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Development and validation of an analytical protocol for the sampling and quantitative analysis of ions on the surface of unstable historic glass in museum collections using ion-exchange chromatography

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ABSTRACT

The early identification of unstable glass objects in museum collections is essential for their conservation, but as yet cannot be accomplished straightforwardly. Accordingly, this paper describes the development and validation of a simple protocol for quantitative determination of ions characteristic of the chemical decay of historic glass, using surface swabbing combined with ion-exchange chromatography. The establishment of a robust protocol is an important step in the development of an early warning system for the chemical deterioration of unstable glass. Using a model system, the protocol was validated for specificity, linearity, accuracy, precision, limits of detection, and limits of quantification for 10 anionic species (fluoride, acetate, formate, chloride, nitrite, bromide, nitrate, carbonate, sulfate and phosphate) and 6 cationic species (lithium, sodium, ammonium, potassium, magnesium and calcium). Good validation parameters ($R^2 > 0.995$; $RSD < 5\%$; Recovery 90–100%) were obtained for acetate, formate, nitrite, nitrate, phosphate, lithium, sodium, potassium, magnesium and calcium. Chloride ($R^2 = 0.934$; $RSD = 13.6\%$; recovery 71.4%) and carbonate ($R^2 = 0.993$; $RSD = 10.3\%$; recovery 120%) had poor validation parameters. Sulfate had low recovery (78.2%), but high reproducibility ($RSD = 4.32\%$) with $R^2 = 0.997$. Limits of quantification were below 1 mg/L for all analytes, which is satisfactory for the study of unstable glass in museum collections. The validated sampling protocol was trialled using artificially aged unstable glass fragments, which resulted in a high relative standard deviation (between 1 and 30%). The ability to achieve improved care of historic glass by application of the validated protocol in museum collections is discussed in the context of a pilot study undertaken at the Rijksmuseum, Amsterdam.

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1. Introduction

Chemical deterioration of historic glass objects on display and in storage in museum collections is a problem of long-standing concern for conservators and curators. Chemical changes induced by atmospheric moisture can result in associated changes in appearance which may render a glass unfit for display and may ultimately lead to the complete disintegration of the object [1–4]. It

has been estimated that up to 30% of glass collections may consist of unstable objects [4–8]. In such collection surveys, the classification of glass objects as stable or unstable is most often based on visual examination, which can be inconclusive because of uncertainty in attributing changes in appearance to chemical instability of the glass or to other phenomena which can broadly be described as soiling. Additionally, the deterioration of glass is not always visible to the naked eye, especially in the early stages of the degradation process [5]. It is, however, crucial to be able to discriminate between unstable and stable glass objects in order to be able to develop and implement long-term conservation strategies for these vulnerable objects. Accordingly, this paper describes the development and validation of a non-destructive ion-exchange

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Fig. 1. Bottle with engraved inscription: “*Blusch den geest niet uit*” [“Do not extinguish the spirit”], The Netherlands, 1686, Rijksmuseum, Reg. No. BK-NM-744. Photo credit: Rijksmuseum. Before (a) and after (b) the removal of a moist film resulting from degradation of the glass.

chromatography protocol for the early identification of unstable glass in museum collections.

Historic vessel glass generally consists of three main components: a network former, a network modifier and a network stabiliser. The network modifier (usually soda or potash) is added to a network former (typically silica for historic glasses) to lower the melting temperature. This addition to the glass batch results in a glass which will chemically be very unstable, and therefore a third component (usually lime) is added to the glass batch, which acts as a network stabiliser [1,9]. When melted together, these three components fuse into a viscous liquid, which can be worked into many shapes using a variety of techniques [10]. Upon cooling, an amorphous network forms consisting of covalent silicon-oxygen bonds (Si–O), ionic monovalent metal-oxygen bonds ($M^+ - O^-$), and ionic divalent metal-oxygen bonds ($O^- - M^{2+} - O^-$) [9]. The main monovalent modifier cations are the alkali ions sodium and potassium, while the most prevalent divalent stabiliser cation is calcium. Other elements may be present as impurities or as deliberate additives to modify the properties of the glass, such as its colour [1,11].

It has been demonstrated that the chemical stability of a glass largely depends on the ratio of the three main glass constituents. When a glass contains a high concentration of alkali oxides and a low concentration of stabilizing elements, it is generally regarded as unstable [12]. However, it has been shown that the chemical stability of glass depends on the overall glass composition, and predicting the stability of glass based on the composition alone is difficult [13]. The deterioration of historic glass is generally associated with changes in the chemical composition of the glass as a result of ion-exchange processes between the glass and water; in the case of museum glass this is atmospheric moisture [14–16]. During this process, cations from within the glass leach out and are replaced by protons, with the simultaneous movement of molecular water into the surface layer of the glass [14,17]. Inside the glass, this causes the formation of an altered surface layer, low in alkali ions and rich in silica [18–20]. Additionally, the leached cations may react with atmospheric compounds to form salts on the outside surface of the glass [21–23].

As a result of these processes, changes in the appearance of historic glass objects may occur, the two main changes being the accumulation of salts on the glass surface, and the formation of a network of hairline cracks (often referred to as *crizzling* [12,24]). In the first instance, ions present on the surface may take the

form of crystalline salts or, if they deliquesce, the presence of a moist film. Fig. 1 shows the effect of cleaning on the appearance of an object upon which a very visible moist film has developed. Whether or not salts deliquesce depends on their deliquescence relative humidity (DRH) and the ambient relative humidity (RH). The occurrence of these phenomena is often described as *glass sickness*. These changes are a result of the irreversible deterioration phenomena described above, and prevention of the development of these symptoms is the main goal in the preservation of historic glass objects. The current work considers the deterioration of glass objects in museum collections, but deterioration also occurs on other forms of historic glass such as historic enamels or miniature painting and daguerreotype cover glasses [25–27]. In addition, when unstable glass is in juxtaposition with metals, the formation of unusual metal corrosion products can occur [28–32]. The prevention of the advancement of glass deterioration is, therefore, not only relevant for the conservation of vessel and decorative glass items but equally essential in the prevention of deterioration in other objects containing glass parts.

Currently there is no straightforward, non-destructive method to identify unstable glass in museum collections before changes in appearance occur. Quantitative analysis of the glass composition is usually not an option as it requires destructive sampling, while non-destructive analytical techniques such as x-ray fluorescence spectrometry [33] are not sensitive enough for quantitative detection of unstable glass. Moreover, no sufficiently precise relationship between glass composition and stability has yet been developed that allows for the clear-cut prediction of unstable historic glass, especially at the borderline of stability and instability. The ratio of different constituents in the glass has been used to indicate glass stability, but as yet this is only valid for specific glass types and cannot be generalised for the diverse glass collections in museums [34]. The use of other non-invasive spectroscopic techniques to measure changes in the chemical structure of the glass has been investigated by others. For example, Raman spectroscopy has been investigated as an indicator of the changes in the structure of glass [35]. Although it was possible to separate stable calcium silicate and lead silicate glasses from potentially unstable alkali silicate glasses, the subsequent discrimination between stable and unstable alkali silicate glasses requires rigorous spectral peak deconvolution, if possible at all. Fiber optic reflectance spectroscopy appears to be a promising technique to measure the hydration layer

thickness [36], and Fourier transform infrared spectroscopy [37] has also been used to measure changes in the glass structure. While these spectroscopic techniques are demonstrably of value in the study of unstable glass, they have yet to provide conservators with a clear-cut assessment method for determining glass stability.

Our approach to the incontrovertible categorisation of historic glass as unstable is based on the rationale that the presence of ions on unstable glass surfaces at very low levels can provide evidence that an object is deteriorating, even when no visual changes can be observed. With few exceptions, the cations originate from the glass itself [2,12], while the anions originate from the atmosphere surrounding the glass. In earlier work it has been demonstrated that ion chromatography (IC) is a suitable technique for the identification of both cations and anions associated with glass deterioration in concentrations below part per million (ppm) levels [8,25]. In relation to the deterioration of glass, IC has also been used to qualitatively identify crystalline salts [21]. The variety of ionic species found on unstable glass surfaces in these studies demonstrates that the formation of salts is a more complex process than initially thought [38]. Moreover, in the course of these investigations it became apparent that the development of a reproducible sampling protocol is necessary, as the results obtained varied greatly due to different sampling materials and methods used in different places. This paper, therefore, describes the development and validation of an analytical protocol for the reliable identification and quantification of ions indicative of glass deterioration for the in-situ investigation of museum objects.

The main application of the protocol is the investigation of large glass collections. In order to make sampling as straightforward as possible, a surface swabbing protocol was developed. This allows for the in-situ sampling of objects by conservators, without the need for the objects to travel. In conservation research surface swabbing and IC analysis has been used successfully, for example, in the study of cellulose nitrate artefact degradation products [39,40], but no validated method for the identification of ionic species on the surface of unstable glass has been published. Prior to validation of the method presented in this paper, efforts have been made to select appropriate sampling materials, which do not interfere with the IC analysis or contaminate the samples, and polyester swabs were identified as the most suitable sampling materials [41,42].

The study of the atmospheric deterioration of 'pristine' decorative glass has received considerably less attention than the two other main groups of glass which enter museum collections, namely archaeological glass or cathedral stained glass. In both these cases a weathered corrosion layer has often formed on the glass prior to museum acquisition as a result of interaction with aqueous solutions and the modes of formation of the respective corrosion layers have been intensively investigated [43]. The existing models of archaeological glass corrosion have been particularly well summarised by Lenting *et al.* [44,45], taking account of relevant studies in nuclear glass dissolution kinetics and extending these models on the basis of their own isotope tracer glass corrosion experiments to create a updated, coupled glass dissolution-silica precipitation model [46].

On the other hand, despite a recent upsurge in international research activity [16], the study of atmospheric degradation of museum vessel glass in display or storage cabinets has received scant analytical chemistry attention in terms of the study of specific historical glass items in collections; most studies have focused on the analysis of replica glasses with historical compositions [12,18,19,22,47–49]. Furthermore, the real-life situation is complicated by the involvement of atmospheric pollutants (notably acetic and formic acid off-gassing from wood or wood products used in storage and/or display cabinets [50–52]), which may react with cations leached from the glass to form salt-laden liquid films

of varying pH on the glass surface. It is in this context that the novel IC protocol validated below provides, for the first time, the possibility of a simple analytical early-warning system for unstable museum vessel glass in order to prioritise those items which require isolation for special care so as to avoid irreversible disfiguration as a result of the deterioration process. The benefits of implementation of the validated protocol are exemplified by a pilot study undertaken at the Rijksmuseum, Amsterdam.

2. Materials and methods

2.1. Ion chromatography

Anion concentrations were determined using a Dionex ICS-2100 IC system equipped with a Dionex DS6 conductivity detector, an Ionpac AS17-C 2×250 mm analytical column and AG17-C 2×50 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 $0.37 \text{ mL} \cdot \text{min}^{-1}$ 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 2×250 mm analytical column and a CG12-A 2×50 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 $0.25 \text{ mL} \cdot \text{min}^{-1}$. 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 into an injection loop with volume of 7 μL . All standards and samples were prepared using HPLC grade deionised water (Millipore Simplicity, 18.2 Ultrapure $18.2 \text{ M}\Omega \cdot \text{cm}$ water system). No glassware was used in the preparation of solutions and samples to avoid contamination.

2.2. Stock solutions, standard solutions and blanks

Cation standard solutions were prepared using a Dionex six-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 solutions of sodium acetate and sodium formate prepared by weighing and dissolving in deionized water. Standard solutions for experimental work were prepared by dilution of these stock solutions. Blanks consisted of deionised water. The contribution of blank swabs to the total ion concentration is reported in earlier work [41].

2.3. Sample preparation and sampling method

Samples were prepared by depositing a total of 40 μL of a standard solution on a sheet of Melinex in four locations, each with 10 μL , within a specified area demarcated by a Teflon sheet with a 32 mm diameter circular cut-out to restrict the sampling area (as demonstrated in a museum context in Fig. 2). Before application of the standard solution the Melinex sheets and Teflon templates were cleaned with ethanol and deionised water and left to dry in a fumehood.

Fig. 2. The sampling protocol demonstrated by one of the authors (GV) at the Corning Museum of Glass.

The applied standard solutions were sampled using polyester TexWipe® TX761 Alpha 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 as much of the solution left on the surface as possible.

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.

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 [53]. The validation of the sampling and analytical method was performed for the following ions related to glass deterioration: sodium, potassium, magnesium, calcium, acetate, formate, chloride, nitrate, carbonate and sulfate. Additionally, the sampling protocol was validated for lithium, ammonium, fluoride, nitrite, bromide and phosphate since these ions were present in the Dionex stock solution anyway. The protocol was validated separately for cationic and anionic compounds as they are analysed on two separate IC systems.

2.4.1. Determination of linearity, range, LOD and LOQ

A calibration curve was made using samples obtained by following the procedure described in Section 2.3 using seven anionic and seven cationic standard solutions with varying ion concentrations, deionized water was included as a blank standard solution. The ion concentrations of the standard solutions before sampling and extraction can be found in the supplementary information. The maximum concentration of ions in the standard solutions was determined by the maximum capacity of the analytical column – 12.5 nmol (AS-17C) and 7.5 nmol (CS-12A) – per analyte per injection. The calibration curve was used to assess linearity, range, LOD and

LOQ. The LOD and LOQ for each ion of interest were calculated using the following equations: $\text{LOD} = 3.3 \cdot \sigma / S$ and $\text{LOQ} = 10 \cdot \sigma / S$. In which 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 subtracted by the calculated peak area according to the calibration curve parameters.

2.4.2. Determination of recovery, repeatability and accuracy

The recovery was determined by applying the sampling and extraction protocol in tenfold. The results of the analyses of these samples were compared to results of a reference solution, with the same concentration. 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 threefold, while blanks were prepared in fivefold.

2.5. Artificial ageing experiments

In order to investigate the applicability of the validated protocol on a glass surface, an experiment was performed using a large piece of unstable flat glass. This glass originated from a historic desk, from which it was removed during restoration because moisture was accumulating on the bottom surface of the glass and damaging the wood underneath. Visual inspection of the glass confirmed the unstable nature of the glass, as a network of hairline cracks was forming. One piece of ca. $15 \times 15 \text{ cm}^2$ (sample code KvL-i) was cut from the glass and was placed in a climate chamber (Heraeus Vötsch VC0020) for three weeks at 70% RH and 70°C to age the glass and induce the deposition of ions on the surface. Prior to ageing, the glass was cleaned using a mixture of ethanol and deionised water (1:1 volume ratio) and was left to dry in the fume hood before being placed in the climate chamber. Six sample locations were identified on outlines of the glass samples traced on Melinex. Three samples were taken after cleaning, but prior to ageing. After ageing, six samples were taken; three from the same locations as prior to ageing and three on new locations. A borosilicate glass sample was included in the ageing chamber as a reference.

2.6. Application of the analytical protocol to the study of museum objects

The validated IC protocol was implemented in the study of 40 vessel glass objects from the Rijksmuseum collection. During a collection survey, a subset of objects was created which were left untreated and available for non-destructive research purposes. The objects investigated were chosen from this subset. Three samples were taken from a flat area on the exterior surface of the main body of each glass in order to obtain the most reliable and comparable results. Ion concentrations were determined for all validated ions.

3. Results and discussion

3.1. Method validation

3.1.1. Specificity

Separation of the ions of interest was achieved using the chromatographic methods described above. Co-eluting occurred in two instances: fluoride and acetate, and bromide and nitrate (Fig. 3a). 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

Fig. 3. Chromatograms showing the separation of anions (a) and cations (b) in stock solutions.

Table 1

List of validated ions with their retention time (RT), studied concentration range (CR), calibration curve parameters (slope, y-intercept, R^2 and the residual sum of squares (RSS)), accuracy (in percentage recovery, $n = 10$), precision (in percent repeatability, $n = 10$) and the lower limits of detection and quantification (LOD and LOQ respectively, as determined by evaluation of the calibration curve). The calibration curves consist of 8 points, with point 1 (blank) measured in fivefold and points 3, 5 and 7 measured in threefold.

Compound	RT (min)	CR (mg/L)		Slope	y-intercept	R^2	RSS	Accuracy (% recovery)	Precision (% RSD)	LOD (mg/L)	LOQ (mg/L)
		Low	High								
Lithium	3.58	0.003	1.43	1.00	-0.003	>0.9994	<0.001	95.7 ± 3.5	3.5	0.008	0.024
Sodium	4.27	0.057	5.70	0.33	0.029	0.9991	0.003	94.8 ± 5.0	4.2	0.140	0.423
Ammonium	4.82	0.011	0.57	0.67	0.010	0.9973	0.286	99.2 ± 2.9	2.9	0.648	1.964
Potassium	6.11	0.023	11.42	0.12	0.004	0.9992	0.001	92.0 ± 5.7	4.1	0.258	0.781
Magnesium	8.71	0.011	5.71	0.45	-0.004	0.9998	0.001	89.5 ± 4.6	4.4	0.067	0.203
Calcium	10.93	0.057	28.57	0.33	0.022	0.9997	0.026	91.8 ± 4.8	4.4	0.404	1.223
Fluoride	2.36	0.010	0.38	0.55	-0.004	0.9977	0.0002	100.7 ± 7.2	6.8	0.020	0.060
Acetate	2.64	0.050	2	0.15	0.007	0.9997	0.0000	101.4 ± 3.1	3.0	0.038	0.116
Formate	3.44	0.043	1.71	0.24	-0.003	0.9994	0.0002	94.3 ± 2.2	2.2	0.046	0.141
Chloride	6.96	0.014	0.57	0.30	0.030	0.9337	0.0036	71.4 ± 25.7	13.6	0.164	0.496
Nitrite	7.94	0.048	1.9	0.24	-0.004	0.9994	0.0002	96.9 ± 2.4	2.2	0.049	0.148
Bromide	9.75	0.048	1.9	0.19	-0.003	0.9981	0.0002	98.5 ± 3.8	3.8	0.090	0.274
Nitrate	10.11	0.048	1.9	0.19	-0.003	0.9990	0.0002	91.9 ± 2.9	2.9	0.063	0.192
Carbonate	13.25	0.050	2	0.045	0.13	0.9926	0.0001	120.0 ± 16.6	10.3	0.185	0.561
Sulfate	14.62	0.071	2.85	0.21	-0.013	0.9966	0.0021	78.2 ± 4.3	4.3	0.179	0.542
Phosphate	16.37	0.071	2.85	0.079	-0.007	0.9960	0.0003	95.8 ± 3.1	3.1	0.194	0.588

in the case of cover glasses of daguerreotypes [25]. The cations could be baseline separated (Fig. 3b). The standard deviation of the retention time (RT) varied between 0.020 and 0.118 minutes for the anions and between 0.004 and 0.134 minutes for the cations.

3.1.2. Linearity and range

The applied protocol was linear within the studied range (Table 1). The coefficient of determination (R^2) was larger than 0.999 for all compounds except for ammonium, fluoride, bromide, carbonate, sulfate and phosphate which gave an R^2 larger than 0.99 (Table 1). The calibration curve of chloride had 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. The calibration curves for each investigated ion can be found in the supplementary data. The fact that chloride shows a poor linear response can be attributed to the high and irreproducible amount of chloride present in the blanks. 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 increase of R^2 to 0.998 for sulfate and phosphate, and a slight increase of R^2 to 0.994 for carbonate.

Ammonium, acetate and formate show a non-linear response in the ion chromatography systems, 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 concentra-

tions the proportion of the compound in non-dissociated state is larger and therefore the relative amount detected by the IC system decreases with increasing concentration. 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.

3.1.3. Accuracy

The recovery of anions after blank subtraction varies from 71.4% to 101.4%. The recovery of chloride (71.4%) and sulfate (78.2%) is low compared to the other anionic components, which show a recovery ranging from 91.9% to 101.4%. Carbonate shows a recovery above 100%, probably due to the absorption of carbon dioxide into the eluent resulting in a high carbonate concentration in the background. The recovery of cations varies from 89.5% to 99.2% (Table 1).

The low recovery of chloride and sulfate is less straightforward to explain and currently unclear. 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. An experiment to investigate this notion was carried out by application of a stock solution directly to a swab and subsequent extraction. The solutions obtained were compared to the original extracted solutions and

Fig. 4. Anion concentrations of solutions obtained by application of a stock solution directly on a swab and subsequent extraction compared to solutions obtained by swabbing a stock solution from a Melinex surface and subsequent extraction and to the relevant reference solution. ($n = 6$).

the reference solution described in paragraph 2.4.2. Fig. 4 shows the results of this experiment. All anionic compounds showed good recovery for the solutions applied directly to the swab, so an interaction between the swab and the analyte is not occurring. In particular, sulfate showed an excellent recovery of $97.7 \pm 0.6\%$, which is much higher than the recovery of sulfate during the validation experiments. Thus, the low recovery of chloride and sulfate for the model systems remains unexplained.

3.1.4. Repeatability

The relative standard deviation (RSD) for both the anionic as the cationic compounds is $<5\%$ for all compounds except for fluoride (6.8%), chloride (13.6%) and carbonate (10.3%) (Table 1). The presence of fluoride is not expected in the study of historic glass. Chloride is an interesting ion in the study of glass deterioration because of its possible presence as a result of surface contamination by sodium chloride, but its high and irreproducible presence in the blanks is problematic. Carbonate is an ion often deemed to be 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 4.3%. This means that, under the validation conditions, the actual concentration of sulfate can be calculated, despite the lower recovery.

3.1.5. 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 1).

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 paper 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 [25]. 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 paper. Moreover, the aim of the pilot study was different from the intended appli-

cation of the protocol validated in this paper, as it merely 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 with the swab. The current protocol, in contrast, 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 the full identification of deterioration products on unstable glass and the pilot study is, therefore, the most suitable for comparison 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 been found only occasionally in low concentrations on the surface of unstable glass [21,54], 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.

3.2. The applicability of the protocol as an early warning system for unstable glass

The main implementation strategy of the sampling protocol is as an early warning system for unstable glass in museum collections. Therefore, it is crucial to be able to obtain reliable analytical results for the prime ionic species associated with historic glass deterioration. These species include sodium, potassium, magnesium, calcium, acetate, formate, chloride, carbonate and sulfate. Results of the validation presented above provide a good indication of the reliability of the analysis of these ions. Some important factors influencing the results of the validation experiments in relation to the application of the protocol as an early warning system for unstable glass are discussed below.

3.2.1. Sodium, potassium and chloride

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 [21,56], it may be a key marker-ion in the identification of unstable glass objects. Although the presence of sodium on the surface of unstable glass can be related to chemical deterioration of the material, it can also be attributed to the ubiquitous presence of sodium chloride in the atmosphere [55] and to handling of the glass. 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 usefulness of sodium as a marker ion for unstable glass. Therefore, more research is required on historical glass objects to determine levels of sodium which are specifically related to deterioration.

As confirmed in a recent study [57], the leaching of 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% [21,25]. 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.

3.2.2. Carbonate

Carbonate is often associated with glass deterioration and environmental recommendations for the prevention of deterioration of unstable glass are often based on the DRH of potassium carbonate at 42% [38]. In actuality, the presence of carbonate on unstable glass surfaces has not often been reported [21,54]. Be that as it may, because of the commonly accepted association of carbonate with glass deterioration [2] 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 in the eluent before degassing [58], so there is always a carbonate peak 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 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 [25]. 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 future work.

3.3. Artificial ageing experiments

Before ageing of the glass sample KvL-i, all ion concentrations were below their LOQ. After ageing the main anionic compounds detected were acetate and formate. The main cationic compounds found were sodium and potassium. No other ions were detected above their LOQ. The samples taken from the unstable glass were compared to ions present on a borosilicate glass, see Fig. 5. The relative standard deviation of the ion concentrations measured after ageing is shown in Table 2.

There is a large standard deviation for the ions detected, much larger than during the validation experiments. An explanation for the high RSD of these samples can be sought in three factors. First,

Fig. 5. Concentration (µg/L, log-scaled) of acetate, formate, sodium and potassium of samples taken from unstable glass KvL-i and from a borosilicate reference glass before and after artificial ageing (n = 6). The absence of bars for acetate and formate indicates that these ions were not found in the corresponding samples.

Table 2

Ion concentrations of samples taken from artificially aged glass and their relative standard deviation (n = 6).

Analyte	Concentration (mg/L)	RSD (%)
Sodium	8.86	21.52
Potassium	12.87	25.27
Acetate	1.86	13.05
Formate	5.07	30.94

there is a difference in the substrate surface from which the samples were collected. During validation, an inert substrate material (Melinex polyester), was used to create similar circumstances for each sample, while the samples in the artificial ageing studies were all obtained from unstable glass surfaces. It is to be expected that all ions on a polyester surface can be removed by swabbing because the ions are less likely to form a weak ionic bond to the substrate than when ions are present on the surface of unstable glass. If ions are weakly bonded to the surface it is possible that they are not all efficiently collected by swabbing, which would increase the RSD of the samples. Second, the action of swabbing the surface may have an effect on the altered surface layer of the glass, which in turn influences the amount of ions sampled. Basically, there are two types of ions which could be collected during sampling: the 'free ions' on the surface of the glass, present in the form of salts, and the mobile ions which are present in the altered surface layer. Based on the validation results it is likely that all free ions are sampled from the glass surface, but variations in the amount of ions which are leached from the altered surface layer might explain the increase in RSD. The deterioration of glass causes a decrease in density of the surface layer of the glass [2,59], which potentially results in the retention of some of the anions that migrate to the surface due to deterioration processes. Third, little is known about the homogeneity in which the deterioration products are distributed across the surface of unstable glass. It has been observed that salts are distributed heterogeneously across the surface of unstable glass [22], but on a much smaller scale (< 0.01 mm²) than the sampling area applied in this study. Therefore, it remains unclear how the deterioration products are distributed across the glass surface on a larger scale, but it could be that local differences in the amounts of ions on the surface exist. This a factor which needs to be taken into account when studying glass

Fig. 6. Sodium (a) and potassium (b) concentrations of samples taken from objects from the Rijksmuseum grouped according to their condition as determined by visual inspection.

deterioration and requires further attention. All these factors need to be included in the study of the formation of deterioration products on unstable glass surfaces and the high RSD of ions present at a high concentration needs to be investigated further.

3.4. Application of the analytical protocol to the study of museum objects

In order to achieve optimal care of glass in museum collections the unambiguous categorisation of unstable items is necessary but up to now has not been possible, especially for glass in the early stages of deterioration. The development of a quantitative and minimally invasive analytical technique to address this problem thus gives conservators the ability to overcome this deficiency in collections' care. This section describes the initial results from the study of Rijksmuseum vessel glass objects using IC and discusses the outcomes in relation to other studies of glass deterioration.

The Rijksmuseum glass collection includes c. 1500 vessel glass objects. For a collection survey of 320 objects selected for a reinstallation carried out in 2009, a system was developed to classify glass stability according to the appearance of objects, with categories ranging from perfect condition (A) to heavily deteriorated and unfit for display (E) (see Lamain et al. [8] for a full description of the categories). It was found that a substantial number of objects showed signs of deterioration (categories D and E), but for most of the objects it was unclear whether surface changes were related to glass deterioration. These objects were classified in categories B and C and they comprise approximately 80% of the investigated objects.

Since the conservators were sometimes uncertain in making the distinction between categories B and C and between categories C and D, some objects were labelled B/C or C/D. The results of the subsequent IC investigation were grouped according to the classification of the conservators. A description of the objects and their classification can be found in the supplementary material.

A wide variety of ions was found on the surface of the glass objects (Figs. 6 and 7). Sodium and/or potassium were detected in most of the samples, which is in line with their known behaviour to leach from glass networks. Objects from categories B, B/C, and C generally show low sodium and potassium concentrations, whereas the concentration of these ions is considerably higher for samples from categories C/D, D, and E. Acetate, formate and carbonate were the main anions found on the surface of the objects, predominantly in categories C/D, D and E. However, carbonate was only detected

when acetate and/or formate were present in very low concentrations or were not detected at all. Chloride, nitrate and phosphate were detected in varying amounts, but in much lower concentrations. Sulfate was detected in higher amounts, but only in the two objects from category E. No lithium, magnesium, calcium, nitrite or bromide were detected above the quantification limits.

The analytical evidence corroborates the classification of the conservators for those objects designated as unstable (categories D and E). The same is true for objects from category C/D, with the exception of two objects: BK-NM-789-A and BK-NM-789-B. The reports made after visual inspection indicate that these objects both had a 'clear haze' and 'potentially dried out droplets', while other objects in the same group were described as having a moist surface layer which is more definitively associated with advanced glass degradation than a white haze on the surface. Therefore, these two objects may have been misassigned to their categories.

For the glasses classified in categories B, B/C and C it is more difficult to discriminate between stable and unstable glass because the objects show a range of designations representing the condition of the glass surface. As a result the description of the condition of these objects is often unclear and terms as 'slightly hazy', 'mildly greasy', 'dirty', 'dried up droplets' and 'moist' are used throughout these three categories. None of these descriptions allows a sufficiently precise assessment of the level of glass degradation to assist collections' care decision making. In contrast, the IC results provide clear-cut numbers which represent the condition of the glass surface and allow for direct inter-object condition comparison.

The prime goal of the application of the IC protocol is to be able to distinguish between chemically stable and unstable glass objects based on the presence of ions on the surface, in particular when visual examination is inconclusive in determining if progressive degradation is taking place. The results described above clearly demonstrate that IC is a valuable tool in the classification of glass stability. They confirm that the analytical protocol can add precision to a visual classification of unstable glass by conservators and can be used to focus attention on the display and storage environmental conditions for the preservation of those objects for which the amount of ions on the surface is high. Future studies on both model glasses and museum objects will refine the discrimination which can be achieved in assessing the susceptibility of glass items within museum collections to undergo degradation.

Furthermore, the validation of this new analytical methodology for the benefit of glass collections' care also provides the basis to contribute, ultimately, to a better understanding of the complex,

Fig. 7. Acetate (a), formate (b) and carbonate (c) concentrations of samples taken from objects from the Rijksmuseum grouped according to their condition as determined by visual inspection.

imperfectly understood processes of museum glass deterioration and the kinetics of the underlying chemical reactions. The interaction between glass and water and the subsequent alteration of the glass structure is a very complex process involving many aspects such as congruent glass dissolution, diffusion reactions, hydrolysis and condensation reactions and growth of secondary phases and several models for the processes involved have been developed (see e.g. [46,60–63]). In particular, the rate at which the alteration of the glass structure occurs is an important topic in the study of glass decay relevant to the study of the use of glass as storage material for radioactive waste [61]. In relation to historic collections, the validated IC analytical protocol now permits SIMS and other analytical studies of the chemical changes occurring within the glass matrix [18,19,22,57,64] to be complemented by quantitative data on the ionic species simultaneously forming on the glass surface. This advance thus rectifies a restrictive deficit in the arsenal of available analytical techniques required for a full understanding of the contribution of the diverse factors which contribute to atmospheric degradation of glass in collections.

4. Conclusions

The research presented in this study was motivated by the need to validate a simple method for the identification and quantification of ionic species on the surface of unstable glass. The use of ion chromatography as the main analytical tool resulted in good separation and quantitative analysis of components associated with

glass deterioration, while swabbing was confirmed as a suitable sampling method to remove deposited ions. The sampling and extraction procedures proved to be accurate, precise and with good limits of quantification for the components of interest. This is of particular relevance in the use of marker ions for glass deterioration since, based on accepted glass deterioration mechanisms and on previous analytical studies, the presence of traces of sodium, potassium and, potentially, calcium ions on the glass surface are likely to be indicative of glass deterioration. For sodium to be a useful marker ion, the interference from adventitious sodium chloride needs to be taken into account and so quantification of the chloride concentration will be important for determination of the amount of sodium chloride on the glass surface. However, because of its poor validation parameters, chloride concentrations need to be regarded with caution. The detection and quantification of carbonate, an important but little investigated anionic component of glass deterioration, is limited by the IC equipment but as a result of the validation parameters obtained the interpretation of carbonate concentrations in samples is more feasible than anticipated.

The research presented in this paper 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. In a pilot experiment with samples obtained from artificially aged unstable glass, the high relative standard deviation found points to the relevance of imperfectly understood aspects of the glass deterioration process. This will therefore be the subject of continuing research; the developed protocol

will be used to explore intricate aspects of glass deterioration on a wide range of objects from museum collections in a bid to identify reliable marker ions for unstable glass and thereby enable the protocol to be utilised for pinpointing glass instability definitively.

The pilot project at the Rijksmuseum has fulfilled its primary purpose; namely, assessment of the novel IC analytical protocol in a museum setting in order to detect glass deterioration before the onset of visible alteration of the glass surface or when such surface changes do not unambiguously indicate glass instability. In addition, implementation of this newly-developed strategy at the Rijksmuseum has underscored its potential to extend the current understanding of mechanisms and kinetics of atmospheric deterioration of vessel glass in greater detail than heretofore. The focus of ongoing research therefore centres on not only the refinement of the use of the protocol as an early warning system for the detection of unstable glass but also, concurrently, the study of poorly-understood mechanistic issues concerning variations in the leaching behaviour of alkali and alkaline earth cations with respect to glass composition, along with the chemical consequences of the different environmental conditions which induce cation leaching from glass.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Guus Verhaar: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Maarten R. van Bommel:** Conceptualization, Methodology, Data curation, Writing - review & editing, Supervision. **Norman H. Tennent:** Conceptualization, Methodology, Writing - review & editing, Supervision.

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Supplementary materials

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