Evaluating PFAS Treatment Method - Ionic Bridging with Divalent Cations

A Major Qualifying Project

Submitted to the faculty of
WORCESTER POLYTECHNIC INSTITUTE
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Degree of Bachelor Science
in
Environmental Engineering and Civil Engineering

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Report Submitted to:
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Abstract

Per- and polyfluorinated alkyl substances (PFAS) define a large group of non-biodegradable fluorinated organic compounds that have garnered widespread attention because of mounting evidence of their ubiquity, prevalence in drinking waters and wastewaters, and potential negative health effects. Variations of the PFAS group are currently found all over the country and over 40,000 U.S. locations are known to emit PFAS into the air through industrial processes.

PFAS are a growing challenge to the environment and the economy, especially concerning the complexities of treating PFAS in water and the significant costs of treatment. In this research, a novel treatment approach using adsorption to treated glass spheres was developed to remove PFOA from water. The effect of divalent cations on adsorption effectiveness was evaluated with the bench scale testing.

Capstone Design Statement

The Accreditation Board for Engineering and Technology (ABET) has established criteria for students graduating in a Bachelor's program in engineering. Among these criteria includes a major engineering design project that integrates engineering standards and applies the knowledge and skills acquired throughout the student's previous coursework.

Students at Worcester Polytechnic Institute (WPI) fulfill this requirement through completion of a Major Qualifying Project (MQP), which serves as the capstone design experience. This MQP demonstrates a rotational adsorption system that utilizes ionic bridging to separate PFAS, specifically PFOA from water. The design of the system was developed through thorough research of the surfactant properties of PFAS and the effectiveness of divalent cationic interactions between PFOA and magnesium chloride. Our team theorized that interactions with the head of the PFAS chain and divalent cations, paired with the adsorption added from interactions at the air-water interface, would create enough activation energy required to extract a significant amount of PFOA from the contaminated source.

To increase the available surface area for potential binding between PFOA and divalent magnesium cations, our team used hollow glass spheres coated with magnesium chloride. This pivotal step facilitates the ion-bridging process between PFOA and the added cations during the reaction. The spheres serve as sites for ionic bridging to occur, enabling the extraction of PFOA. The sphere-salt mixture underwent heating to 715 degrees Celsius in an oven to melt the magnesium chloride onto the spheres. Following this heating process, the coated spheres were introduced into PFOA-contaminated water. This mixture was then spun at a steady rate for 45 minutes. Next, the vessel containing the sample is removed from the device and brought to rest in a refrigerator at 5 Celsius until all hollow glass spheres have returned to the surface.

The sample then underwent Solid Phase Extraction (SPE) based on an adapted version of EPA Method 537.1. This method utilized methanol as the primary carrier. The sample was then brought through a RapidVap until completely dry and prepped for Liquid Chromatography using a methanol water solution.

Professional Licensure Statement

Professional Engineers have a high status of credibility for implementing engineered designs and having bigger responsibilities and project positions from the employer. Given the everyday usage of many of these implemented designs and their importance in transportation, housing, and business, potential clients and clients are able to put a high level of trust in the competency of these Professional Engineers. A PE must undergo four steps in order to complete their license: a four year degree from an accredited institution, four years of apprenticeship under a PE, the completion of the Fundamentals of Engineering exam (FE), and finally the Principles and Practice of Engineering exam (PE). A PE licensure is a legal requirement for engineers and also represents a huge achievement for each individual that obtains it.

Each aforementioned accredited institute must have an academic program approved by the state in order to be a valid program for the four year program step of the licensure process. State approval is often based on prior approval by the Accreditation Board for Engineering and Technology (ABET), a non-profit non-governmental organization, or another organization of similar stature (e.g Canadian Accreditation Board). This approval process itself takes around a year and a half and ensures every program follows their set policies and criteria (Accreditation Board for Engineering and Technology, 2023). During the Engineer in Training (EIT) apprenticeship step of the process, the National Council of Examiners for Engineering and Surveying (NCEES) will conduct assessments to make sure EITs meet laid out qualifications and standards and that they are accountable for their work (National Council of Examiners for Engineering and Surveying, 2023). EITs usually take their FE exam shortly before or after the completion of their four year degree; it is a six hour exam held year round by the NCEES. The specific FE exam that an EIT takes depends upon their discipline and specifications for progression in their desired line of work, and their four years of supervised engineering will begin upon passing the exam. While the engineering experience is in the EIT's chosen path of work, the experience teaches them about a broad range of topics and aspects of professional engineering that increase in difficulty over time (National Council of Examiners for Engineering and Surveying, 2023). After this four year process the EIT is eligible to take the PE exam, which lasts about eight hours and is closed book (National Council of Examiners for Engineering and Surveying, 2023). Upon completing and passing the PE exam the EIT will be awarded PE licensure.

Executive Summary

Background and Goal

Since the 1940s, per- and polyfluorinated alkyl substances (PFAS) have been extensively manufactured and employed across various industries due to their cost-effectiveness and advanced chemical properties. However, heightened awareness of PFAS contamination in drinking water, soil, and even human bloodstream has spurred stricter regulations and a shift away from their use. This project specifically concentrates on devising a novel technique for extracting perfluorooctanoic acid (PFOA) using divalent magnesium cations. Building upon previous experiments, this project hopes to find a potentially revolutionary method for extracting PFAS at low costs.

Methodology

This project aims to observe the ionic bridging that occurs between divalent magnesium cations and PFOA. PFOA contains long carbon chains that are attracted to the positive charge of the magnesium. To facilitate this interaction, additional advection and surface area are introduced into the system. A rotational apparatus and hollow glass spheres fulfill these requirements. By baking the magnesium chloride on the hollow glass spheres at 715 Celsius, the magnesium chloride becomes the anhydrous salt: Mg^{2+}. These coated spheres are then added to PFOA contaminated water at levels anticipated in natural environments. The rotational device then spins end-over-end, allowing collisions between the divalent cations and the carboxyl group at the head of the PFOA chain.

Subsequently, the project employs a Solid Phase Extraction (SPE) and RapidVap Unit, following an adapted version of EPA Method 357.1 as detailed in the appendix. The resultant samples are prepared for analysis on a High Performance Liquid Chromatograph (HPLC) within a methanol solution and later, the LC-QOTF.

Results/Analysis

External standards were prepared at a concentration of 0.04 ppm. Each experimental run aimed to lessen this concentration by half at least. Through the application of SPE and the RapidVap unit, the samples were prepared for liquid chromatography analysis. The HPLC

chromatograms for the tests did not prove any conclusive results. These graphs were compared to theoretical results from Restek to see relevant peaks. The LC-QOTF determined the exact concentrations of PFOA left within the system.

Conclusions/Recommendations

Based on our findings, we have come to the conclusion that there should be alterations within the rotation device in order to simplify extraction. This would include incorporating a mold within to hold the samples that are utilized in the experiment. Utilizing LC-QOTF as an effective analysis tool could prove to yield accurate results. We also recommend using serial dilutions throughout the process to ensure minimal waste accumulation. The experiment proved to be unsuccessful with PFOA remaining at high concentrations within the system.

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Chapter 1: Introduction and Background

1.1 Introduction to PFAS

Per- and polyfluorinated alkyl substances (PFAS) define a wide group of non-biodegradable compounds produced in industrial settings that have garnered widespread attention because of mounting evidence for their ubiquity, prevalence in US drinking water, and negative health effects[1].

Long-chain PFAS and short-chain PFAS are the two categories most often used to characterize this class of compounds. Long-chain PFAS such as Perfluorooctanoic acid (PFOA), as shown in Figure 1, is a man-made perfluorinated compound (PFC) that was introduced in the environment after World War II. PFOA is a stable chemical consisting of an eight carbon chain that is resistant to thermal, microbial and chemical degradation allowing it to build up in the environment over time[2]. The C-F bond is the strongest covalent bond in organic chemistry that contributes to PFOA's outstanding thermal stability and is evident in its boiling point of 372°F[3]. They also exhibit mutually hydrophobic and lipophobic properties, which can be attributed to the low polarizability of fluorine atoms. The extremely slow biodegradation of PFAS, if it takes place at all, results in long half-lives of 8 to 111 years in the soil, allowing PFAS to accumulate in the environment, specifically in soil and groundwater[4]. Understanding the physical and chemical properties of PFAS is critical to begin constructing effective treatment practices.

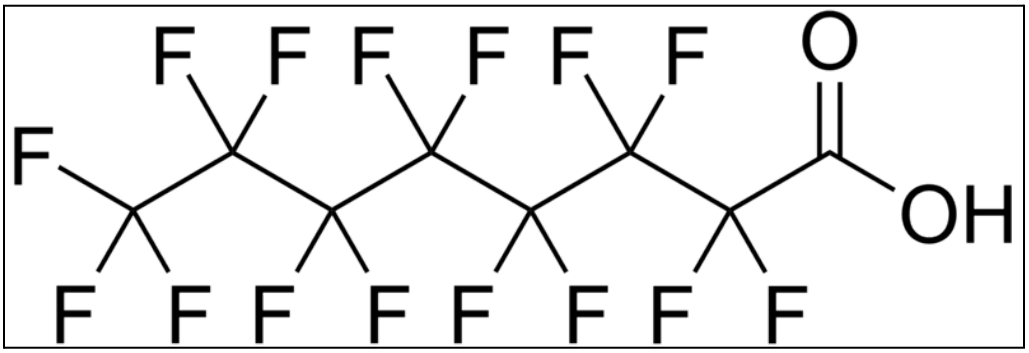

Figure 1. PFOA molecular structure

[1] Gagliano, “Removal of poly- and perfluoroalkyl substances”
[2] Buckley, “Effect of mono- and di-valent cations on PFAS”
[3] McNamara, “Comparison of Activated Carbons for Removal of Perfluorinated Compounds”
[4] Gagliano

1.1.1 Utilization of PFAS and Widespread Existence in the Environment

PFAS have been in production since the 1940s and have been used in a range of products, encompassing firefighting foam, water-repellent sprays, nonstick cookware, food packaging, and textiles designed to resist stains or water[5]. As a result of these compounds being used in a vast array of industries, PFAS is, with little exaggeration, present in almost everything. However, the chemical properties that make PFAS beneficial for consumer products, make the compound a risk to the environment and human health.

While being in hundreds of different manufactured products, the most concerning part, and the issue our team hopes to address first and foremost, is its presence in the air, ground, and water. The Environmental Working Group (EWG), an American Activist group that specializes in research and advocacy in the areas of toxic chemicals and drinking water pollutants, has identified well over 40,000 U.S. locations that pour PFAS into the air via emissions between textile mills and other industrial manufacturing sites. These compounds eventually find their way into water sources, landfills, and the soil, where they accumulate[6] and affect all forms of life in the area. Due to their notable water solubility and the ease with which they migrate into the subsurface environment, PFAS present substantial threats to both human health and the aquifer system and the critical factor is that because of their resistance to decompose, they biomagnify as they move up the food chain[7]. Although dozens of PFAS compounds of varying chain lengths and compositions have been detected in water around the country, the US Environmental Protection Agency (USEPA) has shown particular concern regarding longer chained PFASs with eight or more carbons, such as PFOA[8].

1.1.2 Environmental and Human Health Impacts of PFAS

Epidemiological and toxicological evidence for the health effects of PFASs is growing rapidly. Studies of the general public have linked elevated levels of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) with increased cholesterol, thyroid disease, and weakened immune response[9].

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[5] Gagliano
[6] Spanne, “What are PFAS”
[7] Gagliano
[8] McNamara
[9] Andrews, “Population-Wide Exposure to Per- and Polyfluoroalkyl Substances”

Human exposure to PFAS occurs primarily through drinking water, regardless of whether the water comes from surface water or groundwater[10]. PFOA is not metabolized in the body and its tissue distribution in humans is still unknown, however, a study from 2007 shows it is likely to be present primarily in the liver, kidney, and blood[11]. According to the US Centers for Disease Control and Prevention, PFAS has entered the bloodstream of 98% of the US population at a detectable level[12]. The existing lifetime drinking water health advisory from the EPA stands at 70 ng/L for the combined concentration of PFOA and PFOS in drinking water. According to a study done by the Environmental Working Group, "it is estimated that >200 million people in the United States consume water that contains PFOS and PFOA in concentrations of 1 ng/L or higher." Additionally, the authors of the study estimate that between "18 and 80 million people in the United States consume water that contains PFOS and PFOA at concentrations of 10 ng/L or higher"[13].

1.1.3 PFAS Chemistry

To construct a suitable treatment practice for PFOA, the first step is to understand their unique chemical structure. As mentioned previously, the strong C-F bonds within PFAS molecules allow for extreme resistance and strength in these compounds. In addition, the lone fluorine atoms create an electrostatic shield, allowing for kinetic stability and protection from nucleophilic addition or subtraction[14]. This makes PFAS reactions rare and turns the compound inert. This is also a reason for why breaking down PFAS is taxing and requires extreme temperatures or extreme water conditions. However, pulling the PFAS molecules from water only requires the interaction with the head of the PFAS chain and the divalent cation. This is an event referred to as ion-bridging interactions. Use of divalent cations are important as the biggest factor affecting ion exchange is the ionic charge[15]. The Mg^{2+} has already proven to experimentally work and this is a new way of testing the ionic bridging occurring.

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[10] Kennedy, Gerald L. Jr. "The toxicology of perfluorooctanoate"
[11] Steenland, "Epidemiologic Evidence on the Health Effects of Perfluorooctanoic Acid"
[12] McNamara
[13] Andrews
[14] Leung, "Physicochemical properties and interactions of perfluoroalkyl substances (PFAS)"
[15] Leung

1.1.4 Critical Micelle Concentration

The critical micelle concentration (CMC) refers to the capability of micelle structures to form[16]. Micelle structures are when the molecules aggregate and form masses. For PFAS, this value determines the surfactant's movements of micelle structures on the surface. This alters the energy within the system and therefore the surface tension. This surface tension is important, as "before reaching the CMC, the surface tension decreases sharply with the concentration of the surfactant"[17]. The CMC value of PFOA that was observed for this experiment was 45.54 mg/L. There are many differences with this CMC value in text and experimental work. Multiple experiments have found that this value is disputed. Some reports state that the CMC for PFOA could be as low as 0.0108 mg/L[18]. This experiment will treat the 45.54 mg/L value as accurate unless proven otherwise in our experimentation.

1.2 Previous Success With Divalent Cations

Recently, there have been discoveries that divalent cations can interact with PFAS in such a way that they are extremely helpful with the removal of compounds from water sources. This is due to the hardness of the water and the way cations affect the air-water interface[19]. By interrupting this interface, the PFAS can break away from the water molecules and attach to the divalent cations. Previous experiments have utilized a foam fractionation unit in which there is PFAS-infused water and a steady stream of the desired cation. There were measured concentrations as the system continued and it was seen that there was a steady decrease in the PFAS concentration levels[20]. There was success in this experiment in removing both the larger and smaller chains.

> "The addition of salt to anionic surfactant solutions impacts....the electrostatic repulsion between the surfactant head groups, permitting increased adsorption or higher concentration of surfactants (SDS and PFAS) at the interface"[21]

This quote from Buckley states very succinctly why the addition of cationic molecules assists in the collection of PFAS. There are more reasons though, including that the cations decrease

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[16] Ma, "Molecular designs of enhanced oil recovery chemicals"
[17] Ma
[18] US EPA. "National Recommended Water Quality Criteria - Aquatic Life Criteria | US EPA,"
[19] Buckley
[20] Buckley
[21] Buckley

water's surface tension. This would then allow for the transfer of PFAS to be easier and more fluid. The efficiency of the removal of PFAS would also then be directly correlated to the charge density as proven experimentally[22]. The two cations that have been previously successful are Mg^{2+} and Ca^{2+}. There were anomalies within the Ca^{2+} compared to the Mg^{2+}. The magnesium trials ended up being the more successful experiments.

1.3 Hollow Glass Spheres

The use of hollow spheres in this experiment is to increase the surface area on which the potentially binding between PFOA and the divalent magnesium cations can occur. It also adds a solid phase interaction which will assist in the disturbance of the air-water interface. The addition of the hollow glass spheres also provide the advection necessary for the reaction to occur. This is critical as the breaking of this interface is what allows for the PFOA to ion-bridge with the added cations. These spheres have diameters of approximately 65 micrometers.

1.4 Background of SPE, RapidVap, and LC machines

Solid Phase Extraction (SPE) is utilized for prepping the sample for the end goal of liquid chromatography by extracting the analyte from the water within. This is due to the packing material within the column. The columns utilize polystyrene divinylbenzene (SDVB), a compound that prohibits the perfluorooctanoic acid from flowing through. Methanol is utilized to elute the PFOA from the column as per the adapted version of EPA Method 357.1. This mixture of methanol, PFOA, and potentially small amounts of water is then taken for further experimentation. The RapidVAP unit allows for our PFOA to drop out of solution in a solid form. This happens by applying agitation to the sample while simultaneously supplying nitrogen at a high temperature. The system also alters the pressure in order to affect the physical condition of the mixture. Lastly, Liquid Chromatography is used to separate the individual parts within a mixture and examine the signals given off from the components. The liquid enters in what is referred to as the "mobile phase" which then flows through a gradient valve and eventually the column. The results are sent to a computer connected to the instrumentation.

[22] Buckley

1.5 Project Statement

The goal of the project is to successfully remove PFOA from contaminated water through the ionic relationship available between PFAS and divalent cations while increasing surface area and solid interactions. We are striving to accomplish this goal by utilizing magnesium chloride and hollow glass spheres/beads in a rotational system where there is constant motion. This constant motion should provide the interactions necessary at the air-water interface for the PFAS to separate from the water and adhere to the magnesium.

Chapter 2: Methodology

The goal of this project was to determine a novel treatment model for PFAS within water streams. To achieve this, our team constructed a new experiment based upon previously established and tested theory to determine if better treatment methods are available. For this report, our team utilized the ionic bridging relationship between divalent magnesium cations and PFOA. Our aim was to increase the extraction levels possible by increasing the surface area within the system along with adding a solid phase interaction.

2.1 PFOA Batch Creation

To properly observe the effects of the divalent cations on PFAS removal, all concentrations must be maintained efficiently throughout the experiment. With this goal in mind, our team determined that a batch process would be the most efficient method of testing in terms of repeating the same standards over multiple iterations. The intention is for each experimental run to begin at approximately a concentration of 0.04 ppm PFOA. This concentration choice was predicated on the high sensitivity of the Liquid Chromatography instrument, with a focus on averting any potential carry-over effects. To achieve this, the experiment utilized a ratio of 0.545 milligrams of PFOA per 13.625 liters of reagent water. It is important to note that when dealing with small concentrations such as this one, there is a large room for error. Because each trial used 250 mL of PFOA contaminated water and from this one batch, we were able to complete all of our trials. There will also be internal/external standards that will be produced to compare the resulting plots from experimental trials and are mentioned in greater detail below in the HPLC procedure (see Section 2.5).

2.2 Hollow Glass Spheres and Magnesium Chloride

To ensure proper coating of the magnesium chloride onto the glass spheres, our team decided to bake the sphere-salt mixture in a furnace at ~715 degrees Celsius for a period of 24 hours. This process is fundamental as it evaporates the hydrated water, resulting in the formation of anhydrous salt and leaving behind the ionic charged molecule. To start, the magnesium chloride was weighed to ensure a 10 milliMolar (mM) concentration within a water solvent observing a pH of 7, as successful experiments previously have followed a similar procedure[23].

[23] Buckley

We then weighed out a ratio with ~0.5083 g of magnesium chloride and ~0.5 g of hollow glass spheres. Sample calculations for the amounts of chemicals/spheres can be found in Appendix B and see Appendix A-4 for the lab baking procedure.

As part of our experiment, we systematically adjusted the composition of hollow glass spheres and magnesium chloride added to each 250mL sample. Our objective is to comprehend how altering the quantity of hollow glass spheres can inform us about the optimal mixture needed to significantly reduce PFOA levels when scaling up the process. Following the baking process and the determination of the appropriate quantity of coated spheres for each trial, the magnesium-coated spheres were introduced into the PFOA-contaminated water, preparing them for the Rotational Advection Component phase.

2.3 Rotational Mixing Component Procedure

To contain the PFAS sample with the hollow glass spheres, our team decided to use a 1000 mL (1 L) Nalgene® bottle for its compatibility with the experiment and the size. Sizing considerations were taken into account owing to the restricted dimensions of the rotational device. Also, rotating the 250 mL sample within this voluminous container facilitated complete spinning, ensuring optimal reacting at the air-water interface. An image of the rotational device with samples in the vessel can be found below as Figures 2 and 3.

Figure 2. Rotational device image with samples.

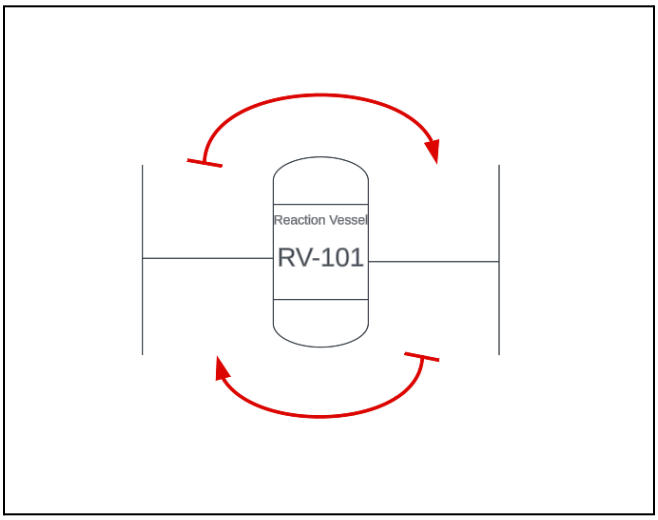

Figure 3. Reaction vessel diagram. Made from LucidChart.

The 1000 mL Nalgene® bottle will then undergo a 60 minute spinning phase to maximize the binding of magnesium with the PFOA molecule head. The rotational motion, combined with the presence of solid particles (glass spheres), provides the necessary advection to disrupt the air-water interface. This disruption facilitates the transfer of PFOA from the water solution to bind with magnesium through ionic bridging. Once the time duration has ended, the rotational device is shut down and the samples are removed from the device and ready to be filtered.

2.4 Filtering

The glass spheres are then filtered from the PFOA spiked solution, with any excess moisture going to the hazardous waste. The remaining PFOA infused water then undergoes solid phase extraction (SPE) to prepare for the Liquid Chromatograph (LC).

2.5 Sample Preparation

Following our novel process' completion, the resulting sample then had to be subjected to solid phase extraction to allow for testing by means of a liquid chromatograph. An adapted version of the EPA's Method 537.1 would provide the background and the standards for our team's procedure for the sample's preparation through SPE. If the steps for the SPE procedure cannot be completed within the timeframe of the lab period, the samples (still remaining within

the 1000 mL Nalgene® bottle) can be loaded into a refrigerated storage at around ~14 degrees Celsius, however 7 degrees Celsius would be ideal.

2.6 Solid Phase Extraction

Firstly, following the sample after the rotational device and/or the refrigerated storage, the SPE run may be prepared. An important note for this process included that the SPE cartridge cannot become dry otherwise the conditioning phase would have to be reset. 15 mL of pure methanol followed by 18 mL of reagent water must be extracted through the cartridge without letting the liquid line drop below the edge of the packing.

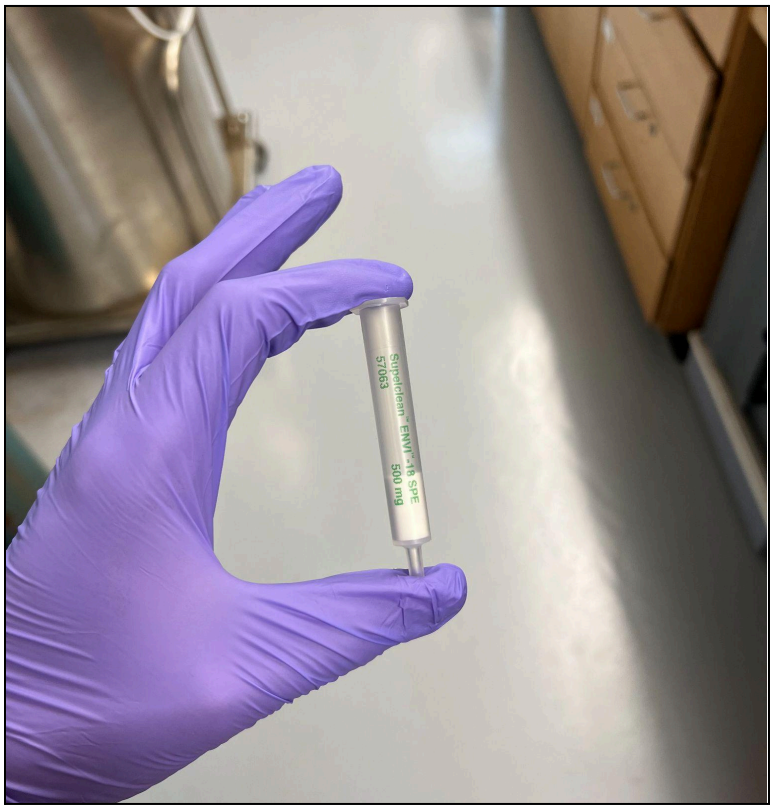

Figure 4. Image of the packing for the SPE cartridge within the lab.

After all of the liquid had been run through the cartridge, an additional 2 mL of reagent water is added to each cartridge, sample transfer tubes are attached from the sample to the solid phase extraction unit, and a vacuum is turned on with a flowrate of 10-15 mL/min. The vacuum is run until all of the sample has been processed within the SPE unit, and the sample is then collected. The complete lab procedure may be found in Appendix A-2.

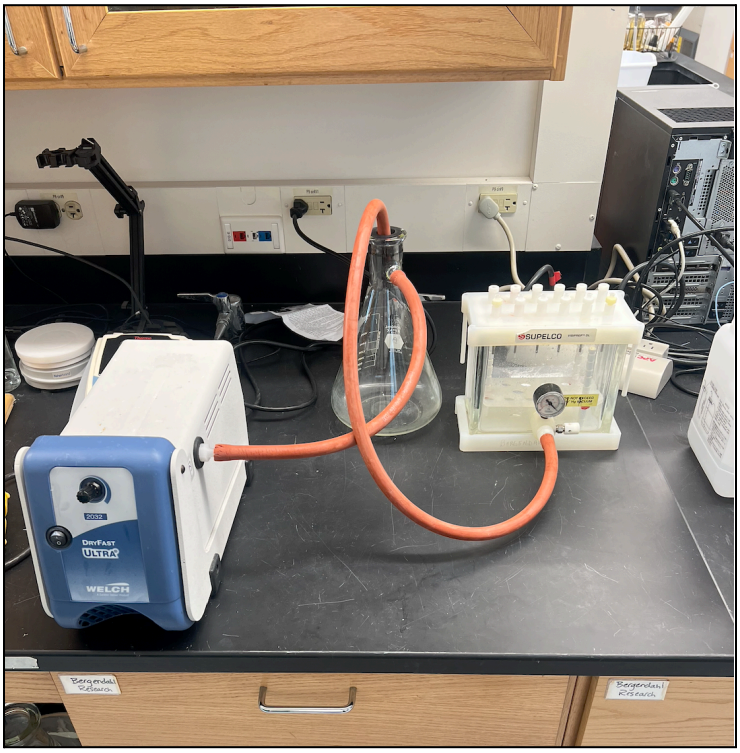

Figure 5. Solid phase extraction image within the lab.

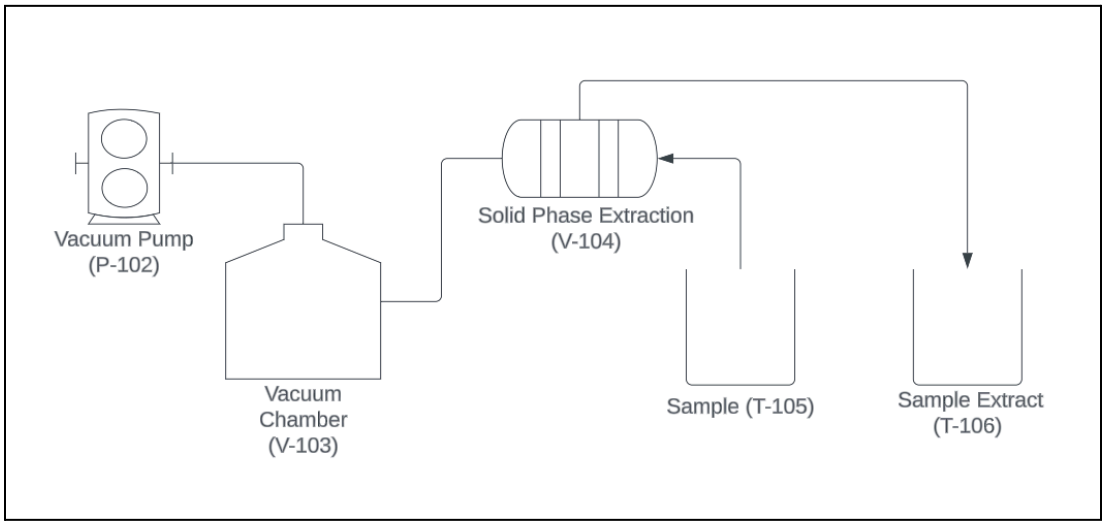

Figure 6. Solid phase extraction diagram. Made from LucidChart.

2.7 RapidVap Operation

Following the SPE procedure, the resulting sample then had to be concentrated to dryness under a gentle stream of nitrogen within the RapidVap unit. This is to ensure all of the water and methanol from the SPE are removed from the sample for the LC. The RapidVap conditions that

were set for our samples were: 68ºC for the nitrogen stream, speed is 22, and a time of 250 minutes. After the RapidVap process is concluded, the sample is taken out of the RapidVap and placed into a collection vial with an added mixture of methanol:water (96%:4%). The sample has the internal standards (IS) added to the collection vial and then is brought over to the HPLC for testing. A more indepth version of this procedure may be found in Appendix A-3.

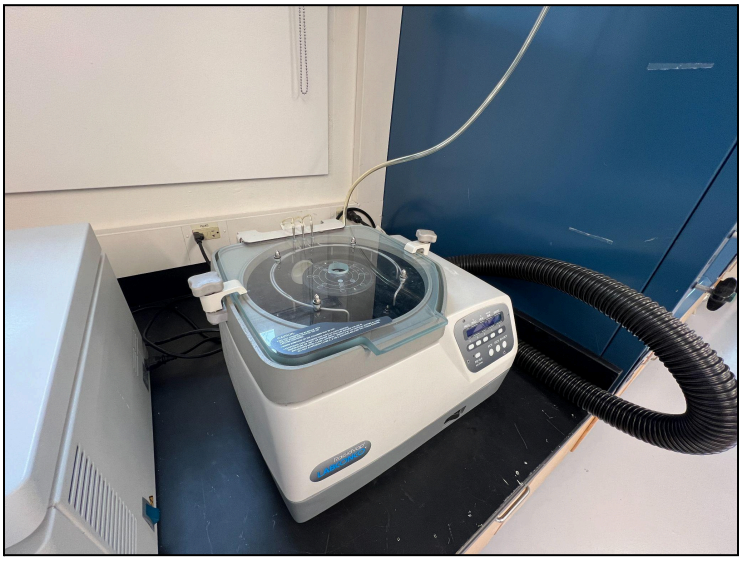

Figure 7. RapidVap image within the lab. White tubing line at the top of the image is the nitrogen line.

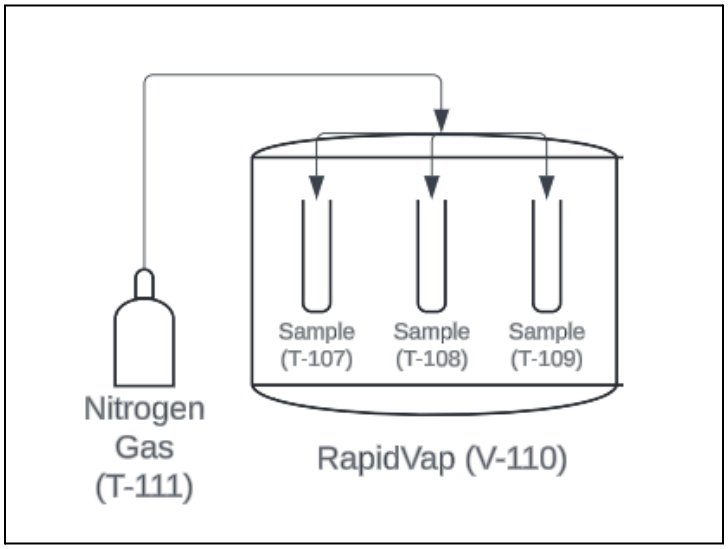

Figure 8. RapidVap process diagram. Made from LucidChart.

2.8 HPLC Testing

For the HPLC analysis, our team used an Agilent 6546 LC/Q-TOF, 3 x 50 mm, 1.8 µm. Our team expected the PFOA peak at around 12 minutes within the column, however there are other factors that will change this result. One important note for our team was to ensure that our samples are not too highly concentrated. With running a sample that is too high for the HPLC to process, carryover becomes a risk for testing. Carryover is when a concentrated sample does not get fully processed by the LC, and the sample spills over into the next sample, thus disrupting all of the concentration measurements.

Figure 9. HPLC image within the lab.

2.9 Glassware Cleaning

Our team cleaned all containers/glassware with a 1% methanol wash, a detergent wash and then a final tap water wash to ensure all excess waste is properly cleaned off of the glassware. Then all of the hazardous materials/waste is then properly disposed of in the designated storage bottles found within the lab. An additional note of concern is to avoid sample contact with glass as PFAS may be associated with the glass surface. All cleaning notes and procedures may be found in Appendix A of this report.

Chapter 3: Results and Evaluation

This section of the report presents the findings obtained from the experiment utilizing our novel method. A total of 12 samples were taken to report the method with two of the samples failing to be tested due to experimental error and other encountered issues. Samples 3 and 8 were unable to undergo the HPLC analysis due to filtration issues. These samples were found to have particles that were too large for the equipment's sensitivity standards. Within the 12 samples, the amount of hollow glass spheres coated with magnesium varied to determine the efficiency of the spheres within the rotational device. Following this the sample bottle size within the rotational device also was varied to study the air-water interface effect when the area was reduced within the same parameters of the experiment. These changes allowed for the determination of upscaling this process and allowed to see the effects of greater and less advection to the contaminated water system.

3.1 Varying Magnesium Chloride Concentration

As previously stated, the hollow glass spheres with baked magnesium were varied to view the overall effect of the advection process with the PFOA. By lowering the amount (to around 0.8 grams), our team expected there to be more PFOA contained within the final sample and the opposite to the greater amounts (1.2 grams). This variation provided useful information into developing an upscaled version of the experiment with the use of a fluidized bed that is discussed further in the chapter. Table 1 displays the final weight of the hollow glass spheres and the magnesium together before they were added to the instrument. These values were recorded down to the 0.1

Table 1. PFOA Tests/Data. An expanded version of this table may be found in Appendix C.

Trial #	Hollow Glass Spheres (g) and Magnesium Chloride (g)
1	1.0100
2	1.2000
~~*3*~~	~~0.8060~~
4	0.9500
5	1.2000
6	1.0100
7	1.2000
~~*8*~~	~~1.0434~~
9	1.0500
10	0.8500
11	1.0500

3.2 Control Tests/Test Results

The purpose of a control test to include a trial is to provide a baseline against the results to be able to see a change and/or a difference. Within our control tests, our team held one sample from each batch to have a baseline for each different trial group. This provides our team with two different data views: where our team can view the overall PFAS lost due to transfer (either through adhesion to the glass/materials or some other experimental error) and the overall change from the other samples. Along with the control tests, a reference PFOA spike made from the Restek Pro EZLC Chromatogram Modeler Software was used to understand where the PFOA spike may appear within the samples.

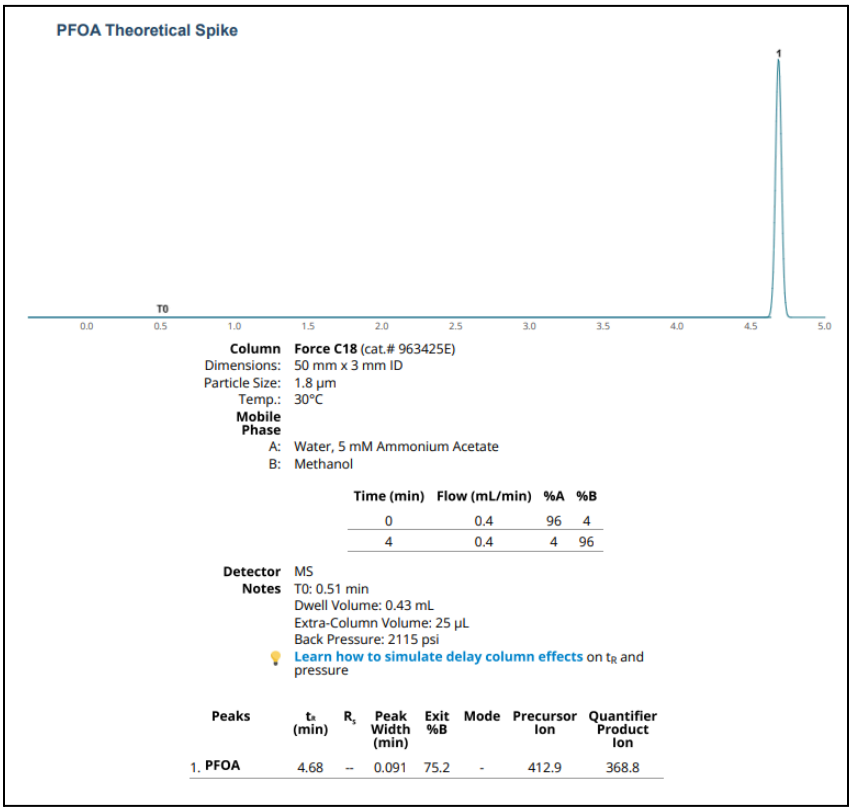

Figure 10. Restek Software PFOA Model spike used for referencing test samples.

Figure 10 displays the resulting peak from perfluorooctanoic acid that is expected in HPLC. This software assumes perfect conditions and no operating errors when producing the spikes. Appendix D includes all data obtained from the HPLC experimentation including the chromatograms with concentrations and peaks. This collected data was inconclusive as the peaks showed a similar result to the Restek software, but proved to show any decrease in concentration.

The samples were then sent to undergo LC-QOTF for further analysis with results displayed in Table 2.

	MS Peak Area	Conc. (ng/l)	Conc. (ppm)
Test 1	93889538	989850	0.98984974
Test 2	81512490	859331	0.85933147
Test 4	64627316	681274	0.68127416
Test 5	64627316	681274	0.68127416
Test 6	69463033	732268	0.7322677
Test 7	32778703	345425	0.34542461
Test 9	56481515	595375	0.59537518
Test 10	93866208	989604	0.98960372
Test11	62288446	656610	0.65661035
batch	96244679	1014685	1.01468514

Table 2. The resulting concentrations observed from LC-QOTF

When examining the results from LC-QOTF, it is clear to see that all samples have extremely high levels of PFOA. These samples were made with a concentration of what was measured to be 0.04 ppm. The table displays that none of the samples were near this level and were much higher. This could be due to contamination from glassware being improperly cleaned. It is important to note that the batch's concentration was approximately 1 ppm with every test being lower. That being said, it is clear that this extraction method does not work as there are extremely high levels of PFOA within the system still.

3.3 Data Comparison

Despite the inconclusive batch tests from HPLC, the data from the actual tests showed trace amounts of PFOA within the tests as trace concentrations. As seen from the figures in Appendix D, some of the samples display a trace peak around the 4.68 minute peak that would have represented PFOA. This discrepancy between the data received and the Restek Model might have been due to experimental error or other factors. A table stating the potential PFOA peaks within the graphs can be found below as Table 3.

Table 3. Comparison of Actual vs. Restek Model.

	Minutes
Restek Peak	4.680
Trial 1	4.569
Trial 5	4.704
Trial 9	4.746

3.4 Reactor Design Evaluation

For those interested in replicating the outlined experiment, certain modifications to the rotational device are advisable. Utilizing 3D printing technology to create molds for holding various reaction vessels would be advantageous. Design software like CAD can facilitate this process efficiently. While the experiment employed various packing materials to ensure system stability, the adoption of a 3D printed mold would enhance operational efficiency for operators.

Additionally, the rotational device occasionally experienced operational issues, necessitating troubleshooting measures. To enhance efficiency, we recommend implementing a more reliable system for future experiments.

3.4.1 Reactor Sizing/Upscaling

Upscaling this project would require a transitioning from laboratory-scale testing to larger, more practical applications where careful consideration of factors such as cost-effectiveness, efficiency, and scalability are fundamental. Adapting the experimental methods and technologies of this project to accommodate larger volumes of water while maintaining the effectiveness of PFAS removal is the goal. Addressing logistical challenges such as system integration, regulatory compliance, and environmental impact is crucial in the upscaling process. Due to the fundamental importance of the air-water interface in this experiment, our team proposes utilizing a fluidized-bed reactor (FBR) . Common dimensions allow for a height of 1760 mm with an inside pipe diameter of 100 mm. In these reactors, solid particles are suspended and behave like a fluid when a gas or liquid flows through them. Initially, the particles settle due to gravity, but as the fluid flow increases, they become buoyant, forming a

fluidized bed. This reactor would provide the perfect system for the magnesium chloride coated spheres to interact with PFOA at the air-water interface.

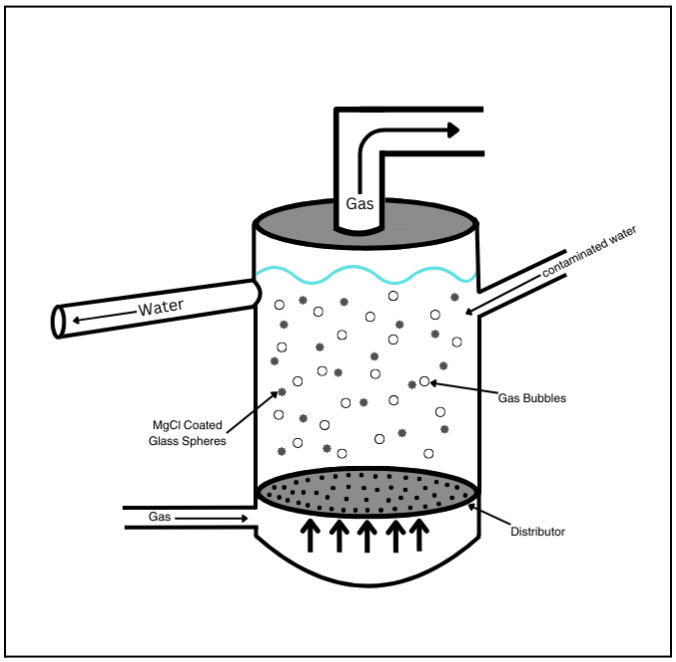

Figure 11. Fluidized Bed Diagram Drawing

In order to recycle the large volume of glass microspheres in an upscaled reactor, they must be recoated with magnesium chloride after each use. This necessitates its own upscaled process of spraying, baking, and cooling large batches of spheres before reentering them into the churning reactor. Ultimately, successfully upscaling this novel PFAS water treatment processes presents significant potential for effectively addressing widespread contamination issues and safeguarding water resources on a broader scale.

3.4.2 Baking MgCl and Hollow Glass Spheres

Heating hydrated magnesium chloride to its melting point of 715 degrees Celsius results in the loss of water from the compound, transforming it into the anhydrous salt required for the ionic bridging process. This melting step is pivotal to the experiment's success. The spheres used in the experiment play a crucial role in providing the necessary advection and surface area. Initially, these spheres were not subjected to baking until our team had the opportunity to present our project at a conference hosted by the New England Water Environment Association. This

exposure allowed us to interact with professionals in the PFAS industry, leading to the refinement of our methodology.

Chapter 4: Conclusion and Recommendations

The reported hypothesis on the effect of divalent cations in a rotational mixing system proved to be inconclusive from the results obtained from the HPLC. However, LC-QOTF determined the method to be unsuccessful. With the water retaining a high PFOA concentration after experimentation, the magnesium did not interact as it was expected to.

4.1 Experimental Error

Within the data, there are indicators of PFOA present within some of the samples however without the support from the batch, the data is inconclusive. The largest portion of experimental error that would have resulted in this outcome would likely have been from the adhesion of PFOA to the surfaces of the glassware and other laboratory equipment used to run the experiment. The areas within the procedure where this might have occurred would have been the pipette transfer tools used to transfer the sample from the solid phase extraction device to the RapidVap or the RapidVap transfer to the HPLC test vials. Another source of error would have come from the overall batch creation within the experiment. When creating a large batch with such a low concentration of PFOA, there is a large error percent due to the reality of it not being well-mixed. Improper cleaning could have also led to contamination. Lastly, the final potential source of error could be the HPLC itself, due to its overall new introduction to the laboratory.

4.2 EPA's Method 537.1

The use of the established EPA Method 537.1, was referenced extensively throughout the SPE and HPLC procedures. The modified procedure allowed for our team to follow the EPA's method to extract and prepare a contaminated PFOA water sample for LC testing.

4.3 Further Research and Recommendations

This project operates under the assumption that readers possess a basic understanding of how certain laboratory equipment functions, including Solid Phase Extraction (SPE), Liquid Chromatography (LC), and RapidVap.

Looking ahead, there is potential for exploring the substitution of calcium divalent cations, which could yield promising results. Both magnesium and calcium salts facilitate ionic bridging, and investigating how calcium fares in this experiment would be intriguing. Calcium has proven to be successful in the past. Altering the container size for the experiment could

prove to yield different results. Changing the area allows for more/less interactions between the salt and PFOA.

Incorporating LC-QOTF as an analytical device as opposed to HPLC would also be interesting. The HPLC did not find conclusive results for this project, and LC-QOTF produced definitive results. Utilizing samples found from nearby water sources instead of spiking reagent water would also be an interesting test. As this project is to prove if this system would be effective, everything used was under certain conditions. Actually applying it would be a good test.

References:

Gagliano, Erica. et al. “Removal of poly- and perfluoroalkyl substances (PFAS) from water by adsorption: Role of PFAS chain length, effect of organic matter and challenges in adsorbent regeneration,” *Water Research*, vol. 171 (2020), https://doi.org/10.1016/j.watres.2019.115381.

Buckley, Thomas. et al. “Effect of mono- and di-valent cations on PFAS removal from water using foam fractionation – A modelling and experimental study,” *Separation and Purification Technology*, vol. 286 (2022), https://doi.org/10.1016/j.seppur.2022.120508.

McNamara, James. et al. “Comparison of Activated Carbons for Removal of Perfluorinated Compounds From Drinking Water,” *Journal AWWA* 110, no. 1 (2018): E2–14. https://www.jstor.org/stable/26653669.

Spanne, Autumn. “What are PFAS,” *Environmental Health News,* (2022).

Andrews, David. and Naidenko, Olga. “Population-Wide Exposure to Per- and Polyfluoroalkyl Substances from Drinking Water in the United States,” *Environmental Science & Technology Letters,* vol. 7 (2020): 931-936. https://doi.org/10.1021/acs.estlett.0c00713.

Steenland, Kyle, Tony Fletcher, and David A. Savitz. “Epidemiologic Evidence on the Health Effects of Perfluorooctanoic Acid (PFOA),” *Environmental Health Perspectives*, vol. 118 (2010): 1100–1108. http://www.jstor.org/stable/27822994.

Leung, Shui Cheung Edgar. et al. “Physicochemical properties and interactions of perfluoroalkyl substances (PFAS) - Challenges and opportunities in sensing and remediation,” *Science of The Total Environment*, vol. 905 (2023). https://doi.org/10.1016/j.scitotenv.2023.166764.

Ma, Qisheng, Tang, Yongchun. “Chapter 5 - Molecular designs of enhanced oil recovery chemicals,” *Gulf Professional Publishing*, vol. 3 (2023): 281-319. https://doi.org/10.1016/B978-0-12-823363-4.00006-6.

US EPA. “National Recommended Water Quality Criteria - Aquatic Life Criteria | US EPA,” *US EPA*. (2015).

Shoemaker, J. and Tettenhorst, Dan. “Method 537.1 Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and

Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)," *U.S. Environmental Protection Agency,* (2020).

Kennedy, Gerald L. Jr. et al. "The toxicology of perfluorooctanoate," *Critical reviews in toxicology,* vol. 34 (2004): 351-84. https://doi.org/10.1080/10408440490464705

Accreditation - ABET. (2023, September 13). ABET. https://www.abet.org/accreditation/

Boston, Catherine Moore. Banacos, Natalie. and Heiger-Bernays, Wendy. "Per- and Polyfluoroalkyl Substances: A National Priority for Safe Drinking Water." *Public Health Reports (1974-)*, vol 134 (2019): 112–17. https://www.jstor.org/stable/26629202.

NCEES. (2023, April 20). *Why licensure matters | NCEES*. https://ncees.org/licensure/why-licensure-matters/

Kuzniewski, S. "Document details - EPA's detection methods, the drinking water treatability database, and innovative technologies for PFAS remediation," *Environmental Remediation and Innovations*, vol 32 (2022): 309-323. https://www.jstor.org/stable/26629202.

Smith, Sanne. et al. "Foam fractionation for removal of per- and polyfluoroalkyl substances: Towards closing the mass balance" *Science of The Total Environment,* vol. 871 (2023). https://doi.org/10.1016/j.scitotenv.2023.162050.

Wang, Jianlong, and Niven, Robert. "Unification of surface tension isotherms of PFOA or GenX salts in electrolyte solutions by mean ionic activity," *Chemosphere*, vol. 280 (2021). https://doi.org/10.1016/j.chemosphere.2021.130715.

Costanza, Jed. et al. "Accumulation of PFOA and PFOS at the Air-Water Interface," Environmental Science & Technology Letters, vol 6 (2019): 487-491. https://doi-org.ezpv7-web-p-u01.wpi.edu/10.1021/acs.estlett.9b00355

Appendices:

Appendix A: In-Lab Procedure for Rotational Device, SPE, and Standard Setup

NOTE: All glassware and items used within this experiment will be washed with a methanol wash and then another regular wash. An additional note of concern is to avoid sample contact with glass as PFAS may be associated with the glass surface.

Approximate Lab Timeline:

- Setup - 10 minutes
- Treatment Method w/ Rotational Device - 60 minutes
- Sample Filtration - 20 minutes
- Cleanup/SPE Setup - 120 minutes
- Sample Runthrough- 160 minutes
- Sample Extraction - 10 minutes
- Sample Collection - 10 minutes
- RapidVap - 250 minutes

Appendix A-1: Hollow Glass Sphere Procedure:

1. Set up 1000 mL Nalgene® bottle for rotational device
   - 1.1. First, fill 1000 mL of water into the Nalgene® bottle
   - 1.2. Secondly, fill ~0.500 ± 0.01 g of hollow glass spheres
     - *Step 1.2 and 1.3 were amended for the baking process of the magnesium chloride to the hollow glass spheres; That procedure may be found at the bottom of this paper as Step-A (or Appendix A-4).*
   - 1.3. Following this, add ~0.5083 ± 0.01 g of magnesium chloride ($MgCl_2$)
     - *See Step 1.2's comment.*
   - 1.4. Mix bottle
   - 1.5. Lastly, weigh out ~1 ± 0.1 mg of PFOA and add to the Nalgene® bottle
     - *Note: the weight measurements for the PFOA does not have a large margin of error due to the measuring equipment's standards.*
2. Place Nalgene® bottle into the rotational device with contents sealed (*add parafilm to ensure seal on bottle for hazard concerns*).
3. Turn on the rotational device and wait ~45 minutes to ~60 minutes
4. Following the rotational period, separate the glass beads from the contaminate magnesium/water mixture.
   - *4.1. Using filter paper and a funnel, filter the hollow glass spheres and MgCl*
5. *(From this step follow the EPA method precisely)* The samples are then loaded into a refrigerated storage (14°C is fine but 7°C is better). This step is in place if SPE cartridge preparation cannot be completed in allotted time.

Appendix A-2: SPE Trial and RapidVap:
TO NOTE BEFORE SPE TRIAL*:*

- Throughout the preparation, the cartridge is not to be allowed to go dry as the conditioning phase would have to be reset. The SPE large volume sampler tube should take care of this caution.
- For LC-MS testing, the samples are handed over to proper lab technicians to run within the LC-MS.

1. Rinse each cartridge with 15 mL of methanol (pure) followed by a rinse of 18 mL of reagent water, *without letting the water drop below the top edge of the packing: if the cartridge goes dry the conditioning must be started over.*
2. Add 2-3 mL of reagent water to each cartridge. *This step is responsible for preventing the packing from drying out before the sample is added.*
3. Attach sample transfer tubes and turn on the vacuum.
4. Begin to add the sample through vacuum and adjust the flowrate of the vacuum to a flow of 10-15 mL/min (10-15 inches of Hg).
5. After the entire sample has passed through, add two 7.5-mL aliquots of reagent water to the sample bottle and run that through the cartridge.
6. Following the sample passing through the cartridge, the final step includes drawing air through the cartridge for 5 minutes at high vacuum (10-15 inches of Hg).
7. After the drying air, turn off and release the vacuum. Lift the SPE manifold top and put in a collection vial to now collect the SPE sample. Turn on the vacuum to low settings and add 4 mL of methanol to the sample bottle to run through the cartridge.
8. Following the 4 mL an additional 4 mL of methanol is added to the sample bottle for a second dilution.
9. Following this, remove the SPE sample from the manifold and shut down the vacuum.
10. Storage of the SPE sample should be in a dark, room temperature area (28^{o}C), if the RapidVap section cannot be completed within the given lab period.

RapidVap Procedure:

1. Take the SPE sample and place the vial into the RapidVap unit.
2. Concentrate the extract to dryness under a stream of nitrogen in a RapidVap. This is used to remove all of the water/methanol mix at around 60-65^{o}C. Other settings for the RapidVap include a speed of 22 and setting the time for approximately 4 and a half hours.
3. Add the appropriate amount of 96%:4% (vol/vol) of methanol:water solution and the IS[24] to the collection vial to bring the volume to 1 mL and vortex. Transfer a small aliquot with a plastic pipet to a polypropylene autosampler vial.

[24] Adding 10 µL of the 2 ng/µL IS to the extracts (2 ng/mL IS concentration yields 20 ng/mL in the 1 mL extract).

Appendix A-3: Sample Volume Determination:

1. If the level of the sample was marked on the sample bottle, use a graduated cylinder to measure the volume of water required to fill the original sample bottle to the mark made before extraction.
    - *For HPLC testing, the samples are handed over to proper lab technicians to run within the HPLC.*
2. Then determine to the nearest 2 mL on each sample. If using weight to determine volume, weigh the empty bottle to the nearest 1 gram and determine the sample weight by subtraction of the empty bottle weight from the original sample weight.
3. Assume a sample density of 1.0 g/mL and in either case, the sample will be used in the final calculations of the analyte concentration.

Appendix A-4: For Baking Magnesium Chloride with Hollow Glass Spheres

A. Weigh out a total of ~0.5083 g of magnesium chloride on a scale and add to a hot plate for the furnace. Then add approximately ~0.5 g of hollow glass spheres to the same hot plate.
    - *One important note is that when putting the testing materials into the furnace, to accomplish multiple tests, our team put greater sums of the materials together. Rather than a singular 1 g total sample for the furnace, our team weighed out several tests worth of the materials to provide a more efficient process.*
B. Pace the sample into the furnace for 24 hours at ~715^{o}C.
C. Once the 24 hours have been completed, allow the hot place and sample to cool before using the sample for a trial.

Appendix B: Sample Calculations and Lab Notes

Appendix B-1: PFOA Batch Concentration Calculation

0.04 ppm Solution:

16 ng/ 4 mL
4 ng / 1 mL
0.000004 mg / 1 mL
0.000004 mg / 0.001 L
0.04 mg / 1 L

Appendix B-2: Restek Pro EZLC Chromatogram Modeler Calculations

For Restek Reading Software: **Agilent ZORBAX RRHD Eclipse Plus C18, 3 × 50 mm, 1.8 µm**
For help: https://www.restek.com/articles/pro-ezlc-chromatogram-modeler-help

Calculating Dwell Volume:

$$V = \pi r^2 L = \pi(1.5\,mm)^2(50\,mm) = 353.43\ mm^3$$

$$353.43\,mm^3 * (0.001\,mL/1\,mm^3) = 0.353\,mL * 0.5^{@} = 0.1767\,mL$$

@ - approximating the free space within the column in a packed column at 50%

$$Dwell = 0.1767mL + 0.25mL = 0.427\,mL$$

Appendix C: Trial Spreadsheet/Information

Table 3. PFOA Tests/Data (expanded version).

Trial #	Control Batch #	Hollow Glass Spheres (g)	Magnesium Chloride (g)	Water (mL)	Rotational Device	Filter	Vacuum/SPE	RapidVap	IS and ES	HPLC	Notes:
1	1.0	1.0009		250.0	☑	☑	☑	☑	☑	☑	
2	1.0	1.2009		250.0	☑	☑	☑	☑	☑	☑	
~~*3*~~	~~1.0~~	~~0.8060~~		~~250.0~~	☑	☑	☑	☑	☐	☐	sample became invalid
4	1.0	0.9526		250.0	☑	☑	☑	☑	☑	☑	
5	1.0	1.2012		250.0	☑	☑	☑	☑	☑	☑	
6	1.0	1.0026		250.0	☑	☑	☑	☑	☑	☑	
7	1.0	1.2110		250.0	☑	☑	☑	☑	☑	☑	
~~*8*~~	~~1.0~~	~~1.0434~~		~~250.0~~	☑	☑	☑	☑	☐	☐	sample became invalid
9	1.0	1.0475		250.0	☑	☑	☑	☑	☑	☑	
10	1.0	0.8537		250.0	☑	☑	☑	☑	☑	☑	
11	1.0	1.0534		250.0	☑	☑	☑	☑	☑	☑	500 mL test bottle
CONTROL BATCH	N/A	N/A		250.0	N/A	N/A	☑	☑	☑	☑	this is the control batch to ensure that our system had PFOA

	Hollow Glass Spheres and MgCl Batch #
This batch of HGS and MgCl was taken 3/26 at 1.0093 g	Batch A
This batch of HGS and MgCl was taken 3/26 at 1.2093 g	Batch A
This batch of HGS and MgCl was taken 3/26 at 0.8060 g	Batch A
This batch of HGS and MgCl was taken 3/26 at 0.9526 g	Batch A
This batch of HGS and MgCl was taken 3/28 at 1.2012 g	Batch B
This batch of HGS and MgCl was taken 3/28 at 1.0026 g	Batch B
This batch of HGS and MgCl was taken 3/29 at 1.2110 g	Batch B
This batch of HGS and MgCl was taken 3/29 at 1.0434 g	Batch B
This batch of HGS and MgCl was taken 3/29 at 1.0475 g	Batch B (0.77 g) and Batch C (0.2775)
This batch of HGS and MgCl was taken 3/29 at 0.8537 g	Batch C
This batch of HGS and MgCl was taken 4/2 at 1.0534 g	Batch C

Batch Notes:
BATCH #1: 0.04 mg/L of PFOA (0.04 ppm)
Batch A: 4.0 g of MgCl and HGS
Batch B: 6.0 g of MgCl and HGS

Appendix D: Sample Graphs/Data

Sample Name	: Test 1		
Sample ID	:		
Data Filename	: PFAS_Analysis_Test4_4102024_012.lcd		
Method Filename	: PFAS_Method.lcm		
Batch Filename	: PFAS_Analysis_Test4.lcb		
Vial #	: 2-12	Sample Type	: Unknown
Injection Volume	: 10 uL		
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Date Processed	: 4/10/2024 1:28:36 PM	Processed by	: System Administrator

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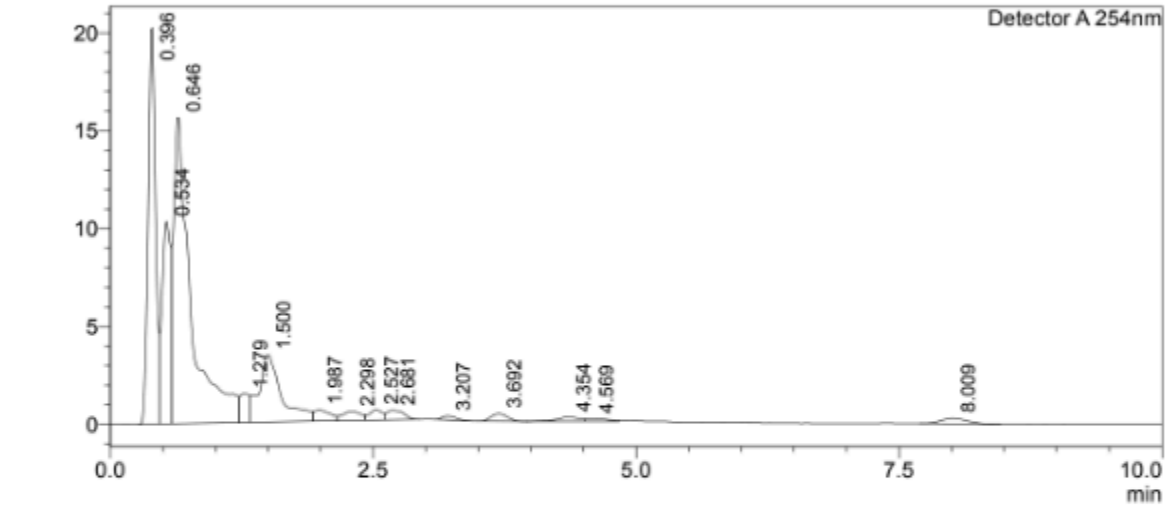

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	0.396	98338	20207	0.000			
2	0.534	59897	10314	0.000		V	
3	0.646	180306	15616	0.000		SV	
4	1.279	9248	1477	0.000		V	
5	1.500	50840	3438	0.000		V	
6	1.987	6075	560	0.000		V	
7	2.298	5762	456	0.000		V	
8	2.527	4471	518	0.000		V	
9	2.681	5329	479	0.000		V	
10	3.207	1822	198	0.000			
11	3.692	4295	382	0.000			
12	4.354	3602	234	0.000			
13	4.569	2202	152	0.000		V	
14	8.009	4904	283	0.000			
Total		437090	54315				

Detector B Channel 1

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
Total							

Figure 12. Test 1's results from the HPLC test.

<Sample Information>

Sample Name	: Test 2		
Sample ID	:		
Data Filename	: PFAS_Analysis_Test4_4102024_013.lcd		
Method Filename	: PFAS_Method.lcm		
Batch Filename	: PFAS_Analysis_Test4.lcb		
Vial #	: 2-13	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 4/10/2024 1:28:58 PM	Acquired by	: System Administrator
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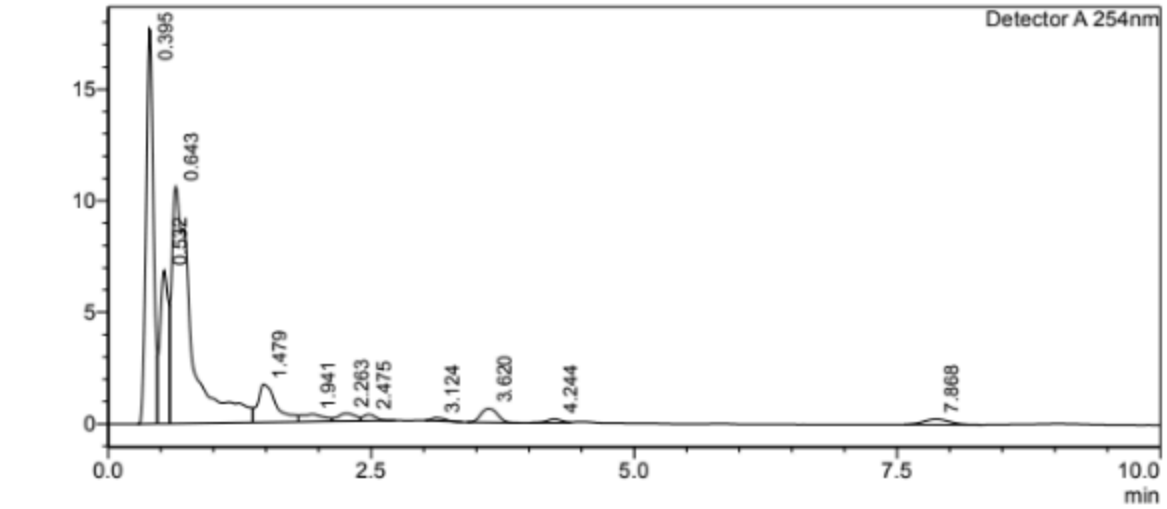

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	0.395	83394	17696	0.000			
2	0.532	38520	6854	0.000		V	
3	0.643	137525	10594	0.000		SV	
4	1.479	21317	1696	0.000		V	
5	1.941	4850	328	0.000		V	
6	2.263	4068	339	0.000		V	
7	2.475	2339	281	0.000		V	
8	3.124	1224	142	0.000			
9	3.620	6777	627	0.000			
10	4.244	1624	163	0.000			
11	7.868	4017	241	0.000			
Total		305656	38962				

Detector B Channel 1

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
Total							

Figure 13. Test 2's results from the HPLC test.

<Sample Information>

Sample Name	: Test 4		
Sample ID	:		
Data Filename	: PFAS_Analysis_Test4_4102024_011.lcd		
Method Filename	: PFAS_Method.lcm		
Batch Filename	: PFAS_Analysis_Test4.lcb		
Vial #	: 2-11	Sample Type	: Unknown
Injection Volume	: 10 uL		
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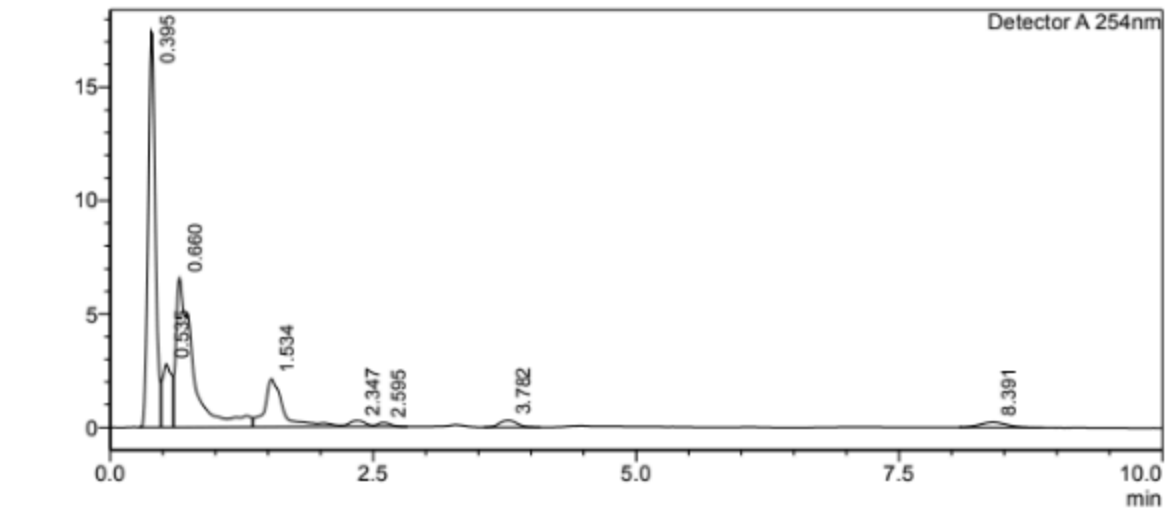

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	0.395	81324	17431	0.000		V	
2	0.535	17042	2776	0.000		V	
3	0.660	74217	6559	0.000		SV	
4	1.534	25880	2108	0.000		SV	
5	2.347	2820	257	0.000		V	
6	2.595	1429	170	0.000		V	
7	3.782	3376	290	0.000			
8	8.391	3811	222	0.000			
Total		209899	29814				

Detector B Channel 1

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
Total							

Figure 14. Test 4's results from the HPLC test.

<Sample Information>

Sample Name	: Test 5		
Sample ID	:		
Data Filename	: PFAS_Analysis_Test4_4102024_010.lcd		
Method Filename	: PFAS_Method.lcm		
Batch Filename	: PFAS_Analysis_Test4.lcb		
Vial #	: 2-10	Sample Type	: Unknown
Injection Volume	: 10 uL		
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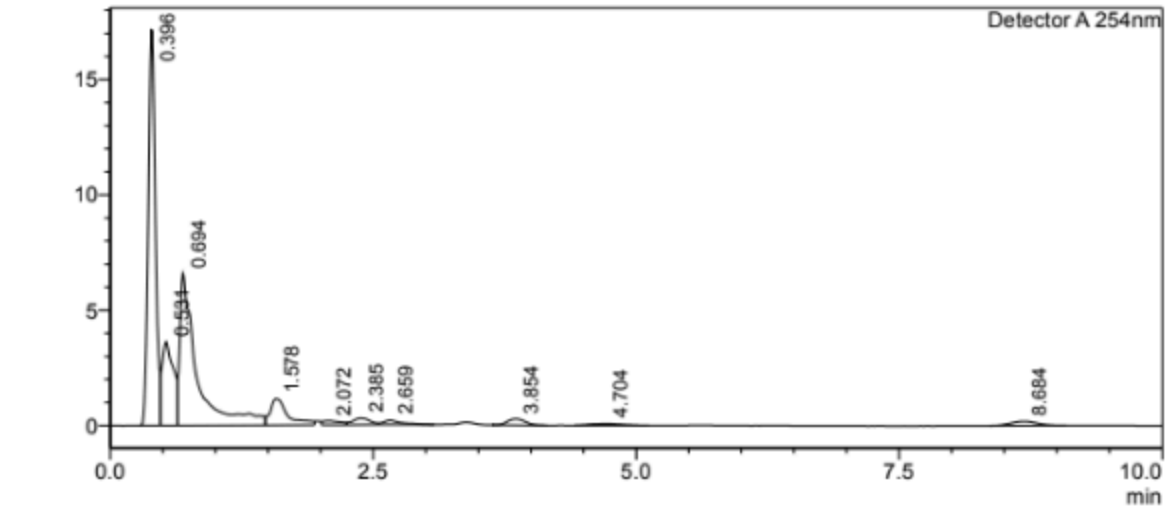

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	0.396	79586	17138	0.000			
2	0.531	27948	3615	0.000		V	
3	0.694	72669	6581	0.000		SV	
4	1.578	13256	1133	0.000		V	
5	2.072	2078	180	0.000		V	
6	2.385	3262	279	0.000		V	
7	2.659	2301	188	0.000		V	
8	3.854	3172	270	0.000			
9	4.704	1588	75	0.000			
10	8.684	3176	187	0.000			
Total		209035	29646				

Detector B Channel 1

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
Total							

Figure 15. Test 5's results from the HPLC test.

<Sample Information>

Sample Name	: Test 6		
Sample ID	:		
Data Filename	: PFAS_Analysis_Test4_4102024_014.lcd		
Method Filename	: PFAS_Method.lcm		
Batch Filename	: PFAS_Analysis_Test4.lcb		
Vial #	: 2-14	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 4/10/2024 1:39:24 PM	Acquired by	: System Administrator
Date Processed	: 4/10/2024 1:49:27 PM	Processed by	: System Administrator

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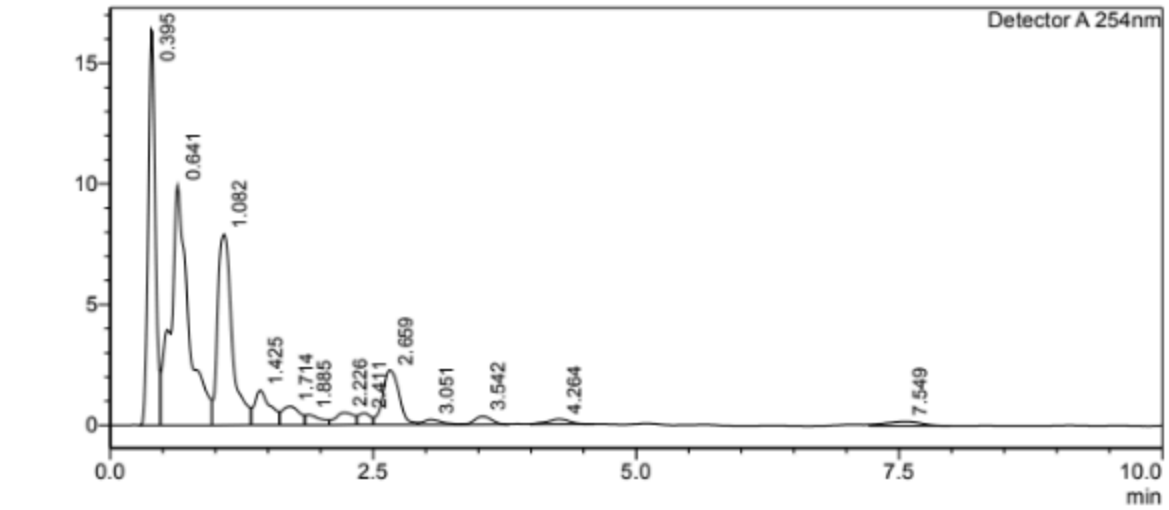

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	0.395	74942	16373	0.000		V	
2	0.641	119121	9911	0.000		V	
3	1.082	76167	7898	0.000		V	
4	1.425	14941	1441	0.000		V	
5	1.714	8949	765	0.000		V	
6	1.885	4162	414	0.000		V	
7	2.226	5998	497	0.000		V	
8	2.411	3837	478	0.000		V	
9	2.659	24293	2259	0.000		V	
10	3.051	2410	198	0.000		V	
11	3.542	3645	325	0.000		V	
12	4.264	3061	209	0.000		V	
13	7.549	4159	173	0.000		V	
Total		345684	40942				

Detector B Channel 1

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
Total							

Figure 16. Test 6's results from the HPLC test.

<Sample Information>

Sample Name	: Test 7		
Sample ID	:		
Data Filename	: PFAS_Analysis_Test4_4102024_005.lcd		
Method Filename	: PFAS_Method.lcm		
Batch Filename	: PFAS_Analysis_Test4.lcb		
Vial #	: 2-5	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 4/10/2024 12:05:37 PM	Acquired by	: System Administrator
Date Processed	: 4/10/2024 12:15:40 PM	Processed by	: System Administrator

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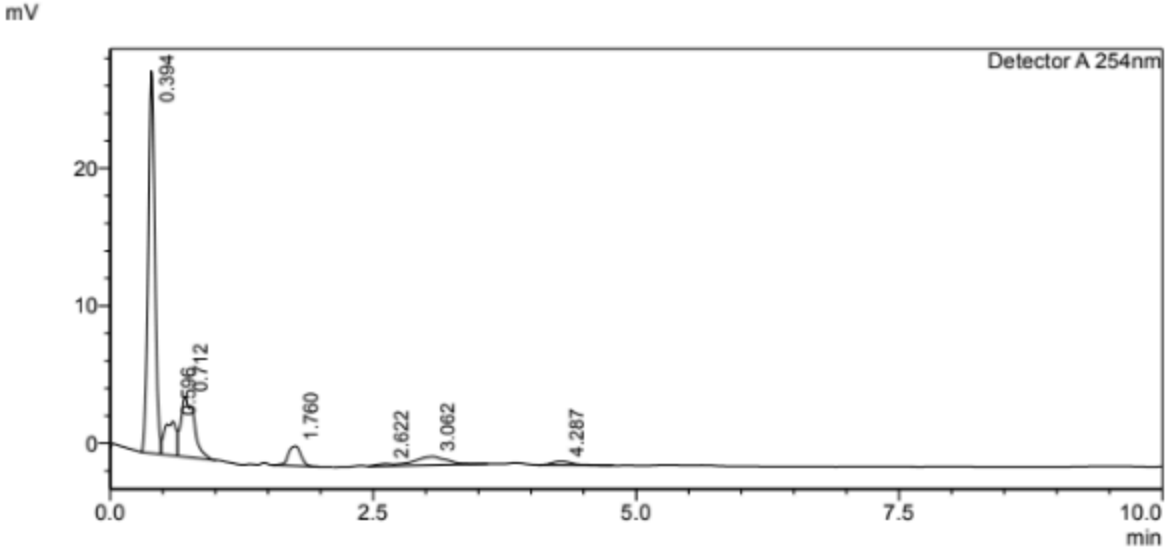


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	0.394	119350	27785	0.000			
2	0.596	19004	2463	0.000		V	
3	0.712	38316	4361	0.000		V	
4	1.760	11757	1432	0.000			
5	2.622	1579	150	0.000		V	
6	3.062	13294	613	0.000		V	
7	4.287	3647	267	0.000			
Total		206949	37071				

Detector B Channel 1

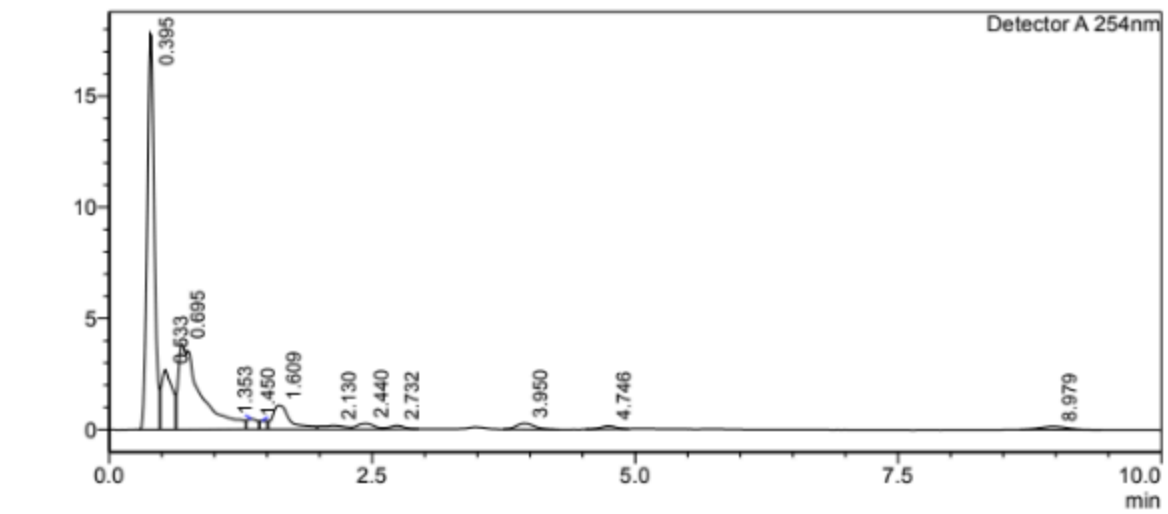
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
Total							

Figure 17. Test 7's results from the HPLC test.

<Sample Information>

Sample Name	: Test 9		
Sample ID	:		
Data Filename	: PFAS_Analysis_Test4_4102024_009.lcd		
Method Filename	: PFAS_Method.lcm		
Batch Filename	: PFAS_Analysis_Test4.lcb		
Vial #	: 2-9	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 4/10/2024 12:47:17 PM	Acquired by	: System Administrator
Date Processed	: 4/10/2024 12:57:19 PM	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	0.395	81930	17781	0.000			
2	0.533	19064	2674	0.000		V	
3	0.695	57000	3830	0.000		V	
4	1.353	3100	455	0.000		V	
5	1.450	1809	370	0.000		V	
6	1.609	12366	1058	0.000		V	
7	2.130	2389	156	0.000		V	
8	2.440	2738	238	0.000		V	
9	2.732	1406	154	0.000		V	
10	3.950	2950	256	0.000			
11	4.746	1281	132	0.000			
12	8.979	2468	136	0.000			
Total		188501	27240				

Detector B Channel 1

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
Total							

Figure 18. Test 9's results from the HPLC test.

<Sample Information>

Sample Name	: Test 10		
Sample ID	:		
Data Filename	: PFAS_Analysis_Test4_4102024_008.lcd		
Method Filename	: PFAS_Method.lcm		
Batch Filename	: PFAS_Analysis_Test4.lcb		
Vial #	: 2-8	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 4/10/2024 12:36:51 PM	Acquired by	: System Administrator
Date Processed	: 4/10/2024 12:46:54 PM	Processed by	: System Administrator

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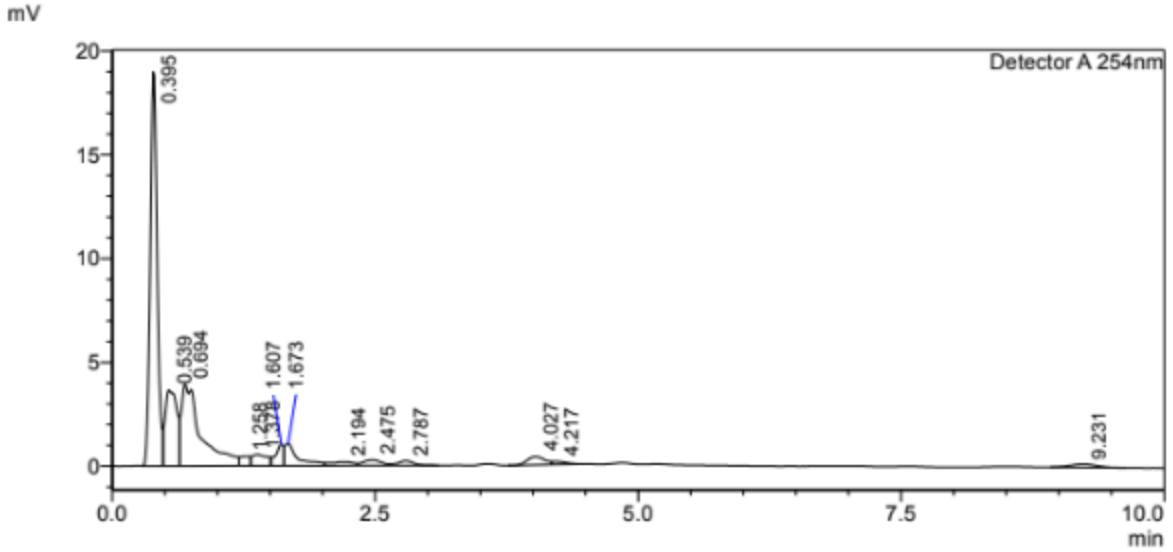

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	0.395	86006	18980	0.000		V	
2	0.539	28822	3655	0.000		V	
3	0.694	50912	3944	0.000		V	
4	1.258	2912	458	0.000		V	
5	1.378	5473	544	0.000		V	
6	1.607	5399	1017	0.000		V	
7	1.673	9190	1054	0.000		V	
8	2.194	2795	180	0.000		V	
9	2.475	3222	263	0.000		V	
10	2.787	2326	222	0.000		V	
11	4.027	4747	398	0.000			
12	4.217	1388	160	0.000		V	
13	9.231	2690	154	0.000			
Total		205882	31029				

Detector B Channel 1

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
Total							

Figure 19. Test 10's results from the HPLC test.

<Sample Information>

Sample Name	: Test 11		
Sample ID	:		
Data Filename	: PFAS_Analysis_Test4_4102024_006.lcd		
Method Filename	: PFAS_Method.lcm		
Batch Filename	: PFAS_Analysis_Test4.lcb		
Vial #	: 2-6	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 4/10/2024 12:16:02 PM	Acquired by	: System Administrator
Date Processed	: 4/10/2024 2:36:12 PM	Processed by	: System Administrator

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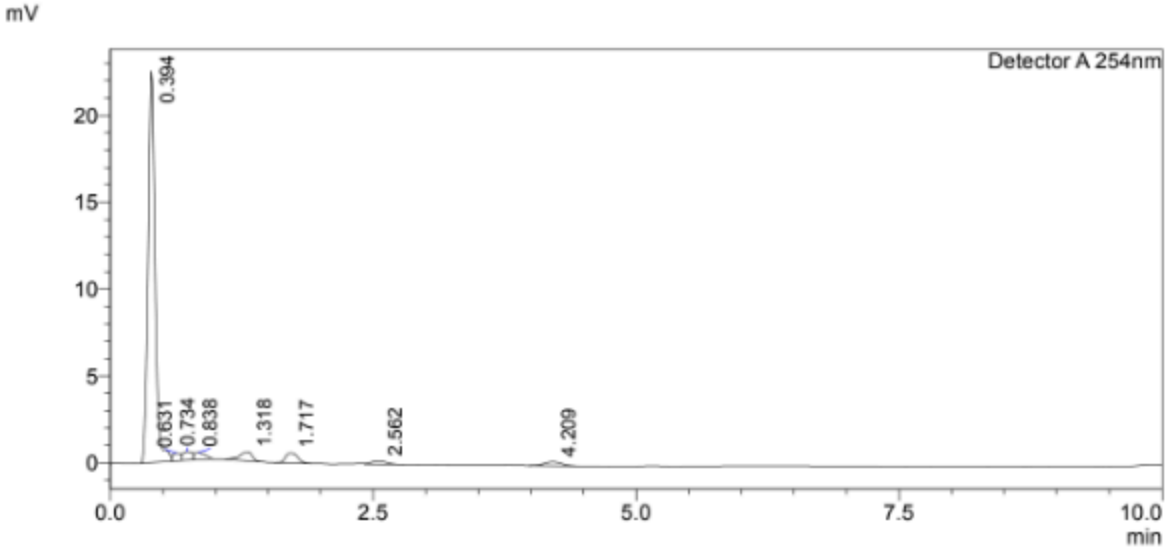


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	0.394	103049	22537	83.002		M	
2	0.631	2441	440	1.966		V M	
3	0.734	2908	498	2.343		V M	
4	0.838	2651	392	2.135		V M	
5	1.318	4009	497	3.229		M	
6	1.717	4590	565	3.697			
7	2.562	1909	179	1.538		V	
8	4.209	2596	223	2.091			
Total		124153	25331				

Detector B Channel 1

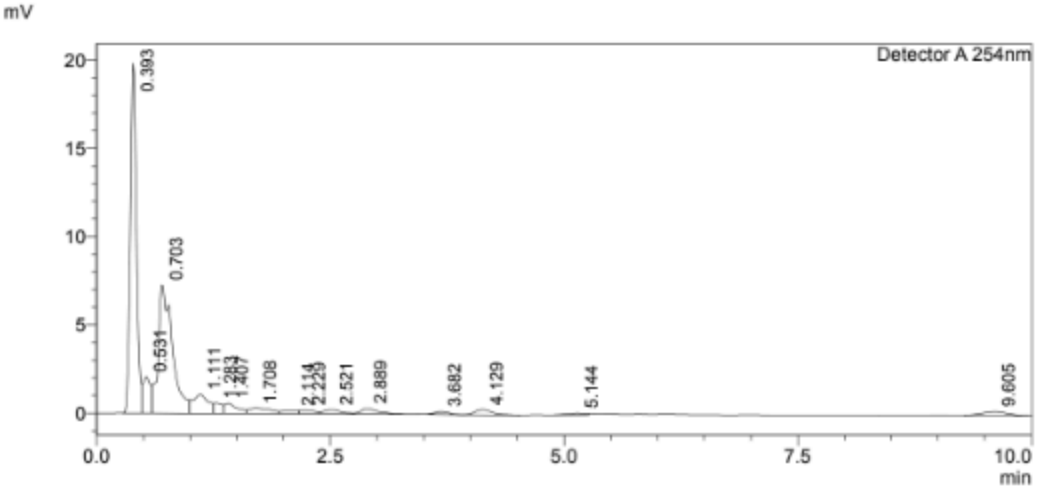
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
Total							

Figure 20. Test 11's results from the HPLC test.

<Sample Information>

Sample Name	: Batch		
Sample ID	:		
Data Filename	: PFAS_Analysis_Test4_4102024_007.lcd		
Method Filename	: PFAS_Method.lcm		
Batch Filename	: PFAS_Analysis_Test4.lcb		
Vial #	: 2-7	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 4/10/2024 12:26:27 PM	Acquired by	: System Administrator
Date Processed	: 4/10/2024 12:36:29 PM	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	0.393	89713	19837	0.000		V	
2	0.531	11825	2072	0.000		V	
3	0.703	77000	7272	0.000		V	
4	1.111	12645	1075	0.000		V	
5	1.283	3549	586	0.000		V	
6	1.407	5491	571	0.000		V	
7	1.708	5234	322	0.000		V	
8	2.114	2229	194	0.000		V	
9	2.229	2180	208	0.000		V	
10	2.521	3045	234	0.000		V	
11	2.889	3939	311	0.000		V	
12	3.682	1723	163	0.000		V	
13	4.129	3755	293	0.000			
14	5.144	1296	87	0.000			
15	9.605	3890	216	0.000			
Total		227513	33441				

Detector B Channel 1

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
Total							

Figure 21. Batch/Control results from the HPLC test.