INTRODUCTION
1.1 Unstable glass in museum collections

This dissertation is devoted to the chemical deterioration of vessel glass in museum collections. In particular, this study focuses on glass sickness. This term is often used to describe visual changes that occur on glass surfaces as a result of chemical deterioration, and is of particular relevance for objects which have not been exposed to extreme conditions and have been stored indoors for most of their lifetime. The deterioration processes of other types of glass, especially archaeological glass and stained-glass windows, are different topics which are not covered in this dissertation. The preservation of glass in museum collections is of great importance to museum curators and conservators. However, as described in detail throughout this dissertation, the deterioration of glass in museum collections has not received a great amount of attention with the result that conservators are often uncertain which glasses are at risk of deteriorating before changes in appearance occur. As these changes in appearance are a result of irreversible deterioration of the chemistry of the glass it is of vital importance to be able to distinguish those glasses prone to deterioration from those which are stable, before changes in appearance occur and a valuable object potentially becomes unfit for display.

Whether or not a glass will show signs of chemical deterioration depends mainly on two factors: the composition of the glass itself and the environment in which the glass is stored. The importance of the glass composition for its stability was recognized by glassmakers and researchers as early as the 17th century when both Antonio Neri and George Ravenscroft described glass decay in their manuscripts and patents (Neri, 1612; Ravenscroft, 1674), and changed their methods for glassmaking accordingly. The increased knowledge on glass-making and awareness of the importance of composition resulted in the widespread production of glass around the world from the 18th century onwards (Tait, 2012). It was, however, not until the beginning of the 20th century when the chemical structure of glass was investigated and scientists started to understand the chemical principles of glass deterioration.

Zachariasen (1932) was the first to publish on the arrangement of atoms in the glass structure. His papers (Zachariasen 1932, 1935) allowed for the investigation
of chemical and physical behaviour of glass, and monographs on this topic were published from mid-twentieth century onwards (e.g. Morey, 1954; Volf, 1984). The advancement of knowledge on glass chemistry also increased the interest for glass deterioration in museum collections. Robert Organ (1957) published a paper on preferred climate conditions for the storage of unstable glass. In the 1970s, important advances were made in the understanding of the chemistry of deterioration of glass in museum collections. The chemical nature of unstable glass was investigated by Robert Brill (1972, 1975, 1978) who combined compositional data of deteriorating historic glass and experimental data obtained from artificial ageing studies to determine the importance of the ratio of glass constituents for glass stability. At the same time he studied the effect of the environment on the deterioration of glass and demonstrated the adverse effect of moisture in the atmosphere on glass deterioration. The role of atmospheric water in glass deterioration was further investigated in the 1960s, 70s, 80s and 90s in research papers (for example Douglas and El-Shamy, 1967; El-Shamy et al., 1975; Ernsberger, 1980; Bunker, 1994). The mechanisms of glass deterioration are described in detail in Chapter 2.

Typical phenomena related to glass sickness are weeping (Figure 1.1) and crizzling (Figure 1.2). Weeping is the formation of a moist layer or droplets on the surface of the glass, whereas crizzling is a term used to describe the formation of a fine network of hairline cracks (Brill, 1975; Kunicki-Goldfinger, 2008). Both phenomena originate from the chemical alterations of the glass structure during deterioration. During the deterioration process cations leach out of the glass network and are replaced by hydrogen ions. This is accompanied by the migration of molecular water into the glass surface, resulting in the formation of an altered surface layer rich in molecular water. Weeping is associated with the formation of hygroscopic salts on the glass surface, which form as atmospheric molecules react with leached ions. The exact nature of these salts is not fully understood, but published papers suggest the formation of formate and carbonate salts (Robinet et al., 2004; Eremin et al., 2005; Fearn, McPhail and Oakley, 2005; Fearn et al., 2006). Crizzling is related to the dehydration of the top layer of the glass, which may consist of up to 20% of water due to hydration of the surface layer during its lifetime. The dehydration of this layer causes a major loss in volume causing internal stress,
which is released through the formation of cracks (Kunicki-Goldfinger, 2008). Both processes often develop gradually, but the onset of crizzling in particular may develop rapidly when a sudden drop in the storage relative humidity occurs (Koob, 2006).

The above-mentioned problems occur on vessel glasses, or objects in which glass is part of the materials used, in museum collections across the world. Despite the fact that only few museums have undertaken and published condition surveys of glass collections, it is evident that glass deterioration in museum collections is a significant problem. At the Victoria and Albert Museum (V&A) 6500 vessel glasses were investigated, of which circa 400 (6%) showed clear signs of glass deterioration (Oakley, 1990). Although the survey was very comprehensive, it did not enumerate potentially unstable glasses without visual signs of decay, most likely because those early signs of deterioration had been removed during cleaning campaigns. Therefore, the actual number of unstable objects is probably

![Figure 1.1. Fluteglass, height 38.4 cm, ca. 1600-1700. Rijksmuseum, Reg. No. BK-NM-10754-287. Droplets have formed on the inside of the glass as can be seen in the detail (left). Photos: © Rijksmuseum](image-url)
considerably higher. At the National Museums of Scotland (NMS), the British glass collection was surveyed for signs of deterioration and about 20% of the objects were labelled as unstable (Cobo del Acro, 1999; Eremin et al. 2005). In 2013 Burghout and Slager (2013) published their findings of a glass collection survey at Museum Boijmans van Beuningen (MBVB). Over 4000 objects were investigated, of which 105 (3%) were classified as unstable and showing signs of deterioration. Another 566 objects (14%) were identified as being potentially unstable.

The impetus for the research presented in this dissertation was a collection survey by the conservators at the Rijksmuseum, in particular Bodill Lamain. As she was reviewing the condition of vessel glasses in the collection she tried to categorize the glasses into five groups ranging from perfect condition to heavily

Figure 1.2. Fully crizzled and discoloured flagon with spout and ovoid body, height 13.9 cm, ca. 1700. Rijksmuseum, Reg. No. BK-NM-804. Photo: © Rijksmuseum.
deteriorated and unfit for display, but noticed that this was often difficult as signs of glass deterioration are not always clearly visible and the early stages of glass deterioration could not be distinguished from other surface effects (Lamain et al., 2013). Evaluation of the condition was urgent, as the survey was carried out in preparation of the display of objects in the refurbished museum, but no clear-cut method existed for the definite identification of unstable glass. It was particularly hard to determine whether a glass had an altered appearance due to glass deterioration, or due to other effects, such as the deposition of contaminants on the surface or the effect of handling the objects.

What these surveys demonstrate is that a large number of glass objects in museums are in danger of further decay. Simultaneously, they highlight the difficulty of classifying glass objects as ‘sick glasses’. Several methods have been developed for the categorization of unstable glass based on its appearance. Koob (2006) described five stages of crizzling, which is a useful tool in the categorization of unstable glass, but often hard to use when the degradation patterns are not as evident as the formation of cracks on the surface. The five categories developed by the Rijksmuseum (Lamain, 2013) incorporate the notion of the formation of a greasy or altered surface layer, but the descriptions used – such as ‘surface haze’, ‘greasy appearance’, or ‘spotty’ – are often ambiguous and do not necessarily describe the stability of the glass.

As an alternative to visual examination of glass, a large body of research has been devoted to the technical study of unstable glass. Much research concerning glass sickness has been aimed at understanding the chemical nature and composition of unstable glass (e.g. Brill, 1975; Kunicki-Goldfinger et al., 2009), its causes and underlying chemical mechanisms (e.g. Brill, 1972; Brill 1978, Hogg et al., 1999; Fearn, McPhail and Oakley, 2004, 2005; Koob, 2006), and controlling the environment in which the glass is kept (e.g. Organ, 1957; Roemich, 1999; Oakley, 2001). The non-destructive identification of unstable glass at an early stage in its development has, however, received less attention. Ulitzka and Touchard (1991) proposed a method to “detect glasses in danger and to find a way to protect them” (p. 872) using x-ray fluorescence analysis to determine the composition of the glass, but the follow-up of this proposal has not been published. Neelmeijer and Mäder (2005) studied the use of ion beam analysis (IBA) techniques (PIXE and PIGE) for
the determination of silicon concentration differences between the altered surface layer and the unaltered bulk glass. The disadvantage of this method is that IBA is not widely available and that the object will need to travel to the research facility. Spectroscopic techniques such as Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy have been used to study glass deterioration (Earl, 1999; Robinet et al., 2006), but they are unable to provide a clear-cut assessment of glass stability. Consequently, no straightforward method exists for the unambiguous identification of glass objects in large collections.

The identification of unstable glass objects, especially those not yet showing visible signs of deterioration, is at the heart of this dissertation. Since this problem originates from conservators experiencing trouble with how to deal with glass deterioration in the collections they are responsible for, this work has a strong connection with practical implications for preservation and conservation of glass. It is of prime significance to realise that deterioration of unstable glass is an irreversible process, which cannot be stopped completely. Conservation actions are therefore often aimed at slowing down chemical deterioration through controlling the environment in which the objects are kept. However, no consensus has been reached on the ideal storage conditions for unstable glass objects. As a result, glass collections are often stored in the same climate which is used for other objects, but which is not necessarily preferential for the glass. Glass collections often consist of thousands of objects and due to the nature of the material they have a range of different compositions and may not benefit from similar conservation strategies. Being able to pinpoint those glasses at risk of further decay would greatly benefit conservators as they would then be able to take specific measures for those unstable objects, rather than for an entire collection. Not being able to identify those objects at risk may lead to the advancement of deterioration and the potential loss of scores of objects in a single collection. In order to investigate such a large number of objects, a straightforward method should be used.

The development of a straightforward method is, however, not straightforward. For the investigation of glass collections there are three challenges that need to

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1 Kunicki-Goldfinger (2008) provides an overview of climate conditions used for the storage of glass. Suggested relative humidity values range from 22% to 55%.
be addressed. Firstly, the method should be sensitive enough to discriminate between stable and unstable glass even when there seem to be no differences to the naked eye. Secondly, the method should be non-invasive and straightforward so that a conservator can gather samples from many objects in a short period. This is of particular importance as glass collections can be comprised of several thousands of objects. Third, the method should be able to quantitatively analyse samples. Quantitative analysis is crucial as only then a discrimination between unstable, potentially unstable and stable glass objects can be made.

Despite the fact that there is a large body of research devoted to the study of historic glass, much remains unclear about the exact mechanisms of deterioration (Geisler et al., 2015; Schalm and Anaf, 2016) and on the identification of unstable glass objects in museum collections. The identification of unstable glass objects and the development of appropriate conservation strategies to prevent glass deterioration are high on the agenda of glass conservators and curators, but scientific information on both topics is lacking. Therefore, the core aim of this study is to support conservators in making better assessments of glass stability and suitable conservation strategies, as well as contributing to the current body of knowledge on glass deterioration processes.

1.2 Terminology

The term glass sickness is used to describe the visual changes that occur on the glass surface as a result of the inherent chemical instability of the glass composition. During discussions the use of the word sickness has often led to the misconception that it is a phenomenon that can be ‘cured’ or is ‘contagious’, while this is not the case. This misunderstanding may also be a result of the fact that glasses which are stored near each other simultaneously develop ‘symptoms’ of ‘glass sickness’, while this is not a result of objects infecting each other with glass sickness, but rather a result of the similar unfavourable environmental conditions and the fact that these objects are of unstable composition in the first place. Despite the ambiguity that is accompanied by such terminology, conservation professionals are not afraid to compare object decay to human health. For example, the term bronze disease is used to describe the corrosion of copper due to a specific interaction
of bronze with chloride (Scott, 1990). It can be argued that the term ‘glass sickness’ strikingly describes the phenomena that it is associated with, somewhat resembling ‘human sickness’. Who is not familiar with the weeping/sweating as a consequence of a fever, or the cracks (crizzling) that form on the human skin in dry weather? Since ‘glass sickness’ is also a term much more appealing to the imagination than glass deterioration, it is used in the title of this dissertation. For the sake of clarity however, the term will be avoided as much as possible in the rest of the dissertation. Instead, the difference between ‘sick’ and ‘healthy’ glass will be described by the more neutral terms ‘unstable’ and ‘stable’ respectively.

When studying different sources on glass deterioration one quickly drowns in different, often unclear terms describing the same phenomenon or the use of one word with a different meaning in different contexts. Schalm and Anaf (2016) have made a list of terms they encountered during their review of glass deterioration literature. It includes term as ‘sick glass’, ‘ill glass’, ‘glass disease’, ‘gel layer’, ‘leached layer’, ‘crust with gel lamination’, ‘deteriorated glass surface’, ‘corroded glass layer’, ‘hydrated surface layer’, ‘altered glass’, ‘altered layer’, et cetera. As a result, there is no consensus on terms used to describe the effects of chemical deterioration of glass and this diversity of unclear terminology remains. Kunicki-Goldfinger (2008) provides the notion that there has been a history of unclear terminology concerning the deterioration of glass objects, especially in the field of conservation of cultural heritage objects. He suggested that “conservation surveys focus on the presence of two main characteristics – crizzling and moisture – accompanied by additional information gathered on a more detailed level” (p. 48). And while it is true that these two main characteristics are the two most notable phenomena, they are not mutually exclusive and both exist in different gradations.

Streamlining the used terminology used in the field of glass conservation is a large task and it does not fall within the scope of this dissertation to achieve this. However, this dissertation does require some terminology to describe changes in appearance and chemistry of glass. The terms used throughout this dissertation will be explained when necessary, chapter 2 is central in this as most of the terminology will be introduced and explained there.
1.3 A short historical perspective on glassmaking

The time and place of the origin of glass production, or vitreous materials, is unknown. Nonetheless, it is recognised that the development of techniques for glaze and glassmaking go hand in hand with scientific, economic and societal advancements in the Near and Middle East and Europe. Though important in the understanding of glass history and the development of glassmaking techniques, this section will only briefly describe this topic, focusing on aspects particularly relevant to the understanding of glass deterioration. The objects studied in this dissertation include mostly European vessel glasses, and therefore the history of glass production before the Roman Empire will be covered only briefly in this section, as this exceeds the scope of this dissertation.

In *Naturalis Historia* Pliny the Elder provides an account of the discovery of glassmaking (see Rasmussen (2012) for a summary) that is not likely to be true, but which provides an interesting perspective. He describes how Phoenician merchants who were shipping blocks of *nitre* (sodium carbonate) were cooking on a sandy beach in modern day Israel, using the nitre as support for their pots. The fusion of sand, nitre and wood/plants used as fuel for the fire was said to result in the formation of glass. Though plausible (Rasmussen, 2012), it is unlikely that this is the actual first time glass was produced. More likely, glass was discovered as a by-product of metallurgy (Tite, Shortland and Paynter, 2002; Rasmussen, 2012). The most important developments in the early history of glass production described by Rasmussen (2012) and Tite (2002) include the creation of Egyptian faience (fourth millennium BC), the use of glass as independent material in Egypt and Mesopotamia (from ca. 2500 BC), and the introduction of glass as a major industry in Egypt and Mesopotamia (from 1500 BC). A historic perspective on glass production is provided by Seth Rasmussen (2012), while a superlative overview of historic glass production techniques is provided by Hugh Tait (2012). The two most important periods in European glass production are described below.

The first major technical advances in glass production were accomplished by the Romans. The invention of glassblowing in modern day Syria around 100 BC induced what is referred to as the *first golden age of glass* (Axinte, 2011): a major
increase in glass production centres throughout the Roman Empire during the first to the fourth century AD. Different glassmaking techniques were developed, including the production of clear glass, layered glass structures in different colours and the production of flat glass (see for example Tait, 2012). During the following centuries the developments in glassmaking technologies declined after the fall of the Roman Empire. It was not until around the tenth century AD that glass production technology was reintroduced and improved in Venice. A period which is referred to as the second golden age of glass (Axinte, 2011) spanned the 13th to 17th century followed developments in Venice, such as the establishment of a glassmakers’ guild (1268). During this period the famous cristallo, very clear glass, was produced in Venice (Rasmussen, 2012; Tait, 2012). After this period, glass played a crucial role in the advancement of scientific knowledge by the introduction of scientific equipment such as microscopes, thermometers, barometers, chemical glassware, mirrors, lenses and so on (MacFarlane and Martin, 2004). A modern society without glass is unimaginable, both as a material used in everyday life, in scientific equipment, as well as in works of art.

The deterioration phenomena we see today, and which are the subject of this dissertation, are also recorded in historic sources. In particular, the problem of crizzling has been known since at least the seventeenth century. In a translation of Neri’s handbook on glass technology L’Arte Vetraria (Neri, 1612) Christopher Merret (1662) notes: “glass of lead, ’tis a thing unpractised in our furnaces and the reason is, because of the exceeding brittleness thereof … could this glass be made as tough as that of crystalline, ’t would far surpass it in the glory and beauty of its colours”, referring to the beauty of lead glass, but at the same time recognizing the problem of the chemical instability (“brittleness”) of the glass. Despite the comments by Merret on the instability of lead glass, George Ravenscroft applied for a patent for the “Art and manufacture of a particular sort of cristalline glasse resembling rock christall” in 1674. This glass indeed contained high concentrations of lead and, due to its unstable composition, degraded. This led to the submission of two certificates that slightly changed the glass manufacturing technique from the initial patent in 1676 (MacLeod, 1987). The certificates mention that the glasses had been observed to “crizzel and decay” and to “crizzel and spoil” (MacLeod, 1987). The fact that Ravenscroft changed his recipe within two years
demonstrates that the onset of crizzling is a process that can occur within a short period of time after production. After the change in the recipe, the stability of the Ravenscroft glasses increased. However, the fact that Ravenscroft glasses are still known to crizzle in museums is evidence that the solution to the crizzling problem was not completely found in 1676 (MacLeod, 1987). In addition, in 20th century glass making, for art glass and even scientific sample bottles, crizzling has remained an issue to the present day.

Finally, an important example of highlighting the effect the glass batch formulation has on the stability of glass is the deterioration of cristallo. These Venetian objects are often regarded as highlights of glass collections in museums, but also prove to be the most challenging to conserve as they often display signs of advanced deterioration. This is a result of the experimentation of glassmakers who were attempting to create high quality, clear glass by purification of the raw materials used for glassmaking. This resulted in the inadvertent removal of stabilizing elements from the glass batch, thus creating glasses of unstable composition (Brill, 1975). These endeavours of craftsmen several centuries ago now pose a problem for conservators of glass collections. The research presented in this dissertation aims to contribute to a better understanding of how to prevent deterioration of these priceless objects.

1.4 Research questions

The overall scope of this dissertation is to gain a better understanding of glass deterioration mechanisms in order to identify potentially unstable glass objects in museum collections and make recommendations on suitable conservation strategies for these objects. The main issue in this research is:

How can unstable glass objects in museum collections be identified using non-destructive, readily-available methods before irreversible changes in appearance occur and how can further deterioration of these objects be prevented?

To test this main question five research steps will be addressed:

1. What chemical mechanisms are currently associated with glass
deterioration in the literature, which analytical techniques are available for the non-destructive investigation of glass deterioration and what are the leading conservation strategies?

Chapter 2 provides a theoretical framework for the other, experimental chapters in this dissertation. It gives insight in the current knowledge on glass deterioration relevant to the museum context. It also explores the way in which chemical deterioration of glass objects in museum collections have been studied. An overview of current conservation strategies is also provided, based on the existing literature on glass conservation, as well as on visits and personal communication with glass conservators. The overview of these three topics (glass deterioration, analytical studies and conservation strategies) provides the context for the experimental results in the following chapters.

2. Which ionic compounds are found on the surface of unstable glass? What are potential consequences of their presence for conservation of glass objects?

In order to answer this research question an analytical technique capable of quantifying the presence of ions in low concentrations with straightforward sampling and interpretation of the results is necessary in order to facilitate collaboration between scientists and conservators. Ion chromatography (IC), a form of high performance liquid chromatography (HPLC), is such a technique and it is at the heart of this thesis. An extensive description of the technique is provided in Chapter 3. This second research question forms the core of the third chapter in which the analysis of samples taken from clearly deteriorating objects will be presented. The results of these analyses are of qualitative nature and act as a proof of principle for the use of ion chromatography (IC) for the analysis of samples removed from glass surfaces using a swabbing protocol (the potential of IC was discussed in a preliminary paper (Lamain et al., 2013) in an earlier publication). The results provide crucial information for the subsequent development and validation of a robust sampling and analytical protocol. The potential sources of ions will be explored and their nature will be compared to ions found by other scholars. Based on the ions detected, some considerations on preventive conservation strategies will be presented as well. Primarily, this chapter provides essential information for the development of a method for the
quantitative analyses of ions on the surface of unstable glass, which is necessary for the discrimination between stable and unstable glass.

3. **How can ions on the surface of unstable glass be analysed quantitatively?**

Chapter 4 describes the development and validation of a sampling and analytical protocol aimed at the quantitative identification of ions on glass surfaces. The ions under investigation are the ones identified in Chapter 3, supplemented by ions which are used for calibration of the IC systems. An important aspect of the protocol is that the sampling should be very straightforward and can be carried out by a conservator while the final analysis is done by the scientist using advanced equipment in a laboratory setting.

4. **Which ions can be attributed to the deterioration of glass, and which ions have another source?**

Chapter 5 steps out of the museum context and investigates the deterioration of glass in a controlled environment. Unstable glass fragments are artificially aged and the deterioration products are sampled using the validated protocol described in Chapter 4. This provides insight into the origin of the ions found on the surface of the glass, acts as a test-case for the analytical protocol, explores ways of artificially aging glass and enables the discussion on potential marker ions for unstable glass. Furthermore, because these glass samples can be analysed destructively, this provides the opportunity to explore the relationship between glass composition and the deterioration products found on the glass surface.

5. **Can the concentration of ions found on the surface of glass objects in museum collections be related to their chemical stability?**

In the final experimental chapter, Chapter 6, the museum context is explored in more depth. Samples taken from vessel glasses from the Rijksmuseum and Museum Boijmans van Beuningen are analysed. The objects under investigation have all been classified in the past according to their condition based on visual examination by conservators. The outcomes of the sample analyses will be compared to this classification. This chapter will further investigate the potential marker ions for unstable glass and the use of the determined ion concentrations in the development of an early warning system for unstable glass.
1.5 Samples

Two different types of samples were used in these studies. Initially, samples were obtained from glass objects from museum collections. For Chapter 3, samples taken from objects, known with certainty to be unstable, from The Rijksmuseum, The Corning Museum of Glass and The Hamburg Museum were investigated. For Chapter 6, samples were collected from objects from The Rijksmuseum and Museum Boijmans van Beuningen. These samples were taken from objects classified as both stable and unstable, in this case multiple samples were taken for each object.

The second types of samples were taken from unstable glasses which could be used for destructive testing and artificial aging. These samples include a large piece of flat glass which was replaced during the restoration of a 19th century desk, replica glasses from the Corning Museum of Glass with compositions which simulate those of unstable historic glass, plus quartz and borosilicate glass as reference materials. These samples were used for Chapters 4 and 5.

1.6 Outline of the dissertation

The dissertation consists of seven chapters: an introduction, 5 research chapters and a final conclusions chapter which acts as a synthesis of all the experimental chapters. The dissertation was written as a single body of research, but the chapters can be regarded as individual research papers. Chapter 2 is a literature review paper on the current understanding of glass deterioration in museum collections. Chapter 3 is the first research paper and is largely based on a paper published in the peer-reviewed preprints of the conference Recent Advances in Glass and Ceramics Conservation of the ICOM-CC Glass and Ceramics Working Group interim meeting 2016 in Wroclaw, Poland. Chapter 4 is a research paper focusing on quantitative analysis of ions on glass surfaces, Chapter 5 concentrates on artificial ageing studies and Chapter 6 describes the investigation of museum objects. The final chapter, Chapter 7 is a synthesis of the previous chapters and summarises the most important conclusions of the research. It also provides recommendations for future work and describes the practical implications for the field of the conservation of glass.
1.7 References


