UREAP APPLICATION FORM

Thompson Rivers University
Office of Research and Graduate Studies

First Name: Jessica

Last Name: Whitehouse

Student ID: T00682230 Start Date of Project: (01/May/2024)

Please complete all sections of this application form.

1. FACULTY MENTORS INFORMATION

1.1 Who is your Primary Faculty Mentor? Dr. Sharon Brewer

1.2 Who is your Secondary Faculty Mentor? Dr. Robin Kleiv

NOTE: Your Primary and Secondary Faculty Mentors must each complete a Faculty Mentor Support Form. Forms can be found under the attachments tab within your TRU Romeo UREAP application and on the TRU UREAP webpage under information and Forms for Faculty Mentors..

2. PROJECT DESCRIPTION

2.1 Provide an abstract of your proposed research: (maximum 1500 characters)

Throughout the 2024 summer break, our goal is to investigate the development of a greener, faster, and safer analytical method compared to the current standard liquid-liquid microextraction method to detect and determine the concentration of haloacetic acids (HAAs) in treated drinking water. HAAs are among the results of water disinfection, classified as disinfectant by-products (DBPs), which are produced during the water treatment cycle, both in municipal water treatment and civilian water treatment. There are over thirty different forms of HAAs, many of which are labeled as suspected carcinogens, with only five being monitored annually in the Kamloops municipal treated water, these being monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, and dibromoacetic acid[1,2]. Investigating the use of dispersive liquid-liquid extraction combined with derivatization for the determination of HAAs in water would potentially allow the levels of HAAs in local water to be regularly monitored and compared to Canadian guidelines.

2.2 Provide a brief literature review for your proposed research: (maximum 3500 characters)

Haloacetic acids (HAAS) are disinfectant by-products (DBPs) which are produced when water is disinfected by chlorination. While there are thirty variations of HAAs, only monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), and dibromoacetic acid (DBAA) are monitored in the Kamloops municipal drinking water report[1,2]. Of these, DCAA and DBAA, have been labeled as “reasonably anticipated to be a human carcinogen”, along with four others that are detected in most drinking water[1].

The US EPA designed the current standardized method for determining HAAs in drinking water which hasn’t been updated since 2003. This method requires reducing the pH of a 40 mL sample to a pH of 0.5, extraction with 4 mL methyl tert-butyl ether (MTBE), two hours of heating, and neutralization[3].

The method that I will be basing my research on can be directly compared to this standardized method. One improvement is that the proposed method will heat smaller sample volumes for less time[3,4,6]. Another factor is the increase in awareness of green chemistry in the non-standard method. The non-standard method includes small reagent volumes, very few exceeding 3 µL per analysis, and the main n-octanol extraction needs only 1.8 µL of n-octanol compared to the 4 mL of MTBE that the EPA method uses to extract HAAs along with 40 mL of sample needed for the EPA method and only 7 mL needed for the non-standard method[3,4,6].

The determination of the HAAs relies on GC-MS, an instrument that separates vaporized ions. As a gas, the ion travels through a column, interacting with the stationary phase. After passing through a mass analyzer, the mass spectrometer sorts the compound fragments by their mass charge ratio, which is shown by spectra. Since HAAs are not volatile in order to analyze them with our GC-MS instrumentation volatile derivatives need to be formed. The reaction I will investigate derivatizes HAAs to form volatile methyl esters using sulfuric acid and methanol with the aid of a catalyst, trifluoroacetic anhydride[4].

In the City of Kamloops water treatment plan, the drinking water is tested annually for HAAs in four locations near the edges of the city. These locations include the Lac Le Jeune booster, the Knutsford Hill booster, the Campbell Creek Super Save Gas Station, and the Nobel Creek booster[2]. These are excellent locations for HAA sampling, as they are far from the city's treatment plant which would mean that they have the highest chance of interacting with organic matter after disinfection which leads to the formation of HAAs[1]. The disadvantage to this HAA monitoring plan is the schedule of sampling. With annual sampling, the city does not account for the correlation between HAA concentration and seasonal variations. The monitoring plan does not follow the Health Canada recommendation of quarter-annual HAA monitoring, as the concentration of HAAs rises as the average temperature rises[5].

There is a considerable gap in published literature in regards to HAA testing in pools and hot tubs. As it stands, the only method being applied to these scenarios is the standard EPA method, which was above shown to be lesser in efficiency when compared to the new, non-standard methods[4,6]. This offers new territory in applying this method to pools and hot tubs to test the validity of the method's use for the large concentrations of HAAS found in pools and hot tubs.

2.3 What is the hypothesis or research question for your proposed research? Include any specific objectives: (maximum 500 characters)

The research question for my project is "Is an analytical method using dispersive liquid-liquid extraction combined with derivatization suitable for the determination of HAAs in Kamloops water samples?" Specifically, I will investigate the development of a literature-based method using dispersive liquid-liquid extraction combined with derivatization for the analysis of HAAs, determine the method's relevant figures of merit, and assess its suitability for a range of Kamloops waters.

2.4 Provide a description of the research methodology/methodologies and analysis that you intend to employ in completing this research: (maximum 1500 characters)

The proposed analytical method has multiple parts: sampling, extraction, derivatization, and determination. Each step will start from the optimum conditions reported in the literature[4,6]. The first step is to test and optimize the GC-MS parameters provided by the non-standard literature method[4,6]. This will allow for ease and hastening of the determination of the HAAs. This will include the investigation of the impact on detection capabilities from ion selection, which will be essential in optimizing the GC-MS methodology. Next, the simultaneous derivatization and extraction method from the literature will be tested and optimized. By using an efficient extractant solvent, heating temperature, catalyst, and reaction time from literature, these being respectively 1 mL n-octanol, 25 °C, 0.5 μL trifluoroacetic anhydride, and 10 minutes, I will be able to test the derivatization and extraction while making any necessary adjustments, specifically, I am interested in comparing types of glassware to optimize the extraction process[4,6]. After finalizing the overall method, multiple samples of Kamloops waters will be analyzed and compared to the accepted limit of HAAs. Sample types will include tap water from various locations across the city, along with samples from various private pools and hot tubs that were filled with Kamloops drinking water.

2.5 Provide a description of how your research will significantly impact your field of study:

(maximum 1500 characters)

With the current minimal testing of HAAs in Kamloops' treated water, success in developing a green and efficient method of detection and monitoring of HAAs could help to increase the occurrence of testing within the city. This could also expand to seasonal monitoring of HAAs, as the increase in organic matter introduced during early spring would impact the concentration of HAAs. As HAAs are suspected carcinogens, it would be imperative to keep HAA levels below the federal limit of 0.08mg/L, which would require frequent testing and monitoring.

While municipal HAA testing impacts drinking water, a simple HAA detection method could also be applied to civilian water disinfection, such as hot tubs and swimming pools. As this water is not monitored by the municipal facilities, it would be up to the property owners to test themselves or take to a testing facility, to monitor their waters for HAAs and compare them to the federal guidelines. As someone who works in the hot tub and swimming pool industry, I see that an unfortunately high amount of civilians do not take proper care of their water treatment, and with the added risk of carcinogenic HAAs being untested, having a method to measure the amount of HAAs could increase the awareness of possible hazards of improperly treated water to civilians.

2.6 Describe your plans to disseminate your research findings: (maximum 500 characters)

The results of this research will be displayed as a printed poster at the TRU Undergraduate Research Conference once completed. The UREAP report will also be shared with relevant local industry partners.

2.7 List the references that you have cited throughout your research proposal observing the appropriate citation style for your discipline: (maximum 3500 characters)

[1]National Toxicology Program, United States Department of Health and Human Services. Report on Carcinogens. *Monograph on Haloacetic Acids Found as Water Disinfection By-Products*, last revived March 2018. https://ntp.niehs.nih.gov/sites/default/files/ntp/about_ntp/monopeerrvw/2017/july/haafinalmonograph_508.pdf (accessed 2024-02-22).

[2]Kamloops Center for Water Quality, City of Kamloops. *Drinking Water Annual Report*, 2022. https://www.kamloops.ca/sites/default/files/2023-06/IH%20Annual%20Drinking%20Water%202022_REP.pdf (accessed 2024-02-20).

[3]United States Environmental Protection Agency, Office of Ground Water and Drinking Water. Method 552.3. *Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Microextraction, Derivatization, and Gas Chromatography with Electron Capture Detection*, 1st Ed., revised July 2003. https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=901V0400.txt (accessed 2024-02-20).

[4]Bidgoli, A.; Mohammad, S. Single-drop microextraction with in-microvial derivatization for the determination of haloacetic acids in water sample by gas chromatography–mass spectrometry. J. Chrom. A. **2008,** *1216* (7), 1059-1066. DOI:10.1016/j.chroma.2008.12.064

[5]Federal-Provincial-Territorial Committee on Health and the Environment, Federal-Provincial-Territorial Committee on Drinking Water. Guidelines for Canadian Drinking Water Quality: Guideline Technical Document. *Haloacetic acids*. 2008. https://health.canada.ca/publications/healthy-living-vie-saine/water-haloacetic-haloacetique-eau/alt/water-haloacetic-haloacetique-eau-eng.pdf (accessed 2024-02-20).

[6]Al-shatri, M.; Basheer, C.; Nuhu, A. Determination of Haloacetic Acids in Bottled and Tap Water Sources by Dispersive Liquid-Liquid Microextraction and GC-MS Analysis. Sci. World. J. **2014**, vol2014, ID 695049. DOI: 10.1155/2014/695049

3. PROJECT TIMELINE WITH BENCHMARKS

3.1 Provide a timeline for your project that includes key benchmarks: (maximum 1000 characters)

May:

Begin training on the gas chromatography-mass spectrometer, optimize temperature program and GC-MS settings

June:

Learn extraction and derivatization techniques, optimize the extraction and derivatization procedures

July:

Test developed method on prepared standards of suitable concentration ranges

August:

Testing developed method on real water samples

Write final UREAP report

NOTE: Please refer to the UREAP Help Guide for a project timeline example. Students must demonstrate a willingness to engage in 12 weeks or equivalent of sustained research per the Terms of Reference.

4. OPERATING GRANT BUDGET PROPOSAL

4.1 The UREAP award offers up to $1000 toward direct research expenses. These expenses must be preapproved by the UREAP committee in the adjudication phase. Use the provided template under the Attachments tab in the TRU Romeo UREAP application to complete your budget proposal. Copy amount from the TOTAL AMOUNT line of the budget here. Total Amount: $ 1000.00

4.2 Additional budget information: (maximum 500 characters)

If I am not successful in obtaining the Operational Grant, the supplies will be provided by my faculty mentors.

5. CONTRIBUTION TO ACADEMIC/PROFESSIONAL GOALS

5.1 Describe how this project will contribute to your academic and/or professional goals:

(maximum 1000 characters)

This project will have many positive outcomes towards my academic and professional goals. In the area of academics, I will have the opportunity to grasp a deeper understanding of the process of developing a method. This applies to my education as I am currently enrolled in the Applied Analytical Chemistry course, which is majorly dedicated to the details required to create a proper experimental procedure. This will also apply to the upper-level lab courses that I will be taking in the upcoming years as many of them require the students to create their procedures, therefore allowing me to be well-versed in method development before entering the lab.

For my professional goals, this research will provide valuable laboratory experience and a test of patience in problem-solving. In industry and professional academia, there is a requirement for problem-solving skills, which can only be developed with experience. This project will allow me to hone my critical and creative thinking to solve outside-of-the-box problems.

NOTE: Include your role in conceiving of the project, your role in the implementation of the project, and your overall academic objectives – explaining how this project will help to advance those objectives.