X-RAY MICROANALYSIS OF ANCIENT GLASSY MATERIALS: A COMPARATIVE STUDY OF WAVELENGTH DISPERSIVE AND ENERGY DISPERSIVE TECHNIQUES*

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Sensitivity, precision and accuracy of quantitative microanalysis of major, minor and trace elements present in ancient glasses by energy dispersive spectrometry (EDS) is compared to that by wavelength dispersive spectrometry (WDS). Although there are certain problems with EDS due to peak overlaps and background noise, the precision and minimum detection limits of EDS for most of the important elements in ancient glasses were found to compare favourably to those of WDS. Both EDS and WDS, when quantified by comparison to glass standards, can produce reliable results which are adequate for most technological questions.

INTRODUCTION

Quantitative chemical analysis of ancient glassy materials, such as glass artefacts, glazes and enamels, can reveal important information for the classification and history of glass. The chemical composition may supply clues as to the raw materials used, the production techniques and the conditions of manufacture for a particular time and place, thus helping to define the history of glass technology (Brill 1968; Henderson 1985; Sayre and Smith 1967; Verità and Toninato 1990). Moreover comparison of compositional data can help with the identification or authentication of glass objects (Newton and Brill 1985).

A wide range of techniques, each with its own advantages and disadvantages, has been used to analyse glass composition, including wet chemical analysis, atomic absorption and inductively coupled plasma atomic emission spectrometry, and X-ray fluorescence. However, X-ray microanalysis in the electron microprobe or scanning electron microscope, using either wavelength dispersive spectrometry (WDS) or energy dispersive spectrometry (EDS), is increasingly adopted. The advantages of these techniques include the small sample size ($< 1 \text{ mm}^3$) and the ability to distinguish and analyse, or exclude, inclusions, opacifiers and weathered areas. Furthermore, the techniques are faster than the conventional methods, and the sample is not destroyed, so it is available for further investigations.

On the other hand, there are limitations to the methods. They have poor sensitivity to trace elements (discussed below) and to elements lighter than Na. Peak overlap for some

elements can be problematic with EDS, while in WDS the high energy of the electron beam can cause migration of Na away from the point of analysis. The problem of analysing ancient glasses with WDS has partly been discussed in previous works (Henderson 1988; Verità and Hreglich 1986; Verità and Biavati 1989) but not the use of EDS. It is known that EDS detectors have inferior performances in comparison with WDS spectrometers; in particular, they have an inferior peak resolution and overlap between adjacent EDS peaks will be severe in some instances. Detection limits are also seriously degraded as a much larger proportion of background continuum is sampled under individual EDS peaks. Finally, EDS has a limited total count rate capability and, therefore, theoretically, the EDS data are less precise as compared with the WDS data. In spite of these limitations, EDS is often more readily available than WDS or other analytical methods to museums and laboratories engaged in the analysis of works of art and archaeological materials. Some studies have been published using EDS for glass analysis (Bimson and Freestone 1988; Freestone 1993; Philippon *et al.* 1988; Vandiver 1982) but often EDS has been used only for semi-quantitative analysis or f˄r the analysis of glass types which are not of historical interest (Charbonneau 1988). On the other hand, studies carried out on silicate minerals with EDS systems (Dunham and Wilkinson 1978) and comparisons with WDS performance of X-ray fluorescence (Potts *et al.* 1985) suggest that good results should be expected also for EDS microanalysis of ancient glassy materials.

The aim of the present work is to examine and compare WDS and EDS for quantitative analysis of glasses. In order to assess the reliability of both techniques for elements commonly found in ancient glassy materials, their precision and accuracy in the analyses of major and minor glass components and their sensitivity as concerns trace elements have been determined.

MATERIALS AND METHODS

Reference glasses

Twenty-two reference glasses were analysed to produce data for precision, accuracy and sensitivity of EDS compared to WDS. The glasses were chosen so as to cover the whole range of the major glass components of the main compositional groups of ancient glasses and to include most minor elements of interest. Samples were international standards or well-characterized glasses, analysed in at least two different laboratories by conventional chemical methods. The considered specimens include:

four synthetic glasses produced by Corning with a complex composition (up to 28 constituents) reproducing the main categories of ancient glasses, analysed in a round robin by 12 different laboratories (Brill 1972);

four soda-lime and two potash-lime glasses with a simple composition (six to ten constituents);

ten soda-lime and three potash-lime glasses with different contents of trace elements in a significant range; in this group four original ancient glasses are included;

and four lead glasses with a PbO content ranging between 5 and 37 wt. %.

The ranges of concentration of the glass components covered by the reference glasses are reported in Table 1.

Table 1 *Ranges of glass compositions investigated; in parentheses the number of reference glasses containing the element is indicated. Minimum detection limits expressed in parts per million are also reported for WDS and EDS, determined as three standard deviations of the background*

Element	Range of composition (wt. %)		Minimum detection limits (ppm)			
			WDS (20 sec; 15 kV/100 nA)		EDS (400 sec; 30 kV)[1]	
F	0–5.0	(3)	600	$K\alpha$;TAP		[2]
Na_2O	1.0–18.0	(16)	150	$K\alpha$;TAP	1500	$K\alpha$
MgO	0.1–5.5	(15)	100	$K\alpha$;TAP	2000	$K\alpha$
Al_2O_3	0.1–5.0	(14)	100	$K\alpha$;TAP	3000	$K\alpha$
SiO_2	55.0–72.0	(16)	100	$K\alpha$;TAP	3000	$K\alpha$
P_2O_5	0–4.0	(10)	120	$K\alpha$;TAP	5000	$K\alpha^3$
SO_3	0.05–0.6	(12)	200	$K\alpha$;TAP	1500	$K\alpha^4$
Cl	0–1.0	(10)	80	$K\alpha$;PET	350	$K\alpha$
K_2O	0.2–20.0	(16)	40	$K\alpha$;PET	800	$K\alpha$
CaO	0–10.0	(14)	50	$K\alpha$;PET	560	$K\alpha$
TiO_2	0.03–2.0	(9)	180	$K\alpha$;PET	400	$K\alpha$
Cr_2O_3	0.03–0.2	(3)	160	$K\alpha$;PET	370	$K\alpha$
MnO	0.1–1.2	(10)	150	$K\alpha$;PET	470	$K\alpha$
Fe_2O_3	0.1–1.7	(13)	200	$K\alpha$;LiF	450	$K\alpha$
CoO	0–0.3	(4)	200	$K\alpha$;LiF	380	$K\alpha$
NiO	0–1.0	(3)	200	$K\alpha$;LiF	600	$K\alpha$
CuO	0–2.7	(5)	300	$K\alpha$;LiF	620	$K\alpha$
ZnO	0–5.0	(4)	200	$L\alpha$;TAP	650	$K\alpha$
As_2O_3	0–2.0	(4)	200	$L\alpha$;TAP	2500	$L\alpha^3$
ZrO_2	0–1.0	(3)	250	$L\alpha$;TAP	1700	$L\alpha$
SnO_2	0–0.5	(6)	350	$L\alpha$;TAP	5000	$L\alpha^3$
Sb_2O_3	0–2.2	(7)	600	$L\beta$;PET	6000	$L\alpha^3$
BaO	0–7.0	(6)	300	$L\alpha$;PET	3000	$L\alpha^3$
PbO	0–5.0	(4)	400	$M\alpha$;PET	5000	$M\alpha^3$
PbO^5	5.0–37.0	(4)				

[1] MDL for Na, Mg, Al, Si, K, Ca were determined with EDS at 200 sec, 15 kV.

[2] Due to the presence of the oxygen $K\alpha$ peak, fluorine is detected in the windowless EDS detector only for concentrations of at least 3 wt. %.

[3] High values due to peak overlaps.

[4] In glasses containing less than 1 wt. % PbO.

[5] Major components of high lead oxide glasses were excluded from regressions because of the intense matrix effect.

Sample preparation technique

Glass is usually a very homogeneous material and small flakes are generally representative of the chemical composition of the glass artefact. Nevertheless, some precautions should be taken to make X-ray microanalysis really representative of the bulk glass composition. First, the analysed area must be polished before analysis. All ancient glass artefacts, even those exhibiting a glossy, well-preserved surface, are covered by modified layers whose chemical composition is completely different from the bulk. Indeed, it should be recalled that in the usual conditions of X-ray microanalysis (energies of the electron beam ranging between 10 and 30 kV), the thickness of the analysed layer is only a few microns. Second,

heterogeneities (stones, microcrystals, glassy cords or knots) could be present; such 'defects' can be easily detected and must be excluded from the analysed area.

In the present work, the glass objects were sampled by scratching or flaking a small piece off with a diamond-edged scribe, making sure to remove some unweathered glass. The fragments were fixed on a double-sided adhesive tape which was then laid on the perfectly flat bottom surface of a mould. The samples were embedded in an epoxy or acrylic resin and afterwards the glass surface was exposed by grinding the specimen with a low grade $(20-30 \mu m)$ silicon carbide or diamond abrasive paper (water as a lubricant). The samples were then finally polished using a hard surface nylon disc running at $\geqslant 300$ rpm and cerium oxide powder or diamond paste (grade $3 \mu m$ or less) and water as a lubricant. Following this procedure, it was possible to obtain a well-polished surface maintaining the sample flatness and minimizing relief and edge rounding of the glass fragments. Since glasses are poor conductors of electrons a carbon coating was applied to the polished cross-section to prevent localized charging of the specimen surface and any resulting distortion of the electron beam. Unknown and reference glasses were coated at the same time. It was found that good results can be achieved also by sputtering a thin film of metallic nickel on to the sample; gold coating should be avoided because it has an important absorbing effect on emerging X-rays and produces a marked signal loss, especially for light elements. The low beam energy required by EDS systems allows uncoated glass samples to be analysed but only for qualitative purposes: the intensity and the position of the X-ray peaks are unstable and not reproducible.

Instrumental and analytical conditions

The WDS system used was a microprobe SX-50 produced by CAMECA (France), located at the Stazione Sperimentale del Vetro, Venezia-Murano, Italy. This is equipped with two vertical and one inclined spectrometers (PET-TAP-LiF crystals). The detectors were Argon-CH_4 10% gas flow-counters adjusted to the ideal voltage of each element to be analysed. The major elements were analysed at 15 kV, 15 nA and 10 seconds of counting time and trace elements at 15 kV, 100 nA and 20 seconds counting time. Backgrounds were detected on both sides of the peaks.

The energy dispersive spectrometer was a Kevex model Delta IV, attached to a modified Amray 1100 (1600T) scanning electron microscope (SEM), located at the Metropolitan Museum of Art, New York. This EDS model is equipped with a normal beryllium window detector, and does not detect elements below the atomic weight of sodium. Peak calibration is first checked using an aluminium and copper standard. Analyses were done with beam intensity adjusted to give an input rate of approximately 1700 counts per second (cps), using a time-factor of 12 micro-seconds for an average dead-time of 25%. Channel width was set at 10 eV per channel. The major components of the glasses were analysed at 15 kV for 200 seconds live-time. Other minor and trace components were analysed at 30 kV for 400 seconds. After acquisition of the EDS spectrum, the escape peaks were removed automatically, and the background noise was removed with careful manual modelling. Weight percentages of oxides were calculated from cps data (net counts per second) compared to well-analysed reference glasses. Counts per second for each oxide were obtained using the Kevex Quantex software integration deconvolution routine, using the minimum size integration windows. Data for elements with peak overlap, such as Sb and Ca, were obtained using the Gaussian deconvolution routine to separate the counts for each element.
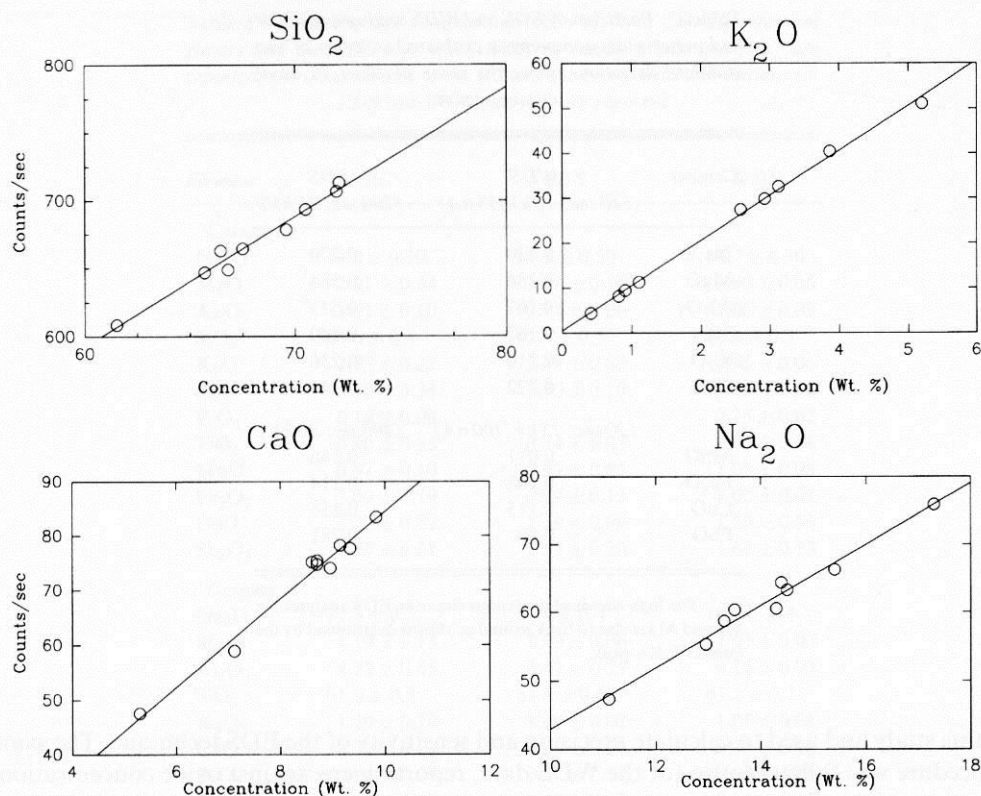
Figure 1   *Plots of net counts per second against concentrations for SiO$_2$, K$_2$O, CaO and Na$_2$O for nine soda-lime-silica glasses (all with less than 1 wt. % lead oxide).*

Each glass was analysed on six different spots and the mean values and standard deviations were calculated. For each element, the total net counts were determined by subtracting the background from the peak counts; the cps were determined by dividing the net counts by the counting time. The total net counts and cps were then used to determine the precision and sensitivity of WDS and EDS following the procedure reported hereafter. The total time taken for analysis (spectra acquisition and data processing) is similar for the two techniques, in the order of a few minutes.

The stability of the devices was assured by repeating the analysis of a reference glass systematically every other sample; due to the high stability of the instrument, no instrumental drift was detected with the SX-50, and correction was taken into account for the SEM.

RESULTS AND DISCUSSION

Figure 1 shows the plots of EDS net cps against concentrations for Na$_2$O, SiO$_2$, K$_2$O and CaO for nine soda-lime-silica glasses containing less than 1 wt. % lead oxide. The good linearity demonstrates that only a negligible matrix effect exists in these ranges of composition. The same regression curves were plotted for all the other elements of interest

Table 2   *Precision of EDS and WDS analyses of major and minor glass components evaluated in terms of two standard deviations about the mean at 10 wt. % oxide concentration*

Element	WDS (10 sec; 15 kV/15 nA)	EDS (200 sec; 15 kV)
Na_2O	0.220	0.270
MgO	0.186	0.584[1]
Al_2O_3	0.167	0.577[1]
SiO_2	0.167	0.140
K_2O	0.210	0.236
CaO	0.222	0.244
	(20 sec; 15 kV/100 nA)	(400 sec; 30 kV)
MnO	0.071	0.146
Fe_2O_3	0.108	0.114
CuO	0.115	0.155
PbO	0.50	0.281

[1] The high standard deviations found in EDS analyses for Mg and Al are due to background problems determined by the intense Si,$K\alpha$ peak.

in this study and used to calculate precision and sensitivity of the EDS technique. The same procedure was followed also for the WDS data, reporting cps against oxide concentration.

Precision and accuracy

The precision of EDS and WDS data for major and minor glass components may be evaluated from the results shown in Table 2. To assist in the evaluation of errors, precision is expressed in terms of two standard deviations (2σ) about the mean at 10 wt. % oxide concentration.

An assessment of these data suggests that the results obtained by the two techniques are broadly comparable. The only exception concerns magnesium and aluminium; the high standard deviation found in EDS analyses of these oxides is due to errors in the subtraction of the intense and curved shape background determined by the close Si,$K\alpha$ peak. The precision observed in the determination of major and minor components is acceptable for the analysis of ancient glassy materials with both WDS and EDS techniques. The present investigation has not been extended to the analysis of high lead glasses (PbO higher than 5 wt. %) because of the important matrix effect due to this heavy element. However, by using a ZAF correction program in these analyses it could be observed that the results are similar to those obtained for the other categories of ancient glassy materials.

In order to evaluate accuracy of the two methods, three of the synthetic Corning glasses (the high-lead glass C was excluded) reproducing the main categories of ancient glasses were analysed six times. The average raw data (net counts) were corrected to concentrations using a PAP program (for WDS) and based on glass and pure oxide international standards and using the regression curves counts/concentration previously reported (for EDS).

Table 3 *Recommended composition (RC) of three Corning reference glasses and the EDS and WDS analyses (mean of six analyses) are reported; the uncertainties in the RC and the two standard deviations for EDS and WDS analyses are reported*

Element	RC	EDS	WDS
Corning A			
Na_2O	14.5 ± 0.10	14.5 ± 0.50	14.7 ± 0.30
MgO	2.81 ± 0.44	2.71 ± 0.15	2.90 ± 0.06
Al_2O_3	1.01 ± 0.10	0.94 ± 0.06	1.00 ± 0.03
SiO_2	66.6 ± 0.4	67.3 ± 0.5	66.4 ± 0.5
K_2O	2.93 ± 0.22	2.89 ± 0.05	2.95 ± 0.06
CaO	5.30 ± 0.34	5.30 ± 0.10	5.40 ± 0.08
P_2O_5	0.14 ± 0.06	—	0.15 ± 0.02
TiO_2	0.80 ± 0.05	0.74 ± 0.05	0.85 ± 0.04
MnO	0.97 ± 0.10	0.99 ± 0.05	1.05 ± 0.08
Fe_2O_3	1.09 ± 0.14	0.99 ± 0.13	1.05 ± 0.08
CuO	1.22 ± 0.22	1.19 ± 0.06	1.30 ± 0.06
Sb_2O_3	1.55 ± 0.21	1.55 ± 0.20	1.62 ± 0.13
Corning B			
Na_2O	17.3 ± 0.2	17.4 ± 0.4	17.0 ± 0.4
MgO	1.19 ± 0.15	1.09 ± 0.06	1.05 ± 0.02
Al_2O_3	4.22 ± 0.45	4.41 ± 0.25	4.25 ± 0.05
SiO_2	61.5 ± 0.3	61.8 ± 0.6	61.2 ± 0.7
K_2O	1.10 ± 0.10	1.09 ± 0.02	1.05 ± 0.02
CaO	8.71 ± 0.27	8.80 ± 0.25	8.70 ± 0.18
P_2O_5	0.84 ± 0.09	0.87 ± 0.15	0.90 ± 0.05
TiO_2	0.10 ± 0.03	0.10 ± 0.03	0.11 ± 0.02
MnO	0.23 ± 0.04	0.24 ± 0.04	0.23 ± 0.02
Fe_2O_3	0.35 ± 0.06	0.35 ± 0.03	0.32 ± 0.03
CuO	2.70 ± 0.21	2.81 ± 0.10	2.75 ± 0.07
Sb_2O_3	0.46 ± 0.09	—	0.40 ± 0.03
Corning D			
Na_2O	1.32 ± 0.22	1.32 ± 0.12	1.40 ± 0.05
MgO	4.09 ± 0.18	4.06 ± 0.22	4.19 ± 0.10
Al_2O_3	5.43 ± 1.07	5.56 ± 0.18	5.20 ± 0.08
SiO_3	55.2 ± 0.3	54.4 ± 0.6	55.2 ± 0.6
K_2O	11.5 ± 0.65	11.7 ± 0.24	11.6 ± 0.16
CaO	15.0 ± 0.35	15.1 ± 0.32	14.8 ± 0.23
P_2O_5	4.00 ± 0.26	3.84 ± 0.35	3.93 ± 0.12
TiO_2	0.40 ± 0.04	0.30 ± 0.06	0.38 ± 0.04
MnO	0.47 ± 0.12	0.43 ± 0.06	0.51 ± 0.04
Fe_2O_3	0.50 ± 0.04	0.48 ± 0.05	0.47 ± 0.06
CuO	0.40 ± 0.20	0.35 ± 0.12	0.43 ± 0.07
Sb_2O_3	0.86 ± 0.12	—	0.82 ± 0.10

The accuracy was evaluated by comparing the means of the six EDS and WDS analyses, with the accepted values of the three Corning glasses; results are reported in Table 3. In this table also the uncertainties in the recommended composition and the standard
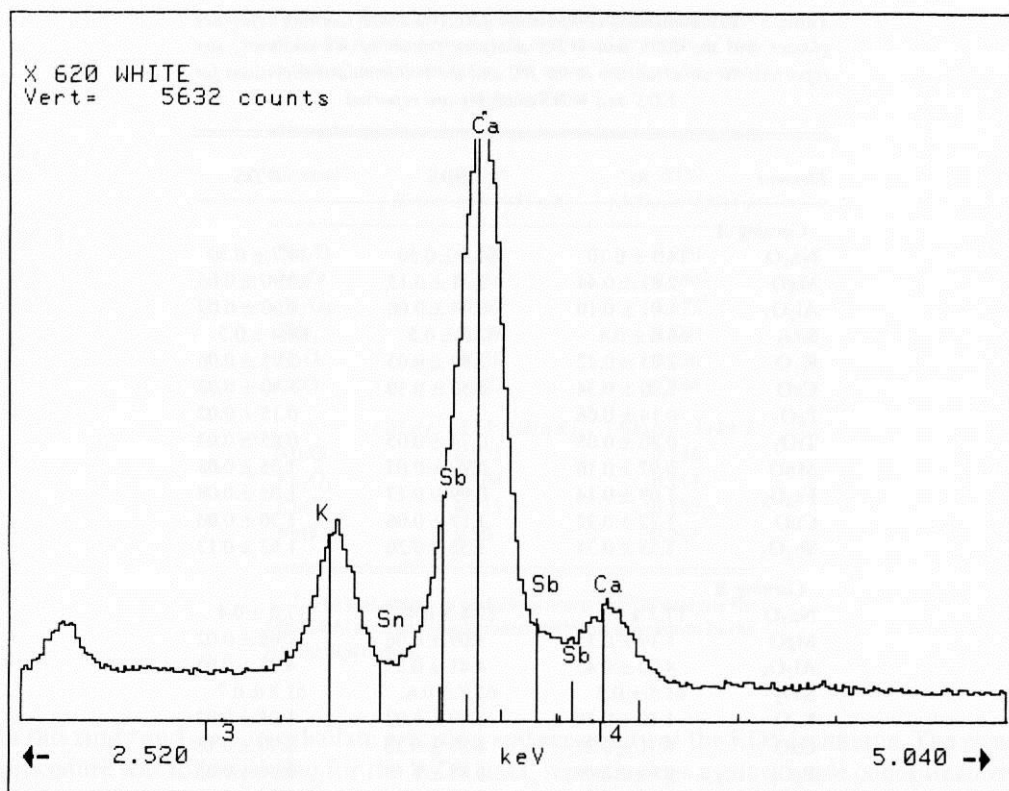
Figure 2   *EDS spectrum of opaque white Egyptian glass showing peak overlap of potassium/calcium and tin/antimony.*

deviation of the six EDS and WDS analyses are reported. An assessment of these data suggests that the results obtained by the two techniques are broadly comparable, and match very closely the accepted compositions. Exceptions are observed only for Pb and Sb, when present in concentrations close to the detection limit of WDS, which are not detectable with EDS.

It is interesting to observe that for many elements the uncertainties in the recommended composition are of the same order of magnitude or sometimes greater than the errors claimed by either EDS or WDS techniques. It can be concluded that the accuracy of microanalytical analyses of ancient glasses, if appropriate correction programs are used, is mainly determined by the uncertainties in the recommended composition of the reference glasses.

Sensitivity

Twenty-three trace elements of interest in the study of ancient glasses were analysed both with WDS and EDS techniques under routine analytical conditions. The sensitivity is determined as three standard deviations (3σ) of the background; the results expressed in ppm are reported in Table 1 as minimum detection limits (MDL). It can be observed that
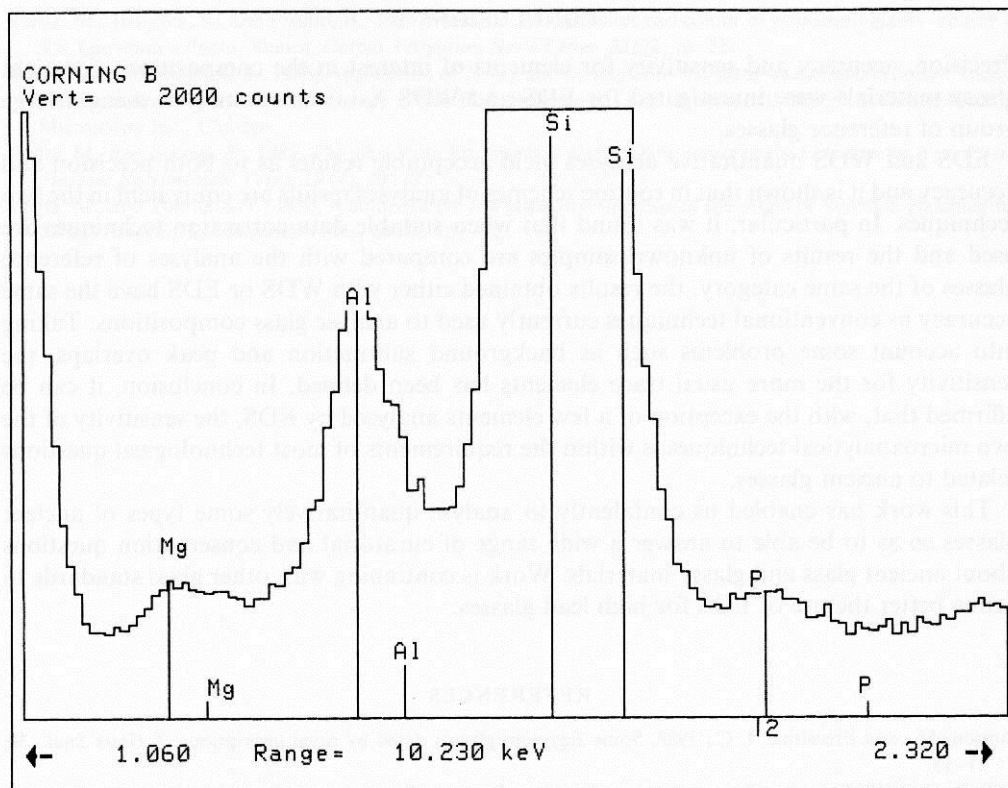
Figure 3   *EDS spectrum of Corning glass B showing large Si,Kα peak and P,Kα, Al,Kα and Mg,Kα peaks.*

for both techniques the detection limit varies according to the atomic number of the element concerned: light and heavy elements are less easy to detect.

As expected, the sensitivity is lower with the EDS technique by one to two orders of magnitude; even so, for many elements such as Na, Mg, Al, Cl, K, Ca, Mn, Fe and Cu it can be stated that the sensitivity of both WDS and EDS is sufficient for the analysis of ancient glasses. For other elements such as P, As, Sn, Sb, Ba and Pb, the MDL of the EDS technique are much higher owing to peak overlap. Figures 2 and 3 are partial EDS spectra showing peak overlap of the Ca,Kα and Sb,Lβ peaks, K,Kα and Sn,Lβ and interference of the Si,Kα peak with Mg, Al and P Kα peaks.

Some tests performed using peak deconvolution programs showed that in certain cases they yield excellent results and the MDL of these elements may lower to 800–1500 ppm. In other cases, for instance the P/Si overlap or in the cases of Sn and Sb determination in high potassium, high calcium glasses, deconvolution has no appreciable effects on sensitivity. Fluorine is not detectable in glasses with standard beryllium window EDS detectors; only using windowless or advanced thin window EDS detectors is fluorine detectable and only for concentrations beyond 3 wt. %. Such limitation is probably due to the O,Kα peak overlap; in fact, fluorine is detectable in concentrations lower than 1 wt. % in calcium fluoride crystals. It should be stressed that detection limits can be lowered by using counting times longer than the 20 and 400 seconds used for WDS and EDS respectively.

CONCLUSIONS

Precision, accuracy and sensitivity for elements of interest in the composition of ancient glassy materials were investigated for EDS and WDS X-ray microanalysis using a large group of reference glasses.

EDS and WDS quantitative analyses yield acceptable results as to both precision and accuracy and it is shown that in routine schemes of analyses results are equivalent in the two techniques. In particular, it was found that when suitable data correction techniques are used and the results of unknown samples are compared with the analyses of reference glasses of the same category, the results obtained either with WDS or EDS have the same accuracy as conventional techniques currently used to analyse glass compositions. Taking into account some problems such as background subtraction and peak overlaps, the sensitivity for the more usual trace elements has been defined. In conclusion, it can be affirmed that, with the exception of a few elements analysed by EDS, the sensitivity of the two microanalytical techniques is within the requirements of most technological questions related to ancient glasses.

This work has enabled us confidently to analyse quantitatively some types of ancient glasses so as to be able to answer a wide range of curatorial and conservation questions about ancient glass and glassy materials. Work is continuing with other glass standards to define better the use of EDS for high lead glasses.

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