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Developing a Portable Prototype to Utilize an Electrospun Colorimetric Sensor for the Detection of Trihalomethanes in Water

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Developing a Portable Prototype to Utilize an Electrospun Colorimetric Sensor for the Detection of Trihalomethanes in Water

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Executive Summary

Problem Statement

As a result of using chlorine in water disinfection processes, trihalomethanes (THMs) are created. THMs are one type of many disinfection by-products (DBPs) that occur as a result of this treatment. The Environmental Protection Agency (EPA) recognizes chloroform, bromoform, bromodichloromethane, and dibromochloromethane as THMs. Exposure to trihalomethanes is known to negatively affect human health in ways that include kidney problems and increased cancer risk. A method that can be utilized in field testing to recognize these chemicals will make the process faster and cheaper than current procedures, which require samples to be tested in labs. THMs must be detected at 80 parts per billion (ppb) in water to reach the EPA maximum containment level. Past work by Max Duckworth, which characterized an electrospun membrane and testing procedure, was recreated and a prototype for field testing was developed for the progression of this work. As a part of the procedure, a camera is required to take pictures of results. It is out of the ordinary in the present day for someone not to have a cellphone, so this work utilized a Moto X4 camera to test the abilities of this common technology.

Results

The experimental procedures were completed according to optimal parameters determined in Duckworth's previous work. Solutions made up of cyclohexane, acetone, dimethyl formamide, and 2.6 wt% polypropylene were used for electrospinning. At this weight percent, the membrane is hydrophobic, preventing water from interacting with reagents when running the colorimetric reaction. The Fujiwara reaction occurs when pyridine is mixed with a base, like sodium hydroxide, causing a red/yellow color change in the presence of THMs. Water reduces

the intensity of the color change, which was quantified using ImageJ software. A 3D printed prototype for THM detection was designed to keep the experimental procedure essentially the same, but usable in different environments. When using the previously determined procedure, the average color intensity of water contaminated with 250 and 80 ppb of bromoform was 87.6 and 66.6, respectively, with standard deviations of 26.8 and 21.1. Using the developed prototype with this procedure resulted in an average intensity of 93.8, with a standard deviation of 8.2 for 250 ppb. The average intensity when using the prototype with 80 ppb was 74.0 and standard deviation of 12.1. Compared to Duckworth's data, this was a more broad distribution. Testing using a lower bromoform concentration of 8 ppb did not produce visible results. T-testing results of 0.003 and 3.23×10^{-6} (for the regular procedure and prototype procedure respectively) indicated that the differences in the 250 and 80 ppb data sets were statistically significant. The t-test comparing regular procedure data and prototype data of identical bromoform concentrations (0.25 for 250 ppb and 0.19 for 80 ppb) determined that the means of the data were not significantly different.

Conclusions

Though the data sets of 250 and 80 ppb were determined to be significantly different for both the original and prototype procedures, the average intensities and standard deviations were very different than those determined in Duckworth's research, which is thought to be attributed to the camera used. At this point in time, cell phone cameras in general are not precise enough to reliably recreate the previous experimental data. The differences between the original and prototype procedures were determined to be insignificant. This indicated that the prototype worked in the same manner as the original procedure. One way of avoiding issues that may arise from using different cameras is to create a card that indicates colors and examples of the

colorimetric response to different THM concentrations. When working on field testing, this could be used to visually confirm the presence of THMs at a less precise, yet useful level. An indicating card would provide a quick confirmation of contaminant detection without quantifying the exact concentration level.

Broader Implications

Completing this research gave me the chance to work largely independently in a lab setting. I learned to work with new procedures and equipment, like those used in electrospinning. I was able to collaborate with and get advice from Dr. Monty and the graduate students of the Monty Lab Group when needed. Creating a field testing prototype gave me exposure to SolidWorks, 3D printing, and the University of Akron MakerStudio, which I had previously never used. I appreciate that I have been able to experience the successes and setbacks of scientific research, and work on a project intended to aid in environmental improvement.

The results of this work could benefit society by creating to a quick, cheap, and portable method of THM detection in water. If such a testing method becomes feasible, contamination will be detected and treated more often, leading to safer drinking water overall.

Future Work

The progression of this work would consist of additional testing with a high quality camera, working to confirm the calibration curve created by Duckworth, which relates THM concentration to color intensity. The prototype should be modified to use a durable material that can be tested many times, and the difference, or lack thereof, between the original and prototype test methods should be determined. Calibration curves using other THMs should be created using the same procedures as used in this research.

Introduction

Contaminant detection in water is vital to ensure safe use, and various types of chemical contaminants are regulated by the U.S. Environmental Protection Agency (EPA). One category of contaminants are trihalomethanes (THMs), which include chloroform, bromoform, bromodichloromethane, and dibromochloromethane [1, 2]. These chemicals are formed as by-products when disinfectants like chlorine are used as water treatment to remove contaminants in drinking water [1,2]. When chlorine is added to water, it reacts with naturally occurring organic and inorganic matter, creating multiple disinfection by-products (DBPs), which include THMs [2]. The EPA recognizes potentially detrimental health effects as a result of long term exposure to trihalomethanes, including increased cancer risk and problems with the liver, kidneys, and central nervous system. The maximum contaminant level of total THMs in water allowed by the EPA is 80 parts per billion (ppb), and the EPA notes maximum contaminant level goals of zero ppb of bromoform and bromodichloromethane, 60 ppb of dibromochloromethane, and 70 ppb of chloroform [3]. THM exposure occurs through inhalation, dermal absorption of shower and bath water, and ingestion of drinking water [2].

The ability to detect THMs in water is important for human health, and past detection methods have to be able to determine THM concentration at the ppb scale. The work described in this report seeks to recreate experimental methods completed by Max Duckworth, who completed characterization of an electrospun membrane used in combination with the Fujiwara reaction to create a colorimetric sensor to detect bromoform and chloroform in ppb concentrations [4]. A portable prototype, created to utilize this method of THM detection in the field, was tested in order to further this research.

Detection of THMs and other DBPs is commonly completed using liquid-liquid extraction and gas chromatography, and the EPA's official method of DBP detection utilizes these methods [5]. Samples are required to be analyzed in laboratory studies in order to determine THM concentration, and must often be concentrated in order to quantify contaminants [6]. The detection method of this work seeks to eliminate the need for samples to be transported and studied in labs, and to remove the concentration step. The overall goal is to make this process faster and less expensive than traditional procedures, and to create a prototype that can be used in the field for contaminant testing.

Background

Electrospinning is a technique by which a polymer solution flows through a needle which acts as a capillary tube. The needle and a grounded collecting plate are connected to a high voltage power source. At a critical voltage, the surface tension of the solution in the tip of the needle is overcome by the applied electric field. A jet of solution is sent in a whipping motion to the collecting plate and the solution solvent evaporates, which results in polymer nanofibers forming on the plate. Many different polymers in solution are able to be spun for a large variety of applications, including in the textile and medical industries [7].

One method of detection of THMs is the Fujiwara reaction. Using pyridine and a base, commonly sodium hydroxide (NaOH), a colorimetric reaction occurs in the presence of THMs and other halogenated compounds [8]. A visible color change is created, and this ranges from red to yellow/brown depending on concentration. In past procedures, the Fujiwara reaction has been used for detection ranging from 1-100 ppm, but it has been modified in order to lower the detection limit [9]. Water hinders the color intensity of the reaction, and preventing it from contacting reagents will help to achieve detection at lower concentrations [8].

Experimental Methods

A solution for electrospinning was made in order to create nanofiber membranes. The procedure to make the solutions required 8 grams of cyclohexane, and 1 gram each of acetone and dimethyl formamide, and 267 mg of polypropylene placed in a 20 milliliter (mL) scintillation vial. Duckworth determined that a 2.6 wt% polypropylene solution was the most hydrophobic when testing solutions from 1 to 4 wt% [4]. Electrospinning solutions were heated for approximately 24 hours at 70 °C. The solution was loaded into a plastic 10 mL syringe attached to tubing, which connected to a 21 gauge blunt needle placed vertically in the top of a box used to enclose the process. The needle and foil were connected to a high voltage power supply via alligator clips. Using Duckworth's procedure for creating nanofiber mats, the parameters for electrospinning included a distance of 25 cm from the foil collecting plate to the needle, a solution flow rate of 25 ml/h, and 25 kV from the power source. Figure 1 shows a diagram of the experimental electrospinning setup. The solution was pumped into the tip of the needle, and the syringe pump and power source were turned on at the same time. A single nanofiber mat was created by running the electrospinning process for about ten minutes. Once complete, the membranes were allowed to dry before cutting into 4 by 4 centimeter squares.

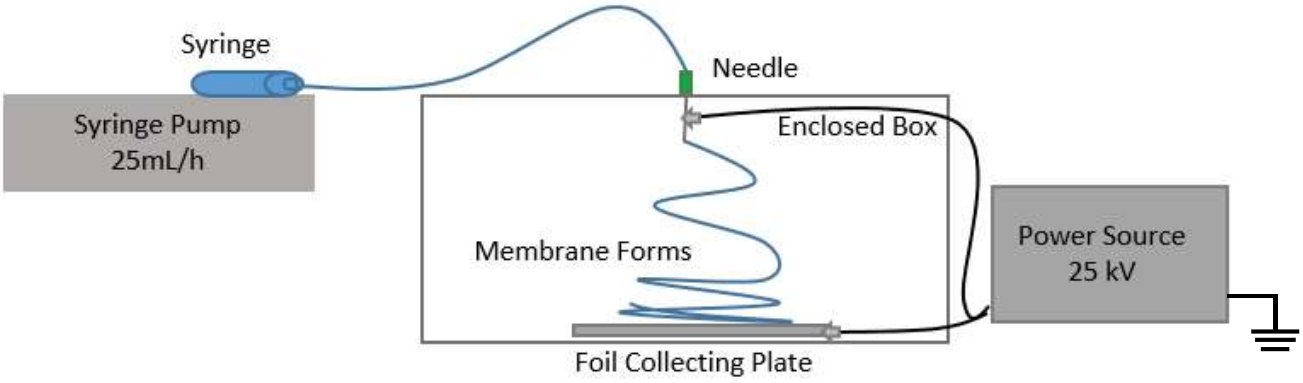

Figure 1: Diagram of the experimental electrospinning setup.

In order to test for the presence of bromoform, a supersaturated solution of NaOH in ethanol was made, as well as a solution of deionized water and bromoform in a known concentration on the ppb scale. A 20 mL scintillation vial of bromoform solution was placed in a water bath on a 70 °C heating plate. A membrane piece was placed between two Teflon blocks which fit over the opening of the vial. The membrane could be seen through a circular hole in the middle of each block (Figure 2). Heating the vial caused the THM to evaporate, condensate on the membrane, and pass through the nanofibers. Water was prevented from passing through the membrane due to the hydrophobicity. Initially, 75 microliters each of pyridine and supersaturated sodium hydroxide were added to the top of the membrane. For the rest of the procedure, a 9:1 volumetric ratio of pyridine to NaOH solution (144:16 microliters) was added using pipettes at a rate necessary for wetting the membrane, generally every 3 to 5 minutes. Following the previous procedure, pictures of the membrane were taken from 10.5 cm above the setup after reagent additions [4]. Photos were taken using a Moto X4 cell phone camera, watching for a visible color change that included yellow/brown spots. At THM concentration on the part per million scale, the visible color change was pink or red [4]. The procedure was run long enough to ensure a visible color appearance before ending each test, which usually lasted about thirty minutes.

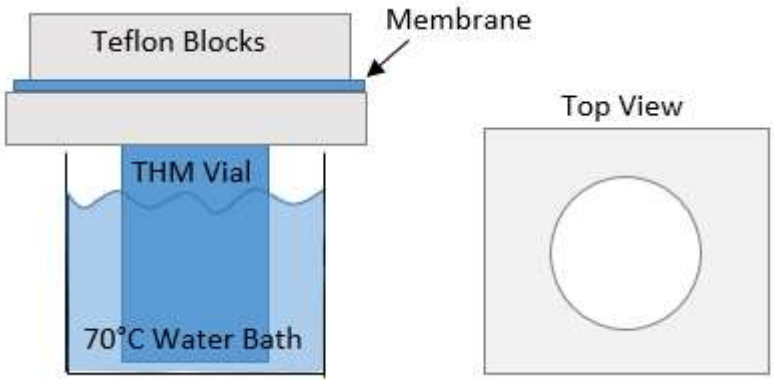

Figure 2: Diagram of Fujiwara reaction experimental setup.

A prototype for the use of this process in field testing was developed. For the first round of prototype testing, a relatively simple addition to the setup of the process was created. Mimicking the Teflon pieces used in the original procedure, a rectangular block, 3D printed using PLA, was made to be able to fit over the opening of a 20 mL scintillation vial. During the creation of the prototype, a test block was used to run the Fujiwara reaction. It was determined that the reaction could not take place on directly on the block, as the membrane fused to the material. Sides were built up on the piece so that the Teflon blocks could sit inside without moving. Multiple views of the prototype can be seen below in Figures 3A and 3B. The procedure for using the prototype was exactly the same as the original test method, aside from the fact that the Teflon blocks and membrane rested inside the PLA piece. The prototype was 3D printed in the University of Akron MakerStudio.

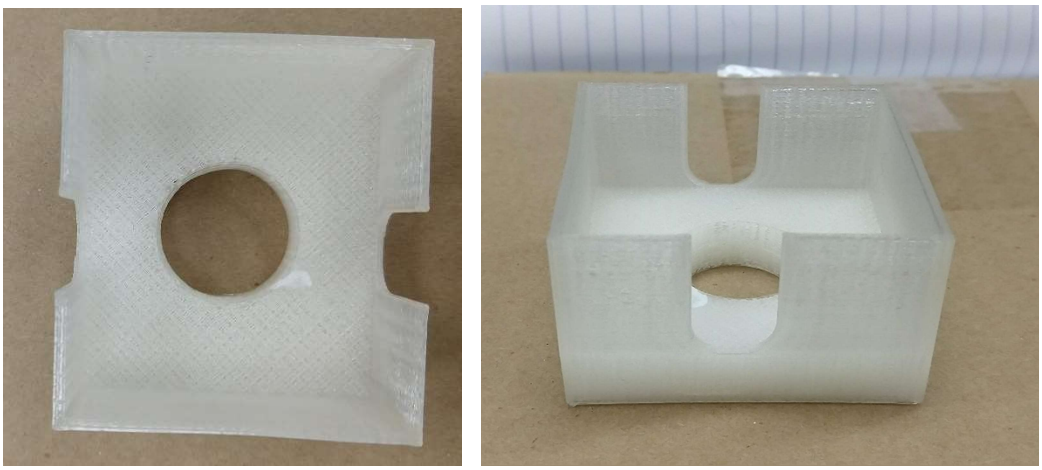

Figure 3A and 3B: Top and side view of membrane testing prototype

ImageJ software was used to quantify the intensity of the color change in each reaction. Following the process that Duckworth used, the pictures taken of each reaction test were opened using ImageJ, and the area of color change was selected. The area color was inverted and the mean intensity was measured using measurement tools in ImageJ [4].

Data and Results

All testing was completed using 2.6 wt% membranes in a 70 °C water bath. The Fujiwara reaction was run using a 9:1 ratio of pyridine to supersaturated sodium hydroxide solution. These conditions were the optimal parameters as determined in Duckworth's research. The same concentrations of bromoform tested previously were used [4]. The images were analyzed for color intensity of reaction, and the average values and standard deviation of the data sets are seen in Table 1. Bromoform concentrations of 250 and 80 ppb were seen visually during testing and in pictures taken, both when using the original method of testing and the prototype. During this testing, a lower concentration of 8 ppb was not seen to produce visible results.

Table 1: Average and standard deviation of the intensity of the Fujiwara reaction.

Bromoform concentration (ppb)	Intensity	
Normal Testing	**Average**	**Standard Deviation**
250	87.6	26.8
80	66.6	21.1
Prototype Testing		
250	93.8	8.2
80	74.0	12.1

These results are to be compared to the results seen by Duckworth, which can be seen in Table 2. Examples of the results seen on membranes can be seen in Figure 4.

Table 2: Average and standard deviation of the color intensity seen by Duckworth in testing [4].

	Intensity	
Bromoform concentration (ppb)	**Average**	**Standard Deviation**
250	136.3	4.9
80	127.6	8.7
8	114.5	6.4

T-tests were completed using Excel in order to determine whether the data sets were statistically different. The data included in the t-tests only consisted of runs in this round of testing, and did not include Duckworth's data. The t-tests results comparing 250 and 80 ppb for regular testing was 0.003 and was 3.23×10^{-6} for the prototype. Being less than 0.05, these results indicated that the two sets of data (the 250 and 80 ppb concentrations) were statistically different. Between the original and prototype data sets of the same concentration, t-tests were also completed. For the 250 ppb bromoform concentration, comparing the regular and prototype testing data, the t-test value was 0.25, and for the 80 ppb bromoform concentration, the t-test value was 0.19. These results indicated that there was not a statistically significant difference between the means of the original and prototype test data. This is promising for the use of a similar prototype in field testing. Being that the EPA limit for THMs is 80 ppb, the results are encouraging for future practical testing of water samples.

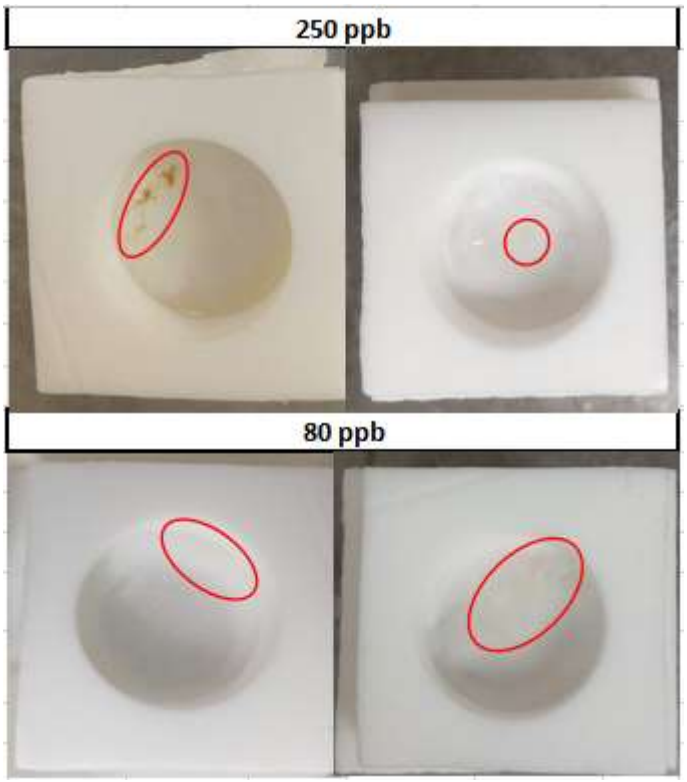

Figure 4: Examples of visible colorimetric reactions of different bromoform concentrations.

Discussion/Analysis

Using the same technique tested by Duckworth, the results of the previous study were attempted to be confirmed and furthered with the creation of a prototype for field testing. Physically, the experiment ran in the same manner, including electrospinning 2.6 wt% membranes for optimal hydrophobicity, using a 70 °C water bath to produce an intense color change, and adding pyridine and supersaturated sodium hydroxide in a 9:1 ratio when running the Fujiwara reaction. Though these experiments were completed in the same manner, the image analysis produced very different results than those seen previously. This can be attributed to the camera used. It was attempted to use a Moto X4 camera, an average cell phone camera that anyone completing testing could be reasonably expected to own. Duckworth's data used a more precise camera, and resulted in a less spread out color intensity data set, seen in Table 2.

Though the t-tests indicated that there was a significant difference between the 250 and 80 ppb data sets, more testing should be completed. The experimental data was generally more spread out than seen previously and did not follow the calibration curve determined by Duckworth, which appears to be due to the camera quality [4]. It will be necessary to make sure that different cameras can repeat the results seen by Duckworth. The t-tests between the regular and prototype testing indicated that the prototype worked in the same manner as the original test method. The testing for the original and prototype procedures used the same camera and were tested under the same conditions. This is promising for the development of a field testing device. Different materials for the prototype must be considered. The PLA was seen to fuse to the membrane during early testing, and the prototype began to show signs of deterioration due to prolonged heat exposure after many tests. A material that can withstand contact with the chemicals and applied heat will be necessary for repeated testing.

Future tests should use the Nikon Coolpix S9100 as used previously. If other high quality cameras are used, it must be confirmed that they can detect a color change at the concentrations previously tested, and that the data follows the concentration curve determined by Duckworth. In the future, cell phone cameras may be sufficient to complete these procedures, but for the time being, better quality cameras should be used. Ideally, a visual analysis will be used to determine THM presence during field work. A card with pictures indicating concentration present could be used to confirm results. An example of an indicating card can be seen below in Figure 5. More ppb concentrations should be tested in order to create a card that encompasses a wider range of the results seen in the Fujiwara reaction.

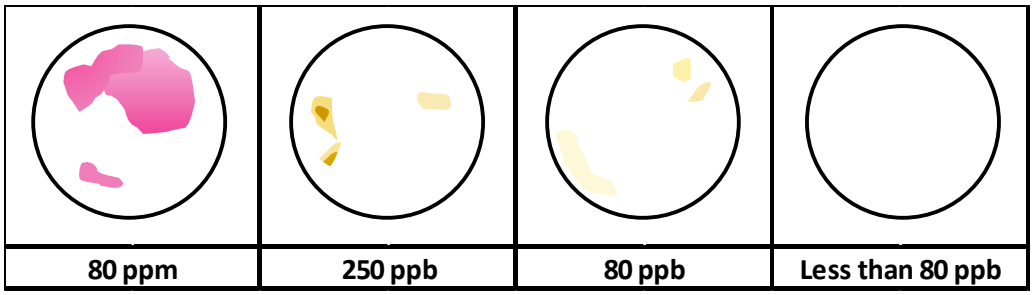

Figure 5: Example card indicating the potential look of the colorimetric reaction for visual confirmation of THMs.

This work confirmed that the 2.6 wt% electrospun membrane can be used to detect THMs at the ppb concentration. Continued work needs to be completed in order to affirm the previously determined concentration curve, and differences in picture quality must be considered. Development began on a prototype that can be used with the same procedure as previous testing. Further iterations of prototypes should determine a suitable material. The future completion of this research is intended to create a functioning device for THM detection at the EPA maximum contaminant level of 80 ppb in field testing, while being cheaper and faster than current methods.

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Appendices

Table A1: Intensity data for the Fujiwara reaction compiled using ImageJ for 250 ppb bromoform using the original method.

250 ppb					
Tested					
3/22/2019		3/27/2019	3/28/2019	3/29/2019	
Mebrane Sample					
11/14/2016 1	2/27/19 B1	11/14/16 2A	3/15/19 B2	2/1/19 B1	3/15/19 2A2
Intensity					
102.33	103.403	63.659	68.327	54.003	45.088
145.282	100.532	65.032	94.059	57.967	96.927
87.728	97.574	93.088	98.238	56.338	95.369
147.358	103.96	93.652	106.203	58.688	58.963
131.078	106.534	95.199	88.508	57.44	54.003

Table A2: Intensity data for the Fujiwara reaction compiled using ImageJ for 80 ppb bromoform using the original method.

80 ppb		
Tested April 1, 2019		
Membrane		
3/7/19 2A1	3/15/19 2A1	3/5/19 B1
Intensity		
105.242	56.231	57.373
82.595	53.086	54.051
101.667	48.517	39.285
96.171	53.664	39.617
104.975	59.972	52.839
78.838	63.703	48.926

Table A3: Intensity Data for the Fujiwara reaction compiled using ImageJ for 250 ppb bromoform when completing the procedure with the prototype.

250 ppb with Prototype		
Tested April 10, 2019		
Membrane		
2/27/19 B2	3/12/19 1A3	2/22/19 B
Intensity		
99.992	102.494	95.353
94.988	88.194	94.45
109.456	83.388	100.796
95.036	81.256	89.384
107.96	81.256	88.159
95.298	95.602	84.935

Table A4: Intensity data compiled using ImageJ for 80 ppb bromoform when completing the procedure with the prototype.

80 ppb with Prototype		
Tested April 11, 2019		
Membrane		
3/7/19 B1	4/4/19 A1	4/4/19 A2
Intensity		
75.603	74.794	42.356
95.906	78.368	76.99
73.511	79.388	76.757
82.088	78.099	71.262
77.329	79.891	70.729
75.338	77.32	45.799

Table A5: T-test results when comparing the two bromoform concentrations to each other for the original procedure and the procedure with the prototype. This also includes T-test data comparing 250 ppb for the original and prototype methods, and 80 ppb for original and prototype methods.

T-Test Results	
250 ppb and 80 ppb Original Method	0.003
250 ppb and 80 ppb using Prototype	3.23E-06
250 ppb Original and Prototype	0.25
80 ppb Original and Prototype	0.19