Experimental:

2.1. Reagents and Chemicals

Table 2. Reagents used for dispersive liquid-liquid microextraction and the adapted EPA method.

Reagent	Manufacturer
Haloacetic Acid Mix	Restek
99% 1-Octanol	Thermo Scientific
Octyl chloroacetate	Sigma Aldrich
Trifluoroacetic anhydride (1 g x 10)	Avantor
Trifluoroacetic anhydride (10 mL)	Sigma Aldrich
>99.9% Acetone	Sigma Aldrich
>99.5% Methyl-t-butyl Ether	Supelco
Anhydrous Ethanol	Commercial Alcohols
Sodium Sulfate	Caledon
99.8% Methanol	Ultrapure
99% Sulfuric Acid	Sigma Aldrich

2.2. Preparation of Standards

2.2.1 Dispersive Liquid-Liquid Microextraction Standards



Scheme 2. The steps to create standards and samples for the dual extraction and derivation method.

2.2.2 GC-MS Adapted EPA Standards

From pure methyl dichloroacetate, an 82.9ppm stock was created by diluting in MTBE.

Using the purchased HAA mixture, a 20.0ppm stock solution was created by diluting in MTBE. This stock was used to spike LC-MS grade water before reacting following Scheme 3.



Scheme 3. The steps to create standards and samples for the GC-MS adapted EPA method.⁶

2.3. Sampling Locations and Sample Collection

2.3.1 Tap Water Samples

Two tap water samples were collected from varying locations across Kamloops, BC: a residential house in the Dallas neighbourhood and a residential house in the Aberdeen neighbourhood.

Before each sample was taken, the faucet head was wiped down with a clean disposable cloth and the water was turned on for 30 seconds before filling the sample bottle.

The residential tap water samples were preserved with ~12mg of ammonium chloride, filled to create zero headspace, and stored in a refrigerator immediately. These samples were analyzed after four days.

2.3.2 Swimming Pool Water Samples

Two samples were collected from saltwater-based pools in the Dallas neighborhood of Kamloops, BC. These samples were preserved with ~12mg of ammonium chloride, filled to create zero headspace, and stored in a refrigerator immediately. These samples were analyzed after four days.

2.3.3 Spa Water Samples

Two spa samples were collected from chlorine-based spas in Kamloops, BC, one in the Dallas neighbourhood and one in the Upper Sahali neighborhood. Both samples were preserved with ~12mg of ammonium chloride, filled to create zero headspace, and stored in a refrigerator immediately. These samples were analyzed after four days.

2.4. Instrumentation

The samples and standards were analyzed using the Agilent 7890B GC system paired with the Agilent 5977A MSD system along with a PAL liquid autosampler system.

2.5. Method development

2.5.1 Dispersive Liquid-Liquid Microextraction Method

The base of this method is from Al-shatri et al, with adjustments to the temperature program and the sample and standard preparation.⁵

On the GC-MS, a bakeout program was created and run between each sample to ensure no solvent carry-over as the octanol's retention time is less than a minutes from the HAA peaks.

The standard GC-MS method went through many iterations to optimize retention time and separation along with adjustments to the SIM ions selected for analysis. This was finalized with the following GC-MS method:

Inlet temperature	200°C
Ion source temperature	200°C
Carrier gas flow rate	2 mL/min
Carrier gas pressure	50 kPa
Injection volume	0.2 μL
Pre-washes with octanol	2
Post-washes with octanol	2
Temperature and hold #1	40°C for 1 minute
Ramp rate #1	25°C/min
Temperature and hold #2	180°C for 4 minutes
Ramp rate #2	30°C/min
Final temperature and hold	250°C for 2 minutes
Solvent delay	5.7 minutes
SIM	79, 95, 48, 76, 121, 123, 139, 36,
	110, 127, 129, 131, 120, 122, 173
Scan range	35-230

Table 3. GC-MS Method for dispersive liquid-liquid microextraction.

To determine the retention time of octyl chloroacetate, the derivative of MCAA, standards were prepared by diluting the purchased chemical in acetone and octanol. This aided in determining the timing of the solvent delay as to not cut off any HAA peaks and identifying the retention time of MCAA product.

2.5.2 GC-MS Adapted EPA Method

This method was based on the procedure and temperature program listed by Chiavelli et al. $^{\rm 6}$

Table 4. GC-MS Method for the adapted EPA method.

Inlet temperature	200°C
Ion source temperature	200°C
Carrier gas flow rate	2 mL/min
Carrier gas pressure	50 kPa
Injection volume	1 μL
Pre-washes with MTBE	2
Post-washes with MTBE	2
Temperature and hold #1	40°C for 1 minute
Ramp rate #1	2.5°C/min
Temperature and hold #2	65°C
Ramp rate #2	10°C/min
Temperature and hold #3	85℃
Ramp rate #3	20°C/min
Final temperature	205°C
Post run temperature	210°C for 7 minutes
Solvent delay	3 minutes
SIM	3 min(59, 64, 77), 8.3 min(59, 83, 85, 111), 10
	min (59, 117, 119)
Scan range	35-230

To determine the retention time of methyl dichloroacetate, standards were prepared by diluting pure methyl dichloroacetate with MTBE. These standard concentrations were 0.55, 0.83, 1.1 and 10 ppm.

A 20.0ppm HAA stock in MTBE was used to spike LC-MS grade water to 0.025, 0.050, 0.100, and 5.00 ppm following Scheme 3.

2.6 Ion Selection

2.6.1 Dispersive Liquid-Liquid Microextraction Ions

The base for ion selection was based on the ions chosen by Saraji and Bidgoli with a few adjustments.⁹ For methyl chloroacetate, the ions selected were 70, 79, 95 m/z. While 79 and 95

m/z were chosen as characteristic ions for MCAA, 70 m/z would produce a larger signal than either ion and act as a beacon.⁹ Unfortunately, the octanol has a very similar structure and overpowered the MCAA peaks making it difficult to determine an exact retention time.

The ions selected to identify DCAA were 41, 43, 48, 56, and 76 m/z. While 48 and 76 m/z are used as characteristic peaks, the 41:43 m/z ratio were specifically useful to identify DCAA. There was also the 56:69 m/z ratio that was used to confirm the peak.

In the case of DBAA, there were multiple characteristic peaks that could have been used, but the 120:121:122 m/z ratio was the most helpful and reliable. TCAA was also simple to choose ions for, as the recommended ions, 110 and 121 m/z, were consistently prominent along with 57 m/z.² With a similar trend, the ions for BCAA were the recommended ions, 127, 131, and 129 m/z along with 57 m/z being used as a beacon.⁹

2.6.2 GC-MS Adapted EPA lons

The ions for each molecule were selected from Chiavelli and Birch, focusing on the three chlorinated products.^{6,10} For methyl chloroacetate, 59, 64, and 77 m/z were chosen. The 64 and 77m/z ions are characteristically not seen in the mass spectrum of MTBE, and therefore excellent identifiers. While 59m/z is seen within the mass spectrum of MTBE, it is at a significantly higher ratio in methyl chloroacetate and can still be used as character peak.

Methyl dichloroacetate compared four ions: 59, 83, 85, and 111m/z. The ratio between 83:85 m/z was immensely useful as characteristic ions as they could easily be compared to the reference mass spectrum.¹¹ Selecting the ions for methyl trichloroacetate used a similar logic with 59, 117, and 119 m/z as there is a characteristic ratio between 117:119 m/z and 59 m/z used as a beacon.