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ORIGINAL PAPER

Critical assessment of the elemental composition of Corning archeological reference glasses by LA-ICP-MS

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Abstract Corning archeological reference glasses A, B, C, and D have been made to simulate different historic technologies of glass production and are used as standards in historic glass investigations. In this work, nanoseconds (193, 266 nm) and femtosecond (800 nm) laser ablation were used to study the elemental composition of Corning glasses using laser ablation inductively coupled plasma mass spectrometry. The determined concentrations of 26 oxides (Li_2O, B_2O_3, Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, V_2O_5, Cr_2O_3, MnO, Fe_2O_3, CoO, NiO, CuO, ZnO, Rb_2O, SrO, ZrO_2, SnO_2, Sb_2O_5, BaO, PbO, Bi_2O_3) are compared with values reported in the literature. Results show variable discrepancies between the data, with the largest differences found for Cr_2O_3 in Corning A; Li_2O, B_2O_3, and Cr_2O_3 in Corning B; and MnO, Sb_2O_5, Cr_2O_3, and Bi_2O_3 in Corning C. The best agreement between the measured and literature values was found for Corning D. However, even for this reference, glass re-evaluation of the data was necessary and new values for PbO, BaO, and Bi_2O_3 are proposed.

Keywords Glass · Standards · Archeometry · LA-ICP-MS

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Introduction

The knowledge about the elemental composition of historic glasses is crucial for establishing their age, provenance, or the technology used for their production [1–6]. The required chemical information can be obtained from instrumental techniques, which offer variable sensitivity as well as limits of detection [7–10] exploiting various reference materials to support method validation and evaluation of the measurement uncertainty. The limited collection of available solid reference materials limits the quality assurance and quality control when analyzing solids. Archeometrical analyses are additionally complicated by the uniqueness of the analyzed historic objects, and measurements need to be performed non-destructively or pseudo non-destructively using micro-sampling [7, 11–21].

For historic glass analysis, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a good choice, because it offers direct micro-sampling by focused laser beam and fast multielemental determination with low detection limits [7, 22–25]. This method has been widely and successfully used for elemental analysis of historic glasses [5, 11, 21, 26–29], although the lack of suitable matrix-matched solid standards is still recognized as an important limitation and prevents insights into the accuracy achievable with this technique.

Glass standards in analysis of historic objects

Taking into account the widely varying composition of historic glass, the selection of appropriate matrix-matched solid reference materials is difficult [2, 11]. The most popular glass reference materials are those which are available from NIST (National Institute of Standards and Technology) in form of wafers. These have been widely used as calibration materials

for LA-ICP-MS analysis of historic glass [21, 27–30]. The silicate matrix (Si-Na-Ca-Al) of NIST SRM 610 to 617 is doped with the well-known concentrations of 61 elements. However, the composition of historic glasses usually differs considerably from the major element composition of these reference materials. To meet these analytical needs, Corning archeological reference glasses: A, B, C, and D have been produced by the Corning Museum of Glass (USA). These materials reflect the different technologies of historic glass production. Glasses A and B mimic the composition typical for Egyptian, Mesopotamian, Roman, Byzantine, and Islamic glasses; C is similar to glasses from East Asia, and D reflects glasses, which have been produced from the seventeenth to the nineteenth centuries [2, 31, 32].

High purity synthetic oxides and carbonates, NaCl, $NH_4H_2PO_3$, alumina hydrate, natural $ZrSiO_4$, and SiO_2 have been used as precursor materials to produce the Corning glasses [31]. Trace elements have been mixed in two groups (Ti, Sn, B, Ba, Sr, Li, Rb and V, K, Ag, Zr, Ni, Zn, Bi) and ball-milled prior to incorporation. The precursor mixtures were melted, stirred, and quenched in deionized water, then crushed, and re-melted again. The rehomogenized melt was poured into 1-cm-thick sheets. Two groups of elements can be distinguished in the elemental composition of Corning glasses [31, 32]. The first group includes the elements which oxides have been determined by a number of techniques, i.e., gravimetry, polarography, flame photometry, atomic absorption, X-ray fluorescence, or neutron activation (SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, MnO, P_2O_5, TiO_2, Sb_2O_5, CuO, PbO, CoO, BaO, SnO_2, SrO, and ZnO). The second group includes the oxides for which nominal compositions were calculated from mass fractions of the precursor constituents added to the batch (B_2O_3, Li_2O, Rb_2O, V_2O_5, Cr_2O_3, NiO, ZrO_2, Bi_2O_3). It can be assumed that the results obtained by several laboratories should be more reliable then indicative information about the contents of the oxides calculated for the second group, although Corning archeological reference glasses are not characterized by a metrologically valid procedure. These glasses have been mainly used for estimation of the precision and accuracy of measurements in several investigations of historic glass objects [5, 11, 17, 27, 29, 30, 33–40], because large amounts of elemental concentration data have been published for them [11, 27, 31, 32, 37–40]. The contents of the literature values of the oxides used in this study are from Vicenzi [32] who referred to Brill [2] (Table 1).

Brief revision of the literature

Brill [2, 31] coordinated the first interlaboratory investigations of elemental compositions of the Corning archeological reference glasses and published recommended and nominal values. Tentative recommended values were given in 1971 [31], with emphasis that these preliminary values would need further evaluation. The final compositions of Corning glasses were published by Brill [2] in 1999, and they were then used as the recommended ones [32]. These values have been used for calibration in quantitative analyses of historic glasses and to check the accuracy of the methods used, although the principles of quality control were not always sufficiently documented [33, 40–43]. The deficiency of information about the obtained precision and accuracy can be noticed in some reports [33, 40, 43] as well as the lack of identifying the Corning glass used [42]. In some cases, even when the accuracy and precision were given and discussed in the text, the detailed results of these control measurements were omitted [17, 34, 35].

Corning C and D were used by Kuisma-Kursula [36, 37] to determine the accuracy of the measurements. Bronk and Freestone [38] validated the usefulness of the scanning electron microscopy/energy-dispersive X-ray analysis in analyzing glass objects with the use of Corning A and B. They described the influence of the procedure used for the preparation of the Corning glasses to the final results and reported problems with quantification of some oxides (Sb_2O_5, PbO in Corning B). Other authors [39] reported inconvenience of quantification of SnO_2, in Corning C. The most comprehensive and multitechnique (electron probe micro-analysis (EPMA), LA-ICP-MS, secondary ion mass spectrometry) investigations of Corning archeological reference glasses were described by Vicenzi et al. [32]. This study reports the determination of minor and trace elements and their distribution in the Corning glasses. The agreement of the presented EPMA results with recommended values is highly variable, while the general agreement between LA-ICP-MS and previously published data is within 5% to 20%. EPMA measurements validated heterogeneous distribution of some elements (SrO, ZnO in all glasses, and BaO, SnO_2 in Corning B), while LA-ICP-MS indicated relatively high degree of the compositional uniformity of all the Corning glasses which were examined using 193 nm laser with beam diameter of 23 μm. The details of the LA-ICP-MS results have been discussed for Corning A, B, and D. A value of the MnO content in Corning C has been reported here for the first time [32].

LA-ICP-MS has also been applied by Shortland et al. [30] for the determination of trace elements in glass objects using Corning A as a quality control for the accuracy of the measurements. The authors concluded that the agreement of their results with the values recommended by Vicenzi et al. [32] was rather poor. It is important to note that the most significant discrepancies have been observed for Cr_2O_3 (161%), PbO, SnO_2, and SrO (about 30%). The quantitative results of MnO in Corning C with a mean content of 0.001 wt.% obtained in our laboratory [11] or published by Dussubieux [26, 27] varied strongly from the value given

Table 1 Major, minor and trace element oxide compositions of Corning archeological reference glasses A, B, C, D [32], and NIST 610

	Corning A, wt.%	Corning B, wt.%	Corning C, wt.%	Corning D, wt.%	NIST SRM 610, wt.%
SiO_2	66.56	61.55	34.87	55.24	70.20
Al_2O_3	1.00	4.36	0.87	5.30	1.880
Fe_2O_3	1.09	0.34	0.34	0.52	0.058
MgO	2.66	1.03	2.76	3.94	0.077
CaO	5.03	8.56	5.07	14.8	11.50
Na_2O	14.3	17.0	1.07	1.20	12.80
K_2O	2.87	1.00	2.84	11.3	0.059
MnO	1.00	0.25	0.82	0.55	0.056
P_2O_5	0.13	0.82	0.14	3.93	0.078
TiO_2	0.79	0.089	0.79	0.38	0.072
Sb_2O_5	1.75	0.46	0.03	0.97	0.039
CuO	1.17	2.66	1.13	0.38	0.054
PbO	0.12	0.61	36.7	0.48	0.045
CoO	0.17	0.046	0.18	0.023	0.052
BaO	0.56	0.12	11.4	0.51	0.047
SnO_2	0.19	0.04	0.19	0.10	0.050
SrO	0.10	0.019	0.29	0.057	0.059
ZnO	0.044	0.19	0.052	0.10	0.056
B_2O_3	0.20	0.02	0.20	0.10	0.115
Li_2O	0.01	0.001	0.01	0.005	0.104
Rb_2O	0.01	0.001	0.01	0.005	0.047
V_2O_5	0.006	0.03	0.006	0.015	0.079
Cr_2O_3	0.001	0.005	0.001	0.003	0.057
NiO	0.02	0.10	0.02	0.05	0.057
ZrO_2	0.005	0.025	0.005	0.013	0.059
Bi_2O_3	0.001	0.005	0.001	0.003	0.040

by Vicenzi [32]. Dussubieux [27] reported for few elements, not only Mn in Corning C, that the concentrations provided by Brill [2] might not be accurate.

Aim of the work

The evaluation of the published data revealed various inconsistencies between the recommended and determined values of several constituents of Corning archeological reference glasses, which are of interest to both archeologists and art historians. Corning archeological reference glasses are widely used as calibration or validation materials for the analysis of historic glass. Therefore, the reliability and usefulness of the available data requires a careful re-examination.

The aim of this work was focused on a detailed investigation of the composition of Corning archeological reference glasses A, B, C, and D using LA-ICP-MS. Therefore, various nanosecond (λ=193, 266 nm) and femtosecond (λ = 800 nm) laser wavelengths were used for sampling. The quantification scheme is based on NIST 610, and the results of each individual sampling using commonly applied wavelengths for archeological studies are summarized and discussed in comparison to literature data.

Experimental

Samples and standard

Three different types of archeological reference glasses, which were fabricated to mimic historic glass recipes, were investigated: Corning glass A and Corning glass B are Na-rich/Ca-bearing silicates; Corning Glass C is rich in Pb and Ba while Corning Glass D is K- and Ca-rich silicate [31, 32] (Table 1).

Standard glass NIST SRM 610 was used as the external standard. The similarity of the bulk composition of NIST 610 to the composition of the Corning glasses [32] was considered to be close to the matrix composition of the Corning glass matrix. Therefore, reduced influence of element fractionation effects on the calculated results was

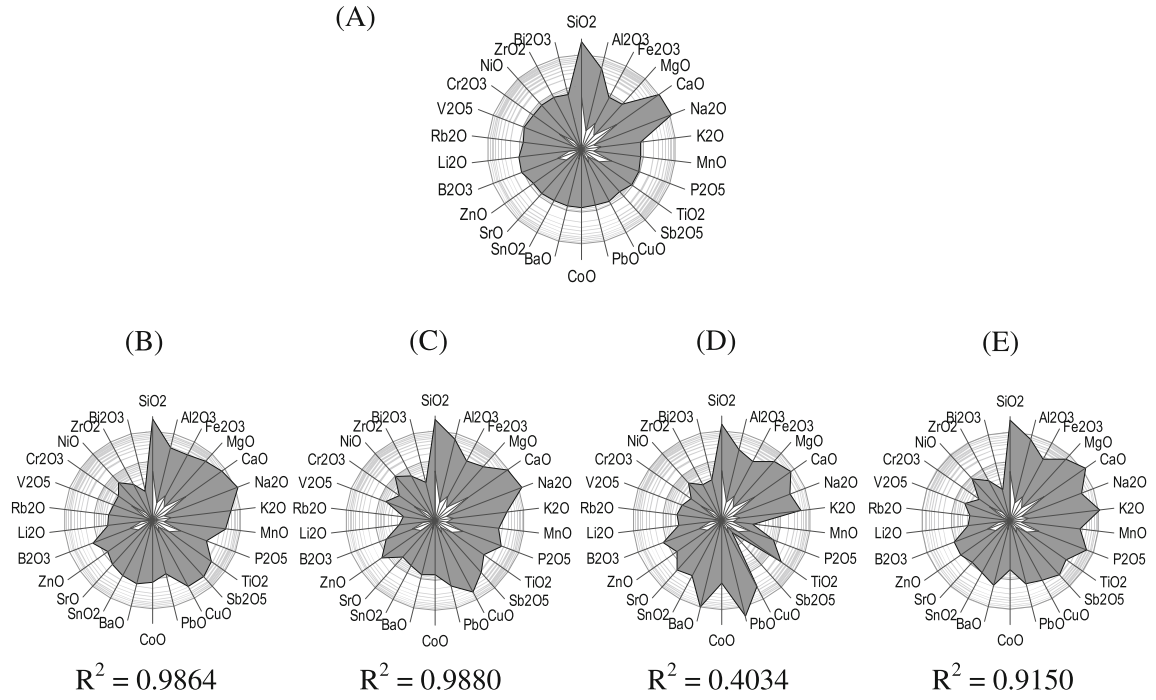

Fig. 1 The relationship between the oxides concentration in calibration: NIST 610 (*A*) and unknown samples: Corning A (*B*); Corning B (*C*), Corning C (*D*), and Corning D (*E*). *White patterns* in the *middle* part of the chart visualizes limits of detection for the respective elements. The values of R^2 given below the charts show correlation coefficient of the NIST vs Cornings

assumed. The comparison of the calibration materials and samples with the correlation coefficient indicating the relationship between the oxides concentration in calibration and unknown samples is given in Fig. 1. The matrix-matching is acceptable for three of the four investigated glasses (R^2= 0.9864 for Corning A; R^2=0.9880 for Corning B, and R^2= 0.9150 for Corning D), and it is most significantly different for the Corning C (R^2=0.4034), when compared with the other glasses.

Instrumentation

LA-ICP-MS was used in this study with the involvement of three different laser systems (Table 2):

1. The laser ablation system LSX-200$^+$ (CETAC, USA) combining a stable, environmentally sealed 266-nm UV laser (Nd–YAG, solid-state, Q-switched) was coupled to inductively coupled plasma mass spectrometer ELAN 9000 (Perkin Elmer SCIEX, Canada). All experiments were performed using Ar as the carrier gas.
2. The 193-nm ArF-Excimer laser (GeoLas Compex, MicroLas, Goettingen, Germany) was coupled to ELAN 6100 (Perkin Elmer, Norwalk, CT, USA).
3. The Ti/sapphire femtosecond laser system (Legend, Coherent Inc., Santa Clara, CA, USA) was coupled to Elan DRC II (Perkin Elmer SCIEX, Thornhill, Canada). All ablations

Table 2 Instrumental settings, operating conditions, and data acquisition parameters

Laser system parameters and settings			
Laser ablation characteristics and settings			
Wavelength, nm	193	266	800
Pulse duration	15 ns	5 ns	150 fs
Energy density, Jcm^{-2}	23.9	15.9	15.1
Beam diameter, μm	40	100	130
Repetition rate, Hz	10	10	5
ICP MS characteristics and settings			
RF Power	1370	1050	1350
Neb. gas flow rate	0.85	0.98	1.0
Plasma gas flow rate	16.7	16.0	17.0
Carrier gas	He	Ar	He
ICP MS data acquisition parameters			
Scanning mode		Peak hopping	
Dwell time, ms		10	
Pre-integration time, s		30	
Integration time, s		60	
Isotopes monitored	^{7}Li, ^{11}B, ^{23}Na, ^{25}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{39}K, ^{42}Ca, ^{48}Ti, ^{49}Ti, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{61}Ni, ^{65}Cu, ^{66}Zn, ^{85}Rb, ^{88}Sr, ^{90}Zr, ^{118}Sn, ^{121}Sb, ^{135}Ba, ^{137}Ba, ^{208}Pb, ^{209}Bi		

which were carried out using the 193 and 800 nm lasers were performed using He as the sample carrier gas, which was mixed with Ar before entering the ICP.

For all measurements, the samples were placed inside the ablation cell with NIST SRM 610. The calibration material was measured twice at the beginning and twice at the end of each run to correct for instrumental drift using the algorithm proposed by Longerich et al. [44]. Seven replicate single point ablations at locations randomly selected on the glass surface were carried out on each sample. Transient signals were recorded and evaluated for subsequent elemental quantification. The LA-ICP-MS signals were background-corrected and integrated using LAMTRACE program developed by Jackson [45]. Table 3 summarizes the average limits of detection for the different types of laser wavelengths used for sampling (for crater diameter, see operating conditions, Table 2).

The results for all samples were calculated using SiO_2 as the internal standard, applying the data displayed in Table 1. Normalization was performed to the total content reported by Vicenzi [32] as 99.79 wt.% for Corning A; 99.33 wt.% for Corning B; 99.80 wt.% for Corning C; and 99.97 wt.% for Corning D. Therefore, although the initial contents of SiO_2 as the internal standard were given according to the literature [34], the final contents differed from these recommended values after normalization.

Table 3 Calculated limits of detection (LOD) for the different types of laser wavelengths used for sampling

wt.%	LOD_{193}	LOD_{266}	LOD_{800}
SiO_2	0.02110	0.01640	0.00925
Al_2O_3	0.00018	0.00012	0.00004
Fe_2O_3	0.00068	0.00048	0.00019
MgO	0.00015	0.00030	0.00010
CaO	0.00553	0.02040	0.00134
Na_2O	0.00007	0.00003	0.00017
K_2O	0.00016	0.00006	0.00008
MnO	0.00006	0.00001	0.00001
P_2O_5	0.00103	0.00089	0.00074
TiO_2	0.00024	0.00028	0.00007
Sb_2O_5	0.00004	0.00004	0.00002
CuO	0.00009	0.00003	0.00004
PbO	0.00002	0.00002	0.00002
CoO	0.00001	0.00001	0.00001
BaO	0.00004	0.00002	0.00002
SnO_2	0.00002	0.00003	0.00000
SrO	0.00001	0.00001	0.00001
ZnO	0.00015	0.00060	0.00004
B_2O_3	0.00042	0.00023	0.00034
Li_2O	0.00006	0.00002	0.00004
Rb_2O	0.00001	0.00001	0.00001
V_2O_5	0.00003	0.00002	0.00001
Cr_2O_3	0.00045	0.00015	0.00007
NiO	0.00005	0.00070	0.00008
ZrO_2	0.00001	0.00001	0.00001
Bi_2O_3	0.00001	0.00001	0.00001

Results and discussion

Analysis of corning archeological reference glasses by means of LA-ICP-MS

The results of Corning archeological reference glasses [31, 32] measured using various laser wavelengths and pulse width for sampling by LA-ICP-MS are given in Table 4. It was found that the results acquired with different laser wavelengths varied significantly and that the 193 nm ns or 800 nm fs lasers provided the comparable results, while the 266 nm ns laser showed most significant deviations.

Homogeneity of Corning glasses

The homogeneity of the Corning glasses has already been reported by Vicenzi et al. [32]. The majority of the concentrations of the elements reported in Table 4 were determined with relative standard deviations less than 5%. The mean Sb_2O_5 in Corning C is the only exception, with the high relative standard deviations obtained for the all laser wavelengths used in this study (RSD=19% for 193 ns-laser, RSD=12% for 266 ns-laser, and RSD=26% for 800 fs-laser ablation). The mean Sb_2O_5 in Corning C was calculated consequently as equal to the c=0.0001 wt.%. irrespective of the laser wavelength. However, these results suggest an inhomogeneous distribution of Sb in Corning C.

Comparison of the results obtained after ablation by means of 193 ns, 266 ns, and 800 Fs lasers

The ratios of the measured to the literature [32] values for each oxide element of the Corning glasses are displayed in Fig. 2.

The deviations of the results acquired within this study to the recommended values caused variable shapes of radar-charts for the overall chemical composition of particular Corning glasses (Fig. 2). Analogous shapes of the charts for different laser wavelengths could be obtained if the interaction of these lasers with sample of identical composition was similar. However, it is known that both laser wavelength and pulse duration affect the degree of fractionation, therefore, some differences of the results were expected. Fractionation effects often are reduced by the use of shorter wavelengths (e.g., ns-193 nm) and shorter

Table 4 Major, minor, and trace element oxide compositions of Corning archeological reference glasses A, B, C, and D

wt.%	193 nm	266 nm	800 nm	193 nm	266 nm	800 nm
	Corning A			Corning B		
SiO_2	67.82 (0.4)	NA	68.90 (0.2)	62.02 (0.3)	57.72 (3.1)	63.94 (0.3)
Al_2O_3	0.820 (2.4)	NA	1.08 (3.2)	4.63 (1.3)	7.76 (1.6)	4.02 (1.4)
Fe_2O_3	0.979 (1.3)	NA	0.979 (0.1)	0.311 (1.5)	0.268 (0.7)	0.307 (1.2)
MgO	2.50 (1.6)	NA	2.11 (0.4)	0.988 (0.7)	1.18 (2.0)	0.789 (1.7)
CaO	4.94 (1.9)	NA	5.36 (3.3)	8.75 (1.4)	13.7 (0.6)	9.12 (1.2)
Na_2O	13.4 (0.7)	NA	13.6 (1.2)	16.5 (0.5)	13.9 (2.0)	16.0 (0.6)
K_2O	3.46 (1.1)	NA	2.46 (1.2)	1.30 (1.4)	0.876 (2.6)	0.827 (2.5)
MnO	1.13 (1.3)	NA	0.969 (0.7)	0.241 (1.2)	0.238 (0.9)	0.230 (0.9)
P_2O_5	0.085 (0.8)	NA	0.088 (1.1)	0.611 (0.8)	0.417 (2.8)	0.633 (1.2)
TiO_2	0.739 (2.2)	NA	0.771 (3.7)	0.099 (1.9)	0.145 (1.1)	0.101 (0.9)
Sb_2O_5	1.86 (1.0)	NA	1.44 (1.4)	0.418 (1.8)	0.289 (1.1)	0.401 (0.8)
CuO	1.10 (1.8)	NA	1.19 (0.5)	2.82 (1.7)	2.23 (4.4)	2.57 (0.6)
PbO	0.073 (0.9)	NA	0.059 (2.9)	0.532 (2.5)	0.388 (1.5)	0.331 (2.3)
CoO	0.170 (1.3)	NA	0.167 (0.7)	0.043 (0.8)	0.037 (2.4)	0.043 (1.0)
BaO	0.46 (2.2)	NA	0.278 (3.3)	0.077 (2.5)	0.109 (3.0)	0.052 (5.1)
SnO_2	0.171 (1.1)	NA	0.173 (0.7)	0.024 (0.9)	0.022 (4.2)	0.024 (0.4)
SrO	0.106 (1.8)	NA	0.110 (2.4)	0.017 (1.9)	0.028 (2.3)	0.019 (1.0)
ZnO	0.048 (1.6)	NA	0.051 (2.4)	0.211 (1.7)	0.177 (1.4)	0.216 (0.9)
B_2O_3	0.274 (5.3)	NA	0.214 (1.1)	0.036 (6.4)	0.021 (0.9)	0.032 (3.4)
Li_2O	0.011 (2.9)	NA	0.011 (1.9)	0.003 (4.6)	0.002 (4.3)	0.003 (0.9)
Rb_2O	0.009 (1.4)	NA	0.010 (0.4)	0.001 (2.3)	0.001 (6.4)	0.001 (1.1)
V_2O_5	0.007 (2.3)	NA	0.007 (1.2)	0.034 (1.2)	0.029 (2.1)	0.033 (0.6)
Cr_2O_3	0.003 (4.9)	NA	0.003 (8.0)	0.010 (3.1)	0.008 (2.1)	0.009 (2.4)
NiO	0.023 (2.2)	NA	0.028 (11)	0.094 (1.1)	0.079 (3.1)	0.091 (1.5)
ZrO_2	0.005 (2.7)	NA	0.006 (3.8)	0.023 (2.7)	0.053 (1.6)	0.025 (1.9)
Bi_2O_3	0.001 (3.0)	NA	0.001 (5.7)	0.004 (2.4)	0.004 (0.7)	0.004 (0.8)
	Corning C			Corning D		
SiO_2	31.41 (0.5)	32.87 (2.1)	28.36 (0.3)	28.36 (1.2)	56.59 (3.3)	57.11 (0.2)
Al_2O_3	0.736 (1.2)	1.58 (2.2)	0.772 (0.8)	5.19 (3.0)	4.82 (1.9)	4.40 (0.9)
Fe_2O_3	0.262 (0.8)	0.244 (3.5)	0.277 (0.9)	0.460 (2.1)	0.459 (2.9)	0.480 (0.8)
MgO	2.50 (0.7)	3.00 (1.4)	2.02 (1.1)	3.87 (1.3)	4.43 (0.6)	3.86 (0.9)
CaO	4.75 (0.8)	8.24 (0.7)	4.84 (0.4)	14.7 (2.4)	18.3 (2.4)	15.5 (0.6)
Na_2O	0.966 (0.6)	1.17 (1.4)	0.848 (1.3)	1.30 (1.4)	1.31 (2.1)	1.31 (1.0)
K_2O	3.21 (0.3)	1.87 (1.4)	2.45 (1.8)	14.2 (0.7)	8.69 (1.5)	11.1 (0.2)
MnO	0.001 (3.1)	0.001 (3.6)	0.001 (4.8)	0.597 (1.1)	0.499 (3.3)	0.531 (0.8)
P_2O_5	0.068 (1.8)	0.054 (3.9)	0.062 (0.4)	3.05 (0.9)	2.26 (4.4)	3.08 (0.8)
TiO_2	0.706 (0.6)	1.10 (1.6)	0.753 (0.4)	0.356 (2.7)	0.413 (2.9)	0.371 (0.6)
Sb_2O_5	0.0001 (19)	0.0001 (12)	0.0001 (26)	0.961 (1.9)	0.572 (3.4)	0.780 (0.3)
CuO	1.10 (0.5)	1.00 (2.7)	1.15 (0.4)	0.370 (1.6)	0.356 (1.7)	0.37 (0.9)
PbO	39.8 (0.5)	34.2 (2.7)	47.8 (0.4)	0.241 (1.4)	0.213 (2.2)	0.222 (0.7)
CoO	0.164 (0.4)	0.150 (4.9)	0.170 (0.7)	0.018 (1.3)	0.018 (2.8)	0.020 (6.6)
BaO	13.3 (0.6)	13.4 (2.1)	9.47 (2.2)	0.291 (1.8)	0.374 (3.2)	0.285 (3.6)
SnO_2	0.163 (0.8)	0.173 (1.5)	0.172 (0.8)	0.084 (1.9)	0.080 (6.9)	0.088 (0.8)
SrO	0.333 (0.5)	0.439 (4.1)	0.308 (1.5)	0.055 (2.6)	0.070 (5.1)	0.059 (0.3)
ZnO	0.042 (1.1)	0.050 (3.3)	0.046 (0.5)	0.102 (1.6)	0.097 (3.7)	0.104 (0.7)
B_2O_3	0.187 (1.3)	0.154 (2.3)	0.167 (1.0)	0.105 (3.0)	0.083 (1.3)	0.107 (0.7)
Li_2O	0.009 (2.4)	0.008 (3.2)	0.008 (0.8)	0.006 (1.3)	0.006 (3.4)	0.006 (0.9)
Rb_2O	0.008 (0.5)	0.008 (5.0)	0.010 (0.3)	0.005 (2.0)	0.005 (1.7)	0.005 (1.1)

Table 4 (continued)

wt.%	193nm	266nm	800nm	193nm	266nm	800nm
V_2O_5	0.006 (0.9)	0.006 (2.2)	0.007 (0.6)	0.017 (1.1)	0.017 (2.3)	0.018 (0.6)
Cr_2O_3	0.002 (3.3)	0.002 (8.1)	0.003 (8.3)	0.003 (4.1)	0.003 (2.2)	0.004 (1.0)
NiO	0.018 (1.4)	0.016 (6.9)	0.022 (4.7)	0.048 (1.4)	0.048 (3.3)	0.053 (10)
ZrO_2	0.004 (1.4)	0.012 (6.3)	0.006 (0.4)	0.011 (4.9)	0.014 (1.9)	0.012 (0.7)
Bi_2O_3	0.004 (1.1)	0.005 (4.2)	0.007 (1.0)	0.001 (3.7)	0.001 (2.9)	0.001 (1.8)

The average results expressed in weight percentage [wt.%] obtained after ablation of the glasses with various laser wavelengths are given in the subsequent columns—193, 226, or 800 nm, respectively

RSD values are given in brackets (percent)

NA not analyzed

pulse widths (e.g., fs-800 nm) [46, 47], and the results obtained with these laser wavelengths for the most of elements were comparable.

The analyzed Corning glass results obtained using a 266 nm laser differed to some extent from the results obtained using ablation with 193- and 800-nm wavelength lasers. The most pronounced difference was observed for the soda–lime–silica glass (Fig. 2, Corning B) but can also be seen in the pattern for the high-lead-and-barium glass (Fig. 2, Corning C). The differences of the respective results for potash–lime–silica glass (Fig. 2, Corning D) are low. The highest differences in all samples were observed for Al_2O_3, CaO, ZrO_2, Bi_2O_3, SrO, and K_2O when ablating at 266 nm when compared with 193 or 800 nm lasers. Inconsistent results for PbO were obtained for the high-lead-and-barium glass (Corning C).

Apart from the mentioned inconsistencies, some systematic variations from the recommended values for each Corning glass can be noticed, and these values will be discussed in more detail. Independent of the lasers used for ablation,

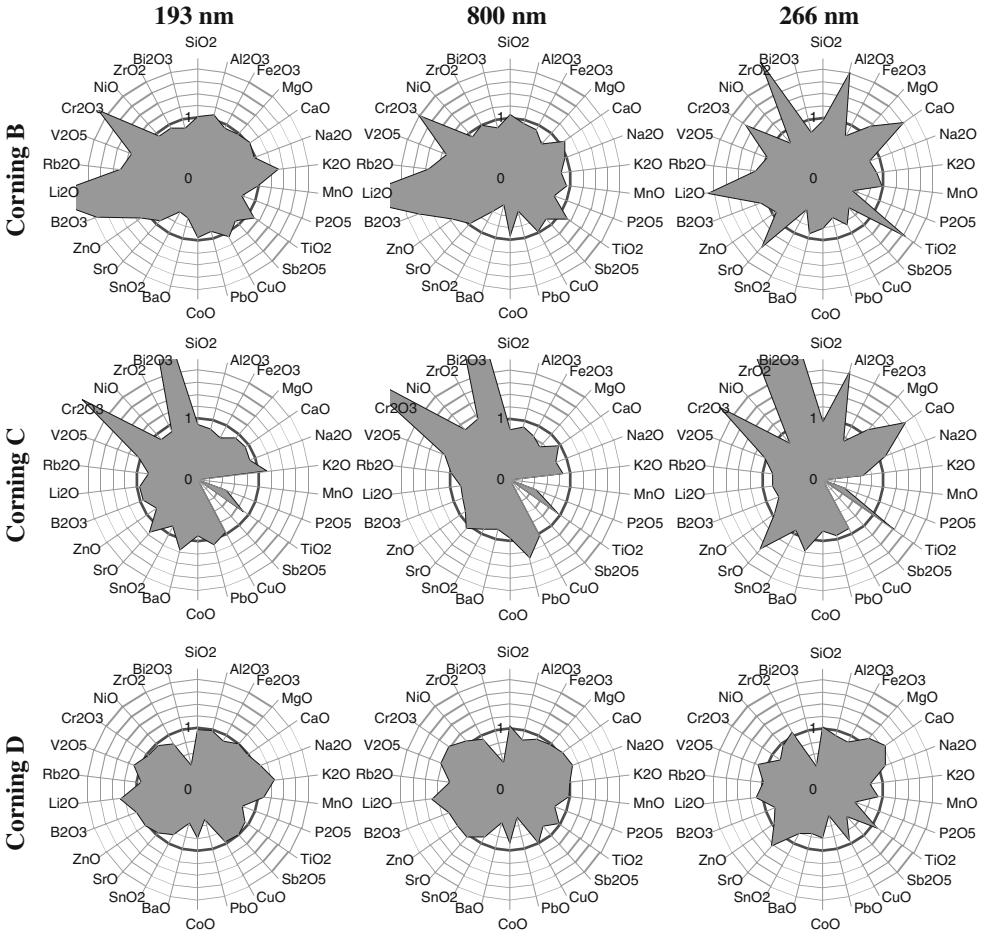

Fig. 2 The ratios of the measured to the recommended values calculated for the results obtained by means of LA-ICP-MS for Corning B, C, and D after ablation by 193, 800, and 266 nm lasers

all data showed an underestimation of SnO_2 and overestimation of Li_2O and Cr_2O_3 in Corning B as well as underestimation of MnO and Sb_2O_2 and overestimation of Cr_2O_3 and Bi_2O_3 in Corning C with respect to the recommended values [32]. The data for Corning D are in good agreement with the data reported by Brill [31], which indicates and accurate characterization. However, Bi_2O_3, PbO, and BaO differ significantly and indicate an overestimation in the literature.

The 266 nm shows the largest and non-coherent, with the other lasers (193 ns and 800 fs lasers), deviations from the expected values, therefore, the quantitative results obtained using this laser wavelength are excluded from the further comparisons. The use of 193-nm laser wavelength creates smaller particles which are more effectively transported and ionized in the plasma and thus exhibit less elemental fractionation compared with 266 nm lasers [48]. Also, the use of femtosecond laser pulses (800 nm) has been reported to be beneficial for LA-ICP-MS measurements [49]. Therefore, the data acquired using these two types of lasers will be discussed in more detail.

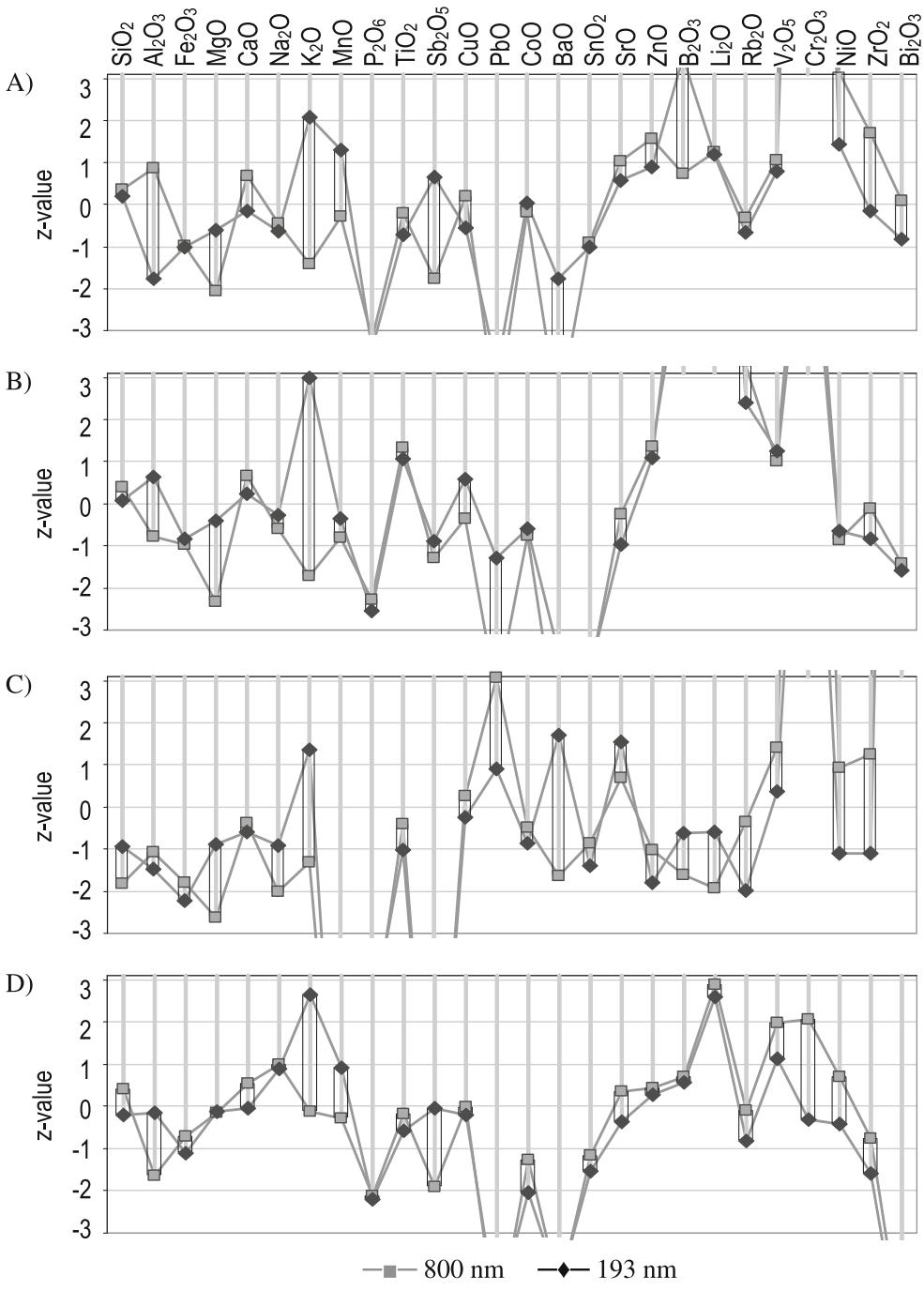

Fig. 3 z-Score values for the LA-ICP-MS results of Corning glasses analyzed using 193 and 800 nm laser ablation

Recommended and determined values for 800 and 193 nm lasers

The recommended contents of the oxides were compared with data acquired using 800 and 193 nm. Discrepancies between these values were evaluated using the z-scores for each individual result. The target standard deviation was assigned as 10% of the recommended value for each element, because the information about the relative standard deviations could only be extracted from the report describing individual results of four repetitive inductively coupled plasma-optical emission spectrometry measurements of Corning glasses from Brill [2]. The calculated values of RSDs exceeded 10% for three oxides: PbO in Corning A (X_{rec}=0.120 wt.%, SD_t=0.043 wt.%, RSD=35.5%), Al_2O_3 in Corning C (X_{rec}=0.870 wt.%, SD_t=0.115 wt.%., RSD=13.2%), and Sb_2O_5 in Corning C (X_{rec}=0.025 wt.%, SD_t=0.006 wt.%, RSD=23.1%). The high RSD of the mean content was confirmed by our LA-ICP-MS study only for Sb_2O_5 in Corning C. Therefore, the SD_t applied was taken from Brill [2].

Generally, the z-scores are acceptable (within ±2; 95%) and unacceptable when the score is outside ±3 (greater than 99%), and questionable with intermediated values. The calculated z-score values for the oxides in Corning glasses were used to indicate discrepancies between the measured and recommended data (Fig. 3). The values which were outside the calculated threshold for both wavelengths (193 and 800 nm) indicated the need of a re-evaluation of the recommended concentrations in the Corning glass. Most of the results acquired in this study agree with the published and recommended values [2, 31, 32], but some discrepancies were found for different oxides in all Corning glasses (Fig. 3). The results of P_2O_5, PbO, BaO, and Cr_2O_3 were found unacceptable in Corning A; BaO, SnO_2, B_2O_5, Li_2O, Cr_2O_3, and BiO_3 in Corning B; MnO, P_2O_5, Sb_2O_5, Cr_2O_3, and Bi_2O_3 in Corning C; and PbO, BaO, and Bi_2O_3 in Corning D.

Re-evaluation of the elemental composition of Corning archeological reference glasses

Although the use of fs laser typically decreases laser-induced elemental fractionation, increased errors due to mass-load-induced matrix effects in the ICP can influence the quantification capabilities and figures of merit such as accuracy [50–53]. Furthermore, a detailed study about the influence of the wavelength on the accuracy needs further validation and has not been studied as extensively as for a 193 nm ns laser ablation system.

Therefore, the re-evaluation of the recommended values is proposed using the mean of seven LA-ICP-MS measurements at 193 nm. These values are summarized in Table 5 with their standard deviations (SD) and compared with values from literature [2, 27, 30–32].

Table 5 New data set expressed in wt.%

		Brill [2]	**Brill** [31]	**Vicenzi** [32]	NEW_{193}±SD	Literature data [27, 30]
Corning A	**P_2O_5**	**0.13**	**0.13**	**0.13**	0.0847±0.0007	0.0341±0.0022 [30]
	PbO	**0.12**	**0.05**	**0.12**	0.0725±0.0007	0.0596±0.0022 [30]
	BaO	**0.56**	**0.55**	**0.56**	0.46±0.01	0.3905±0.0125 [30]
	Cr_2O_3	0.001	0.001	0.001	0.0033±0.0002	0.0018 [30]
Corning B	**BaO**	**0.12**	**0.10**	**0.12**	0.077±0.002	0.08±0.02 [27]
	SnO_2	**0.04**	**0.03**	**0.04**	0.0241±0.0002	0.021±0.001 [27]
	B_2O_3	0.02	0.02	0.02	0.035±0.001	–
	Cr_2O_3	0.005	0.005	0.005	0.0096±0.0003	–
	Bi_2O_3	0.005	0.005	0.005	0.0042±0.0001	–
Corning C	**P_2O_5**	**0.14**	**0.10**	**0.14**	0.068±0.001	0.07±0.03 [27]
	MnO	–	–	**0.82**	0.0011±0.0000	0.0013±0.0002 [27]
	Sb_2O_5	**0.03**	–	**0.03**	0.0001±0.0000	0.0002±0.0001 [27]
	Cr_2O_3	0.001	0.001	0.001	0.0023±0.0001	–
	Bi_2O_3	0.001	0.001	0.001	0.0040±0.0001	–
Corning D	**PbO**	**0.48**	**0.25**	**0.48**	0.241±0.003	0.23±0.01 [27]
	BaO	**0.51**	**0.33**	**0.51**	0.291±0.005	0.38±0.09 [27]
	Bi_2O_3	0.003	0.002	0.0025	0.0012±0.0000	–

Bold font was used to indicate the oxides for which recommended values were given by Brill [2]; normal-font entries indicate nominal composition. The preliminary, tentative values proposed by Brill [31] are also shown here

Conclusions

Three types of archeological reference glasses, reflecting different historical technologies of glass production, were investigated using LA-ICP-MS. The results obtained using different laser wavelengths and pulse durations (nanoseconds, 193 and 266 nm, and femtoseconds, 800 nm) were compared among each other and to recommended values from the literature. Comparison of the re-evaluated values which were proposed here with the data recommended by Brill [2, 31] indicated that some tentative values [31] were closer to the data set generated in this study using a 193 and an 800 nm laser for sampling then the values published later on [2]. The recommended quantification especially of PbO in Corning A, BaO in Corning B, P_2O_5 or Sb_2O_5 in Corning C, and PbO or BaO in Corning D were overestimated in the final report [2], comparing to the published preliminary results [31].

Based on this LA-ICP-MS study, some significant discrepancies were found. The data indicate that the 266 nm laser ablation used for sampling is not suitable for quantification of these glasses using NIST 610 for calibration. Therefore, the data set generated in this study using a 193 and an 800 nm laser for sampling was compared with the recommended glass composition. The concentrations of P_2O_5, PbO, BaO, and Cr_2O_3 in Corning A, as well as BaO, SnO_2, B_2O_5, Li_2O, Cr_2O_3, and BiO_3 in Corning B differ most significant, and some new values are proposed. This confirms reports in the literature where the determination of some trace elements, including Sn, have been reported to be difficult (Corning B). Similar reports on Cr, Rb, and Bi in Corning C have been found. Therefore, corrected values for MnO, P_2O_5, Sb_2O_5, Cr_2O_3, and Bi_2O_3 in Corning C and PbO, BaO, and Bi_2O_3 in Corning D are also reported. All other oxides contents in the various Corning glasses were quantified by LA-ICP-MS with good agreement to the data reported in the literature [2, 31, 32].

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