Sonochemical Defluorination of Perfluorinated Compounds by Activated Persulfate Ions

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Sonochemical Defluorination of Perfluorinated Compounds by Activated Persulfate Ions

by

Kevin M. Gray

A Thesis

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of the

WORCESTER POLYTECHNIC INSTITUTE

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in

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APPROVED:

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Professor Paul Mathisen (Committee Member)

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Dr. Jose Alvarez Corena (Committee Member)
Abstract

Polyfluorinated compounds (PFCs) are a class of anthropogenic chemicals that have been found in groundwater and wastewater around the world. Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are primarily used for industrial surfactants, and aqueous film forming foams (AFFFs). These PFCs and many of their constituents have been found to be carcinogenic to humans and other animals. A simple method for defluorination of these compounds is needed. Advanced oxidation of PFOS, PFHxS, and PFBS-k was carried out using activated sodium persulfate through ultrasonic irradiation with the following condition; [PFC] = 20 millimolar (mM), [Na$_2$S$_2$O$_8$] = 25 mM, pH = 7, and 25°C. Fluoride concentrations were quantified by ion chromatography (IC). In laboratory experiments, batch reactions of PFBS solutions were conducted in purified water at different pH conditions and N$_2$S$_2$O$_8$: PFBS molar ratios of 1:1, 2:1, 10:1, and 100:1 respectively. Solution pH was maintained at 7 using HNO$_3$. Of the three compounds, PFHxS had the greatest defluorination (11%) after 120 minutes reaction time. However, PFBS-K had the greatest increase in defluorination (115%) between the control ultrasound (US) experiment and the combination experiment. When Na$_2$S$_2$O$_8$ was increased, the defluorination ratio of PFBS decreased. This decrease was partly attributed to scavenging reactions between SO$_4^{2-}$ and S$_2$O$_8^{2-}$. These results show a synergism between ultrasonic irradiation and activated sodium persulfate as a form of advanced oxidation. Recommendations for further research into defluorination of PFOS and its constituents by ultrasonic degradation include: the use of high performance liquid chromatograph with accompanying mass spectrometry (HPLC/MS), the use of an ultrasonic probe with alternate frequencies, and the effects of surface tension on defluorination.
Acknowledgements

I would like to thank Worcester Polytechnic Institute (WPI) Department of Civil and Environmental Engineering for providing me with the resources to complete this experiment. I thank my advisor Professor John Bergendahl for offering me his expertise and time throughout my graduate education at WPI. I would also like to thank him for his guidance through every phase of this project. I would like to thank Dr. Wenwen Yao for her help in running the ion chromatograph (IC). I also thank her for her assistance in the laboratory when the IC needed repairs, chemicals needed to be purchased, or equipment ordered. I would like to thank Professor Paul Mathisen and Dr. Jose Alvarez Corena for being part of my research committee. I would also like to thank my parents Dr. Nancy and Mr. Michael Gray for their continued support and understanding. Once again I would like to thank WPI for giving me the opportunity to complete this research and obtain my Masters of Science in Environmental Engineering.
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Chapter 1: Introduction

Polyfluorinated compounds (PFCs) are a class of anthropogenic chemicals that have been incorporated into a vast variety of products within the last several decades. The primary compounds best known as PFCs are perfluorosulfonates (PFSAs), which includes perfluorooctane sulfonate (PFOS), and perfluorocarboxylic acids (PFCAs), which contains perfluorooctanoic acid (PFOA). These chemicals have been used as coating agents for nonstick cookware, carpets, and clothing, packaging coatings, industrial surfactants, emulsifiers, electrical wire casings, chemical resistant tubing, and aqueous film forming foams (ATSDR 2018). Concerns for these chemicals has increased due to their adverse characteristics which include but are not limited to: toxicity, food chain bioaccumulation, half-life longevity in humans, and high degradation resistance.

Figure 1 illustrates the chemical structures of various perfluorsulfonic acids, categorized by their carbon chain length group. This research focused on the degradation of three perfluorosulfonates utilizing the combination of ultrasonic irradiation and sodium persulfate. The perfluorosulfonates in question are potassium perfluorooctanesulfonate (PFOS), tridecafluorohexane-1-sulfonic acid potassium salt (PFHxS), and potassium nonafluoro-1-butanesulfonate (PFBS-K).
Chapter 2: Background

PFOS, PFHxS, and PFBS-K are compounds for which fluorine has replaced hydrogen on all the carbons within the compound, except the carbons associated with functional groups. The fluorinated regions allow for unique physical and chemical characteristics, including thermal stability, hydrophobic and surfactant properties. Table 1 contains the properties and chemical formulas of each of these compounds as well as the sodium persulfate, the oxidant used for degradation. Appendix A contains the control ultrasound and sodium persulfate results. Appendix B contains the ultrasound and sodium persulfate combination results.

<table>
<thead>
<tr>
<th>Perfluorinated Compound</th>
<th>CAS Number</th>
<th>MW</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium Perfluorooctanesulfonic Acid (PFOS)</td>
<td>2975-39-3</td>
<td>538.22 g/mol</td>
<td>C₈F₁₇KO₃S</td>
</tr>
<tr>
<td>Potassium Perfluorohexane-1-sulfonate (PFHxS)</td>
<td>3871-99-6</td>
<td>438.20 g/mol</td>
<td>C₆F₁₃KO₃S</td>
</tr>
<tr>
<td>Potassium Perfluorobutane-1-sulfonate (PFBS)</td>
<td>29420-49-3</td>
<td>338.10 g/mol</td>
<td>C₄F₉KO₃S</td>
</tr>
<tr>
<td>Sodium Persulfate</td>
<td></td>
<td>238.10 g/mol</td>
<td>N₂S₂O₈</td>
</tr>
</tbody>
</table>

These properties were perfect for extinguishing aqueous film forming foams (AFFFs) (EPA 2016; Place 2012). With the increase in PFC production, government and regulatory bodies have been working towards regulating the production of these compounds (Zushi, 2011). The EPA has collaborated with several companies working toward voluntarily discontinuing the production of PFOS and its related compounds between 2000 and 2002. Additionally, in the U.S., a series of Significant New Use Rules (SNUR) were established to restrict the use of materials that contained these compounds. Most recently, the EPA established the PFOA Stewardship Program that aimed
to reduce the emissions of PFOA by 95% by 2010 and to eliminate long-chain PFCs by 2015 (USEPA, 2001).

A 2001 study found the presence of PFOS in the blood of many wildlife species found from a wide range of locations across the world (Giesy 2001). This sparked concern after PFCs were found in both humans and the blood of animals inhabiting locations far from human interaction (Houde 2006, Butt 2010). The variety in locations lead to the understanding that PFCs undergo transportation from temperate regions to Polar Regions where they can accumulate uninterrupted. Additionally, animals that are well known to accumulate persistent organic

Figure 1: General structures for perfluorosulfonic acids
pollutants (POPs) were found to be susceptible to accumulating PFOS as well as other long chain PFCAs (Smithwick 2006, Butt 2008). Other studies have documented PFC concentrations in waterbodies worldwide. Areas with direct industrial emissions have been documented with the highest concentrations of PFCs ranging from 11000 ng/L (Saito 2004, Nakayama 2010). PFOS levels within the ocean are typically lower by around 3 orders of magnitude (Yamashita 2005).

Another environmental concern is the bioaccumulation through food chains. Long chain length compounds with 8 fluorine carbon bonds are more bioaccumulative than those with fewer (Conder 2008, Martin 2003). In rodents and monkeys, PFOS exposure increased liver weight, decreased body weight, and showed a steep dose response curve for mortality (Saito 2004). By exposing rodents to high PFOS levels in their food, a 2002 study observed an increase in hepatocellular adenomas and thyroid follicular cell adenomas (3M Company, 2002). Similarly, pregnant mice who were fed PFOS showed reduced growth rate for pups as well as neonatal mortality (Lau, 2007). It was discovered that the PFOA pathway for carcinogenicity is mediated by the peroxisome proliferator-activated receptor-alpha (PPAR-α) pathway (USEPA Science Advisory Board, 2006). However, within humans, the importance of this pathway is strongly debated.

While the documentation of PFOS toxicity in animals has shown relatively consistent results, the documentation of health effects in human workers exposed to these compounds has been inconsistent (Steenland, 2010). A 2003 study of PFOS and PFOA concentration in workers found that circulating blood levels of PFCs were hundreds of times more than those who do not work in an occupation that has exposure to these compounds (Olsen, 2003). However, these results are hardly conclusive, due to the small population of those who are exposed to these
compounds and at what levels of exposure is difficult to ascertain. Additionally, those who are exposed to PFCs are usually exposed to other compounds that might have similar toxicities which would interfere with the data. An increase in bladder cancer mortality from a yearlong exposure to PFOS was discovered by a 2003 study (Alexander, 2003). A subsequent reevaluation of this study in 2007 observed that the increase in bladder cancer mortality was similar to that of the general U.S. population (Alexander, 2007). Studies that focus on the general population have also shown inconsistent results. Nevertheless, the studies suggest a number of important potential health effects. Some key findings from these studies found decreased sperm counts (Joensen, 2009), a decrease in birth weight and size (Apelberg, 2007), thyroid disease (Melzer, 2010), and elevated cholesterol (Nelson, 2010). In response to the widespread environmental contamination and potential health issues, the U.S. EPA has issued various provisions and health advisories for PFOS and PFOA in drinking water (ATSDR, 2018). Their advisories state to consume below 200 ng/L PFOS and 400 ng/L PFOA (ATSDR, 2018).

Remediation and treatment of PFOA and PFOS has been found to be challenging. Several technologies have emerged over the years including adsorption, advanced oxidation, filtration, sonochemical decomposition, and air-sparged hydrocyclone (ASH) technology. Currently the most common remediation technique for water is the use of granular activated carbon (GAC) to adsorb the pollutants (Fujii, 2007). Studies have found that GAC can consistently remove PFOS concentration at the microgram per liter scale with an efficiency of greater than 90% (Fujii, 2007). However, organic matter within wastewater samples has shown a decrease in PFC removal due to competition (Fujii, 2007). Filtration has also shown high removal efficiency with around 99% removal of initial concentrations ranging from 0.5-1500 mg/L (Tang 2006). These authors also
observed that with increased PFOS concentrations came a decrease in permeate flux. Additionally, most wastewater contaminated with PFOS required pre-treatment before reaching the membrane or reverse osmosis (RO) system.

PFOS and PFOA are resistant to oxidation due to the strength of the carbon-fluorine bonds that make up the PFC compounds. Being the most electronegative element, fluorine resists oxidation. Furthermore, fluorine is the most powerful inorganic oxidant with a reduction potential of 3.6 V (Wardman, 1989). This reduction potential makes fluorine thermodynamically unfavorable when trying to form the fluorine atom with any one-electron oxidant. In order to overcome the difficulty associated with fluorine, studies have tested a wide range of reagents and advanced oxidation processes (AOPs). Advanced oxidation processes have been utilizing powerful hydroxyl or sulfate radicals as primary oxidizing agents since the 1980s. Further use of AOPs became broadly applied in wastewater treatment due to the degradation ability of these radicals to destroy organic and inorganic pollutants. AOPs differ from oxidants such as chlorine due to their rare use as disinfectants. Hydroxyl radicals have a rather short half-life causing the detention times for disinfection to be prohibitive as the radical concentrations are low (Tchobanoglous, 2003). However, these radicals are extremely powerful at deconstructing pollutants into less, or even non-toxic, products.

A number of studies found that the highly reactive sulphate and hydroxyl radicals could drive the oxidation process and degrade PFOA to fluorine and carbon dioxide (Ross, 2012; Hori, 2005; Wang, 2010). However, smaller chains of perfluorocarboxylic acids formed during initial oxidation requiring further oxidation to completely mineralize the compounds. This degradation was accomplished with light-activated persulfate with 50 mM $\text{[S}_2\text{O}_8^2-$ and 4 hours of irradiation.
Further research found that heat-activated persulfate could also effectively degrade PFOA (Hori, 2008). 374 micromoles of PFOA and 50.0 micromoles of sodium persulfate were heated to 80°C for 6 hours (Hori, 2008). Their estimated yield of fluorine ions and carbon dioxide molecules were 77.5% and 70.2% respectively conclusively demonstrating mineralization of PFOA. However, degradation of PFOS and PFOA at the mg/L level has been found ineffective when using advanced oxidation processes.

Sonochemistry is defined by the utilization of acoustic fields to generate chemical reactions within a solution. Sound waves cause bubbles in solution to collapse resulting in high vapor temperatures that catalyze pyrolysis and combustion of chemicals. A 2005 study found pyrolysis would decompose PFCs at the bubble – water interface (Moriwaki, 2005). The sonochemical mechanism works by applying an ultrasonic field to an aqueous solution in order to begin nucleation of cavitation bubbles. The bubbles will expand until reaching a radius maximum. Transient bubbles then undergo a quasi-adiabatic compression which releases kinetic energy resulting in high temperatures, on average 5000 K (Didenko, 1999; Ciawi, 2006). 28% PFOS decomposition after 60 minutes under air atmosphere was reported by a single study (Moriwaki, 2005). Recently, studies have shown that organic matter does not affect degradation rates of PFCs due to preferential adsorption of PFCs to the bubble – water interface (Cheng, 2008).

This research investigated the effectiveness of advanced oxidation for treating PFOS contaminated water. It was hypothesized that PFOS degradation can be achieved in water by a combination of ultrasonic irradiation and sodium persulfate. It was also hypothesized that higher doses of sodium persulfate would achieve greater PFOS degradation. Therefore the following objectives were formed:
- Develop a method to perform equilibrium batch reactor ultrasonic irradiation experiments with PFC contaminated water,
- Develop a method to quantify defluorination of PFOS, PFHxS, and PFBS-K using the Ion Chromatograph (IC) in the Worcester Polytechnic Institution (WPI) Environmental Engineering Lab,
- Evaluate the effect of ultrasound and sodium persulfate on defluorination of PFOS, PFHxS, and PFBS-K.
Chapter 3: Methodology

Chemicals

Potassium perfluorooctanesulfonate 98%, Tridecafluorohexane-1-sulfonic acid potassium salt 98%, and Potassium nonafluoro-1-butanesulfonate 98% were purchased from Aldrich (ST. Louis, MO). Sodium Persulfate 98% and Sodium Sulfate Anhydrous were purchased from Fisher Scientific (Pittsburg, PA).

Experiments

All water used was purified with a Barnstead Nanopure water system (Barnstead RO/Nanopure system, Thermo Scientific, Marietta, Ohio). Glassware used was rinsed 4 times with tap water, and then rinsed 4 times with purified (DO) water. Finished solutions were disposed within labeled hazardous waste containers. Their beakers were rinsed 4 times with a combination of tap water and dish soap, then rinsed 4 times with purified water. The glassware was then air dried for 24 hours before being washed and used again.

Laboratory and Sample Preparations

Before solutions were prepped the sonicator (Qsonica Q700, 100W, 20kHz, USA) and the water cooling system were powered on. The cooling pump was monitored until the desired temperature of 25°C was reached before continuing with the experiments. 2 milliMolar (mM) stock solutions were prepared for all three perfluorinated compounds in 500 mL beakers. These solutions were labeled and covered with Parafilm M, all-purpose laboratory film, then stored in a hood until ready to be used. The experimental solutions were prepared by taking 5 mL of the desired 2 mM stock solution and adding it to 500 mL of purified water. Solutions were stirred for
5 - 10 minutes on a magnetic stir plate, or until particulates in solution became fully dissolved. For ultrasound control experiments, no sodium persulfate was added to the experimental solution. Rather, the 500 mL beaker was placed directly into the sonication booth (Figure 2) and sonicated for 120 minutes with samples drawn every 15 minutes. For sodium persulfate control experiments, 25 mM of Na₂S₂O₈ were added to the 20 mM experimental solution, covered and left on a magnetic stir plate for 120 minutes, with samples drawn every 15 minutes.
Ultrasonic Degradation using Sodium Persulfate and Ion Chromatograph Analysis

Ion chromatography (IC) analyses were performed to determine fluoride concentrations in the samples. Prior to IC analysis, fluoride calibration curves were generated using 10, 50, 100, 300, 600, and 1000 μg/L fluoride standard solutions (Appendix C contains these curves). A method for ultrasonic irradiation of perfluorinated compounds using activated persulfate ions was developed. The following steps were followed to perform the sonication and IC analysis of PFCs:

1. Using an electronic scale, a foil crucible was weighed and zeroed.
2. Sodium persulfate (Na$_2$S$_2$O$_8$) was measured in the foil crucible to the desired mass. The white powder was then added to the 20 mM experimental solution.
3. In order to reach the desired pH of 7, 1 N sodium hydroxide (NaOH) was added to the solution.
4. The solution was magnetically stirred for 5 minutes before being transferred to the sonication booth.
5. Once in the booth, the sonication probe was lowered halfway into the 500 mL solution.
6. The initial sample, at t=0, was taken when the sonication probe was first plunged into the sample, but before the sonication began. Once that sample was drawn, the sonication booth door was sealed and the sonication process was initiated. Sample t = 120 min was drawn after the sonicator was stopped at its allotted 2 hour run time.
7. 5 mL of the solution was transferred to IC vials every 15 minutes. Samples were capped.

8. The IC vials were placed in a Dionex Autosampler.

9. Chromeleon, a Thermo Fisher Scientific software package, was used to program methods and sequences to run and analyze samples through the IC.

10. 100 mL of each sample was injected into the IC by the Dionex automatic sample injector using an autosampler syringe.

11. The injected sample was analyzed by a 2100 Series Ion Chromatograph from Dionex.

Fluoride and sulfate ion concentrations were measured with a Dionex ICS-2100 (manufacturer, location) which consisted of a Dionex automatic sample injector, a degasser, a pump, a guard column, a separation column, and a conductivity detector with a suppressor device. The mobile phase was an aqueous solution containing NaHCO$_3$ (1.7 mM) and Na$_2$CO$_3$ (1.8 mM). The flow rate was 2 mL/min.

The amount of fluoride ($C_0$) in each compound was calculated as follows:

$$Total\ Initial\ Fluoride\ (C_0) = X_0 \ast 19 \ast N$$  \hspace{1cm} (1)

Where $X_0$ is the initial concentration (mM), 19 is the molar mass of fluoride (g/mol), and $N$ is the number of fluoride molecules in 1 mole of the compound.
Acid Digestion

Acid digestion was performed to evaluate defluorination of PFCs by nitric acid. The following method was followed for the acid digestion of the samples:

1. 5 mL of concentrated HNO₃ was combined with 50 mL of 2 mM PFOS solution.
2. The solution was heated on a hot plate to bring volume down to 5 ml.
3. The solution was brought back up to desired volume (5 mL) with purified water.
4. Due to the viscous nature of the solution, a filter was used to remove excess foam.
5. A 5 mL IC vial was filled with solution.
6. The sample was placed in the IC making sure to label the sample “Acid Digestion.”

A control test was also completed, where steps 1-6 were followed but with only HNO₃ and purified water.
Chapter 4: Results & Discussion

Experiments to determine the effect of activated sodium persulfate and ultrasound on the degradation of PFCs were done at an initial neutral pH of 7. The sodium persulfate doses used were 25, 50, 250, and 2,500 mM. A fluoride calibration curves was generated using 10, 50, 100, 300, 600, and 1000 μg/L fluoride standards which can be seen in Figure 3. This curve was used to quantify fluoride levels in multiple experimental runs and their IC results can be found in Appendix C.

![Figure 3: 99.99% Calibration curve for fluoride generated using 10, 50, 100, 300, 600, and 1000 μg/L fluoride standards.](image)
Defluorination of PFCs

US degradation (100W, 20 kHz) of 20 mM PFOS with 25 mM sodium persulfate and without sodium persulfate was conducted for 120 minutes. Fluoride degradation was calculated through the following equation:

\[ F \text{ Removal \%} = \frac{c_0 - c}{c_0} \times 100 \quad (2) \]

Where \( c_0 \) is the initial amount (\( \mu g/L \)) of fluoride in 20 mM PFOS (associated with the organic PFS molecules), and \( c \) is the number of fluoride (\( \mu g/L \)) that remained with the organic PFS molecules after 120 min retention time. \( c \) was calculated by

\[ F\text{louride Concentration}\ (C) = c_0 - c_r \quad (3) \]

Where \( c_r \) is the concentration of free fluoride (\( \mu g/L \)) liberated from the organic PFAS molecules due to defluorination after 120 minutes of reaction. Control experiments were conducted to determine whether exclusively sodium persulfate or exclusively ultrasound would cause defluorination of the target compounds. Results for the control sodium persulfate experiments showed less than 0.1% defluorination. This corroborates similar findings that illustrate sodium persulfate alone is not able to degrade perfluorinated compounds (Lin, 2015), presumably because the oxidation strength of persulfate is not strong enough to break C-F bonds.

When exposed solely to ultrasound for 120 minutes, PFHxS released the most fluoride molecules at 558.8 \( \mu g/L \) (11\% defluorination). US of both PFOS and PFBS resulted in low amounts of defluorination: PFOS released 92.89 \( \mu g/L \) fluoride (1.4\%) and PFBS-K released 140.36 \( \mu g/L \) fluoride (4.2\%). When subjected to both ultrasound and 25 mM sodium persulfate, both PFOS
and PFBS showed greater defluorination after 120 minutes than US alone. Figures 5, 6, and 7 compare each compound’s degradation under different combination of US and persulfate.

Figure 5: Effects of persulfate addition on defluorination of PFHxS ([PFHxS]₀ = 20mM; [Sulfate]₀ = 0mM, 25mM; initial pH = 7; T = 25 °C; power = 100W).

Figure 4: Effects of persulfate addition on defluorination of PFOS ([PFOS]₀ = 20mM; [Sulfate]₀ = 0mM, 25mM; initial pH = 7; T = 25 °C; power = 100W).
Sodium persulfate addition to the ultrasound system resulted in greater defluorination of PFOS and PFBS respectively. Only PFHxS showed little to no change in defluorination after 120 minutes. PFOS had a 27% increase in fluoride concentration with the addition of 25 mM sodium persulfate. Similarly, US of PFBS produced the greatest increase (115%) in fluoride concentration after addition of 25mM sodium persulfate. However, the increase in fluoride concentration only amounted to defluorination ratios of 1.7% and 8.9% for PFOS and PFBS-K, respectively.

In 2015 Lin et al. reported two reactions through which PFOA removal is achieved with treatment using ultrasound and sodium persulfate. They entitled the two reactions the “direct” and “indirect” reaction (Lin, 2015). The “direct” reaction describes the process of bubble formation and destruction known as cavitation. Perfluorinated compounds have strong polarities, therefore, when exposed to cavitation they migrate to the bubble-water interface (Zhao, 2008). At this interface, interfacial tension is decreased allowing for better adsorption.
Therefore, when cavitation occurs the target compounds are adsorbed onto the bubble surface and destroyed when the bubble erupts. The “indirect” reaction refers to the formation of sulfate ions during ultrasonic irradiation. This formation occurs through the following equations:

\[ H_2O \rightarrow OH \cdot + H \cdot \] (4)

\[ OH \cdot + SO_4^{2-} \rightarrow OH^- + SO_4^- \cdot \] (5)

\[ SO_4^- \cdot + PFOS \rightarrow F^- + CO_2 + SO_4^{2-} \] (6)

In order to test the effects of higher sodium persulfate dosage, PFBS was chosen as the primary contaminant due to the fact that it had the greatest increase in defluorination at 25 mM sodium persulfate dose. Figures 8 shows PFBS exposed to increasing amounts of sodium persulfate.

![Figure 7: Effects of persulfate dosage on defluorination after 120 minute reaction time.](image)
With a small increase in persulfate concentration, the amount of free fluoride increased. However, once the persulfate concentration increase beyond 25 mM, lower amounts of fluoride were released. This phenomenon was illustrated in 2013 by Hao et al. when analyzing sonochemical degradation of ammonium perfluorooctanoate with persulfate addition. This phenomenon occurs due to excessive $\text{SO}_4^{2-}$ which can cause the following reactions:

\[
\text{SO}_4^{-} \cdot + S_2O_8^{2-} \rightarrow \text{SO}_4^{2-} + S_2O_8^{-} \cdot \quad k = 6.1 \times 10^5 \text{ M}^{-1} \text{s}^{-1} \quad (7)
\]

\[
\text{SO}_4^{-} \cdot + SO_4^{-} \cdot \rightarrow S_2O_8^{2-} \quad k = 4 \times 10^8 \text{ M}^{-1} \text{s}^{-1} \quad (8)
\]

These reactions could compete with the PFBS/ $\text{SO}_4^{2-}$ reaction; therefore, higher dosages of sodium persulfate could impede defluorination of these compounds. Follow up tests with PFOS that illustrate this phenomenon are shown in Figure 9. The IC results for PFOS can be found in Appendix B.

![Figure 8: Sulfate interference with defluorination of PFOS at higher sodium persulfate dose.](image)
The Effects of pH and Temperature on Defluorination

The effects of temperature and pH on perfluorinated compounds have been studied in various previous reports. Several studies observed that the degradation rate was highest at a pH of 6.0 and would decrease with either an increase or decrease in pH (Hao, 2014; Liu, 2012; Liang, 2007). They attributed the observation to formed $SO_4^-\bullet$ undergoing the following reactions:

$$SO_4^-\bullet + H_2O \rightarrow OH\bullet + H^+ + SO_4^{2-}$$ \hspace{1cm} (9)

at all pHs and,

$$SO_4^-\bullet + OH^- \rightarrow SO_4^{2-} + OH\bullet$$ \hspace{1cm} (10)

at alkaline pH.

The generated $OH\bullet$ has been shown poor reactivity with PFCs in aqueous solutions (Lutze, 2018). Therefore, in alkaline pH solution $OH^-$ could be a scavenger for $SO_4^-$, and result in decreased PFC degradation. While acidic solutions, $SO_4^-\bullet$ creation could increase due to acid catalyzation (Liang 2007). The higher $SO_4^-\bullet$ generation could favor reactions between radicals, reactions between radicals and scavengers, or reactions between radicals and organics shown in equation 7 and 8. Ultimately, higher pH conditions inhibit the persulfate oxidation of PFCs more than lower pH conditions (Hao 2014). Additionally, pH values were gathered before and after 120 minutes reaction time to investigate whether any pH changes occur due to the reactions. During these tests, initial pH was not fixed to 7, but rather, unaltered and recorded in Table 2.
Table 2: pH values before and after 120 minutes of ultrasonic irradiation.

<table>
<thead>
<tr>
<th>Test</th>
<th>Compound</th>
<th>Initial pH</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PFBS</td>
<td>5.54</td>
<td>4.20</td>
</tr>
<tr>
<td>2</td>
<td>PFBS</td>
<td>5.61</td>
<td>4.47</td>
</tr>
<tr>
<td>3</td>
<td>PFBS</td>
<td>5.15</td>
<td>4.25</td>
</tr>
<tr>
<td>1</td>
<td>PFHxS</td>
<td>5.22</td>
<td>4.04</td>
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<tr>
<td>2</td>
<td>PFHxS</td>
<td>5.04</td>
<td>3.94</td>
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<tr>
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<td>PFHxS</td>
<td>5.78</td>
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<tr>
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<td>PFOS</td>
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<tr>
<td>3</td>
<td>PFOS</td>
<td>5.17</td>
<td>4.79</td>
</tr>
</tbody>
</table>

Temperature effects have also been previously studied. It was observed that 25°C provides the greatest effectiveness for degradation and defluorination for the temperatures evaluated (Lin, 2015). This is suspected to be partially due to lower surface tension at higher temperatures, which can interface with cavitation at the bubble-water interface. Additionally, oxidant-assisted ultrasound has been found to have an optimal temperature of 25°C for its reaction kinetics (Liu, 2012).

**Acid Digestion of Perfluorinated Compounds**

Acid digestion was run in order to determine if perfluorinated compounds could be degraded to their constituents by nitric acid. The test resulted in a heavy viscous solution that had to be filtered before IC analysis. The digestion process resulted in heavy foaming due to the surfactant properties of PFOS. Figure 10 illustrates the control versus the digestion of PFOS. The results show that after 4 hours of heating and 24 hours of cooling, digestion released 1.14 μg/L of fluoride which equates to a defluorination ratio of 0.02. This amount is more than contact with sodium persulfate, but much less than the combination of ultrasound and sodium persulfate. Further digestion attempts were not pursued.
Figure 9: Acid Digestion IC Results
Chapter 5: Conclusions

The intent of this research was to determine the effectiveness of ultrasonic irradiation and sodium persulfate oxidation of water contaminated with three perfluorosulfonates (PFOS, PFHxS, and PFBS-K), as well as the optimum dosage of Na$_2$S$_2$O$_8$ for the treatment of perfluorosulfonates. Ultrasonic irradiation and sodium persulfate were found to be synergistic as a form of advanced oxidation. A combination of 25 mM Na$_2$S$_2$O$_8$ and 120 minutes of ultrasonic irradiation (100W, 20 kHz) was found to cause greater defluorination in both PFOS and PFBS than with just one treatment process. The combination of US and Na$_2$S$_2$O$_8$ increased defluorination in PFOS by 27% and PFBS by 115%. However, when the Na$_2$S$_2$O$_8$ dosage was increased, the defluorination ratio in PFBS decreased drastically. The drastic decrease in defluorination was attributed to high scavenging potential of SO$_4$$^{-}\bullet$. Therefore, the greatest dosage of Na$_2$S$_2$O$_8$ was found to be 25 mM, or a 1:1 ratio of perfluorinated compound to sodium persulfate. Finally, acid digestion of PFOS was found to be an ineffective process of defluorination. 5 mL of HNO$_3$ digested 50 mL of 2mM PFOS. This digestion resulted in a defluorination ratio of less than 0.1%.
Chapter 6: Engineering Implications and Future Research

Ultrasonic irradiation as a process to activate sodium persulfate is effective at a laboratory bench scale. Results indicated that defluorination of perfluorinated compounds can be measured with ion chromatography. However, the actual degradation of these perfluorinated compounds should be investigated by direct measurements in the future. The use of a high-performance liquid chromatograph with accompanying mass spectrometry has been found to accurately measure PFC degradation (Lin, 2015; Zhao 2008). It would be beneficial to know if the PFCs are being broken down into smaller carbon chain compounds, which might account for the low defluorination ratios. Future research should be aimed at determining if ultrasonic irradiation combined with activated sodium persulfate causes smaller carbon chain formation.

Past research has shown that surface area plays a role in ultrasonic degradation of PFOA (Lin, 2015; Liu, 2012). Future research should consider the effectiveness of increased cavitation on PFOS and its constituents. Previous work has shown higher frequencies produce heightened cavitation and greater bubble production. By using a sonicator that can vary frequency it may be found that PFCs degrade greater within a specific frequency range. Higher frequencies mean higher energy costs, but research needs to be done to determine what optimal energy input is required for greater defluorination.

Other ways to remove PFCs exist and should be investigated. Granular activated carbon (GAC) is the leading removal technique for PFCs. However, this process is expensive and does not degrade the compound. Once adsorbed, the GAC filter needs to be disposed of accordingly. Disposal costs, manufacturing costs, energy costs, and ease of operation should all factor into choosing a treatment method. Investigating other forms of activating sodium persulfate could be
beneficial to lowering these costs. Similarly, analyzing at other advanced oxidation processes such as Fenton’s oxidation, or $\text{O}_3/\text{UV}$ would be useful in determining effectiveness of PFC removal.

A batch system laboratory bench scale was used in this research. The use of other reactor types should be considered for future tests. Continuous stirred tank reactors (CSTRs) or plug flow reactors (PFRs) provide a continuous flow of solution. CSTRs benefit from greater mixing for chemical addition and rapid stabilization of pH, temperature, and concentration. PFRs offer the ability of variable dosing. Multiple dosing or continuous dosing can be achieved in a PFR. Different configurations of these reactors should also be tested. Ultimately, varied reactor setups and types should be considered for future research.
Reference List


EPA. Risk Management for Per- and Polyfluoroalkyl Substances (PFASs) under TSCA. 2016
www.epa.gov/assessing-and-managing-chemicals-under-tsca/perfluorooctanoic-acid-pfoa-
perfluorooctyl-sulfonate


Liang, C.J.; Wang, Z.S.; Bruell, C.J. Influence of pH on persulfate oxidation of TCE at ambient temperatures. Chemosphere. 2007. 66. 106-113


Smithwick, M.; Norstrom, R. J.; Mabury, S. A.; Solomon, K.; Evans, T. J.; Stirling, I.; Taylor, M. K.; Muir, D. C. Temporal trends of perfluoroalkyl contaminants in polar bears (Ursus maritimus) from two locations in the North Ame

Steenland, K.; Fletcher, T.; Savitz, D. A. Epidemiologic evidence on the health effects of perfluorooctanoic acid (PFOA). Environ. Health Perspect. 2010, 118 (8), 1100–1108


Appendix A: Control Experiment IC Results

<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS/min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.28</td>
<td>Fluoride</td>
<td>BMB*</td>
<td>0.007</td>
<td>0.037</td>
<td>1.0393</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.01 0.04 1.04

---

Operator: donlocal  Timebase: CEE11_1  Sequence: KEVIN 05092018

5/11/2018  9:35 AM

---

ANION_report\Integration

Chromeleon (c) Dionex 1996-2008  
Version 6.80 SR10 Build 2818 (166959)
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS*min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.017</td>
<td>0.077</td>
<td>23007</td>
</tr>
</tbody>
</table>

**TOTAL:**

| | | | | 0.02 | 0.08 | 2.30 |

---

**Graph Image:**

A chromatogram showing peak analysis for a sample named “PFBS-persulfate-0min.” The graph displays various peaks with retention times and heights, with the highest peak at approximately 4.274 minutes, labeled as “Fluoride.” The analysis was performed using a program labeled “AutoSample_anyloop_35min_MB.”
<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td></td>
<td></td>
<td>µS/min</td>
<td>µS</td>
<td>ppb</td>
</tr>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.018</td>
<td>0.086</td>
<td>2.5087</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.02 0.09 2.51

---

**Graph:**

KEVIN 05092018 #4 [modified by donlocal]  
ECD_1

---

ANION_report/Integration

Chromeleon (c) Dionex 1996-2008  
Version 6.80 SR10 Build 2818 (166959)
Sample Name: PFBS-persulfate-30min
Sample Type: unknown
Program: AutoSample_anyloop 35min_MB
Inj. Date/Time: 09/05/18 15:13

<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS·min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.012</td>
<td>0.061</td>
<td>1.7074</td>
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</tbody>
</table>

TOTAL: 0.01 0.06 1.71
Sample Name: PFBS-persulfate-45min
Sample Type: unknown
Program: AutoSample_anyloop 35min_MB
Inj. Date/Time: 09/05/18 15:49
Inj. Vol.: 100.0
Dilution Factor: 1.0000
Operator: n.a.
Run Time: 35.00

<table>
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<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS*min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM *</td>
<td>0.012</td>
<td>0.059</td>
<td>1.6268</td>
</tr>
</tbody>
</table>

TOTAL: 0.01 0.06 1.63

ANION_report/Integration

Chromeleon (c) Dionex 1996-2008
Version 6.80 SR10 Build 2818 (166959)
Operator: donlocal  Timebase: CEE11_1  Sequence: KEVIN 05092018

Sample Name: PFBS-persulfate-60min
Sample Type: unknown
Program: AutoSample anyloop 35min_MB
Inj. Date/Time: 09/05/18  16:26

<table>
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<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.25</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.012</td>
<td>0.061</td>
<td>1.6289</td>
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</tbody>
</table>

TOTAL: 0.01 0.06 1.63

KEVIN 05092018 #7 (modified by donlocal)
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<th>No.</th>
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<th>Type</th>
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<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.011</td>
<td>0.056</td>
<td>1.5155</td>
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</table>

**TOTAL:**  
0.01  
0.06  
1.52

---

**Sample Name:** PFBS-persulfate-75min  
**Sample Type:** unknown  
**Program:** AutoSample_anyloop 35min_MB  
**Inj. Date/Time:** 09/05/18 17:02  
**Inj. Vol.:** 100.0  
**Dilution Factor:** 1.0000  
**Operator:** n.a.  
**Run Time:** 35.00

---

**ANION_report/Integration**

Chromeleon (c) Dionex 1996-2008  
Version 6.80 SR10 Build 2818 (166959)
**Sample Name:** PFBS-persulfate-90rin  
**Sample Type:** Unknown  
**Program:** AutoSample anyloop 35min_MB  
**Inj. Vol.:** 100.0  
**Dilution Factor:** 1.0000  
**Operator:** n.a.  
**Run Time:** 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time min</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area μS/min</th>
<th>Height μS</th>
<th>Amount ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.25</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.010</td>
<td>0.053</td>
<td>1.3838</td>
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</tbody>
</table>

**TOTAL:** 0.01 0.05 1.38
Sample Name: PFBS-persulfate-105min  
Sample Type: unknown  
Program: AutoSample_anyloop 35min_MB  
Inj. Date/Time: 09/05/18 18:15  
Inj. Vol.: 100.0  
Dilution Factor: 1.0000  
Operator: n.a.  
Run Time: 35.00

<table>
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<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS*min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4.25</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.010</td>
<td>0.056</td>
<td>1.3926</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.01 0.06 1.39
Sample Name: PFBS-persulfate-120min
Sample Type: unknown
Program: AutoSample_anyloop 35min_MB
 kj Date/Time: 09/06/18 18:52

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM *</td>
<td>0.012</td>
<td>0.063</td>
<td>1.7360</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.01 0.06 1.74

KEVIN 05092018 #11 [modified by donlocal]  ECD_1
**Sample Name:** PFBS-US-15min  
**Inj. Vol.:** 100.0  
**Sample Type:** unknown  
**Dilution Factor:** 1.0000  
**Program:** AutoSample_annyloop 35min_MB  
**Operator:** n.a.  
**Inj. Date/Time:** 09/06/18 20:06  
**Run Time:** 35.00

<table>
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<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.224</td>
<td>1.123</td>
<td>31.153</td>
</tr>
</tbody>
</table>

**TOTAL:**  
Area: 0.22  
Height: 1.12  
Amount: 31.15

---

KEVIN 05092018 #13 [modified by donlocal] PFBS-US-15min

**ANION_report/Integration**

Chromeleon (c) Dionex 1996-2008
Version 6.80 SR10 Build 2818 (166959)
### Sample Information

- **Sample Name:** PFBS-US-30min
- **Sample Type:** unknown
- **Program:** AutoSample_anyloop 35min_MB
- **Inj. Vol.:** 100.0
- **Dilution Factor:** 1.0000
- **Inj. Date/Time:** 09/05/18 20:41
- **Operator:** n.a.
- **Run Time:** 35.00

### Results

<table>
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<th>No.</th>
<th>Time min</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area µS/min</th>
<th>Height µS</th>
<th>Amount ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.385</td>
<td>1.919</td>
<td>53.6205</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.39   1.92    53.62

---

**Graph:**

A graph showing the analysis of PFBS-US-30min, with peaks identified for various analytes, including Fluoride at 4.271 µS.

**ANION_report/Integration**

*Chromeleon (c) Dionex 1996-2008 Version 6.80 SR10 Build 2818 (166069)*

---

42
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS/min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM  *</td>
<td>0.501</td>
<td>2.455</td>
<td>69.636</td>
</tr>
</tbody>
</table>

**TOTAL:** 3.50 2.45 69.64
**Sample Name:** PFBS-US-60min  
**Inj. Vol.:** 100.0  
**Sample Type:** unknown  
**Dilution Factor:** 1.0000  
**Program:** AutoSample_anyloop 35min_MB  
**Operator:** n.a.  
**Inj. Date/Time:** 09/05/18 21:54  
**Run Time:** 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS*min)</th>
<th>Height (µS)</th>
<th>Amount (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM*</td>
<td>0.629</td>
<td>3.046</td>
<td>87.4131</td>
</tr>
</tbody>
</table>

**TOTAL:**  
Area: 0.63  
Height: 3.05  
Amount: 87.41

---

**Graph:**

*Graph showing the analysis of PFBS-US-60min, with peaks identified including Fluoride.*

**Chromatogram:**

*Chromatogram from KEVIN 05092018 #16 (modified by donlocal) showing the separation of Peaks with retention times and heights.*
**Sample Name:** PFBS-US-75min  
**Inj. Vol.:** 100.0

**Sample Type:** unknown  
**Dilution Factor:** 1.0000

**Program:** AutoSample_anyloop 35min_MB  
**Operator:** n.a.

**Inj. Date/Time:** 09/05/18  22:31  
**Run Time:** 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (μS*min)</th>
<th>Height (μS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.28</td>
<td>Fluoride</td>
<td>BM  *</td>
<td>0.728</td>
<td>3.347</td>
<td>101.2340</td>
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</tbody>
</table>

**TOTAL:** 0.73  3.65  101.28

---

[Graph showing the analysis results for PFBS-US-75min with peak heights and areas, including a peak labeled 'Fluoride' at 4.28 minutes.]

---

**ANION_report/Integration**  
**Chromeleon (c) Dionex 1996-2008**  
**Version 6.80 SR10 Build 2818 (166959)**
### Analysis Results

<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µg/min)</th>
<th>Height (µg)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>RM *</td>
<td>0.847</td>
<td>4.034</td>
<td>117.8882</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.85 4.03 117.69

---

**Graphical Representation:**

A chromatogram showing the analysis of PFBS-US-90min, with peaks at various retention times. The peaks are labeled with their respective compounds and areas. The graph includes a peak labeled 'Fluoride' at 4.274 min with an area of 0.847 µg/min.

---

**Additional Information:**

- **Sample Name:** PFBS-US-90min
- **Sample Type:** unknown
- **Program:** AutoSample_anyloop 35min_MB
- **Inj. Date/Time:** 09/05/18 23:07
- **Inj. Vol.:** 100.0 µL
- **Dilution Factor:** 1.0000
- **Operator:** n.a.
- **Run Time:** 36.00 min
**Sample Name:** PFBS-US-105min  
**Sample Type:** unknown  
**Program:** AutoSample_anyloop 35mln_MB  
**Injection Volume:** 100.0  
**Dilution Factor:** 1.0000  
**Operator:** n.a.  
**Inj. Date/Time:** 09/05/18 23:44  
**Run Time:** 35.00

<table>
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<th>No.</th>
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<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.926</td>
<td>4.431</td>
<td>128.7019</td>
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</tbody>
</table>

**TOTAL:**  
Area: 0.93  
Height: 4.43  
Amount: 128.70

---

**Graph:**  
- **KEVIN 05092018 #19 (modified by donlocal)**  
- **ECD 1**  
- **Axes:**  
  - X-axis: Time (min)  
  - Y-axis: μS  
- **Peaks:**  
  - Fluoride at 4.27 min

---

**Software:**  
- Chromleon (c) Dionex 1996-2008  
- Version 6.80 SR10 Build 2818 (166959)
<table>
<thead>
<tr>
<th>No.</th>
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<th>Area (μS*min)</th>
<th>Height (μS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Fluoride</td>
<td>SM</td>
<td>1.01</td>
<td>4.769</td>
<td>140.3614</td>
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<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
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<td></td>
<td>1.01</td>
<td>4.77</td>
<td>140.38</td>
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Chromeloon (c) Dionex 1996-2008
Version 6.80 SR10 Build 2818 (166959)

ANION_report/Integration
<table>
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<th>Height (μS)</th>
<th>Amount (ppb)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>total</td>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

---

**Graph:**

Graph showing a peak at around 18.817 minutes with a height of 0.300 μS.

---

**Table:**

<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
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<th>Area (μS*min)</th>
<th>Height (μS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>total</td>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>No.</td>
<td>Time (min)</td>
<td>Peak Name</td>
<td>Type</td>
<td>Area (µS*min)</td>
<td>Height (µS)</td>
<td>Amount (ppb)</td>
</tr>
<tr>
<td>-----</td>
<td>------------</td>
<td>-----------</td>
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<td>---------------</td>
<td>-------------</td>
<td>--------------</td>
</tr>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.012</td>
<td>0.059</td>
<td>1.6079</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.01 0.05 1.61
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS*min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.010</td>
<td>0.053</td>
<td>1.3308</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.01 0.05 1.33
**Sample Name:** PFHxS-persulfate-30min  
**Inj. Vol.:** 100.0  
**Program:** AutoSample_anyloop 35min_MB  
**Run Time:** 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS*min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.008</td>
<td>0.047</td>
<td>1.1156</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.01 0.05 1.12
Sample Name: PFHxS-persulfate-45min
Sample Type: unknown
Program: AutoSample_anyloop 35min_MB
Inj. Vol.: 100.0
Dilution Factor: 1.0000
Operator: n.a.
Inj. Date/Time: 10/05/18 14:40
Run Time: 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (μS/min)</th>
<th>Height (μS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM *</td>
<td>0.009</td>
<td>0.053</td>
<td>1.2652</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TOTAL: 0.01</td>
<td>0.05</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Kevin 05102018 #6 [modified by donlocal]

Chromeleon (c) Dionex 1996-2008
ANION_report/Integration
Version 6.60 SR10 Build 2818 (166959)
Sample Name: PFHxS-persulfate-60min
Sample Type: unknown
Program: AutoSample anyloop 35min MB
Inj. Date/Time: 10/05/18 15:16
Run Time: 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS*min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.007</td>
<td>0.045</td>
<td>1.0289</td>
</tr>
</tbody>
</table>

**TOTAL:**

0.01 0.05 1.03

---

**Graph:**

[Graph showing a chromatogram with peaks labeled.]
<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.006</td>
<td>0.047</td>
<td>1.0588</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.01 0.05 1.06
Sample Name: PFHxS-persulfate-90min  Inj. Vol.: 100.0
Sample Type: unknown  Dilution Factor: 1.0000
Program: AutoSample_anyloop 35min_MB  Operator: n.a.
Inj. Date/Time: 10/05/18  16:29  Run Time: 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.008</td>
<td>0.050</td>
<td>1.1511</td>
</tr>
</tbody>
</table>

TOTAL: 0.01 0.05 1.15
<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area µS/min</th>
<th>Height µS</th>
<th>Amount ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>8M</td>
<td>0.009</td>
<td>0.051</td>
<td>1.1821</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.01 0.05 1.18

---

**Sample Name:** PFHxS-persulfate-105min
**Inj. Vol.:** 100.0
**Sample Type:** unknown
**Dilution Factor:** 1.0000
**Program:** AutoSample_anyloop_35min_MB
**Operator:** n.a.
**Inj. Date/Time:** 10/05/18 17:06
**Run Time:** 35.00
<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS/min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM *</td>
<td>0.008</td>
<td>0.050</td>
<td>1.0823</td>
</tr>
</tbody>
</table>

**TOTAL:**

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01</td>
<td>0.05</td>
<td>1.08</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

*Kevin 05102018 #11 [modified by donlocal]*

---

*ECD_1*

---

**Sample Name:** PFHxS-persulfate-120min  
**Inj. Vol.:** 100.0

**Sample Type:** unknown  
**Dilution Factor:** 1.0000

**Program:** AutoSample anyloop 35min MB  
**Operator:** n.a.

**Inj. Date/Time:** 10/05/18 17:42  
**Run Time:** 35.00
Sample Name: PFHxS-US-0min  Inj. Vol.: 100.0
Sample Type: unknown  Dilution Factor: 1.0000
Program: AutoSample anyloop 35min_MB  Operator: n.a.
Inj. Date/Time: 10/05/18 18:19  Run Time: 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area µS/min</th>
<th>Height µS</th>
<th>Amount ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM *</td>
<td>0.011</td>
<td>0.055</td>
<td>1.5543</td>
</tr>
</tbody>
</table>

TOTAL: 0.01  0.05  1.55
Sample Name: PFHxS-US-15min
Sample Type: unknown
Program: AutoSample_anyloop 35min_MB
Inj. Date/Time: 10/05/18 18:55

<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (μS*min)</th>
<th>Height (μS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.499</td>
<td>2.573</td>
<td>69.4182</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.50 2.57 69.42
Sample Name: PFHxS-US-30min  Inj. Vol.: 100.0
Sample Type: unknown  Dilution Factor: 1.0000
Program: AutoSample_anyloop 35min_MB  Operator: n.a.
Inj. Date/Time: 10/05/18 19:32  Run Time: 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS/min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM</td>
<td>1.035</td>
<td>5.937</td>
<td>143.9476</td>
</tr>
</tbody>
</table>

**TOTAL:** 1.04 5.94 143.95
Sample Name: PFHxS-US-45min  Inj. Vol.: 100.0
Sample Type: unknown  Dilution Factor: 1.0000
Program: AutoSample_anyloop 35min_MB  Operator: n.a.
Inj. Date/Time: 10/05/18 20:08  Run Time: 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area μS*min</th>
<th>Height μS</th>
<th>Amount ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM *</td>
<td>1.540</td>
<td>7.447</td>
<td>214.1080</td>
</tr>
</tbody>
</table>

**TOTAL:** 1.54  7.45  214.11
Sample Name: PFHxS-US-60min
Sample Type: unknown
Program: AutoSample anyloop 35min_MB
Inj. Date/Time: 10/05/18  20:45
Run Time: 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.28</td>
<td>Fluoride</td>
<td>8M</td>
<td>2.079</td>
<td>9.899</td>
<td>286.9796</td>
</tr>
</tbody>
</table>

TOTAL: 2.08  9.90  286.98
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (μS/min)</th>
<th>Height (μS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.29</td>
<td>Fluoride</td>
<td>RM</td>
<td>2.547</td>
<td>12.038</td>
<td>354.0875</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TOTAL:</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TOTAL:** 2.55, 12.04, 354.09

---

**Graph:**

- **Title:** Fluoride (Fluoro) Analysis
- **Time (min):** 0.0 to 35.0
- **Concentration (μS):** 18.0
- **Peak Details:**
  - Fluoride: 1.0, 4.287
  - Other peaks with minor contributions

---

**Technical Details:***

- **Sample Name:** PFHxS-US-75min
- **Injection Volume (μL):** 100.0
- **Sample Type:** unknown
- **Dilution Factor:** 1.0000
- **Program:** AutoSample_anyloop 35min_MB
- **Date/Time:** 10/05/18 21:21
- **Run Time:** 36.00

---

**Note:**

This analysis was conducted using a Dionex HPLC system. The ECD detector was configured to detect fluoro-specific peaks accurately. The chromatogram shows a clean separation of Fluoride from other potential interferences, confirming its presence at the specified concentration.
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (μS/min)</th>
<th>Height (μS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.28</td>
<td>Fluoride</td>
<td>BM *</td>
<td>3.032</td>
<td>14.292</td>
<td>421.5017</td>
</tr>
</tbody>
</table>

**TOTAL:**

3.03
14.29
421.50

---

**Note:**

- Sample Name: PFHxS-US-90min
- Sample Type: unknown
- Program: AutoSample_anyloop 35min_MB
- Operator: n.a.
- Inj. Date/Time: 10/05/18 21:58
- Run Time: 35.00
**Sample Name:** PFHex-US-105min  
**Inj. Vol.:** 100.0  
**Sample Type:** unknown  
**Dilution Factor:** 1.0000  
**Program:** AutoSample.anyloop 35min_MB  
**Operator:** n.a.  
**Inj. Date/Time:** 10/05/18 22:34  
**Run Time:** 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time min</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area µS/min</th>
<th>Height µS</th>
<th>Amount ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.28</td>
<td>Fluoride</td>
<td>BM</td>
<td>3.576</td>
<td>16.653</td>
<td>497.1132</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TOTAL:</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.58</td>
<td>16.65</td>
<td>497.11</td>
</tr>
</tbody>
</table>

**Kevin 05102018 #19 [modified by donlocal] PFHex-US-105min**

ECD_1

---

**ANION_report/Integration**

Chromeleon (c) Dionex 1996-2008

Version 6.80 SR10 Build 2818 (166959)
<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.28</td>
<td>Fluoride</td>
<td>BM *</td>
<td>4.020</td>
<td>18.677</td>
<td>558.812</td>
</tr>
<tr>
<td><strong>TOTAL:</strong></td>
<td></td>
<td></td>
<td></td>
<td>4.02</td>
<td>18.68</td>
<td>558.81</td>
</tr>
</tbody>
</table>

Sample Name: PFHxS-US-120min
Sample Type: unknown
Program: AutoSample_anyloop 35min_MB
Inj. Date/Time: 10/05/18 23:11
Inj. Vol.: 100.0
Dilution Factor: 1.0000
Run Time: 35.00
<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td></td>
<td></td>
<td>µS*min</td>
<td>µS</td>
<td>ppb</td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
<td></td>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

![Graph](image-url)
**Sample Name:** blk  
**Inj. Vol.:** 100.0  
**Sample Type:** unknown  
**Dilution Factor:** 1.0000  
**Program:** AutoSampler_anyloop_26min_MB  
**Operator:** n.a.  
**Inj. Date/Time:** 09/05/18 13:12  
**Run Time:** 26.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS*min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.28</td>
<td>Fluoride</td>
<td>BMB*</td>
<td>0.007</td>
<td>0.037</td>
<td>1.0393</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.04  

---

**Diagram:**
- Labelled peaks: 1 - Fluoride (4.280), 2 - T1094, 3 - T10987

---

ANION_report/Integration  
Chromeleon (c) Dionex 1995-2008  
Version 6.80 SR10 Build 2818 (156959)
Sample Name: PFBS-persulfate-0min
Sample Type: unknown
Program: AutoSample_anyloop 35min_MB
Inj. Date/Time: 09/05/18 14:00
Inj. Vol.: 100.0
Dilution Factor: 1.0000
Operator: n.a.
Run Time: 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.017</td>
<td>0.077</td>
<td>2.30E7</td>
</tr>
</tbody>
</table>

TOTAL: 0.02 0.08 2.30
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS*min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.018</td>
<td>0.086</td>
<td>2.5087</td>
</tr>
</tbody>
</table>

**TOTAL:**

|      | 0.02       | 0.09       | 2.51       |

**Graph:**

![Graph of Fluoride analysis](attachment:image.png)
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS*min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>SM *</td>
<td>0.012</td>
<td>0.061</td>
<td>1.7074</td>
</tr>
</tbody>
</table>

**TOTAL:**

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01</td>
<td>0.06</td>
<td>1.71</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[Graph showing chromatogram with peak labeled as 'Fluoride' at 4.26 minutes, peak height of 0.061 µS, and area of 0.012 µS*min]
### Analyte Information

- **Sample Name:** PFBS-persulfate-45min
- **Sample Type:** unknown
- **Program:** AutoSample anyloop 35min MB

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area μS/min</th>
<th>Height μS</th>
<th>Amount ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4.27</td>
<td>Fluoride</td>
<td>8M *</td>
<td>0.012</td>
<td>0.059</td>
<td>1.6268</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.01 0.05 1.63
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS*min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.25</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.010</td>
<td>0.053</td>
<td>1.3838</td>
</tr>
</tbody>
</table>

**TOTAL:**

|     |            |           |      | 0.01          | 0.05        | 1.38         |

![Graph of Fluoride Peak](image)
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS*min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4.25</td>
<td>Fluoride</td>
<td>BM +</td>
<td>0.010</td>
<td>0.056</td>
<td>1.3926</td>
</tr>
</tbody>
</table>

**TOTAL:**

<table>
<thead>
<tr>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.05</td>
</tr>
<tr>
<td>No.</td>
<td>Time (min)</td>
</tr>
<tr>
<td>-----</td>
<td>------------</td>
</tr>
<tr>
<td>1</td>
<td>4.27</td>
</tr>
</tbody>
</table>

**TOTAL:**

0.01  0.05  1.74

---

![Graph of Fluoride Peak](attachment:graph.png)
<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area μS*min</th>
<th>Height μS</th>
<th>Amount ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.010</td>
<td>0.056</td>
<td>1.4555</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.01  0.05  1.45
<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area μS/min</th>
<th>Height μS</th>
<th>Amount ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.224</td>
<td>1.123</td>
<td>31.1638</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.22 1.12 31.18
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS/min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.386</td>
<td>1.9/9</td>
<td>53.6205</td>
</tr>
</tbody>
</table>

**TOTAL:**

| 0.32 | 1.92 | 53.62 |

---

**Graph:**

The graph shows a chromatogram with peaks labeled as Fluoride at 4.27 minutes. The peak height and area are presented above each peak. The total area under the curve for Fluoride is 53.62 ppb.
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS*min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.501</td>
<td>2.455</td>
<td>69.6356</td>
</tr>
</tbody>
</table>

**TOTAL:**

|       |     |       |      | 0.50 | 2.45 | 69.84 |

---

**KEVIN 05092018 #15 [modified by donlocal] PFBS-US-45min**

**ECD_1**

---

**ANION_report/Integration**

**Chromeleon (c) Dionex 1996-2008**

**Version 6.80 SR10 Build 2818 (166959)**
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS/min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM *</td>
<td>0.629</td>
<td>3.046</td>
<td>87.4131</td>
</tr>
</tbody>
</table>

**TOTAL:**

|            | 0.63 | 3.05 | 87.41 |

**Graph Image:**

- KEVIN 05092018 #16 (modified by donlocal) PFBS-US-60min
- ECD 1

---

Operator: donlocal  Timebase: CEE11_1  Sequence: KEVIN 05092018  
5/11/2018  9:35 AM
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS·min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.28</td>
<td>Fluoride</td>
<td>BM^*</td>
<td>0.728</td>
<td>3.547</td>
<td>101.2840</td>
</tr>
</tbody>
</table>

**TOTAL:**

- 0.73
- 3.55
- 101.25

---

**Graph:**

- **Title:** KEVIN 05092018 #17 [modified by donlocal] PFBS-US-75min
- **Component:** ECD
- **Concentration Range:** 0.0 - 5.00 µS
- **Time Range:** 0.0 - 35.00 min
- **Peaks:**
  - Fluoride at 4.28 min
  - Other peaks indicated at specific times and concentrations.

---

**Technical Details:**

- **Operator:** donlocal
- **Sequence:** KEVIN 05092018
- **Sample Name:** PFBS-US-75min
- **Inj. Vol.:** 100.0 µL
- **Sample Type:** unknown
- **Program:** AutoSample Anyloop 35min_MB
- **Inj. Date/Time:** 09/05/18 22:31
- **Run Time:** 15.00 min
- **Dilution Factor:** 1.0000

---

**Software:**

- Chromeleon (c) Dionex 1996-2008
- Version 6.80 SR10 Build 2818 (166959)

---

**Page Reference:**

- Page 16
- 5/11/2018 9:35 AM
Sample Name: PFBS-US-90min  Inj. Vol.: 100.0
Sample Type: unknown  Dilution Factor: 1.0000
Program: AutoSample_anyloop 35min_MB  Operator: n.a.
Inj. Date/Time: 09/05/18 23:07  Run Time: 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS*min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>8M *</td>
<td>0.847</td>
<td>4.034</td>
<td>117.6882</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.85 4.03 117.69
<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (\mu S/min)</th>
<th>Height (\mu S)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM  *</td>
<td>0.926</td>
<td>4.431</td>
<td>128.7019</td>
</tr>
</tbody>
</table>

**TOTAL:**

|      | 0.93 | 4.43 | 128.70          |

**Graph:**

The graph shows a trace analysis with peaks labeled as Fluoride at 4.27 minutes. The trace is labeled as KEVIN 05092218 #19 [modified by donlocal].

*Note: The graph details are not fully transcribed due to the image resolution.*
<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area [µS*min]</th>
<th>Height [µS]</th>
<th>Amount [ppb]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM*</td>
<td>1.01</td>
<td>4.769</td>
<td>140.3614</td>
</tr>
</tbody>
</table>

**TOTAL:**

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.01</td>
<td>4.77</td>
<td></td>
<td></td>
<td></td>
<td>140.36</td>
</tr>
</tbody>
</table>

---

ANION_report/Integration

88
### Sample Information

**Sample Name:** blk  
**Inj. Vol.:** 100.0  
**Sample Type:** unknown  
**Dilution Factor:** 1.0000  
**Program:** AutoSampler anyloop 26min MB  
**Operator:** s.a.  
**Inj. Date/Time:** 10/05/18 00:57  
**Run Time:** 26.00

### Table: Peak Integration

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td></td>
<td></td>
<td>µS/min</td>
<td>µS</td>
<td>ppb</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TOTAL:</td>
</tr>
</tbody>
</table>

### Graph

The graph shows a chromatogram with peaks labeled 'blk' and 'ECD_1'. The graph is labeled 'KEVIN 05092018 #21'.
### Appendix B: Experimental IC Results

#### Sample Information
- **Sample Name:** PFOS-US-NaSO4-0min
- **Inj. Vol.:** 100.0
- **Sample Type:** unknown
- **Dilution Factor:** 1.0000
- **Program:** AutoSample_anyloop 35min_MB
- **Operator:** n.a.
- **Inj. Date/Time:** 03/05/18 15:06
- **Run Time:** 15:00

#### Analysis Table

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.28</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.025</td>
<td>0.121</td>
<td>3.4520</td>
</tr>
</tbody>
</table>

**TOTAL:**
- 0.02
- 0.12
- 3.45

#### Graph

![Graph showing IC results](image)
<table>
<thead>
<tr>
<th>No.</th>
<th>Time min</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area μS*min</th>
<th>Height μS</th>
<th>Amount ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.29</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.148</td>
<td>0.683</td>
<td>20.525</td>
</tr>
</tbody>
</table>

**TOTAL:**

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.15</td>
<td>0.68</td>
<td></td>
<td>20.52</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[Graph showing the concentration of Fluoride over time]
<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.29</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.314</td>
<td>1.470</td>
<td>43.5201</td>
</tr>
</tbody>
</table>

**TOTAL:**

|       |      |          |      | 0.31  | 1.47   | 43.52  |

---

**Graph:**

- 0.00 µS
- 1.00 µS
- 2.00 µS
- 3.00 µS
- 4.00 µS
- 5.00 µS
- 6.00 µS

- 0.00 min
- 5.00 min
- 10.0 min
- 15.0 min
- 20.0 min
- 25.0 min
- 30.0 min
- 35.0 min

**Legend:**

- Fluoride

---

**Report Information:**

- Operator: donlocal
- Timebase: CEE11_1
- Sequence: Kavin 05032018
- Page: 12
- Date: 5/4/2018
- Time: 9:25 AM

---

**Graph Information:**

- Software: Chromelon (c) Dionex 1996-2008
- Version: 6.80 SR10 Build 2818 (166959)
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS/min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.29</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.42</td>
<td>2.046</td>
<td>58.7563</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.42 2.05 58.78
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS*min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.528</td>
<td>2.581</td>
<td>73.4125</td>
</tr>
</tbody>
</table>

**TOTAL:**

0.53     2.58   73.41
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS/min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.621</td>
<td>3.03</td>
<td>86.3675</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TOTAL:</td>
<td>86.36</td>
</tr>
</tbody>
</table>

Kavin 05032018 #14 [modified by donlocal]
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS:min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.28</td>
<td>Fluoride</td>
<td>BM*</td>
<td>0.71</td>
<td>3.463</td>
<td>99.2975</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.71 3.46 99.39
Sample Name: PFOS-US-NaSO4-120min
Sample Type: unknown
Program: AutoSample_anyloop 35min_MB

Inj. Vol.: 100.0
Dilution Factor: 1.0000

Inj. Date/Time: 03/05/18 19:58
Run Time: 15.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS*min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.28</td>
<td>Fluoride</td>
<td>BM *</td>
<td>0.850</td>
<td>4.156</td>
<td>118.1441</td>
</tr>
</tbody>
</table>

**TOTAL:**

0.85 4.15 118.14
**Sample Name:** PFHxS-combine-0min  
**Sample Type:** unknown  
**Program:** AutoSample anyloop 35min_MB  
**Inj. Vol.:** 0.00  
**Dilution Factor:** 1.0000  
**Operator:** a.a.  
**Run Time:** 35.00  
**Inj. Date/Time:** 11/05/18 13:55

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS·min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TOTAL:</td>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

---

![Graph](attachment:image.png)

**KEVIN 05112018 #3**

**PFHxS-combine-0min**

**ECD-1**

**ANION_report/Integration**

**Chromeleon (c) Dionex 1996-2008**

**Version 6.80 SR10 Build 2818 (166959)**
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (μS·min)</th>
<th>Height (μS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.817</td>
<td>3.933</td>
<td>111.8263</td>
</tr>
</tbody>
</table>

**TOTAL:** 0.82 3.53 111.83
Sample Name: PFHxS-combine-30min  Inj. Vol.: 100.0
Sample Type: unknown  Dilution Factor: 1.0000
Program: AutoSample_anyloop 35min_MB  Operator: n.a.
Inj. Date/Time: 11/05/18 15:08  Run Time: 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM</td>
<td>1.387</td>
<td>6.716</td>
<td>10.988</td>
</tr>
</tbody>
</table>

TOTAL: 132.57 57.72 109.34

[Graph showing the results of the analysis]
Sample Name: PFHxS-combine-75min  Inj. Vol.: 100.0
Sample Type: unknown  Dilution Factor: 1.0000
Inj. Date/Time: 11/05/18 16:57  Run Time: 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS/min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM</td>
<td>2.815</td>
<td>13.205</td>
<td>385.5147</td>
</tr>
</tbody>
</table>

TOTAL: 2.82  13.20  385.51
### Sample Information
- **Sample Name:** PFHxS-combine-90min
- **Sample Type:** unknown
- **Program:** AutoSample anyloop 35min_MB
- **Inj. Date/Time:** 11/05/18 17:34
- **Run Time:** 35.00

### Analysis Results

<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS*min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM</td>
<td>3.223</td>
<td>14.954</td>
<td>441.3558</td>
</tr>
</tbody>
</table>

**TOTAL:** 3.22 14.95 441.38

---

**Graph:**

- **Title:** KEVIN 05112018 #0
- **Sample:** PFHxS-combine-90min
- **Column:** ECD_1

**Peak:**

1. **Fluoride:** 4.27 µS

---

**Software:** Chromeleon (c) Dionex 1996-2008
**Version:** 6.80 SR10 Build 2818 (166959)
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS/min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>8MB</td>
<td>3.964</td>
<td>16.421</td>
<td>541.4216</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>3.95</td>
<td>16.42</td>
<td>541.42</td>
</tr>
<tr>
<td>No.</td>
<td>Time (min)</td>
<td>Peak Name</td>
<td>Type</td>
<td>Area (μS·min)</td>
<td>Height (μS)</td>
<td>Amount (ppb)</td>
</tr>
<tr>
<td>-----</td>
<td>------------</td>
<td>-----------</td>
<td>------</td>
<td>---------------</td>
<td>-------------</td>
<td>--------------</td>
</tr>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM</td>
<td>3.889</td>
<td>17.769</td>
<td>532.5422</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
<td></td>
<td></td>
<td>3.88</td>
<td>17.77</td>
<td>532.54</td>
</tr>
</tbody>
</table>
**Sample Name:** PFBS-combine-T=0  
**Inj. Vol.:** 100.0  
**Sample Type:** unknown  
**Dilution Factor:** 1.0000  
**Program:** AutoSample_anyloop 35min_MB  
**Operator:** n.a.  
**Inj. Date/Time:** 14/05/18 13:31  
**Run Time:** 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td></td>
<td>µS/min</td>
<td>µS</td>
<td>ppb</td>
<td></td>
</tr>
<tr>
<td>TOTAL:</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Graph:**

The graph shows the KEVIN 05142018 #3 with the PFBS-combine-T=0 sample. The trace extends from a minimum of -0.50 µS to a maximum of 3.50 µS, with time markers from 0.0 to 35.0 minutes.
Sample Name: PFBS-combine-T=15
Sample Type: unknown
Program: AutoSample__anyloop 35min_MB
Inj. Date/Time: 14/05/18 14:07
Inj. Vol.: 100.0
Dilution Factor: 1.0000
Operator: n.a.
Run Time: 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM *</td>
<td>0.479</td>
<td>2.068</td>
<td>64.343</td>
</tr>
</tbody>
</table>

TOTAL: 0.47 2.07 64.34
<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td></td>
<td></td>
<td>µS/min</td>
<td>µS</td>
<td>ppb</td>
</tr>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM *</td>
<td>0.851</td>
<td>4.398</td>
<td>116.578</td>
</tr>
</tbody>
</table>

**TOTAL:**

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.85</td>
<td>4.40</td>
<td>118.57</td>
</tr>
</tbody>
</table>

KEVIN 05142018 №6 [modified by donlocal]
Sample Name: PFBS-combine-T=60  Inj. Vol.: 100.0
Sample Type: unknown  Dilution Factor: 1.0000
Program: AutoSample_anyloop 35min_MB  Operator: n.a.
Inj. Date/Time: 14/05/18  15:57  Run Time: 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM</td>
<td>1.178</td>
<td>5.694</td>
<td>161.3199</td>
</tr>
</tbody>
</table>

**TOTAL:**
1.18 5.62 161.32

KEVIN 05142018 #7 (modified by donlocal)
Sample Name: PFBS-combine-T=75  Inj. Vol.: 100.0
Sample Type: unknown  Dilution Factor: 1.0000
Program: AutoSample_aniloop 35min_MB  Operator: n.a.
Inj. Date/Time: 14/05/18 16:33  Run Time: 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM *</td>
<td>1.369</td>
<td>6.210</td>
<td>187.446</td>
</tr>
</tbody>
</table>

TOTAL: 1.37  6.21  187.46

---

KEVIN 05142018 #8 (modified by donlocal)
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS×min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM *</td>
<td>1.648</td>
<td>7.386</td>
<td>225.7302</td>
</tr>
</tbody>
</table>

**TOTAL:** 1.65 7.39 225.73

---

**Sample Name:** PFBS-combine-T=90  
**Inj. Vol.:** 100.0  
**Sample Type:** unknown  
**Dilution Factor:** 1.0000  
**Program:** AutoSample_anyloop 35min_MN  
**Operator:** n.a.  
**Inj. Date/Time:** 14/05/18 17:10  
**Run Time:** 35.00

---

**Graph:** Graph showing Fluoride peak at 4.26 minutes with an area of 1.648 µS×min and a height of 7.386 µS, resulting in an amount of 225.73 ppb.
Sample Name: PFBS-combine-T=105  Inj. Vol.: 100.0
Sample Type: unknown  Dilution Factor: 1.0000
Program: AutoSample_anyloop 35min_MB  Operator: n.a.
Inj. Date/Time: 14/05/18  17:46  Run Time: 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time  min</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area μS/min</th>
<th>Height μS</th>
<th>Amount ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.27</td>
<td>Fluoride</td>
<td>BM</td>
<td>1.990</td>
<td>8.175</td>
<td>267.0855</td>
</tr>
</tbody>
</table>

**TOTAL:** 1.52 8.22 267.08
Sample Name: PFBS-combine-T=120  Inj. Vol.: 100.0
Sample Type: unknown  Dilution Factor: 1.0000
Program: AutoSample_anyloop 35min_MB  Operator: s.a.
Inj. Date/Time: 14/05/18 18:23  Run Time: 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area μS min</th>
<th>Height μS</th>
<th>Amount ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.26</td>
<td>Fluoride</td>
<td>BM</td>
<td>2.205</td>
<td>9.281</td>
<td>301.8846</td>
</tr>
</tbody>
</table>

**TOTAL:** 2.20 5.28 301.88

KEVIN 05142018 #11 [modified by donlocal] ECD_1
### Sample Information
- **Sample Name:** PFBS T= 15
- **Sample Type:** unknown
- **Program:** AutoSample anyloop 35min MB
- **Inj. Vol.:** 100.0
- **Dilution Factor:** 1.0000
- **Operator:** a.a.
- **Inj. Date/Time:** 08/06/18 14:28
- **Run Time:** 15:00

### Analysis Results

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>µS*min</td>
<td>µS</td>
<td>ppb</td>
</tr>
<tr>
<td>TOTAL</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

**Graph**

The graph shows a chromatogram with peaks labeled for various times and areas. The peaks are labeled with specific times and areas, indicating the detection of PFBS at different retention times.

---

*ANION_report/Integration*  
*Chromeleon (c) Dionex 1996-2008*

Version 6.80 SR10 Build 2818 (166959)
<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area μS*min</th>
<th>Height μS</th>
<th>Amount ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TOTAL:</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

![Graph showing data for PFBS T= 45](image-url)
Sample Name: PFBS T= 60
Sample Type: unknown
Program: AutoSample_anyloop 35min_MB
Inj. Vol.: 100.0
Dilution Factor: 1.0000
Inj. Date/Time: 08/06/18 16:18
Operator: n.a.
Run Time: 35.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area μS*min</th>
<th>Height μS</th>
<th>Amount ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOTAL:</td>
<td></td>
<td></td>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Chromelcos (c) Dionex 1996-2008
ANION_report/Integration
Version 6.80 SR10 Build 2818 (166959)
Sample Name: PFBS T= 75
Sample Type: unknown
Program: AutoSample_anyloop 35min_MB
Inj. Date/Time: 08/06/18 16:54
Inj. Vol.: 0.000
Dilution Factor: 0.0000
Operator: s.a.
Run Time: 15.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td></td>
<td></td>
<td>µS*min</td>
<td>µS</td>
<td>ppb</td>
</tr>
<tr>
<td>TOTAL:</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Kevin 060818 #8
PFBS T= 75
ECD_1

Chromleon (c) Dionex 1996-2008
ANION_report/Integration
Version 6.80 SR10 Build 2818 (166959)
Sample Name: PFBS T= 105
Sample Type: unknown
Program: AutoSample_anyloop 35min_MB
Inj. Date/Time: 06/06/18 18:07

<table>
<thead>
<tr>
<th>No.</th>
<th>Time min</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area µS*min</th>
<th>Height µS</th>
<th>Amount ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TOTAL:</td>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

![Graph of PFBS T= 105](image)
<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS/min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TOTAL</td>
<td></td>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

---

**Sample Name:** PFBS T=0  
**Inj. Vol.:** 100.0  
**Sample Type:** unknown  
**Dilution Factor:** 1.0000  
**Program:** AutoSample anyloop 35min_MB  
**Operator:** n.a.  
**Run Time:** 35.00

Chart showing the chromatogram with peak areas and integrals.
# Appendix C: Calibration Curve IC Results

Operator: donlocal  Timebase: CEE11_1  Sequence: Kavin 05032018  

<table>
<thead>
<tr>
<th>Sample Name:</th>
<th>10ppb</th>
<th>Inj. Vol.:</th>
<th>100.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Type:</td>
<td>Standard</td>
<td>Dilution Factor:</td>
<td>1.0000</td>
</tr>
<tr>
<td>Program:</td>
<td>AutoSampler_anyloop 26min_MB</td>
<td>Operator:</td>
<td>n.a.</td>
</tr>
<tr>
<td>Inj. Date/Time:</td>
<td>03/05/18  12:21</td>
<td>Run Time:</td>
<td>26.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Time min</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area µS*min</th>
<th>Height µS</th>
<th>Amount ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.30</td>
<td>Fluoride</td>
<td>BM *</td>
<td>0.060</td>
<td>0.300</td>
<td>8.3389</td>
</tr>
</tbody>
</table>

**TOTAL:**

|   | 0.06 | 0.30 | 8.34 |

---

![Graph showing calibration curve and peak analysis](image-url)

Kavin 05032018 #3 [modified by donlocal]  
10ppb  
ECD_1

---

ANION_report/Integration  
Chromeleon (c) Dionex 1996-2008  
Version 6.80 SR10 Build 2818 (166959)
Sample Name: 50ppb
Sample Type: standard
Program: AutoSampler_anyloop 26min_MB
Inj. Date/Time: 03/05/18 12:49

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.28</td>
<td>Fluoride</td>
<td>8M</td>
<td>0.329</td>
<td>1.627</td>
<td>45.786</td>
</tr>
</tbody>
</table>

TOTAL: 0.33 1.63 45.78
<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.29</td>
<td>Fluoride</td>
<td>BM</td>
<td>0.70</td>
<td>3.437</td>
<td>97.524</td>
</tr>
</tbody>
</table>

**TOTAL:**

<table>
<thead>
<tr>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.70</td>
<td>3.44</td>
<td>97.52</td>
</tr>
</tbody>
</table>

---

**Graph Description:**

- **Peak 1:** Fluoride at 4.29 minutes
- **Peak 2:** unidentified at 4.63 minutes
- **Peak 3:** unidentified at 8.07 minutes
- **Peak 4:** unidentified at 17.67 minutes

**Graph Details:**

- **Time Scale:** 0.0 to 26.0 minutes
- **Concentration Scale:** 0.0 to 5.0 μS

**Integration Software:**

- **Software:** Chromeleon (c) Dionex 1996-2008
- **Version:** 6.80 SR10 Build 2818 (166959)

---

**Operator:** donlocal  
**Timebase:** CEE11_1  
**Sequence:** Kavin 05032018  
**Inj. Vol.:** 100.0  
**Dilution Factor:** 1.0000  
**Operator:** s.a.
Sample Name: 300ppb
Sample Type: standard
Program: AutoSampler anyloop 26min_MB

Inj. Date/Time: 03/05/18 13:44
Run Time: 26.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (µS*min)</th>
<th>Height (µS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.29</td>
<td>Fluoride</td>
<td>BM *</td>
<td>2.130</td>
<td>10.206</td>
<td>296.0979</td>
</tr>
<tr>
<td>TOTAL:</td>
<td></td>
<td></td>
<td></td>
<td>2.13</td>
<td>10.21</td>
<td>296.10</td>
</tr>
</tbody>
</table>

Kavin 05032018 #6 [modified by donlocal] 300ppb

ANION_report/Integration

Chromeleon (c) Dionex 1996-2008
Version 6.80 SR10 Build 2818 (166959)
Sample Name: 600ppb
Sample Type: standard
Program: AutoSampler anyloop 26min_MB
Inj. Date/Time: 03/05/18 14:11
Run Time: 36.00
Inj. Vol.: 100.0
Dilution Factor: 1.0000
Operator: s.a.

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area (μS/min)</th>
<th>Height (μS)</th>
<th>Amount (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.30</td>
<td>Fluoride</td>
<td>BM</td>
<td>4.337</td>
<td>19.123</td>
<td>602.9694</td>
</tr>
</tbody>
</table>

**TOTAL:**

4.34 19.12 602.97
<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Peak Name</th>
<th>Type</th>
<th>Area</th>
<th>Height</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.31</td>
<td>Fluoride</td>
<td>RM</td>
<td>7.192</td>
<td>29.604</td>
<td>999.8651</td>
</tr>
</tbody>
</table>

**TOTAL:**

|     |     |       |      | 7.19 | 29.60 | 999.87 |

---

*Graph showing the analysis of Fluoride with peak areas, heights, and calculated amounts.*
Calibration Batch Report

Sequence:  Kavin 05032018
Program:  AutoSampler anyloop 26min MB
Inj. Date/Time:  05/03/18 14:39
Operator:  CEE11
Run Time:  26.00

Fluoride  External  ECD 1
Area [µS/min]  ppb
0  500  1,200
0.0  2.0  4.0  6.0  8.0

Fluoride  External  ECD 1
Area [µS/min]  ppb
0  500  1,200
0.0  2.0  4.0  6.0  8.0

AN.ON_report/Calibration(Batch)  PeakNet 6 (r) Dionex 2001 - 2006
Version 6.80 SR10 Build 2818 (166959)
Sequence: Kavin 05032018
Inj. Vol.: 100.0
Program: AutoSampler_anyloop 26min_MB
Operator: n.a.
Inj. Date/Time: 05/03/18 14:39
Run Time: 26.09

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time min</th>
<th>Peak Name</th>
<th>Cal.Type</th>
<th>Points</th>
<th>Offset (C9)</th>
<th>Slope (C1)</th>
<th>Curve (C2)</th>
<th>Coeff.Det. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.31</td>
<td>Fluoride</td>
<td>Lin</td>
<td>6</td>
<td>0.000</td>
<td>0.007</td>
<td>0.000</td>
<td>99.9933</td>
</tr>
</tbody>
</table>

AVERAGE: 0.0000 0.0072 0.0000 99.9933