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Glass sickness: Detection and prevention

Investigating unstable glass in museum collections

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4

THE DEVELOPMENT AND VALIDATION OF AN ANALYTICAL
PROTOCOL FOR THE QUANTITATIVE DETECTION OF IONS IN
DETERIORATION PRODUCTS ON THE SURFACE ON UNSTABLE
HISTORIC GLASS USING ION-EXCHANGE CHROMATOGRAPHY

4.1 Introduction

Currently there is no method to identify unstable glass in museum collections before these changes in appearance occur. Quantitative analysis of the glass composition is usually not an option as it requires destructive sampling. Non-destructive analytical techniques are not sensitive enough for quantitative detection of elements indicative of glass stability (see for example Kaiser and Shugar (2016) on x-ray fluorescence spectrometry of glass). However, the hypothesis being explored in this dissertation is that very low concentrations (ppm and sub-ppm) of ionic species on unstable glass surfaces will provide evidence that an object is deteriorating, even when no visual changes can be observed. In order to be able to test this hypothesis a robust sampling and analytical protocol is necessary. This protocol needs to be not only reliable but also very straightforward for the in-situ investigation of museum objects.

Prior to the initiation of the research for this dissertation it was demonstrated that ion chromatography (IC) is a suitable technique for the identification of both cations and anions associated with glass deterioration in concentrations below ppm levels (Lamain et al. 2013). In relation to the deterioration of glass, IC has been used for qualitative identification of salt formation as crystalline surface products (Eremin et al. 2005). The research of this dissertation has extended that study to ionic species in moist films and droplets on unstable glass surfaces comprising vessel glass, daguerreotypes and portrait miniature cover glasses (Chapter 3). The variety of ionic species on unstable glass surfaces in both these studies have demonstrated that the formation of salts is a more complex process than initially thought (Organ, 1956) and modes of formation of these salts remain unclear. Moreover, it became apparent that the development of a more reproducible sampling protocol is necessary, as without that the results varied greatly due to different sampling materials and methods used in different institutions (Chapter 3). The quantitative analysis of ions on the glass surface is not only applicable to the assessment of glass stability, it is also necessary in the investigation of the sources of these ions. The results presented in Chapter 3 provide a start for the explanation of the large variety of ions on the glass surface, but it became evident that a more reliable and quantitative analytical protocol is required.

The sampling protocol developed in this chapter is based on surface swabbing. With this simple approach the conservator (or curator) responsible for the glass collection can take the sample non-invasively in the depot without the necessity of the presence of an analytical scientist to gather the sample. In that way the objects studied do not need to be transported, as the sample itself can be transported, which is not only safer, but also more cost-efficient. Most conservators are familiar with the use of swabs and so, in combination with their low-cost and ease of use, they have great potential for this application. In conservation research, surface swabbing combined with IC analysis has been used successfully, for example, in the analysis of cellulose nitrate artefact degradation products (Quye et al. 2011a, 2011b). Prior to validation of the method presented in this chapter, the use of different sampling materials which do not interfere with the IC analysis or pollute the samples (Chapter 3; Verhaar, 2012; Lamain et al., 2013).

The aim of the research presented in this chapter is therefore the validation of a sampling and analytical protocol for the quantitative identification of ionic species found on unstable glass surfaces. The ions investigated are sodium, potassium, magnesium, calcium, acetate, formate, chloride, nitrate, carbonate and sulfate. Additionally, the protocol has been validated, as described below, for lithium, ammonium, fluoride, nitrite, bromide and phosphate. The presence of these ions on the surface of unstable glass is not anticipated, but their presence in the stock solutions used allows for their validation as well. This may be beneficial for the application of the resultant protocol in other fields of research and demonstrates the wider applicability of IC. The use of an IC system provides the opportunity to analyse glass deterioration products in liquid solutions quantitatively; the scope and limitations for the quantification of all relevant ions are the prime aspect of this chapter. The validation of a sampling and sample preparation protocol is important in order to enable inter-object comparisons, which is crucial for the discrimination between stable and unstable glass objects in museum collections.

4.2 Materials and methods

4.2.1 Ion chromatography 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, 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 0.5 to 45 mM at a flow rate of 0.37 mL·min⁻¹ over a runtime of 22 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 aqueous solutions.

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 which is protected by a CG12-A 2x50 mm guard column, and a Dionex cation electrolytically regenerated suppressor (CERS 500). A solution of 20 mM 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 aqueous solutions.

Samples were stored in polypropylene vials and injected using a Dionex AS-AP autosampler with an injection volume of 7 µL. All standards and samples were prepared using HPLC grade deionised water (Millipore Simplicity, 18.2 Ultrapure 18.2 MΩ·cm water system). To avoid contamination, no glassware was used in the preparation of solutions and samples.

4.2.2 Stock solutions, standard solutions and blanks

Cation standard solutions were prepared using a Dionex 6 cation stock solution (lithium, sodium, ammonium, potassium, magnesium, calcium). An anionic stock solution was made by mixing a Dionex seven-anion IC-standard solution (fluoride, chloride, nitrite, bromide, nitrate, sulfate, phosphate), a Dionex carbonate

IC-standard solution and sodium acetate and sodium formate solution prepared by weighing and dissolving these salts in deionized water. Standard solutions for experimental work were prepared by dilution of these stock solutions. Blanks consisted of HPLC grade water.

4.2.3 Sample preparation and sampling method

The use of cotton swabs in Chapter 3 was underpinned by the fact that they were the most practical in use and the least polluting to the samples of the materials tested (see Lamain et al., 2013 for an overview of other experiments carried out to optimise ion extraction). Although the cotton swabs provided satisfactory results in that stage of the research, lowering the blank contributions to the ion concentrations is beneficial for the validated protocol. In particular, because the amount of sodium extracted from the cotton swabs is significant compared to the amount of sodium sampled from the surface. Therefore, the use of polyester swabs (Texwipe Alpha® TX761) was investigated.¹ Blank extractions were carried out to investigate the contribution of these swabs to the total ion concentrations in the samples as explained in Chapter 3. The results of the blank extractions are shown in Figure 4.1. It is evident that, for each ion under investigation, the blank contribution of the polyester swabs is significantly lower than the contribution of the cotton swabs. Therefore, the polyester swabs were used in the validation of the analytical protocol.

In order to replicate the presence of aqueous droplets on weeping glass, samples were prepared by applying four drops of 10 μL of a standard solution on a sheet of Melinex within a specified area. Four drops were used to have an even spread of the solution on the sampling surface, while a volume of 10 μL provided a feasible pipetting volume. A Teflon template was placed on top of the Melinex surface to restrict the sampling area (Figure 4.2). Before application of the standard solution the Melinex sheets and Teflon templates were cleaned with ethanol and deionised water and left to dry.

¹ These swabs were provided by Cees Bruggink (InIon Chromatography) and Mandy Slager (private conservator).

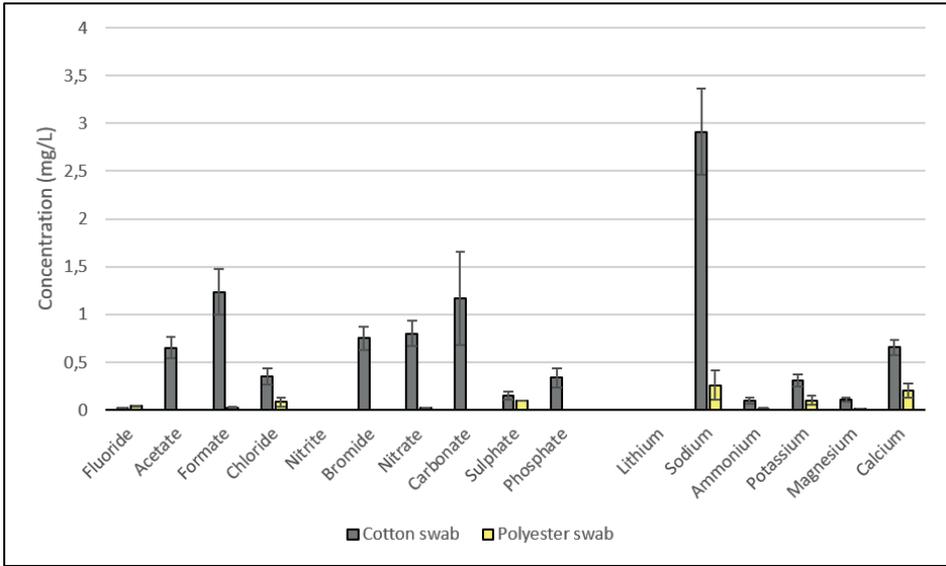


Figure 4.1. Ion concentrations of cotton swab and polyester swab blank extractions.

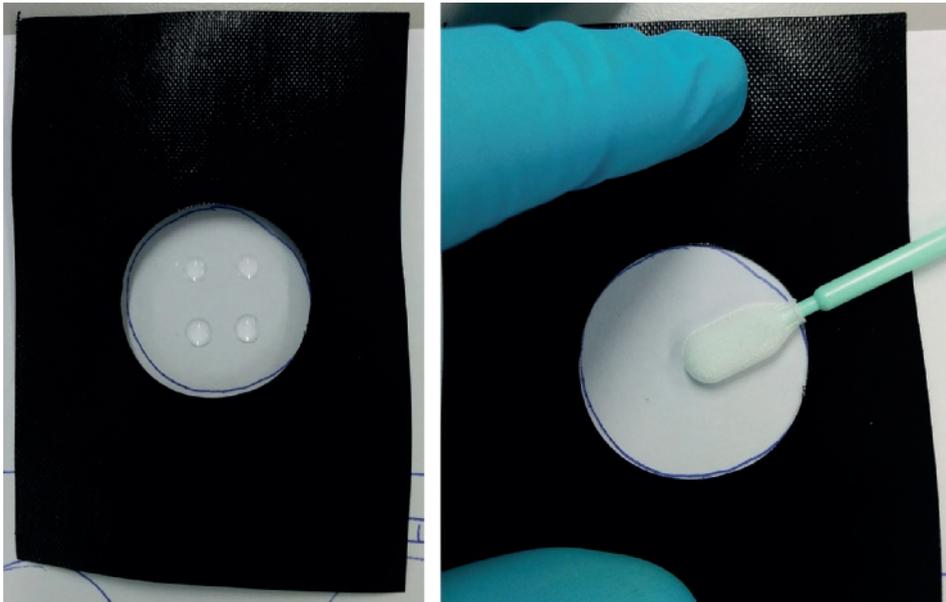


Figure 4.2. sample preparation and sampling using a Teflon template and polyester swabs.

The applied standard solutions were sampled using the polyester swabs of which one side was moistened with 50 μL of deionized water while the other side of the swab was not moistened. The applied standard solution was sampled by swabbing the sampling area in two perpendicular directions using the moistened side of the swab, the same sampling pattern was repeated with the un-moistened side of the swab to absorb any solution left on the surface.

After sampling the swabs were placed in polypropylene centrifuge tubes for extraction in 1.31 mL deionized water for an hour, resulting in a total dilution of the standard solution applied on the Melinex of 35 times. The swabs were then removed and the remaining solution was centrifuged for 4 minutes at 5000 rpm. The top 900 μL was collected using a Finnpiptette and transferred to a polypropylene vial for IC analysis.

4.2.4 Validation of the analytical protocol

The method was validated for specificity, linearity, range, accuracy, precision, limit of detection (LOD) and limit of quantification (LOQ) according to the ICH Harmonised Tripartite Guideline (ICH, 2014). The validation of the sampling and analytical method was performed for the following ions related to glass deterioration: sodium, ammonium, potassium, magnesium, calcium, acetate, formate, chloride, nitrate, carbonate and sulfate. Furthermore, the sampling protocol was validated for lithium, ammonium, fluoride, nitrite, bromide and phosphate since these ions were present in the Dionex stock solutions anyway. The protocol was validated separately for cationic and anionic compounds as they are analysed on two different systems.

4.2.5 Linearity, range, LOD and LOQ

A calibration curve was made to assess linearity, range, LOD and LOQ. Seven anionic and seven cationic standard solutions with varying ion concentrations were used to construct the calibration curve, deionized water was included as a blank standard solution (Table 4.1). Two factors determined the maximum concentration of ions in the standard solutions: the maximum capacity of the

Table 4.1: Ion concentrations (mg/L) of the standard solutions used for the experiments.

Standard solution concentrations (mg/L)									
Analyte	Calibration curve experiments								Repeatability experiments
	1 (Blank)	2	3	4	5	6	7	8 (stock)	
Lithium	0	0.1	0.5	1	2	5	10	50	10
Sodium	0	0.4	2	4	8	20	40	200	40
Ammonium	0	0.4	2	4	8	20	40	200	40
Potassium	0	0.8	4	8	16	40	80	400	80
Magnesium	0	0.4	2	4	8	20	40	200	40
Calcium	0	2	10	20	40	100	200	1000	200
Fluoride	0	0.33	0.67	1.33	2.67	5	10	13.33	6.67
Acetate	0	1.8	3.5	7	14	26	53	70	35
Formate	0	1.5	3	6	12	23	45	60	30
Chloride	0	0.5	1	2	4	7.5	15	20	10
Nitrite	0	1.67	3.33	6.67	13.33	25	50	66.67	33.33
Bromide	0	1.67	3.33	6.67	13.33	25	50	66.67	33.33
Nitrate	0	1.67	3.33	6.67	13.33	25	50	66.67	33.33
Carbonate	0	1.8	3.5	7	14	26.5	53	70	35
Sulfate	0	2.5	5	10	20	37.5	75	100	50
Phosphate	0	2.5	5	10	20	37.5	75	100	50

analytical column (respectively 12.5 and 2.5 nmol per analyte per injection for the AS-17C column for the CS-12A column) and the concentration of ions in the stock solutions used to prepare the standard solutions. The minimum value of the studied range was determined by the empirical observations made on the minimum amount of ions which could be detected by the IC systems. The combination of these three parameters (column capacity, ion concentration in stock solutions and detection limits of the IC system) resulted in a range in which the ion concentration in the most concentrated standard was 40 times the ion concentration in the most diluted standard for anions and 500 times for cations. The LOD and LOQ for each ion of interest were calculated using equations 4.1 and 4.2.

$$LOD = 3.3 \cdot \sigma / S \quad (\text{Equation 4.1})$$

$$LOQ = 10 \cdot \sigma / S \quad (\text{Equation 4.2})$$

In these relationships σ is the residual standard deviation of the regression line and S is the slope of the calibration curve. The residuals were calculated by taking the absolute value of the measured peak area with subtraction of the calculated peak area according to the calibration curve equation.

4.2.6 Repeatability and accuracy

The recovery was determined by applying the sampling and extraction protocol to ten samples which were prepared in the same way. The results of the analyses of these samples were compared to results of a reference solution with the same concentration as the sample solutions would have at 100% recovery. The reference solution was prepared by adding four times 10 μL of the stock solution to a sample vial containing 1310 μL of deionized water, to which another 50 μL of deionized water was added. Reference solutions were prepared and analysed in threefold, blanks were prepared in fivefold and the samples were prepared in tenfold.

4.3 Results and discussion

4.3.1 Method validation

Specificity

Separation of the ions of interest was achieved using the chromatographic methods described above. For the anionic system there are two instances in which components are co-eluting: fluoride and acetate, and bromide and nitrate (Figure 4.3 a). This is not problematic for the study of unstable glass museum objects as the detection of fluoride on unstable glass surfaces is not anticipated and bromide has only been identified in rare instances where the glass was in contact with other materials, for example in the case of cover glasses of daguerreotypes (Chapter 3). The cations could be baseline separated (Figure 4.3 b).

Linearity and range

The applied protocol was linear within the studied range (Table 4.2). The coefficient of determination (R^2) was larger than 0.999 for all compounds except for ammonium, fluoride, bromide, carbonate, sulfate and phosphate showing an

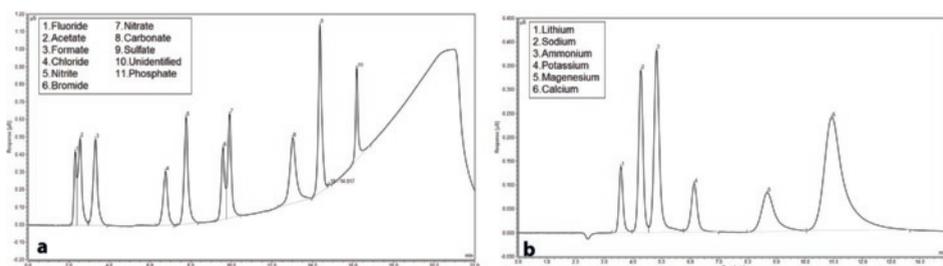


Figure 4.3. Chromatograms showing the separation of anions (a) and cations (b).

R^2 larger than 0.99 (Table 4.2). Chloride showed a relatively poor R^2 of 0.93. The calibration curve for sodium contained one outlier, which was identified using the Grubbs test for outliers. This value was omitted from the calculations. Appendix 4.1 shows the calibration curves for each investigated ion. The fact that chloride shows a poor linear response can be attributed to the high and irreproducible amount of chloride present in the blanks (see the calibration curve for chloride in

Table 4.2: List of ionic compounds validated in the study together with the retention time (RT), studied concentration range (CR) and calibration curve parameters (slope, y-intercept, R^2 and the residual sum of squares (RSS)).

Compound	RT (min)	CR (mg/L)		Slope	y-intercept	R^2	RSS
		Low	High				
Lithium	3.575	0.003	1.428	1.001	-0.003	>0.9994	<0.001
Sodium	4.268	0.057	5.7	0.326	0.029	0.9991	0.003
Ammonium	4.816	0.011	0.57	0.669	0.010	0.9973	0.286
Potassium	6.111	0.023	11.42	0.116	0.004	0.9992	0.001
Magnesium	8.712	0.011	5.71	0.458	-0.004	0.9998	0.001
Calcium	10.933	0.057	28.57	0.337	0.022	0.9997	0.026
Fluoride	2.358	0.010	0.38	0.552	-0.0038	0.9977	0.0002
Acetate	2.635	0.050	2	0.1533	0.0066	0.9997	0.0000
Formate	3.437	0.043	1.71	0.2428	-0.0029	0.9994	0.0002
Chloride	6.964	0.014	0.57	0.3007	0.0301	0.9337	0.0036
Nitrite	7.935	0.048	1.9	0.2389	-0.0043	0.9994	0.0002
Bromide	9.751	0.048	1.9	0.1911	-0.0032	0.9981	0.0002
Nitrate	10.106	0.048	1.9	0.1911	-0.0030	0.9990	0.0002
Carbonate	13.246	0.050	2	0.0455	0.1327	0.9926	0.0001
Sulfate	14.62	0.071	2.85	0.2141	-0.0136	0.9966	0.0021
Phosphate	16.365	0.071	2.85	0.0788	-0.0072	0.9960	0.0003

Appendix 4.1). The studied range of carbonate, sulfate and phosphate lies below the limits of detection for two out of seven calibration points. Therefore, the linearity of the studied range is less than the other compounds. Omission of these values from the calculations results in an improvement of R^2 to 0.998 for sulfate and phosphate. For carbonate omission of these values results in a slight increase of R^2 to 0.994.

Ammonium, acetate and formate have a non-linear response in the ion chromatography systems used, due to the fact that the ratio of the dissociated state of these compounds (detectable by IC) and non-dissociated state (not detectable by IC) depends on the concentration of the compound in solution. For higher concentrations the proportion of the compound in non-dissociated state is larger and therefore the relative amount detected by the IC system is smaller. This effect can be accounted for by making a quadratic calibration curve for a larger range. Through application of this method to the results of ammonium, a calibration curve with R^2 of 0.999 was derived. Acetate and formate have a linear response for the range studied, but extension of the range will result in a non-linear response. However, when a sample has an ion concentration that falls outside of the linear range, it can be diluted to obtain a concentration within the linear range.

Accuracy

The recovery of anions after blank subtraction varies from 71.37% to 101.37%. The recovery of chloride (71.37%) and sulfate (78.15%) is low compared to the other anionic components, which show a recovery ranging from 91.93% to 101.37%. Carbonate shows a recovery above 100%, potentially originating from the characteristics of carbonate detection in the IC system which causes a high blank concentration of carbonate. The recovery of cations varies from 89.45% to 99.16% (Table 4.3).

The low recovery of chloride and sulfate is less straightforward to explain and currently unclear. Two steps in the validation experiments could cause a difference in the extracted solution and the reference solution. Firstly, the amount of sampled chloride and sulfate could be affected by the interaction between these ions and the surface to which they were applied. If chloride and sulfate have an affinity with the surface to which the standard solutions were applied, they might

Table 4.3: Validated ionic compounds and their recovery, repeatability, limit of detection (LOD) and limit of quantification (LOQ).

Compound	Recovery (%)	Repeatability (RSD)	LOD (mg/L)	LOQ (mg/L)
Lithium	95.67 ± 3.51	3.51%	0.008	0.024
Sodium	94.75 ± 4.97	4.20%	0.140	0.423
Ammonium	99.16 ± 2.93	2.93%	0.648	1.964
Potassium	91.96 ± 5.68	4.09%	0.258	0.781
Magnesium	89.45 ± 4.61	4.39%	0.067	0.203
Calcium	91.77 ± 4.83	4.42%	0.404	1.223
Fluoride	100.71 ± 7.16	6.78%	0.020	0.060
Acetate	101.37 ± 3.12	2.96%	0.038	0.116
Formate	94.25 ± 2.19	2.21%	0.046	0.141
Chloride	71.37 ± 25.68	13.57%	0.164	0.496
Nitrite	96.87 ± 2.41	2.15 %	0.049	0.148
Bromide	98.47 ± 3.82	3.81%	0.090	0.274
Nitrate	91.93 ± 2.92	2.87 %	0.063	0.192
Carbonate	120.02 ± 16.59	10.26 %	0.185	0.561
Sulfate	78.15 ± 4.28	4.32 %	0.179	0.542
Phosphate	95.81 ± 3.08	3.05 %	0.194	0.588

be retained on the surface during sampling. Secondly, the extraction of these ions could be less efficient than the other ions investigated. In that case, the ions should partly be retained by the swabs. Both processes were not investigated during the validation experiments, but if these ions turn out to be relevant for future research of glass surface deposits, or other application, these issues should be investigated.

Repeatability

The repeatability for both the anionic as the cationic compounds is <5% for all compounds except for fluoride, chloride and carbonate, for which the RSDs were 6.78%, 13.57% and 10.26% respectively (Table 4.3). The presence of fluoride is not expected in the study of historic glass. Chloride could be an interesting ion in the study of glass deterioration, but its high and irreproducible presence in the blanks is problematic. Carbonate is an ion often associated with the formation of deposits on glass surfaces, but its irreproducible recovery and low repeatability provides less confidence in its quantitative analysis. Despite the fact that sulfate has a lower recovery than the other components, it has a high repeatability with a RSD of

4.32%. This indicates that the results of analysis of sulfate using the presented protocol are reliable as the repeatability is high, but the ion concentration might need a correction for the low recovery

Limits of detection and quantification

Limits of detection ranged from 0.038 to 0.185 mg/L for anions and from 0.067 to 0.648 mg/L for cations. The limits of quantification ranged from 0.116 to 0.561 mg/L and from 0.203 to 1.964 mg/L for the cations (Table 4.4).

The LOD and LOQ of the validated method are of main interest in the study of unstable glass, as the proposed method is aimed at the quantitative detection of the ions of interest in low concentrations. The LOD and LOQ presented in this chapter are below the concentration of ions found on unstable glass objects in a pilot study in which the concentration of ions was larger than 1 mg/L for all detected ions (Chapter 3). However, the sampling method used in that study had not been validated, and it is therefore difficult to compare those results to the results presented in this chapter. Moreover, the aim of the proof of principle was different than the intended application of the protocol validated in this chapter. Chapter 3 focused on the identification of ions in droplets and moist layers on the surface of unstable glass, which meant that there were no requirements to the sampling protocol other than collecting the moisture in the swab. The validated protocol is aimed at sampling surfaces ranging from those on which no moisture has accumulated to clearly moist surfaces and a uniform sampling procedure is therefore crucial. Nonetheless, no other study has been directly aimed at identification of deterioration products on unstable glass and therefore this proof of principle is the most suitable study to compare with the results from this validation study. It is reassuring that the LOD and LOQ of all components are lower than the ion concentrations found on the objects included in the proof of principle, with the exception of ammonium, which has a higher LOQ than the other components. However, ammonium has only been found occasionally in low concentrations on the surface of unstable glass (Robinet et al., 2004; Eremin et al., 2005), hence this ion is less relevant for glass degradation studies.

The analytical protocol described in this paper could be modified if the quantification limit appears to be insufficient in the study of glass objects, for

example by decreasing the extraction volume or increasing the sampling area to increase the sensitivity of the method.

4.3.2 The application of the protocol in an early warning system for unstable glass

The main application of the validated protocol is as an early warning system for unstable glass. Therefore, it is essential to be able to obtain reliable analytical results for ionic species associated with glass deterioration. These species are sodium, potassium, magnesium, calcium, acetate, formate, chloride, carbonate and sulfate. The results of the validation presented above provide good confidence in the reliability of the analysis of these compounds. Some important factors in relation to the application of the protocol as an early warning system for unstable glass are discussed below.

Sodium, potassium and chloride

The presence of sodium and chloride on the surface of museum objects made of glass can have many sources. Although the deposition of sodium on the surface of unstable glass can be related to chemical deterioration of the material, two other sources of sodium are its deposition due to the ubiquitous presence of sodium chloride in the atmosphere (see e.g. Nazaroff et al., 1992) and as a result of handling, which has recently been studied (Haverkamp, 2017). The presence of both sodium and chloride may therefore not be useful for the identification of unstable glass objects. As sodium is often associated with the formation of deterioration products on the surface of unstable glass, for example in the form of sodium formate (Schmidt, 1992; Eremin et al., 2005), it may be a key marker ion in the identification of unstable glasses. The quantitative detection of both sodium and chloride is therefore important to be able to identify which proportion of sodium may originate from the glass and which proportion is a result of the deposition of sodium chloride. Due to poor reproducibility and the presence of chloride in blank samples on the Melinex surfaces, the presence of sodium chloride on glass surfaces may limit the use of sodium as a marker ion for unstable glass. However, more research is required on historical glass objects to determine typical levels of sodium which could be related to deterioration.

Potassium, besides sodium, is often associated with the structural chemical changes of the glass surface and may therefore be identified on these surfaces. An important compound detected on unstable glass surfaces is potassium formate as it has a low deliquescence relative humidity (DRH) of 17%. This means that it will deliquesce in virtually any storage environment and it may well be that detection of this compound is pivotal in the development of storage and conservation recommendations. It is encouraging that the validation parameters are good for potassium.

Carbonate

Carbonate is often reported to be associated with glass deterioration (Kunicki-Goldfinger, 2008) and environmental recommendations for the prevention of deterioration of unstable glass are often based on the DRH of potassium carbonate at 42 % (Organ, 1957). This compound has however not been identified on unstable glass surfaces in subsequent studies (Robinet et al., 2004; Eremin et al., 2005). Because of the association of carbonate with glass deterioration it is of interest to detect it quantitatively on the surface of unstable glass. However, quantitative IC analysis of carbonate is problematic for two reasons. First, carbonate is formed in the mobile phase of the chromatographic system due to the absorption of carbon dioxide (Wan Isahak et al., 2015) in the eluent before degassing, so there is always a relatively large response in the blanks. Second, carbonate is a weak acid ion of carbonic acid, which dissociates into bicarbonate and carbonate, depending on the pH of the solution. Bicarbonate cannot, however, be detected using the IC setup employed in this research.

In this study, carbonate was included in the validation and the results were better than anticipated. It was possible to determine the LOD and LOQ based on a calibration curve with an acceptable R^2 of 0.9926. However, in the pilot study, carbonate was only detected in one instance (Chapter 3). Therefore, the question remains whether or not carbonate will be suitable for the identification of unstable glass objects and the study of glass deterioration mechanisms. Further investigation on the presence of carbonate on the surface of unstable glasses will be discussed in Chapters 5 and 6.

4.4 Conclusions

The research presented was aimed at the validation of a simple method for the identification of ionic compounds on the surface of unstable glass. The use of ion chromatography as the main analytical tool provided good separation and quantitative analysis of components associated with glass deterioration, while swabbing proved to be a suitable sampling method to collect solutions containing compounds similar to those found on unstable historic glass surfaces. The sampling and extraction methods proved to be accurate, precise and with good limits of quantification for most studied components. Chloride is unsuitable as an indicator for glass instability and its presence in samples indicates that the sodium contents of these samples should be regarded with care. The detection of carbonate is limited by the IC equipment and quantitative detection should be regarded with caution, but the implementation of the limits set by the validation presented in this chapter allows for the interpretation of carbonate concentrations in samples. The work presented in Chapter 5 and Chapter 6 will provide more insights into the detection of carbonate on unstable glass surfaces.

The research presented in this chapter is fundamental for the conservation of historic glass in museum collections. It provides the opportunity for quantitative analysis of unstable glass surface deposits in low concentrations, as expounded in subsequent chapters. Further work will explore the relation between the glass composition and deterioration products that form on the glass surface. The protocol will be used to study both the stability and deterioration mechanisms of historic glass in museum collections by analysing not only what compounds are deposited on the glass surface, but also in what quantities these compounds are found on the glass surface. This will lead to the identification of potential marker ions for unstable glass and the protocol will be applied to museum objects which appear to be in different stages of deterioration, but where visual examination is inconclusive about the condition of the glass.

4.5 References

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Appendix 4.1 Calibration curves of validated ions

