RESEARCH PAPER

The Corning Archaeological Reference Glasses: New Values for “Old” Compositions

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The Corning Archaeological Reference Glasses are widely used as standards in the chemical analysis of archaeological and historical glasses, as their compositions were designed to approximate those of major glass types in antiquity. Since their development in the 1960s, their compositions have been revisited and updated. This paper provides a brief overview of the Corning glasses, and addresses two of the last three elements to be re-evaluated: the recommended values for the concentrations of $\text{SO}_3$ and Cl were, until now, based on theoretical values. Data for these elements were collected using electron microprobe, and used together with published data to suggest new values. Finally, a complete list with the most up-to-date compositions for the four Corning glasses is compiled for the benefit of other analysts.

Keywords: Archaeometry; glass; analysis; corning; reference standards; methodology

Introduction

The Corning Archaeological Reference Glasses are widely used as standards in the analysis of archaeological and historical glasses, as their compositions were designed to approximate those of major glass types in antiquity. Scientific analysis of glass has played an important role in archaeology in recent years, in the study of raw materials, provenance determination, glass-making technology, the organisation of production and the recycling of glass (cf. Rehren and Freestone, 2015). Reference standards are used in chemical analysis to calibrate the equipment, to test the performance of the analytical equipment and the quality of the data generated, and to indicate the degree to which data are comparable with other data. To achieve this, the reference material must be homogeneous and its composition well-characterised.

Since the development of the Corning glasses, their elemental compositions have been re-evaluated and new updated values suggested, most recently by Wagner et al (2012). However, the concentrations of three elements were not re-examined in that study and the values are still based on theoretical values. This paper provides a brief overview of the Corning reference glasses and recommendations for new values for the concentrations of two of these elements; sulphur and chlorine. These elements can be studied to understand technological processes involved in the making of glass. Sulphur concentrations can be an indicator of the chemical properties giving the glass its colour and the redox conditions of the furnace (Schreurs and Brill, 1984;
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Beerkens, 2003; Freestone and Stapleton, 2015), whereas chlorine concentrations serve as a marker of repeated melting or recycling (Al-Bashaireh et al., 2016), the addition of salt as a raw material (Gérth, Wedepohl and Heide, 1998; Wedepohl, 2003), and the melting temperature of the glass (Rehren, 2000). Both elements are also related to deterioration processes (Schreiner et al., 1999).

Overview of the Corning Archaeological Reference Glasses

Robert Brill and The Corning Museum of Glass initiated, and were central to, a project to improve the analysis of archaeological glass by developing four reference glasses with compositions similar to those of common ancient glasses: Corning A and B are soda-lime silicate glasses that were designed to resemble ancient Egyptian, Mesopotamian, Roman, Byzantine and Islamic plant ash and natron glasses; Corning C is a high-lead, high-barium glass, similar to some East Asian glasses; and Corning D is a potash-lime silicate glass based on Medieval European compositions (Brill, 1965, 1972).

The glasses were prepared using chemicals of known purity that were weighed out according to the target compositions and ball-milled for 16 hours to ensure homogeneous mixing before melting (details of the procedure described in Brill 1965 and in Brill 1972). Theoretical compositions were calculated based upon the mixtures (published in Brill, 1972). Sulphur and chlorine were added to the mixtures using sodium sulphate and sodium chloride, and their ultimate concentrations estimated assuming 70% retention of SO$_3$ and 80% retention of Cl. The glasses were distributed to multiple laboratories (cf. Brill, 1972 Appendix I) for analysis by numerous methods without prior knowledge of their theoretical composition, and “tentative” compositions were then recommended (Brill, 1972 Appendix IV). In 1999, Brill published new recommended values for the four glasses based upon replicate analyses by inductively coupled plasma optical emission spectrometry (ICP-OES), though the traces were still based upon the theoretical compositions (Brill, 1999: analytical procedure detailed in Appendix A, theoretical compositions in Appendix B, and recommended reference compositions in Appendix D).

Vicenzi and colleagues (2002) evaluated the usefulness of the Corning glasses as secondary standards, focusing on the minor and trace elements and impurities, and using the analytical methods of electron probe microanalysis (EPMA), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and secondary ion mass spectrometry (SIMS). The primary focus of this paper was the spatial heterogeneity of the glasses (and thus their basic suitability as secondary standards) rather than the confirmation or re-evaluation of the recommended values from Brill (1999), and they concluded that the Corning glasses were suitably homogeneous for use as secondary standards.

However, various published articles reported some discrepancies between their measured analyses of some elements in the Corning glasses and the published recommended compositions (including Kuisma-Kursula and Räsänen, 1999; Kuisma-Kursula, 2000; Bronk and Freestone, 2001; Falcone et al., 2002; Vicenzi et al., 2002; Shortland et al., 2007; Dussubieux et al., 2008; Wagner et al., 2008; Dussubieux et al., 2009). This prompted the study by Wagner et al. (2012) with the purpose of testing the published recommended compositions of the Corning glasses and where needed, suggesting new values for some elements. Using LA-ICP-MS with three different laser systems, they suggested new values for elements whose results were separated by 3σ from the previously recommended values. The concentrations of sulphur, chlorine and silver were not tested by Wagner and colleagues.

Re-evaluation of Sulphur and Chlorine Concentrations

The impetus for this paper came from an observation that, firstly, the measured values for SO$_3$ and Cl in some of the Corning glasses in analytical work at the UCL Institute of Archaeology consistently differed from the recommended values, and secondly, many
published papers also reported similar disagreement (see references listed in Table 2). The theoretical concentrations of SO₃ and Cl in the Corning glasses were admittedly approximate due to the unpredictable loss of these elements during the glass melting process (described in detail in Brill, 1972). That it is unsurprising that measured results for these elements show poor agreement with the theoretical recommended values is explicitly acknowledged by Vicenzi (et al 2002: 722); however, the low degree of confidence in these concentrations make it highly important to re-evaluate those values in order to better characterise the composition of these glasses and to further their usefulness as reference standards.

The concentrations for Ag in the Corning glasses, which are also currently based upon theoretical values, will not be addressed here, as it is present in concentrations below the limits of detection of the equipment (see below); also Corning C will not be addressed as this high-lead, high-barium glass is not

Table 1: Mean and standard deviation of n analyses for SO₃ and Cl in Corning A, B and D, expressed as oxide weight percent (wt%).

| Source                        | Method  | A (n = 80) | B (n = 91) | D (n = 97) |
|-------------------------------|---------|------------|------------|------------|
|                               | SO₃     | Cl         | SO₃        | Cl         | SO₃        | Cl         |
| Kuisma-Kursula & Räisänen 1999 | SEM-EDS | 0.14       | 0.09       |            | 0.17       | 0.16       |
| Kuisma-Kursula 2000          | EPMA-WDS|            |            | 0.15       | 0.17       |
| Bronk & Freestone 2001       | SEM-EDS | 0.17       | 0.09       | 0.55       | 0.17       |            | 0.19       | 0.16       |
| Vicenzi et al. 2002          | EPMA-WDS| 0.13       | 0.09       | 0.45       | 0.16       | 0.19       | 0.16       |
| Schoer & Rehren 2007         | EPMA-WDS| 0.09       | 0.09       | 0.41       | 0.15       |            |            |
| Freestone et al. 2010        | SEM-EDS |            |            |            | 0.32       | 0.17       |
| Freestone et al. 2015        | EPMA-WDS| 0.14       | 0.09       | 0.50       | 0.16       |            |            |
| Cholakova, Rehren and Freestone 2015 | EPMA-WDS | 0.15       | 0.09       | 0.51       | 0.17       |            |            |
| This paper                   | EPMA-WDS| 0.14       | 0.09       | 0.49       | 0.17       | 0.20       | 0.16       |
| Mean                         |         | **0.14**   | **0.09**   | **0.48**   | **0.16**   | **0.23**   | **0.16**   |
| Standard deviation           |         | 0.019      | 0.006      | 0.048      | 0.011      | 0.023      | 0.009      |
| Previously recommended values (Brill 1999) | | 0.10      | 0.10      | 0.50      | 0.20      | 0.30      | 0.40 |
| Percentage change            |         | 37.0       | −10.2      | −3.2       | −18.9      | −23.7      | −59.6      |

Table 2: Published results for SO₃ and Cl for Corning A, B and D alongside results of the current paper, expressed as oxide weight percent (wt%). The mean of all studies is compared with the recommended theoretical values published in Brill (1999).
used in most glass analysis in these laborato-
ries and therefore no data was available.

**Methodology**
The Corning Archaeological Reference
Glasses A, B and D are used as secondary
standards for electron microprobe analysis
in the UCL Institute of Archaeology Wolfson
Archaeological Science Laboratories. The data
used for this paper has been collected by the
author over the past two years (2015–2016)
as part of research involving the analysis of
medieval glass. Samples of the Corning glasses
were embedded in epoxy resin, polished to
1 μm with diamond paste, and vacuum-coated
in carbon. Analyses were carried out using a
JEOL JXA-8100 Electron Probe Microanalyser
with attached wavelength dispersive spec-
trometers (EPMA-WDS). Standard procedure
for glass analysis in the Wolfson Archaeological
Science Laboratories is to take area measure-
ments with magnifications of 800x and a
working distance of 11mm giving a raster area
of 150 x 110 μm, with an accelerating voltage
of 15kV and a beam current of 50nA, and with
30s count time on each element peak and 10s
count time per background measurement.
Analytical totals had a mean of 99.5%, and
the data were not normalised.

Data compiled from several publications
were also used. This was limited by the fact
that some publications using the Corning
glasses do not publish their measurements
of the standards and others did not report
values for the elements of interest. The data
taken from published works were generated
using EPMA or scanning electron microscopy
(SEM) with either attached WDS or energy
dispersive spectrometers (EDS). For a com-
parative study of WDS and EDS systems in
the analysis of glass, see Verità et al. (1994).

As the previously accepted values are
based on theoretical compositions, a sta-
tistical test for difference is not considered
appropriate. The recommended values in
this paper, calculated as the mean average
of nine publications, are the first based upon
actual measurement.

**New Values for Chlorine and Sulphur
Concentrations**
The mean and standard deviation of the
results for SO$_3$ and Cl in Corning A, B and D
as measured by the author using EPMA-WDS
are given in Table 1, and it is also noted that
the standard deviation of the results for SO$_3$
in all three Corning glasses are greater than
those for Cl. These results are compared with
data from eight other publications (Table 2).
The Cl concentrations are in good agreement,
whereas the SO$_3$ results are more variable. This
variability is largely due to the convention of
reporting sulphur as an oxide rather than the
measured element, resulting in a reported
standard deviation that has been multiplied
by 2.497 (the conversion factor of S to SO$_3$),
and furthermore means that the concentra-
tions are closer to detection limits than the
oxide concentration suggests. The sulphur
concentrations as measured by EDS tend to
be higher than those by WDS; the overlapping
S-K$\alpha$ and Pb-M$\alpha$ lines may have had a small
effect on those results. Variation between
laboratories and machines is also evident, for
example in the consistently lower SO$_3$ val-
ues reported by Schoer & Rehren (2007) and
Kuisma-Kursula (2000).

The best agreement with the recom-
manded values (Brill, 1999) is for SO$_3$ in
Corning B and Cl in Corning A; the most
significant disagreement is found in Cl con-
centrations in Corning D. Estimated reten-
tion rates were assumed to be the same for
all three glasses (Brill, 1972), but instead the
solubility would be dependent on the com-
position of each glass; for example, the soda
concentrations (Freestone et al., 2015).

The lack of a complete up-to-date list of
concentrations for the Corning glasses has
meant that some papers use recommended
concentrations based upon the initial theo-
retical values published by Brill (1972) and
reiterated again in Brill (1999), others use the
“tentative recommended compositions” also
published in Brill (1972), whereas others are
using values whose origins are not known to
this author and are presumably based upon
Table 3: Updated compositions for Corning Archaeological Reference Glasses A, B, C and D (wt%).

|     | A          | B          | C          | D          |
|-----|------------|------------|------------|------------|
| SiO₂ | 66.56 c    | 61.55 c    | 34.87 c    | 55.24 c    |
| Na₂O | 14.3 b     | 17.0 b     | 1.07 b     | 1.20 b     |
| CaO  | 5.03 b     | 8.56 b     | 5.07 b     | 14.8 b     |
| K₂O  | 2.87 b     | 1.00 b     | 2.84 b     | 11.3 b     |
| MgO  | 2.66 b     | 1.03 b     | 2.76 b     | 3.94 b     |
| Al₂O | 1.00 b     | 4.36 b     | 0.87 b     | 5.30 b     |
| P₂O₅ | 0.0847 d   | 0.82 b     | 0.068 d    | 3.93 b     |
| SO₃  | 0.14 e     | 0.49 e     | 0.10 a     | 0.23 e     |
| Cl   | 0.09 e     | 0.16 e     | 0.10 a     | 0.16 e     |
| TiO₂ | 0.79 b     | 0.089 b    | 0.79 b     | 0.38 b     |
| MnO  | 1.00 b     | 0.25 b     | 0.0011 d   | 0.55 b     |
| Fe₂O₃| 1.09 b     | 0.34 b     | 0.34 b     | 0.52 b     |
| CoO  | 0.17 b     | 0.046 b    | 0.18 b     | 0.023 b    |
| NiO  | 0.020 a    | 0.099 b    | 0.020 a    | 0.050 a    |
| CuO  | 1.17 b     | 2.66 b     | 1.13 b     | 0.38 b     |
| ZnO  | 0.044 b    | 0.19 b     | 0.052 b    | 0.10 b     |
| SnO₂ | 0.19 b     | 0.0241 d   | 0.19 b     | 0.10 b     |
| Sb₂O₅| 1.75 b     | 0.46 b     | 0.0001 d   | 0.97 b     |
| BaO  | 0.46 d     | 0.077 d    | 11.4 b     | 0.291 d    |
| PbO  | 0.0725 d   | 0.61 b     | 36.7 b     | 0.241 d    |
| Li₂O | 0.010 a    | 0.001 a    | 0.010 a    | 0.005 a    |
| B₂O₃ | 0.200 a    | 0.035 d    | 0.200 a    | 0.100 a    |
| V₂O₅ | 0.006 a    | 0.036 b    | 0.006 a    | 0.015 a    |
| Cr₂O₃| 0.0033 d   | 0.0096 d   | 0.0023 d   | 0.0025 a   |
| Rb₂O | 0.010 a    | 0.001 a    | 0.010 a    | 0.005 a    |
| SrO  | 0.10 b     | 0.019 b    | 0.29 b     | 0.057 b    |
| ZrO₂ | 0.005 a    | 0.025 a    | 0.005 a    | 0.0125 a   |
| Ag₂O | 0.002 a'   | 0.010 a'   | 0.002 a'   | 0.005 a'   |
| Bi₂O₃| 0.001 a    | 0.0042 d   | 0.0040 d   | 0.0012 d   |

a Brill 1972. Theoretical values, nominal compositions calculated from precursor mass fractions (uncontested by Wagner et al. 2012); 'Ag₂O concentrations were not addressed by Wagner and colleagues.
b Brill 1999.
c Brill unpublished data, reported in Vicenzi et al. 2002
d Wagner et al. 2012 data.
e Adlington 2017 (current paper).
unpublished work shared between researchers. To address this problem, a full list of elements for the four Corning glasses has been compiled with the most up-to-date recommended concentrations and with references to the published origin of each value, reported in Table 3; it is suggested that these values are used in future work.

Summary
The Corning Archaeological Reference Glasses are important secondary standards used in the analysis of archaeological and historical glass, and so it has been important to verify their usefulness as standards (cf. Vicenzi et al., 2002) and corroborate their compositions (cf. Wagner et al., 2012). The compositions of three elements in these glasses have not been re-examined and are theoretical values based upon batch calculations. This paper revisited the concentrations of sulphur and chlorine in Corning A, B and D, after the author observed consistent disagreement with the recommended values both in her own analytical work and in published research, and new values were recommended based on a mean average of published and new results. These results here are tentative and are expected to be revised again when a more thorough, directed approach can be taken; in particular, results for $SO_3$ in all glasses, especially Corning D, vary widely in the published data used in this paper. However, the contribution of this work will give analysts a better understanding of the composition of these standards and of the performance of their equipment. Finally, a complete, up-to-date list of compositions has been compiled for the benefit of other analysts using the Corning glasses.

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Competing Interests
The author has no competing interests to declare.

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