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Weeping Glass: The Identification of Ionic Species on the Surface of Vessel Glass Using Ion Chromatography

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Keywords:

Weeping glass; glass sickness; glass deterioration; ion chromatography

Abstract

Aqueous films on the surface of unstable vessel glass were analysed. Five cation and eight anion species from eleven glass items in the Rijksmuseum, Amsterdam, the Hamburg Museum and the Corning Museum of Glass have been quantified by ion chromatography. Sodium, potassium, magnesium and calcium cations and acetate, formate, chloride, nitrate, carbonate and sulfate anions are deemed most significant. The results indicate that the compositions of moist films on weeping glass are more complex than generally recognised. The findings are discussed in relation to the sources of the ions and the implications of their diversity for the choice of a suitable relative humidity (RH) for display and storage of unstable vessel glass. The compounds which may form have deliquescence RH values which span the range 11-99%, demonstrating the difficulty of making recommendations about storage RH to prevent the onset of weeping.

Introduction

This paper is part of a more extensive investigation 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 two main purposes; firstly, to gain a better understanding of the origin of ions and, secondly, 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 carbon dioxide or with 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 relative 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 pro-

posed 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, the preliminary results of which are presented and discussed in this paper, 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. A detailed description of the IC technique and the sampling protocol adopted for our research has been reported previously (Lamain et al. 2013). Using the IC setup chosen, quantification 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.

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 paper is still being refined for use as an early-warning system for detecting unstable glass, and validation for quantitative comparisons between different objects is yet to be achieved. Nonetheless, for understanding the phenomenon of weeping glass and for discussing the choice of optimal display and storage

RH values, important progress is already achievable by consideration of the relative quantities of the ions present. This paper 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.

Experimental

Objects and samples

Five vessel glasses from the Rijksmuseum (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 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.

Sampling and extraction

Samples were taken using a previously-developed sampling protocol (Lamain et al. 2013) for which the sampling materials have been evaluated (Verhaar, van Bommel, and Tennent 2015). 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

Collection	Object no.	Description	Sample codes
	BK-KOG-139	Bottle, c. 1675-1700, Dutch	RM_BK-KOG-139_1 RM_BK-KOG-139_2
Rijksmuseum	BK-NM-758	Bottle, Willem Jacobszoon van Heemskerck (engraver), c. 1675-1685, Dutch	RM_BK-NM-758
	BK-NM-776	Glass, Anonymous, c. 1550-1600, Venice	RM_BK-NM-776
	BK-NM-7995	Wine glass, Anonymous, c. 1600-1650, Venice	RM_BK-NM-7995
	BK-NM-9811	Wine glass, Anonymous, c. 1675-1700, Dutch	RM_BK-NM-9811
Corning Museum of Glass	92.3.36	Goblet, 1600-1699, Venice	CMOG_92.3.36_1 to CMOG_92.3.36_4iii
	1912.438	Miniature painting, Portrait of an unknown man, possibly from the Goos Family, c. 1810	HM_1912.438
	1912.452	Miniature drawing, Portrait of Rosalie Cohen with her son Albrecht, 1820	HM_1912.452
Hamburg Museum	1929.223	Miniature painting, Portrait of Karoline Amalie Herzfeld, c. 1805	HM_1929.223
	1932.174	Daguerreotype, Portrait of Johan Gottfried Unbehagen as teacher, 2 nd third 19 th C.	HM_1932.174
	1934.295	Daguerreotype, Portrait of Lady Kunhardt, 2 nd third 19 th C.	HM_1934.295

Table 1: List of objects and sample codes included in this study.

the USA but never arrived. Therefore, the samples from the CMOG were obtained (by NHT) 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 soluble 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. Extraction of blank swabs was also carried out for comparison.

Analysis

Anion concentrations were determined using a Dionex ICS-2100 IC system equipped with a Dionex DS6 conductivity detector, an Ionpac AS17-C 2x250 mm analytical column and 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 and a CG12-A 2x50 mm guard column, and a Dionex cation electrolytically regenerated suppressor (CERS 500). A 20 mM solution of methane sulphonic 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).

Results and discussion

Blanks

In order to determine the contribution of the blank swabs to the total amount of ions in the extracted solution, dry cotton swabs were extracted and the solutions were analysed using IC and compared to the deionised water blank. For the sampling of the objects from the RM and the HM collections cotton swabs from a drugstore were used. Anal-

ysis of the extracted solutions of blank swabs indicated that the contribution of sodium is most significant and exceeds the concentration of sodium in the deionised water blank (Verhaar, Van Bommel, and Tennent 2015). 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 samples 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 1-4). In this way, the contribution of the swab material to the concentration of each ion can be easily appreciated.

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 in figures 1 and 2. For the RM and HM samples the major cations found were sodium and potassium. Calcium and magnesium were present in small amounts. Large amounts of formate and chloride were found during anion analysis of the RM and HM 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) 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

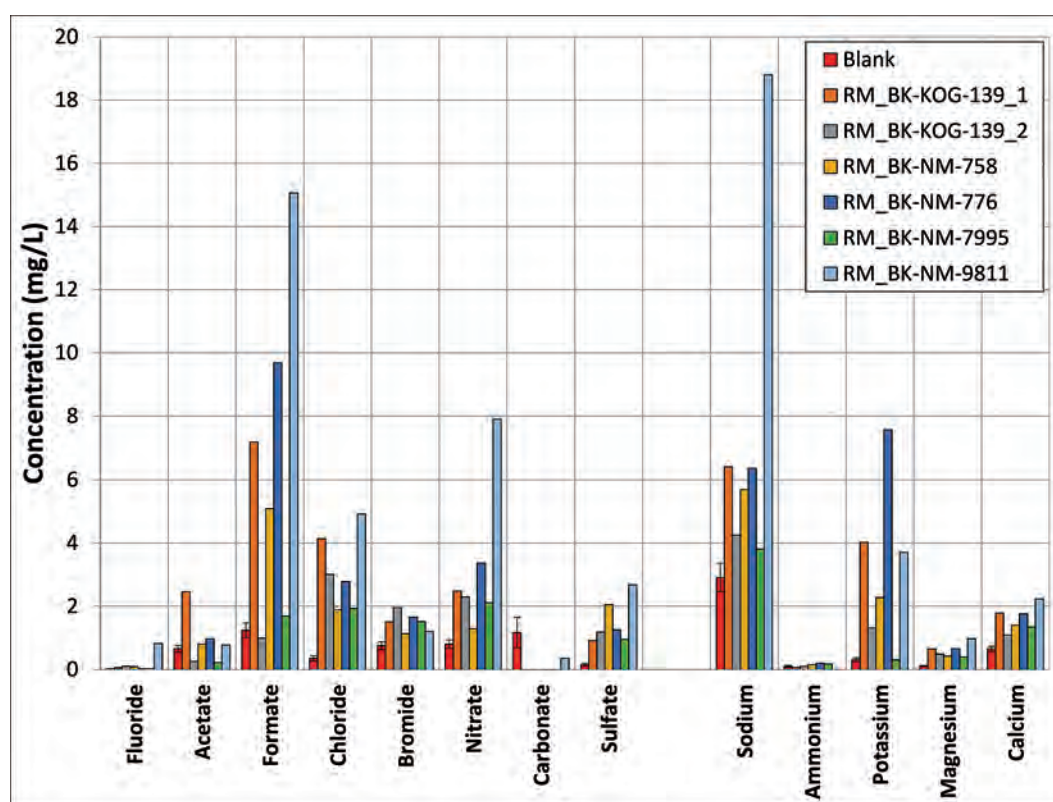


Fig. 1. Anion and cation concentrations for the samples from the Rijksmuseum.

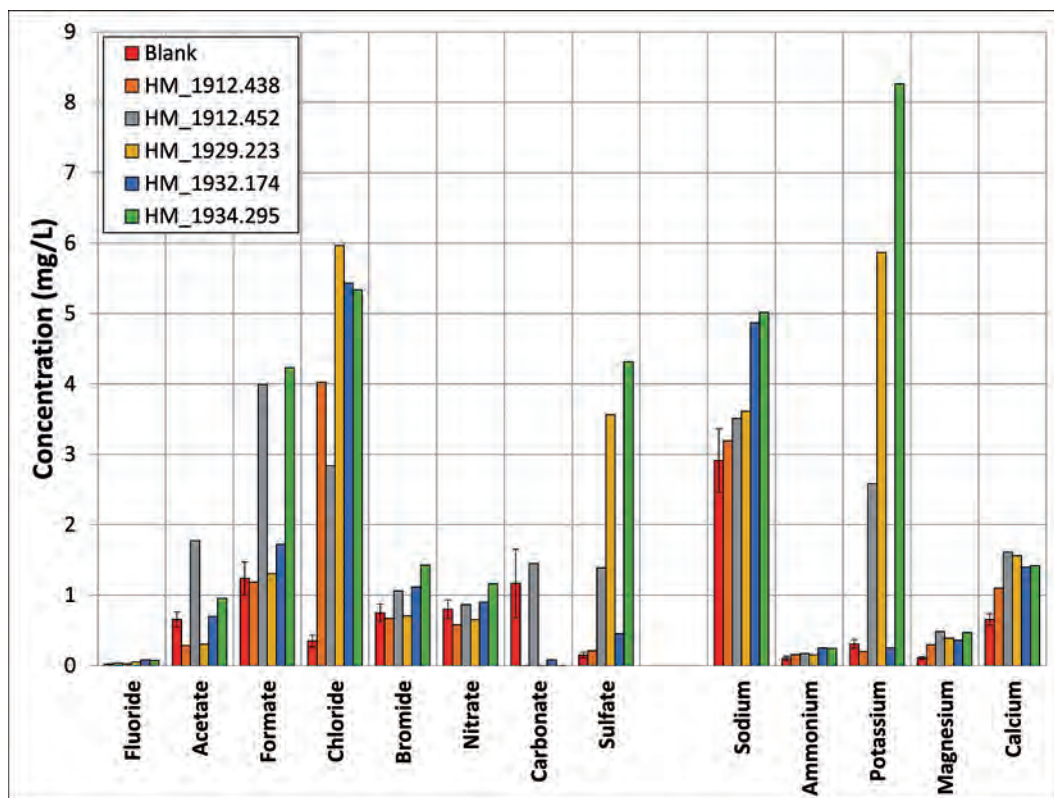


Fig. 2. Anion and cation concentrations for the samples from the Hamburg Museum.

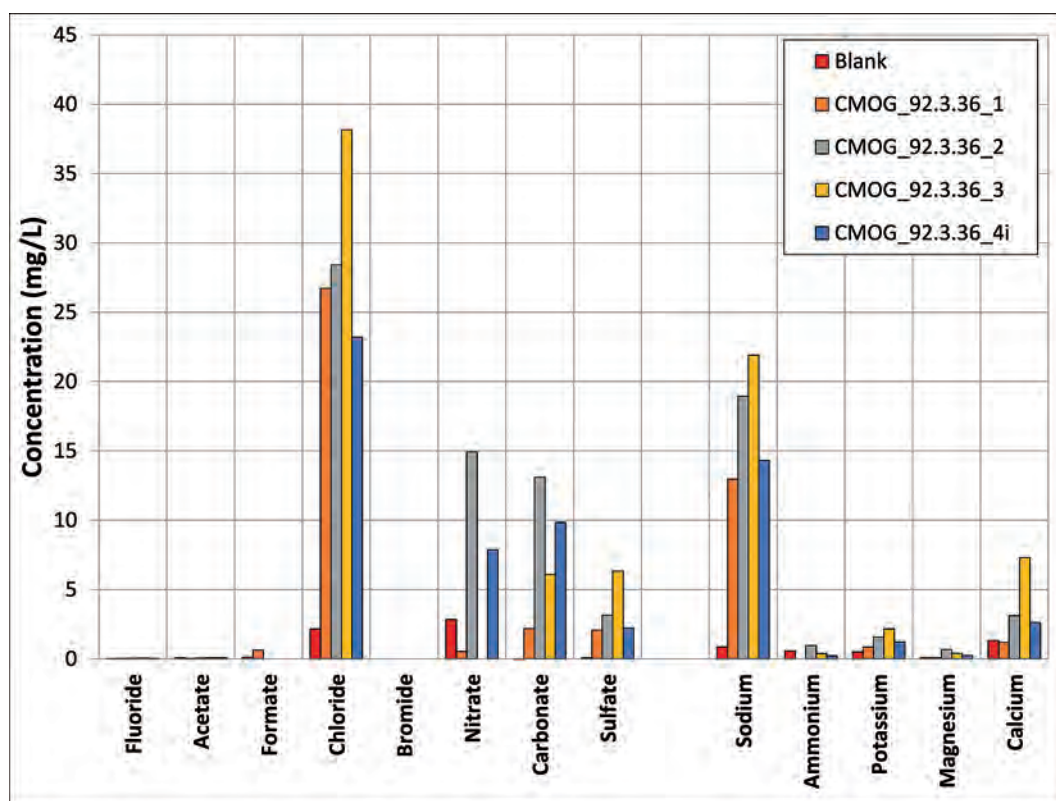


Fig. 3. Anion and cation concentration for samples CMOG_92.3.36_1-4i.

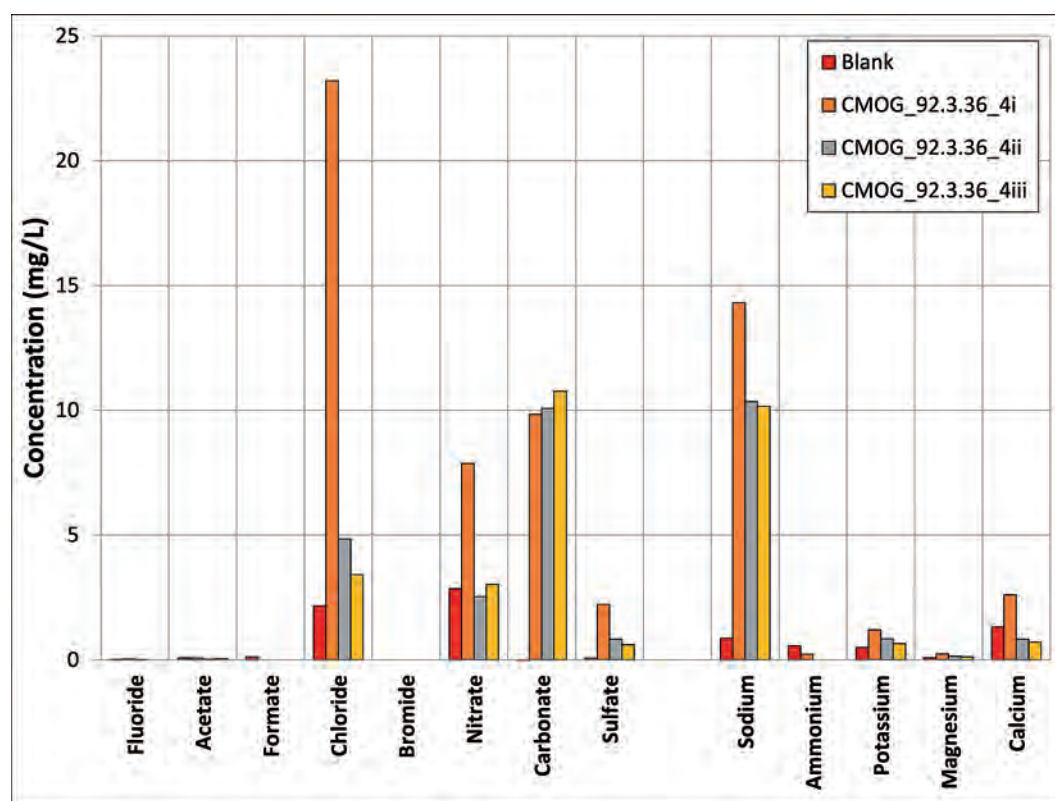


Fig. 4. Anion and cation concentration for samples CMOG_92.3.36_4i-4iii.

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.

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. To date, several issues in the development of a robust analytical protocol have been tackled (Lamain et al. 2013; Verhaar, Van Bommel, and Tennent 2015). 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, yet to be completed, is the optimisation and validation of the sampling protocol for glass surfaces. As a result, at present, inter-comparisons between objects are 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 our ultimate goal—an early warning system for detecting glass deterioration—experiments towards an optimal sampling procedure are planned as the next phase of our research programme.

Nonetheless, the results presented in figures 1–4 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 our current ability to draw conclusions from the ion chromatograph 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 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 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 4 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 from our study also suggest that sodium formate is one of the main compounds on the surface of weeping glass, the equally large concentrations of different 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 our results. For the RM glasses (figure 1), 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 2 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 forma-

Deliquescence Relative Humidity				
Anion	Sodium salt	Potassium salt	Magnesium salt	Calcium salt
Acetate	43.5-45.2% (8)	23% (5)	n.d.	100% (6)
Formate	50.2-52.1% (8)	16-17% (3)	n.d.	n.d.
Chloride	75% (5)	85% (5)	33% (5)	32% (2)
Nitrate	75% (5)	95% (5)	54% (5)	11 % (1)
Carbonate	91% (4)	43% (5)	~100% *	~100% (7) *
Sulfate	84% (10)	97% (5)	41-56% (9) **	n.d.

Table 2: Room temperature values for the deliquescence relative humidity of salts possibly associated with weeping glass surfaces. (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) Kreamer, Hunsche, and Noga (2009); (7) Onasch, McGrau, and Imre (2000); (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

tion 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. 1992). Of particular relevance, these levels were found to be similar to those outdoors for museums with no HVAC systems. 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. 1992).

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, 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 1-3 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).

Conclusions

The results obtained in this study 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 as this research programme develops. The primary target of future research will be the development of a reproducible sampling protocol aimed at drawing conclusions from inter-object comparisons. This research will largely be based on analyses of deterioration products on the surface of artificially aged synthetic glasses with a composition comparable to unstable historic glass. This will, in addition to the results presented in this paper, allow exploration of the relationship between the composition of the surface liquid film and the glass itself, providing more insight into the nature of unstable glass. Finally, recommendations for storage and conservation strategies will be based on the study of synthetic glasses in varying environments as an extension to the study of museum objects.

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