Concentrating 6:2 FTOH using a Bubbler System: A novel method for treating PFAS in wastewater

A Major Qualifying Project

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Report Submitted to:
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Abstract

PFAS is a class of chemicals used in many industries because of their ability to form an interface. Yet, they pose a concern to human health and do not break down in the environment. Removing PFAS from water and wastewater is vital to preventing bioaccumulation. Our project capitalized on the surfactant nature of PFAS to design a batch reactor system with four graduated cylinders to remove a volatile PFAS species, 6:2 FTOH, from water by bubbling. We intended for evenly spaced liquid samples to undergo solid phase extraction (SPE) followed by injection into a GC-MS device. 6:2 FTOH concentration sample results would be compared to the initial 6:2 FTOH concentration before bubbling to determine if bubbles captured and removed PFAS from water. Though we did not test the effectiveness of bubbling, our standardization and sample-testing procedures revealed new information on 6:2 FTOH. Our reactor design is able to test our hypothesis along with other factors such as pH, ionic strength, and cosurfactants.

Capstone Design Statement

The Accreditation Board for Engineering and Technology (ABET) has set requirements for students to graduate with a Baccalaureate program in engineering. One of these requirements includes a major engineering design that incorporates the engineering standards based on the knowledge and skills the students acquired through their previous coursework.

Worcester Polytechnic Institute (WPI) completes the capstone design through the Major Qualifying Project (MQP). This MQP demonstrates the design of a batch aeration system that contains mechanical components to separate PFAS into high and low concentrations.

The design of the system was developed through research on aeration systems and related treatment processes with adsorption. We theorized that with the surfactant properties of PFAS, it would adsorb onto the bubbles and create a high concentration at the top of the reactor and a low concentration at the bottom of the reactor. Some of the main factors that could affect the design were the pore sizes, reactor height, and PFAS adsorption to other materials other than bubbles.

The design consisted of four main batch reactors that were 1-liter glass graduated cylinders. This was chosen because of its tall and thin characteristics, allowing a longer contact time between the bubbles and the surfactant: PFAS. Air was delivered into the open system through a compressed air outlet into ½” ID plastic tubing. The tubing was connected to a four-way hydraulic manifold that split the airstream into four different streams labeled A, B, C, and D. Each line was connected to a 0-4 L/min rotameter to measure the flow of the air entering the system. Then the inlet line was fed into the reactor and connected to a porous stone at the bottom of the reactor. The porous stone diffused the air to create our bubbler system. This system was designed to be run for 30 minutes with a static air flow rate to allow a long enough contact time between the bubbles and the PFAS to create meaningful separation. Once the run time was over, another set of tubing (¼” ID) at the bottom of the system was connected to a four-way peristaltic pump. The pump would allow us to take samples from all four systems simultaneously to create less variability in sample collection along with causing as little mixing as possible.

After sample collection, the samples would be analyzed after a solid phase extraction (SPE). SPE was originally designed based on current EPA methods. However, EPA methods were originally designed for a liquid chromatograph-mass spectrometer (LC-MS). Because of this, the procedures needed to be modified. These modifications included using different carriers such as methylene chloride, methanol, and ethyl acetate. We also used both Supelco Envi-18 Tubes and Agilent Bond Elute LMS. When running the analysis, the tubes were conditioned with the carrier, followed by conditioning with regent water. The sample water was then run through SPE. The PFAS was eluted with the carrier then the sample was analyzed in the GC-MS. In situations where the carrier could not be injected into the GC-MS, a RapidVap evaporated the solvent. Reconstitution of the sample with a solvent followed evaporation so that the sample could be injected into the GC-MS.

Professional Licensure Statement

Professional Engineers (PEs) have the credibility to implement engineered designs, the trust of potential clients and clients, as well as greater responsibility attributed to them from their employers. When we utilize structures in our everyday lives, such as cross a bridge or ride an elevator, we trust the competence of the engineer(s) that configured them. Likewise, a PE must have successfully completed four general steps to earn their licensure: four years of engineering under the mentorship of a PE, a four-year degree from an accredited institution, the Fundamentals of Engineering (FE) exam, and the Principles and Practice of Engineering (PE) exam.

Not only is professional licensure a symbol of achievement, it is a legal requirement for today's engineers. The National Council of Examiners for Engineering and Surveying (NCEES) assesses future engineers, or Engineers in Training (EIT) to ensure they meet standards, have the qualifications, and can be held accountable in their profession (National Council of Examiners for Engineering and Surveying, 2023). Educational institutions must have a state-approved engineering program for an EIT to meet four-year degree requirements. Programs are approved by non-profit, non-governmental organizations such as the Accreditation Board for Engineering and Technology (ABET). For ABET, the accreditation process is about 18 months long and determines compliance with set policies and criteria (Accreditation Board for Engineering and Technology, 2023).

An EIT may choose to take the FE shortly before or after completion of an accredited engineered program. The exam is offered by NCEES throughout the year and is taken online over the course of six hours (National Council of Examiners for Engineering and Surveying, 2023). There are different branches of engineering FE exams may test on and the one the EIT takes depends on their specifications and discipline, such as chemical or mechanical engineering. Upon receiving a passing score on the exam, an EIT must also complete four years of qualifying engineering experience. The supervised experience must take place under the engineering path of the EIT and allow them to enhance and apply technical skill (National Council of Examiners for Engineering and Surveying, 2023). It must also be an encompassing experience providing the EIT exposure to multiple aspects of professional engineering that increase in task complexity over the course of the four-year experience (National Council of Examiners for Engineering and Surveying, 2023). Finally, a passing score on the PE exam is needed before applying for and receiving licensure. Similar to the FE exam, the PE exam is an online test. It is about two hours longer than the FE exam and is a closed-book test (National Council of Examiners for Engineering and Surveying, 2023). PE licensure is awarded upon successfully completing all four requirements and application approval.

Executive Summary

Background and Goal

Per- and polyfluorinated alkyl substances, commonly known as PFAS, are a broad class of chemicals gaining notoriety for their prevalence in urban and natural environments. PFAS are a concern to human health, so removing them from wastewater before they can enter the environment is paramount for preventing buildup and bioaccumulation within the environment. The goal was to separate PFAS from water and create a concentrated waste stream of aqueous PFAS using bubbles as a collector.

Methodology

We started by designing a batch reactor system to produce gas bubbles that PFAS would theoretically adsorb onto, thus creating a concentrated PFAS layer at the top of the reactor as the bubbles rose through the water. We made a standard curve with PFAS in a methylene chloride solution using gas chromatography-mass spectrometry (GC-MS). Porous stones placed at the bottom of the reactors produced bubbles with compressed air, and we had in-line valves and rotameters for each reactor. Sampling tubes placed at the bottom of each reactor used a peristaltic pump to retrieve the sample. We adapted a sample preparation method for LC-MS-MS from EPA Method 537.1. In our methodology, evaporation using a RapidVap and reconstitution with methylene chloride followed solid phase extraction (SPE) before injection into GC-MS for analysis.

Results and Discussion

We designed the reactors to allow airflow control and monitoring for each reactor body. These air tubes then went to porous stones that made uniform bubbles. PFAS molecules would collide with the rising bubbles and either dissolve into the air phase or adsorb to the surfaces of the bubbles. However, we could not find the exact mechanisms and mass transfer phenomena within the literature. We planned on operating the reactors for 30 minutes. We placed the sample collection tube on the bottom of the reactor to minimize disturbance of the water column. Once we pumped the samples, we would need to use our sample preparation methodology to be able to analyze them in a GC-MS. Starting with SPE, we tried two reversed-phase cartridges: Supelclean Envi-18 and Agilent Bond Elute LMS. Using both cartridges, we tried eluting with methylene chloride before injecting directly into the GC-MS, and we tried eluting the Agilent Bond ELute LMS cartridges with methanol, evaporating with a RapidVap, reconstituting with methylene chloride, and finally injecting into the GC-MS. All of these trials failed. For the methylene chloride elution trials, we believe it was because the methylene chloride did not dissolve the 6:2 FTOH from the column. For the methanol elution trials, we believe that both the 6:2 FTOH and methanol evaporated in the RapidVap. This meant we needed to find a solvent that would dissolve 6:2 FTOH from the SPE cartridge and work as a mobile phase in GC-MS. Ethyl acetate has potential for this, but our results were inconclusive.

Conclusions and Recommendations

We need further methodological development for utilizing GC-MS. Ethyl acetate as a mobile phase for PFAS analysis in GC-MS has promise. The treatment system developed in this project for PFAS removal from water may be a cost-efficient way of creating a concentrated

waste stream for PFAS, which would improve overall treatment effectiveness. Further research into mass transfer mechanisms using a surfactant and bubbles will likely amend the treatment process.

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1.0 Background

1.1 Introduction to PFAS

Per and polyfluorinated alkyl substances (PFAS) refers to a broad class of chemicals gaining notoriety for their prevalence in urban and natural environments (Zodrow et al., 2022). Their notoriety arises from widespread usage of PFAS in consumer products and their resistance to breaking down by biotic and abiotic processes (Kotthoff et al., 2015; Washington et. al, 2010; Sáez et al. 2008). Their resistance to degradation has earned this class of chemicals the moniker “forever chemicals”. These forever chemicals can be found in numerous products, including cleaning products and fire-fighting foams. What makes PFAS useful for these products are the surfactant nature and the strong and stable carbon-fluorine bonds that resist bonding and degradation. The surfactant nature comes from the combination of a hydrophilic head functional group and a hydrophobic tail that contains carbon-fluorine bonds (Sáez et al. 2008). The hydrophobic tail has a portion of the tail that follows the pattern C_nF_{2n+1}. Perfluorinated substances have all available bonding sites on the carbon tail fluorinated, and polyfluorinated substances have some bonding sites replaced with hydrogen atoms. The tail portion of PFAS molecules can also be classified by the number of carbon atoms it contains; generally long chain PFAS molecules are considered either six or seven carbon atoms long, however definitions can vary. PFAS species are also commonly acids, with this dissociation occurring at the head group (Buck et al., 2011). PFAS are surfactants, or surface active agents, which are a kind of chemical that adsorbs to interfaces because of this bipole nature. They align their nonpolar tails to face the most nonpolar side of an interface and their polar heads to the most polar side of an interface. In an aqueous solution, this would mean that the heads of the surfactants are aligned to face the water phase, and the tails face the other phase. This is the case for the reactor in this project, with the nonpolar phase being air bubbles rising through a column of water. Surfactants act as a bridge between the two phases, and this results in two main effects: decreasing surface tension and decreasing interface tension. Surfactants also will form micelles at high enough concentrations; micelles are groups of surfactants that align in a predictable manner with either the head or tail facing the inside of the group and the other side facing the solvent phase. The lowest concentration that makes this effect is called the critical micelle concentration (Farn, 2006).

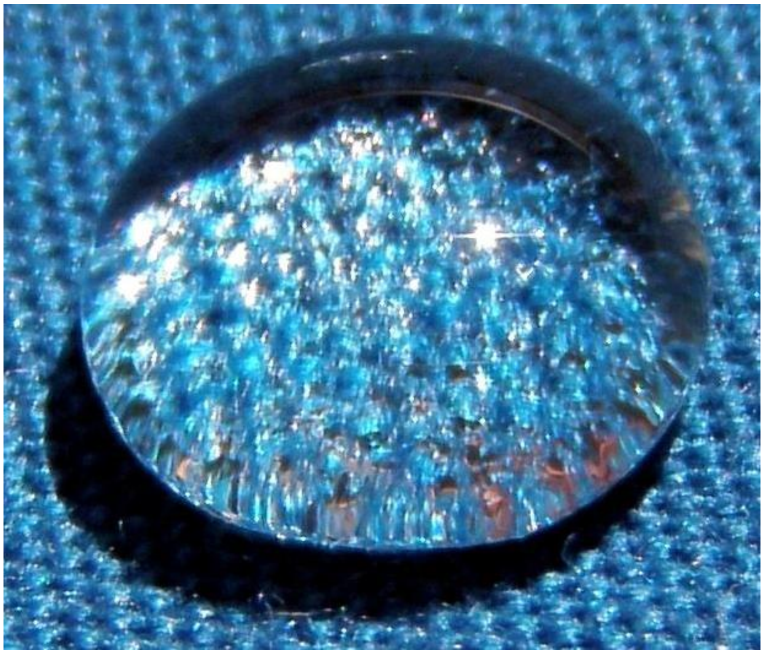


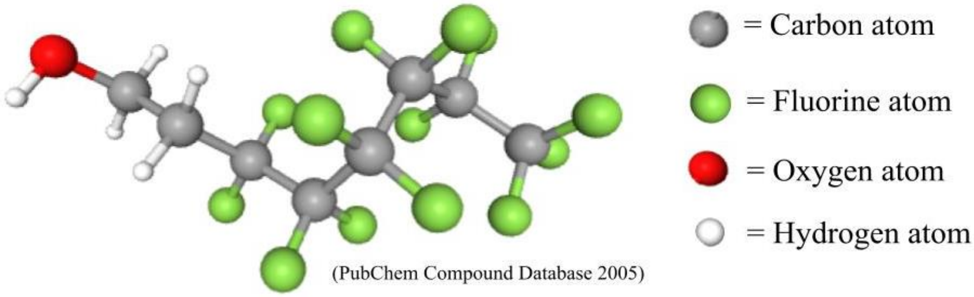
Figure 1. PFAS has properties that make it a common part of water repellent fabrics. Image from Brocken Inaglory under the Creative Commons Attribution-Share Alike 3.0 Unported.

As an inert chemical with repellant characteristics, PFAS lends itself to being a common surfactant material in industry (Kotthoff et al., 2015; Zanolli, 2019). Yet, the same properties that make PFAS beneficial in consumer products may make it a human health risk, and this risk will continue to accumulate in the environment due to PFAS resisting degradation (Huet, 2022). As the potential toxicity, carcinogenicity, and bioaccumulation of this emerging contaminant poses a global health concern, companies and organizations continue searching for novel, inexpensive, and effective treatment methods (Peake, 2020). This past July in 2022, the United States Environmental Protection Agency (USEPA) awarded $25,000 to students of the University of Missouri to design an affordable filtration system for treating PFAS in drinking water (Beisser, 2022). As more treatment options become available, it is important to make a distinction between the kinds of PFAS that different treatment operations target. PFAS can be distinguished into two types: volatile and non-volatile substances. This project focuses on volatile PFAS species due to analytical device restrictions. Currently, there are few treatment methods on the market for volatile forms of PFAS (Liu et al., 2019).

1.2 About 6:2 FTOH

One such group of volatile PFAS substances are fluorotelomer alcohols (FTOH). Such substances include repeating units of strong carbon-fluorine bonds along a carbon backbone with some number of alcohol functional groups at one end (Liu et al., 2019). Specific molecules of the FTOH group are referred to by the number of fluorinated carbons in a ratio to the number of carbon ethyl alcohol groups. Many of the strong FTOH molecules include two carbon ethyl alcohol groups. Amongst those molecules, the number of fluorinated carbons dictates their strength in relation to each other (Liu et al., 2019). More fluorinated carbon bonds equate to greater stability, thermal conductivity, and hydrophobic properties (Liu et al., 2019). Such properties make them useful in products like plastics, stain repellents, and resin. An example of a hydrophobic fabric is shown in Figure 1. Once items containing FTOH are disposed of, they collect in the environment and can biodegrade into perfluorinated carboxylic acids (PFCAs) (D'Eon & Mabury, 2007). PFCAs are persistent in the environment and are known to bioaccumulate in the blood of animals, including humans (D'Eon & Mabury, 2007).

Manufacturers usually use one or more of four forms of fluorotelomer alcohols: 4:2 FTOH, 6:2 FTOH, 8.2 FTOH, and 10.2 FTOH. 6:2 FTOH consists of six fluorinated carbons and two carbon ethyl alcohol groups configured as shown in Figure 2 below.



(PubChem Compound Database 2005)

Figure 2. Stick and ball figure of 6:2 FTOH. Image from PubChem PubChem Identifier: CID 69537 https://pubchem.ncbi.nlm.nih.gov/compound/69537#section=3D-Conformer

At room temperature, 6:2 FTOH is a clear liquid that boils at around 91-93°C and has a pungent odor (Doug Discovery, 2022). It has an aqueous solubility of 18.8 mg/L and Henry's constant 2.30984 gas conc./aq conc. (Wu & Chang, 2011).The surface adsorption potential of 6:2 FTOH could allow it to be removed from an aqueous solution via bubbling.

1.3 Air-liquid Mass Transfer Theory

There are two mechanisms for PFAS removal in our reactor: liquid to air mass transfer and interfacial adsorption.

Air-liquid water treatment processes tend to be used for the removal of volatile contaminants and dissolved gasses. Pollutant can be transferred from either phase, but this paper will focus on transfer of pollutant from the liquid phase to the air phase, or desorption using a bubbler (Crittendon et al., 2012).

All air-liquid processes are governed by mass transfer between the air and liquid phases. Transfer of mass between phases occurs at the air-liquid interface. The driving forces between the mass transfer is the surface concentration of pollutant in both phases, the surface area of the interface, and the Henry’s constant of the pollutant. The pollutant moves from high concentration to low concentration through diffusion to reach equilibrium. In the case of this paper, 6:2 FTOH will move from a high relative concentration in a wastewater stream to a lower concentration of an incoming gas. The likelihood of the pollutant to move between gas and liquid phases is defined by the pollutant’s Henry’s constant. For the purposes of this paper, we will use a unitless form of the Henry’s constant with [gas concentration/aqueous concentration] (Edzwald, 2011). The movement between the two phases is also dependent on the surface area between them; more pollutants are able to move over higher surface area. This principle is important for the design of any reactor that uses an air-liquid process. For any air-liquid process, the closer the system gets to equilibrium, the slower the process becomes. There are other factors that may affect the mass transfer rate, such as pH (Droste, 2019), ionic strength, and surfactants (Edzwald, 2011).

1.4 Aeration Bubbler

The interfacial adsorption of PFAS in our reactor is similar to dispersed air floatation (DAF). DAF usually refers to dissolved air floatation, but it can also refer to dispersed air floatation. Both methods remove charged particles from water, but dispersed air floatation uses much larger bubbles that are produced by a sparger or diffuser. The smaller bubbles in dissolved air floatation help increase removal, which makes dissolved air flotation more common than dispersed air floatation. A possible schematic for DAF is shown in Figure 3 below. In conventional DAF, the input stream of water requires a preparation step of coagulation and flocculation. The ideal floc particle size for DAF is below 100 micrometers, smaller than gravity style settling tanks, because larger particles would increase the density of bubbles, hindering rise (Edzwald, 2010).

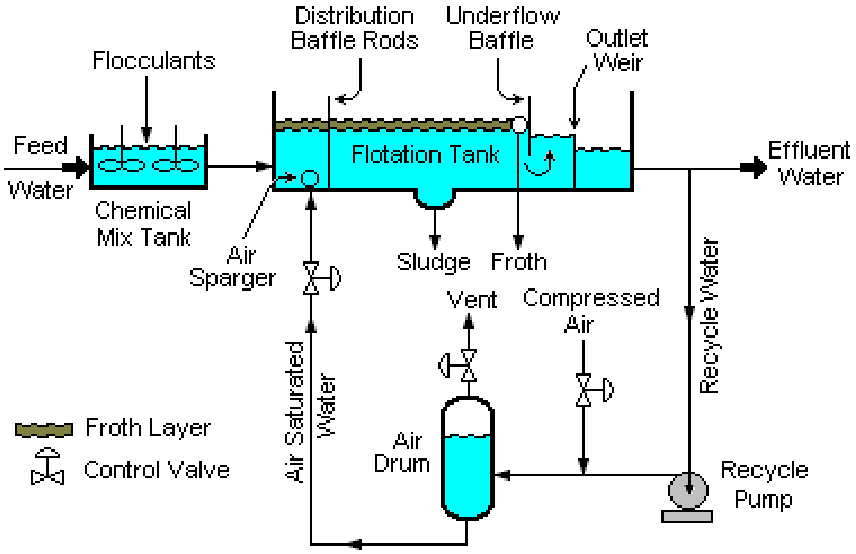


Figure 3. A possible schematic for DAF removal. Image from Mbeychok.

Our application is similar to DAF because it is a surface active process using large bubbles. Unlike DAF, our process does not remove discrete particles; it relies on the surfactant nature of PFAS to adsorb onto the interface of the rising bubbles. Because of this difference, the system cannot be completely modeled as if it were DAF. There is currently no theoretical model for mass transfer of surfactants onto bubbles as the current body of literature is uninterested in this particular mass transfer phenomena. Instead, focus and research is put into other forms of surfactant removal (Palmer & Hatley, 2018), surfactant effects on DAF (Basařová & Zedníková, 2018), surfactant effects on bubble rise (Cuenot et al., 1997), and surfactant effects on the geometry of moving bubbles (Clift et al., 1978). However, some theory of DAF could be applied: the bubbles must collide with surfactant molecules for them to be removed, the bubbles will be denser with more surfactant adsorbed, and the collisions between the molecules and bubbles will be determined by the molecule size and bubble size.

Bubbling air through surfactant-polluted water will have some amount of both mechanisms: dissolving into the air within the bubble, and adsorbing onto the surface of the bubble. It is likely that the ratio of these two mechanisms will be different for each individual chemical, and this ratio and overall removal could be impacted by unique properties such as Henry's constants, critical micelle concentration, surface activity, and charge (Kancharla et al., 2022), along with factors relating to known DAF and aeration principles like concentration, bubble size, and contact time. Not only are the mechanisms themself not well defined, but the equilibrium between those two processes would be another factor to investigate. It is possible that the system will be thermodynamically favorable at one set ratio between the two, or it could change to favor a higher surface concentration ratio or vice versa over the rise time of the bubble. If PFAS or surfactant removal via bubbler shows promise, then further research should be done into exactly how these two competing mechanisms work.

1.5 Foam Fractionation Theory

This bubbling process is called either bubble fractionation or foam fractionation; foam fractionation refers to a process that forms a stable foam at the top of the column of water, and bubble fractionation refers to a process that does not form a stable foam (Stevenson and Li, 2017). A visual of foam or bubble fractionation is shown in Figure 4 below. Foam fractionation has proven to remove high amounts of PFAS from contaminated water in pilot scale removal projects, however it is still relatively unknown as a commercial process (Smith et al., 2022). There is some evidence to show that foam fractionation works better for long chain PFAS molecules, likely because these species are more hydrophobic, which would strengthen the adsorptive surfactant properties of the molecule. A foam fractionation removal project in

Australia for treatment of contaminated groundwater had over 99.5% removal of long chain PFAS including PFOS, PFHxS, and PFOA (Burns et al., 2021).

Figure 4. This image is an example of a foam or bubble fractionation bubbler. If a stable foam forms on top of the column, it would be considered foam fractionation. If a stable foam does not form, then it would be considered bubble fractionation.

There is varied evidence as to the effect of pH on removal from foam fractionation, and this likely indicates that pH does not affect the process much. There is some evidence to show that some additions to the influent water may increase removal; cosurfactants and dissolved ions have shown promise to do this (Smith et al., 2022).

The major difference between bubble fractionation and foam fractionation is where the higher concentration of surfactant is after treatment. In bubble fractionation, the bubbles pop, leaving high concentration of surfactant in the bulk phase of the liquid at the top of the column of water. In foam fractionation, the surfactant stabilizes the foam that is generated at the top of the column of water. This means that there is a concentration gradient between the high concentration of surfactant still adsorbed to the bubble, and the bulk concentration of surfactant that is in any liquid that has been carried by the foam that is produced by the reactor (Stevenson & Li, 2017).

2.0 Methodology

The goal of this project was to identify a novel treatment model for PFAS. To do this, we needed to both construct a reactor to test our hypothesis, and we needed to find an analysis method to verify any treatment that the reactor may do. This lead us to identify three goals:

1. Design and build a reactor to test our hypothesis
2. Develop a sample preparation procedure for GC-MS
3. Develop GC-MS settings for reliable and accurate results

2.1 Reactor Design

Our hypothesis for removal of PFAS is that using the surfactant properties of PFAS, we could bubble air through a column of water and have the PFAS adsorb to the surface of the bubbles and rise to the top of the column of water. We then needed a way to contain aqueous sample, bubble air through, and remove samples with minimum disturbance of the water column. To contain the column of water, we decided to use 1-liter graduated cylinders as shown in Figure 5 below. This would give us an easy way to confirm that we had the same volume for consecutive runs, and it would give us a way to confirm sampling volumes.

The next part of our design related to air entering the column of water. We needed to have a consistent, repeatable air flow rate that creates a consistent bubble size. We used a compressed air intake from a bench that flowed into a manifold with individual valves for flow control within 0-4 L/min, which is what our rotameters measured. Then the air flowed through individual in-line rotameters for flow monitoring. From there the ¼ inch inner diameter tubes ran to porous stones to produce bubbles. The porous stones had an unknown pore size and were used because of their availability. We ran the reactors for 30 minutes for each run at a static air flow rate.

Once the reactor was done with the treatment run, we would need to take the sample out of the cylinders. To do this, we placed another set of ⅜ inch inner diameter tubes at the bottom of the cylinders. These tubes ran to Masterflex L/S standard digital drive peristaltic pump heads that were connected to the same pump for convenience. They were at the bottom for consistency between runs. We planned on running the peristaltic pumps at a low flow rate to minimize disturbance of the column through the Bernoulli's effect. Further discussion of our reactor design is in 4.0 Conclusion and Recommendations. Our sampling was done with a peristaltic pump attached to tubes placed at the bottom of each cylinder. The sampling flow rate was the same for each cylinder.

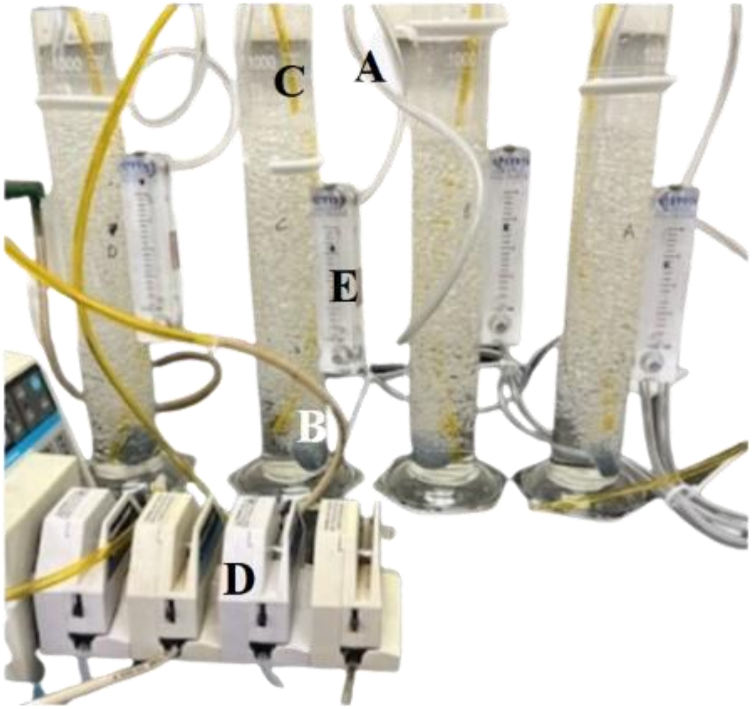


Figure 5. Annotated reactor: A is the air input tube, B is the porous stone, C is the sampling tube, D is the Masterflex peristaltic pump, E is the rotameter, and not pictured is the manifold with valves for individual air flow rates.

2.2 Sample Preparation and Storage

All samples were prepared with purified water (Thermo Scientific Nanopure) and 6:2 FTOH purchased as 97% purity from Oakwood Chemical (Estill, South Carolina). All samples were stored without headspace in a $4^{O}C$ laboratory refrigerator. The solvents used were methylene chloride 99.9% purity from Fisher Scientific (Pittsbrgh, Pennsylvania), methanol 99.9% purity from Fisher Sci (Pittsburgh, Pennsylvania), and ethyl acetate from Pharmco.

2.3 Sample Preparation

Before we could run our reactor, we needed a viable analysis method. We had a GC-MS available to us, but the EPA PFAS analysis procedures all use LC-MS. Our first idea was to try to adapt EPA Method 537.1 for use in GC-MS. The reactor produces aqueous samples, but we needed to reconstitute the PFAS from the samples into a solvent that could be run in the GC-MS. We originally used methylene chloride for this purpose, so we needed a way to dry the sample from the reactor to then reconstitute with methylene chloride. Our first idea was to dry the samples in a RapidVap under a gentle nitrogen stream, but 6:2 FTOH has a lower boiling point than water at $92^{O}C$, so the samples needed to first go through a separation method that does not use evaporation. We decided to use SPE for this first step. With SPE, we could titrate our aqueous sample through a cartridge, and elute with a solvent of our choice. If this solvent was able to go into the GC-MS, then we would inject our samples directly from this step.

2.4 SPE Procedure

We used both Supelco Envi-18 Tubes (bed wt. 500mg, volume 3mL) and Agilent Bond Elute LMS (bed wt. 500mg, volume 6mL). We first conditioned the tubes with 3mL of methanol followed by 3mL of reagent grade water. We then eluted aqueous 6:2 FTOH samples through these tubes at 1mL/min. Once the solutions eluted fully, we eluted the remaining 6:2 FTOH with methylene chloride or methanol. Our process is laid out in Figure 6 below.

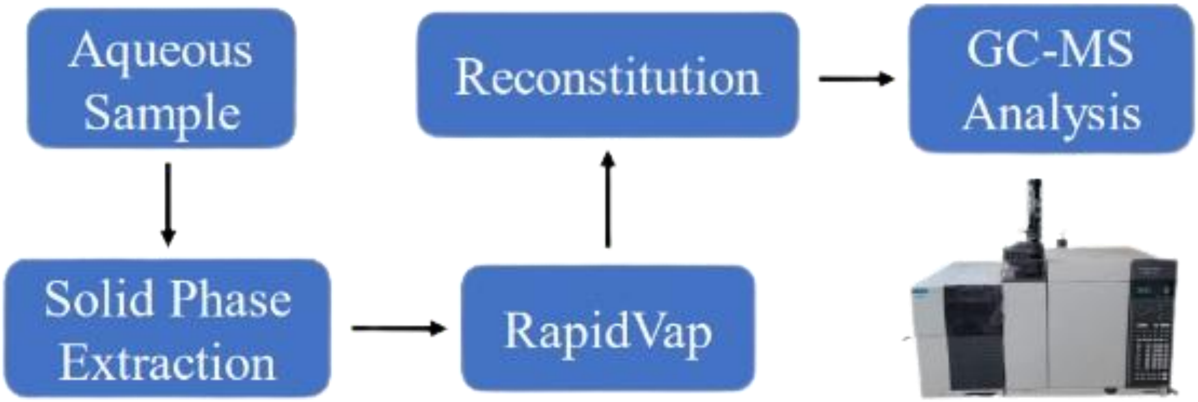


Figure 6. Flowchart of sample preparation and analysis procedure. Also pictured is the Agilent Technologies 7890B GC system with a 5977B MSD.

If we could not inject the SPE elution solvent into the GC-MS, we needed to use a RapidVap nitrogen dryer to dry the solvent. We set the RapidVap to 45^{O}C with no spinning and a nitrogen flow rate of 10 psi. Once the solvent was dry we reconstituted the 6:2 FTOH into methylene chloride, then injected into the GC-MS.

2.5 GC-MS Procedure

For GC-MS analysis on an Agilent Technologies (Santa Clara, CA) 7890B system with a 5977B MSD, we needed to find settings that would give a sharp, distinct peak of 6:2 FTOH dissolved in methylene chloride. This required trial and error to find the appropriate ramp settings for our column. We used a splitless injection of 1µg and initially used settings from Ayala-Cabrera et al. (2020) but we found that an oven temperature of 250^{O}C, an initial temperature of 50^{O}C, and a single ramp of 2^{O}C/min to a final temperature of 80^{O}C provided distinct peaks of 6:2 FTOH with the Agilent 19091S-433UI HP 5ms ultra inert 30m x 250µm x 0.25µm column in our GC-MS. We made a standard curve with 6:2 FTOH dissolved directly in methylene chloride for potential analysis. However, we were not able to use methylene chloride in the GC-MS due to issues with sample preparation. Further discussion of sample preparation is in the Results and Discussion section. We tried using ethyl acetate as a mobile phase in the GC-MS as Wu, Y., and Chang, V. W. (2011) and Portolés T. et al. (2015), however we were not able to adjust the oven settings to create a distinct peak of 6:2 FTOH.

2.6 Glassware Cleaning

All glassware was cleaned with detergent and rinsed with the hottest water available. The glassware was then rinsed with methanol before air drying.

3.0 Results and Discussion

Our reactor design would allow for testing basic foam or bubble fraction along with testing additional parameters such as pH, addition of cosurfactants, and ionic strength.

3.1 Sample Preparation Procedure

The goal of our sample preparation procedure was to take an aqueous sample from the reactor and reconstitute the 6:2 FTOH in a solvent that could be injected into the GC-MS. We wanted to use methylene chloride for GC-MS analysis, so we started SPE elution with methylene chloride. Since our samples were a nonionic, aqueous solution, we decided to use a reverse, or nonpolar phase of SPE cartridges. This phase polarity matches the advised polarity in EPA Method 537.1.

3.2 Supelco Envi-18 SPE Cartridges

We first used Supelco Envi-18 cartridges, which are reverse phase. The stationary phase in the Envi-18 cartridges is bonded silica, while the stationary phase in EPA Method 537.1 is styrene divinylbenzene (SDVB), a different reverse phase media. We selected reverse phase SPE cartridges because reverse phase SPE works best for aqueous solutions with nonionic analytes (Mitra S., 2004). Results from GC-MS analysis provided a chromatogram that did not show the presence of any 6:2 FTOH in the sample after running 6:2 FTOH and methylene chloride through Supelco Envi-18 cartridges. Potential reasons are that the 6:2 FTOH did not adsorb to the bonded silica stationary phase during SPE, or that the methylene chloride was not strong enough as a solvent to elute the 6:2 FTOH from the cartridge.

3.3 Agilent Bond Elute LMS Cartridges

Bonded silica did not work as an SPE media for 6:2 FTOH and methylene chloride, so we changed the SPE columns to Agilent Bond Elute LMS, which is a reverse phase cartridge that uses SDVB. We again tried using methylene chloride to elute the adsorbed 6:2 FTOH from the SPE column, however the GC-MS chromatogram again did not show the presence of 6:2 FTOH. Since this phase matches the EPA Method 537.1 phase, we believed that methylene chloride was not a strong enough solvent to elute the adsorbed 6:2 FTOH, so we needed to consider a new elution solvent.

3.4 Elution with Methanol

EPA Method 537.1 specifies using methanol as the solvent for SPE, and since the procedure was designed for LC-MS, the resulting solution can be injected into the LC-MS without an additional step. However, we could not inject methanol into the GC-MS due to the chance of methanol not fully vaporizing in the oven, so we needed to dry the resulting solution with a RapidVap nitrogen dryer. After we attempted to elute with methanol, we performed RapidVap drying at 45℃ and 10 psi nitrogen flow rate. We chose this drying temperature to be high enough to evaporate the methylene chlorine, but low enough to allow 6:2 FTOH to remain in the sample vial. We then reconstituted the vials with methylene chloride. This attempt also failed to show any 6:2 FTOH in the GC-MS, so we decided to run a control test for the RapidVap.

3.5 RapidVap Control Test

To rule out the RapidVap being a potential source of error for evaporating 6:2 FTOH, we ran a control test for the RapidVap. We mixed two solutions directly with 6:2 FTOH in methanol and dried them in the RapidVap. After reconstitution and GC-MS analysis, one of the samples showed no detection of 6:2 FTOH, and the other sample detected at an order of magnitude lower than expected as shown in Appendices A and B, respectively. If all of the 6:2 FTOH had remained in the sample, it would have detected 375 ppb, but the sample detected at 20.5 ppb as shown in Figure 7 below. After this control test, we decided that the RapidVap was not able to consistently retain all of the 6:2 FTOH in the vial. Because of this inconsistency, we decided to remove it from our sample preparation method. Consequently, we needed to find a solvent that would both elute the 6:2 FTOH from the SPE columns and be suitable for GC-MS analysis.

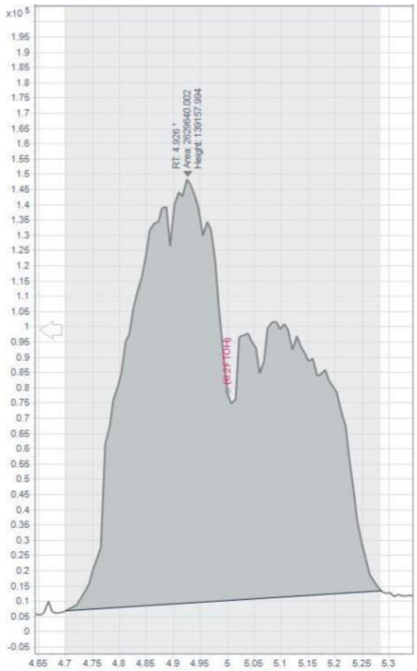


Figure 7. The peak area curve of the RotaVap control test detected less 6:2 FTOH than expected. On the y-axis is abundance and the x-axis is retention time (minutes).

3.6 Ethyl Acetate as a GC-MS Solvent

We found two successful examples in the literature that used GC-MS analysis for 6:2 FTOH, The Effect of Surface Adsorption and Molecular Geometry on the Determination of Henry's Law Constants for Fluorotelomer Alcohols by Wu and Chang (2011) and Gas Chromatography-Tandem Mass Spectrometry with Atmospheric Pressure Chemical Ionization for Fluorotelomer Alcohols and Perfluorinated Sulfonamides Determination by Portolés et al. (2015). Both papers used ethyl acetate to elute 6:2 FTOH through SPE columns before directly injecting into a GC-MS (Wu & Chang, 2011; Portolés et al., 2015). Initially, we attempted to create a standard curve of 6:2 FTOH in ethyl acetate, but the results of this attempt were inconclusive. A potential source of error is that 6:2 FTOH may have eluted with the solvent, causing no 6:2 FTOH to appear on the chromatogram.

3.7 Reactor Design and Use

Some parameters to be evaluated and optimized are provided below. The reactor body is a 1-liter graduated cylinder with compressed air pumped through ½” ID tubing from compressed air through a porous stone located at the base of the graduated cylinder. Air bubbles produced by the porous stone rise through the height of the graduated cylinder. We monitored the air flow rate with in-line rotameters that measured flow from 1L/min to 4L/min. We placed a ¼” ID sampling tube at the bottom of each graduated cylinder that was connected to a peristaltic pump head. Overall, our design is a system of four reactors as shown in Figure 5.

3.7.1 Processing a Stable Foam

There is no consideration in the reactor design of how to process a stable foam, if one forms. If a stable foam forms, we would need a reproducible method of how to remove the foam and collapse it for liquid analysis. The foam would need to be removed mechanically, either broken by physical or chemical means, and finally collected and processed for analysis.

3.7.2 Bubble Size

One parameter that could be easy to change would be bubble size. Collector bubble theory suggests that smaller bubble sizes would result in higher removal efficiencies due to its greater surface area, so it would be an important parameter to investigate (Edzwald, 2011). However, we only had one set of porous stone diffusers, so we could not change the bubble size, and the pore size for these stones was not reported. Using different sized porous stones with defined pore sizes would allow for a more rigorous investigation of the mass transfer phenomena of foam fractionation.

3.7.3 Column Height

Another parameter that would directly affect removal efficiency is the height of the column of water. We planned to take four evenly spaced samples from each reactor, and the height of a 1-liter graduated cylinder might not allow enough stratification to make a removal correlation.

3.7.4 Sampling Methods

The sampling method we intended to use was with a peristaltic pump connected to tubes placed at the bottom of each reactor. We intended to run the peristaltic pump at fairly low flow rates, less than 150 mL/min to cause as little disturbance of the overall column as possible. However, even at low flow rates, the disturbance caused by the sampling may irrevocably affect the concentrations of the samples. A potential fix for this would be a reactor body with a tap at the bottom, similar to a burette.

3.7.5 Additional Parameters to Change

Finally, there are other parameters that could be changed to try to enhance removal. Using a different gas, for example ozone, could potentially increase removal by increasing the polarity difference between phases. Additions like a cosurfactant could also affect the interface and potentially increase removal. There is some evidence to show that addition of ions can also increase removal. We can also test the effect of pH on removal with the original rector design. All of these could be tested after the initial hypothesis test of 6:2 FTOH removal in reagent grade water.

4.0 Conclusions and Recommendations

Our Conclusions and Recommendations can be broken down into five main points:

1. Ethyl acetate as the mobile phase may have promise for PFAS analysis using GC-MS
2. Apply published EPA methods when possible
3. Our reactor design would be able to test our hypothesis
4. Our reactor design could investigate additional species to increase removal
5. Further research into mass transfer phenomena of foam and bubble fractionation would improve this process

4.1 Promise for Ethyl Acetate as a GC-MS Mobile Phase

Wu, Y., and Chang, V. W. (2011) and Portolés T., et al. (2015) were both successful in using ethyl acetate as the elution solvent for SPE and the GC-MS solvent. In our control test for the RapidVap, we found that it was too inconsistent for use in a sample preparation method, so a successful sample preparation solvent must be suitable for both of these tasks. Ethyl acetate shows promise to have both of these properties and should be investigated further.

4.2 Published EPA Methods

Published EPA methods should be used when possible. We lacked access to a LC-MS for this project, therefore we modified EPA Method 537.1 for use in GC-MS. However, we found difficulty using GC-MS for analysis of PFAS. We recommend using the method as published when possible.

4.3 Reactor Design

We believe that the reactor that we designed and built would be able to test our hypothesis. It is possible that a larger reactor would allow for better stratification of 6:2 FTOH throughout the height of the reactor and therefore, improve the accuracy and applicability of a resulting removal correlation. We chose 1-liter graduated cylinders for ease of use and accessibility, but reactor bodies that are closer in size to full-scale, commercial reactors would improve the accuracy and applicability of results. Due to limited availability of porous stones, we used a set of porous stones with a consistent but unknown pore size. Redesigning the reactor may also allow for changing bubble sizes by implementing porous stones of known and varied sizes.

4.4 Addition of Other Species

Our initial intention with our reactor design was to test the hypothesis of surfactant removal with bubbles by using a solution of 6:2 FTOH and purified water. However, our reactor design could accommodate the addition of other species such as cosurfactants (Burns et al., 2021) and metallic ions (Smith et al., 2022) to increase PFAS removal. It could also be used to test the effects of pH on removal efficiency. These factors could be part of a commercial treatment strategy, so they should be investigated. Successful experimentation with our removal mechanisms using 6:2 FTOH could be related to the PFAS class as a whole. All PFAS molecules display some form of surface activity so if 6:2 FTOH is removed by adsorbing to the surface of bubbles, then it could indicate a new form of treatment for the whole class. This is compounded by 6:2 FTOH being short-chained; short-chain PFAS are less hydrophobic than long-chain PFAS, so removal would be higher for long-chain PFAS.

4.5 Further Research into Foam Fractionation

Successful trials for foam fractionation have been done in Sweden (Smith et al., 2022) and Australia (Burns et al., 2021) for treatment of landfill leachate and contaminated groundwater respectively. Their positive results, cost efficiency, and removal efficiency should prove justification to fully define mass transfer correlations for foam and bubble fractionation. Currently, Foam Fractionation Principles and Process Design (Stevenson and Li, 2017) defines practical design considerations for foam fractionation. Further research into the subject would be beneficial for increasing removal efficiency.

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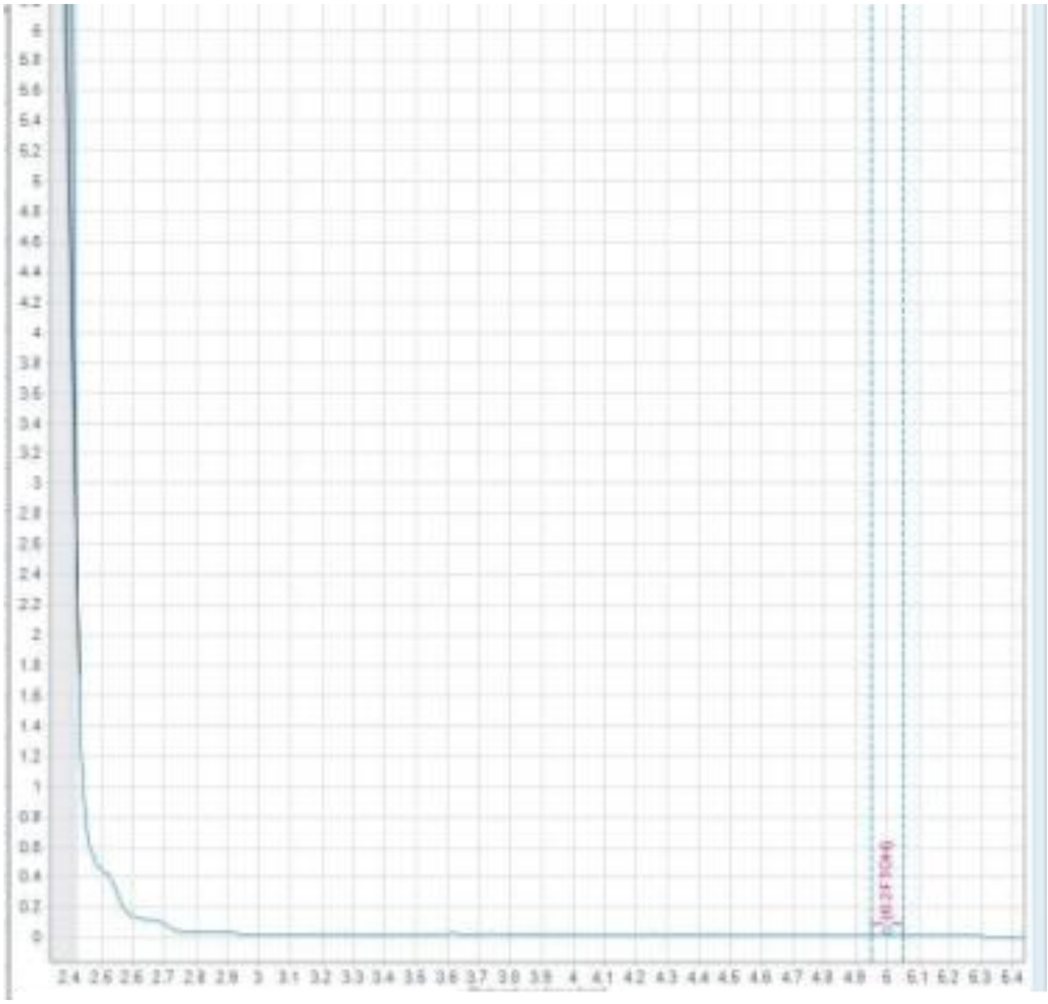
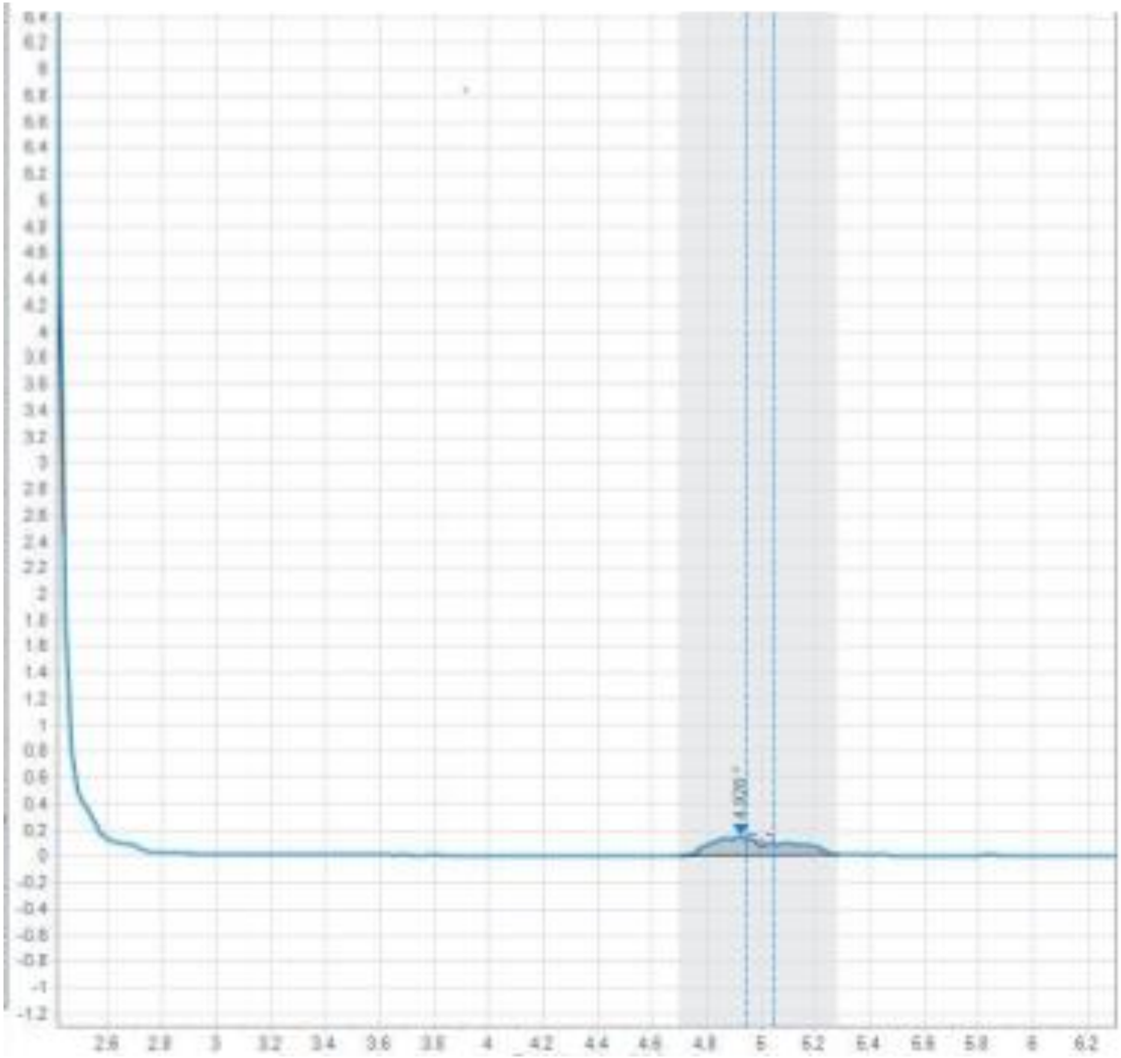
Appendices

Appendix A: Chromatogram of Zero 6:2 FTOH Detection



On the y-axis is abundance and the x-axis is retention time (minutes).

Appendix B: Chromatogram of Lower 6:2 FTOH Concentration than Expected



On the y-axis is abundance and the x-axis is retention time (minutes).