Discussion:

3.1.1 Dispersive Liquid-Liquid Microextraction

To begin developing the temperature program, a set of standards with octyl chloroacetate, the octylated MCAA, diluted in octanol was formed. Unfortunately, due to the octanol, even with drastically increasing the concentration of the octyl chloroacetate, it was still overwhelmed by the octanol peak. To combat this, standards were created using acetone to replace the octanol. While this did show an identifiable peak, it could not be used as a base for the setting a calibration curve. As the octanol seemed to interfere with the magnitude of the product's ion peaks, a consistent baseline could not be met to confidently quantify the octyl chloroacetate. Due to this, the MCAA content in the water samples were not analyzed.

Each type of water sample had its own interesting qualities. Starting with the swimming pool water samples, it is important to note that Pool 1 had no detectable HAAS and Pool 2 had no detectable MBAA. In Pool 2, the highest HAA concentration was found to be DBAA at 2.029ppm and the lowest detectable HAA concentration was DCAA at 0.611ppm. This is puzzling as the concentration of free chlorine in the water should be higher than bromide due to the chloride salt sanitation method. It was predicted that the chlorine variants of the HAAs would be larger than their bromine counterparts due to the use of chlorine sanitation.

Hot tub water showed surprising high concentrations of all the HAAs detected. Hot tub 1 had the highest HAA concentration of all the water samples, with the highest being MBAA at 106.2pmm and the lowest being BCAA at 13.55ppm. Hot tub 2 possessed much lower, albeit still high compared to the recommended limit of 80ppb, HAA concentrations.⁸ The highest was BCAA at 24.81ppm and the lowest was DCAA at 2.734ppm. The hot tubs followed the same trend as the swimming pools as the brominated HAAs were found at a higher concentration compared to the chlorinated HAAs.

In the tap water samples, each sample had a different HAA with the highest concentration. In the Aberdeen tap sample, the HAA with the highest concentration was BCAA at 81.410ppm whereas the HAA with the highest concentration in the Dallas tap sample was MBAA at 14.509ppm. The lowest HAA for Aberdeen was then MBAA at 2.664ppm with the Dallas one being DCAA at 2.635ppm. This again shows the trend that the brominated products are higher than the chlorinated products.

Between all of the types of samples, the HAAs with the highest concentrations were always a brominated variant, which as mentioned above, is an unexpected result. As each of the water samples were sanitized with a chlorine product, it was expected that the chlorinated products would be at a higher concentration compared to the brominated products. While this was unexpected, it leads into many topics to research in the future.

An interesting turn of results was that the pool samples had lower concentrations of HAAs compared to tap water. While there is currently no concrete reason as to why this occurred, a possibility could be due to the constant filtration and circulation of the water. Both of the swimming pools had a filter media of sand, whereas the hot tubs had pleated cartridge filters, and the tap water's only extra filtration after being treated is only for debris.

Nearly all of the samples contained high levels of HAAs, especially when compared to the regulated limit allowed to be detected in Canadian drinking water. The maximum of combined HAAs concentration is indicated by Health Canada as 80ppm, which is drastically small when compared to the individual concentrations of each HAA detected.⁸ While this was expected for the pool and hot tub water due to their open water and higher chlorination, the tap water samples exceeding the federal limits was unanticipated. The one exception was Pool 1, which had no detectable HAAS. While the first assumption as to why Pool 1 had such low levels of HAAs might be care of the water by the owners, this is disproved by the same owners maintaining Spa 2, which had the highest detected levels of HAAs. When later questioned, the owners stated that Pool 1 and Spa 2 were maintained on the same schedule together. Due to this, it is unknown as to why Spa 2 had such high levels of HAAs and why Pool 1 had such low levels of HAAs.

Throughout the development of the derivatization process, several challenges arose, such as in the earlier trials, the TFAA used was transferred into a smaller vial with a Teflon coated septum. The vial was evacuated and filled with nitrogen three times to reduce the degradation of the TFAA. This was necessary due to the original packaging including only a screw cap as the seal. If there was any air left over during the transfer, this could have caused the TFAA to degrade. After one use, the septum appeared to be contaminated. The TFAA then had to be transferred in a glove bag under nitrogen to smaller vials with Teflon coated septa. Each vial could only be used once, as once the septum was pierced, it was contaminated with TFAA and begun to degrade. In the case that the TFAA was degraded before it was used in the reaction, this could be the cause for the difficulty in detecting product peaks before the new TFAA arrived. Overall, the inert Teflon coated septa should not have reacted with the TFAA per Sigma Aldrich. This leads to the possibility that invisible drips landed on top of the septa after piercing or that in the case of the first vial, the septum was over punctured after being evacuated.



Scheme 4. The mechanism of TFAA in water.

When identifying each product, mass spectra from the National Institute of Standards and Technology (NIST) were used as the baseline. The sole exception was DCAA, as no certified mass spectrum could be found. For this compound, the experimental mass spectrum obtained by Bidgoli and Mohammad was used as the reference spectrum.⁹

The most noticeable challenge was the separation of the MCAA and octanol peaks. By using octanol as a rinse in the GC-MS, there was a significant shoulder left by the octanol that overrode the MCAA peak. When analyzing the selected ions, a tentative retention time of 6.15 min was selected due to the small 79 and 95 m/z peaks. These peaks were often overpowered by the octanol peak and proved difficult to pinpoint consistently. Due to the lack of confidence in the retention time of this peak, it was labeled as tentative.

3.1.2 Comparison to GC-MS Adapted EPA Method

When comparing the dispersive liquid-liquid microextraction method outlined in Scheme 2 to the GC-MS adapted EPA method, there are many factors to consider. The first aspect is the greenness of each method. There are twelve principles of chemistry outlined by the American Chemical Society: Prevention, Action Economy, Less Hazardous Chemical Syntheses, Designing Safer Chemicals, Safer Solvents and Auxiliaries, Design for Energy Efficiency, Use of Renewable Feedstocks, Reduce Derivatives, Catalysis, Design for Degradation, Real-time analysis for Pollution Prevention, and Inherently Safer Chemistry for Accident Prevention.¹²

The most obvious improvement between the two methods is in the Catalysis section. In the dispersive liquid-liquid microextraction, TFAA is used as a catalyst to speed up the reaction time reducing it from 2 hours in a water bath to only 10 minutes in a sonicating bath.

The decrease in reaction time also leads into an increase in energy efficiency. Although, the water bath is not the only device that requires power in the EPA method, as it also required 3.5 minutes of vortexing.

Future Work:

There were many aspects that require a mention for future work. The first step would be to adjust the temperature program to reveal the MCAA peak from underneath the octanol peak. With a temperature program that can identify all the HAAs, the next focus would be to develop more specific calibration curves. With the range of concentrations being so broad, multiple calibration curves could be produced, one closer to the 500ppb range and the other covering the larger concentrations that ranged upwards of 100 ppm. With separate curves, it can make calculating the smaller concentrations more precise.

As mentioned in 3.1.1, the brominated HAAs were at a higher concentration than the chlorinated HAAs. In the future, it would be valuable to test the bromine and chlorine content in the sanitizing products as well as maintaining consistency by using the same sanitizing product for each water sample.

Another point of interest for the future is to extend sampling. This could include adding samples from public pools to compare to private pools, samples from chlorine puck pools, saltwater pools, and bromine pools, and also aligning the shock day of the pools and spas. This could also extend to analyzing the HAA content in the water over time, such as right after shocking to the next shock treatment.

To further asses the greenness of the developed method, a step forward would be to investigate and optimize the reaction's atom economy to reduce the amount of wasted reagents.¹²

Conclusion:

A method using GC-MS to determine the concentration of HAAs was developed, along with an increase in greenness compared to the standardized EPA method. This method is suitable to analyze many HAAs, including brominated variants. The real water samples assessed were determined to have higher concentrations of HAAs than the regulation limit of 80ppm with the exception of one swimming pool sample.

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