UNDERSTANDING MULTICOMPONENT OXIDE INTERFACES USING INVERSE GAS CHROMATOGRAPHY

A Thesis in
Chemistry
by
Lymaris Ortiz Rivera

© 2011 Lymaris Ortiz Rivera

Submitted in Partial Fulfillment of the Requirements for the Degree of

Master of Science

August 2011
The thesis of Lymaris Ortiz Rivera was reviewed and approved* by the following:

Karl T. Mueller
Professor of Chemistry
Thesis Advisor

Thomas E. Mallouk
Evan Pugh Professor of Materials Chemistry and Physics

Carmen Enid Martínez
Associate Professor of Environmental Soil Chemistry

Carlo Pantano
Distinguished Professor of Materials Science and Engineering

Barbara Garrison
Shapiro Professor of Chemistry
Head of the Department of Chemistry

*Signatures are on file in the Graduate School
ABSTRACT

Multicomponent complex oxides, especially sodium aluminoborosilicate glass fibers, are important materials used for thermal insulation in buildings and homes. The surfaces of fibers that are used in such materials must be reactive to adhesives and other organics, and stable against chemical attack by humidity. The reactive sites present on the glass surface, and their roles in binding different chemical species, require investigation so that the materials can be tailored to meet specific demands. In this study the interaction of a small probe molecule (acetic acid) with sodium aluminoborosilicate glass fiber is investigated with the final goal of a predictive understanding of the oxide surface reactivity with carboxylic functional polymers. In order to study the nature of the interaction of probe molecules to the oxide surface, inverse gas chromatography coupled to mass spectrometry (IGC-MS) and inverse gas chromatography temperature programmed desorption (IGC-TPD) are utilized. After dosing of sodium aluminoborosilicate glass fibers with acetic acid, the mass spectrum shows that carbon dioxide and water are the most abundant species that elute from the GC column at a constant temperature of 100°C, due to the presence of sodium carbonate on the fiber surface. IGC-TPD-FID and IGC-TPD-MS studies show four different regimes, one at low temperatures and three at higher temperatures. IGC-TPD-MS studies show that at the low temperature, acetic acid elutes as an intact species, revealing that at these temperatures physisorbed acetic acid is being removed. At higher temperatures, elution of acetic acid is observed from a more strongly physisorbed species (based on the temperature range of desorption) and a new species, ethenone, is also observed. Ethenone is a product of the decomposition of carboxylate species at high temperatures, which suggest that the formation of carboxylate species is occurring
as an interaction of the acetic acid with the sodium aluminoborosilicate glass. Also, at higher temperatures (600°C) water desorbs as a product of silanol group condensation as well as the removal of chemisorbed water in the glass. Coupling previous NMR studies with the results of this work, we have discovered that both sodium from the glass itself and sodium found in sodium carbonates formed near the surface (presumably from interaction of the untreated glass with atmospheric carbon dioxide) can be the sites of interaction with the carboxylic acid, with the majority of binding occurring with the sodium in the glass surface.
# TABLE OF CONTENTS

LIST OF FIGURES .................................................................................................................. vii

LIST OF TABLES .................................................................................................................. x

ACKNOWLEDGEMENTS ........................................................................................................ xi

Chapter 1 Silica and Glass Surfaces ...................................................................................... 1

1.1 Introduction ...................................................................................................................... 1
1.2 Silica Surface ..................................................................................................................... 3
1.3 The Surface Chemistry of Silica ...................................................................................... 4
1.4 Multicomponent Glass Formation and Surface Chemistry .............................................. 5
  1.4.1 Adsorption Processes ................................................................................................. 6
1.5 Multicomponent Glass Structure .................................................................................... 7
  1.5.1 Glass-forming Elements ............................................................................................. 7
  1.5.2 Glass-forming Oxides ................................................................................................. 8
1.6 Sodium Aluminoborosilicate Glasses ............................................................................. 8
1.7 References ....................................................................................................................... 11

Chapter 2 Inverse Gas Chromatography ............................................................................ 13

2.1 Introduction ...................................................................................................................... 13
2.2 Inverse Gas Chromatography ......................................................................................... 14
2.3 Inverse Gas Chromatography Temperature Programmed Desorption ......................... 15
2.4 Inverse Gas Chromatography coupled to Mass Spectrometry ....................................... 17
2.5 References ....................................................................................................................... 19

Chapter 3 Studies of the Reactive Surface in Sodium Aluminoborosilicate Glass Systems .... 20

3.1 Introduction ...................................................................................................................... 20
3.2 Background ...................................................................................................................... 21
3.3 Experimental Methods .................................................................................................... 22
  3.3.1 Materials ..................................................................................................................... 22
  3.3.2 IGC-MS ....................................................................................................................... 23
  3.3.3 IGC-TPD...................................................................................................................... 24
  3.3.4 Processing of Spectra ................................................................................................ 25
    3.3.4.1 Pure Acetic Acid Subtraction ............................................................................. 26
    3.3.4.2 Extracted Ions Chromatogram ......................................................................... 26
    3.3.5 X-ray Photoelectron Spectroscopy ........................................................................ 27
    3.3.6 Acid Leaching Procedure ....................................................................................... 27
3.4 Results and Discussions .................................................................................................. 28
  3.4.1 Sodium Aluminoborosilicate Glass Studies by IGC-MS ............................................ 28
  3.4.2 Sodium Aluminoborosilicate Glass Studies by IGC-MS: $^{13}$C Enriched Acetic Acid as Probe Molecule .............................................................. 34
3.4.3 Leaching Experiments ............................................................................................... 36
3.4.4 Deconvolution of Previous NMR Studies .................................................................. 41
3.4.5 Temperature Programmed Desorption Studies of Sodium Aluminoborosilicate Glass ................................................................. 44
3.4.5.1 Temperature Programmed Desorption Studies of Sodium Aluminoborosilicate Glass: $^{13}$C Enriched Acetic Acid .................. 50
3.4.6 Temperature Programmed Desorption Studies of Leached Sodium Aluminoborosilicate Glass ......................................................... 53
3.4.6.1 Temperature Programmed Desorption Studies of Leached Sodium Aluminoborosilicate Glass: $^{13}$C Enriched Acetic Acid .............. 57
3.5 Summary ......................................................................................................................... 61
3.6 References .......................................................................................................................... 62

Chapter 4 Conclusions and Future Directions ............................................................... 63

4.1 Conclusions ...................................................................................................................... 63
4.2 Future Directions .............................................................................................................. 64
LIST OF FIGURES

Figure 1-1. Silica surface. ............................................................... 3

Figure 1-2. Formation of water film on glass by adsorption. ......................... 6

Figure 1-3. Glass surface sites where reaction with water can occur. 7

Figure 2-1. Schematic of the differences between Conventional Gas Chromatography and Inverse Gas Chromatography. ....................... 15

Figure 2-2. Experimental set-up for Temperature Programmed Desorption Inverse Gas Chromatography with a Flame Ionization Detector. 16

Figure 2-3. Experimental set-up for Inverse Gas Chromatography coupled to Mass Spectrometer. .................................................. 18

Figure 3-1. $^1$H-$^{13}$C CP MAS NMR spectra of $^{13}$C enriched acetic acid dosed onto (A) sodium aluminoborosilicate glass and (B) Cab-O-Sil. 21

Figure 3-2. Silyl ester. ........................................................................ 22

Figure 3-3. Sample preparation for an IGC-TPD experiment. ....................... 25

Figure 3-4. Different reactions from the interaction of acetic acid with basic sites on the surface of sodium aluminoborosilicate glass fibers. ...................... 29

Figure 3-5. IGC chromatogram of sodium aluminoborosilicate glass dosed with acetic acid at 100 °C. The mass spectrum in the box corresponds to the area marked with the circle. ........................................... 30

Figure 3-6. Mass spectrum of carbon dioxide. ......................................... 30

Figure 3-7. Background spectrum. ...................................................... 30

Figure 3-8. IGC-MS of sodium aluminoborosilicate glass dosed with acetic acid at 100 °C. The mass spectrum in the box corresponds to the area marked with the circle. .................................................. 31

Figure 3-9. Mass spectrum of water. .................................................... 31

Figure 3-10. IGC -MS of sodium aluminoborosilicate glass dosed with acetic acid at 100 °C. The mass spectrum in the box corresponds to the area marked with the circle. .................................................. 32

Figure 3-11. IGC chromatogram of pure acetic acid at 100 °C. The mass spectrum in the box corresponds to the area marked with the circle. ......... 33
Figure 3-12. Subtracted mass spectrum corresponds to the area marked with the circle in ................................................................. 33

Figure 3-13. Extracted ion method applied to IGC chromatogram of sodium aluminoborosilicate glass dosed with acetic acid at 100 °C................................. 34

Figure 3-14. Mass spectrum of $^{13}$C enriched acetic acid......................... 35

Figure 3-15. IGC chromatogram of sodium aluminoborosilicate glass dosed with $^{13}$C-acetic acid at 100 °C. The graph in the box corresponds to the respective areas marked with the circles and letters.................. 36

Figure 3-16. IGC chromatogram of leached sodium aluminoborosilicate glass dosed with acetic acid at 100 °C........................................................................ 38

Figure 3-17. IGC-MS spectra of (A) leached sodium aluminoborosilicate glass and (B) fresh sodium aluminoborosilicate glass dosed with acetic acid at 100 °C ........................................................................ 40

Figure 3-18. Extracted ion method applied to IGC chromatogram of leached sodium aluminoborosilicate glass dosed with acetic acid at 100 °C........... 41

Figure 3-19. I) $^1$H-$^{13}$C CP MAS NMR spectra of $^{13}$C enriched acetic acid dosed onto (A) freshly pulled sodium aluminoborosilicate glass and (B) sodium carbonate$^5$, II) $^1$H-$^{13}$C CP MAS NMR spectra of $^{13}$C enriched acetic acid dosed onto sodium aluminoborosilicate glass.................................................. 42

Figure 3-20. Deconvoluted $^1$H-$^{13}$C CP MAS NMR spectra of $^{13}$C enriched acetic acid dosed onto sodium aluminoborosilicate glass. ................................. 43

Figure 3-21. Deconvoluted $^1$H-$^{13}$C CP MAS NMR spectra of $^{13}$C enriched acetic acid dosed onto sodium aluminoborosilicate glass, the light blue line correspond to the $^1$H-$^{13}$C CP MAS NMR spectra of $^{13}$C enriched acetic acid dosed onto sodium carbonate. ........................................................................ 44

Figure 3-22. Decomposition of sodium carbonate.......................................... 45

Figure 3-23. IGC-TPD-FID and IGC-TPD-MS profiles of sodium aluminoborosilicate glass dosed with acetic acid ............................................................... 45

Figure 3-24. IGC-TPD-FID and IGC-TPD-MS profiles of sodium aluminoborosilicate glass dosed with acetic acid at (A) constant temperature of 100 °C and (B) temperature programmed desorption plot from 100-600 °C. 46

Figure 3-25. Peaks of interest from IGC-TPD-MS profile of sodium aluminoborosilicate glass dosed with acetic acid.......................................................... 48

Figure 3-26. Mass spectra of peaks of interest from Figure 3-25.................... 48
Figure 3-27. Subtracted mass spectra of peaks of interest from Figure 3-25 .......................... 48

Figure 3-28. Extracted ion method applied to IGC-TPD-MS of sodium aluminoborosilicate glass dosed with acetic acid ............................................................... 49

Figure 3-29. IGC-TPD-FID and IGC-TPD-MS profiles of sodium aluminoborosilicate glass dosed with $^{13}$C acetic acid ................................................................. 51

Figure 3-30. Peaks of interest from IGC-TPD-MS profile of sodium aluminoborosilicate glass dosed with $^{13}$C acetic acid ................................................................. 51

Figure 3-31. Mass spectra of peaks of interest in Figure 3-30. .............................................. 52

Figure 3-32. Subtracted mass spectra of peaks of interest from Figure 3-30 ...................... 52

Figure 3-33. Extracted ion method applied to IGC-TPD-MS of sodium aluminoborosilicate glass dosed with $^{13}$C enriched acetic acid ........................................... 53

Figure 3-34. Comparison of TIC from IGC-TPD-FID of fresh and leached sodium aluminoborosilicate glass dosed with acetic acid ................................................. 54

Figure 3-35. Comparison of TIC from IGC-TPD-MS of fresh and leached sodium aluminoborosilicate glass dosed with acetic acid ................................................. 54

Figure 3-36. IGC-TPD-FID and IGC-TPD-MS profiles of leached sodium aluminoborosilicate glass dosed with acetic acid ...................................................... 56

Figure 3-37. Peaks of interest from IGC-TPD-MS profile of leached sodium aluminoborosilicate glass dosed with acetic acid ...................................................... 56

Figure 3-38. Mass spectra of peaks of interest in Figure 3-37. .............................................. 56

Figure 3-39. Subtracted mass spectra of peaks of interest from Figure 3-37 ...................... 56

Figure 3-40. Extracted ion method applied to IGC-TPD-MS of leached sodium aluminoborosilicate glass dosed with acetic acid ................................................. 57

Figure 3-41. IGC-TPD-FID and IGC-TPD-MS profiles of leached sodium aluminoborosilicate glass dosed with $^{13}$C enriched acetic acid ........................................... 58

Figure 3-42. Peaks of interest from IGC-TPD-MS profile of leached sodium aluminoborosilicate glass dosed with $^{13}$C enriched acetic acid ........................................... 58

Figure 3-43. Mass spectra of peaks of interest of Figure 3-42. .............................................. 59

Figure 3-44. Subtracted mass spectra of peaks of interest from Figure 3-42 ................. 59

Figure 3-45. Extracted ion method applied to IGC-TPD-MS of leached sodium aluminoborosilicate glass dosed with $^{13}$C enriched acetic acid ........................................... 60
LIST OF TABLES

Table 3-1. Surface Composition (At%) by XPS of sodium aluminoborosilicate glass. ........................................................................................................................................ 28

Table 3-2. Surface Composition (At%) by XPS of fresh sodium aluminoborosilicate glass and leached sodium aluminoborosilicate glass. ....... 37
ACKNOWLEDGEMENTS

This thesis represents a very important milestone in my professional and personal development. I would like to thank the people that contributed directly or indirectly to the realization of this goal. First of all, I would like to acknowledge the National Science Foundation (NSF) under grant CHE-0809657, for the funding to make this project possible. This work was conducted in collaboration with Penn State University, Jonhs-Manville and Dow Chemical (previously Rohm Haas) under the NSF program “Grant Opportunities for Academic Liaison with Industry (GOALI)”. I would like to express my sincere gratitude to my advisor, Dr. Karl T. Mueller. Thank you Dr. Mueller for letting me being a part of your research group, and for constant encouragement. I also want to thank Dr. Carlo Pantano, although not an official committee member, who took on the role of advisor and gave me extraordinary feedback and advice. Also, thanks to Victor Bakaev, who took time to teach me how to use the IGC, set up the mass spectrometer for my experiments, helped with data analysis, and gave great advice and direction. Also, I would like to thank Joy Banerjee for the XPS sample preparation and data collection.

I am very thankful for my graduate committee, who contributed to the completion of this milestone. I would also like to thank the Mueller group member’s past and present, for unconditional help and support throughout the research process. I would like to thank Rebecca Golombeck, who introduced me to the IGC world. Thanks to Rebecca Sanders, Kelly Murphy, and David Roach, for all the help with the NMR set up, reading my papers and NUTS troubleshooting. Thanks to Daniel Suchy, for being a good partner in this project and helping me with the NMR data.
In addition, I want to express my sincere gratitude to the special people that provided their unconditional support, guidance and sincere friendship: Noelsís Márquez, Wilnelia Marrero, Liza Díaz, Emil Hernández, Sandra Rodríguez and all my friends. They made this experience a unique one and I am very fortunate to have them in my life. I would like to give a very special acknowledgement to Amin Espah Borujeni, thanks for all the support, advice, tolerance and the great moments and adventures. Doostat daram!

Finalmente, quiero agradecer toda mi familia, pero en especial a las personas más extraordinarias de este mundo, mis padres Margarita Rivera and Gilberto Ortiz, mi hermana, Tanialis Ortiz y mi cuñado, Joel López. A ellos agradezco infinitamente, porque su amor incondicional, inspiración y confianza hicieron de este sueño una meta realizada. A ellos le dedico este logro. (Last but not least, I want to thank my family, especially the most extraordinary people in this world, my parents, Margarita Rivera and Gilberto Ortiz, my sister, Tanialis Ortiz and my brother-in-law, Joel López. I am extremely thankful for them, because their unconditional love, inspiration and courage made this dream a realized goal. I dedicate this achievement to them.)
Chapter 1
Silica and Glass Surfaces

1.1 Introduction

The applications of glass fibers are diverse; they are used for insulation, filtration, and reinforcements. Glass fiber is grouped with rock/slag wool and refractory ceramic fiber into the family of synthetic vitreous fibers (SVF). SVFs are human-made, fibrous materials with an amorphous (vitreous, i.e., non-crystalline) molecular structure. Glass fiber is manufactured in two basic forms: glass wool and glass textile filament. Glass wool is primarily used for thermal and acoustical insulation in buildings, air handling systems, pipe covers, automobiles, aircraft, mobile homes, and a wide variety of appliances and equipment. A small proportion of glass wool (less than 1% in the US) is manufactured as special application fiberglass, which is used for high efficiency particulate air filters, specialty filter papers, battery components, and aerospace insulation. Textile glass filament is coarser than glass wool; it is used in draperies, screening, electrical yarns, and industrial fabrics and as reinforcement in roofing paper, shingles, plastics, papers, rubber, and other materials. Even though glass fibers are useful in many applications, their surfaces are the target of chemical attack, which causes a weakening of the glass fibers causing changes in their thermal and mechanical properties.

Coatings are usually applied to a fiber for adhesive binding or coupling to a polymer matrix. Generally, the coatings used are thermally or UV cured organic polymers cross-linked with a resin or silane coupling agents. These coatings also protect
the surface from chemical damage that can weaken the glass surface\textsuperscript{5}, and so must be stable against humidity and water attack.

The study of the reactive sites on the glass surface, especially those that are responsible for the linkage between the glass fiber surface and an organic coating, is of great importance. These polymeric systems often possess a variety of organic functional groups. Companies had been using formaldehyde in the adhesive binders for fiberglass insulation, but formaldehyde is a sensitizing agent and a suspected carcinogen and long-term exposure to formaldehyde has been linked to asthma and dermatitis\textsuperscript{1}, and for this reason, formaldehyde-free polyacrylics are now being developed for the binders.

In this study, acetic acid has been selected as a probe molecule representative of the carboxylic acid functional group found in many polyacrylic adhesive polymers. It is desirable to investigate the interaction of acetic acid with the surface of the glass fiber in order to understand multicomponent glass surface chemistry and reactivity, which differs from the reactivities measured for single-component oxides such as silica and alumina. Methods such as inverse gas chromatography coupled to mass spectrometry (IGC-MS) and inverse gas chromatography temperature programmed desorption coupled with mass spectrometry (IGC-TPD-MS), will be used to study the reactive surface sites of the glass fibers, specifically sodium aluminoborosilicate glass fibers. The final goal of our team project is to utilize green alternatives in order to replace the formaldehyde binders that are currently used in fiberglass production, and this particular study focuses on understanding the chemical implications for the glass surface of utilizing formaldehyde-free coatings that are based on acrylic acid chemistries.

Given the complexity of multicomponent glasses surfaces, the structure and reactive surface of the most abundant building block of the glasses studied here will first be introduced.
1.2 Silica Surface

Silica is a naturally occurring material in minerals. The primary use of silica is in the production of glass, but it not limited to this product. Due to the ability to modify the surface chemistry of silica, it is used in a broad range of applications such as catalysis, biotechnology, filtration and chromatography.

The surface of silica terminates in either a siloxane group or one of the several forms of silanol groups as show in Figure 1-1. Siloxane groups are Si-O-Si bridges, and the bridging oxygen is considered to be on the surface. The silanol groups can be divided into isolated silanol groups, geminal silanols, and vicinal silanols. Isolated silanol groups are species in which the surface silicon atom has three bonds into the bulk structure and the fourth bond terminates as an OH. Geminal silanols are species with two bonds to bridging oxygens and two hydroxyl groups attached to the silicon. The geminal silanols are too close to hydrogen bond with each other, whereas the free hydroxyl groups are too separated. Vicinal silanols or hydrogen bonded silanols are species in which one nearby silanol is hydrogen bonded to another nearby silanol.

![Figure 1-1. Silica surface.](image-url)
1.3 The Surface Chemistry of Silica

The chemistry on the surface of silica depends on the nature of attractive forces existing between the adsorbate (usually a small molecule) and adsorbent (the silica), and these attractive forces will dictate the type of adsorption that will occur at the surface. Adsorption can be classified as physical adsorption (physisorption) or chemical adsorption (chemisorption). The interaction between adsorbate and adsorbent may be due to chemical bonding, hydrogen bonding, hydrophobic bonding, or van der Waals forces.

Van der Waals’ type forces dictate physical adsorption, or physisorption, because the forces of attraction between the molecules of the adsorbate and the adsorbent are weak. Due to the weak nature of the forces in physisorption, heating or decreasing the pressure of the adsorbate can reverse this process. Otherwise, in chemical adsorption or chemisorption, the forces of attraction between the adsorbate and the adsorbent are very strong forming chemical bonds in this type of interaction.

Silanol groups are responsible for the interaction of species with the silica surface. The bulk of the silica structure is composed of siloxane groups, and this functionality is formed by condensation during silica formation. Otherwise, silanol groups are formed by incomplete condensation or chemical attack after condensation.

Hydroxyl groups play an important role on the silica surface because hydrogen bonding is the most common method of adsorption at the silica-adsorbate interface. Silanols are proposed to be the water adsorption sites, which explain the hydrophobic character of silica with low silanol densities\(^6\).

Silica glass has a random distribution of surface hydroxyls, which is attributed to its amorphous nature. This amorphous nature of silica is responsible for the adsorption
process at the silica surface. The adsorption of water on a silica surface may be compared with that of other molecules of similar size. The adsorbate molecule may be large enough to occupy more than one adsorbing site. Studies performed by Garrone and Ugliergo\(^7\) showed that the main interactions of SiOH to the O end of CO, to the O end of N\(_2\)O, to the O atoms in H\(_2\)O, and to the N atom in NH\(_3\) are due to hydrogen bonding.

Studies of temperature programmed desorption up to 850K of silica performed by Dinh et al.\(^8\) showed that the physisorbed water can be removed from the silica within 1 hour at 320K. The chemisorbed water in silica cannot be completely removed and the removal temperature is about 500K in a high vacuum condition.

### 1.4 Multicomponent Glass Formation and Surface Chemistry

Glass is a term frequently used to mean the fusion product of inorganic materials, which have been cooled to a rigid condition without crystallizing. There are well-defined properties that characterize glasses from other states of matter (liquids and crystalline solids). For example, glasses lack long-range periodic order of the constituent atoms. Therefore, they more closely resemble liquids and not crystalline solids in their atomic distribution.\(^9\) Unlike crystals, glasses do not have a sharp melting point and do not cleave in preferred directions. Glasses, like liquids, are isotropic, a property that is of immense value in their use for a variety of purposes.\(^10\)

A glass is generally obtained by rapidly cooling a liquid below its freezing point and this has been considered as a part of the definition of the glassy state, although glasses may also be obtained by compressing a liquid or by vapor deposition. The classical explanation for the formation of a glass is that when a liquid is cooled, its fluidity
decreases and, at certain temperature below the freezing point, becomes nearly zero. The liquid becomes rigid. The glassy state has a more phenomenological definition than a generic one: “a glass is a state of matter which maintains the energy, volume and atomic arrangement of a liquid, but for which the changes in energy and volume with temperature and pressure are similar in magnitude to those of a crystalline solid.”

1.4.1 Adsorption Processes

One of the most important properties of a solid surface is adsorption. Adsorption is classified as physisorption if it involves only van der Waals’ forces and chemisorption if an exchange or sharing of electrons also takes place. Both are shown schematically in Figure 1-2, which is relevant to a typical soda-lime-silicate glass.

![Figure 1-2](image.png)

**Figure 1-2.** Formation of water film on glass by adsorption.

The chemisorption of water, commonly termed hydroxylation or hydrolysis, is thought to dominate the surface chemical behavior of pristine silicate glasses. There are a number of sites where chemisorption of water may occur, as shown in Figure 1-3.
These reactions are fundamental because they produce silanol groups, responsible for the physical adsorption and clustering of water.

\[
\equiv \text{Si}^+ + \text{H}_2\text{O} \rightarrow \equiv \text{Si-OH} + \text{H}^+
\]

\[
\equiv \text{Si-O}^- + \text{H}_2\text{O} \rightarrow \equiv \text{Si-OH} + \text{OH}^-
\]

\[
\equiv \text{Si-O-Si} \equiv + \text{H}_2\text{O} \rightarrow 2(\equiv\text{Si-OH})
\]

\[
\equiv \text{Si-OX} + \text{H}_2\text{O} \rightarrow \text{Si-OH} + \text{XOH} \text{ where X = Li, Na, K, Ca, Ba, Pb, etc.}
\]

Figure 1-3. Glass surface sites where reaction with water can occur.\(^9\)

1.5 Multicomponent Glass Structure

The ability of a substance to form a glass does not depend upon a particular chemical or physical property. Any substance, if cooled sufficiently fast, could be obtained in the glassy state.\(^{10}\) Many glass-forming liquids are often, although not without exception, liquids which are very viscous at the melting point; liquids which do not form glasses have much lower viscosities.

1.5.1 Glass-forming Elements

Of all elements in the Periodic Table, only a few in Groups V and VI, such as P, O, S, Se, Te can form a glass on their own.
1.5.2 Glass-forming Oxides

B_2O_3, SiO_2, GeO_2 and P_2O_5 readily form glasses on their own and are commonly known as ‘glass formers’ for they provide the backbone in other mixed-oxide glasses. As_2O_3 and Sb_2O_3 also produce glass when cooled very rapidly. TeO_2, SeO_2, MoO_3, WO_3, Bi_2O_3, Al_2O_3, Ga_2O_3 and V_2O_5 will not form glass on their own, but each will do so when melted with a suitable quantity of a second oxide, so they are also called “conditional glass-formers”.

1.6 Sodium Aluminoborosilicate Glasses

The applications of aluminoborosilicate glasses are various, such as optical components, chemical and heat-resistant containers, the sequestration of radioactive waste, and glass fiber. The structure of this type of glass is complicated because of the uncertain role of aluminum oxide (Al_2O_3). In particular, the extent and nature of mixing of the network-forming cations (Si, B and Al) are still unclear, but have an important role in controlling viscosity, network cation diffusivity, and other properties affected by the configurational entropy. The composition of these glasses, which is formed of silica (SiO_2) and boron oxide (B_2O_3), one network intermediate (Al_2O_3) and some modifiers (such as alkali and alkali earth oxides), make the structure of the glass both complicated and interesting.

The structure of the boron and the aluminum are of great interest in aluminoorosilicate glasses. Boron can be found in either tetrahedral or trigonal coordination with oxygen, comprising BO_4\(^-\) groups (B\(^{IV}\)) and BO_3 groups (B\(^{III}\)), respectively. The trigonal species are further broken down into symmetric and
asymmetric trigonal boron groups.\textsuperscript{18-20} A symmetric trigonal boron group refers to boron that is connected to three bridging oxygens. Otherwise, an asymmetrical trigonal boron group refers to boron that is connected to one or two non-bridging oxygens (NBO). The addition of alkali oxides causes some changes in the coordination of the boron species, from B\textsuperscript{III} to B\textsuperscript{IV}. The addition of more alkali oxides causes a disturbance in the borate structure, called the borate anomaly, which change compositional trends and properties. At the root of this phenomenon is the conversion of B\textsuperscript{III} to B\textsuperscript{IV}, which occurs until a maximum is reached. An increasing formation of NBO asymmetric B\textsuperscript{III} groups is observed with the remaining addition of alkali oxides.\textsuperscript{21-23}

Aluminum is a network forming cation in aluminoborosilicates with alkali or alkaline-earth network modifiers, such as Ca, Sr, Na and K. In sodium aluminoborosilicate glasses, the aluminum is found in two possible coordinations, octahedral and tetrahedral (Al\textsuperscript{VI} and Al\textsuperscript{IV}), respectively. But it is expected that most of the aluminum is present in tetrahedral coordination.

The coordination of aluminum in Al\textsubscript{2}O\textsubscript{3} is octahedral, but the alkali or alkaline-earth oxides addition to aluminum oxide changes the octahedral aluminum coordination to a tetrahedral coordination.\textsuperscript{24, 25} This coordination change occurs in order to balance local charges. Due to the complexity of these systems, it is very difficult to propose a structural model.\textsuperscript{26}

The surfaces of glasses differ from the composition of the bulk, and this is due to the interactions that occur between the surface and the environment, which is of great importance when studying vapor deposition. The ability to absorb molecules in the vapor phase is a characteristic property of solid surfaces. The phenomenon of adsorption results from the solid interacting with the field of force surrounding the adsorbate molecule.\textsuperscript{27}
It is known that in silica the reactive sites are the silanol groups on the surface. The addition of new species to glasses systems alters the reactivity of the glass. It is the main goal of this project to investigate the reactivity of the surfaces of sodium aluminoborosilicate glasses, and how they interact with organic probe molecules.
1.7 References


Chapter 2

Inverse Gas Chromatography

2.1 Introduction

Understanding the adsorption of a polymer coating onto a glass surface requires a thorough knowledge of the reactive sites on the glass surface. The specific bonds that form when multicomponent aluminoborosilicate glasses are dosed with simple organic molecules are of primary importance for determining the potential reactivity of different surface coatings.

Inverse gas chromatography temperature programmed desorption coupled to a flame ionization detector (IGC-TPD-FID) is an analytical technique useful for studying the surface properties of a material by examining the adsorption-desorption behavior of a probe molecule. This technique can be applied to study the surface chemistry of a broad range of samples based on the high sensitivity and stability of the flame ionization detector (FID). Also, IGC enables the distribution of the strength of adsorption sites on the oxide surface to be visualized as peaks in a desorption plot. However, IGC-TPD-FID is unable to identify the surface species reacting with the probe molecule. IGC can be coupled to mass spectrometry to study the identity of the substances that are coming off as a result of the interaction of the probe molecule, which in the work presented here is acetic acid, with a multicomponent glass surface.
2.2 Inverse Gas Chromatography

As more complex chemistries and molecules are utilized for the alteration of glass surfaces, there is an increased need for an understanding of surface phenomena beyond the usual surface area and adsorption isotherm. This interest has led to the introduction of a more sophisticated gas chromatography technique, called Inverse Gas Chromatography (IGC). This technique, widely used for characterization and study of surface properties of many materials was invented in 1967 and its theory and methodology was developed in the beginning of 1976, as a consequence of the increasing interest by researchers in the materials science field.\(^1\)\(^2\) IGC was first developed as a technique for the study of synthetic polymers, but its applications have broadened to different areas such as biological polymers, copolymers, polymer blends, glass fibers, carbon fibers, coal, and solid food. IGC is a powerful technique in the analytical chemistry field because it is convenient and its basic instrumentation is inexpensive, rugged, and widely available.

IGC is an extension (but an inverse sense) of conventional gas chromatography (GC) or Analytical Gas Chromatography (Figure 1-1). The main difference between GC and IGC relies on the fact that in IGC the surface species of interest are introduced as the stationary phases (packing material). In conventional GC, the technique is used to separate and analyze the compounds of an injected gas mixture pulse, while the surface properties of the packed column are known. However, in IGC the injected molecules, called probes, are introduced into the column to investigate their interactions with the solid surface of the packing material. Except for the reversal of roles of the mobile and stationary phases, the theoretical principles and instruments are basically the same both for GC and IGC.\(^3\)
The IGC method provides information on the surface chemistry of a wide range of differing samples based on the very high sensitivity, linearity, and stability of the flame ionization detectors employed in IGC. Especially useful is the ability of IGC to probe and characterize the heterogeneity of adsorption on oxide surfaces. The heterogeneity of oxide surfaces refers to the distribution of both weak and very strong adsorption sites.

![Diagram: Conventional Gas Chromatography and Inverse Gas Chromatography](image)

**Figure 2-1.** Schematic of the differences between Conventional Gas Chromatography and Inverse Gas Chromatography.

### 2.3 Inverse Gas Chromatography Temperature Programmed Desorption

Inverse Gas Chromatography Temperature Programmed Desorption (IGC-TPD) is a technique used to investigate the energetics of adsorption on surfaces. During a typical TPD experiment, a clean surface is exposed to a known concentration or pressure of adsorbate gas, which after adsorption results in an initial coverage. The sample is then heated with a programmed temperature ramp:

\[
T(t) = T_o + \beta \cdot t 
\]

*Equation 2-1*
where $\beta$ is the linear heating rate, $t$ is the time and $T_0$ is the initial temperature. As the temperature increases, the desorption rate will increase until some temperature, $T_{\text{max}}$, where the desorption rate begins decreasing as the remaining adsorbate concentration is depleted.

Also, TPD can be used to investigate adsorption heterogeneity; this can be accomplished by a variation in the adsorbate concentration. For example, at low adsorbate concentration, the adsorbate is expected to occupy the highest-energy adsorption sites. The adsorbate will first enter a weak physisorption minimum and diffuse across the surface before finding a chemisorption minimum. As the surface concentration increases, the adsorbate will fill progressively weaker sites.

Heterogeneous surfaces contain more than one type of adsorption sites. There are two types of adsorption heterogeneity, adsorbate-induced and intrinsic heterogeneity. Adsorbate-induced heterogeneity refers to the coverage-dependent changes in surface potential; this means that on a homogeneous surface, sites neighboring an adsorbed molecule may differ slightly in energy from those sites far from

---

**Figure 2-2.** Experimental set-up for Temperature Programmed Desorption Inverse Gas Chromatography with a Flame Ionization Detector.
other adsorbed species. This adsorbate-induced heterogeneity can lead to islanding or non-uniform coverage, depending on the adsorbate-adsorbate interactions.

On the atomic scale, inorganic surfaces (such as aluminoborosilicate glasses) are expected to be compositionally, structurally, and energetically heterogeneous. This heterogeneity is primarily due to the disorder of the atomic structure and the heterogeneity of bonding environments. Inorganic glasses have a wide range of cation environments, bond-lengths, and bond-angles, which lead to a different local electronic structure, and expectedly different adsorptivity than crystalline structures.

The heterogeneity in the absorbent surface is adsorbate dependent. This means that surfaces can be heterogeneous with respect to one adsorbate, and be homogeneous with respect to a different adsorbate. Oxide surfaces, like the ones on aluminoborosilicate glasses, are generally heterogeneous with respect to more polar molecules such as carbon monoxide, water, or alcohols. These molecules interact through stronger, directional bonds such as hydrogen, ionic, or even covalent bonding. These more polar molecules can be used to discriminate surface sites with different characteristics, based upon the interactions between the probe molecule and the surface site.

2.4 Inverse Gas Chromatography coupled to Mass Spectrometry

Inverse Gas Chromatography is often coupled to other selective techniques such as spectroscopy, more specifically mass spectrometry. These methods offer great advantages for the identification of reaction products associated with dissociative chemisorption, desorption or thermal decomposition.
Figure 2-3. Experimental set-up for Inverse Gas Chromatography coupled to Mass Spectrometer.

Usually, IGC is coupled with detection via a FID because it provides information on the surface chemistry of a wide range of differing samples based on very high sensitivity, linearity, and stability. However, the FID does not provide any information regarding the identity of the desorbed molecules that result from the interaction of probe molecules with oxide surfaces. Coupling IGC with a mass spectrometer as a detector offers better understanding of the species that result from the interactions of probe molecules with target surfaces.
2.5 References


Chapter 3

Studies of the Reactive Surface in Sodium Aluminoborosilicate Glass Systems

3.1 Introduction

Chemical knowledge obtained from single oxide materials is often applied to multicomponent oxides even though it is widely recognized that unique reaction sites exist at the surface of the more complex systems. In this work, the increased complexity of multicomponent surfaces and the resulting implications for polymer binding are being studied through analysis of chemical interactions of acetic acid with sodium aluminoborosilicate glass fibers. Multicomponent complex oxides, especially aluminosilicate glass fibers, are important materials used as reinforcement agents in thermal insulation in buildings and homes.\(^1\) The surfaces of these fibers are functionalized or coated for specific applications.

In this work the interactions of small organic molecules such as acetic acid with multicomponent glass were probed using a combination of inverse gas chromatography coupled with a mass spectrometer (IGC-MS) and inverse gas chromatography in the temperature programmed desorption mode (IGC-TPD). The aim of this project was to investigate the reactive sites on sodium aluminoboroaluminosilicate glass fibers, with the final goal to utilize green alternatives in order to replace the resins and formaldehyde binders that are currently being used in fiberglass production.
3.2 Background

The surfaces of multicomponent glasses are very complex systems and much less information is known about the molecular interactions at the glass surface. It is widely known that for silica, one important set of reactive sites are the silanol groups on the surface, but much less is known about specific reactive sites at multicomponent glass surfaces.

In a previous study by Daniel Suchy, sodium aluminoborosilicate glass was treated using a probe molecule, acetic acid, and was analyzed by solid state nuclear magnetic resonance (NMR). The results of this study demonstrate that the surface of multicomponent glass behaves differently than a model silica surface, in this case Cab-O-Sil®, as demonstrated in Figure 3-1. The principal cause of this behavior is the lack of an equivalent number of reactive silanol groups (for acetic acid adsorption) on the multicomponent glass surface.

Figure 3-1. $^1$H-$^{13}$C CP MAS NMR spectra of $^{13}$C enriched acetic acid dosed onto (A) sodium aluminoborosilicate glass and (B) Cab-O-Sil.$^2$
The NMR spectra in Figure 3-1 show two peaks for Cab-O-Sil® (B) and one peak for the sodium aluminoborosilicate glass (A) after both samples were dosed with $^{13}$C enriched acetic acid. DRIFTS studies combined with NMR of Cab-O-Sil® dosed with acetic acid relate the up-field peak at 178 ppm with physisorbed species and the peak at 172 ppm is from chemisorbed species; studies identify this peak as a silyl ester$^{4,5}$ (Figure 3-2). The same studies indicated that the peak at around 182 ppm for the sodium aluminoborosilicate glass was related to the formation of a carboxylate structure.

![Figure 3-2. Silyl ester.](image)

From the previous NMR and DRIFTS studies, it was determined that sodium plays an important role in the reactivity of the glass surface. In this study, IGC-MS and IGC-TPD coupled to a flame ionization detector (FID) and MS are used to elucidate information regarding the reactive surface sites on sodium aluminoborosilicate glass fibers, analyzing the reaction products of this interaction and learning about absorption energies.

3.3 Experimental Methods

3.3.1 Materials

Analytical columns for IGC experiments consisted of quartz tubing (6.3 mm outer diameter, 4 mm inner diameter, Technical Glass Products) with a length of 23 cm. The quartz tubing was cleaned by immersion in a concentrated sulfuric acid, chromium trioxide
solution (Chromerge, Fisher Scientific) for 24 hours. The tubing was well rinsed with purified water and non-denatured ethanol before it was dried.

Sodium aluminoborosilicate glass fibers were drawn using a custom-built fiber drawing system. Bulk glass marbles (with a commercial glass wool composition, courtesy of Johns-Manville) were melted at 1000 °C in a single tip platinum-rhodium crucible and allowed to equilibrate for 1 hour. The melted glass then passed through a 2 mm i.d. tip and was drawn at 4.6 m/s onto a Teflon cylinder. Fibers were drawn for 15 minutes under standard laboratory conditions (<25% RH and 25 °C) and analyzed immediately or stored under vacuum for future analyses.

The monofilament glass has a nominal diameter of 5µm. Monofilament fibers were packed into the column by tying wax-free dental floss around the center of a 52 cm long monofilament bundle. The strand of floss was then used to pull the fibers through the column ensuring alignment of the fibers along the column dimension. The column was packed as densely as possible to maximize the amount of surface area available for adsorption. On average, 3 g of fibers could be packed within the 23 cm column.

### 3.3.2 IGC-MS

Inverse gas chromatography (IGC) is an analytical technique used for the study of surface properties of a material by examining the retention behavior of a probe molecule. IGC-MS experiments were performed using a standard GC/MS instrument (HP 5890 series II GC equipped with a 5792 mass selective detector). The injector temperature was at 60 °C and the oven temperature was set at 100 °C.

Once the column is loaded in the GC, it is conditioned under UHP helium (10 ml/min) at 200 °C for 30 minutes before any experiment begins. A typical IGC analysis
consisted of an injection of 1µL of acetic acid (HPLC grade, 99% purity) using a Hamilton syringe (7000 series, Hamilton Company, Reno, NV). Before injection the mass selective detector (MSD) is turned on and a time delay of 0.5 minutes precedes the actual injection. The time delay is carried out with the purpose of obtaining a background spectrum for subtraction from the obtained spectrum (see section 3.3.4).

**3.3.3 IGC-TPD**

IGC-TPD experiments were performed using both a FID and a MS detector. Given the fact that the FID is a detector with high sensitivity and stability, it is widely used to study the surface chemistry of a broad range of samples. The FID was fueled by ultra-high purity (UHP) hydrogen and air (Ultra Zero) and was operated at 250 °C. The IGC system was modified to access higher temperatures by installing a home-built 15 cm long resistively heated tube furnace, which was capable of heating just the analytical column to 650°C. The furnace temperature was measured using a K-type thermocouple, which resided alongside the sample column within the tube furnace. To maintain the placement of the thermocouple and to remove temperature gradients in the oven, a home built copper tube insert was used. A programmable controller (Watlow-982) maintained the temperature of the furnace within 2 °C during a 20 °C/min ramp.

IGC-TPD experiments were conducted using a different sample preparation, but the column conditioning remained the same. Monofilaments were packed into the column by tying wax-free dental floss around the center of a 52 cm long monofilament bundle. The strand of floss was then used to pull the fibers through the column ensuring alignment of the fibers along the column dimension, but the fibers were centered in the column at about 12 cm (Figure 3-3), to have exactly the same length as the tube furnace.
Figure 3-3. Sample preparation for an IGC-TPD experiment.

Once the column is loaded in the GC, it is conditioned under UHP helium (10ml/min) at 200 °C for 30 minutes before the experiment begins. A typical IGC-TPD analysis consisted of an injection of 1µL of acetic acid (HPLC grade, 99% purity) using a Hamilton syringe (7000 series, Hamilton Company, Reno, NV). For this type of experiment, the injection of the probe molecule is followed by a 3-minute dwell at 100 °C while the excess probe molecules elute. The sample was then heated using the tube furnace at 20 °C/min to 600 °C where it was held for 10 minutes before returning to 100 °C.

3.3.4 Processing of Spectra

An IGC chromatogram consists of separate points, each point containing the entire MS spectrum. The MS spectra were scanned in the interval of m/z values from 10-70 a.u. (The maximal value of m/z cannot exceed the molecular weight of the probe molecule (acetic acid) which is 60.05 g/mol.)

There are two standard procedures the MS software allows one to carry out with those spectra. One is background subtraction: The background spectrum was recorded during the first 0.5 min before injection of acetic acid. It was subtracted from all the target
spectra. The other procedure is averaging. This procedure allows one to average spectra in a predetermined area. Circles in the figures presented in this work indicate such areas. If one believes that the spectra from separate points in the chromatogram are basically identical, one can considerably increase the signal to noise ratio by using the averaging procedure.

3.3.4.1 Pure Acetic Acid Subtraction

Another subtraction procedure used in this work is subtraction of the pure acetic acid spectrum from a target spectrum. The goal of this subtraction is to discover the reaction products, which may appear due to interaction of acetic acid with the glass surface. The pure acetic acid subtraction is performed using a special Microsoft Excel module developed for this work. First, the mass spectrum of pure acetic acid is obtained, the three lines with highest abundance in this spectrum are selected, and then the same three lines are searched for in the target spectrum. A ratio of abundance for each of the three lines in the target and pure acetic acid spectra is made and an average is calculated. Then, all the lines in the pure acetic acid spectra are multiplied by that averaged ratio and subtracted from the target spectrum. The resulting spectrum is called the subtracted spectrum.

3.3.4.2 Extracted Ions Chromatogram

The MS software allows one to select from the total ion current (TIC) plot (which corresponds to all m/z values in the scan interval), the plot corresponding to the current from a separate ion (m/z value) or the group of m/z values corresponding to various
fragments of a molecule. In IGC-MS experiments we selected ions with m/z values of 17 and 18 for water, m/z values of 12, 16, 28 and 44 for carbon dioxide and m/z values of 12, 13, 14, 15, 16, 17, 19, 24, 25, 26, 28, 29, 31, 40, 41, 42, 43, 45, 46, 60 and 61 for acetic acid. When $^{13}$C enriched acetic acid was used as the probe molecule the selected ions were 12, 13, 14, 15, 16, 17, 28, 29, 30, 31, 41, 42, 43, 44, 46, and 61. For IGC-TPD-MS experiments the selected m/z values were 17 and 18 for water, m/z values of 12, 13, 14, 15, 16, 21, 24, 25, 26, 28, 29, 40, 41, 42 and 43 for non-enriched ethenone, m/z values of 13, 14, 15, 16, 17, 22, 25, 26, 27, 29, 30, 41, 42, 43, 44 and 45 for $^{13}$C enriched ethenone, m/z values of 12, 16, 28 and 44 for non-enriched carbon dioxide and m/z values of 13, 17, 29 and 45 for $^{13}$C enriched carbon dioxide. The selected ions for each species correspond to the lines that appear in the spectra of the pure species.

3.3.5 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) analyses were performed on an instrument with a monochromatic Al K$\alpha$ source (Kratos, Axis Ultra, England). Spectra were collected with a photoelectron take off angle of 90° and 40 eV pass energy. All spectra were referenced to the C 1s binding energy at 285.0 eV.

3.3.6 Acid Leaching Procedure

A pH=3 solution was made from proper dilution of 18 M H$_2$SO$_4$. Fibers were immersed in 1 L solution at 50 °C for 60 s. Then, the fibers were rinsed with 500 mL of de-ionized water at 50 °C. Excess water was removed by blotting the fibers with lint free tissue and placement of the blotted fibers in a vacuum oven at 125 °C for 1 hour.
3.4 Results and Discussions

3.4.1 Sodium Aluminoborosilicate Glass Studies by IGC-MS

The multicomponent monofilament glass studied in this work has both alkali and alkali-earth content, as shown in Table 3-1. The amount of sodium present near the surface, which is significantly greater than the amount of other alkali elements, is capable of participating in carboxylate complex formation. This suggests that when the multicomponent monofilament glass is dosed with acetic acid, the lack of reactive silanol groups makes the basic sites in the glass surface the primary site for interactions. This observation is supported by a previous study\(^3\), which found that the interaction of acetic acid with the multicomponent glass mainly occurs at basic sites producing sodium carboxylate.

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Ca</th>
<th>Mg</th>
<th>K</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8.2</td>
<td>2.3</td>
<td>0.8</td>
<td>0.3</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 3-1. Surface Composition (At%) by XPS of sodium aluminoborosilicate glass.

A previous study\(^6\) performed by Rob Schaut in Dr. Pantano’s group demonstrated that sodium aluminoborosilicate glasses have carbonate on their surfaces. The fact that the acetic acid is reacting with basic sites in the fiber and also the presence of carbonate on the fiber can lead us to hypothesize different reactions that can be taking place at the glass surface (Figure 3-4):
Figure 3-4. Different reactions from the interaction of acetic acid with basic sites on the surface of sodium aluminoborosilicate glass fibers.

The proposed reactions in Figure 3-4 suggests that: A) the acetic acid interacts with the chemisorbed Na that is in the glass, producing sodium carboxylate; B) the acetic acid interacts with the sodium carbonate that is in the glass surface producing sodium carboxylate, carbon dioxide and water. IGC-MS and IGC-TPD-MS can be used to test these hypotheses by analyzing the eluting species of the interaction.

The IGC chromatogram of sodium aluminoborosilicate glass dosed with acetic acid at 100 °C shows two shoulders at the beginning of elution and then a strong peak (Figure 3-5). The mass spectrum shows that the first shoulder is primarily composed of species with m/z of 12, 16, 22, 28 and 44 as shown in Figure 3-5. The mass spectrum for the first shoulder looks very similar to the mass spectrum of carbon dioxide (Figure 3-6), which demonstrates that at the beginning of the reaction the main eluting species is carbon dioxide. This spectrum belongs to carbon dioxide, which is coming from the interaction of acetic acid with some species in the glass.
**Figure 3-5.** IGC chromatogram of sodium aluminoborosilicate glass dosed with acetic acid at 100°C. The mass spectrum in the box corresponds to the area marked with the circle.

**Figure 3-6.** Mass spectrum of carbon dioxide.7

**Figure 3-7.** Background spectrum.
The second shoulder in the IGC-MS for the sodium aluminoborosilicate glass dosed with acetic acid shows species with m/z of 12, 15, 16, 17, 18, 22, 28 and 44 as depicted in Figure 3-8. The species with m/z 17 and 18 correspond to water, whose spectrum is shown in Figure 3-9, and m/z 44 belongs again to carbon dioxide. The second shoulder contains water and carbon dioxide, but carbon dioxide has a higher abundance than water, and higher than the abundance of carbon dioxide in the first shoulder. The water elutes later in the profile because it interacts more strongly with the glass surface than does the carbon dioxide.

Figure 3-8. IGC-MS of sodium aluminoborosilicate glass dosed with acetic acid at 100 °C. The mass spectrum in the box corresponds to the area marked with the circle.

Figure 3-9. Mass spectrum of water.
The major peak of the chromatogram at around 1.5 minutes (Figure 3-10) has a complicated mass spectrum with high abundance for the m/z of 43, 45 and 60. The probe molecule is acetic acid with molecular weight of 60 g/mol. The mass spectrum for pure acetic acid (Figure 3-11) is acquired by the injection of acid in an empty column. This spectrum looks very similar to the spectrum obtained at the higher abundance peak of the sodium aluminoborosilicate glass dosed with acetic acid. This observation suggests that what is obtained at the major peak is mostly the elution of acetic acid. Carbon dioxide and water were detected in the subtracted spectrum, as shown in Figure 3-12, but the abundances are low in comparison with the content in the shoulders.

Figure 3-10. IGC-MS of sodium aluminoborosilicate glass dosed with acetic acid at 100 °C. The mass spectrum in the box corresponds to the area marked with the circle.
Figure 3-11. IGC chromatogram of pure acetic acid at 100 °C. The mass spectrum in the box corresponds to the area marked with the circle.

Figure 3-12. Subtracted mass spectrum corresponds to the area marked with the circle in Figure 3-10.

Figure 3-13 shows the profile obtained using the extracted ion method (described in section 3.3.4.2) for the injection of acetic acid to sodium aluminoborosilicate glass. This profile shows that carbon dioxide appears mostly in the shoulders and the water appears
in the second shoulder. Also, this plot shows that what elutes at the highest abundance peak is acetic acid.

![Figure 3-13](image)

**Figure 3-13.** Extracted ion method applied to IGC chromatogram of sodium aluminoborosilicate glass dosed with acetic acid at 100 °C.

### 3.4.2 Sodium Aluminoborosilicate Glass Studies by IGC-MS: $^{13}$C Enriched

**Acetic Acid as Probe Molecule**

The results from sodium aluminoborosilicate glass dosed with acetic acid showed that carbon dioxide and water are eluting together with acetic acid at 100 °C. Even when carbon dioxide and water are obtained as a product in the proposed reaction B in the scheme in Figure 3-4, some additional portion of carbon dioxide could form from acetic acid decomposition. To confirm the mechanism of carbon dioxide formation, $^{13}$C enriched acetic acid was used as a probe molecule. If the carbon dioxide is coming from the acid itself, carbon dioxide will have a m/z of 45, instead of 44.
The mass spectrum for the injection of $^{13}$C enriched acetic acid to sodium aluminoborosilicate glass (Figure 3-15) shows the elution of carbon dioxide with m/z of 44 and water with m/z of 18. Point C has been obtained by subtraction of the pure $^{13}$C enriched acetic acid spectrum shown in Figure 3-14. The data shown in Figure 3-15 shows that the carbon dioxide is not coming from the acetic acid because no signal at m/z of 45 was observed. Instead, the carbon dioxide was formed from the carbonate species on the surface.

![Mass spectrum of $^{13}$C enriched acetic acid.](image)

**Figure 3-14.** Mass spectrum of $^{13}$C enriched acetic acid.
3.4.3 Leaching Experiments

The surface composition of the glass suggests that the amount of sodium present in the surface is significantly greater than the amount of other elements that are capable of participating in carboxylate complex formation (as shown in Table 3-1). Also, cations with a charge greater than +1 are known to form bonds to acetate with various conformations, which result in different chemical shifts and therefore multiple peaks \(^8,9,10\) which is not observed in the recent NMR studies\(^1\). This observation leads to the hypothesis that if the amount of sodium is reduced from the surface, then less sodium carbonate is on the surface and a decreased amount of carbon dioxide should be formed.

To further test this idea, leaching experiments at low pH were performed on fresh sodium aluminoborosilicate glass. XPS data were obtained on both the fresh sodium
aluminoborosilicate glass and leached sodium aluminoborosilicate glass in order to compare any changes in the surface composition. XPS experiments were performed in collaboration with Joy Banerjee from the Dr. Pantano Group at the Materials Research Institute at Penn State. Leaching removes more than half of the surface sodium and carbonate content compared to what was present in the fresh sodium aluminoborosilicate glass (Table 3-2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>O</th>
<th>Na</th>
<th>Ca</th>
<th>Mg</th>
<th>K</th>
<th>C</th>
<th>B</th>
<th>Si</th>
<th>Al</th>
<th>CO$_3^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh pulled</td>
<td>48.4</td>
<td>8.2</td>
<td>2.3</td>
<td>0.8</td>
<td>0.3</td>
<td>18.6</td>
<td>4.5</td>
<td>15.3</td>
<td>1.9</td>
<td>2.8</td>
</tr>
<tr>
<td>Leached</td>
<td>41.9</td>
<td>3.5</td>
<td>2.1</td>
<td>0.5</td>
<td>-</td>
<td>34.4</td>
<td>-</td>
<td>16.6</td>
<td>2.1</td>
<td>1.1</td>
</tr>
</tbody>
</table>

*Table 3-2.* Surface Composition (At%) by XPS of fresh sodium aluminoborosilicate glass and leached sodium aluminoborosilicate glass.

An IGC-MS experiment was performed on leached sodium aluminoborosilicate glass dosed with acetic acid, and the chromatogram is shown in Figure 3-16. The chromatogram looks very similar to the pure acetic acid chromatogram (Figure 3-11) and very different from the interaction of acetic acid with fresh sodium aluminoborosilicate glass (Figure 3-5). The fact that the chromatogram for the leached sodium aluminoborosilicate glass looks similar to the spectrum of the pure acetic acid suggests that there is no specific interaction taking place between the acid and the leached glass, because the chromatogram of acetic acid is the elution of the acid in an empty column. The leached sodium aluminoborosilicate glass spectrum (Figure 3-16) does not have the two shoulders at the beginning of elution that were seen in the chromatogram of interaction of acetic acid with fresh sodium aluminoborosilicate glass (Figure 3-5). The
leached sodium aluminoborosilicate glass spectrum (Figure 3-16) demonstrates a very small shoulder at approximately 1 min. The difference in shape between the fresh sodium aluminoborosilicate glass and the leached sodium aluminoborosilicate glass suggest that the two glasses interact differently with the acid.

Figure 3-16. IGC chromatogram of leached sodium aluminoborosilicate glass dosed with acetic acid at 100 °C.

A comparison between fresh sodium aluminoborosilicate glass and leached sodium aluminoborosilicate glass after both were dosed with acetic acid is shown in Figure 3-17. Traces I, II and III of Figure 3-17 show the mass spectra of the circled areas from the different chromatograms. In general, carbon dioxide and water are obtained from both type of glasses but the leached sodium aluminoborosilicate glass shows considerably less (about 3 times less) carbon dioxide and water than the fresh sodium aluminoborosilicate glass. These results are related with the amount of sodium carbonate that is present at the surface of the fiber. Because the leached fiber has less sodium on it and therefore less formation of sodium carbonate in the surface, the acid does not have enough sodium carbonate sites to interact with and most of the acid elutes. This observation would explain
the similarity in shape between the pure acetic acid chromatogram and the leached sodium aluminoborosilicate glass, as well the difference between fresh and leached sodium aluminoborosilicate glasses dosed with acetic acid.
Figure 3-17. IGC-MS spectra of (A) leached sodium aluminoborosilicate glass and (B) fresh sodium aluminoborosilicate glass dosed with acetic acid at 100 °C.
Figure 3-18. Extracted ion method applied to IGC chromatogram of leached sodium aluminoborosilicate glass dosed with acetic acid at 100 °C.

Figure 3-18 shows the profile obtained using the extracted ion method after the injection of acetic acid to leached sodium aluminoborosilicate glass. This profile demonstrates that carbon dioxide appears at the small shoulder at one minute. The ion representative of water appears later in the chromatogram but with a very low abundance. Also, carbon dioxide and water have a very low abundance during the progress of the experiment and mostly molecules that are eluting under these conditions are acetic acid.

3.4.4 Deconvolution of Previous NMR Studies

IGC results demonstrate that the acetic acid is interacting with sodium carbonates producing carbon dioxide and water, but is difficult to confirm if acetic acid is also interacting with the sodium that is in the glass. Recent NMR studies\(^2\) demonstrate that when sodium aluminoborosilicate glass is dosed with acetic acid a different chemical shift is observed than when sodium carbonate is dosed with acetic acid, as shown in plot I of
Figure 3-19. The conclusions of this NMR study\textsuperscript{2} were that acetic acid interacts with sodium aluminoborosilicate glass differently than it does with sodium carbonates, producing carboxylate with sodium as a sorbed carboxylate species. In the same study\textsuperscript{2} it was inferred that acetic acid is just interacting with the sodium that is in the glass, because of the difference in chemical shifts. But, if a closer look is given to the NMR spectra in plot II of Figure 3-19 it can be seen that a small shoulder appears at the same chemical shift for the interaction of acetic acid with sodium carbonate.

\textbf{Figure 3-19.}\ I) \textsuperscript{1}H-\textsuperscript{13}C CP MAS NMR spectra of \textsuperscript{13}C enriched acetic acid dosed onto (A) freshly pulled sodium aluminoborosilicate glass and (B) sodium carbonate\textsuperscript{2}, II) \textsuperscript{1}H-\textsuperscript{13}C CP MAS NMR spectra of \textsuperscript{13}C enriched acetic acid dosed onto sodium aluminoborosilicate glass.

If a deconvolution is performed in the \textsuperscript{1}H-\textsuperscript{13}C CP MAS NMR spectra of \textsuperscript{13}C enriched acetic acid dosed onto sodium aluminoborosilicate glass (Figure 3-20), two peaks can be resolved. The peak with the higher intensity has a chemical shift of 179 ppm, and the low intensity peak has a chemical shift of 181 ppm. If the \textsuperscript{1}H-\textsuperscript{13}C CP MAS NMR spectrum of \textsuperscript{13}C enriched acetic acid dosed onto sodium carbonate is compared with the deconvoluted
spectra (Figure 3-21), it can be observed that the peak at 181 ppm corresponds to the interaction of the acetic acid with sodium carbonate near the surface. The peak at 179 ppm is due to the interaction of the acetic acid with the sodium in the glass, as proposed in previous NMR studies.\textsuperscript{2} The deconvoluted spectra (Figure 3-20) demonstrate that the majority of the binding is happening with the sodium that is in the glass rather than in the sodium carbonate in the surface, with a ratio of 0.56:0.44.

![Deconvoluted \textsuperscript{1}H-\textsuperscript{13}C CP MAS NMR spectra of \textsuperscript{13}C enriched acetic acid dosed onto sodium aluminoborosilicate glass.](figure3-20.png)
**3.4.5 Temperature Programmed Desorption Studies of Sodium Aluminoborosilicate Glass**

IGC-TPD-MS can also confirm the formation of sodium carboxylate. If the glasses are exposed to a temperature programmed desorption regime, the decomposition of carboxylate species should be observed at higher temperatures. Studies have shown that sodium carboxylate species start decomposing at higher temperatures, around 450 °C, with carbon dioxide and etheneone being decomposition products. If sodium carbonate is present in the fiber surface, its decomposition occurs at higher temperatures as well, around 400 °C, producing sodium oxide and carbon dioxide as shown in Figure 3-22.
Before performing IGC-TPD-MS experiments, an IGC-TPD-FID is collected to verify the elution profiles at different temperatures, from 100 °C to 600 °C. Figure 3-23 shows the complete profile for IGC-TPD-FID and the IGC-TPD-MS spectra from the injection of acetic acid onto sodium aluminoborosilicate glass. The sharp peak represents the products of the interaction of acetic acid with the glass at 100 °C, which were carbon dioxide and water at the beginning of the peak and the highest abundance peak represent the excess of acetic acid.

If a closer look is given to the portion at constant temperature (100 °C) in Figure 3-23, the plot of Figure 3-24 A is obtained. This plot shows IGC-TPD-FID and the IGC-TPD-
MS chromatograms of the injection of acetic acid onto sodium aluminoborosilicate glass at a constant temperature of 100 °C, and it can be seen that the IGC-MS spectrum is similar to the chromatogram in Figure 3-5. The injection of acetic acid is done at 0.5 minutes with the purpose of being able to make background subtraction. The temperature is held constant for 3.5 minutes (plot A) and then the temperature is ramped as shown in plot B of Figure 3-24. The signals from the respective detectors are decreased in plot B of Figure 3-24 with the purpose of providing a more clear understanding of the desorption plots. The shape of peaks in the two chromatograms in plot B is different, as well as the scales because the detectors in both techniques have different sensitivities. The FID is sensitive to carbon-containing species and the MS is sensitive to all ions.

Figure 3-24. IGC-TPD-FID and IGC-TPD-MS profiles of sodium aluminoborosilicate glass dosed with acetic acid at (A) constant temperature of 100 °C and (B) temperature programmed desorption plot from 100-600 °C.

If a mass spectrum analysis (Figure 3-26) is performed on each of the four peaks selected in Figure 3-25, it can be seen that peaks A and B in Figure 3-25 are mostly due to the elution of acetic acid because their spectra are very similar to the spectrum of pure acetic acid (Figure 3-11). Based on the difference in temperature, it can be inferred that
peak A, which appears at lower temperature (around 150 °C) is due to physisorbed acetic acid. Peak B appears at higher temperatures (around 340 °C), and this peak can be attributed to strongly physisorbed acetic acid. The mass spectrum of peak C also shows the elution of acetic acid but an ion with m/z of 42 has a higher abundance. This ion is associated with ethenone, which has a mass of 42 g/mol, and is a product of decomposition of carboxylate species. Peak D is strong in the MS spectrum but low in the FID. The mass spectrum for this peak shows that water is the predominant species. The FID is not sensitive to water, which explains the low intensity in the IGC-TPD-FID spectrum. Due to the high temperature at which water appears and the intensity of this peak, it can be attributed to the condensation of silanol groups, which start to condense at temperatures above 400°C\textsuperscript{13}. Also, these glasses have a lot of water in their surface that will not elute at lower temperatures.

If a subtraction of acetic acid is performed (see section 3.3.4) in peaks A, B and C (Figure 3-27) it is determined that peak A shows the elution of water and carbon dioxide, but the abundances are low (around 600 units). The instrument noise is about 500 units, so this spectrum can be considered as instrumental noise. This observation leads to the conclusion that peak A arises only from the elution of physisorbed acetic acid.

The subtracted spectrum of peak B shows the presence of carbon dioxide and water, with abundances higher than the instrumental noise (about three times higher). The temperature at which this peak appears, 370 °C, is close to the sodium carbonate decomposition temperature of 400 °C. Peak B is due to acetic acid that is more strongly absorbed, possibly from strongly physisorbed acetic acid and the decomposition of carbonates in the glass surface.

The subtracted spectrum of peak C shows the presence of ethenone, carbon dioxide and water. This observation leads to the conclusion that peak C is due to the
decomposition of both carboxylate species and carbonates. To further test this idea, $^{13}\text{C}$ enriched acetic acid was used as a probe molecule (see section 3.4.5.1).

**Figure 3-25.** Peaks of interest from IGC-TPD-MS profile of sodium aluminoborosilicate glass dosed with acetic acid.

**Figure 3-26.** Mass spectra of peaks of interest from Figure 3-25.

**Figure 3-27.** Subtracted mass spectra of peaks of interest from Figure 3-25.
Figure 3-28 shows the profile obtained using the extracted ion method for the IGC-TPD-MS after the injection of acetic acid to sodium aluminoborosilicate glass. This profile shows an increase of ethenone and carbon dioxide at around 470 °C. This is due to the decomposition of carboxylate and carbonates. At lower temperature no significant increase is observed in any ions with the exception of acetic acid: physisorbed acetic acid at lower temperatures and strongly physisorbed acetic acid at higher temperatures. At 600°C water is the only species eluting due to silanol condensation as well as chemisorbed water being released from the glass.

![Graph](image)

**Figure 3-28.** Extracted ion method applied to IGC-TPD-MS of sodium aluminoborosilicate glass dosed with acetic acid.
3.4.5.1 Temperature Programmed Desorption Studies of Sodium Aluminoborosilicate Glass: $^{13}$C Enriched Acetic Acid

To further test the idea that sodium carboxylate species and carbonates are decomposing at higher temperatures, the IGC-TPD-MS experiment was performed after dosing sodium aluminoborosilicate glass with $^{13}$C enriched acetic acid, shown in Figure 3-29. Using this probe molecule, the carbon dioxide that is produced from the decomposition of sodium carboxylate should have an m/z of 45 because it will be $^{13}$C labeled, as well as the ethenone with an m/z of 43. Similarly to the IGC-TPD-MS spectrum of sodium aluminoborosilicate glass dosed with non-enriched acetic acid, the IGC-TPD-MS spectrum of glass dosed with $^{13}$C enriched acetic acid has four peaks. A mass spectrum analysis (Figure 3-31) is performed on each of the four peaks selected in Figure 3-30.

The mass spectra of peaks A and B (Figure 3-31) show the elution of $^{13}$C enriched acetic acid (Figure 3-14). The mass spectrum of peak C shows a considerably increase in the line for the ion with m/z of 43, but also enriched acetic acid is observed. Peak D is due to the elution of water. To make more concrete conclusions about the precedence of ions in each spectrum, a subtraction of the spectrum from pure $^{13}$C enriched acetic acid was performed.

Figure 3-32 shows the subtracted spectra of peaks A, B and C. Peak A shows mostly water, but the abundance scale is considerably low, which suggests that the obtained spectrum belongs to instrumental noise. This observation leads to the conclusion that peak A at around 170 °C is due to physisorbed acetic acid onto the glass.

The subtracted spectrum of peak B shows the presence of ions with m/z of 45, 44 and 18, but the abundance scale is close to the instrumental noise range (500 units), which suggests that the obtained spectrum is mostly produced from instrumental noise.
Peak B is obtained from acetic acid that is strongly adsorbed (possibly physisorbed on strong adsorption sites) to the glass based on the higher desorption temperature, around 370°C.

The subtracted spectrum of peak C shows the presence of ions with m/z of 43 (higher abundance), 44, 45, and 18. Ethenone that is $^{13}$C enriched has a mass of 43 g/mol. The line with m/z of 43 is therefore due to the decomposition of carboxylate that is enriched. Carbon dioxide can be produced from the decomposition of carboxylate as well as decomposition of carbonate. The line with m/z 44 is due to carbon dioxide that is the product of carbonate decomposition. Otherwise, the line with m/z of 45 is due to carbon dioxide eluting from carboxylate decomposition. Peak C is due to the decomposition of carboxylate and carbonate species in the glass.

**Figure 3-29.** IGC-TPD-FID and IGC-TPD-MS profiles of sodium aluminoborosilicate glass dosed with $^{13}$C acetic acid.

**Figure 3-30.** Peaks of interest from IGC-TPD-MS profile of sodium aluminoborosilicate glass dosed with $^{13}$C acetic acid.
Figure 3-31. Mass spectra of peaks of interest in Figure 3-30.

Figure 3-32. Subtracted mass spectra of peaks of interest from Figure 3-30.

Figure 3-33 shows the profile obtained using the extracted ion method for the IGC-TPD-MS after the injection of $^{13}$C enriched acetic acid to sodium aluminoborosilicate glass. This profile shows an increase of ethenone and carbon dioxide (enriched and non-enriched) at around 470 °C. This is due to the decomposition of carboxylate and carbonates. At lower temperatures an increase in the $^{13}$C enriched ethenone is observed, but after subtraction that ion was not obtained which means that at lower temperatures, ethenone is eluting from the acid itself. At 600 °C water is the only species eluting due to silanol condensation as well as chemisorbed water in the glass.
Figure 3-33. Extracted ion method applied to IGC-TPD-MS of sodium aluminoborosilicate glass dosed with $^{13}$C enriched acetic acid.

3.4.6 Temperature Programmed Desorption Studies of Leached Sodium Aluminoborosilicate Glass

As shown in previous XPS data (Table 3-2), leaching removes more than half of the surface sodium and carbonate content compared to the amount present in the fresh pulled sodium aluminoborosilicate glass. A comparison between IGC-TPD-FID (Figure 3-34) of fresh and leached sodium aluminoborosilicate glass dosed with acetic acid shows that the leached chromatogram has a lower abundance profile. Also, the peak at around 470 °C, is different in the leached glass, and later in this chapter the species that form this peak in the leached fiber will be examined. Similarly, the comparison of IGC-TPD-MS (Figure 3-35) for fresh and leached sodium aluminoborosilicate glass shows that the leached glass has less signal than the fresh glass. The identity of each peak will be examined in the following sections.
If a mass spectrum analysis (Figure 3-38) is performed on each of the four peaks selected in Figure 3-37, it can be seen that peaks A, B and C are due mostly to the elution of water and acetic acid. Peak D shows the elution of water due to the condensation of...
silanol groups as well as elution of chemisorbed water, as seen before with the fresh sodium aluminoborosilicate glass.

If a subtraction of acetic acid is performed in peaks A, B and C (Figure 3-39) it was found that peaks A and B are due to the elution of water. This observation leads to the conclusion, as observed with fresh glass, that peak A is due to physisorbed acetic acid and peak B is due to acetic acid that is strongly physisorbed onto the glass surface.

The subtracted spectrum of peak C shows the presence of ethenone, carbon dioxide and water. Less ethenone and carbon dioxide are obtained in comparison with the subtracted spectrum for the same temperature peak for the fresh glass (Figure 3-27). As concluded for the fresh glass, peak C is obtained due to decomposition of carboxylate as well as carbonate. This conclusion agrees with the reduction of sodium in the glass surface, leading to a decrease in the production of ethenone and carbon dioxide. \(^{13}\)C enriched acetic acid will be used to corroborate the presence of carbon dioxide from carbonate species in the leached glass, because carbon dioxide is a product of decomposition of carboxylate species as well.
Figure 3-36. IGC-TPD-FID and IGC-TPD-MS profiles of leached sodium aluminoborosilicate glass dosed with acetic acid.

Figure 3-37. Peaks of interest from IGC-TPD-MS profile of leached sodium aluminoborosilicate glass dosed with acetic acid.

Figure 3-38. Mass spectra of peaks of interest in Figure 3-37.

Figure 3-39. Subtracted mass spectra of peaks of interest from Figure 3-37.

Figure 3-40 shows the profile obtained using the extracted ion method for the IGC-TPD-MS of the injection of acetic acid to leached sodium aluminoborosilicate glass. This profile shows an increasing amount of ethenone and carbon dioxide at around 440 °C. This increase is due to the decomposition of carboxylate and carbonates. At 600 °C water is the only species eluting due to silanol condensation as well as chemisorbed water in the
glass. Also, the profile for the elution of water for the leached glass is different from the fresh glass because the former has more water in its surface due to the leaching procedure. During this procedure, the glass is exposed to water.

![Graph showing Temperature Programmed Desorption Studies of Leached Sodium Aluminoborosilicate Glass](image)

**Figure 3-40.** Extracted ion method applied to IGC-TPD-MS of leached sodium aluminoborosilicate glass dosed with acetic acid.

### 3.4.6.1 Temperature Programmed Desorption Studies of Leached Sodium Aluminoborosilicate Glass: $^{13}$C Enriched Acetic Acid

To further test the idea of formation of carboxylate and verify whether carbonates are present in the leached glass and decomposition is seen at higher temperatures, an IGC-TPD-MS experiment was performed dosing leached sodium aluminoborosilicate glass with $^{13}$C enriched acetic acid, shown in Figure 3-41.

A mass spectrum analysis (Figure 3-43) is performed on each of the four peaks selected in Figure 3-42. As shown in Figure 3-43, peaks A, B and C are due mostly to the elution of water and acetic acid, but a higher abundance of water is seen in peaks B and
the same behavior was observed in the leached fiber dosed with non-enriched acetic acid. As in previous spectra for fresh glass, peak D shows the elution of water due to silanol group condensation and chemisorbed water.

If a subtraction of $^{13}$C enriched acetic acid is performed in peaks A, B and C (Figure 3-44) it was observed that peaks A and B are due to the elution of water. The subtracted spectrum of peak C shows ions with m/z of 18 (stronger), 42, 43 and 45. Based on the ions present in this spectrum, water, $^{13}$C enriched ethenone and $^{13}$C enriched carbon dioxide, are the species eluting at this temperature. No carbon dioxide with m/z of 44 is eluting within this temperature from the leached glass, which suggests that no carbonates are present in this glass.

**Figure 3-41.** IGC-TPD-FID and IGC-TPD-MS profiles of leached sodium aluminoborosilicate glass dosed with $^{13}$C enriched acetic acid.

**Figure 3-42.** Peaks of interest from IGC-TPD-MS profile of leached sodium aluminoborosilicate glass dosed with $^{13}$C enriched acetic acid.
Figure 3-43. Mass spectra of peaks of interest of Figure 3-42.

Figure 3-44. Subtracted mass spectra of peaks of interest from Figure 3-42.

Figure 3-45 shows the profile obtained using the extracted ion method for the IGC-TPD-MS of the injection of $^{13}$C enriched acetic acid to leached sodium aluminoborosilicate glass. This profile shows an increasing amount of enriched and non-enriched ethenone and enriched carbon dioxide at around 450 °C. This increase is due to the decomposition of carboxylate. Even when enriched acetic acid was used in this experiment, this probe molecule is not completely enriched producing ethenone that is not enriched. The elution of water is observed during the duration of the experiment but an increased amount is observed at higher temperatures (600 °C).
Figure 3-45. Extracted ion method applied to IGC-TPD-MS of leached sodium aluminoborosilicate glass dosed with $^{13}$C enriched acetic acid.
3.5 Summary

Previous studies have shown that silanol groups play an important role in the reactive surface of silica, but not much information is known about the reactive surface of multicomponent glasses. In this study it was demonstrated that sodium-containing species, and especially sodium carbonates, play an important role in determining the reactivity of sodium aluminoborosilicate glasses. It was demonstrated that when sodium aluminoborosilicate glasses are dosed with acetic acid, the main sites of interaction are the sodium carbonates in the glass surface and the sodium present in the glass. These conclusions were made using NMR data and IGC-MS as well as temperature programmed desorption experiments. Using temperature programmed desorption experiments, it was demonstrated that the acetic acid is absorbed into the glass surface as both weak and strongly physisorbed species. Also, carboxylate formation was observed and leaching experiments demonstrate that the amount of sodium in the glass is reduced after quick exposure to acid, producing less carboxylate formation. This work demonstrated that in sodium aluminoborosilicate glasses, the sodium in the glass and sodium carbonates in the surfaces could be the interface between the glass surface and possible coatings used for surface protection.
3.6 References


7. www.nist.gov


Chapter 4
Conclusions and Future Directions

4.1 Conclusions

IGC-MS and IGC-TPD-MS were used to understand the interaction of acetic acid with sodium aluminoborosilicate glass surfaces. XPS data demonstrate that the surfaces have a high sodium content and presence of carbonate at the surface. Sodium in the glass and sodium carbonate on the surface were proposed as possible reactive sites for acetic acid introduced to the surfaces. The IGC-MS experiment shows the formation of carbon dioxide and water as a result of the interaction of acetic acid with a multicomponent glass. At lower temperatures (100 °C), use of $^{13}$C-labelling proved that the carbon dioxide was arising as a product of direct reaction of the acetic acid with sodium carbonate on the surface. Leaching experiments are shown to decrease the sodium and carbonate content in the glass surface giving as a result a decrease in the formation of carbon dioxide as shown in the IGC-MS spectra.

IGC-TPD-MS experiments show that acetic acid interacts with the glass surface as a weak and strong physisorbed species. Also, IGC-TPD-MS shows that at higher temperatures the decomposition of sodium carbonate and carboxylate species are both observed. Presumably, then, even as the acetic acid is interacting with the sodium carbonate as observed in IGC-MS studies, further bonding of acetate moieties to sodium from the glass surface is indicated. While previous NMR studies concluded that the sodium in the glass is the primary source of interaction of carboxylic acid with the glass, a careful re-interpretation of the NMR data was performed here. Coupling the NMR
studies with the results of this work, it was found that both sodium in the glass and the sodium carbonates near the surface can be the sites of interaction, and the ratio of sites under the dosing conditions used previously was 0.56:0.44, with the majority of binding to the sodium in the glass surface sites.

4.2 Future Directions

Multicomponent glass fibers are very complex systems and the discoveries presented in this work serve as a piece of information that can aid in the study of the broad topic of oxide surface reactivity. Performing long term aging experiments to study the formation of more carbonates on the surface and their impact on glass surface reactivity, and coupling NMR and IGC in aging experiments will lead to even more valuable information on surface reactivity. Also, studies of more extreme leaching experiments in which the sodium is removed completely from the surface, or the use of sodium free glasses, should be conducted in order to have a better understanding of the glass surface reactivity. Furthermore, utilizing molecular modeling in these complex systems can help to elucidate important information about the complexity of the surfaces of multicomponent glass.