

The Effects of Acid Rain on the Visible Light Absorption of Stained Glass

Francis Ricci

Red Hook Central High School
103 West Market St.
Red Hook, NY 12571

Abstract

The effect of acid rain on stained glass windows is felt by many churches and other historic buildings worldwide, especially in Europe. As a result, the relationship between the traditionally dark interiors of these European churches and the acid rain that corrodes the stained glass was studied. Specifically, the effects of specific pHs of acid rain on the visible light absorption of stained glass over time were examined.

In order to study this topic, various samples of modern stained glass were exposed to acidic solutions at specific pHs. The visible light absorption of these samples was measured using an Ocean Optics Chemistry USB 4000 NIR-VIS spectrometer over a period of eight weeks, with one absorption measurement per week. These absorbance spectra were then compared to analyze the specific impact of pH on the samples of stained glass.

It was found that pH affects the visible light absorption of stained glass in three main ways. First, after breaking through an initial outer layer on the glass, the visible light absorption of stained glass will continue to increase as it is exposed to acidic solutions over a period of time. Second, the lower the pH of the acidic solution that the samples of stained glass are exposed to, the higher the visible light absorption of the samples of stained glass. Finally, a greater change in the pH of the solution over the course of the experiment lead to a greater change in the visible light absorption of the samples exposed to that solution.

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Table of Contents

List of Figures	5
Introduction	6
Materials and Methods	8
Results	9
Discussion	13
Works Cited	15

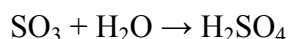
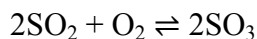
List of Figures

Figure 1.....	Wavelength vs. Absorbance by week.....	pg. 9
Figure 2.....	Wavelength vs. Absorbance by pH.....	pg. 10
Figure 3.....	Absorbance vs. Time by pH.....	pg. 11
Figure 4.....	Change in pH vs. Change in Absorbance by week.....	pg. 12

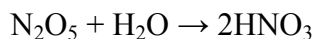
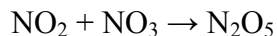
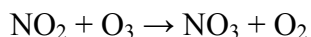
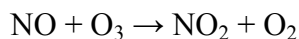
Introduction

There are many dangerous environmental problems facing the world today, but one of the most physically damaging is acid deposition. Acid deposition is harmful to various aspects of the biosphere, notably bodies of water, soil, and trees.¹ In addition, it damages manufactured structures, such as metal and masonry, through the dissolution of carbonates.² Interestingly, acid deposition also affects stained glass, through the corrosion of the glass itself and the corrosion of the glazing system.²

Acid deposition is primarily composed of sulfuric and nitric acids, which are formed largely as a result of human emissions of sulfur and nitrogen oxides.³ Acid deposition is approximately 66% composed of sulfuric acid, and 33% composed of nitric acid.³ Sulfuric acid is formed from sulfur dioxide by the following mechanism:³



Nitric acid is formed from nitrogen monoxide by the following mechanism:³

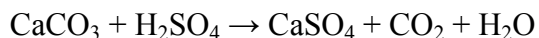


In addition to sulfuric and nitric acids, acid deposition also contains small amounts of nitrous, hydrochloric, formic, carbonic, and acetic acids.⁴ There are also trace amounts of pyruvic, glyoxylic, oxalic, butanedioic, and propanedioic acids.⁴ The pH of acid deposition ranges from 1.5 to 4.5, with normal rain having a pH of 5 to 6.¹

Stained glass itself has a relatively complex and variable chemical composition. Most glass is composed primarily of silicon dioxide, sodium carbonate, calcium carbonate, and magnesium oxide.⁵ The pigments in stained glass are caused by a wide range of chemical compounds, depending on the color of the glass.⁶ The red glass used in this investigation was probably colored by selenium, as a selenide, and by iron and chromium, as oxides.⁶

Stained glass is particularly susceptible to the ravages of acid deposition, particularly wet deposition, which is commonly known as acid rain.⁷ Acid rain leeches alkaline ions from the glass, which results in the formation of a superficial silica gel layer and causes the precipitation of insoluble salts.⁷ Eventually, acid rain will cause craters and pits to form in the stained glass.⁷ These reactions result in a diminished transparency of the glass.⁸

In addition, the sulfuric acid in the acid rain can react with calcium carbonate in the stained glass through the following reaction:³



This reaction causes a change in pH because the sulfuric acid is broken up and converted to calcium sulfate and water.

This investigation intends to provide insight into the extent to which acid rain causes a darkening of stained glass. This is of particular importance in determining the degree to which it is necessary to modify existing stained glass windows to protect them from acid rain, based on the average pH of rain in the area in which the windows are located.

In order to investigate this topic in the most accurate manner possible, a visible light spectrometer was used to measure the visible light absorption of samples of stained glass. These samples were exposed to solutions of sulfuric and nitric acids at specific pHs, in order to determine the effect of each of these pHs on the visible light absorption of the stained glass samples.

The light spectrometer measures light absorption by passing a beam of light through the sample, and measuring which wavelengths are absorbed or reflected by the sample, and which wavelengths are able to pass through. These measurements generate a graph of wavelength vs. absorbance. It is then possible to compare the graphs of samples exposed to different pHs, determining exactly how the absorbance of a sample varies with the pH of the sample's solution.

Materials and Methods

In order to have a wide range of data for the investigation, solutions with pHs ranging from 2.0 ± 0.2 to 7.0 ± 0.2 , in increments of $1.0 \pm .2$, were used, giving a total of six solutions. In order to reduce random error, all of the samples were taken from the same piece of stained glass, and used three samples of stained glass in each solution. A red piece of glass was used because red light appears on one of the ends of the visible light spectrum, so there would not be a sudden drop in absorbance in the middle of the spectra; instead the drop would occur at the end. It would not have been a problem if the drop had occurred elsewhere, but since color was only being used as a control, red was used as a matter of convenience, because a graph with a drop at the end would be easier to analyze than a graph that had a low absorbance section in the middle. In further experimentation, effects on glasses of different colorations could be analyzed. All of the samples were the same size, and measured 5 cm x 5 cm x 0.5 cm. Each sample was assigned a number, from one to eighteen, which correlated to a specific pH, to ensure that each solution always contained the same three samples. Because the pH of the solutions changed over time, the solutions were replaced every week, after the absorbance measurements were taken.

Each sample of stained glass was specially prepared prior to experimentation. First, a file was used to score the glass with its assigned number, in the top right corner. This served two purposes. The scoring ensured that each sample of glass could be matched to the proper solution. It also allowed the absorbance spectra for each sample to be tracked over time. Next, two indentations were filed out of the bottom front edge of each sample. They were spaced at the same distance apart as the sides of the spectrometer, so that each sample would be placed in the spectrometer in exactly the same position for each measurement. This was necessary because the light absorbance of the glass was not precisely uniform across the sample.

The solutions were prepared using sulfuric and nitric acid, in a ratio of 2:1. Each of the stock solutions was first diluted to a $0.100 \text{ mol dm}^{-3}$ solution, before being diluted to the proper pHs. However, because the pH of the distilled water used for the dilutions was around 5.3, due to carbonic acid formed by dissolved carbon dioxide, it was not possible to dilute the solutions to a pH above 5.3. As a result, for the solutions at pHs of 6 and 7, the solutions were made by the dilution of a sodium hydroxide solution.

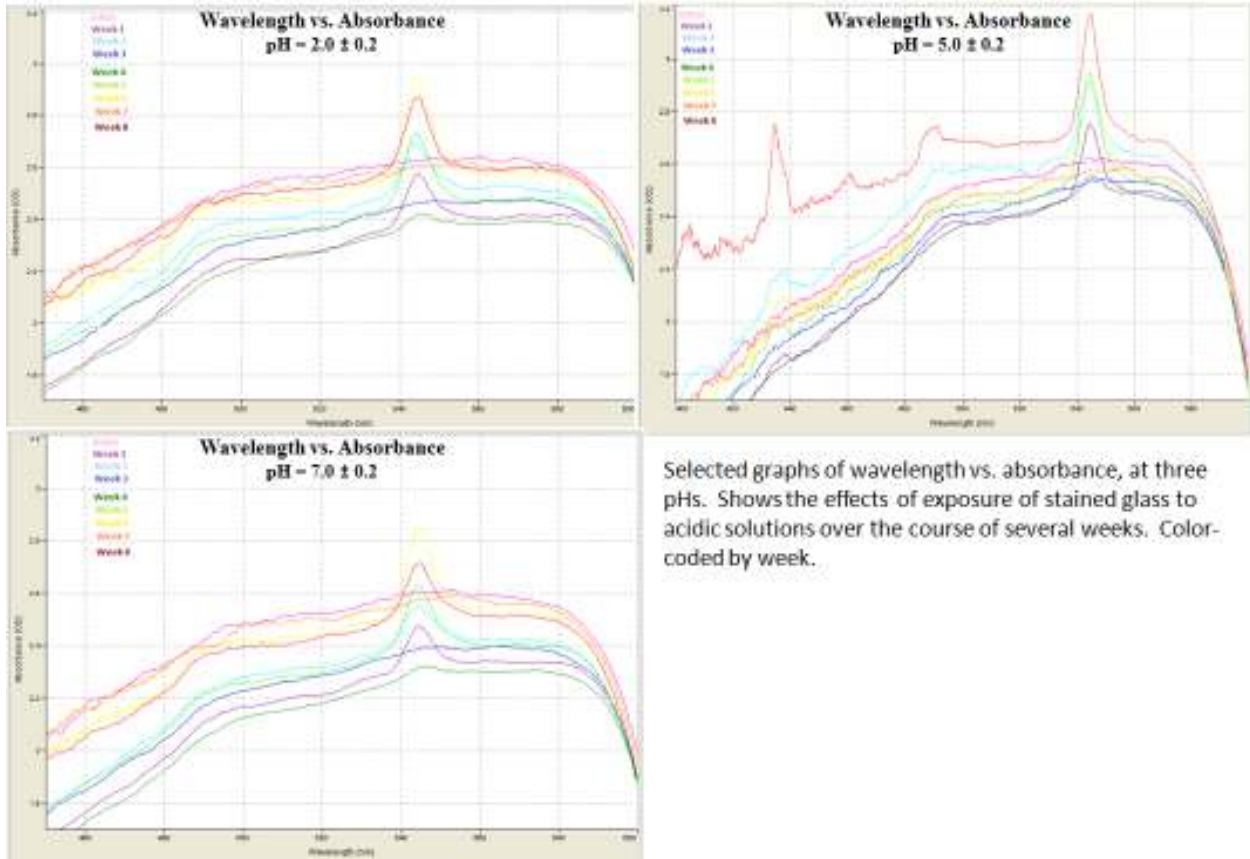
Before submerging the stained glass in the acid solutions, initial absorbance measurements were taken for each sample. Absorbance measurements were taken using an Ocean Optics Chemistry USB 4000 NIR-VIS spectrometer, which measured absorbance in the visible light and near infrared spectrum. After the initial measurements were taken, the samples were submerged in the acid solutions. One 250 mL beaker was used for each pH, and three samples of stained glass were placed vertically into each beaker, in a triangular formation, so that both sides of each sample were fully exposed to the solution. 200 mL of solution were used for each beaker. At the end of each week, the pH of each solution was measured, to monitor changes in pH over the course of the week. After this, the samples were removed from the

solution and fully dried, so that absorbance measurements could be taken. After the measurements were taken, the solutions were replaced and the samples were submerged in the solutions in the same manner as before. This was repeated for eight weeks, so that a total of nine absorbance measurements were taken for each sample: one at the end of each week of the experiment, plus the initial measurements. The absorbance measurements were taken on a weekly basis, because preliminary experiments suggested that a week was long enough for an appreciable change in absorption to occur, while being short enough to allow for enough measurements across the course of a few months.

Results

Figure 1 is composed of selected absorbance spectra from selected samples of stained glass, and each graph tracks a single stained glass sample across the length of the experiment. These three graphs involve an overlay of nine different spectra: the initial spectrum and the eight experimental spectra. Although not present in the first few weeks, there is a general upward trend in the absorbance of the glass beginning with week 4, and continuing through the end of the experiment. This trend is most pronounced in the sample at a pH of 2.0 ± 0.2 , but it is also existent in the samples at the other pHs. The pHs of 2.0, 5.0, and 7.0 were chosen to show the effects of a highly acidic solution, a slightly acidic solution, and a neutral solution. Graphs of this trend are shown at all tested pHs in Figure 3.

Figure 1



Selected graphs of wavelength vs. absorbance, at three pHs. Shows the effects of exposure of stained glass to acidic solutions over the course of several weeks. Color-coded by week.

Figure 2 is composed of graphs of absorbance spectra for each pH during a given week. Each of the three graphs is an overlay of six different absorbance spectra, one for each of the pHs tested, and each corresponds to one of the weeks of the experiment. The first graph shows the spectra after the first week of experimentation, at week one, the second graph shows the spectra midway through the experiment, at week four, and the third graph shows the spectra after the final week of the experiment, at week eight. The graph of the absorbance spectra at the initial measurement before experimentation showed no correlation, as would be expected, and was not included.

The graphs show a distinct relationship between the pH and absorbance of the samples of stained glass. It is clear that the samples that were exposed to solutions of lower pHs have higher absorbance than those that were exposed to higher pHs. In addition, these absorbance spectra support the previous observation that the absorbance increases over time, beginning with week four, as the absorbance between 500 and 520 nm ranges from about 2.15 to 2.40 during week four, and from 2.40 to 2.65 during week eight. The 500 to 520 nm range is especially meaningful in this analysis, because the graph is flattest in this area, allowing for clear determination of the specific absorbance ranges. However, it can also be noted that the overall absorbance between 400 and 600 nm ranges from 1.70 to 2.55 during week 4, while ranging from 2.00 to 3.10 for the same range during week 8. This also suggests a general trend of increasing absorption over time.

Figure 2 also shows that as stained glass is exposed to acidic solutions over time, its absorbance spectra become increasingly jagged. The spectra for the initial readings and for week four show gently curving lines, while the spectra for week eight show lines with a rougher curvature, especially for the more acidic solutions.

Figure 2

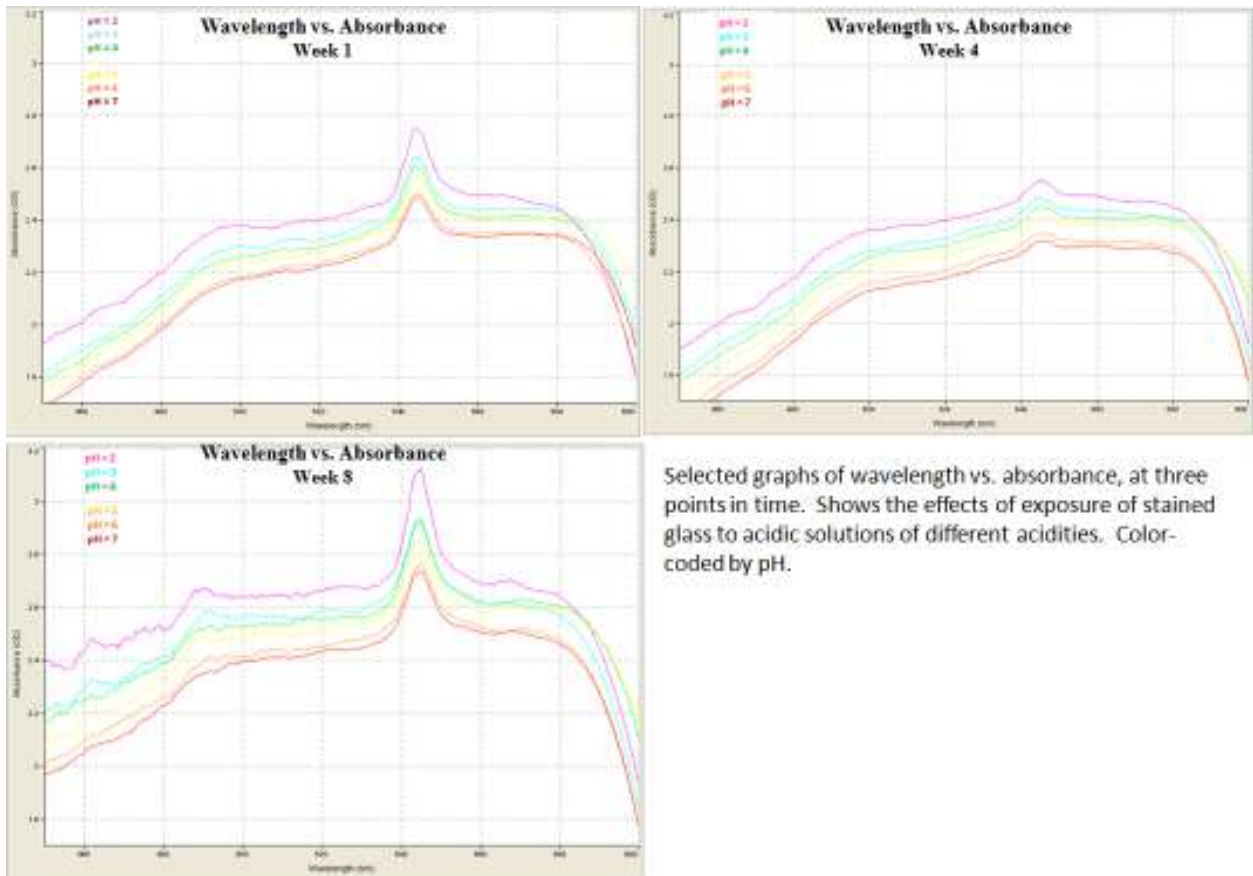


Figure 3 is compilation of each of the spectra obtained from the experiment. The absorbance spectra from each of the 18 samples across all 8 weeks were analyzed at 500.13 nm, and the absorbance at this wavelength was determined using the SpectraSuite Spectroscopy software. 500.13 nm was chosen because it is where most of the spectra begin to level off, which minimizes error. Each of the absorbance values was then plotted on one of three graphs, which graph pH versus absorbance for a given week. Three graphs were used so that there would only be one point per pH per week on each graph, without averaging the data, and still allowing all of the data to be presented. It would be inaccurate to average the data for the samples at the same pH because they are different, independent samples, which began from different initial conditions.

These graphs support the same trends presented by the specific selected data presented previously. The most notable characteristic of the graphs is that as the pH increases, the absorbance decreases, except in the initial measurements. This observation can be made by noting that the curves for lower pHs lie above the curves for higher pHs on the graph, with the curve for a pH of 2 lies above that for the pH of 3, and so on. In addition, these general graphs support the previous observation that, in general, beginning with week four, the absorbance increases, especially at low pHs. This trend can be observed by noting that the curves are generally upward-sloping beginning with week 4, although there is some variation in this trend with specific pHs, especially during week 8. During week 8, the trend of increasing absorbance only holds true for the solutions whose pHs are below that of the distilled water used for the experiment (pHs 2 through 5). This spread of the absorption values could be examined through further study, based on where the trend heads after this week for the various pHs.

Figure 3

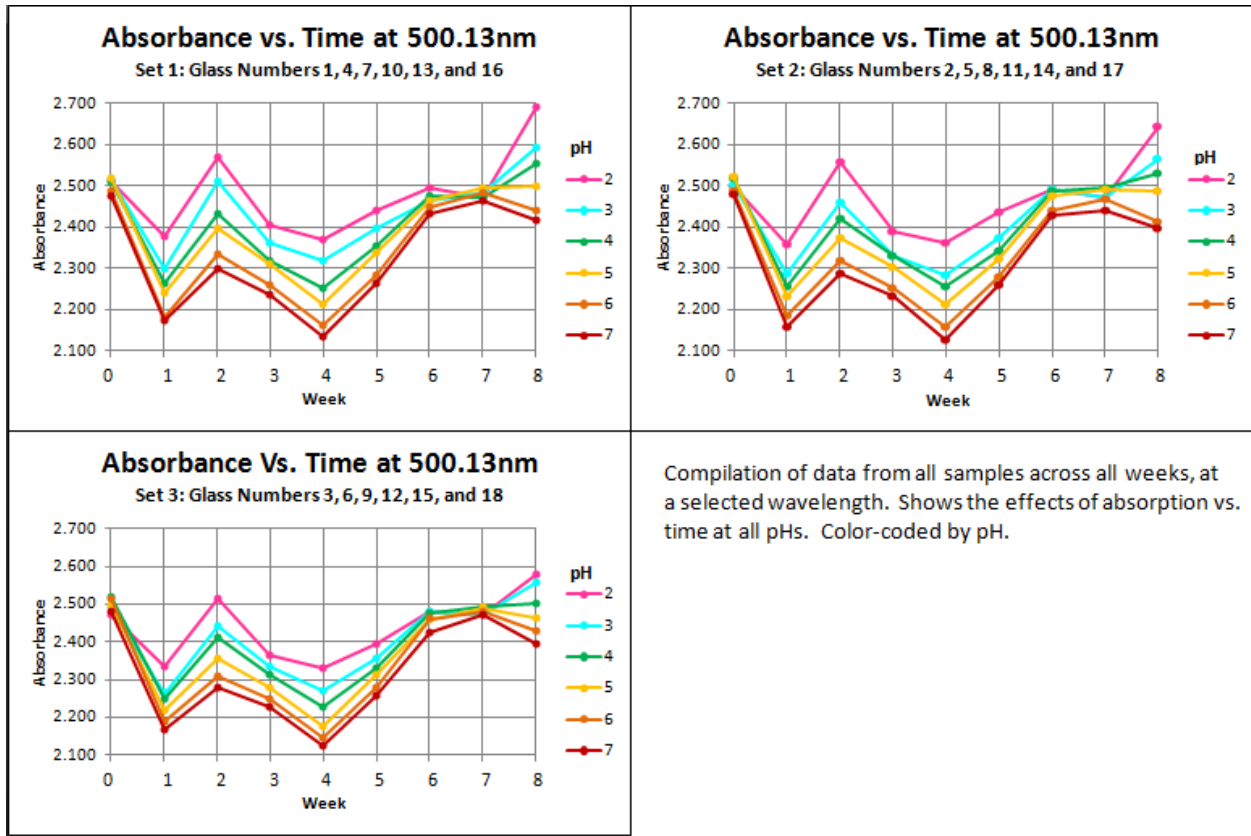
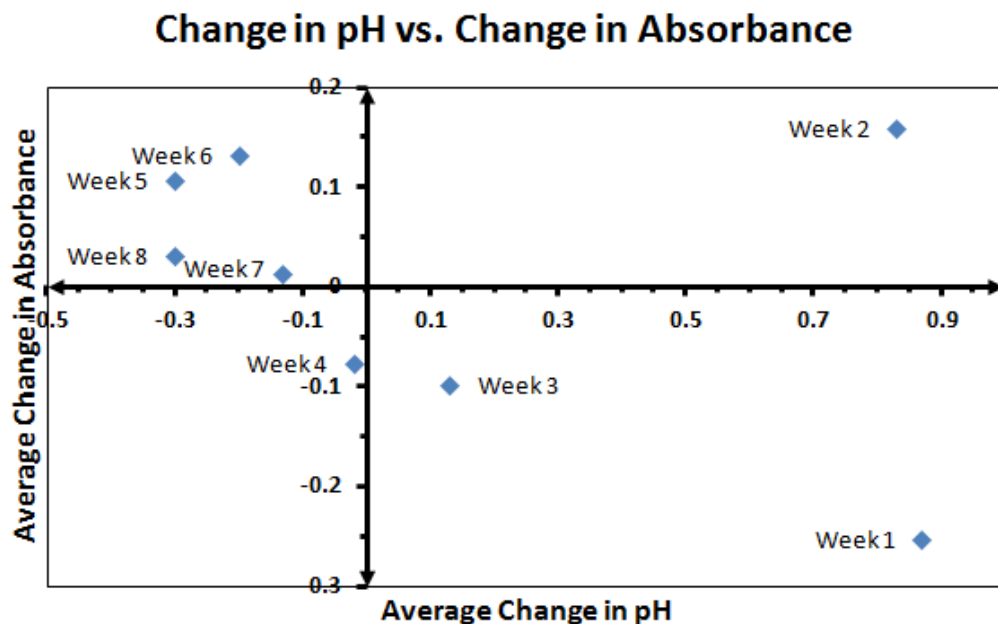


Figure 4 shows the effect that the change in pH had on the change in absorbance of the stained glass, average measurements were taken. The average change in pH was calculated, based on the initial and final pHs of each solution each week. The average change in absorbance was calculated, based on the difference in absorbance across all of the samples between the previous week and the week being tested. It is acceptable to average the absorption data in this case, because the change in absorption is being measured, which accounts for initial conditions, unlike in Figure 3.

The graph of average change in pH vs. average change in absorbance suggests that a greater change in pH leads to a greater change in absorbance. Although there is not a specific, direct relationship between the average change in pH and the average change in absorbance, there is a more basic relationship, namely that the points that had high values for change in absorbance also had high values for change in pH, with the points that had low absorbance values having low pH change values. In addition, for the second half of the experiment, the values for change in pH are negative, while the values for the change in absorption are positive. They are also grouped closer together than during the first half of the experiment.

Figure 4



Shows the effects of the average pH change of solution on the average change in absorption of the samples during a given week.

Discussion

The data collected suggests that pH influences the visible light absorption in three main ways. First, after a period of initial exposure, increased exposure to a solution of acidic pH will cause an increase in the visible light absorption of stained glass. The absorption continues to increase as the length of time the glass is exposed to the acidic solution is increased. This is very significant in relation to stained glass windows in churches and other buildings, because it means that over time, stained glass windows will become darker and darker, as the stained glass absorbs more and more of the visible light. This means that very old buildings in areas with a lot of acid rain will need to find a way to protect their windows, or install additional lighting to compensate for the additional light absorbed by the stained glass windows.

Second, more acidic solutions had a greater impact on the visible light absorption of the samples of stained glass. While all of the solutions impacted the visible light absorption of the samples of stained glass, the solutions with low pHs resulted in samples with the highest absorbance. This is also significant in relation to stained glass windows in buildings, because it means that buildings in areas with highly acidic rain should be more concerned with the affect the acid rain will have on their stained glass than those in areas with relatively neutral rain.

Third, larger changes in the pH of the solutions indicated larger changes in the visible light absorbance of the samples in the solutions. Over the course of a week, large changes in pH resulted in large changes in visible light absorption, while small changes in pH resulted in small changes in visible light absorption. This suggests that the pH change in the solution is a result of the extent to which the reaction with the stained glass occurred. A greater change in pH would suggest a more complete reaction. This makes sense from a formulaic standpoint as well, because the reaction between calcium carbonate and sulfuric acid involves neutralizing the acid in solution, while simultaneously breaking down the calcium carbonate in the stained glass. This would cause an increase in visible light absorption of the glass, by making the pigments in the glass more concentrated, due to the fact that the pigments are not affected by this reaction.

There were several sources of error in this experiment, including temperature fluctuations, evaporation, inaccuracies of measuring instruments, and shortcomings in the experimental method. Temperature fluctuations affected the experiment primarily by altering the concentration of carbonic acid, and as a result the pH, of the solutions while the experiment was occurring.

Evaporation also affected the experiment while it was occurring, by altering the relative concentrations of solute and solvent in the solutions, which slightly altered the pHs of the solutions. However, it also affected the solutions while they were in storage prior to being used for the experiment, because the solutions were made up two weeks beforehand. The effect of evaporation on the solutions in storage was minimized by using glassware with tightly sealed

lids, so that water vapor could not escape the container. Nevertheless, some of each solution did evaporate, as was indicated by the condensation on the inside of the glassware.

There was also some uncertainty in the accuracy of the measuring instruments, which resulted in error. For example, the pH probe that was used to check the starting pHs of the solutions and to measure the final pHs of the solutions had an uncertainty of ± 0.2 . This is a relatively high uncertainty, and it could significantly affect the measurements for the average change in pH of the solutions, as the values for average change in pH fell between -0.30 and 0.87. This would result in an uncertainty higher than the measured value for some of the average changes in pH. In addition, it could cause some values for change in pH to change from positive to negative or vice versa.

Finally, there was some error in the experimental method that was used. First, the experimentation occurred in an environment that was not at a controlled temperature, which affected the pHs of the solutions. Second, the time between absorbance measurements was not exactly constant at one week, but fluctuated in the time of day that the measurements were taken. In addition, because the measurements were taken during the school day, the samples of stained glass were not exposed to the acidic solutions while they were in school, before and after being tested. This was a total of about eight hours per week that the samples were not in solution. Finally, although the solution at a pH of 7.0 acted as the control in this experiment, these samples underwent changes similar to the samples at other pHs, so it was not the best choice for a control.

In order to best improve the experiment, the error associated with experimental method should be minimized. First, if the experiment were carried out indoors, where it would only experience limited temperature fluctuations, the pH changes due to changes in carbonic acid concentration would be minimized. Second, the interval of time between each absorbance measurement could be held constant by choosing a specific time of day, such as 3:00 pm, at which the measurements would always be taken. In addition, if the samples of stained glass were brought directly to the lab to have their absorbance measurements taken, and then immediately brought back to the site of the experiment, the amount of time per week that the samples would spend in the solutions would be maximized, while also being brought closer to a constant value. Finally, in addition to using a solution with a pH of 7.0, it would be beneficial to test samples of stained glass each week that were not exposed to a solution of any kind, in order to compare the stained glass in the solutions to unaffected samples. This would imitate the conditions faced by stained glass windows in churches that experience little or no rain.

Finally, this investigation leaves some unanswered questions. Why do some weeks have sudden peaks in absorbance in all samples at around 545 nm, while others do not, seemingly without a pattern? Since there is no exterior coating on the glass,⁹ why did it take a few weeks before the absorbance began to increase steadily?

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