Glass sickness: Detection and prevention
*Investigating unstable glass in museum collections*
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THE IDENTIFICATION OF IONIC SPECIES ON THE SURFACE OF VESSEL GLASS USING ION CHROMATOGRAPHY

This chapter is based on the following paper:


Contribution of the authors:

1. Conceptual ideas
2. Experimental work
3. Data interpretation
4. Preparation of the manuscript
5. Project supervision
3.1 Introduction

This scoping chapter describes the first part of the extensive experimentation primarily designed to pinpoint glasses of unstable composition where visual inspection is inconclusive in assigning surface effects, often described by terms such as ‘haze’ or ‘cloudiness’, to an unstable glass composition (Lamain et al., 2013). The focus of the research presented herein is, in contrast, an investigation of those glasses incontrovertibly displaying signs of deterioration, specifically the presence of the distinct moist films or droplets on the surface which characterise weeping glass. This investigation is motivated by the need to understand more precisely the identity of ionic species present in these aqueous films for three main purposes; firstly, to provide a proof of principle for an analytical protocol for the identification of ionic species on unstable glass surfaces, secondly, to gain a better understanding of the origin of ions, and thirdly, to be better placed to provide sound, analytically-based recommendations for storage and display environmental conditions for weeping glass.

The nature of the species present depends on the glass composition and, specifically, the ions leached from the glass by the action of atmospheric moisture, the reaction of these ions with atmospheric molecules (e.g. carbon dioxide or gaseous atmospheric pollutants), and, additionally, the surface deposition of ionic compounds from the atmosphere or from handling. These three sources of ions can potentially give rise to a wide range of crystalline products or ionic solutions on the surface of unstable glass objects in museum collections. Whether these species remain in solution or crystallise as efflorescence salts depends on the deliquescence relativity humidity (DRH) of the crystalline compounds and the relative humidity (RH) of the storage or display environment. At any RH above its DRH, a compound will exist as an aqueous solution, whereas at RH levels below the DRH it will be in a crystalline state. This consideration underpinned the choice of a recommended storage RH for unstable vessel glass in museums, first proposed by Organ (1957). He argued that, in order to avoid the effect of weeping, glass should be maintained at a RH below 42% so as to prevent the deliquescence of potassium carbonate, the compound which he considered would have the lowest DRH of all those that might form on glass. This has remained a prime recommended storage or display target RH for unstable glass to the present
day (see, for example, Erhardt and Mecklenburg, 1994; Koob, 2006; Kunicki-Goldfinger, 2008).

However, despite almost sixty years of general acceptance of this recommendation, no analytical study has been undertaken specifically to explore its validity. A number of studies have subsequently identified crystalline compounds on the surface of unstable glass items in museums but no comprehensive identification and quantification of the species present in solution on the surface has been reported. Accordingly, the focus of this ongoing analytical study is the elucidation of the composition of the aqueous films on weeping glass.

In this research, ion chromatography (IC) is the main analytical technique used as it provides the possibility to quantify low concentrations of cations and anions in aqueous solutions. Using the IC setup chosen, quantification of ion concentrations in aqueous solutions is achieved for thirteen cations and anions of which we consider sodium, potassium, magnesium, calcium, acetate, formate, chloride, nitrate, carbonate and sulfate most relevant to the formation of salts on the surface of unstable glasses. A detailed description of the IC technique will be provided in section 3.2. The development of a qualitative sampling protocol for the research and the implementation of IC as a suitable technique to analyse ions related to glass deterioration were undertaken previously, prior to initiating the research presented in this dissertation (Lamain et al., 2013), but at that point the protocol was not applied to the study of museum objects. That research was based on a master-thesis in which the applicability of ion chromatography as an analytical tool for the study of ions related to glass deterioration was investigated (Verhaar, 2012).

Using IC as the main analytical technique provides three major advantages. Firstly, the analytical procedure is relatively straightforward and allows rapid analyses of samples from many objects. Secondly, the technique offers low detection limits (ideally, parts per million or even parts per billion), with the ability to detect ions on artefact surfaces where no apparent surface alteration has taken place (Tennent et al., 1992). Thirdly, sampling can be very straightforward. By using simple cotton swabs a representative sample from the glass surface can be obtained. The protocol used in this chapter is refined in subsequent chapters for use as an early-warning
system for detecting unstable glass and validation, in particular, for quantitative comparisons between different objects is part of the research presented later in this dissertation (Chapter 4). Nonetheless, for understanding the phenomenon of weeping glass and for discussing the choice of optimal display and storage RH values, important conclusions are already achievable by consideration of the relative quantities of the ions present. This chapter therefore reports results of IC analyses of eleven unstable glass items from three museums: the Rijksmuseum, Amsterdam, the Hamburg Museum and the Corning Museum of Glass.

3.2 Ion Chromatography

Ion chromatography is a form of high performance liquid chromatography (HPLC) and enables the separation of ionic species in aqueous solutions. The principle behind the technique is that ionic species – which are pumped through the system at high pressure – are separated in a chromatographic column. A fixed injection volume of the sample is introduced to the flow path via an injection valve after which it migrates through the IC system as depicted in Figure 3.1. The inside of the column is packed with a stationary phase which consists of a resin of small spherical beads with ion-exchange sites with a charge opposite to the target ions. This means that anions and cations have to be analysed on different systems using analytical columns with different stationary phases. The sample is pumped through the column with an eluent – the mobile phase – which competes for ion-exchange sites on the stationary phase with ions from the sample (Figure 3.2). The concentration of the competing ions in the eluent can be adjusted according to the samples analysed. If separation with a constant eluent concentration, called isocratic analysis, is insufficient for separation of all ionic species in the sample, the eluent concentration can be changed during the analysis, this is called a gradient. Compounds with stronger ionic interaction with the stationary phase provide more competition for ion-exchange sites and are more retained than those showing less affinity to the stationary phase resulting in a separation of the different ionic species.

The separated ions can be detected by a variety of methods, but conductivity detection is most commonly used in IC systems. The conductivity of the solution
passing through the conductivity cell is continuously monitored, and when ions pass through the detector they cause an increase in conductivity. This response is recorded and presented as peaks in a so-called chromatogram (Figure 3.3). The surface area of a peak is generally directly proportional to the ion concentration, which enables quantitative analysis after proper calibration. A suppressor is used to reduce the background signal caused by the conductivity of the eluent. Through ion exchange mechanisms the conductivity of the eluent is decreased, while conductivity of the sample ions increases as they are converted to highly conducting species. For example, in a cation suppressor a strongly alkaline anion exchange resin is used to exchange hydroxide ions with the anionic component of the acidic eluent, thus forming water and reducing the conductivity of the eluent. Simultaneously, the anionic component of the analyte is exchanged for hydroxide ions, creating highly conductive species such as sodium hydroxide.

The first developments in ion chromatography using conductivity detectors were carried out some 40 years ago following the work by Small, Stevens and Bauman (1975). In a pioneering paper they described a method to use a conductivity cell for continuous monitoring of the conductivity of a solution, while using suppression to decrease the background signal originating from the conductivity of the eluent. Since then, important innovations for the evolution of the technique have been achieved (Lucy, 2003) and the technique is still being innovated (Haddad, Nesterenko and Buchberger, 2008). Currently, IC is an important technique in analytical chemistry and several textbooks are available (e.g. Fritz and Gjerde, 2009; Weiss, 2016). Applications of IC are found in environmental science (e.g. Saigne, Kirchner and Legrand, 1987; Nonomura, 2004), food science (e.g. Zhu et al., 2005) and clinical science (e.g. Green et al., 1982; Bhattacharyya and Rohrer, 2012).

In conservation research, IC has been used for the identification of corrosion products (see e.g. Paterakis, 2003; Wang, 2007a, 2007b) and salt efflorescence (see e.g. Tennent et al., 1992; Backbier, Rosseau and Bart, 1993; Gibson et al. 1997a; Gibson et al. 2005; McCabe, McKinley and Smith, 2008; Ruiz-Agudo et al., 2011), studying the deterioration of cellulose nitrate and cellulose acetate artefacts (Quye, et al., 2011a., 2011b; Littlejohn et al., 2013) and the detection of pollutants in storage and display cases (see e.g. Gibson et al., 1997b; Tétreault et al., 2003; Hodgkins, Grzywacz and Garrell, 2011).
Figure 3.1. Schematic overview of a typical ion chromatography system (from: Dionex Corporation, 2012)

Figure 3.2. Schematic overview of ion elution (from: Sequant, 2007)
Of particular importance in the research of deterioration products on cultural heritage is the ability of IC to detect ionic species which are invisible to the naked eye (Tennent et al. 1992). In the study of historic glass deterioration, IC has only rarely been used as a main analytical tool: Robinet et al. (2004) and Eremin et al. (2005) used IC and Raman spectroscopy for the identification of crystalline deterioration products on the surface of unstable glass, while Thicket and Pretzel (2010) used IC to measure the formate deposition rate on weeping glass.

Despite the fact that IC is capable of quantitatively identifying species associated with glass deterioration (Verhaar, 2012; Lamain et al., 2013), the technique is not a part of the structural investigation of deteriorating glass. In order to be able to deploy IC to better understand glass deterioration it is necessary to develop a good understanding of its potential and limitations. This chapter therefore, for the first time, presents research on the identification of ionic species found on weeping glass from museum collections, which are in a non-crystalline state. The qualitative results obtained in this chapter act as a proof of principle for the adopted technique and is the foundation for the development of a quantitative analytical protocol to identify unstable glasses in an early stage.

**Figure 3.3.** Example of a cation chromatogram. The horizontal axis represents the retention time (min), the vertical axis represents the conductivity. The peak surface areas are representative of the concentration of the analyte.
3.3 Experimental

3.3.1 Objects and samples

Five vessel glasses from the Rijksmuseum, Amsterdam (RM), five items from the Hamburg Museum (HM) and one vessel glass from the Corning Museum of Glass (CMOG) were included in this study. Table 3.1 lists the objects with their registration numbers and sample codes.

The RM samples were taken from glasses clearly demonstrating signs of deterioration, described by the museum conservators as “droplets”, “greasy” and “wet”. The samples were taken during a condition survey of a part of the glass collection. Of the many samples gathered, a selection of those with pronounced moist surfaces was made for this study.

Samples from the HM were taken from the inside of cover glasses of daguerreotypes and painted miniatures. These glasses exhibited symptoms of glass deterioration in storage which in some cases had led to the formation of corrosion products on the copper frames (Beiner-Büth, 2015). The cover glasses had a moist surface film which appeared greasy.

Four samples were taken from the foot of a Venetian glass from the CMOG, one from each quadrant. Samples CMOG_92.3.36_4i to iii are three samples taken consecutively from one quadrant of the foot. This Venetian glass was considered by the museum conservators to be of unstable composition but at the moment of sampling there were no obvious signs of glass deterioration.

3.3.2 Sampling materials

Three types of cotton swabs were investigated for their potential use in a sampling protocol: handmade pure cotton swabs on plastic sticks, prefabricated sterile swabs used for DNA sampling and prefabricated commercial swabs available from the drugstore, abbreviated respectively as HW, SW, and CW. The presence of ionic species in these swabs was evaluated by aqueous extraction of blank swabs, i.e. swabs that were not used for sampling. In order to minimize interference with the ions of interest, the average concentration of ions after extraction of the blank
swabs was evaluated by comparison to the chromatogram of deionised water.

### 3.3.3 Sampling and extraction

Samples were taken using a previously-developed sampling protocol (Lamain et al. 2013). Sampling at the Rijksmuseum was performed by the conservators in collaboration with one of the authors (GV). A sampling kit was sent to the HM along with sampling instructions. A kit was also sent to the USA but never arrived. Therefore, the samples from the CMOG were obtained with swabs prepared at the museum. All samples were sent back to Amsterdam in closed polypropylene vials.

Sampling was performed using cotton swabs moistened with deionised water. An area of circa 2 cm² was sampled. In order to bring the salts into solution for IC analysis, the swabs were placed in a polypropylene centrifuge tube and extracted for an hour in 1.5 mL deionised water. After removal of the swabs from the centrifuge tube the samples were centrifuged for ten minutes at 2000 rpm to remove possible fibres and other larger particles from the sample.

### Table 3.1: List of objects and sample codes included in this study.

<table>
<thead>
<tr>
<th>Collection</th>
<th>Object no.</th>
<th>Description</th>
<th>Sample codes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rijksmuseum</td>
<td>BK-KOG-139</td>
<td>Bottle, c. 1675-1700, Dutch</td>
<td>RM_BK-KOG-139_1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>RM_BK-KOG-139_2</td>
</tr>
<tr>
<td></td>
<td>BK-NM-758</td>
<td>Bottle, Willem Jacobszoon van Heemskerk (engraver), c. 1675-1685, Dutch</td>
<td>RM_BK-NM-758</td>
</tr>
<tr>
<td></td>
<td>BK-NM-776</td>
<td>Glass, Anonymous, c. 1550-1600, Venice</td>
<td>RM_BK-NM-776</td>
</tr>
<tr>
<td></td>
<td>BK-NM-7995</td>
<td>Wine glass, Anonymous, c. 1600-1650, Venice</td>
<td>RM_BK-NM-7995</td>
</tr>
<tr>
<td></td>
<td>BK-NM-9811</td>
<td>Wine glass, Anonymous, c. 1675-1700, Dutch</td>
<td>RM_BK-NM-9811</td>
</tr>
<tr>
<td>Corning Museum of Glass</td>
<td>92.3.36</td>
<td>Goblet, 1600-1699, Venice</td>
<td>CMOG_92.3.36_1 to CMOG_92.3.36_4ii</td>
</tr>
<tr>
<td>Hamburg Museum</td>
<td>1912.438</td>
<td>Miniature painting, Portrait of an unknown man, possibly from the Goos Family, c. 1810</td>
<td>HM_1912.438</td>
</tr>
<tr>
<td></td>
<td>1912.452</td>
<td>Miniature drawing, Portrait of Rosalie Cohen with her son Albrecht, 1820</td>
<td>HM_1912.452</td>
</tr>
<tr>
<td></td>
<td>1929.223</td>
<td>Miniature painting, Portrait of Karoline Amalie Herzfeld, c. 1805</td>
<td>HM_1929.223</td>
</tr>
<tr>
<td></td>
<td>1932.174</td>
<td>Daguerreotype, Portrait of Johan Gottfried Unbehagen as teacher, 2nd third 19th C.</td>
<td>HM_1932.174</td>
</tr>
<tr>
<td></td>
<td>1934.295</td>
<td>Daguerreotype, Portrait of Lady Kunhardt, 2nd third 19th C.</td>
<td>HM_1934.295</td>
</tr>
</tbody>
</table>
3.3.4 Analysis

Anions were analysed using a Dionex ICS-2100 IC system equipped with a Dionex DS6 conductivity detector, an Ionpac AS17-C 2x250 mm analytical column, protected by an AG17-C 2x50 mm guard column, and a Dionex anion electrolytically regenerated suppressor (AERS 500). The eluent used was potassium hydroxide with a gradient ranging from 1-45 mM at a flow rate of 0.37 mL·min\(^{-1}\) over a runtime of 20 minutes. Eluent concentrations were established using a Dionex EGC-III eluent generator cartridge. A Dionex CR-ATC trap column was used to remove anionic contaminants from the eluent. This setup allows for the analysis of fluoride, acetate, formate, chloride, nitrite, bromide, nitrate, carbonate, sulfate and phosphate ions in concentrations below parts per million levels.

The analysis of cations was performed using a Dionex ICS-1100 IC system equipped with a Dionex DS6 conductivity detector, an Ionpac CS12-A 2x250 mm analytical column, protected by a CG12-A 2x50 mm guard column, and a Dionex cation electrolytically regenerated suppressor (CERS 500). A 20 mM solution of methane sulphonlic acid (Fluka chemicals, >99% pure) was used as eluent at a flow rate of 0.25 mL·min\(^{-1}\). This setup allows for the analysis of lithium, sodium, ammonium, potassium, magnesium, and calcium ions in concentrations down to parts per million levels.

Samples were stored in polypropylene vials and injected using a Dionex AS-AP autosampler. All standards and samples were prepared using HPLC grade deionised water (Thermo Scientific Barnstead Genpure UV-TOC, Ultrapure 18.2 MΩ·cm water, TOC: 1 – 5 ppb).

Calibration of the IC systems was carried out using stock solutions. A Dionex™ Combined Six Cation Standard I was diluted to create six standard solutions to construct a calibration curve for lithium, sodium, ammonium, potassium, magnesium and calcium. For the calibration of the anion analysis three standard solutions were used to create one stock solution which was diluted to create 5 standard solutions. The three standard solutions were Dionex™ Combined Seven Anion Standard I (fluoride, chloride, nitrite, bromide, nitrate, sulfate, phosphate), a Dionex carbonate IC-standard and a combined solution of acetate and formate.
was created by weighing and dissolving their sodium salts. The results of the calibration are listed in Table 3.2.

Table 3.2: Data for the calibration curves of the IC-system. Listed are the calibration range (CR), the y-intercept, the slope and the coefficient of determination ($R^2$).

<table>
<thead>
<tr>
<th>Compound</th>
<th>CR (mg/L)</th>
<th>Low</th>
<th>High</th>
<th>y-intercept</th>
<th>Slope</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>0.01</td>
<td>0.5</td>
<td>-0.004</td>
<td>0.998</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>0.04</td>
<td>2</td>
<td>0.006</td>
<td>0.317</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Ammonium</td>
<td>0.08</td>
<td>4</td>
<td>0.000</td>
<td>0.376</td>
<td>0.999</td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td>0.04</td>
<td>2</td>
<td>0.001</td>
<td>0.212</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.04</td>
<td>2</td>
<td>0.002</td>
<td>0.509</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>0.2</td>
<td>10</td>
<td>-0.023</td>
<td>0.363</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Fluoride</td>
<td>0.033</td>
<td>1.33</td>
<td>-0.093</td>
<td>2.492</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Acetate</td>
<td>0.175</td>
<td>7</td>
<td>0.011</td>
<td>0.569</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Formate</td>
<td>0.15</td>
<td>6</td>
<td>-0.023</td>
<td>0.919</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td>0.05</td>
<td>2</td>
<td>-0.018</td>
<td>1.289</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Nitrite</td>
<td>0.067</td>
<td>2.67</td>
<td>0.044</td>
<td>0.829</td>
<td>0.999</td>
<td></td>
</tr>
<tr>
<td>Bromide</td>
<td>0.067</td>
<td>2.67</td>
<td>-0.027</td>
<td>0.557</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.067</td>
<td>2.67</td>
<td>-0.017</td>
<td>0.769</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Carbonate</td>
<td>0.175</td>
<td>7</td>
<td>0.128</td>
<td>0.088</td>
<td>0.993</td>
<td></td>
</tr>
<tr>
<td>Sulfate</td>
<td>0.25</td>
<td>10</td>
<td>-0.088</td>
<td>0.953</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Phosphate</td>
<td>0.25</td>
<td>10</td>
<td>-0.047</td>
<td>0.411</td>
<td>1.000</td>
<td></td>
</tr>
</tbody>
</table>

### 3.4 Results and discussion

#### 3.4.1 Blanks

In order to determine the contribution of the swabs, which could contains some ions as well, to the total amount of ions in the extracted solution, dry cotton swabs were extracted and the solutions were analysed using IC. These samples are referred to as the blanks. The resulting cation concentrations are listed in Figure 3.4a. At this moment in the research, only the cationic contributions were compared and the ion contributions of the cotton swabs from the drugstore (CW) provided the best results. The use of handmade swabs and sterile swabs was dismissed, as their
contribution to the total sodium concentration exceeds that of the swabs from the drugstore significantly. As the anionic contributions were satisfactory as well (Figure 3.4b), these swabs were used in this research. Furthermore, it was found that the polypropylene centrifuge tubes do not contribute significantly to the concentrations of ions in solution.

For the CMOG samples, swabs were handmade from cotton wool and fine glass rods available in the CMOG conservation studio. Analysis of a single cotton wool blank showed that it contained more calcium and less sodium than the other swabs but no additional swabs were available for confirmatory replicate analyses.

The results of the blank extraction are presented adjacent to the concentration of the ions in the sample solutions (Figures 3.5-3.8) and are labelled ‘blank.’ In this way, the contribution of the swab material to the concentration of each ion can be easily appreciated.

3.4.2  Museum glass samples

The results provide information on the nature of ionic species on the surface of weeping glass. The measured ion concentrations for the RM and HM are listed

![Figure 3.4. The contribution of three types of swabs (from the drugstore [CW], handmade from cotton wool [HW] and sterile swabs used for tissue sampling [SW]) to the cation concentrations (a) and the contribution of the CW swabs to the anionic concentrations (b) as determined through blank swab extraction. n = 10 for each type of swab.](image)
in Figures 3.5 and 3.6. For the RM and HM samples the major cations found were sodium and potassium. One of these ions or a combination of both was detected in most samples and when they were detected their concentration was significantly higher than that of the other cations. Calcium and magnesium were present in small amounts. The principle anions found during anion analysis of the RM and HM samples were formate and chloride. Chloride was detected in every sample, and while formate was not detected in every sample, when it was detected the concentration was generally higher than in the other samples. Sulfate was present in medium to high concentrations and bromide was found in small concentrations. Acetate was only detected in two samples. Fluoride and nitrate were found in RM samples, but not in samples from the HM.

For the CMOG samples (Figure 3.7) the main cation was sodium, with low concentrations of potassium and calcium and trace amounts of magnesium and ammonium. The main anion found was chloride, which was found in all samples, as was sulfate. Acetate, fluoride and bromide were not detected. Nitrate was identified on two samples in high concentrations. Formate was found in only one sample in very low concentration.

The significance of these generalised observations is discussed below. Additionally, attention is focused on the occurrence of carbonate which is considered to be of particular importance in weeping glass studies to date.
Figure 3.5. Anion and cation concentrations for the samples from the Rijksmuseum. The blank sample is the extraction of the blank swab.

Figure 3.6. Anion and cation concentrations for the samples from the Hamburg Museum. The blank sample is the extraction of the blank swab.
Figure 3.7. Anion and cation concentration for samples CMOG_92.3.36_1-4i. The blank sample is the extraction of the blank swab.

Figure 3.8. Anion and cation concentration for samples CMOG_92.3.36_4i-4iii. The blank sample is the extraction of the blank swab.
3.4.3 Interpreting the analytical results

The low detection limits of IC for quantification of the ions of interest offers the potential to permit extremely detailed interpretation of the formation of ionic species on glass surfaces. Several issues in the development of a robust analytical protocol were tackled in the previously mentioned preliminary Masters’ degree research project (Verhaar, 2012; Lamain et al. 2013). In order to ensure that the analytical results can be confidently interpreted as a true quantification of the total ions present on each glass, a crucial additional step is the optimisation and validation of the sampling protocol for glass surfaces. This step is dealt with in Chapter 4; at present, inter-comparisons between objects are, therefore, restricted and the analytical results can only be considered in terms of the range of ions and the relative amounts of these ions in any single sample. Thus, for example, no firm conclusion can be drawn from the consistently lower concentrations present in the HM samples compared to those from the RM. For the success of the ultimate goal – an early warning system for detecting glass deterioration – experiments towards an optimal sampling procedure are part of the next phase of the research programme (see Chapter 4).

Nonetheless, the results presented in Figures 3.5-3.8 provide compelling evidence that the range of ions on the glass surface is more complex than generally thought and that, in consequence, Organ's assessment of weeping glass display and storage requirements (Organ 1957) is an over-simplification that needs to be reconsidered. These issues are discussed in more detail below in terms of the results from the samples from the eleven glasses in this study.

Before addressing the implications of these findings, the results from the single CMOG glass studied are important in an assessment of the ability to draw conclusions from the present ion chromatography results. The value of these results, with six samples all from a single object, is that, even without a rigorously-applied sampling protocol, they provide confidence for our methodology and indicate the steps that need to be taken to improve this.

Figure 3.7 shows that for similar samples from a single object the same ions are detected but there is a spread in concentrations of each ion from sample to sample. In
order to be able to compare ion concentrations between objects, more quantitative
determination of the ions on the glass surface will be necessary. The first steps will
be to improve the sampling efficiency (the percentage of ions gathered from the
glass surface during sampling), the reproducibility (the ability for similar samples
to provide similar quantitative analytical results), and the recovery (the ratio of
sampled ions that is extracted and analysed) based on experiments with mock-
up samples on which a solution of known ion concentrations is applied and with
synthetic glass of unstable composition. It must be borne in mind, however, that
for future inter-comparisons between objects, the uniformity of the ions present
on different areas of the surface in a single object will be an intrinsic uncertainty.

A second experiment carried out with the CMOG glass investigated the results
of repeat samplings from the same area. Three samples were taken consecutively
from the same location (CMOG_92.3.36_4i, 4ii, 4iii). The results presented in
Figure 3.8 demonstrate that the concentration of ions decreases significantly,
especially after the first sampling. Since the sampling procedure for this glass was
not rigorous (ten swipes of the swab over the 12 cm² surface), it was not expected
that all ions would be removed in the first sample; ions could have been collected
in the later samples from previously untouched areas. Interestingly, the only ion
which shows no sequential decrease is carbonate, indicating that further research
into the detection of carbonate is necessary.

**Deliquescence of salts**

In previous studies, sodium formate has been identified as the main crystalline
species on the surface of unstable glass (see, for example: Schmidt 1992; Robinet
et al. 2004; Eremin et al. 2005). Despite the fact that the results reported in this
chapter also suggest that sodium formate is one of the main compounds on the
surface of weeping glass, the large concentrations recorded for other anionic
species also need to be taken into account.

In a key paper (Eremin et al. 2005) it was suggested that, due to the low DRH
(16-17%) of potassium formate, this compound may have a dominant role in the
maintenance of moist surfaces on weeping glass even at moderately low RH (for
example, c. 40%). The likelihood of the formation of this compound on certain
glasses is confirmed by the present results. For the RM glasses (Figure 3.5),
formate was detected as the dominant anionic species in four of the six samples. For each of these samples potassium is also clearly detected, thus supporting the proposition that potassium formate may make an important contribution to the moist surfaces on weeping glasses.

The wide range of ions found on the glasses sampled emphasizes the complex chemistry of the weeping glass phenomenon and the difficulty of making general recommendations about storage or display conditions for unstable glass. Table 3.3 lists the DRH of sodium, potassium, magnesium and calcium salts that may be present on the glass surface, based on the results of this investigation. An added complication is that mixtures of salts result in an overall DRH different from that of the individual salts (Price and Brimblecombe, 1994). A further uncertainty is that such unusual mixtures of ions may lead to the formation of complex compounds, possibly unknown to science. This is a topic of related research interest concerning the juxtaposition of weeping glass with metals (Eggert, 2010). The HM items in this study also show evidence of weeping glass/metal reaction.

**The sources of the ions in the samples investigated**

*Principal ionic components*

It is generally accepted that the sodium and potassium alkali cations on the surface of unstable glass originate from the glass (Kunicki-Goldfinger, 2008) and the results from all samples are in accord with this. For sodium, the identification of high levels of chloride in all samples is indicative of the additional ubiquitous presence of sodium chloride, deposited from handling and/or from aerosols in the atmosphere. The contribution of the latter source was also postulated in the glass studies of Robinet et al. (2004) and finds support in specific investigations devoted to the museum environment where an atmospheric source of sodium chloride was identified in Californian museums (Nazaroff et al., 1993). Of particular relevance, for museums with no HVAC systems, sodium chloride levels were found to be similar to those outdoors. The source of calcium and magnesium, also detected in all samples, is assumed to be the glass itself as these alkali earth elements are also present in unstable glasses (Brill, 1975).
The anions derive from the environment in which the glass is kept, either as a result of off-gassing from storage or display materials or as a result of their presence in the outdoor atmosphere. The detection of formate and acetate is undoubtedly primarily due to the emission of formic acid, acetic acid and formaldehyde from wood or wood composite materials. As mentioned above, chloride is associated with the presence of sodium chloride. The presence of sulfate and nitrate is likely to be due to infiltration of outdoor pollutants into the museum environment (Nazaroff et al., 1993).

The question remains whether detection of formic and acetic acid on the surface of unstable glass can be a result of ambient atmospheric concentrations of carbonyl compounds. IC analytical evidence has recently been adduced for the hypothesis that formate and acetate found on unstable mosaic glass is the result of parts per billion concentrations of ambient formic and acetic acid (Tennent and Carthy 2016). Nevertheless, the storage and display history of the objects is undoubtedly crucial in understanding the formation of salts on the glass surface and in making recommendations for suitable museum environmental conditions. It is, however,

### Table 3.3: Room temperature values for the deliquescence relative humidity of salts possibly associated with weeping glass surfaces.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Deliquescence Relative Humidity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sodium salt</td>
</tr>
<tr>
<td>Acetate</td>
<td>43.5-45.2 % (8)</td>
</tr>
<tr>
<td>Formate</td>
<td>50.2-52.1 % (8)</td>
</tr>
<tr>
<td>Chloride</td>
<td>75 % (5)</td>
</tr>
<tr>
<td>Nitrate</td>
<td>75 % (5)</td>
</tr>
<tr>
<td>Carbonate</td>
<td>91 % (4)</td>
</tr>
<tr>
<td>Sulfate</td>
<td>84 % (10)</td>
</tr>
</tbody>
</table>

(1) Al-Hosney et al. (2005)  
(2) Davila et al. (2010)  
(3) Eremin et al. (2005)  
(4) Erhardt and Mecklenburg (1994)  
(5) Greenspan (1977)  
(6) Kremer, Hunsche, and Noga (2009)  
(8) Peng and Chan (2001)  
(9) Steiger et al. (2011)  
(10) Tang and Munkelwitz (1994)  
* Magnesium and calcium carbonate are poorly soluble in water. Therefore the DRH is estimated to be 100%  
** The DRH of magnesium sulfate depends on the phase of the compound
difficult to trace back the entire storage history – or even the recent history – of objects for study. Frequently, poor documentation on the movement from storage cabinets to display cases, on episodes of cleaning and on changes in the storage location or the materials comprising storage case make it especially difficult to identify those glasses with an impeccable ‘biography’.

**Carbonate**

Since the publication of Organ’s influential paper in 1957, the formation of carbonates of the alkali ions has been regarded as a central process in the degradation of unstable vessel glass. The DRH of potassium carbonate was, and has subsequently remained, the cornerstone of the recommendation he first promulgated for the avoidance of what is generally referred to as weeping (Organ, 1957). Organ, however, carried out no analyses and had no experimental evidence for the actual presence of potassium carbonate on the surface of unstable glass. However at that time, Organ was justified in his supposition that no compound was likely to form on the glass surface with a lower DRH than potassium carbonate. It was only after many years that formates and acetates were recognised as widespread reaction products on vulnerable museum objects (FitzHugh and Gettens, 1971). Still later came the first report of the formation of sodium formate on glass (Schmidt, 1992). In contrast, no clear-cut analytical evidence for the formation of sodium or potassium carbonate on the glass has been published. Furthermore the presence of carbonate salts was sought but not found by Eremin et al. (2005). A possible explanation for the absence of carbonates on unstable glass surfaces is that they may act as intermediates in the formation of other deterioration products, as is thought to occur during the formation of sulfates on medieval stained glass windows (Newton and Davison 1989). The results in Figures 3.5 - 3.8 support the likelihood of chemical conversion of carbonate, formed initially on the glass surface by absorption of carbon dioxide in the atmosphere. At the CMOG, formate and acetate are absent and carbonate is present whereas at the RM and HM carbonate appears to have been consumed with the formation of formate/acetate.

However, calibration of the IC system for the quantitative detection of carbonate is problematic. As a result of absorption of carbon dioxide by the concentrated
potassium hydroxide eluent solution carbonate is formed, which interferes with the analysis. The difficulty of quantifying the carbonate concentration in solutions is underlined by the high relative standard deviation in the blank swab extractions. Furthermore, the quantitative detection of carbonate salts is restricted by the poor solubility in water of magnesium and especially, calcium carbonate. When carbonate is detected it is likely to originate primarily from potassium or sodium carbonate, due to their higher solubility (Lide, 2005). For these reasons, further investigations of the detection of carbonate using IC and further research on the presence of carbonate on the surface of unstable glasses are necessary.

**Bromide and fluoride**

The source of bromide and, to a lesser extent, fluoride in the RM and HM samples is unclear. The presence of these ions in the extracted solutions may be a result of the materials used for sampling or the storage of the samples. As bromide is used in the preparation of daguerreotypes, its presence in the HM samples may originate from the daguerreotypes themselves (Barger and White, 2000).

### 3.5 Conclusions

The results presented in this chapter are of fourfold importance for the care of unstable museum glass. In the first place they demonstrate, though at a preliminary stage, the value of ion chromatography in providing valuable information on the range of species present on glass surfaces. In the second place, they pave the way for establishing relationships between the surface species present and the composition of the glass itself, as well as that of extraneous compounds, notably atmospheric gaseous pollutants. Thirdly, the results are important in the development of an ion chromatography-based analytical approach as an early warning system for pinpointing glasses of unstable composition; they provide a proof of principle of the sampling and analytical protocol. Finally, the findings establish the need to optimise yet further the sampling/sample work-up protocol in order to ensure better efficiency and reproducibility so as to distinguish unambiguously unstable from stable glass at an early stage, prior to a clear visual manifestation of instability.

Of prime significance, the results demonstrate the need for a re-evaluation of
Organ’s recommended target RH to avoid the symptoms of weeping glass. The range of species that have been identified points to the need for a more sophisticated argumentation leading to preferred storage conditions for unstable vessel glass. The species on the glasses sampled from three major museum collections indicate that a greater variety of salts than Organ anticipated may crystallise on the surface. These possibilities need to be considered when making recommendations about display and storage RH intended to preclude the formation of a liquid film as a result of salt deliquescence. In particular, the possibility of potassium formate formation with deliquescence relative humidity of 16-17% means that the prevention of the onset of weeping is more complex than generally accepted. It may be that for certain glasses in certain environments there is no acceptable RH that will prevent weeping. The results also reinforce the concept that the ideal display or storage RH is dependent on both the composition and the environment of an individual glass, a fact not taken into consideration in the specification of a single preferred target RH for all unstable glass.

All the above considerations will be explored further in the remainder of this dissertation. The primary target will be the development and validation of a reproducible sampling protocol aimed at drawing conclusions from inter-object comparisons, which is the topic of Chapter 4.

### 3.6 References


