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GLASS ATMOSPHERIC ALTERATION

CULTURAL HERITAGE, INDUSTRIAL
AND NUCLEAR GLASSES

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LA NATURE DE L'ŒUVRE

The implementation of ion chromatography as a key analytical technique for investigation of unstable glass in museum collections

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Abstract

Conservators often face problems in identifying chemically unstable glass objects in museum collections before changes in appearance occur. This paper describes the development and application of an ion chromatography protocol aimed at identifying unstable glass in museum collections before visible changes appear, based on the build-up of ions on the glass surface as a result of deterioration processes induced by atmospheric conditions. The suitability of different types of swabs for sampling surface deposits from unstable glass was investigated. A validated method, using polyester swabs as the sampling material, was applied to objects from Museum Boijmans van Beuningen. Analysis of museum samples indicated that a distinction could be made between stable and unstable glass objects based on the sodium, potassium, acetate and formate concentrations. The outcomes of this study allow for the further investigation of unstable glass using ion chromatography as a key analytical technique and the development of an early warning system for unstable glass.

Résumé

L'identification des objets en verre de collections muséales chimiquement instables, avant l'apparition des premières manifestations macroscopiques de l'altération de la surface du verre, s'avère être une difficulté majeure pour les conservateurs. La présente publication décrit le développement et l'application d'un protocole de chromatographie ionique visant à identifier les œuvres en verre chimiquement instables au sein des collections, avant que ne soit visible macroscopiquement une dégradation de leur surface d'origine chimique. Ce protocole est basé sur la collecte d'ions accumulés à la surface du verre consécutivement à son altération sous atmosphère humide. La pertinence de différents types de tampons employés pour le prélèvement des dépôts ioniques à la surface des verres chimiquement instables a été étudiée. Une méthode validée, utilisant des tampons en polyester pour les prélèvements, a été mise en œuvre sur des objets de la collection du musée Boijmans van Beuningen. Les résultats des analyses conduites sur ces objets anciens apparaissent très encourageants quant à la possibilité de distinguer les objets en verre stables de ceux instables, sur la base des concentrations obtenues en sodium, potassium, acétate et formate. La chromatographie ionique pourrait ainsi se révéler comme une technique analytique de choix pour l'étude des verres chimiquement instables et leur détection précoce au sein des collections.

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INTRODUCTION

The deterioration of glass in museum collections is a large problem for curators and conservators. Condition surveys carried out at museums throughout Europe indicate that up to 30% of the objects in collections may be unstable, implying that many hundreds of objects are at risk of further decay. These surveys (see for example Cobo del Arco, 1999) were carried out using visual examination, which likely leads to an underestimation of the total number of unstable glass objects, as signs of deterioration are not always visible (Oakley, 1990). It would therefore be beneficial to have reliable instrumental means of analysis for the identification of unstable glass. This paper focuses on the use of ion chromatography (IC) as a versatile analytical tool for the investigation of unstable glass in museum collections.

During the process of glass deterioration, cationic species gradually leach out of the glass network under the influence of atmospheric moisture. This mechanism is referred to as an ion-exchange process and has been described in the conservation literature (see Kunicki-Goldfinger, 2008 for a review). The leached cations migrate to the surface of the glass where they can react with atmospheric molecules and form salts (Kunicki-Goldfinger, 2008). Depending on their hygroscopicity, these salts may attract water from the atmosphere and deliquesce, resulting in the formation of a moist layer on the glass surface. If the glasses are stored at an RH below their deliquescence relative humidity (DRH) these salts will crystallize.

The above-mentioned processes may result in a wide variety of ions present on the surface of unstable glass objects in museum collections (Verhaar *et al.*, 2016). Sodium formate has been identified in several occasions (see *e.g.*, Schmidt, 1992; Robinet *et al.*, 2004; Eremin *et al.*, 2005; Thickett and Pretzel, 2010), the presence of carbonates, sulfates and chlorides has been mentioned (Tichane, 1966; Organ, 1957; Roemich, 1999), and the possible formation of potassium formate was suggested by Eremin *et al.* (2005). IC has been used for the characterisation of crystalline deterioration products (Eremin *et al.*, 2005) and ionic species in moist films and droplets on unstable glass surfaces comprising vessel glass, daguerreotypes and portrait miniature cover glasses (Verhaar *et al.*, 2016).

The current research is part of a project aimed at identifying glass objects in an early stage of deterioration based on the amount of ions on the surface. This study follows preliminary investigations in which IC's applicability and potential for quantitative analysis of surface ionic species in the study of glass deterioration was explored (Lamain *et al.*, 2013; Verhaar *et al.*, 2016). Surface swabbing was chosen as sampling method since most conservators are familiar with the use of swabs and because of its low-cost and ease of use. It has the added bonus that samples can be taken on site in museums by conservators and sent for IC analysis. Surface swabbing and IC analysis has been used successfully in conservation, for example in the study of cellulose nitrate artefact degradation products (Quye *et al.*, 2011a; Quye *et al.*, 2011b). The current paper

describes the selection of suitable sampling materials for the investigation of unstable glass objects.

This paper reports advances in the development of a quantitative analytical IC protocol for the identification of ionic species on the surface of unstable glass. Prior to the work presented in this study it has not been possible to apply IC reproducibly for the quantitative determination of ions present on the surface of unstable glass. In order to achieve this, a validated method was developed to ascertain the reliability of the analytical results. In analytical chemistry method validation is carried out extensively: countless examples of method validation papers can be found in, for example, food chemistry (Spínola *et al.*, 2014) and pharmaceutical studies (Yang *et al.*, 2017) as well as in conservation research (*e.g.* Desauziers *et al.*, 2015). The first results of the application of the IC protocol to the study of museum objects are presented in this paper. The full validation experiments and more extensive research on museum objects will be published later.

EXPERIMENTAL

Ion chromatography analysis

Ion chromatography analysis was carried out using an ICS-1100 IC system for cations and an ICS-2100 system for anions. Details on the chromatographic methods and equipment were published in earlier work by the authors (Verhaar *et al.*, 2016).

Selection of sampling materials

The suitability for sampling of four different types of swabs was investigated: cotton swabs from the drugstore, handmade swabs from cotton wool, sterile swabs used for human tissue sampling and polyester swabs (Texwipe Alpha® TX761) used for precision cleaning in cleanroom environments.

These swabs were placed inside polypropylene vials filled with 1.35 mL of deionized water for an hour to extract ions potentially present in these swabs. These concentrations are referred to as the contribution of the blank to the total ion concentration. Ten replicate extractions were made for each swab type and the average ion concentration and standard deviation were determined.

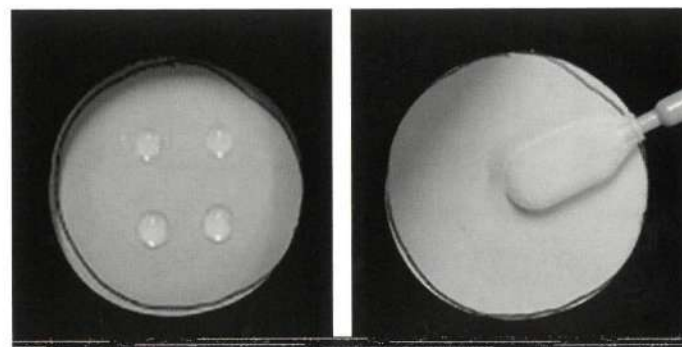


Fig. 1: Sample preparation and sampling using a Teflon template and polyester swabs (© UvA/G. Verhaar).

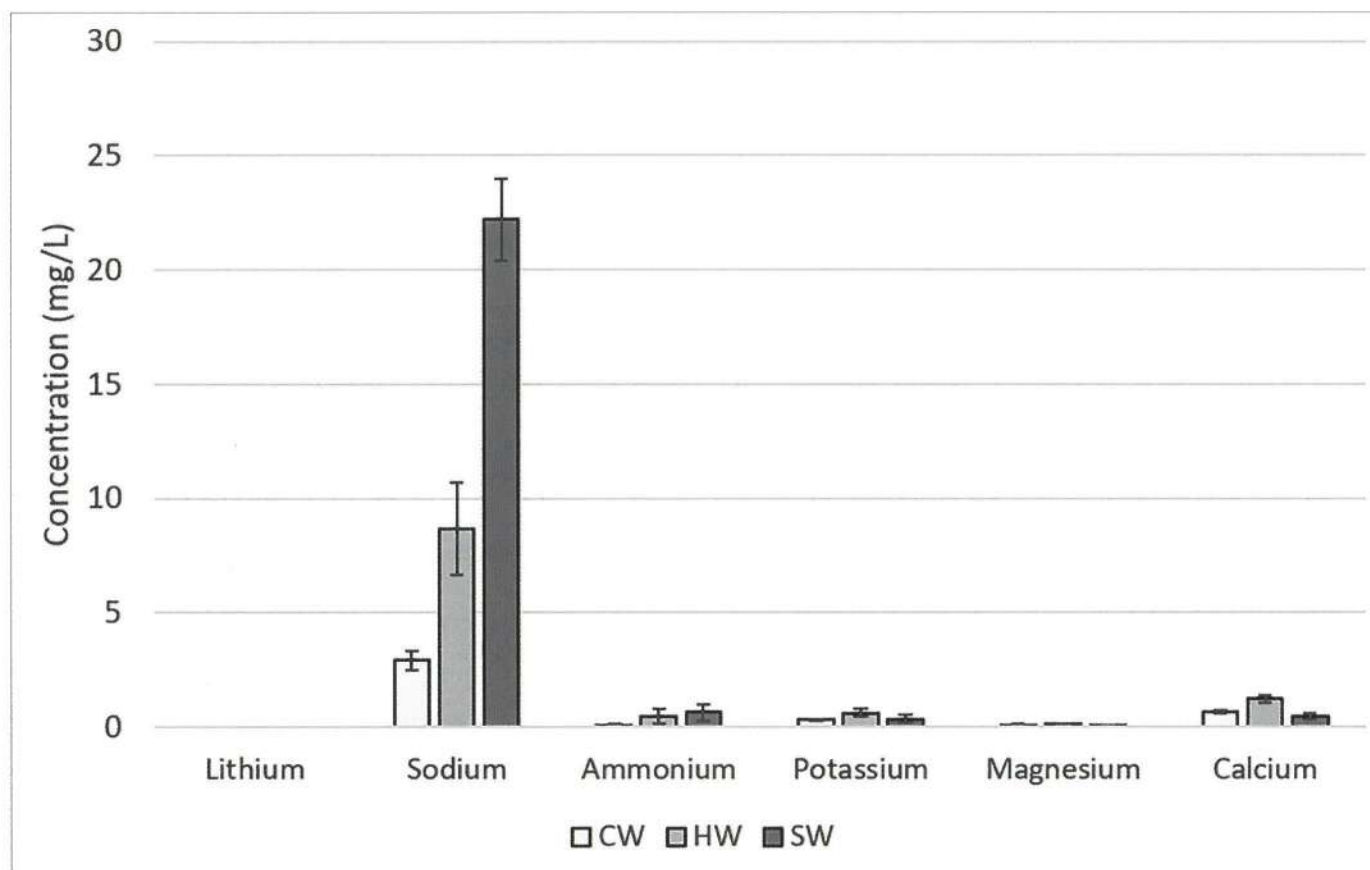


Fig. 2: The contribution to the cation concentrations from three types of swabs: from the drugstore (CW), handmade from cotton wool (HW) and sterile swabs used for tissue sampling (SW) as determined by IC analysis (n = 10 for each type of swab) (© UvA/G. Verhaar).

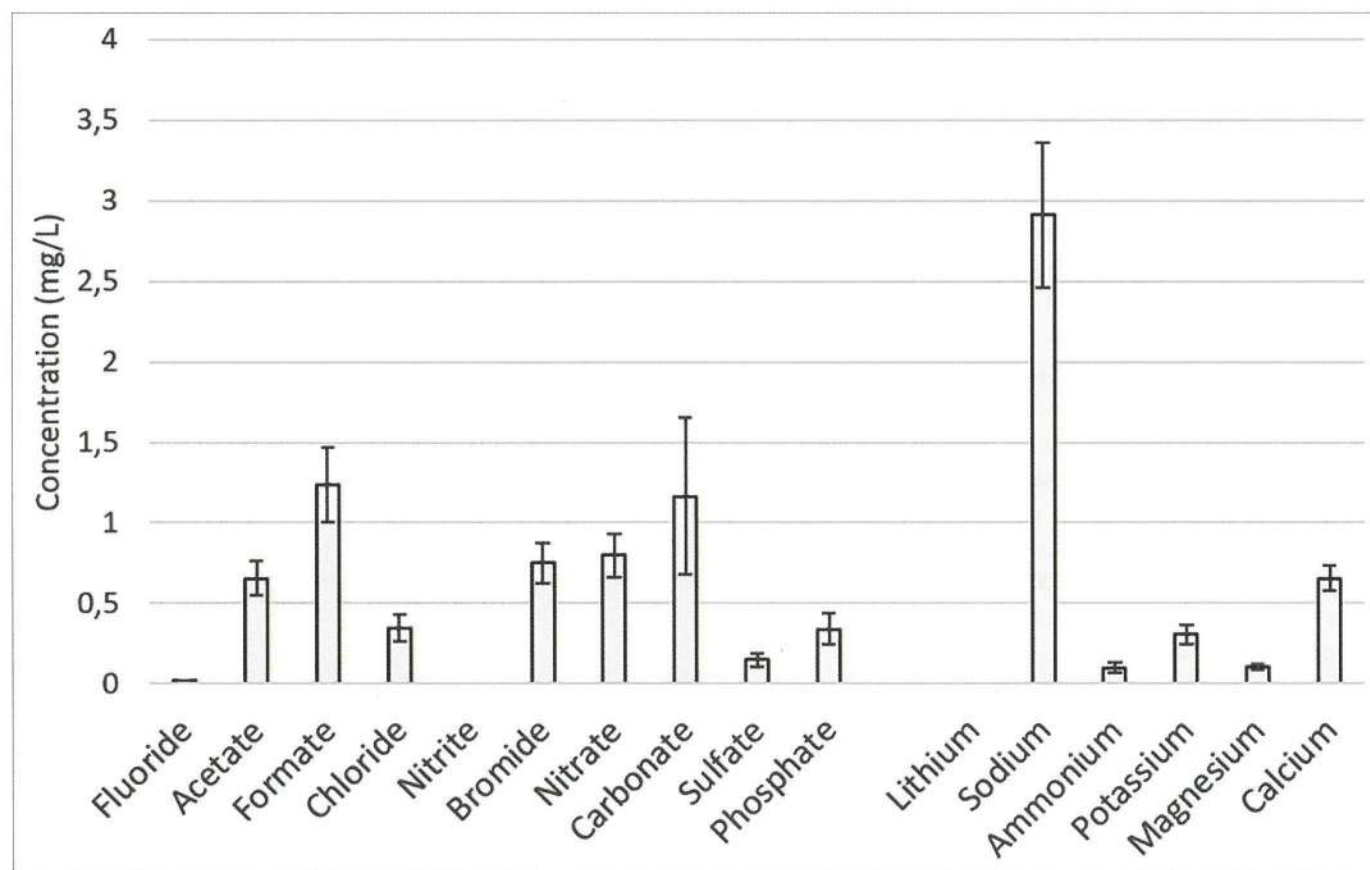


Fig. 3: The contribution of the cotton swab blanks from the drugstore (CW) to the anion concentrations as determined by IC analysis (n = 10) (© UvA/G. Verhaar).

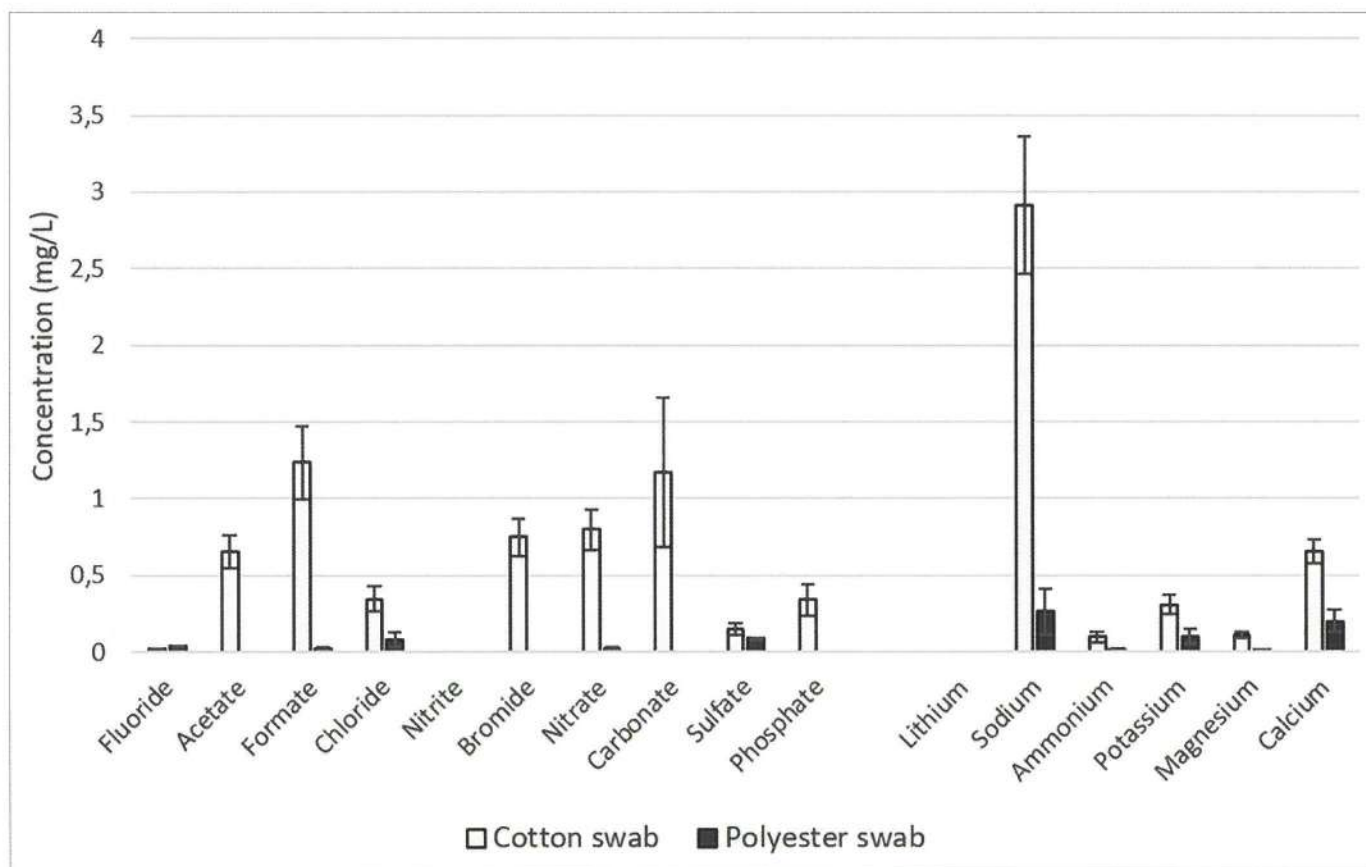


Fig. 4: The contribution of cotton and polyester blank swab blanks to the investigated anion and cation concentrations as determined by IC analysis (n = 10) (© UvA/G. Verhaar).

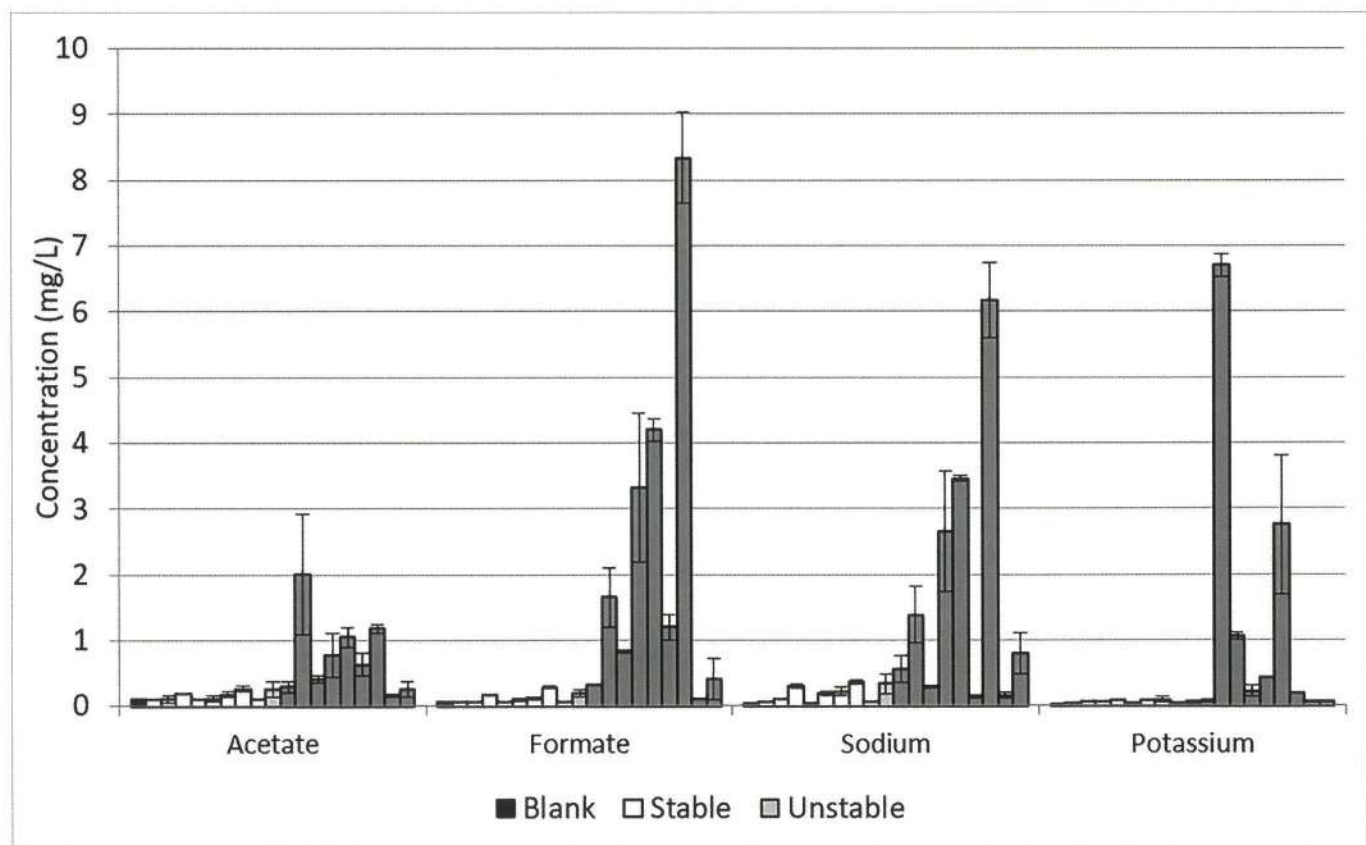


Fig. 5: Ion concentrations for the Museum Boijmans van Beuningen samples for acetate, formate, sodium and potassium as determined by IC analysis (© UvA/G. Verhaar).

Validation of the sampling protocol

A sampling protocol for the reproducible sampling of ionic species on unstable glass surfaces was developed. The protocol consists of the following steps:

1. moisten the swab on one side using 50 μL of deionized water, keeping the other side dry,
2. place a Teflon template over the area to be sampled,
3. using the moistened side of the swab, swipe over the surface in one direction four times back and forth, covering the entire surface as limited by the template,
4. repeat step 3, but in perpendicular direction,
5. repeat steps 3 and 4 with the dry side of the swab to collect as much of the residue as possible,
6. place swab in a 1.5 mL polypropylene centrifuge tube,
7. add 1.35 mL of deionized water to the centrifuge tube for extraction and close the tube,
8. after 60 minutes remove the swab from the tube with cleaned tweezers, be careful not to contaminate the sample,
9. centrifuge the sample at 5000 rpm, over a period of 4 minutes,
10. transfer 900 μL of the solution to a vial for IC analysis,
11. perform IC analysis.

The protocol was validated according to the ICH Harmonised Tripartite Guideline (ICH, 2014). Validation was carried out for the following ions: sodium, potassium, magnesium, calcium, acetate, formate, chloride, nitrate, carbonate and sulfate.

Mock-up samples

In order to validate the above method, mock-up samples were developed. They consisted of a sheet of Melinex upon which four 10 μL drops of ionic solutions were applied. These droplets were then sampled using the described protocol (figure 1). The concentrations of ions in these solutions were varied in order to be able to determine all the validation parameters.

Investigation of museum objects

Eighteen objects from Museum Boijmans van Beuningen (Rotterdam, The Netherlands) were chosen for sampling in consultation with the head of conservation. Eight of these objects were classified as stable and ten of these objects as unstable. At least three samples were taken from the surface of each object. These objects had previously been investigated during a glass collection survey, in which over 4000 objects were included. This project included a condition check and documentation of the condition after visual inspection, cleaning of the objects and storing them in a stable environment after cleaning (Burghout and Slager, 2013). Since all objects were cleaned similarly, a "condition baseline" was created, allowing for the discussion of glass stability based on the concentration of ions subsequently found, 5 years later, on the glass surface.

RESULTS AND DISCUSSION

Selection of sampling materials

Initially three materials were tested for their extraction of six cations into solution: commercially available swabs (CW), handmade cotton swabs (HW) and the sterile swabs (SW). The results of the extraction are presented in figure 2. CW has the lowest contribution to the cation concentrations, and subsequently the contribution of these swabs to ten anion concentrations was also determined (figure 3). Thereafter, they were selected to be used in a pilot study on the qualitative identification of ionic species in droplets on weeping glass (Verhaar *et al.*, 2016).

The pilot study demonstrated the necessity of developing a quantitative analytical protocol in order to be able to make inter-object comparisons. In order to decrease the contribution of the blanks to the ion concentrations the polyester swabs were also blank extracted after the pilot study was conducted. Figure 4 shows the results of this experiment in comparison with the CW swab blank extractions. The polyester swabs yield much lower ion concentrations than the cotton swabs and were therefore selected to be used in the sampling protocol.

Validation of the protocol

Of particular relevance for the deterioration of glass is the validation of sodium, potassium, magnesium, calcium, acetate, formate, chloride, nitrate, carbonate and sulfate. The full validation results will be published elsewhere (Verhaar *et al.*, forthcoming), but some relevant outcomes can be found below.

All cationic species and the anionic species acetate, formate, nitrate and sulfate showed good validation parameters: a linear relation between the amount of sampled ions and the response of the analytical system was achieved, with high reproducibility and accuracy. Sulfate showed lower accuracy, but the reproducibility was high. Chloride and carbonate showed poorer validation parameters. For chloride, this is most likely a result of the high and varying concentration of chloride in the low concentration range, possibly due to unavoidable contamination of the sample by sodium chloride. In that case, a high variation in sodium concentration is also expected, which is not the case. Further research is required to understand this observation. Carbonate is difficult to quantify using the current IC setup, due to its absorption into eluent used in the chromatographic system, but the fact that a linear relationship between the concentration and the response was achieved seems promising for future research. The limits of detection and quantification for all ions were below the ion concentrations measured in the pilot study (Verhaar *et al.*, 2016).

It should be noted that the current system used to validate the analytical protocol is a model system not perfectly representing glass deterioration. It does show that the swabbing protocol can be used to quantitatively analyse the presence of the cations sodium, potassium, magnesium and calcium,

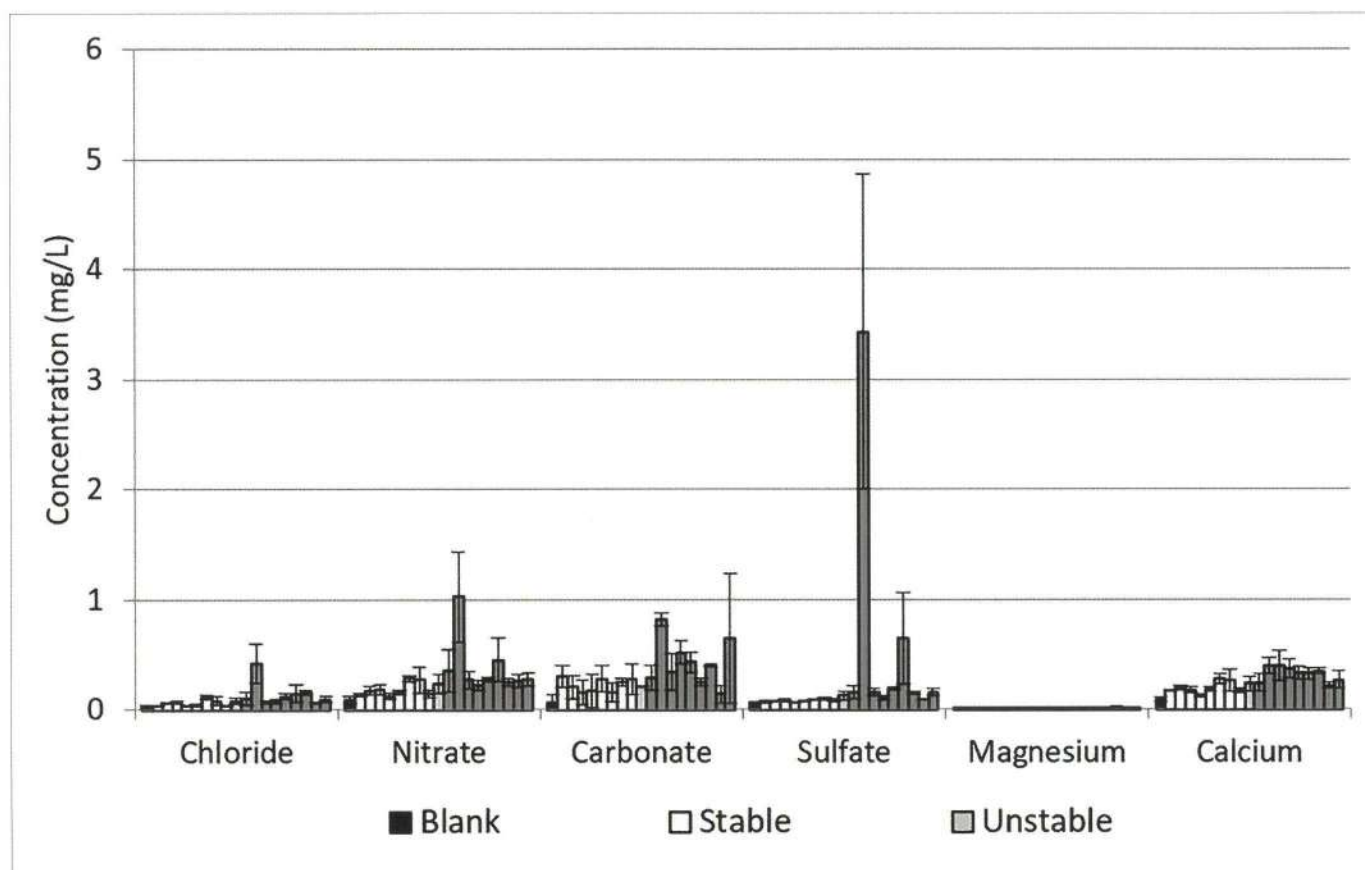


Fig. 6: Ion concentrations for the Museum Boijmans van Beuningen samples for chloride, nitrate, carbonate, sulfate, magnesium and calcium as determined by IC analysis (© UvA/G. Verhaar).

and the anions acetate, formate, nitrate, and sulfate sampled from a surface. However, the Melinex polyester sheet used as a substrate in the mock-ups does not allow for the investigation of the interaction between these ions in solution and the glass surfaces on which they might be found.

Investigation of museum objects

The validated protocol was used to study eighteen objects from Museum Boijmans van Beuningen, Rotterdam. This glass collection was chosen as it contained glasses previously documented as “clearly unstable” and “clearly stable”. As these objects were all cleaned similarly, and stored in the same environment without handling, it might be assumed that all the ions present on the surface are a result of deterioration. It is therefore interesting to evaluate the difference in ion concentrations between the stable and unstable glass objects.

The results of analysis are shown in figures 5 and 6. In the stable group, no ions were detected in a concentration higher than the validated limits of quantification (LOQ). In the unstable group, however, the concentrations of acetate, formate, sodium or potassium exceed the LOQ and are significantly higher for seven out of ten objects. The other three objects show concentrations below the LOQ. This is interesting as there were no visual signs of the formation of a moist layer on the surface of any of the glasses, indicating that IC is a suitable technique for the detection of invisible deterioration products.

These results suggest two significant outcomes of this first application of the protocol to the study of museum objects. Firstly, a high concentration of ions is an indication of glass instability, but a low concentration does not necessarily mean that the glass is chemically stable. Secondly, the developed protocol is suitable for the quantitative detection of ions on the surface of unstable glass and thus allows for further study of glass deterioration processes and the use of IC as an early warning system for unstable glass.

The four ions detected in large concentrations on the objects (sodium, potassium, acetate, formate) seem to be suitable for the use in an early warning system. It is generally recognised that during deterioration sodium and/or potassium ions are deposited on the glass surface by an ion exchange process (Kunicki-Goldfinger, 2008). These ions are therefore prime candidates as marker ions for unstable glass. Accordingly future work will focus on a more detailed investigation of sodium and potassium as indicators for the breakdown of glass. The source of the anionic species is less certain. Acetate and formate are known to originate from the off-gassing of acetic acid, formic acid or formaldehyde from wooden storage cases. However, the glasses investigated were stored in metal cabinets without an apparent source of these compounds. It is therefore of interest to investigate whether or not these ions can originate from the ambient atmosphere in which the glasses were stored. This requires further research.

It should be noted that the relative standard deviation within a single object is still high in some instances. This may be a result of the fact that the accumulation of ions on the surface of the object depends on the location or a result of a deficiency in the analytical protocol, which could not be accounted for in the model system used for validation. Future research will focus on further understanding these observations.

CONCLUSIONS

The development and validation of an ion chromatography analytical protocol provides, for the first time, the opportunity to quantitatively study the presence of ions on the surface of unstable glass objects in museum collections. This allows for the future use of this method in an early warning system for unstable glass, but also for the more fundamental investigation of glass deterioration processes. In particular the use of sodium and potassium as marker ions for unstable glass appears to be a crucial feature to pursue during the development of an early warning system for unstable glass.

Future work will focus on the refinement of the analytical protocol, studying fundamental processes underlying the deposition of ions on unstable glass surfaces and on providing practical guidelines for the safe storage of unstable glass objects in museum collections.

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