Glass sickness: Detection and prevention

*Investigating unstable glass in museum collections*

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THE IMPLEMENTATION OF ION CHROMATOGRAPHY
AS AN ANALYTICAL TOOL FOR THE CLASSIFICATION OF
STABILITY OF GLASS OBJECTS IN MUSEUM COLLECTIONS
6.1 Introduction

The deterioration of glass in museum collections is a large problem for curators and conservators. Condition surveys have been carried out at different museums throughout Europe and estimations of the part of the glass collection which is of unstable nature vary between 10 and 30%. This means that many hundreds of objects are at risk of further decay worldwide. The Boijmans van Beuningen Museum carried out a comprehensive condition survey of the glass collection which demonstrated that 671 objects out of 4005 showed signs of deterioration (Burghout and Slager, 2013). At the Victoria and Albert Museum the condition of 400 glass objects showing clear signs of decay, out of a total of 6500 objects in the collection, was documented (Oakley, 1990; Fearn, McPhail and Oakley, 2005). At the Rijksmuseum the unstable part of the vessel glass collection was estimated to be larger than 10% (Lamain, 2009). The National Museums of Scotland carried out similar research and found that 336 out of 2160 objects (ca. 16%) were deteriorating (Cobo del Acro, 1999). These surveys were all undertaken using visual examination, which possibly leads to an underestimation of the actual total number of unstable glass objects, as signs of deterioration are not always visible (Oakley, 1990). It would therefore be beneficial to have another method for the identification of unstable glass. This chapter concerns the implementation of the IC protocol (Chapter 4) in a museum context to achieve this goal. The main research question is: can unstable glass objects in museum collections be distinguished from stable glass objects based on the concentration of ions detected on the surface of the glass?

In order to answer this question it is important to know which ions can be found on the surface of glass objects. A wide variety of ions can be found on the surface of unstable glass in museum collections, as has been demonstrated in Chapter 3, but very few other studies have focused on the identification of deterioration products on unstable glass surfaces. Those that have all identified sodium formate as the main crystalline compound (Schmidt, 1992; Robinet et al., 2004; Eremin et al., 2005; Thickett and Pretzel, 2010), the possible formation of potassium formate was suggested by Eremin et al. (2005), and the presence of carbonates, sulfates and chlorides has been mentioned as well (Tichane, 1966; Roemich, 1999). The deposition of atmospheric particles on glass surfaces may be another source of
ions. Although it is a problem of particular relevance for window glass (see e.g. Chabas, 2006), it may also occur on vessel glass in museums, depending on the storage conditions. Based on these published studies the principal ions found, by various techniques, on the surface of glass, including window glasses, are: sodium, potassium, calcium, magnesium, chloride, sulfate, nitrate, formate and carbonate.

It is important to understand which of these ions are truly related to glass deterioration and which ions can be attributed to other sources. The statement that a wide variety of ions can be found on the surface of unstable glass was confirmed in Chapter 3, but at that stage in the research it was as yet unclear which ions might be used as indicators to identify unstable glass. The results of the laboratory experiments described in Chapter 5 indicate that sodium and potassium are the main ions associated with the deterioration of glass in controlled environments. Acetate and formate were also detected on the artificially aged glass samples, but their presence depended on the aging environment and acetate and formate were not detected in the final ageing experiments. The presence of sodium and potassium is in line with the compounds found on unstable glass as reported in the studies mentioned above, as is the observation of the accumulation of formate and acetate on unstable glass surfaces. In order to be able to pinpoint unstable glass it is of great relevance to find specific ions which will distinguish the unstable from the stable objects. In previous work only glasses showing clear signs of glass deterioration were investigated, but no comparison was made between ions found on stable objects and ions found on unstable objects. Therefore, this study is designed to compare stable with unstable glass objects based on the nature and concentration of ions found on their surfaces. A vital sub-question which is investigated in this chapter is therefore *which ions act as markers for glass instability.*

This research represents the first time that an analytical protocol has been implemented for the study of glass stability based on what is found on the surface of the glass, rather than looking at the composition of the glass. The latter has been the main strategy for the investigation of glass instability, but no technique has proven to be conclusive in identifying unstable glass objects straightforwardly. An important aspect of this is that only some general observations can be made on the composition of unstable glass, for example that a CaO content of less than
4% results in an unstable glass (Brill, 1975), but crizzling also occurs on glasses containing ca. 10% of CaO (Kunicki-Goldfinger, 2008). Ultimately, it is the glass composition which determines glass stability, but only slight changes in the composition can have a significant effect on chemical stability of the glass (Kunicki-Goldfinger, 2008). Therefore, making an assessment of glass stability is virtually impossible based on the glass composition alone. Rather, studies have focused on the chemical changes in the glass structure associated with glass deterioration. Raman spectroscopy, for example, was used to monitor changes in the silica content and the coordination of cations in the glass network (Robinet et al., 2006), but rigorous spectral peak deconvolution is required in order to separate unstable alkali silicate glasses from the stable alkali silicate glasses. Currently XRF provides no straightforward results to identify unstable glass, and quantitative analysis of the glass composition requires laborious calibration (Kaiser and Shugar, 2013). Other analytical techniques often require destructive sampling to determine the composition of the glass, or transportation of the object to an analytical facility.

In order to avoid these problems the ion chromatography protocol, developed as described in previous chapter, presents a new approach in the evaluation of the stability of glass in a bid to provide quick answers on questions of glass stability, using a straightforward and minimally invasive sampling method. This protocol has been validated using mock-up samples (Chapter 4) and was implemented in artificial ageing studies on flat glass (Chapter 5), but up to this point no tests using a validated protocol for quantitative analysis of ions on the surface of unstable glass have been carried out on actual vessel glasses from museum collections. The research presented in this chapter will therefore also focus on the reliability and ease of use of application of the protocol for museum objects. This involves considering the geometry of the objects, potential differences in ion concentrations on different parts of a single object.
6.2  Methodology

6.2.1  Objects studied

All objects included in this study are from two major museums in The Netherlands: the Rijksmuseum (RM) in Amsterdam and Museum Boijmans van Beuningen (MBvB) in Rotterdam. Both museums have carried out condition surveys of their vessel glass collections in the last 10 years (Lamain et al., 2013; Burghout and Slager, 2013), which enables structured and thorough observations made by conservators to be compared with analytical data gathered by the validated IC protocol described in Chapter 4. A description of the vessel glass collections, the collection surveys and the objects included in this study can be found below.

**Rijksmuseum (RM)**

The Rijksmuseum holds a collection of approximately 1500 vessel glasses ranging from the period of circa 1500-1930, consisting mainly of Dutch and German engraved glass, Venetian glass and façon de Venice. In the past, the glass objects have been stored in different locations, sometimes in unfavourable conditions. They were, for example, on display in wooden showcases and stored in one of the towers of the museum, where climate control was not implemented, and the condition of the glasses was not documented. In 2002 the entire glass collection was moved to a depot where it was stored in climate controlled conditions for the first time. From that moment onwards, the desire arose to monitor and document the condition of the glasses, as well as clean all the objects. During the refurbishment of the Rijksmuseum, between 2003 and 2013, the need to clean those objects chosen to be on display in the renewed Rijksmuseum got prioritised. Therefore, this selection was cleaned and their condition was documented. During this project the conservators observed that a significant proportion of the objects (ca. 25%) was in poor condition, but the reason for this was unclear, although it was assumed that the unfavourable storage conditions in the past and the composition of the glass itself played a key role. However, for certain objects, showing only minor signs of changes in appearance, it was not clear which surface blemishes were due to glass or could be attributed to another source.

In order to be able to better manage priorities for conservation of the glass
collection a system was developed to classify the objects based on their condition. Five categories were developed ranging from *in perfect condition* to *unfit for display* based on visual inspection (see Appendix 6.2 for a full description, this table was published earlier in Lamain et al., 2013). During the survey of the collection carried out after the development of these categories, it turned out that it was difficult to definitively categorize the objects. The developed terminology often insufficiently described the appearance of an object, and when the conservators had the idea that they observed signs of glass deterioration, the visual evidence was not clear to the naked eye and even harder to document in words or images. Therefore, it was decided that additional, analytical, information would be important for the identification of unstable glass. This conclusion was one of the main motivations to start the research presented in this thesis.

After the treatment of the objects which would be displayed after refurbishment, the other objects were cleaned. But for research purposes, a group of 70 objects was left untreated and available for non-destructive research. This selection was called the *buffer collection*. This group contained glasses from all categories and was designed to be representative of the entire vessel glass collection, with the exception of archaeological glass. The glasses included in the present study were selected from the buffer collection and were thus uncleaned. In total 245 samples were taken from 40 objects selected from the buffer collection, details on the objects included in this study can be found in Appendix 6.1.

The samples were taken from three parts of the glass: (1) from the main body, (2) from underneath the object and (3) from the top of the foot, if present. It was generally not possible to obtain more than two samples from the top of and from underneath the foot due to the geometry of the objects. Samples taken from the main body of the glass were taken on the outside of the glass. It was straightforward to obtain these samples as the area is typically large enough to be covered by the Teflon sampling template. It was generally straightforward to obtain three or more samples without any issues concerning geometry.

*Museum Boijmans van Beuningen (MBvB)*

The MBvB holds a glass collection of over 5000 items ranging from diverse origins and periods, with an emphasis on 20th century, especially Dutch, glass. During
a collection survey 4005 objects, including all vessel glasses, were investigated between 2008 and 2011. The remaining part of the collection consists mainly of archaeological glass and stained glass panels. During this survey, entitled the glass project, all glasses were inspected for signs of deterioration, cleaned, and moved to metal storage cabinets. All observations were documented in the collection database (Burghout and Slager, 2013). Currently, the glasses are stored in the MBvB storage facilities in which a climate of 50 ± 5 % RH and 20°C is maintained. The objects included in this study were not removed from the storage cabinets since the glass project.

Three categories were used to classify the condition of the glasses. Category 1 included objects which were not showing signs of deterioration during the glass project, objects in the second category (named category 3) were labelled as potentially unstable, while glasses in the third category (named category 4) showed clear signs of deterioration, either weeping or crizzling. Category 4 was split up into two subcategories: category 4.1 contained the glasses that were weeping, but did not show signs of physical damage (such as the formation of cracks or advanced crizzling) and category 4.2 contained the glasses that were heavily damaged as a result of chemical deterioration and essentially unfit for display. These categories were based on classification systems developed by other institutions (Corning Museum of Glass, Rijksmuseum, British Museum), which ultimately led to the omission of category 2. Of all the glasses investigated, 2.6% showed clear signs of deterioration, 14.1% was classified as potentially unstable and 83.3% of the investigated objects showed no signs of glass deterioration (Burghout and Slager, 2013).

In consultation with the head of conservation, 18 objects were chosen for sampling (Appendix 6.1); due to a tight schedule with a forthcoming relocation of the glass collection it was not possible to collect more samples. During the glass project ten of these objects were classified as unstable (category 4.1) and eight were classified as stable (category 1). No signs of the formation of a moist layer or other surface deposits were observed on any of the objects, except for object V 63 d, which was left uncleaned during the glass project as a reference glass. This provides a good opportunity for the implementation of the IC protocol in the investigation of glass deterioration invisible to the naked eye. As all objects were treated similarly, the
observed differences in ion concentrations are an indication for the rate at which ions are released from the glass after they were treated, which is hypothesised to be an indicator for glass stability throughout this dissertation.

The major difference between the objects studied from the RM and MBvB is the fact that the objects from MBvB were cleaned in the last decade, whereas the objects from the RM were not cleaned. The fact that all objects from MBvB were cleaned provides the opportunity to investigate the ability of IC to discriminate between stable and unstable glass, even when no signs of deterioration can be observed with the naked eye. The accumulation of ions on the surface of the RM samples has taken place over a much longer period, and in unknown conditions. These differences in conservation and storage history will be accounted for in the interpretation of the analytical results.

6.2.2 Analytical procedures

Ion chromatography

Ion chromatography (IC) was carried out for quantitative analysis of anionic and cationic species in aqueous solutions. Details of the equipment used, chromatographic methods, and standard solutions are the same as described in Chapter 4.

Sampling method and sample preparation

The sampling method and sample preparation protocol was the same as described in Chapter 4. Each sample was taken in the storage facilities of the museums, in order to minimize the travelling and handling of the objects. The swabs used for sampling were stored in polypropylene centrifuge tubes and transported to the laboratory. In the laboratory the samples were extracted the next day and the analyses were carried out immediately after extraction and centrifugation.

Major and minor ions

Based on the results obtained in Chapter 5 two groups of ions are identified: the major ions and the minor ions. This classification is maintained throughout this chapter in order to simplify data processing and interpretation. The major ions (i.e. those detected at higher concentration, generally greater than 1 mg/L in the
artificial ageing experiments) are sodium, potassium, acetate and formate. The minor ions were present in lower concentrations (generally below 0.5 mg/L, or, when above this threshold, only observed incidentally in these concentrations) and include chloride, nitrate, carbonate, sulfate and phosphate.

6.3 Results and Discussion

This section will provide a general description of the ions found on the surfaces of the objects sampled. Hereafter, the analytical IC results will be compared to the classification of the objects stability made by the conservator, which is the prelude to a discussion of potential marker ions for unstable glass. First, however, the importance of the sampling location will be discussed, as this is vital in the interpretation of the analytical results.

6.3.1 The importance of sampling location

There may exist a large difference in ion concentrations of different sampling locations on a single object. An example of this is shown in Figure 6.1 which shows the ion concentrations of samples taken from one object, but from three different sampling locations. In this example the ion concentrations in the samples

![Figure 6.1. Sodium and potassium ion concentrations obtained from object BK-NM-9714 for three different sample locations: the main body (n = 3), from underneath the foot (n = 2), and from the top of the foot (n = 2).](image)
taken from underneath the object are significantly higher than the samples from the body of the glass. Averaging of the ion concentrations over all samples (body, underneath and on top of foot) would therefore yield a very high relative standard deviation. Moreover, it is not unlikely that the different parts of a glass have been exposed to slightly different micro-environments.

It can be argued that the body of the glass provides the most reliable analytical results for two reasons. The first relates to the issue of sampling in a reproducible manner. On the body of the glass the sampling template could be placed on a unique position without any problems concerning the geometry of the sampled area. In contrast, the top of the foot of the glass generally curves upwards and narrows towards the stem of the glass. In some cases, in particular for small objects, this leads to problems when delimiting the sampling area on top of the foot. This may lead to a non-reproducible area being sampled, which complicates the comparison of ion concentrations in different samples. Besides, since the body is larger than the foot, more samples can be taken which improves the reliability.

The second reason concerns the exposure to the storage climate. The glass objects are stored standing upwards (with the exception of some large objects which are sometimes stored lying down on a pillow), which means that the main body of the glass is surrounded by the ambient atmosphere, which is likely the same for all objects stored in the same storage cabinets. However, underneath the foot of the glass a microclimate may form due to a lack of ventilation, which may cause local fluctuations in RH. Additionally it has been observed that the deterioration of glass sometimes advances from the bottom of the glass upwards (De Corneillan, 2016). This can occur when glass objects are stored on top of a material off-gassing reactive vapours such as some types of cardboard, plastics (including foam), paper or multiplex. These materials are often used as a barrier between the hard metal surface of the storage cabinets and the object to prevent mechanical damage. Sampling from the inside of objects was avoided, as it may be assumed that dust collects more easily on the inside of the vessel and this is the side that would have been exposed to liquid if the glass was used for drinking or storage of liquids.
6.3.2 General observations

*Rijksmuseum samples*

The storage history of the vessel glasses of the Rijksmuseum since the last conservation treatment is less well known than that of the MBvB collection. This means that, there was no baseline condition at the moment of sampling. However, more objects are available for sampling, which have all been categorized by conservators and are not cleaned, which provides the opportunity to make a more clear distinction between the definitely stable and definitely unstable objects based on the quantitative analysis of ions on the surface.

All sampled RM objects were categorized according to the parameters described in Appendix 6.1. However, as mentioned above, the conservators sometimes had difficulties in making the distinction between categories B and C, and between categories C and D. These objects were labelled B/C and C/D respectively. The IC results were grouped according to the classification made by the conservators (Table 6.1)

<table>
<thead>
<tr>
<th>Category</th>
<th>Number of objects</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>15</td>
</tr>
<tr>
<td>B/C</td>
<td>4</td>
</tr>
<tr>
<td>C</td>
<td>11</td>
</tr>
<tr>
<td>C/D</td>
<td>6</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
</tr>
</tbody>
</table>

A wide variety of ions was detected on the RM samples; the identity of the detected ions was similar to those detected in chapter 3. The major cations detected were sodium and potassium, while the major anions detected were chloride, acetate, formate and carbonate. Sulfate, nitrate, and phosphate were detected in varying amounts, while calcium was identified on some objects, but in low concentrations, marginally above the detection limit for calcium of the analytical protocol, but below the quantification limit (Figures 6.2 and 6.3).
Figure 6.2. Major ion concentrations for all Rijksmuseum objects.

Figure 6.3. Minor ion concentrations for all RM samples.
**Museum Boijmans van Beuningen samples**

The fact that all the objects from MBvB were cleaned a few years before sampling provides a condition baseline. This means that since then, all objects have had the same storage history and that difference in ion concentrations can be assigned to the deterioration of the glass. The major ions detected for the objects in the unstable category are sodium, potassium, acetate and formate (Figure 6.4). Generally, when sodium is detected, low concentrations of potassium are detected and vice versa. No ions were detected in minor concentrations (Figure 6.5), with the exception of one object (204a) which shows higher concentrations of sulfate, nitrate and carbonate. As this is a single observation, these results are treated as outliers, potentially occurring due to an error in the sampling or sample preparation procedure.

![Figure 6.4. Major ion concentrations for the Museum Boijmans van Beuningen samples.](image-url)
6.3.3 Comparing IC data with visual examination

The prime goal of investigating ionic species on the surface of unstable glass with IC is to be able to aid in the categorization of unstable objects, in particular when there are no clear signs of glass deterioration or when deterioration phenomena are unclear. Prior to the investigation presented in this chapter the objects were classified by conservators based on extensive visual inspection, but this categorization was often not straightforward and questions about glass stability remained. Therefore, the question to be answered in this section is: Can IC-analysis of glass surface deposits provide a distinction between stable and unstable glass and how does this compare to the classification based on visual analysis by the conservator?

In order to answer this question it is crucial to understand the conservation context and history of the investigated objects. All objects included in this study were classified by conservators, this categorization is used as a reference for the interpretation of the IC results. For the MBvB samples there was a clear difference in condition of the objects before cleaning during the glass project. Only objects classified as stable and which were classified as clearly unstable were selected for

Figure 6.5. Minor ion concentrations for the Museum Boijmans van Beuningen samples.
investigation during this study. At the moment of sampling there were no visual signs of deterioration on any of the objects, with the exception of one object (V 63 d) which was left uncleaned as a reference glass. Therefore, the results obtained with IC analysis provides information on the ability of the IC protocol to distinguish unstable from stable glass, even when no visual signs of deterioration are apparent.

A trend observed in the MBvB data is that the major ion concentrations are generally significantly higher for the unstable objects than they are for the stable. The minor ions show no difference between the two groups. There are three objects (1a, 1b, v86d) out of ten which do not show elevated ion concentrations, but which were classified as unstable. Interpretation of the data without prior knowledge on the chemical stability of these objects would therefore likely result in their classification as stable, when no other signs of deterioration are apparent (some objects did show incipient crizzling). However, as little is known about the rate in which ions are released from the glass surface, it may well be that the deterioration rate of this glass is low, but that it is of unstable composition. Additionally, the undocumented conservation history prior to the MBvB glass project provides uncertainty in the categorization of the objects during the glass project.

Interpretation of the RM samples is less straightforward. There is more uncertainty in the classification of the objects, due to a greater diversity in phenomena occurring on the surface of the objects. Whereas the MBvB objects were either moist or not (before cleaning), the RM objects show a broader, more complex distribution of surface effects. Terms as 'slightly hazy', 'mildly greasy', 'dirty', 'dried up droplets', 'moist' and 'large droplets' are used to describe the condition of the objects. Therefore a less clear distinction was made between the stable and unstable objects and the interpretation of the data of the RM objects requires more prudence.

Out of the major ions (Figure 6.2) either sodium or potassium, or a combination of both, were detected in most samples, and a sharp increase in concentration seems to occur when going from category C/D to categories D and E. Acetate and formate were detected in some of the samples in categories C/D, D, and E, but not in all samples of these groups and it would therefore be problematic to
use these ions for the categorization of the objects. The minor ion (Figure 6.3) concentrations do not appear to have significant differences between groups. It is striking that carbonate is detected only in the categories C/D, D and E (6 objects), and that sulfate shows higher concentrations in category E (2 objects).

The results as presented above provide confidence that the IC protocol is an appropriate tool to discriminate between glasses that are stable and those that may be unstable. However, a large problem in the conservation of glass is the classification of ‘borderline’ objects, i.e. objects that are potentially unstable, but do not show the obvious signs associated with glass sickness: weeping and crizzling. In some cases there is a discrepancy between the categorization made by visual inspection and the ion concentrations associated with this classification, as the results presented above are not conclusive in discriminating between stable and unstable glass. It may therefore be beneficial to concentrate on particular ions, which may act as marker ions for unstable glass. This approach is discussed in the next section.

6.3.4 Identification of marker ions for glass deterioration

One of the most important aims of this thesis has been to identify markers indicative of the breakdown of unstable glass. The results presented in Chapters 3 and 5 indicate that the major ions associated with glass deterioration, and the ions that are most reliably detectable by IC using the protocol outlined in Chapter 4, are sodium, potassium, formate and acetate. Other ions, such as chloride, sulfate, carbonate and nitrate, were also identified on the surface of unstable glass (Chapter 3 and section 6.3.2), but in varying or minor concentrations close to the limits of detection of the IC protocol, which complicates their use as marker ions for glass deterioration. In some occasions the minor ions are detected in higher amounts, but not structurally and therefore they are unsuitable to predict glass stability.

Out of the four major ions sodium and/or potassium are consistently detected on the surface of unstable glass. This is in line with the existing literature on the leaching of ionic species from the glass surface (see e.g. Fearn, McPhail and Oakley 2004, 2005; Kunicki-Goldfinger, 2008). Of the anionic species investigated
in this dissertation, formate is detected most often on the surface of unstable glass (Schmidt, 1992; Robinet et al., 2004; Eremin et al., 2005; Chapter 3; Chapter 5), but the presence of formate on the surface of unstable glass largely depends on the storage conditions as was indicated in the artificial aging experiments described in Chapter 5. Therefore, this section will mainly focus on the use of sodium and potassium as marker ions for unstable glass. Additionally, the relationship between the presence of acetate and formate on the one hand, and carbonate on the other is investigated, as previous results indicated an inversely proportionate relationship between their concentrations.

Up to this point in the thesis the ion concentrations were reported as mass concentrations instead of molar concentrations, this had three reasons. First, reporting the results in mass concentrations emphasises the low amounts of ions actually detected. Secondly, IC results are usually reported in mass concentrations in comparable studies in the conservation field (see e.g. Quye et al., 2011; Thicket and Pretzel, 2010). Finally, it is a matter of expediency as the calibration of the IC equipment was usually carried out in mass concentrations. However, a more direct way to compare the ion concentrations would be to look at ionic equivalents, for which it is necessary to transform the mass concentrations into molar concentrations. Therefore, in the following section the results will be presented in molar concentrations.

**Sodium and potassium**

The results demonstrate that either sodium, potassium or a combination of the two ions are found on the surface of unstable glass objects. It has been demonstrated earlier that these two ions are indeed most prone to leach from the glass structure as a result of chemical deterioration processes (Douglas and El-Shamy, 1967; El-Shamy et al., 1975; Fearn, McPhail, and Oakley, 2005) and it was therefore anticipated that these two ions, jointly referred to as the alkali ions, were most likely to deposit on the surface of unstable glass objects. Using only one of these ions as a marker for glass deterioration would be insufficient, as soda glass could be unstable and not leach potassium, whereas potash glass would not leach sodium. Therefore it is suggested to use the combination of both ions as a marker for unstable glass by evaluating the total alkali ion concentration in the samples.
The results of adding the sodium and potassium concentrations are shown in Figure 6.6 (MBvB objects) and Figure 6.7 (RM objects). Included in these figures is the sum of the limit of quantification (LOQ) of sodium and potassium (red line, 20 µmol/L). The MBvB results indicate that the sum of the sodium and potassium concentrations for the unstable objects exceeds the LOQ (except for the two objects identified earlier as showing low ion concentrations while being in the unstable category), whereas the concentrations in the stable group are below the LOQ\(^1\).

Similar results are observed in the RM results. The objects categorized as definitely being unstable (categories D and E) all show a sum of alkali ion concentrations above the LOQ. For two objects in category C/D, BK-NM-789-A and BK-NM-789-B, the total alkali ion concentration is lower than the other objects. When reviewing the description of the condition it appears that these glasses are described as having a clear haze and potentially dried out droplets, while the other objects in the same group are all described to have developed a greasy or moist layer, which might explain the different responses. Out of the 30 objects classified in categories B (probably stable), B/C and C (potentially unstable) there are 10 objects showing a response above the LOQ\(^2\). All these objects were described as being lightly greasy, which suggests the deposition of low amounts of hygroscopic salts on the surface indicating potential glass instability. Glasses in the same category that did not show a response above the LOQ are described as being lightly hazy, or slightly dirty or dusty.

The difference in total alkali ion concentrations in the samples emphasizes the need for a concentration threshold for the discrimination between stable and unstable glass. This threshold could then be used to estimate the risk of further decay of the glass and prioritise conservation intervention for certain objects. As the results indicate that the total ion concentration is indicative of glass instability, we can

\(^1\) The limit of quantification itself is not a benchmark for glass stability, but a characteristic of the system used. If a more sensitive system is used, or the analytical protocol is improved, this results in a lower LOQ, which would allow for an even more meticulous study of ion deposition on unstable glass.

categorize the objects based on the total ion concentration. This categorization may provide a more verifiable framework for the evaluation of the condition of glass objects in museum collections. The suggested categorization can be found in table 6.2. As this categorization is based on the rather limited number of sampled objects, the description of the categories is tentative, and expansion of the data set and carrying out extended model studies on the depletion rate and surface deposition of ions are highly recommended. In this respect it is crucial to also include the storage and conservation history of the objects. The ion concentrations on the surface of the MBvB objects are generally lower than those of the RM objects. This can be explained by the fact that the objects from MBvB were cleaned recently, whereas the RM objects were not.

A remark has to be made on the detection of sodium and/or potassium in relation to the glass composition. It is assumed that sodium-rich glasses leach sodium ions and that potassium-rich glasses leach potassium ions. The *mixed alkali effect* occurs when the two alkali species are both constituents of the glass. This phenomenon will affect the amount of sodium and potassium ions leached from the glass. The choice of a target combined sodium + potassium marker ion concentration which indicates unstable glasses will therefore depend on whether sodium and potassium are present alone or in combination. It would therefore be beneficial to take account for this in future research.

Finally, in view of the need to optimise the precision of the determination of the amount of sodium leached from the glass as opposed to the presence of sodium arising from external sources, it would be important to take account of the contribution of sodium chloride by deducting the molar concentration of chloride from the molar concentration of sodium value. In the case of the RM and MBvB samples the contribution of chloride is very small.

![Table 6.2: Suggested categorization of glass objects based on the total alkali ion (Na⁺ and K⁺) concentrations in samples obtained from glass objects using the protocol validated in Chapter 4.](image-url)
**Figure 6.6.** Added average concentrations of sodium and potassium obtained from the MBvB objects. The error is determined by addition of the errors in quadrature, the red line represents the sum of the limits of quantification for sodium and potassium.

**Figure 6.7.** The added average concentrations of sodium and potassium for samples obtained from Rijksmuseum objects. The error is determined by addition of the errors in quadrature, the red line represents the sum of the limits of quantification for sodium and potassium.
6.3.5 Evaluating the use of the sampling protocol in a museum context

As for the artificial aging studies the relative standard deviation (RSD) is larger than during validation. For the museum objects, the RSD varies from 6% to as high as 40% for some objects. This is in some cases higher than the RSD during the artificial aging of unstable glass. This is likely to originate from the fact that the objects have been stored in uncontrolled environments during their lifetime. There could have been pollution on the surface due to handling or a proportion of the deterioration products could have (inadvertently) been removed, resulting in a more heterogeneous distribution of ions on the glass surface. Furthermore, ions could have been extracted from the altered surface layer during sampling, as discussed in Chapter 5. These factors provide room for uncertainty in evaluation of the stability of glass objects based on the concentration of ions on the surface.

In order to better be able to distinguish stable from unstable glass it is essential to better understand the distribution of ions on the glass surface. Even though the evaluation of only the samples taken from the body of an object strongly decreased the RSD, indicating the importance of sample location, the RSD remained high for many objects. Besides understanding the distribution of ions on the surface it might therefore be beneficial to adapt the sampling protocol slightly in order to better understand the distribution of ions on the glass surface. It may, for example, be worthwhile to decrease the sampling area and extraction volume in order to be able to obtain more samples from similar locations on one object.

6.4 Conclusions

The results presented in this chapter are of importance for the field of glass conservation as they demonstrate, for the first time, the ability to investigate the chemical stability of historic glass objects based on the deposition of ions on the surface of these objects. Two groups of objects from two different museums were included in this study: objects from Museum Boijmans van Beuningen (MBvB) and objects from the Rijksmuseum (RM). Although the number of investigated objects requires expansion to improve statistics of data processing, and thereby the validity of the assessment of stability, important conclusions on the applied methodology, the implications for the conservation practice and the potential
future research lines can be drawn.

Firstly, the results demonstrate that the protocol developed is a convincing method for quantitative analysis of ionic species on the surface of glass objects in museum collections and that the protocol has therefore the potential to act as an early warning system for the identification of unstable glass objects in large museum collections. For both the MBvB and RM samples it was demonstrated that a high concentration of sodium and/or potassium is indicative of glass instability, thus relating the analytical results with the condition of the glass. The power of ion chromatography is most convincingly demonstrated by the samples taken from the MBvB objects, where high ion concentrations were observed even when no signs of glass instability could be observed with the naked eye. The group of definitely unstable objects from the RM collection showed a clear increase in ion concentrations when compared to objects which were classified as being “potentially unstable” and “probably stable”. Differentiation between the last two groups is less clear-cut and requires more research.

Secondly, the results point to the identification of sodium and potassium as the most indicative marker ions for unstable glass objects. This is an important step towards the completion of the development of an early warning system by using a straightforward protocol in which a conservator can take a few samples from an object, send it to a laboratory for analysis and get a quick, yet reliable, evaluation of the stability of the object. In this respect it is crucial to take into account the differences in ion concentrations on different parts of the objects. The results in this study indicated that the ion concentrations from samples taken from different parts of the glass may vary significantly, which means that for a good comparison between objects samples taken from similar locations should be compared. The samples taken from the outside of the main body are most suitable for this purpose, as this part of the glass is less likely to be exposed to microclimates. The high RSD of the samples indicates that the amount of ions collected in different samples on the same objects is often divergent. Although the cause for this is at the moment unclear, there are several potential explanations for this observation. The most important is the distribution of deterioration products on the surface of the glass. It is currently unclear how the distribution is determined and whether or not this is a result of inhomogeneous glass deterioration or purely of the agglomeration of...
deterioration products. A second explanation for the high RSD could be found in the nature of the sampled surface. An interaction between the ions on the surface with the surface itself and the potential leaching of ions from the altered surface layer due to the swabbing action could cause an increase in the RSD.

Additionally, the evaluation of the ion concentrations provide the opportunity to make a risk assessment for glass objects. A high concentration of sodium and/or potassium seems to point towards glass instability and therefore the detection of these ions could quickly indicate the necessity to take actions to prevent further deterioration.

Thirdly, the results provide directions for further research lines, not only on fundamental research on glass deterioration but also on practical conservation issues. Most important is the study of those objects which cannot be classified by conservators. At the moment IC results provide hints on glass stability based on the sodium and potassium concentrations, but classification of glasses showing unclear signs of deterioration remains difficult. Part of the problem is that there currently are no other methods to assess glass stability of museum objects non-invasively. At the moment there is no other feedback for interpretation of the IC results than the classification made by the conservators, whereas it is the ultimate goal to reverse this: i.e. the use IC data to classify the condition of the objects. Currently, however, there are no methods to discriminate unstable glass without obvious signs of deterioration from stable glass objects. Even when the elemental composition is fully known, this will only provide a clear-cut indication of glass stability of those glasses with such poor compositions that they will be very unstable and show the related changes in appearance anyway. One possible way to approach this problem is by carrying out extended laboratory research in which the amount of leached ions is measured and related to the total amount of ions deposited on the surface, which requires a combination of two analytical techniques, for example LA-ICP-MS and/or SIMS to measure ion depletion, and IC to measure the surface deposition of the same ions.

Practical implications are that, even though there is no visual evidence for deterioration, ions are still released from unstable glass and monitoring of the glass collection is highly recommended, in particular when it is known that
certain objects have an unstable glass composition. Besides visual inspection, this monitoring should include IC analysis of surface samples. This is particularly important as the amount of ions accumulated on the surface of unstable glass depends largely on the duration for which the glass has been exposed to conditions that promote the leaching of ions. The optimal parameter that identifies glass stability may be the rate of deposition on the surface, but it is impractical to measure this as deterioration processes of glass generally take place over decades. It is therefore promising that the results of the MBvB objects indicate a change in ion concentration on the surface of unstable glass even after a relatively short period of less than a decade.

The results presented in this chapter provide confidence in the developed method in its use as an early warning system for pinpointing unstable glass. We were able to differentiate between stable and unstable glass objects based on the presence of ions on the surface of the glass. The initial success of this innovative approach provides confidence that with the inclusion of complementary compositional research on the depletion of ions and extension of the sample sets and model studies it will be possible to also classify glasses showing unclear changes in appearance and make effective risk assessments for large numbers of glass objects in museum collections.

6.5 References


## Appendix 6.1  Sampled objects

Objects sampled from the Museum Boijmans van Beuningen collection

<table>
<thead>
<tr>
<th>Object number</th>
<th>Description</th>
<th>Date</th>
<th>Category</th>
<th>Deterioration pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 a</td>
<td>Goblet</td>
<td>1529</td>
<td>4.1</td>
<td>No signs of deterioration</td>
</tr>
<tr>
<td>1 b</td>
<td>Lid</td>
<td>1529</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>204 a</td>
<td>Chalice</td>
<td>1675-1700</td>
<td>4.1</td>
<td>Slightly crizzled</td>
</tr>
<tr>
<td>204 b</td>
<td>Lid</td>
<td>1675-1700</td>
<td>4.1</td>
<td>Slightly crizzled</td>
</tr>
<tr>
<td>911</td>
<td>Chalice</td>
<td>1500-1600</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>921</td>
<td>Bowl</td>
<td>1700-1800</td>
<td>4.1</td>
<td>Pinkish hue</td>
</tr>
<tr>
<td>GDP 18</td>
<td>Chalice</td>
<td>1700-1800</td>
<td>4.1</td>
<td>Crizzled and pink</td>
</tr>
<tr>
<td>V 63 d</td>
<td>Wineglass</td>
<td>1921-1923</td>
<td>4.1</td>
<td>Weeping</td>
</tr>
<tr>
<td>V 86 d</td>
<td>Port wineglass</td>
<td>1918</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>V 259</td>
<td>Plate</td>
<td>1982</td>
<td>4.1</td>
<td>No signs of deterioration</td>
</tr>
<tr>
<td>87</td>
<td>Roemer glass</td>
<td>1650-1700</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>573</td>
<td>Goblet</td>
<td>1600-1700</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>708</td>
<td>Plate</td>
<td>1575-1625</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>V 42 f1</td>
<td>Liquor glass</td>
<td>1928</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>V45 a1</td>
<td>Drinking glass</td>
<td>1953</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>V 193 b</td>
<td>Bowl</td>
<td>1938-1939</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>V 1776 a</td>
<td>Jug</td>
<td>1950-2000</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>V 2560 e3</td>
<td>Wineglass</td>
<td>1924</td>
<td>1</td>
<td></td>
</tr>
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</table>
Objects sampled from the Rijksmuseum collection

<table>
<thead>
<tr>
<th>Object number</th>
<th>Description</th>
<th>Date</th>
<th>Category</th>
<th>Deterioration pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>BK-1987-18-A</td>
<td>Decanter</td>
<td>1900 - 1925</td>
<td>B</td>
<td>Lightly greasy, dirty, fingerprints</td>
</tr>
<tr>
<td>BK-1987-18-B</td>
<td>Cup</td>
<td>1900 - 1925</td>
<td>B</td>
<td>Lightly greasy, dirty, fingerprints</td>
</tr>
<tr>
<td>BK-1987-18-C</td>
<td>Cup</td>
<td>1900 - 1925</td>
<td>B</td>
<td>Lightly greasy, dirty, fingerprints</td>
</tr>
<tr>
<td>BK-KOG-1541</td>
<td>Wineglass</td>
<td>1795</td>
<td>B?</td>
<td>Non removable light haze</td>
</tr>
<tr>
<td>BK-KOG-1570</td>
<td>Wineglass</td>
<td>1750 - 1775</td>
<td>B</td>
<td>Very light haze + dirt</td>
</tr>
<tr>
<td>BK-KOG-1572</td>
<td>Chalice</td>
<td>ca. 1775</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BK-KOG-1607</td>
<td>Wineglass</td>
<td>ca. 1850 - 1863</td>
<td>B</td>
<td>Lightly greasy, dirty, fingerprints</td>
</tr>
<tr>
<td>BK-KOG-180</td>
<td>Wineglass</td>
<td>1725 - 1750</td>
<td>B</td>
<td>Lightly greasy, dirty</td>
</tr>
<tr>
<td>BK-KOG-207</td>
<td>Wineglass</td>
<td>1725 - 1750</td>
<td>B</td>
<td>Non removable light haze</td>
</tr>
<tr>
<td>BK-NM-10754-264</td>
<td>Cup</td>
<td>ca. 1800 - 1810</td>
<td>B</td>
<td>Dirt, fingerprint</td>
</tr>
<tr>
<td>BK-NM-10754-80</td>
<td>Cup</td>
<td>ca. 1795</td>
<td>B</td>
<td>Very light haze</td>
</tr>
<tr>
<td>BK-NM-10754-96</td>
<td>Goblet</td>
<td>ca. 1750</td>
<td>B</td>
<td>Light haze, fingerprint</td>
</tr>
<tr>
<td>BK-NM-716</td>
<td>Cup</td>
<td>ca. 1725 - 1750</td>
<td>B</td>
<td>Light haze, fingerprint</td>
</tr>
<tr>
<td>BK-NM-7999</td>
<td>Wineglass</td>
<td>ca. 1760 - 1780</td>
<td>B</td>
<td>Light haze</td>
</tr>
<tr>
<td>NG-NM-10754-83</td>
<td>Wineglass</td>
<td>ca. 1780-1798</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>BK-KOG-206</td>
<td>Wineglass</td>
<td>ca. 1700 - 1725</td>
<td>B/C</td>
<td>Mild pink colour, lightly greasy, light haze</td>
</tr>
<tr>
<td>BK-KOG-209</td>
<td>Wineglass</td>
<td>ca. 1725 - 1775</td>
<td>B/C</td>
<td>Light haze, lightly greasy</td>
</tr>
<tr>
<td>BK-NM-3468</td>
<td>Wineglass</td>
<td>ca. 1750 - 1775</td>
<td>B/C</td>
<td>Dirty, greasy</td>
</tr>
<tr>
<td>BK-NM-733</td>
<td>Wineglass</td>
<td>ca. 1750</td>
<td>B/C</td>
<td>Lightly dirty, greasy, hazy</td>
</tr>
<tr>
<td>BK-18970</td>
<td>Mocking glass</td>
<td>ca. 1725 - 1775</td>
<td>C</td>
<td>Lightly greasy, sligh pink discolouration</td>
</tr>
<tr>
<td>BK-1966-62</td>
<td>Cup</td>
<td>ca. 1800 - 1900</td>
<td>C</td>
<td>Lightly greasy, light haze</td>
</tr>
<tr>
<td>BK-1978-33</td>
<td>Wineglass</td>
<td>ca. 1815 - 1830</td>
<td>C</td>
<td>Lightly greasy, some dirt</td>
</tr>
<tr>
<td>BK-NM-10754-103</td>
<td>Wineglass</td>
<td>ca. 1725 - 1750</td>
<td>C</td>
<td>Greasy (dirty?), light haze</td>
</tr>
<tr>
<td>BK-NM-10754-152</td>
<td>Wineglass</td>
<td>ca. 1750 - 1775</td>
<td>C</td>
<td>Lightly greasy/dirty</td>
</tr>
<tr>
<td>BK-NM-10754-156</td>
<td>Wineglass</td>
<td>ca. 1725 - 1750</td>
<td>C</td>
<td>Lightly greasy, light haze</td>
</tr>
<tr>
<td>BK-NM-10754-349</td>
<td>Wineglass</td>
<td>ca. 1725 - 1775</td>
<td>C</td>
<td>Lightly greasy, light haze</td>
</tr>
<tr>
<td>BK-NM-13178</td>
<td>Wineglass</td>
<td>ca. 1725 - 1750</td>
<td>C</td>
<td>Slightly pink, lightly greasy</td>
</tr>
<tr>
<td>BK-NM-2146-1</td>
<td>Wineglass</td>
<td>ca. 1700-1725</td>
<td>C</td>
<td>Lightly greasy, light haze</td>
</tr>
<tr>
<td>BK-NM-2146-2</td>
<td>Lid</td>
<td>ca. 1750-1800</td>
<td>C</td>
<td>Light haze</td>
</tr>
<tr>
<td>BK-NM-5809</td>
<td>Passglass beaker</td>
<td>ca. 1675 - 1700</td>
<td>C</td>
<td>Lightly greasy, light haze</td>
</tr>
<tr>
<td>BK-NM-10754-14A</td>
<td>Goblet</td>
<td>1800-1900</td>
<td>C/D</td>
<td>Greasy, light haze</td>
</tr>
<tr>
<td>BK-NM-10754-14B</td>
<td>Goblet</td>
<td>1800-1900</td>
<td>C/D</td>
<td>Lightly greasy</td>
</tr>
<tr>
<td>BK-NM-10754-65</td>
<td>Roemer</td>
<td>ca. 1700</td>
<td>C/D</td>
<td>Greasy (dried up droplets?), Haze, Ditry</td>
</tr>
<tr>
<td>BK-NM-789-A</td>
<td>Saltcellar</td>
<td>ca. 1600 - 1699</td>
<td>C/D</td>
<td>Haze, dried up droplets?</td>
</tr>
<tr>
<td>BK-NM-789-B</td>
<td>Saltcellar</td>
<td>ca. 1600 - 1699</td>
<td>C/D</td>
<td>Haze, dried up droplets?</td>
</tr>
<tr>
<td></td>
<td>Description</td>
<td>Date Range</td>
<td>Condition</td>
<td>Condition Details</td>
</tr>
<tr>
<td>-----</td>
<td>----------------------</td>
<td>------------</td>
<td>-----------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>BK-NM-9714</td>
<td>Fluteglass</td>
<td>ca. 1650 - 1675</td>
<td>C/D</td>
<td>Greasy, small droplets</td>
</tr>
<tr>
<td>BK-1980-56</td>
<td>Bottle</td>
<td>ca. 1800 - 1900</td>
<td>D</td>
<td>Large drops on inside, small drops on outside</td>
</tr>
<tr>
<td>BK-KOG-127</td>
<td>Filigree glass pitcher</td>
<td>1600-1700</td>
<td>D</td>
<td>Droplet, moist, greasy</td>
</tr>
<tr>
<td>BK-16476-B</td>
<td>Lid</td>
<td>1688</td>
<td>D/E</td>
<td>Crizzled, Haze, Greasy, Small droplets</td>
</tr>
<tr>
<td>BK-18941</td>
<td>Goblet</td>
<td>1650-1700</td>
<td>E</td>
<td>Crizzled</td>
</tr>
<tr>
<td>BK-KOG-130</td>
<td>Filigree glass cup</td>
<td>1675-1700</td>
<td>E</td>
<td>Moist, greasy layer</td>
</tr>
</tbody>
</table>
Appendix 6.2  Rijksmuseum Glass Condition
Categories

This appendix lists the categories developed by the Rijksmuseum to classify the condition of their glass objects. The categorizations were published earlier by Lamain et al. (2013).

Category A  Glasses in this category are in a perfect condition
No conservation treatment is necessary.

Category B  Symptoms B1–B4 may concern glass degradation
This category contains glasses showing very slight surface changes. It is desirable to clean the glass – after cleaning most of the glasses should have the same appearance as those in category A. Glasses in this category should be monitored after cleaning to see if new surface changes have occurred.

B1 Very slight ‘oily’ appearance which may be an early stage of glass degradation, but can also be unrelated to degradation (grease, etc.)
B2 Very light haze, clearly visible in raking light.
B3 Fingerprints are visible on the surface.
B4 Combination of B1–B3.

Category C  Symptoms C1–C9 may concern glass degradation
This category contains glasses that show probable early stages of glass degradation. Glasses that were treated previously for glass degradation and now appear stable are placed in this category. After cleaning, most glasses (except C7 and C10) should have the same appearance as those in category A. Monitoring is essential in order to detect new surface changes or other symptoms of degradation.

C1 Slight or incipient crizzling; tiny localised cracks on the surface.
C2 Slight discolouration of the glass; suspicion that a colour change has occurred over the years.
C3 Oily surface which may also be localised, manifesting itself as a spotted appearance. This can be an early stage of glass degradation or the presence of external deposits, such as grease.
C4 Harder deposits or haze (which can be scratched away using a fingernail). They may also be localised, giving a spotted appearance.
C5 A fine powder is visible in a cavity (created intentionally during production of the glass) in the glass. The nature and origin of the powder are unclear.
A cavity in the glass (from the manufacturing process) in which a fine powder or light haze is visible.

Archaeological glass that shows iridescence.

A combination of symptoms C1–C6.

A combination of symptoms C1–C6 and symptoms from category B.

Results from earlier treatments and restoration such as glued cracks or fractures and fills.

**Category D**  
Symptoms D1–D6 concern glass degradation  
This category includes glasses with clear symptoms of degradation. Glasses with very unstable or severely aged restoration(s) are also included in this group. It is desirable to clean the glasses (but not D5 and D8). Monitoring is essential in order to detect new surface changes or other degradation symptoms.

D1 Clear crizzling; tiny cracks on large areas of the glass surface.

D2 Clear discolouration of the glass; especially a shift towards purple or pink.

D3 Clear symptoms of weeping glass; small droplets forming on the surface which may appear oily.

D4 Very hard deposits or haze which are difficult to remove.

D5 Archaeological glass with pronounced iridescence.

D6 A combination of the symptoms in category D.

D7 A combination of the symptoms in categories in B, C, and D.

D8 Unstable or severely aged restorations.

**Category E**  
Symptoms E1–E3 concern glass degradation  
This category contains glasses with crizzling that is so advanced that restoration is hardly possible. Glasses in this category can be kept only in storage – the current state is too fragile for display.

E1 Severe crizzling; cracks on large areas of the surface so that the structure of the object is severely affected. Possible flaking.

E2 A combination of different factors; crizzling, discolouration, weeping glass, possibly combined with a surface haze (irremovable) and/or an oily surface appearance.

E3 Severe deterioration such as fractures, complex cracks, and/or missing parts.