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Publication date
2015
Document Version
Final published version
Published in
Glass Deterioration Colloquium - Extended Abstract. - Session I: Glass Deterioration & Conservation

Gerhard Eggert and Andrea Fischer (Eds.)

Glass Deterioration Colloquium – Extended Abstracts

State Academy of Art and Design Stuttgart
Feb. 20th & 21st, 2015

Conference organisers:

STAATLICHE AKADEMIE DER BILDENDEN KÜNSTE STUTTGART
Objektrestaurierung

ICOM
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SESSION I:

GLASS DETERIORATION & CONSERVATION

Identification and documentation of early stages of glass sickness

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Introduction

The identification of early stages of glass sickness is of great importance for conservators and curators. Whereas degradation mechanisms are generally well understood (Brill, 1975; Kunicki-Goldfinger, 2008), identifying the early stages in the deterioration process has been the focus of only a small number of studies (Kunicki-Goldfinger *et al*., 2009). The challenge of distinguishing the first signs of true glass sickness from other surface effects has received little attention. The ability to determine glass stability is of benefit to those responsible for the conservation of historic glass, so as to identify vulnerable items and apply appropriate conservation methods.

The detection of surface deposits is an indication that a glass may be unstable. Deterioration of unstable glass is characterized by exchange of alkali ions (sodium and potassium) from the glass structure with hydrogen ions from atmospheric moisture. The leached alkali ions may form hygroscopic salts on the glass surface through a chemical reaction with gases and vapours in the atmosphere. However, virtually no research on the identification of surface deposits on glass has been published. Organ (1957) described the theoretical processes, but did not provide analytical evidence for the identity of salts on the surface of sick glass. Cobo del Acro (1999) noted that sodium formate was detected as a surface deposit on glass, but did not elaborate. The study was followed by work of Robinet *et al*. (2004) and Eremin *et al*. (2005) who identified crystalline deposits on glass surfaces using ion chromatography and Raman spectroscopy. Although these studies have identified salts on the surface of vessel glass as a result of glass deterioration in combination with a polluted atmosphere, to the best knowledge of the authors similar studies have not been conducted to identify unstable glass degradation products in unpolluted atmospheres.

Therefore, the present study aims at providing a clear-cut analytical protocol to identify unstable glass by chemical analysis of characteristic material on the surface of potentially unstable glass. This may enable the unambiguous discrimination between stable and unstable glass. The initial setup of an ion chromatography (IC) protocol has been reported earlier (Lamain *et al.*, 2013). This paper will report the recent progress of the development of an analytical protocol to assess glass stability.

In particular, sample preparation is addressed in this paper. For analysis with IC the sample should be in aqueous solution and cannot contain particles. In order to be able to analyse deposits on glass surfaces, they need to be transferred from the surface to a sample solution. Therefore, different materials and sampling procedures have been tested for their ability to remove the ions of interest and to release them into water again in a simple, reliable and reproducible manner.

A related topic which is briefly discussed in this paper is the documentation of subtle changes in appearance associated with the early stages of glass sickness. A slight change in lighting conditions or the position of the camera relative to the object can drastically change the appearance of the object in a photograph. Reflectance transformation imaging (RTI) (Earl *et al*., 2011; Malzbender, Gelb, and Wolters, 2001) can prevent this by fixing the position of the camera relative to the object and combining different images with configured lighting conditions to synthesize one image of the deteriorating glass surface.

Experiments and Results

The installation of an ion chromatography system

For the study of glass deterioration and other conservation investigations an ion chromatography system was installed by the Rijksmuseum in the laboratories of the Netherlands Cultural Heritage Agency. It consists of two Dionex ion chromatography systems, for the simultaneous analysis of cations and anions, and a Dionex autosampler connected to both systems. The installed IC systems are capable of quantitative analysis of the following ionic species from a single sample:

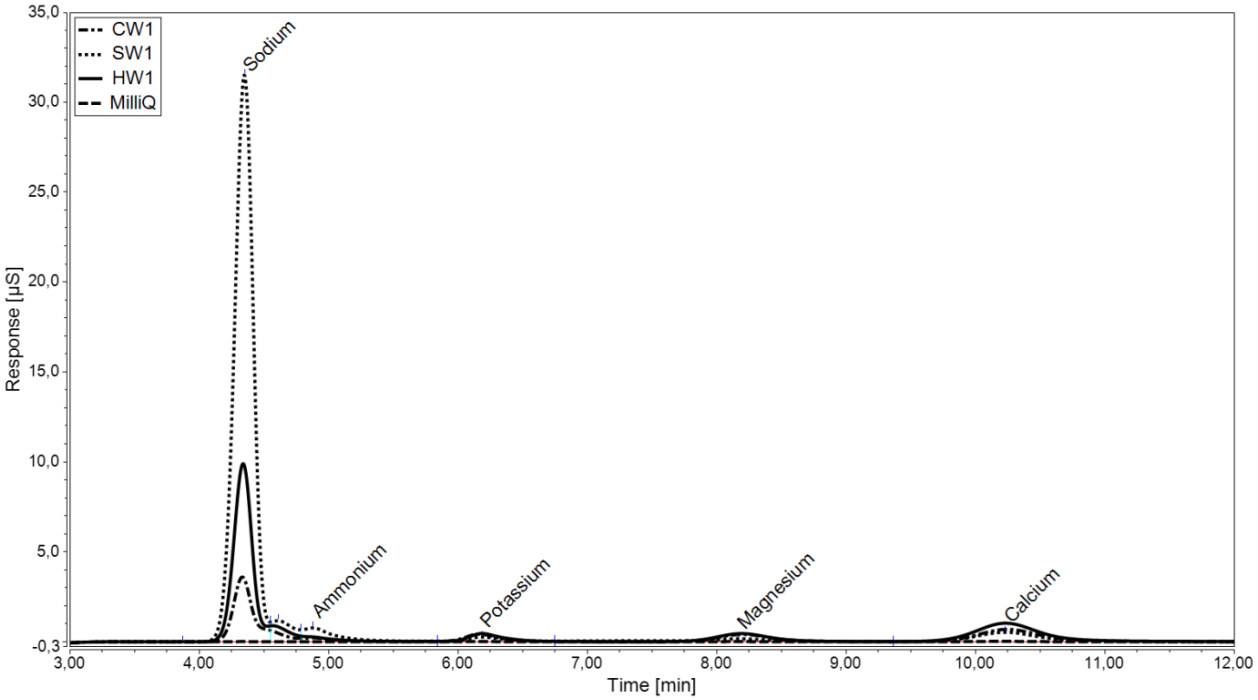

Fig. 1: Results of extraction of blank swabs.

Anions: acetate, formate, carbonate, chloride, fluoride, bromide, nitrite, nitrate, sulphate and phosphate.

Cations: lithium, sodium, ammonium, potassium, calcium, magnesium.

Suitability of sampling materials

Three types of cotton swabs have been investigated on their suitability for the use in a sampling protocol. Handmade pure cotton swabs on plastic sticks, prefabricated sterile swabs and prefabricated commercial swabs available from the drugstore, abbreviated respectively as HW, SW, CW. The presence of elements released during extraction by the swab itself was evaluated by aqueous extraction of blanks (figure 1). These elements might interfere with the analysis of ions of interest and therefore sampling materials from which these elements are extracted in a large amount should preferably not be used in the sampling protocol.

Figure 1 shows that for all sampling materials the sodium peak is large and in particular extracts from sterile swabs (SW1 in the chromatogram) show a large peak in comparison to the blank (MilliQ). This indicates that sodium is extracted from the swab, which may interfere with extraction of actual samples. The sodium peak of the commercially available cotton swabs from the drugstore (CW1 in the chromatogram) is the smallest. Therefore, this type of swab can be considered the preferred type of cotton swab for sampling based on the results of blank extraction experiments.

Sampling ions from glass surfaces

The ability of cotton swabs to remove the ions of interest from a glass surface and to release them into water again has been evaluated. Microscope slides with concave depressions were used as a dummy surface. After application of 50 µL of a test solution[1] with a concentration of sodium ions of 100 $mg \cdot L^{-1}$, the slides were left to dry overnight in the fume hood. After drying the slides were sampled with the cotton swabs moistened with 50 µL of deionized water (MilliQ). Extraction was performed in 950 µL of MilliQ. After centrifugation and filtration the samples were diluted five times, so that at 100% efficiency of the sampling protocol the resulting concentration of sodium in the extracted solution would be 1 $mg \cdot L^{-1}$. The tests were carried out in threefold and for each slide a blank slide was included. A volume of 50 µL of MilliQ was applied on the blank slide instead of the cation standard solution.

1 Dilutions in deionized water of a concentrated mixed cation standard solution were used for calibration and testing. The used test solution was a mixed cation solution with concentration of ions in the following ratio: $Li^+:Na^+:NH_4^+:K^+:Mg^+:Ca^+ = 1:4:8:4:4:20$.

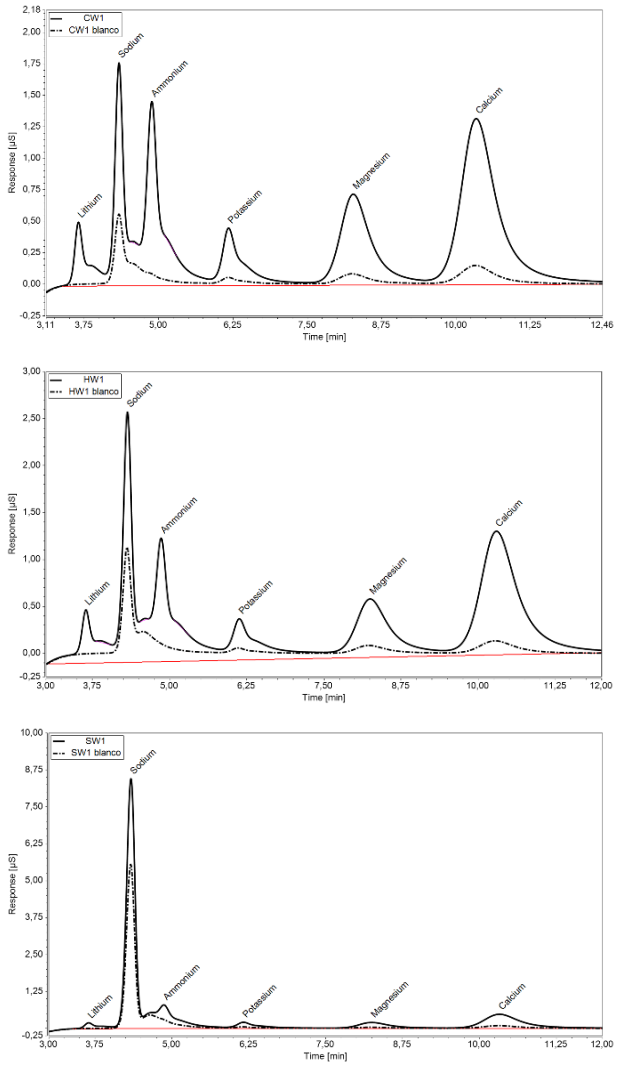

Fig. 2: Results from surface sampling experiments (continuous line) compared to blank samples (dashed line) for the commercially available swabs (top), handmade cotton swabs (center) and sterile swabs (bottom).

The ability to retain ions by moistened swabs and release them again during an extraction in MilliQ was demonstrated by the sampling experiments. Figure 2 clearly shows that the presence of ions in low concentrations on a glass surface by sampling with a moistened cotton swab can be identified. As the sodium peak of the swabs from the drugstore is the lowest, the ions from the test solution are most easily distinguished from the blank sample.

Documenting glass sickness: Reflectance Transformation Imaging

A micro-RTI has been used to document a severely crizzled glass sample. The RTI consists of a hemisphere on which 56 LED lights are mounted on the inside. The LED's are switched on consecutively and for each different position an image from above is captured using a microscopic lens. Software (Monkey Brain) then combines all the images to create a dynamic image of the surface. Currently the research is in an experimental phase and although the results need to be optimized they seem promising and will be presented at the colloquium.

Discussion

The presented experiments and results are the first step in an analytical protocol for the identification of unstable glass. It has been demonstrated that the analytical tool is capable of detecting species, indicative of the breakdown of the glass structure, in low concentrations on glass surfaces. As the reproducibility of the results is still lacking, the protocol will be optimized in the near future to:

- Increase the reproducibility and efficiency;
- Test the potential of other sampling materials;
- Perform sampling on deteriorating glass instead of microscope slides;

The completion of these steps will enable the quantitative analysis of deposits on historic glass surfaces as a result of glass degradation.

The potential of RTI for the documentation of glass sickness needs to be investigated further. However, its ability to visualize minute changes of the glass surface in combination with analytical results of the IC protocol may prove to be of great relevance for the conservation of historic glass.

Acknowledgements

The authors would like to thank Robert van Langh, Isabelle Garachon, Margot van Schinkel, Bodill Lamain and Roosmarijn van Beemen for valuable discussions. Thanks are also due to Martin Jürgens for providing samples of sick glass, Elise van Diejen for ion chromatography work and Rob Erdmann for insights into the problem of imaging glass deterioration.

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