Accuracy, Precision and Detection Limits of SEM–WDS, SEM–EDS and PIXE in the Multi-Elemental Analysis of Medieval Glass

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Accuracy, precision and detection limits of measurements of trace elements of potash, soda and lead reference glasses by wavelength-dispersive spectrometry (WDS) were compared with those by proton induced x-ray emission (PIXE). Accuracy and precision of measurements of major, minor and trace elements in lead glass standard by WDS were compared with those by energy-dispersive spectrometry (EDS). The homogeneity of reference glasses and the effect of spot size of the electron beam on the accuracy and precision were studied. The effects of aluminum pinhole, Kapton foil and zinc foil absorbers on the detection of manganese, iron, arsenic, rubidium, strontium, zirconium and barium in lead glass by the PIXE were investigated. Copyright © 2000 John Wiley & Sons, Ltd.

INTRODUCTION

Quantitative information on the major, minor and trace elements in archeological artifacts including glass, is important in resolving problems connected with manufacturing technology, raw materials and the origin of these objects. In provenance studies of old glass, the role of one element such as arsenic in the early production of Finnish glasswork is rarely conclusive.[1] The best results are obtained through the analysis of several elements. Owing to its flexible network structure, glass can include more than the half of the elements of the Periodic Table. Therefore many kinds of techniques have been used to analyze glass composition, including wet chemical analysis, neutron activation analysis,[2,3] atomic absorption spectrometry,[4] inductively coupled plasma atomic emission spectrometry[5] and x-ray fluorescence spectrometry.[6] The analytical methods used in this study, scanning electron microscopy (SEM) using both wavelength-dispersive (WDS) and energy-dispersive (EDS) spectrometers and proton induced x-ray emission (PIXE), are based on the detection of x-rays. Studies using EDS for glass analysis have been published[7,8] and the problems of analyzing ancient glasses with WDS has been discussed in previous publications.[9,10] A comparative study of WDS and EDS techniques in the analysis of ancient glassy material has been made, but it did not include lead glass, which along with soda and potash glass belongs to the main medieval glass types.[11] The PIXE method has been used in the analysis of archeological material and a few studies included glass analysis.[12,13] The advantages of SEM–EDS and SEM–WDS techniques include the small sample size needed (<1 mm^3) and the ability to analyze

corroded samples. On the other hand, there are limitations to these methods. They have poor sensitivity to trace elements and to elements lighter than Na. Also, the loss of volatile elements (Na) during excitation is a well known phenomenon. In contrast, no chemical changes of the volatile element content during the PIXE analysis of alkali glass fragments have been found, even though structural changes are observed.[14] The sensitivity of the PIXE method at trace element level is significantly better than that of the WDS and EDS methods. According to Reed,[15] the theoretical detection limits in SEM–EDS measurements are about 0.08 wt%. Typical detection limits for WDS detectors are 0.01 wt%.[16] The limits of detection with the macro PIXE system for thick targets are of the order of 1–10 ppm by weight. The PIXE method offers maximum sensitivity when atomic number Z of a detected element is in the range 18–40. The disadvantage of the PIXE method is that the light elements (Na, Al, Mg, Si) important in glass research cannot be detected.

The aims of the present work were to examine and compare WDS and PIXE for the quantitative multi-elemental analysis of trace elements in glasses and to evaluate WDS and EDS as methods for determining major, minor and trace elements in lead glasses. The EDS results have been published previously.[17] This work is an extension of a larger project in which the aims were to analyze the chemical composition of the glass products manufactured in the earliest Finnish glassworks in the 18th and 19th centuries and to find out whether it is possible to identify the manufacturer of glass items based on element composition analysis.[1] The production model of the early Finnish factories was Central European potash glass, often called forest glass owing to its green color, caused by iron and other impurities in the raw materials, such as sand, limestone and birch potash. Because of this Central European glass production model, this research also included a study of differences in chemical composition of potash glass products manufactured by different factories

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in different areas in Central Europe.[18] Both studies concluded that even if variations in absolute concentrations of major, minor and trace elements are not significant, SEM–EDS and PIXE analyses, followed by discriminant analysis of data, is a successful method for identifying the manufacturer. Concentrations of two or three elements are not directly a fingerprint of a manufacturer, but concentrations of 10 or 11 elements which include both major, minor and trace elements used in statistical analyses can resolve the manufacturer problem. For example, in European medieval potash (forest) glass the concentrations of Fe are in the range 1.8–0.1 wt%. If the concentrations of different trace elements such as Fe, Mn, Cu, Sr and Ba vary over the range 1.0–0.1 wt%, then the concentrations of these elements can be measured using the SEM methods or the PIXE method. By choosing a suitable measuring method, the exact knowledge of the accuracy and precision of electron and proton excitation methods in multi-elemental analyses (when the analytical conditions cannot be optimum for all elements) is useful, even if it is well known that electron excitation is less sensitive than proton excitation. A method comparison was made with National Institute of Standards and Technology (NIST) and Corning glass standards. The PIXE results using Corning glass standard D have been published previously.[17] The effects of spot sizes or diameters of the electron beam on accuracy and precision were studied in the SEM–WDS analysis. The effects of different absorbers, Kapton (Du Pont, Switzerland) foil, aluminum pinhole and zinc (Goodfellow, UK) foils on the detection limits of manganese, iron, arsenic, rubidium, strontium, zirconium and barium in lead glass using the PIXE method were studied.

EXPERIMENTAL

Reference glasses

Samples were international glass standards, chosen to cover the whole range of major glass components of the main three compositional groups of medieval glasses and to include most minor and trace elements of interest. Samples for WDS measurements were the Corning glass standards C and D[19] and the NIST glass standard SRM 611. The NIST glass standard SRM 611 contains 61 trace elements at nominal concentrations of 500 ppm by weight in a soda–lime–silica matrix. The same reference glasses were also used in the PIXE measurements. The detection limits of manganese, iron, arsenic, rubidium, strontium, zirconium and barium in lead glass using different filters were evaluated with Corning glass standard C and the NIST glass standard SRM 89. The latter standard is a lead–barium glass powder. For the PIXE measurements the powder was packed in a plastic tube covered by Kapton foil. In WDS measurements absolute concentrations were calculated using the MAC (Micro-Analysis Consultants, St Ives, UK) standard No. 3056. In EDS measurements absolute concentrations were calculated using the same MAC standard. In PIXE measurements absolute concentrations were calculated using the Corning glass standards A and B and the NIST glass standard SRM 620.

Sample preparation

For the SEM measurements, small samples 1 mm in length were usually used. For testing the homogeneity by choosing the measuring points from the whole cross-section of analyzed reference glasses in the present study, samples of 1 cm^2 in area were cut with a diamond saw from the glass standards, mounted on epoxy resin and polished flat. Since glass is a poor conductor, a carbon coating was applied to the polished surface to prevent localized charging and any resulting distortion or reflection of the electron beam.

For the PIXE measurements, glass samples were cleaned with alcohol.

Methods

The WDS analyses of the samples were made at the Institute of Electron Optics of Oulu University, Finland, using a JEOL Superprobe 733 scanning electron microscope with an automatic Link Lemas detector system using a TAP crystal (Na, Mg, Al, Si), PET crystal (P, S, Cl, K, Ca, Ti, Sr, Ba, Zr) and LiF crystal (Mn, Fe, Zn, Cu, Pb). The diameter of the electron beam was 10 and 30 µm. All analyses were made using a 15 kV accelerating voltage and a beam current of 15 nA. All measurements were carried out using a 40 s measuring time for the main elements (20 s at peak position and 20 s at background).

All SEM–EDS values given were taken from our previous work[17] where lead glass samples were 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 electron beam current was 1.2 nA and the measuring time was 50 s.

In the PIXE analyses, the samples were bombarded with a 2 nA external proton beam from the 2.5 MV Van de Graaff accelerator of Helsinki University. The proton energy on the target was approximately 2.4 MeV. The emitted x-rays were detected with a 50×6 mm high-purity germanium detector. Three different filters were used to optimize the measuring system for elements of interest in soda and potash glass. A 150 µm thick aluminum filter, the same filter with a 0.1 mm pinhole, and a 250 µm thick Kapton foil were used to eliminate low-energy characteristic x-rays originating from the major elements in the glass matrix. An aluminum pinhole filter, a 250 µm thick Kapton foil and two 50 and 100 µm thick zinc foil filters were used to optimize measurements of manganese, iron, arsenic, rubidium, strontium, zirconium and barium in lead glass. The measuring time for the sample was about 5 min and the total collected charge was 0.5 µC in lead glass samples. The spectra were collected with the Canberra S-100 measuring program and analyzed with the SAMPO peak fitting program.[20,21]

RESULTS AND DISCUSSION

Diameter of the electron beam in WDS measurements

The effect of spot size on the accuracy and precision of the WDS measurements was studied when the diameters

Table 1. Precisions and accuracies for major, minor and trace elements of the Corning glass standards D and C using the WDS method when the diameter of the electron beam was 10 and 30 μm

Standard	Element	Certified (wt%)	Diameter 10 μm				Diameter 30 μm			
			Present (wt%)	SD (wt%)	RSD (%)	Relative error (%)	Present (wt%)	SD (wt%)	RSD (%)	Relative error (%)
Corning D	Na	0.98	0.97	0.06	6.2	1.0	0.99	0.02	2.0	1.0
	Mg	2.47	2.40	0.04	1.7	2.8	2.39	0.03	1.2	3.2
	Al	2.87	2.69	0.03	1.1	6.3	2.70	0.05	1.8	5.9
	Si	25.81	25.38	0.13	0.5	1.7	25.38	0.13	0.5	1.7
	P	1.74	1.78	0.02	1.1	2.3	1.75	0.07	4.0	0.6
	S	0.11	0.07	0.01	14.3	27.3	0.05	0.01	20.0	54.5
	Cl	0.35	0.17	0.02	11.8	51.4	0.16	0.02	12.5	54.3
	K	9.35	9.32	0.08	0.8	2.3	9.16	0.07	0.7	0.7
	Ca	10.72	11.04	0.13	1.4	3.0	10.91	0.13	1.2	1.8
	Ti	0.24	0.25	0.01	4.0	4.2	0.25	0.01	4.0	4.2
	Mn	0.36	0.45	0.06	13.3	25.0	0.40	0.07	17.5	11.1
	Fe	0.35	0.32	0.06	18.8	8.6	0.34	0.07	20.6	2.8
	Zn	0.08	0.09	0.03	33.3	12.5	0.09	0.04	44.4	12.5
	Ba	0.30	0.32	0.05	15.6	6.7	0.31	0.03	9.7	3.3
	Cu	0.32	0.28	0.04	14.3	12.5	0.29	0.05	17.2	9.4
Corning C	Na	0.84	0.81	0.02	2.5	3.4	0.83	0.01	1.2	1.2
	Mg	1.66	1.56	0.04	2.6	6.3	1.59	0.02	1.2	4.2
	Al	0.54	0.44	0.02	4.5	19.3	0.43	0.01	2.3	20.4
	Si	16.3	16.1	0.04	0.2	1.1	16.10	0.17	1.0	1.2
	P	0.04	0.11	0.05	45.4	25.0	0.05	0.01	20.0	25.0
	S	0.06	0.04	0.02	50.0	33.3	0.04	0.01	25.0	33.0
	Cl	0.11	0.13	0.05	38.5	18.2	0.07	0.01	42.8	36.4
	K	2.32	2.44	0.02	0.8	5.2	2.22	0.16	7.2	4.3
	Ca	3.57	3.63	0.06	1.6	1.7	3.67	0.11	3.0	2.8
	Ti	0.51	0.55	0.04	7.3	7.8	0.54	0.01	1.8	5.9
	Fe	0.22	0.23	0.05	21.7	4.5	0.21	0.02	9.5	4.5
	Zn	0.03	0.08	0.04	50.0	167.0	0.07	0.01	14.3	133.0
	Sr	0.21	0.49	0.35	71.4	133.0	0.14	0.01	7.1	28.6
	Ba	10.83	10.44	0.10	1.0	3.6	10.56	0.15	1.4	2.5
	Cu	0.94	0.97	0.06	6.2	3.2	0.95	0.05	5.3	1.1
	Pb	34.1	32.6	0.7	2.1	4.4	31.6	1.02	3.2	7.3

of the electron beams were 10 and 30 μm. Results for the Corning glass standards D and C are given in Table 1. The precisions are expressed as relative standard deviations (RSD) (standard deviation × 100%/mean) and the accuracies as relative errors ((|observed composition − certified composition|/certified composition) × 100%). The precisions are similar, the exceptions being those for Na, P and S. When the spot size in the measurements is 30 μm, the precision for Na is better than using the smaller diameter. The reason is that the temperature of the sample is reduced when the diameter increases, and sodium as a light element is most sensitive for this heating. The effect of the spot size on the precision of S and P is the reverse. The accuracy for S with the smaller spot size is also better than using the 30 μm diameter electron beam. For Mn and Fe, the accuracies are better in potash (D) glass using the larger spot size, therefore the larger spot was adopted. In the measurements of lead glass standard C, there were no great differences between the precisions and accuracies of the results using a spot size 10 or 30 μm. The accuracies and precisions for Zn and Sr and the precisions for P, S, Ti and Fe were better using the larger diameter electron beam. The accuracy and precision for Cl and the precisions for K and Ca were better using the smaller diameter electron beam.

Accuracy and precision in the WDS and PIXE measurements

The accuracy and precision for Ti, Mn, Fe, Zn, Cu, Zr, Sr and Ba in the WDS and in the PIXE measurements were compared by analyzing the NIST glass standard SRM 611 five times. Results are given in Table 2. At a concentration level of 500 ppm by weight, the precisions for the measured trace elements are 10% or better in the PIXE measurements. The only exception is the precision of Mn, which is nearly 40%. The precisions in the WDS measurements are 25–50%. The accuracies in the PIXE measurements are about 10% or better for Fe, Cu, Zn and Zr and 15–25% for Ti, Mn, Rb, Sr, Ba and Pb. For Ti, Mn, Zn, Rb, Sr, Ba and Pb the accuracies in the WDS measurements are 40–80%, with the exception of the accuracies of Ti and Mn, which are 0.9 and 11%, respectively, and thus better than those in the PIXE measurements. The reason for the poor result in the PIXE measurements is the standard itself, which contains too many (61) trace elements which make the background high and difficult to correct, especially for Ti and Mn. On the other hand, reasonable results for Rb and Pb at this concentration level in the multi-elemental analysis could only be obtained using the PIXE method. The higher accelerating potential of 20 versus 15 kV in the WDS measurements could give better results for Pb.

Table 2. Precisions and accuracies for trace elements of the NIST glass standard SRM 611 and the Corning glass standard D using the WDS and PIXE methods[a]

Standard	Element	WDS					PIXE			
		Certified (ppm)	Present (ppm)	SD (ppm)	RSD (%)	Relative error (%)	Present (ppm)	SD (ppm)	RSD (%)	Relative error (%)
SRM 611	Ti	437	440	160	36.4	0.9	522	54	10.3	19.4
	Mn	485	430	220	51.2	11.3	380	147	38.7	21.6
	Fe	458	705	260	36.9	54.0	482	7	1.4	5.2
	Zn	433	790	330	41.8	82.0	385	8	2.0	11.1
	Cu	444	610	150	24.6	37.0	455	23	5.0	2.5
	Rb	425.7					530	9	1.7	24.5
	Zr	500	300	100	33.3	40.0	548	7	1.3	9.6
	Sr	515.5	790	390	49.4	53.0	427	8	1.9	17.2
	Ba	500	600	300	50.0		573	36	6.3	14.6
	Pb	426					509	18	3.5	19.5
Corning D	Ti	2400	2500	100	4.0	4.2	2200[a]	100	4.5	8.3
	Mn	3600	4000	700	17.5	11.1	3950[a]	80	2.0	9.7
	Fe	3500	3400	700	20.6	2.8	3600[a]	70	1.9	2.8
	Zn	800	900	400	44.4	12.5	900[a]	30	3.3	12.5
	Cu	3200	2900	500	17.2	9.4	3000[a]	100	3.3	6.7
	Rb	46					36[a]	5	13.9	21.7
	Zr	70					120[a]	15	12.5	71.4
	Sr	400					420[a]	10	2.4	5.0
	Ba	3000	3100	300	9.7	3.3	3040[a]	20	0.7	1.3
	Pb	2300					2060[a]	60	2.9	10.4

[a] Previous PIXE values from Ref. 17.

Table 3. Precisions and accuracies of major, minor and trace elements of the Corning lead glass standard C obtained using the WDS method and comparison with the previous values using the EDS method from Ref. 17

Element	WDS					EDS			
	Certified (wt%)	Present (wt%)	SD (wt%)	RSD (%)	Relative error (%)	Previous values[17] (wt%)	SD (wt%)	RSD (%)	Relative error (%)
Na	0.84	0.83	0.01	1.2	1.2	1.1	0.1	9.1	31.0
Mg	1.66	1.59	0.02	1.2	4.2	1.5	0.1	6.7	9.6
Al	0.54	0.43	0.01	2.3	20.4	0.42	0.05	11.9	22.2
Si	16.3	16.09	0.17	1.0	1.2	17.6	0.2	1.1	8.0
K	2.32	2.22	0.16	7.2	4.3	2.13	0.02	0.9	8.2
Ca	3.57	3.67	0.11	3.0	2.8	3.62	0.05	1.4	1.4
Ti	0.51	0.54	0.01	1.8	5.9	0.45	0.10	22.2	11.8
Fe	0.22	0.21	0.02	9.5	4.5	0.18	0.09	50.0	18.5
Zn	0.03	0.07	0.01	14.3	133.0				
Sr	0.21	0.14	0.01	7.1	28.6				
Ba	10.83	10.56	0.15	1.4	2.5	10.70	0.12	1.1	1.2
Cu	0.94	0.95	0.05	5.3	1.1	1.33	0.15	11.3	20.2
Pb	34.1	32.41	0.74	2.3	5.0	34.4	0.4	1.2	0.9
S	0.06	0.04	0.01	25.0	33.3				
P	0.04	0.05	0.01	20.0	25.0				
Cl	0.11	0.07	0.03	36.4					

Comparison of the precisions and accuracies in the present WDS measurements and previously measured PIXE results[17] using the Corning glass standard D (Table 2) show that the precisions are better for Ti, Mn, Fe, Zn, Cu and Ba at a concentration level of 0.3 wt% in the PIXE measurements, but that the accuracies using both methods are similar, about 10%. The concentrations of Rb and Zr in this standard are under 100 ppm by weight and the relative errors in the PIXE measurements have increased to 20 and 70%.

Accuracy and precision in lead glass using WDS and EDS

Accuracy and precision of the WDS and EDS methods in lead glass measurements were compared using the Corning glass standard C. The present WDS results and the previously measured EDS results[17] are given in Table 3. According to Veritá et al.,[11] the results of analyses of soda and potash glass standards obtained by the EDS and WDS techniques are broadly comparable and match

the accepted concentrations very closely. The results of this work comparing lead glass analyses using these two techniques lead to a similar conclusion.

The greatest difference between the results of the EDS and the WDS methods in analyses of lead glass is in measurements of Na. The accuracy and the precision for Na in the WDS measurements are about 1%, whereas in the EDS measurements they are nearly 10 and 30%. The main reason is that the concentration of Na in the Corning glass standard is under 1 wt% and therefore close to the detection limit of the EDS method. The precision and accuracy for Pb are better using EDS than WDS. The results are, however, not directly comparable because the analysis program of the EDS system was corrected in analyses of Pb using different reference materials.

Homogeneity

The PIXE and SEM methods are surface sensitive. According to Mosbah et al.,[22] the range of 2.5 MeV protons in glass is around 60 μm and the maximum depth of analysis is 30–35 μm. Under the usual conditions of SEM analysis, the thickness of the analyzed layer is only a few microns.[11] Because the results of the present study are being judged against results of 'bulk' analyses of homogenized powders, large samples were also used in the SEM analyses. In addition, analysis points were chosen at five widely spaced locations on the glass samples rather than taking five replicate analyses at a single point. On a macro scale glass is fairly homogeneous; therefore, the averages of the analysis results should be comparable to the bulk results. It has been assumed that straggling is insignificant because the cross-section curves for the electron and proton excitation are smooth and do not show resonance-like features such as in excitation curves for nuclear reactions.

The basis for testing the homogeneity is that for a homogeneous sample, the measured standard deviations should fall within the limits $N \pm 3N^{1/2}$, where N is the mean peak counts.[16] Measured standard deviations in the WDS and PIXE measurements for the Corning glass standards C and D and for the NIST standard SRM 611, as well as the theoretical values calculated from count statistics, are given in Table 4. The diameter of the beam was 30 μm in the WDS measurements and 0.8 cm in the

PIXE measurements. According to the WDS results for the Corning reference glass C, the studied elements Ti, Fe, Cu, Zn, Sr, Ba and Pb can be considered homogeneously distributed. On the basis of the PIXE measurements, the same elements, with the exception of Ti, are homogeneously distributed. In addition, Zr is homogeneously and Rb inhomogeneously distributed. In the Corning reference glass D, Ti, Mn, Fe and Ba are homogeneously distributed according to the WDS measurements whereas Zn, Cu and Sr are inhomogeneously distributed. On the basis of the PIXE measurements, Mn and Fe are inhomogeneously distributed, whereas the other studied elements, and also Rb and Zr, which were not measured using the WDS method, are homogeneously distributed. In the soda glass matrix the trace elements are inhomogeneously distributed according to the WDS measurements and homogeneously distributed with the exception of Ti on the basis of the PIXE measurements. The differences between the WDS and PIXE results can be explained by the diameter of the beam but also micro inhomogeneity exists in glass which is consistent with sensitive spectroscopic measurements.[23]

Detection limit

There are many procedures for calculating the detection limits in x-ray spectroscopy. The factors that determine the detection limits in electron and proton x-ray analysis are the counting time, the accelerating voltage, the beam current, the line used to measure the element and the composition of both the sample and the standards. Often the detection limits in the SEM measurements are determined as three standard deviations of the background,[11] whereas in PIXE measurements the detection limits are calculated assuming that the minimum detectable peak is three times the square root of the background at full width at half-maximum intensity (FWHM) of the peak. In this work, detection limits were evaluated under the latter conditions. For the WDS measurements, this means that whole peak areas of some elements were measured. Then the peak and background areas at FWHM were graphically integrated from the whole peak area measurements. The detection limits using the PIXE and the WDS measurements are given in Table 5. The detection limits using the WDS and PIXE measurements are comparable for Ti in soda and potash glass matrix. The real measuring time using the

Table 4. Measured and theoretical standard deviations of trace elements of the Corning glass standards C and D and the NIST glass standard SRM 611, expressed as ppm by weight

Element	Corning C WDS Measured SD	Corning C WDS Theoretical SD	Corning C PIXE Measured SD	Corning C PIXE Theoretical SD	Corning D WDS Measured SD	Corning D WDS Theoretical SD	Corning D PIXE Measured SD	Corning D PIXE Theoretical SD	SRM 611 WDS Measured SD	SRM 611 WDS Theoretical SD	SRM 611 PIXE Measured SD	SRM 611 PIXE Theoretical SD
Ti	100	500	220	190	140	260	130	130	160	60	130	90
Mn					730	740	60	50	220	200	10	15
Fe	240	280	40	70	360	660	60	40	260	220	2	14
Cu	500	900	170	400	500	160	60	100	150	90	20	30
Zn	30	110	40	70	400	360	25	40	330	240	10	30
Rb			50	25			6	7			10	30
Sr	140	600	40	150	240	60	10	20			10	12
Zr			2	5			6	10	100	60	10	30
Ba	1500	3400	2400	8000	300	770	160	460	300	70	40	200
Pb	11000	23000	1660	1870							20	40
As											40	60

Table 5. Detection limits in the present WDS and PIXE measurements expressed as ppm by weight using in the WDS measurements the MAC standard 3056 and in the PIXE measurements the NIST glass standard SRM 611 and Corning glass standard D

Element	WDS Detection limit (ppm)	Absorber	PIXE Detection limit (ppm)
Na	160		
Mg	20		
Al	20		
Si	15		
P	120		
Cl	30		
K	15		
Ca	15		
Ti	20	Kapton	15
Mn	35		7
Fe	30		5
Co			4
Ni			4
Cu	50	Al pinhole	3
Zn	60		3
Pb			2
Rb			2
Sr			2
Zr	100		3
Ba	60		160

PIXE method is about 3 min for each sample and each element, whereas in the present work using WDS the measuring time for each element was 40 s. The whole peak area measurement using the WDS method takes about 30 min when the step is 0.010 mm and the measuring time per step is 0.2 s. Then the WDS measurement of the peak area at FWHM takes about 3 min, which is similar to the PIXE measuring time but notably longer than the real measuring time of 40 s. Hence the detection limits calculated under the present conditions are minimum detection limits for the WDS method; using a measuring time of 40 s the detection limits are higher while the detection limits for the PIXE measurements are experimental and according to the measurements. The concentrations of elements in the PIXE measurements of detection limits were 500 ppm by weight and both Kapton foil and aluminum pinhole

filters were used. In mineralogy, concentrations of trace elements have often been measured using the longer measuring time and higher accelerating voltages in the WDS measurements and the detection limit of one element can be low.[24] In the WDS measurements of old glass, longer measuring times than those used in the present study are possible in multi-elemental analysis, but higher beam currents damage the samples.

Comparing the micro PIXE and the micro synchrotron radiation induced x-ray emission (SXRF) method in natural volcanic glass research, Mosbah *et al.*[22] found that the detection limits were slightly better using the micro SXRF measurements than using the micro PIXE measurements. In steel analysis, the PIXE induced XRF method gave lower detection limits for Ti, V, Mn and Cr than the PIXE method.[25] Hence we can consider that photon excitation could give better detection limits than the macro PIXE method. In particular, total reflection x-ray fluorescence analysis (TXRF) is a powerful analytical tool for trace element determination in various kinds of samples.[26] There are, however, many problems connected with this method in glass research, one of the greatest being that the sample should be very thin.

Al pinhole, Kapton and Zn foil absorbers in lead glass using the PIXE method

In order to optimize the measurements of Mn, Fe, As, Rb, Sr, Zr and Ba in lead glass using the PIXE method, a 150 μm Al absorber, a 150 μm Al absorber with a 0.1 mm diameter pinhole, Kapton (with thickness 250 μm) and Zn foil (with thickness 50 and 100 μm) absorbers were studied using the reference glasses NIST SRM 89 and Corning glass standard C. In lead-rich material the intense Pb L x-ray peaks particularly obscure the analysis of arsenic and strontium. The intense lead peaks also add to the general background throughout the x-ray spectrum. A pure lead sample was measured using different absorbers to obtain the relative intensities of lead peaks. By subtracting the overlapping lead peaks and the intense background induced by lead peaks it was possible to evaluate the intensities of arsenic, strontium, rubidium and zirconium peaks. The S/B ratios, where S is the area of peak at FWHM and B is the background in an equal interval, and the detection limits calculated according the procedure described above are given in Table 6. The zinc

Table 6. Peak to background ratios (S/B) and the detection limits (DL) for Mn, Fe, As and Ba in the NIST lead glass standard SRM 89 and for Rb, Sr, Zr and Ba in the Corning lead glass standard C with different absorbers using the PIXE method

Standard	Element	Content (wt%)	Al pinhole absorber S/B	DL (ppm)	Al 150 μm absorber S/B	DL (ppm)	Kapton absorber S/B	DL (ppm)	Zn 50 μm absorber S/B	DL (ppm)	Zn 100 μm absorber S/B	DL (ppm)
SRM 89	Mn	0.068			0.5	370	2.0	24				
	Fe	0.034			0.5	660	3.5	18				
	As	0.26	16.4	27	36.0	48						
	Ba	1.25	6.0	1200			1.7	1500	11.0	460	6.0	580
	Pb	16.25										
Corning C	Rb	0.009	4.3	12					1.5	15		
	Sr	0.21	2.6	56	2.0	730	1.0	200	0.8	460		
	Zr	0.0037	2.0	2	1.0	4	0.3	10	1.1	8		
	Ba	10.83	16.0	1200	14.7	1380	4.0	5800	47.0	800	25.0	1800
	Pb	34.1										

Table 7. Summary of the present detection limits for Mn, Fe, As, Rb, Sr and Ba in lead glass expressed as ppm by weight using the PIXE method

Element	Content (wt%)	Standard	Absorber	Detection limit (ppm)
Mn	0.068	SRM 89	Kapton	24
Fe	0.034	SRM 89	Kapton	18
As	0.26	SRM 89	Al pinhole	27
Rb	0.009	Corning C	Al pinhole	4
Sr	0.21	Corning C	Al pinhole	60
Zr	0.0037	Corning C	Al pinhole	2
Ba	1.25	SRM 89	Zn (50 μm)	460

foil with 50 μm thickness clearly improves the S/B ratio and the detection limit of Ba. A summary of the detection limits for Mn, Fe, As, Rb, Sr, Zr and Ba in lead glass in the present study is given in Table 7. According to the present work, the best detection limit in lead glass for Mn and Fe can be obtained using the Kapton (thickness 250 μm) absorber and for As, Rb, Sr and Zr the Al (thickness 150 μm) pinhole absorber.

CONCLUSIONS

In provenance studies of old glass, a good result is obtained on the basis of the analysis of about 10 elements; therefore, the SEM and PIXE techniques, as powerful multi-elemental analysis methods, are suitable for resolving problems connected with the origin of old glass artifacts. The SEM–WDS and SEM–EDS methods are suitable for analyzing major and minor components of glass samples. Trace element (<0.1 wt%) analysis is possible using the WDS or the PIXE method. By the PIXE method concentrations from 100 wt% to trace element levels may be detected. The sample preparation for PIXE analysis of glass artifacts is straightforward and after the removal of corrosion layers often direct irradiation is possible. The sample preparation for SEM is time consuming but the sample is not destroyed and is available for further investigations.

The PIXE method is the most sensitive. The detection limits with SEM–EDS, SEM–WDS and PIXE are about 0.1, 0.01 and 0.001 wt%, respectively. Concentrations of some trace elements important in glass research, such as Ti, Mn and Fe, are often in the range 0.1–1.0 wt%; then analysis using any of these three techniques is possible and the knowledge of the accuracy and precision of the analysis method can help one choose the most appropriate technique. The accuracies of WDS measurements of Ti, Mn, Fe, Zn, Cu and Ba with concentrations of 0.5 wt%

are comparable to the values obtained using PIXE, but the precisions are 20–40% whereas in the PIXE measurements they are under 10%, with the exception of Ti. At the level of 0.05 wt% the precisions are about 10% and accuracies 20% in the PIXE measurements, whereas in the WDS measurements they are 20–50 and 40–80% with the exception of the accuracies for Ti and Mn, which are 1 and 11% and thus more comparable to the approximately 20% values for the PIXE measurements.

The only notable effects of spot sizes on the precisions and accuracies are the better accuracies for Mn and Fe in potash and soda glass using the larger 30 μm diameter of the electron beam in the WDS measurements.

The EDS method is comparable to the WDS method in the lead glass analyses. The greatest difference is in the measurement of Na when the concentration of Na is about 1 wt%. The accuracy and precision for Na in the WDS measurements are about 1% but in the EDS measurements they are nearly 10 and 30%.

The SEM and PIXE methods are surface sensitive. On the macro scale (in the PIXE measurements when the diameter of the proton beam was about 0.8 cm) the glass is fairly homogeneous when the measured and theoretical standard deviations of trace element concentrations determined using this method are compared. On the micro scale (in the WDS measurements when the diameter of the electron beam was 30 μm) the glass is homogeneous when the concentrations of trace elements are at a level of 0.5 wt% but inhomogeneous when the concentrations are at a level of 0.05 wt%. Hence the analysis results of the SEM and PIXE methods are comparable with the results of bulk analyses of homogenized powders.

The detection limits of the WDS and the PIXE measurements were calculated assuming that the minimum detectable peak is three times the square root of the background at FWHM. The detection limits in the WDS measurements are 15–160 ppm by weight and in the PIXE measurements 2–15 ppm by weight with the exception of Ba.

According to the present work, the 50 μm thick zinc absorber improves the S/B ratio and the detection limits of Ba at concentration levels of 10.8 and 1.25 wt%. The best detection limits in lead glass for Mn and Fe can be obtained with a 250 μm thick Kapton absorber and for As, Rb, Sr and Zr with a 150 μm thick aluminum absorber with a 0.1 mm diameter pinhole.

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