AN INVESTIGATION IN THE USE OF SOLID PHASE MICROEXTRACTION GAS CHROMATOGRAPHY-MASS-SPECTROSCOPY (SPME-GC/MS) FOR THE ANALYSIS OF THMS FROM WATER SAMPLES

by

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Abstract

Difficulties in sample preservation for semi volatile samples, like trihalomethanes (THMs) in water, often limit the extent of water analyses that may be undertaken to assess a particular water body. Analysis techniques such as liquid-liquid extraction and purge and trap followed by ion exchange (IE) or by high performance liquid chromatography (HPLC) that are currently used only just meet analysis regulatory requirements. Hence, other techniques and their method development are needed to quicken the sampling, extraction and analysis process times. A potential method that may hold promise is the use of head-space solid-phase microextraction (HS-SPME) sampling combined with gas chromatography-mass spectrometry (GC/MS) separation and detection methods. This work has investigated this technique and a method has been developed to assess concentrations of trihalomethanes (THMs) and their derivatives from natural sources of drinking water that are used for the municipality of the Corner Brook, Newfoundland area. Under laboratory conditions, surrogate THM standard samples to include: bromodichloromethane ($CHCl_2Br$), chlorodibromomethane ($CHClBr_2$), chloroform ($CHCl_3$), 1,2-dibromoethane ($C_2H_4Br_2$), and 1,2-dichloroethane ($C_2H_4Cl_2$) of known concentrations (200, 100, 50, 25, 10, 5, 2, and 1 ppm to cover the required analysis range) in methanol samples were analyzed in stirred and sealed vials using head space (HS-SPME) sampling. This was undertaken to fully optimize all sampling and extraction condition parameters, which included (found optimized parameters): choice of type of extraction fiber used (PDMS/DVB), stirring rate of samples (900rpm), extraction temperature of the sample (25^0C), extraction time required (4 min), desorption time of the fiber in the GC injector port for analysis (2 min), and the determination of maximum averaged equilibrium conditions for a number of THM analytes (4 min). Further, an optimized temperature profile for separation by GC for the analysis of this set of THMs was found to be: 30^0C held for 5 minutes, followed by a ramp of 5^0C/min to 50^0C to give a total run time of 9 minutes, when the GC injector port was set at 250^0C, GC transfer line to the MS was 240^0C and the MS source was held at 200^0C. Under the determined optimized conditions water samples were taken from natural waters and analysed for their THM concentrations. Concentrations in the natural water samples were measured at a range of 254 ppb-4.42ppm with good detection limits (< 1ppm) and linear working range (10-1 ppm) of the calibration data. RSDs for SPME extraction averaged between 4.17 and 11.6% for each THM component.

The ease of sampling and extraction of analytes from aqueous solutions by SPME allows for quickening of the sampling and extraction step and hence an overall faster analysis time. The utility of GC/MS allows for separation and subsequent characterization of individual analytes from multiple component analytes. Further, SPME affords THM analysis of the water samples to be carried out either in on-site or in laboratory analysis situations.

1.0 Introduction and Literature Review

The presence of disinfection by-products (DBPs), such as trihalomethanes (THMs), in natural water systems has been a major concern for human health. Bromoform ($CHBr_3$), chlorodibromomethane ($CHCl_2Br$), chloroform ($CHCl_3$), and dichlorobromoethane ($CHCl_2Br$) are typical THMs present in many natural water systems. All of them are suspected of having carcinogenic effects: chloroform and bromodichloromethane are included in Group B2 of the International Agency for Research on Cancer (IARC) cancer group classification, which means that they are probable human carcinogens, whereas bromoform and dibromochloromethane belong to Group C, possible human carcinogens.[1] THM concentrations in local drinking waters need to be closely monitored as they can have adverse effects on the human body at concentrations above 0.9 and 0.09 ppm (mg/L) for the liver and kidney respectively.[2] The maximum allowable contaminant level of THMs, 80 and 100 ppb (µg/L), was set by the US Environmental Protection Agency (EPA) and the European Union (EU) respectively.[3]

Every year, the Government of Newfoundland and Labrador releases a summary of THM concentration levels present in 473 public water supplies around the island.[4] Information given in the summary includes: community name, serviced areas, water source name, average THM levels (ppb), type of water source, number of samples collected, and last season sampled. Concentrations range from as low as <1 ppb to upwards of 566 ppb, as is the case for Boland's Pond in Keels.[4] The document includes information on three ponds analyzed from the Corner Brook region which include Trout Pond (158.15 ppb), Three Mile Pond (117.07 ppb), and Burnt Pond (140.75 ppb). A

detailed breakdown of the Newfoundland and Labrador THM data is shown in appendix A.

Techniques used to study THMs in water include liquid-liquid extraction[5] and purge-and-trap.[6] A HACH spectrophotometer has also been employed in the detection of THMs.[7] Details on the HACH method for THM analysis is shown in Appendix B. THMs must be analyzed within 14 days of sample collection.[8] Some preliminary tests have shown that SPME might show promise for the sampling-extraction and analysis of THMs.[3] A measureable loss of THM concentration has been measured after the 14 day hold time.[4,5] Hence it is important to use analysis methods that allow fast and simple approaches of detection for THMs either directly from water or via a batch analysis that can be accomplished within two weeks. In the latter case, water samples must be preserved by sealing them in brown plastic sampling bottles and stored in refrigerators at temperatures below 4°C.[8]

1.1 Trihalomethanes (THMs)

Classic trihalomethanes (THMs) are halogenated methanes often found in natural waters and sometimes in soft drinks.[9] The four main THMs are bromodichloromethane, bromoform, chlorodibromomethane, and chloroform. THMs can be formed during chlorination of drinking water in a disinfection process, and are known as disinfection by-products (DBPs). The major DBPs produced during chlorination are THMs, Haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones, chloral hydrate, and chloropicrin,[10] where the primary group is the THMs.[11] During disinfection, free available chlorine reacts with dissolved organic carbon present in the drinking water. Reaction with the humic and fulvic acids, being the majority of the dissolved organic carbon, produces

THMs in a haloform reaction.[9] The haloform reaction of free chlorine with a humic model compound is illustrated in Figure 1.1.[12]

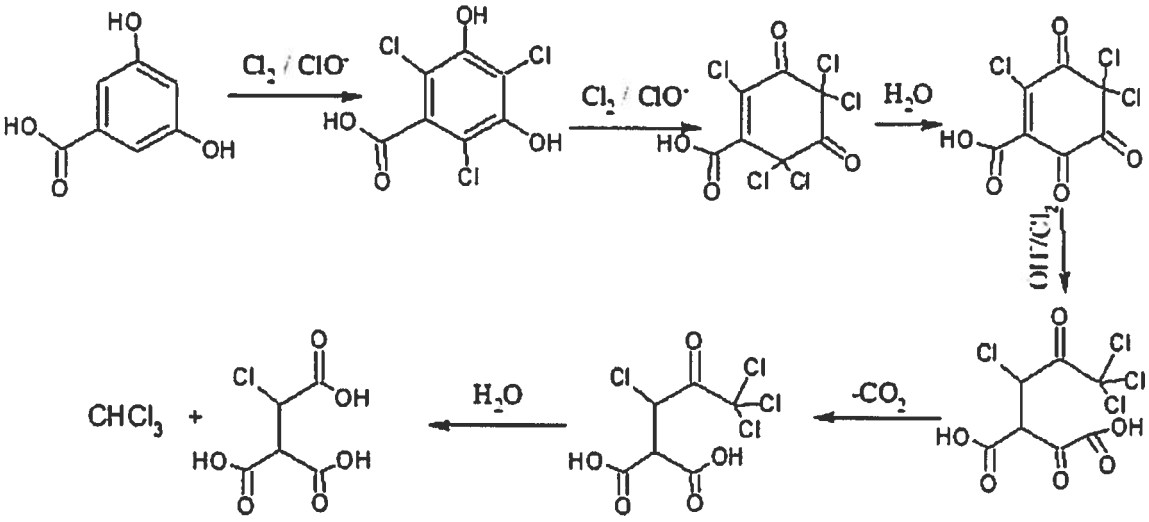

Figure 1.1 Haloform reaction of 3,5-hydroxybenzoic acid at pH > 7.

THMs can be produced in the soil naturally.[13] A number for factors include concentration of hydrogen peroxide and iron (III), where the presence of iron (III) is essential in the formation of natural trihalomethanes.[13] Hydrogen peroxide can be introduced to soils *via* rainwater at concentrations ranging from 2-40 ppt.[14] Hydrogen peroxide in the system stimulates the release of bromodichloromethane, chlorodibromomethane, and chloroform.[13]

A potassium chloride salt also has a linear relationship with the THM concentration.[13] Although natural production of THMs may occur in the soil, their volatility allows for natural transportation into natural water systems by passive diffusion between the atmosphere and surface water. A hypothesized reaction for the formation of

THMs using catechol, resorcin, and hydroquinone as model compounds is shown in Figure 1.2.[13]

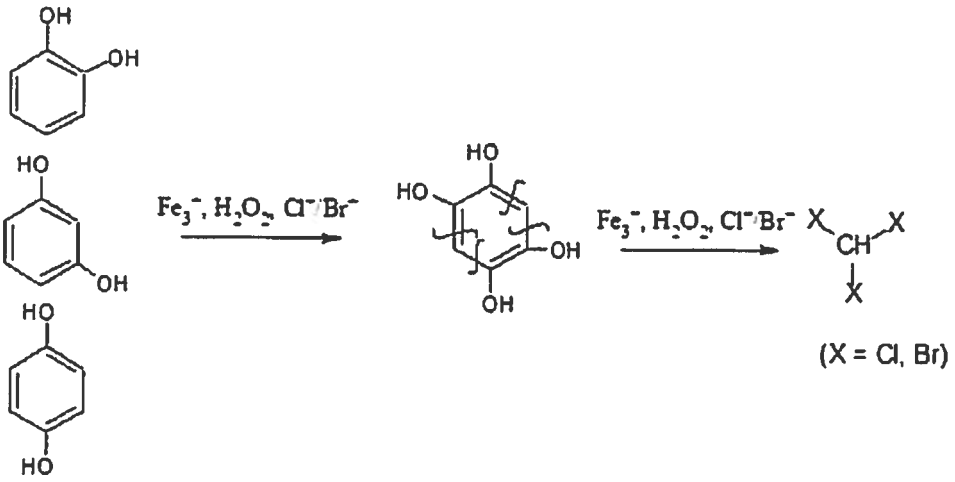

Figure 1.2 Hypothetical degradation pathways of three model compounds in the formation of trihalomethanes

The presence of bromide in a natural water system aids in the production of THMs. Bromide concentration is generally less than 1 ppm in drinking water and on average 100 ppb in surface waters.[8,15] Bromide ion can have a one electron transfer from chlorine to form aqueous bromine. Typical chloride concentrations in surface waters are 10-30 ppm.[15] However, concentrations will vary from one water system to the next. The aqueous bromine then forms hypobromite and hypobromous acid, as shown in reactions (1) – (3).[12]

$$Cl_{2(aq)} + 2Br^-_{(aq)} \longrightarrow 2Cl^-_{(aq)} + Br_{2(aq)} \qquad (1)$$

$$Br_{2(aq)} \longleftrightarrow HOBr_{(aq)} + HBr_{(aq)} \qquad (2)$$

$$HBr_{(aq)} \longleftrightarrow BrO^-_{(aq)} + H^+_{(aq)} \qquad (3)$$

Hypobromite is a better brominating agent than hypochlorite for chlorinating.[12] Brominated THMs are produced through bromination of humic materials in the same way chlorinated THMs are produced. The difference is that a much smaller concentration of aqueous bromine is required for THM production when compared to aqueous chlorine.[16]

Currently, the exact reaction mechanism for bromination or chlorination of humic and fulvic acids is unknown due to the variability in their structures. Many factors determine the extent at which THMs are produced. Factors may include the type and concentration of natural organic matter (NOM), bromide ion concentration, chlorine form and dose, pH, and temperature.[11] Large particulate organic materials found in littoral sediment produces THM precursors at a greater rate (0.33 $\mu g/m^2/day$) than the smaller particulate organic material found in profoundal sediments (0.010 $\mu g/m^2/day$).[16] The increased load of THM precursors from littoral sediments may lead to increased production of THMs upon chlorination. Bromide ion concentration can also affect the THM concentration. The presence of the bromide ion can increase the production of trihalomethanes,[16] therefore a higher concentration of bromide ion in the water will lead to high concentrations of THMs. Chlorine will affect THM concentration in a similar way as the bromide: more chlorine used in the disinfection process produces more THMs if there are sufficient organic materials present.

THM production is altered by pH changes. The haloform reaction (Fig. 1.1) requires basic conditions ($pH \approx 8$).[12] Therefore, reducing pH may reduce the production of THMs from the haloform reaction. Reducing pH also increases the concentration of haloacetonitriles present.[17] In a situation where an analyst were to use pH as a regulatory factor in the control of THM production, a fine balance would need to be found in order

to ensure that the haloacetonitriles do not become problematic. Increased temperature speeds up reaction rates and thus will increase the rate at which THMs are produced. In a previous study looking at factors which affect disinfection by-product formation, chloroform formation was increased as the temperature was increased from 10^0C to 30^0C.[18]

1.2 THM Precursors

Precursors for THM production are formed from many different sources in the water system. These precursors can be categorized into two basic classes: naturally occurring humic substances and non-humic precursors.[15] Proposed structures for humic substances are shown in Figure 1.3:[19]

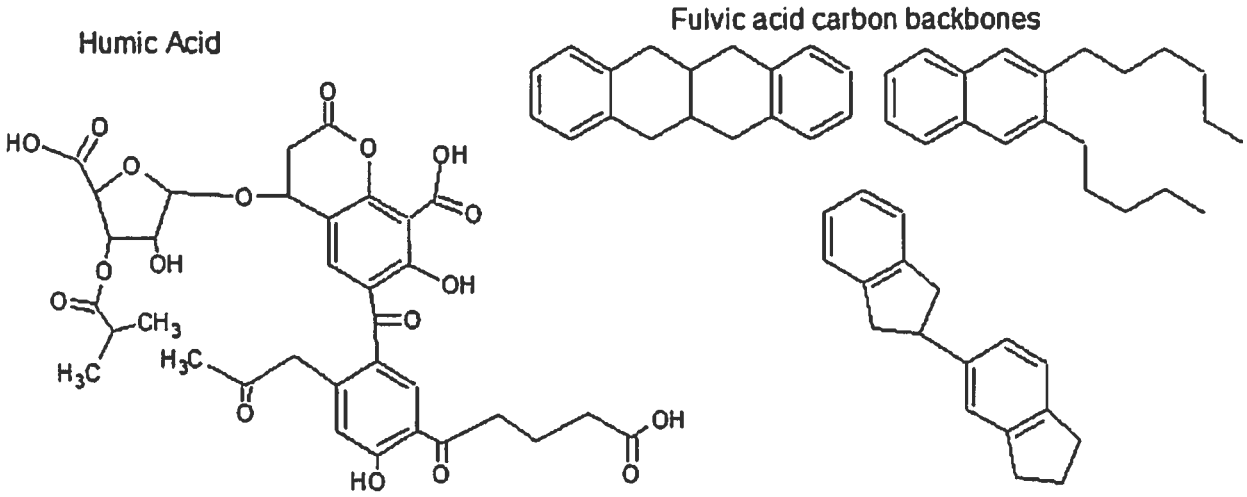

Figure 1.3 Proposed structures for humic acid and fulvic acid carbon backbones.

Non-humic precursors are produced from algal and bacterial cells as well as both living and decaying aquatic plants.[16] The algal precursors are often produced in the form of proteins which cannot be removed easily by coagulation and filtration.[20]

Humic substances constitute the majority of dissolved organic carbon (DOC) in water systems, and thus play an important role in the production of THMs. The DOC originates from aquatic macrophytes, algae, and terrestrial sources.[20] Humic substances tend to be large molecules with varying structures at a range of molecular weights. Molecular weights range can range anywhere from 12,000 to 20,000 g/mol or greater.[21] Humic substances are made up of polymeric humic acids and smaller fulvic acids.

Humic acids refer to the fraction of dissolved organic carbon which precipitates at low pH.[19] From Fig 1.3 it can be seen that they are polymeric in nature and can have molar masses ranging upwards to 20,000 g/mol.[21] An important property about humic acids is that they are refractory, which will ultimately lead to their deposition in sediments.[19]

Fulvic acids (Fig. 1.3) refer to low molecular weight acid soluble compounds.[19] This fraction of DOC tends to be smaller, simple molecules in the range of 12,000 g/mol.[21]

Exact mechanisms for the production of THMs from humic substances are unknown.[22] What is known is that the DBP formed depends heavily on the structure of the initial humic material. The number and type of reaction sites on the humic substance influence the type of DBP formed, where more electrophillic reaction sites influence the formation of THMs over halo acetic acids (HAAs).[23] Functional groups known to generate DBPs are hydroxyl, carbonyl, ester, and carboxylic acid ligands[23] which contain considerable chelating ability. Humic and fulvic acids are the most reactive of the humic substances and are known to be involved in cationic and slightly polar organic pollutant binding.[23]

One of the main techniques used to separate humic substances from other natural organic matter is the use of ion exchange columns coupled with UV/VIS analysis. Common ion-exchange resins for NOM fractionation are Supelite DAX-8 and Amberlite XAD-4. Properties for these resins are shown in Table 1.1.[24,25]

Table 1.1 Properties for DAX-8 and XAD-4 ion exchange resins

Properties	Supelite DAX-8	Amberlite XAD-4
Matrix	acrylic ester	styrene-divinylbenzene
Particle Size	40-60 mesh	20-60 mesh
Pore Volume (mL/g)	0.79	0.98
Sureface Area (m^2/g)	160	750
Density (skeletal, g/mL)	1.23	1.08
Density (wet, g/mL)	1.09	1.02

DAX-8 is an adsorbent resin with moderate polarity and can be used for compounds up to 150,000 g/mol.[24] The resin is most commonly used for the adsorption of humic and fulvic acids.[24] XAD-4 resins are polyaromatic adsorbents for small hydrophobic compounds, chlorinated organics, phenols, surfactants, and pharmaceuticals.[25] DAX-8 and XAD-4columns separates humic materials into very hydrophobic acids and slightly hydrophobic acids respectively,[26] effectively separating out humic and fulvic acids. A direct relationship between total organic carbon and THM precursor concentrations has been found.[27]

1.3 Sampling Methods

Sampling is an integral part of any analysis. Conclusions based on laboratory results from the best possible analysis may be invalidated because the original collection of the samples was inadequate.[8] Two possible sampling techniques for water analysis is spot sampling and time weighted averaging (TWA). Spot sampling is static sampling technique which collects samples from specific points around a sampling area. The

samples are then analyzed on site or brought to a laboratory for detailed analysis. Time weighted averaging (TWA) is a technique whereby THMs are monitored over a long period of time, where episodic changes in THM concentrations are minimized. Unlike spot sampling, which gives very limited estimates, TWA analysis gives a realistic interpretation of the natural water system. Spot sampling essentially takes a picture of a system. This picture is not representative of the system as a whole as changes may occur over a wide time scale. Examples include small changes in pH, salinity, conductivity, and dissolved oxygen. However, TWA requires a longer time period when compared to spot sampling. A single sample analyzed by TWA may take up to a week, while a spot sample can move through an analysis in a few hours.

Due to the need to develop quicker methods for THM analysis, this study will look at THMs in natural water systems around the Corner Brook region using SPME-GC/MS analysis with static sampling methods. The experimental portion will attempt to analyze concentrations of THMs using newly developed methods to utilize SPME sampling techniques.

1.4 Solid-phase Microextraction (SPME) as a Sampling Technique

Solid-phase microextraction (SPME) is a sampling technique which utilizes a polymer fiber on the needle tip to separate the target analyte from its matrix (see Figure 1.5). SPME analysis is easy to use, efficient, cost effective, environmentally friendly, and compatible with separation techniques such as gas and liquid chromatography. The SPME device consists of a plunger, barrel, and needle assembly. The polymer fiber is attached to the needle and can be withdrawn into the barrel with a simple pull of the

plunger. The ease of use when compared to other techniques such as high performance liquid chromatography (HPLC) allows the technique to be very cost effective due to the short operational time, and the fact that the fiber integrates sampling, extraction, and concentration all into a single step.[28] Each of the integrated steps would normally have to be done separately by techniques such as sample collection via grab sampling, separation via GC or HPLC, and concentration through distillation. As one can see each of these preliminary steps is time consuming and therefore costly. With the integration of sampling, extraction, and concentration into a single step, SPME is a quick and potentially lucrative technique for the analysis of many substituents.

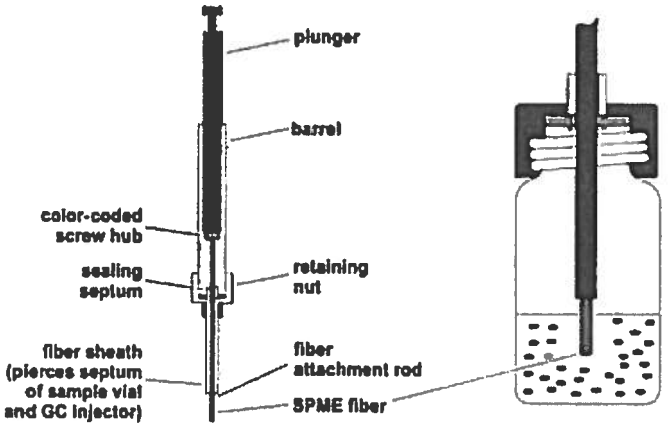

Figure 1.5: Components of a SPME device and method of direct sampling.

SPME can be coupled with instruments such as HPLC or GC-MS for an accurate determination of the analyte in question. The use of SPME coupled with GC-MS was selected for this study due to its ease of use and accuracy of the results capable with the technique.

1.4.1 Equilibrium Extraction Types Using SPME

SPME is a solventless technique. The analyte is adsorbed onto the polymeric fiber through an equilibrium process as shown in equation (6); reducing the cost of the technique and waste produced in the experiment. Two main techniques are used with SPME analysis: headspace extraction and extraction through direct contact with the sample matrix. In direct extraction, the SPME fiber is exposed directly to the sample matrix. The fiber is exposed to the matrix where the analyte is adsorbed onto the fiber in an equilibrium process. In each process the distribution constant of the analyte between the polymeric phase and matrix determines the time at which equilibrium will be reached.

In a gaseous matrix the temperature can have a large impact on the distribution constant (K_{fg}). However, in knowing the temperature of the sample and the heat of vaporization for the target sample, K_{fg} can be calculated by equation (4),[28]

$$\text{Log}_{10}K_{fg} = (\Delta H^{v} / 2.303RT) + [\log_{10}(RT/y_i p^*) - (\Delta H^{v} / 2.303RT^*)] \quad (4)$$

where p^* is the analyte vapour pressure at known temperature T^* and y_i is the activity coefficient of the solute in the coating.[28]

In a liquid matrix, the fiber coating-water distribution is established by equation (5),[28]

$$K_{fw} = K_{fg}K_{gw} \quad (5)$$

where K_{gw} is the gas/water distribution for a given analyte and can be found in Henry's Law constant Tables. Both gas and liquid extractions utilize a direct equilibrium between

the matrix phase and the polymer. However in headspace extraction the relationship is a combination of equillibria.

During headspace extraction one has to consider the multiphase equilibria in a closed system. With a dissolved solid, as the case with dissolved organic carbon, there is an equillibria between the aqueous phase containing the dissolved matter and the gaseous phase of the headspace. Equilibria exist between the headspace of the sample container and the polymeric fiber of the SPME sampling device. Although multiple phases are present, the basis that the concentration of analyte in the aqueous phase equals the concentration of analyte adsorbed onto the polymer still holds true. This is due to the fact that the mass of analyte extracted by the polymer is related to the overall equilibrium of the analyte in the three-phase system.[28] Following the 3-phase equilibrium property that the concentrations of analyte are equivalent between the aqueous and gaseous phases, the total mass of analyte should then remain the same during the extraction process, shown by equation (6).[28]

$$C_0V_s = C_fV_f + C_hV_h + C_sV_s \quad (6)$$

C_0 is the intial concentration of the analyte in the matrix; C_f, C_h, and C_s are the equilibrium concentrations of the analyte in the coating, headspace, and matrix respectively; V_f, V_h, and V_s are the volumes of the coating, the headspace, and the matrix respectively.[28] Knowing the concentration of analyte in each of the phases after equilibrium will allow the analyst to find the initial concentration of the analyte before equilibrium with the SPME fiber. Once the concentration of the analyte and the partition

coefficients is found for both the matrix to headspace (K_{hs}) and headspace to fiber (K_{fh}) equilibriums then the mass can be determined by equation (7).[28]

$$n = (K_{fh}K_{hs}V_fC_0V_s) / (K_{fh}K_{hs}V_f + K_{hs}V_h + V_s) \quad (7)$$

The distribution constant for the matrix/headspace equilibrium is found by comparing the concentration of the analyte in the two phases by equation (8).[28]

$$K_{hs} = C_h / C_s \quad (8)$$

Similarly, the distribution constant for the headspace/fiber equilibrium can be found by equation (9).[28]

$$K_{fh} = C_f / C_h \quad (9)$$

The above equations can be applied to the analysis of THMs by determining their original concentrations in the water sample via the concentrations on the fiber due to its relationship with the equilibrium concentrations found in both the headspace and the sample matrix. Once the partition coefficients are found for each THM, then the original concentrations are easily determined.

1.4.2 Fiber Selection

An important factor in any SPME analysis is the polymer type of the fiber on the needle of the device. There are multiple fibers to choose from when deciding to do an analysis. The range of fibers include poly(dimethylsiloxane) (PDMS), poly(acrylate) (PA), poly(dimethylsiloxane)/poly(divinylbenzene) (PDMS/DVB), poly(ethylene glycol)/ poly(divinylbenzene) (Carbowax/DVB), and poly(ethylene glycol)/template poly(divinylbenzene) (Carbowax/TR).[28] Each of the fibers are available from Supelco.

Choice of fiber depends on the polarity and the molecular weight of the analyte which is shown in Figure 1.6 and Table 1.3.[29,30]

Table 1.3 Fiber selection guide based on polarity of analyte

Analyte Type	Recommended Fiber
Gases and low molecular weight compounds (MW 30-225)	75 µm/85 µm Carboxen/polydimethylsiloxane
Volatiles (MW 60-275)	100 µm polydimethylsiloxane
Volatiles, amines and nitro-aromatic compounds (MW 50-300)	65 µm polydimethylsiloxane/divinylbenzene
Polar semi-volatiles (MW 80-300)	85 µm polyacrylate
Non-polar high molecular weight compounds (MW 125-600)	7 µm polydimethylsiloxane
Non-polar semi-volatiles (MW 80-500)	30 µm polydimethylsiloxane
Alcohols and polar compounds (MW 40-275)	60 µm Carbowax (PEG)
Flavor compounds: volatiles and semi-volatiles, C3-C20 (MW 40-275)	50/30 µm divinylbenzene/Carboxen on polydimethylsiloxane on a StableFlex fiber
Trace compound analysis (MW 40-275)	50/30 µm divinylbenzene/Carboxen on polydimethylsiloxane on a 2 cm StableFlex fiber
Amines and polar compounds (HPLC use only)	60 µm polydimethylsiloxane/divinylbenzene

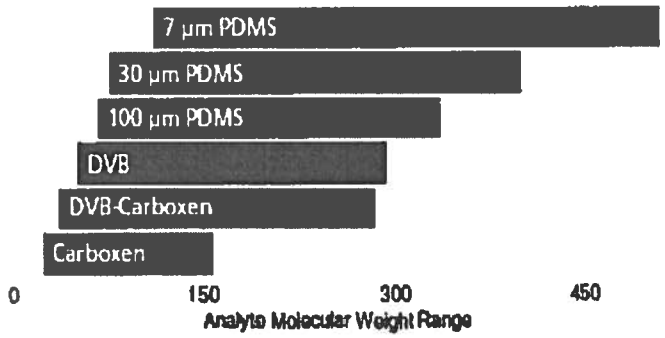

Figure 1.6: SPME fiber selection guide based on analyte molecular weight.

Fiber choice in the analysis of THMs must be made based on the polarity of the THMs and not their molecular weight as they are all very similar in structure. The dipole moments for chloroform, 1,2-dichloroethane, and 1,2-dibromoethane are 1.04, 1.48, and 1.11 respectively.[31] The most useful fibers in extracting THMs are PDMS and PDMS/DVB fibers. PDMS is a good choice as it has the advantage of being able to extract both non-polar and polar compounds by adjusting the extraction conditions.[28] PDMS/DVB polymers are suitable in analyzing more volatile compounds.[29] THMs are known to be volatile and thus PDMS/DVB would also be a suitable choice in fiber.

1.5 Gas Chromatography/Mass Spectroscopy (GC/MS)

Gas chromatography/mass spectroscopy (GC/MS) is a common technique used for the analysis of THM components in natural waters.[6,7] Gas chromatography is a separation technique whereby components are separated based on their affinities towards the stationary phase bound to the column. A mixture of components is introduced to the hot injector port by either direct injection using a gas syringe or by desorption from a SPME fiber. An inert carrier gas carries the mixture of components through the column, where they are separated based on their affinities to the column solid phase. Common carrier gasses include helium, nitrogen, hydrogen, or argon.[32] A typical chromatographic output is shown in Figure 1.7.

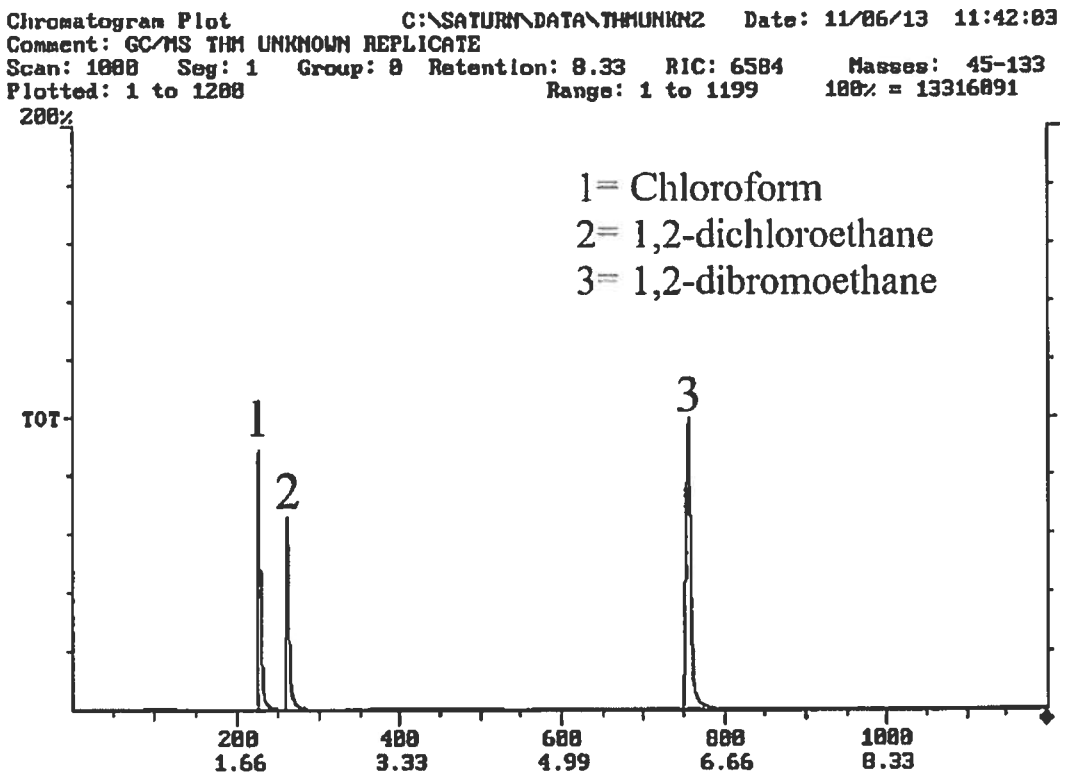

Figure 1.7 Chromatograph for the separation of three THM components

Each component is represented by a peak and each peak is assigned a retention time and a peak area. The retention time is representative of the components affinity towards the column while the peak area is representative of the component concentration.

The temperature of the column has an effect on the retention time and resolution of the component peaks. The resolution is the distance between two peaks in a chromatogram. Increasing the temperature decreases both the retention time and resolution of component peaks. Temperature programming also has an effect on peak resolution. If the temperature of the column is held constant through the entire separation then early peaks are sharp and close together while late peaks tend to be low, broad, and widely spaced.[32] Temperature programming involves changing the temperature at fixed

intervals during separation to attain a maximum resolution between the sample components.[32] The temperature profile normally begins at a low temperature and increases with time to both gain maximum resolution and to ensure all components elute from the column.

It is important to choose the proper column type for an analysis since it has an effect on the retention times, resolution, and sensitivity of the chromatogram. The actual separation of sample components is effected in the column where the nature of the solid support, type and amount of solid phase, method of packing, column length, and temperature are important factors in the determination of the resolution.[32]

There are two main types of columns: packed columns and capillary columns. Packed columns are filled with adsorbent particles that retain components as they pass through the GC. Properties of various porous polymer packings from Propak™ are shown in Table 1.4.[33] Each type of packing has three particle sizes which include 50-80 mesh, 80-100 mesh, and 100-120 mesh.

Table 1.4 Characteristics of GC Propak™ porous polymer packings

*= high purity. DVB = Divinylbenzene; EGDM = Ethyleneglycoldimethacrylate; PEI = Polyethyleneimine; ACN = Acrylonitrile; NV2P = N-vinyl-pyrollidinone; 4VP = 4-vinyl-pyridine.

Polymer	Max operating temp	Surface area (m2/gram)	Tapped bulk density (gram/cc)	Composition	Polarity
A	165°C	526	0.356	DVB*, EGDM*	7
B	190°C	608	0.33	DVB/PEI	8
C	250°C	442	0.322	DVB/ACN	6
D	290°C	795	0.3311	DVB	1
N	165°C	405	0.355	DVB/EGDM	9
P	250°C	165	0.42	DVB/Styrene	3
Q	275°C	582	0.351	DVB	2
R	250°C	344	0.324	DVB/NV2P	5
S	250°C	583	0.334	DVB/4VP	4
T	165°C	250	0.381	EGDM	10

Wall-coated open-tubular (WCOT) columns, the simplest form of a capillary column, are hollow fused-silica columns. A porous polymer is coated onto the fused-silica column at a width of 10-30 μm to retain components as they pass through the column.[34] Wide bore columns give a good compromise between capillary columns and packed columns. These wide bore capillary columns have a wide internal diameter (0.53mm), thick polymer coating, and can be directly substituted directly for packed columns due to their similar sample capacity and flow rates.[34] Properties for packed columns, capillary columns, and wide-bore capillary columns are shown Table 1.5.[34]

Table 1.5 Column types and their properties

	1/8-in. Packed	Wide Bore	WCOT
Inside Diameter (mm)	2.2	0.53	0.025
Film Thickness (μm)	5	1 to 5	0.25
Phase Volume Ratio (β)	15 - 30	130 - 250	250
Column Length (m)	1 to 2	15 - 30	16 - 60
Flow Rate (mL/min)	20	5	1
Effective Plate Height (mm)	0.5	0.6	0.3
Effective Plates/meter	2000	1200	3000
Typical Sample Size		15 μg	50 ηg

A high degree of specific molecular identification can be achieved by interfacing gas chromatography with mass spectroscopy.[32] A GC/MS setup is useful because component peaks can be identified when it elutes from the column in the GC, decreasing the required time for analysis. When the component leaves the GC and enters the MS, it is bombarded with electrons and transformed into positively charged ions.[35] This process is shown in equation (10).[35]

$$A + e^- \rightarrow A^+ + 2e^- \qquad (10)$$

The component ions are then accelerated and deflected by a magnetic field to effectively separate out components and their fragments based on their mass to charge ratio (m/z). Components with a low m/z ratio are deflected more than components with a high m/z ratio. The component is then passed through a detector where it is identified based on its molar mass (m/z ratio). A typical mass spectrum for chloroform is shown in Figure 1.8.

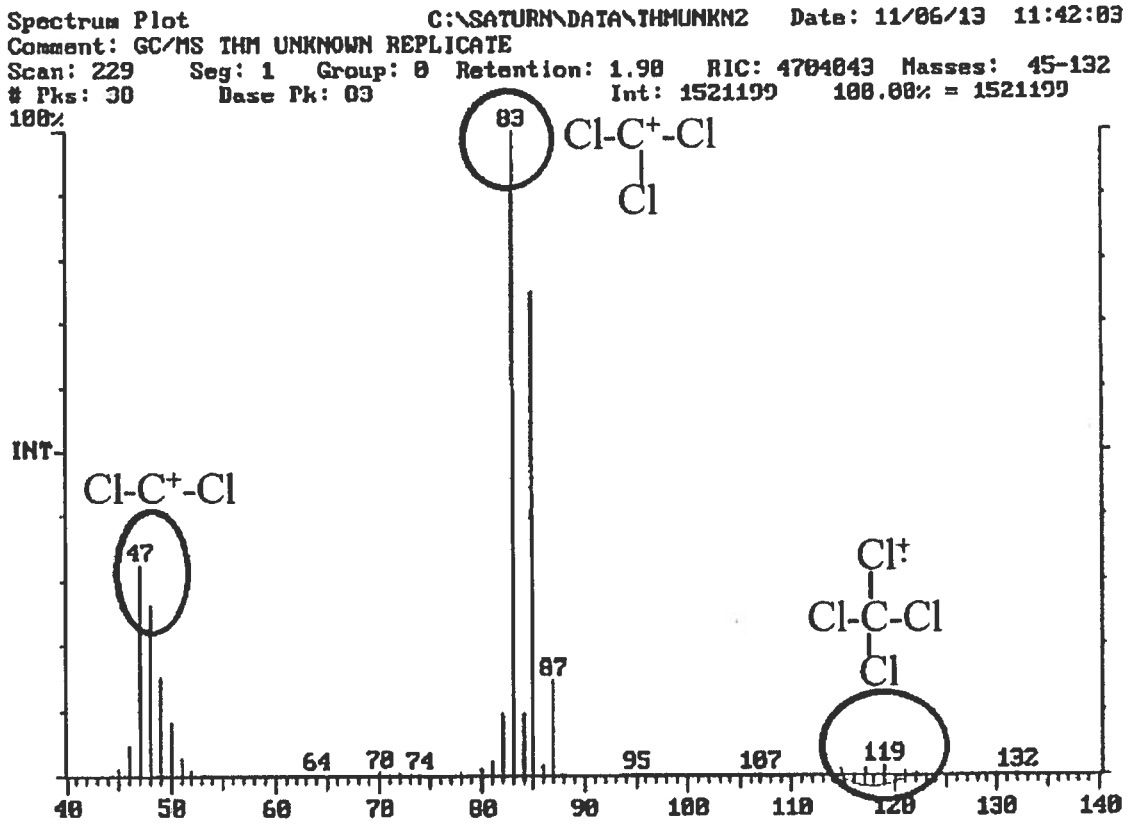

Figure 1.8 Mass spectrum for molecular and fragmentation peaks of chloroform

Establishing the molecular structure of the peak component requires information on the molecular and fragmentation peaks. The molecular peak corresponds to the ionized molecule and gives the molecular weight of the component.[35] Fragmentation peaks correspond to the molecular weight of the fragment ions.[35] Inspection of the mass spectrum in Figure 1.8 for chloroform, with molar mass of 119.38, shows a molecular peak at the 119 m/z ratio. This molecular peak is representative of the chloroform ion. As chloroform is bombarded with electrons, fragment peaks at 83 and 48 are formed. The peak at 83 represents a chlorine atom being cleaved from the structure since 119-83 = 36. Further fragmentation can be seen at 47 m/z where a second chlorine atom is cleaved from chloroform. The fragmentation reaction of chloroform is shown in reaction (11).

$$CHCl_3^+ \xrightarrow{electron} {}^+CHCl_2 \xrightarrow{electron} {}^+CHCl \xrightarrow{electron} {}^+CH \qquad (11)$$

F.W. 119 m/z 84 m/z 49 m/z 14 m/z (Below mass range)

The analytical power for identification in a GC/MS setup makes the technique suitable for the analysis of THMs.

1.6 Ultraviolet/Visible (UV/VIS) Spectrophotometry

Ultraviolet/visible spectroscopy is an analytical method which measures concentrations of analyte based on the absorption of light. The technique is governed by the Beer-Lambert law shown in equation (12).[36]

$$A = \varepsilon * l * C \qquad (12)$$

A is the absorbance (unitless), ε is the molar absorptivity ($L*mol^{-1}*cm^{-1}$), l is the path length (cm), and C is the concentration of analyte ($mol*L^{-1}$). Since the path length and molar absorptivity are constants, the only value which can change is the concentration. Therefore there is a direct correlation between the concentration of analyte and its absorbance at low concentration. At high concentrations the molar absorptivity is no longer constant, making the determination of analyte concentration impossible. The UV/VIS technique will be used as a confirmatory technique to detect the presence of THMs in sample standards. It will not be used as a quantitative technique.

1.7 Aims of the research

The aim of this research is to investigate the development of a SPME extraction method for the analysis of THMs from natural waters. The study will also look at analysis of THMs using a gas chromatogram/mass spectrometer (GC/MS) to ensure quick separation and identification of the THMs.

2.0 Experimental

Chlorodibromomethane and bromodichloromethane was purchased from Alfa Aesar while chloroform, 1,2-dichloroethane, and 1,2-dibromoethane was purchased from Aldrich, BDH AnalaR, and Acros Organics respectively. All standard solutions were prepared in HPLC grade methanol purchased from Fischer Scientific. Each THM stock solution had a purity of greater than 98% while the methanol had a purity of 99.97%. The properties of each component are shown in Table 2.1.[31] Uncertainties for equipment and glassware used in the lab are given in Table 2.2.

Table 2.1 Properties and constants of the chemicals used

A = Chloroform; B = 1,2-dichloroethane; C = 1,2-dibromoethane; D = Bromodichloromethane; E = Chlorodibromomethane; F = Methanol

Compound	A	B	C	D	E	F
CAS Number	67-66-3	107-06-2	106-93-4	75-27-4	124-48-1	67-56-1
Mol. Weight (g/mol)	119.38	98.96	187.86	163.83	208.28	32.04
Density (g/mL)	1.492	1.2454	2.1683	1.983	2.42	0.7914
Boiling Point (°C)	61.5	83.4	131.3	90	118	65
Melting Point (°C)	-63	-35.6	9.8	-57	-22	-97.5
Dipole Moment	1.04	1.48	1.11	1.31		2.87
Water Solubility	Slightly	Slightly	Insoluble	Insoluble	Insoluble	Miscible
Ethanol Solubility	Miscible	Very	Very	Very	Soluble	Miscible
Henry's Constant (atm*L/mol)	0.43	0.14	0.066	0.00212	0.00078	
Purity (%)	99.9	99.5	99	98	98	99.97
Formula	$CHCl_3$	$C_2H_4Cl_2$	$C_2H_4Br_2$	$CHCl_2Br$	$CHClBr_2$	CH_3OH
Supplier	Aldrich	AnalaR	Acros	Aesar	Aesar	Fischer

Table 2.2 Uncertainties of the equipment and glassware used

Equipment	Uncertainty in mL unless otherwise stated
10 mL syringe	± 0.1
500 µL syringe	± 5 µL
0.5 µL syringe	± 0.0003 µL
100 mL Fisherbrand class A pipette	± 0.08
50 mL Fisherbrand class A pipette	± 0.05
25 mL Fisherbrand class A pipette	± 0.03
10 mL Fisherbrand class A pipette	± 0.02
5 mL Fisherbrand class A pipette	± 0.01
25 mL graduated Cylinder	± 0.25
Mass balance	± 0.0002 g
Thermometer	± 0.5°C

2.1 Solvent Selection for THM Standards

Two solvents, a 10% methanol/water solution and a pure methanol solution, were used to make up the THM standards. Solvent selection was done using a Beckman DU 7400 UV-VIS spectrophotometer. The 10%methanol/water solvent was added to a UV-

VIS quartz cell and spiked with one drop of each: chloroform, 1,2-dichloroethane, 1,2-dibromoethane, and 2-chloro-2-methylpropane. THMs added to the pure methanol solution were diluted by adding one equivalent of each THM to 100 mL of solvent. Each solvent was run along with a corresponding blank to ensure the matrix did not interfere with the analysis. A solvent of pure methanol was chosen after comparing the absorbencies of the two spiked samples. Results are tabulated in Appendix C.

2.2 Preparation of Standards for Analysis

Eight standards were prepared *via* serial dilution. An initial 200 ppm standard was prepared by adding 200 µL of each THM component to 1L of HPLC grade methanol. THM components added were: bromodichloroethane, chlorodibromomethane, chloroform, 1,2-dichloroethane, and 1,2-dibromoethane. Subsequent standards of 100, 50, 25, 10, 5, 2, and 1 ppm concentrations were prepared in sealed 100 mL vials via serial dilution from the original 200 ppm standard. A 40 mL headspace vial with a Teflon-Teflon coated septum seal cap was then filled with 30 mL of the prepared standard for analysis. Volumetric flasks were not used in standard preparation to avoid losses due to the volatility of the THMs. Actual concentrations for the 200 ppm standard is illustrated in Table 2.3.

Table 2.3 Actual concentrations of THMs in the 200 ppm standard

Compound	Concentration
Chloroform	200 PPM ± 3.58%
1,2-dichloroethane	200 PPM ± 3.58%
1,2-dibromoethane	200 PPM ± 3.58%
bromodichloromethane	200 PPM ± 3.58%
chlorodibromomethane	200 PPM ± 3.58%

Calculation for 200 ppm standard:

200 ppm = 200 mL / 1,000,000 mL = 0.200 mL / 1,000 mL = 200 μL / 1L,

Uncertainty in 200 PPM standard = uncertainty of methanol addition + uncertainty of THM addn. + uncertainty of transfer to 40 mL headspace vial.

= ((10*0.08 mL)/1000 mL + 5μL/200μL + (3*0.1 mL)/30 mL)*100 = 3.58%

Other calculations in the results were calculated similarly.

2.3 Water Sampling Areas

Sampling areas to assess THM concentrations were chosen in specific regions around the city of Corner Brook. The areas with the highest concentrations of THMs in Corner Brook, according to the 2012 NL Provincial Government Survey,[4] were Trout Pond, Three Mile Pond (Third Pond) and Burnt Pond with estimated total THM concentrations of 158.15 ppb, 117.07 ppb, and 140.75 ppb respectively. Hence samples were taken from the same ponds (Trout Pond and Three Mile Pond) as the likely detection of THMs was possible. Also rough estimates of the THMs were known and were thought to be greater than the determined detection limit of our analysis and of interest because they were above regulatory EPA and Canadian limits of 80 ppb. Such sample concentrations were thought to be indicative of and would give a realistic of THM levels in the surface water around Corner Brook. Locations for Three Mile Pond and Trout pond are illustrated in Figure 2.1.

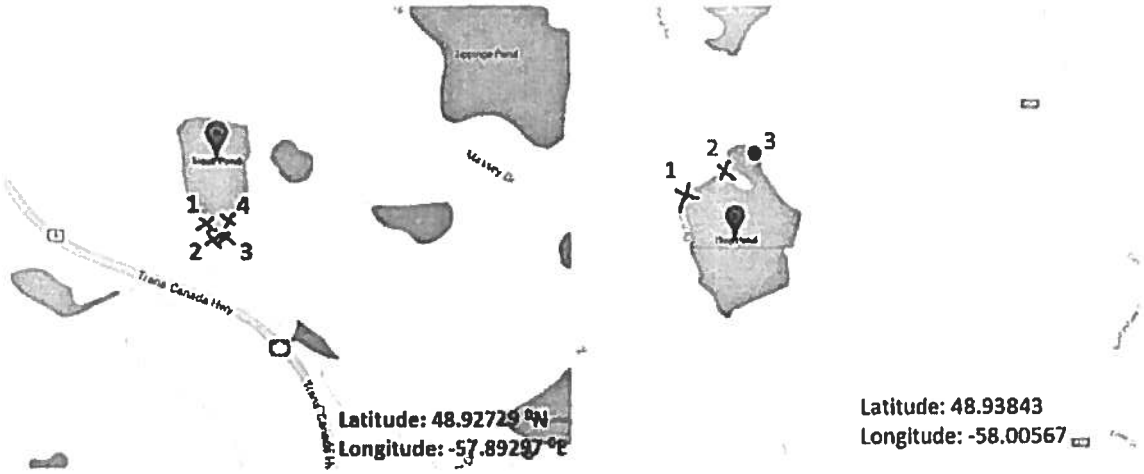

Figure 2.1 Sampling Locations for Trout Pond (left) and Three Mile Pond (right).

The X markings illustrated on each map represent sample locations where spot samples were collected in duplicate. Circular markings represent sample locations where spot samples were collected in triplicate. The description for each mark is listed in Table 2.4.

Table 2.4 Sample location descriptions for Trout Pond and Three Mile Pond

Silt = 0.004-0.031 mm[37]; Sand = 0.0625-2 mm[37]; Pebble = 4-64 mm[37]; Cobble = 65-256 mm[37]

Location	Mark Number and Coordinates	Description
Trout Pond	1 Lat: 48.92567 °N Long: -57.89312 °E	Samples taken from point of land extending from west side of pond. Short grass around bank of land. Bottom topography is sand and pebble sized material.
	2 Lat: 48.92522 °N Long: -57.89273 °E	Samples taken from left side of dock extending from south of the pond. Trees, shrubs, and short grass on bank. Bottom topography is sand, pebble, and cobble sized material.
	3 Lat: 48.92522 °N Long: -57.89254 °E	Samples taken from right side of dock extending from south of the pond. Trees, shrubs, and short grass on bank. Bottom topography is sand, pebble, and cobble sized material.
	4 Lat: 48.92573 °N Long: -5789261 °E	Samples taken from point of land extending from east side of pond. Short grass around bank. Bottom topography is sand and pebble sized material.
Three Mile Pond (Third Pond)	1 Lat: 48.93987 °N Long: -58.00831 °E	Samples taken from northwest of the pond by water intake. No vegetation on bank. Bottom topography is silt with low density of decaying tree leaves.
	2 Lat: 48.94057 °N Long: -5800631 °E	Samples taken from north of the pond on an island spit. Lots of trees and short grass on bank. Bottom topography is silt with high density of decaying vegetation.
	3 Lat: 48.94128 °N Long: -58.00505 °E	Samples taken from north-northeast of the pond in shallow water. High density of trees and short grass on bank. Bottom topography is silt with an intermediate density of decaying vegetation.

2.4 Optimization of Extraction Parameters

All extraction parameters were optimized using a THM standard prepared by spiking 100 mL of 10% methanol/water in a sealed 100 mL vial with one equivalent of each: Chloroform, 1,2-dibromoethane, and 1,2-dichloroethane. A volume of 30 mL was then added to a sealed 40 mL headspace vial equipped with a Teflon-coated stir bar for analysis. Parameters optimized were temperature, spin rate, extraction time, desorption time, and fiber type. All optimizations were done using a PDMS/DVB fiber with 60 µm thickness supplied by Supelco. Headspace volume was held constant at 10 mL for each analysis. The setup for the headspace extractions is illustrated in Figure 2.2.

Figure 2.2 Picture of a SPME headspace extraction setup.

2.4.1 Determination of Optimized Desorption Time

Desorption time was optimized using a 180 ppm THM standard. The PDMS/DVB fiber was inserted into the headspace of the THM standard for a two minute extraction. The Fiber was then pulled into the needle of the SPME apparatus and the needle removed and immediately transferred to the hot injector port of the GC.

Desorption times of 30 seconds, 1 minute, and 2 minutes were tested. An optimized desorption time of 2 minutes was measured to give the largest GC peak area.

2.4.2 Determination of Optimized Extraction Time

The THM standard utilized in the previous optimization was employed for the determination of optimal extraction time. The SPME fiber was exposed to the headspace for a set time period and then immediately injected into the hot injector port of the GC. Extraction times of 0.33, 0.66, 1, 2, 4, 8, and 10 minutes were tested. THM Peak areas for each extraction time was plotted to create an extraction time profile. An optimized extraction time of 4 minutes was determined to be optimum.

2.4.3 Determination of Optimized Spin Rate

The THM standard utilized in previous optimizations was employed for the determination of optimal spin rate. An extraction was carried out at spin rates of 500, 700, 900, and 100 rpm. The SPME fiber was exposed to the headspace for an extraction time of four minutes then immediately injected into the GC port. THM peak areas for each extraction were plotted against spin rate. An optimized spin rate of 900 rpm gave the best and consistent peak areas.

2.4.4 Determination of Optimized Sample Vial Temperature (°C)

The same 180 ppm THM standard utilized in previous optimizations was employed for the determination of optimal extraction temperature. An initial temperature was set at 20°C in an ice bath before extraction. When 20°C was reached the SPME fiber was exposed to the headspace for exactly four minutes at a spin rate of 900 rpm. The

fiber was then pulled back into the plunger and immediately transferred into the injector port of the GC. Extraction temperatures of 25°C, 30°C, 35°C, 40°C, and 45°C were tested. An extraction temperature profile was constructed by plotting peak area against extraction temperature. An optimized temperature of 25^0C was selected.

2.4.5 Fiber Selection

A new spiked 10% methanol/water sample containing one equivalent of each: chloroform, 1,2-dichloroethane, and 1,2-dibromoethane, was prepared for the determination of the optimal fiber type. The three fiber types tested were PDMS/DVB at 60 µm thickness, Carbowax/DVB at 70 µm thickness, and Polyacrylate at 85µm thickness. Before analysis, each fiber was conditioned according to the guidelines given by Supelco. Each fiber was exposed to the headspace for exactly four minutes at a spin rate of 900 rpm and temperature of 25°C. After extraction was complete, the fiber was withdrawn into the SPME needle then immediately inserted into the hot injector port of the GC where it was held for exactly two minutes. PDMS/DVB was chosen to be the best fiber for extraction of THMs.

2.5 Preparation of Natural Water Samples

Fifteen natural water samples were collected and filled to the top in 1 liter brown sample bottles from Trout Pond and Three Mile Pond. After collection, all water samples were analyzed for conductivity, pH, temperature, and dissolved solids. A volume of 25 mL from each sample bottle was added to a 40 mL headspace vial equipped with a Teflon coated stir bar and a Teflon-Teflon coated septum cap. Each sample was stored in the refrigerator at 4^0C to reduce losses between analyses. Five samples were analyzed by

SPME-GC/MS. Samples analyzed were 2, 3, and 6 from Three Mile Pond and 4 and 8 from Third Pond. Three mile pond sample 2 (3P#2) was sampled from the intake at the northwest side of the pond. Three Mile Pond sample 3 (3P#3) was sampled from north-north east near foliage. Three mile pond sample 6 (3P#6) was sampled from north of the pond on an island spit with a large mass of decaying materials in the water. Trout pond sample 4 (TP#4) was sampled from a point of land extending from the west side of the pond. Trout pond sample 8 (TP#8) was sampled from the left side of the dock at the south end of the pond.

Each of the five samples was analyzed in triplicate. Samples were spiked with chloroform, 1,2-dichloroethane, bromodichloromethane, and 1,2-dichloroethane to give concentrations of 1.2, 2.4, 6 and 12 ppm. A standard addition plot was constructed for each THM present in the original water sample.

2.6 UV/VIS Spectrophotometry

The Beckman DU 7400 UV/VIS spectrophotometer was employed in the analysis of the THM standards prepared via serial dilution. A blank of pure methanol was run before each standard to remove matrix effects. Each standard was added to a quartz cell then inserted into the cell holder of the UV/VIS for analysis. The UV/VIS method was used as a validation method rather than an analytical method to ensure that the THMs were dissolved in the solvent. Minimal absorbencies were found when running the THM samples in a 10% methanol/water solution therefore the UV-VIS will not be employed in the analysis of natural water samples. A picture of the UV/VIS setup is shown in Figure 2.3.

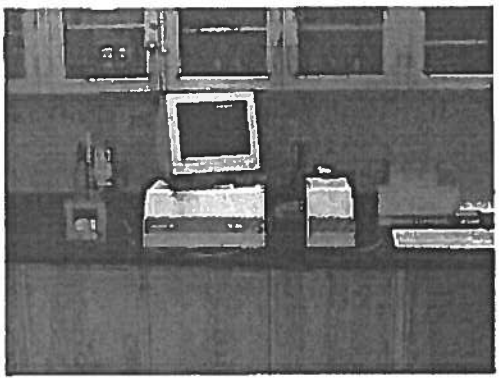

Figure 2.3 Photograph of a Beckman DU-7400 UV/VIS spectrophotometer.

2.7 Optimization of the GC/MS

All THM standards and water samples were analyzed using a Varian Star 3400 Cx / Varian Saturn 3 GC/MS combo. GC/MS parameters needed to be optimized before an analysis could be completed. Following previous laboratory guidelines and course laboratories dealing with THMs, optimal parameters were set and used for the entire analysis. The GC/MS profile employed included an injector port temperature of 250°C and a column transfer line temperature of 240°C with an in source temperature of 200°C. Initial oven temperature was set to 30°C and held for five minutes. A final oven temperature of 50°C was attained by increasing the temperature at a rate of 5°C / minute to attain a total run time of 9 minutes. The GC temperature profile used is illustrated in Figure 2.4.

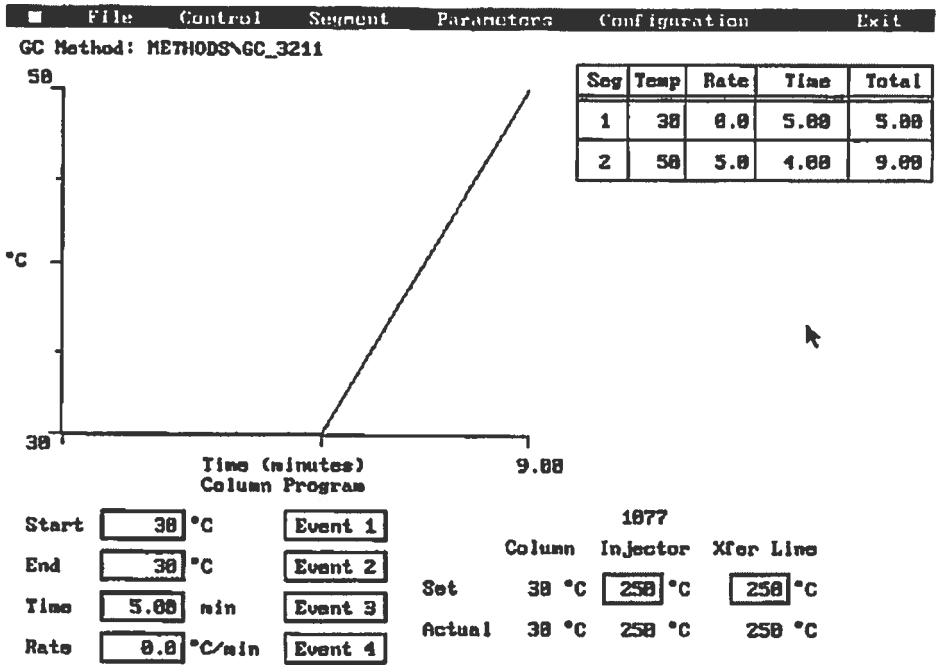

Figure 2.4 Optimized GC temperature profile utilized for THM analysis.

The mass spectrometer was tuned to read samples for the full 9 minutes. Optimized temperatures of 211°C and 200°C were set for the manifold and ion trap detector respectively.

The column employed was a medium polar DB-5, 30 meter silica glass column at 0.25mm thickness with a film thickness of 0.2µm. The medium-polar column was supplied by Supelco. All THM standards and water samples prepared in the laboratory were analyzed using the set GC/MS profile. A picture of the GC-MS setup and is illustrated in Figure 2.5.

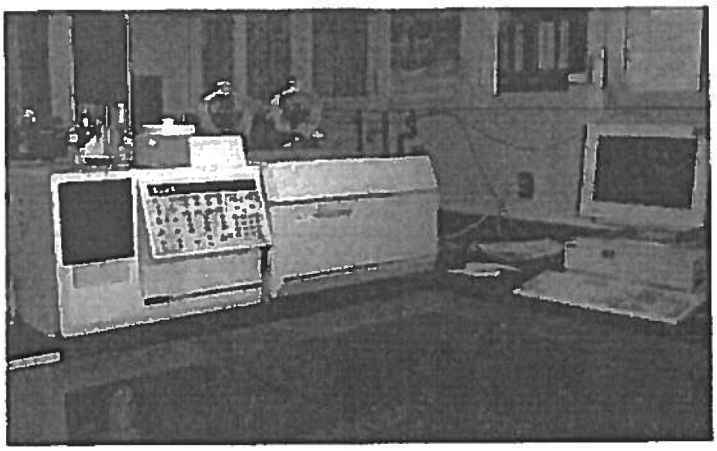

Figure 2.5 Photograph of the gas chromatograph/mass spectrometer

2.8 Sample Analysis

Headspace vials containing a Teflon-coated stir bar and 25 mL of sample was placed inside of a beaker filled with water. A thermometer was placed in the water to monitor sample temperature. The beaker was placed on a hotplate where a temperature of 25°C and spin rate of 900 rpm was set. The sample was given sufficient time to reach equilibrium between the aqueous layer and the headspace. The SPME needle was then inserted into the Teflon septum of the headspace vial and the plunger was pushed down to expose the PDMS/DVB fiber to the sample headspace for 4 minutes. After the extraction was completed, the plunger was depressed to pull the SPME fiber back into the needle housing. The SPME apparatus was then immediately inserted into the hot injector port of the GC, where the plunger was once again pressed down to expose the PDMS/DVB fiber. The fiber was left in the injector port at 250 °C for 2 minutes to allow for the THM components to completely desorb. The sample mixture was then separated into the GC column over a period of 9 minutes. A complete sample analysis which

includes equilibrium time, sample extraction, separation, and MS analysis, requires approximately 25 minutes.

3.0 Results and Discussion

All data in the results were analyzed in triplicate (N=3) to test the quality of the data. Any outlier points that failed the Q-test for small data sets will be present in Tables but will not be presented in Figures or in calibration and other calculations.

3.1 Fiber Optimization and Selection

Accurate analysis of THM components requires optimal extraction parameters when utilizing the SPME device. Desorption time, extraction time, spin rate, extraction temperature, and fiber selection are parameters which need to be optimized for a successful analysis.

3.1.1 Determination of Optimized Desorption Time

Desorption time is an important parameter which prevents carryover of THM components. Any carryover present on the fiber will further contaminate the sample and thus give a systematic error and non-reproducible results for any repeated analyses. Desorption time is determined by a follow-up analysis of the blank SPME fiber after an initial extraction is completed. The fiber is exposed again to the hot injector port until the analyte is completely desorbed from the fiber, removed, and then re-injected after the GCC/MS run is completed. This method ensures no carryover and therefore no cross-contamination of sample analytes. A typical chromatographic output for desorption time is illustrated in Figure 3.1.

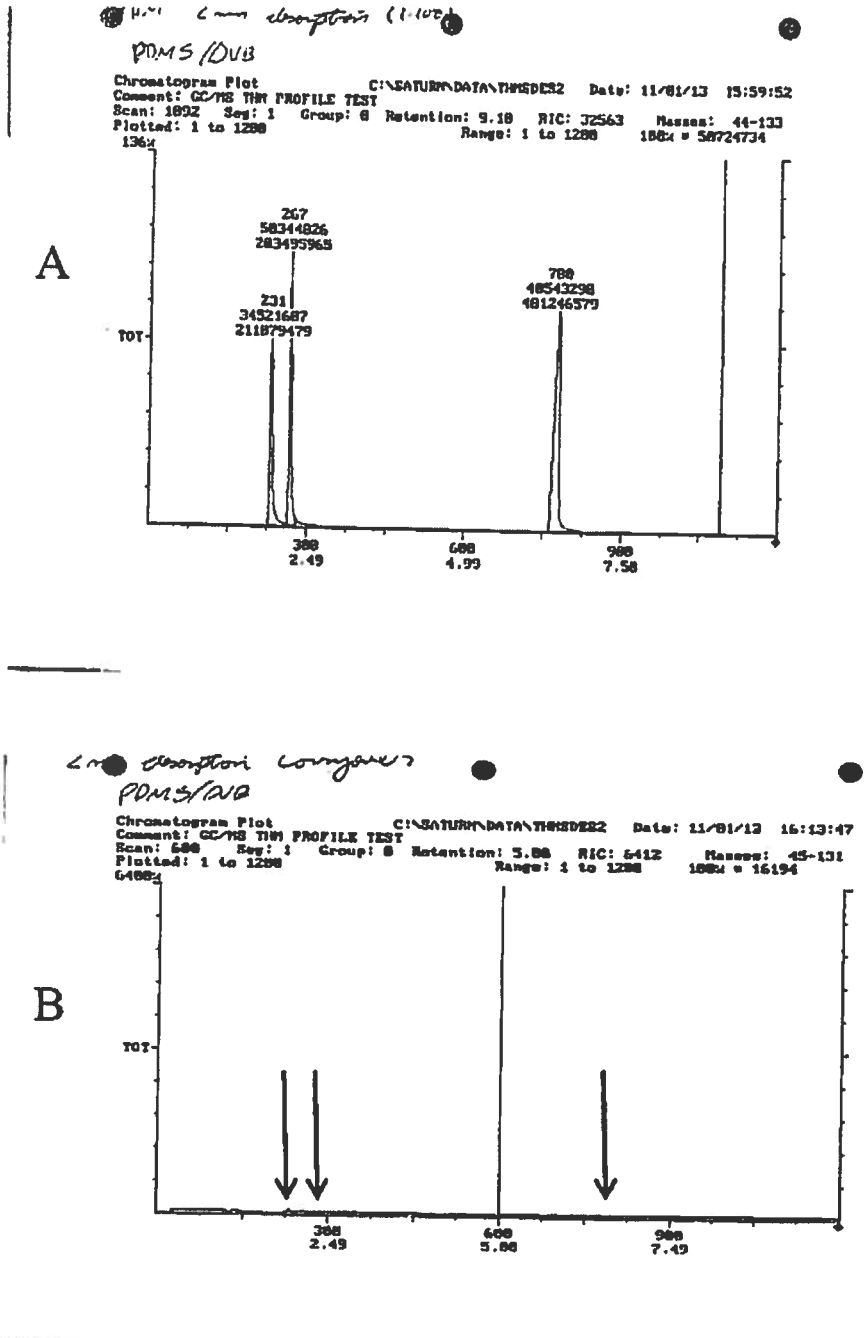

Figure 3.1 A GC spectrum a) showing three analyte peaks well resolved after desorption of the SPME fiber b) Results from the SPME fiber being desorbed again, where no analyte residuals are seen.

3.1.2 Determination of Optimized Extraction Time

SPME extractions are based on three way equilibrium between the aqueous layer, sample headspace, and SPME fiber. Once equilibrium is reached between the sample headspace and SPME fiber, no further analyte is adsorbed in appreciable quantities. Figure 3.2 represents three way equilibrium for the extraction of analyte X.

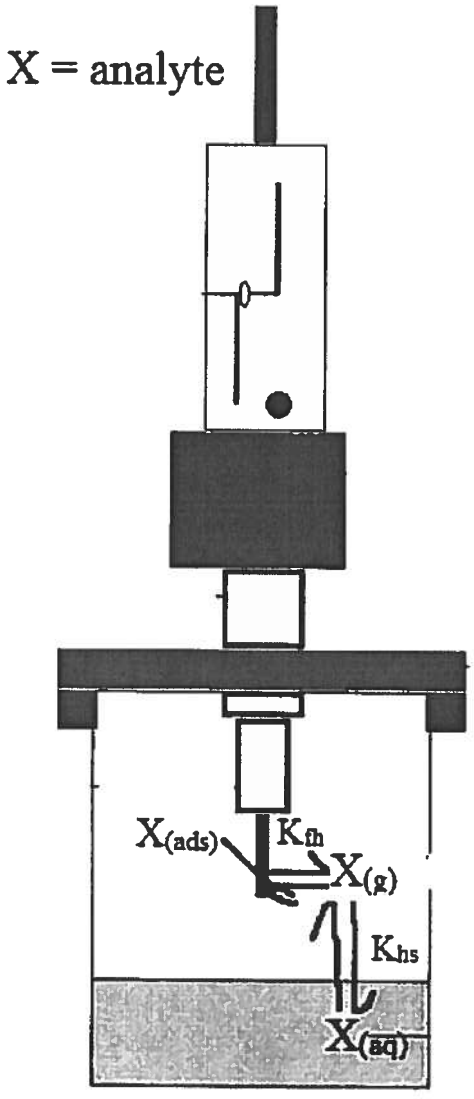

Figure 3.2 Three-way equilibrium for the headspace extraction of analyte X.

The analyte remains constant and corresponds within experimental error to the amount extracted at infinite extraction time (27), illustrated by equation (7).

$$C_0V_s = C_fV_f + C_hV_h + C_sV_s \quad (6)$$

$$n = (K_{fh}K_{hs}V_fC_0V_s) / (K_{fh}K_{hs}V_f + K_{hs}V_h + V_s) \quad (7)$$

The total concentration of analyte (C_0) remains the same during the extraction (eqn. 6). Headspace and sample volumes also remain constant through the course of an extraction. Therefore the total mass of analyte adsorbed depends on the distribution coefficients for the partition between sample-to-headspace (K_{hs}) and headspace-to-fiber (K_{fh}). At equilibrium, these distribution coefficients are constant. Therefore the maximum mass of analyte (n) which can be adsorbed becomes constant at equilibrium.

As illustrated in Figure 3.3, the slope of the line approaches a near zero state around 4 minutes which is an indication of equilibrium conditions. The concentration of analyte extracted after 4 minutes remains relatively constant, as illustrated by the peak areas in Table 3.1

Table 3.1 GC/MS peak area and extraction time for headspace analysis of a 10% methanol/water sample spiked with THMs using 60µm PDMS/DVB fiber

Time	Peak Area (± 5.2%)		
(min)	chloroform	1,2-dichloroethane	1,2-dibromoethane
0	0	0	0
20 seconds	33105559	49766469	33604713
40 seconds	31337763	42510309	35069495
1	34721464	53678533	41435134
2	33133996	34062803	38357145
4	31921216	43145305	37008450
8	31629529	43908552	36400051
10	31295629	43248064	35403094

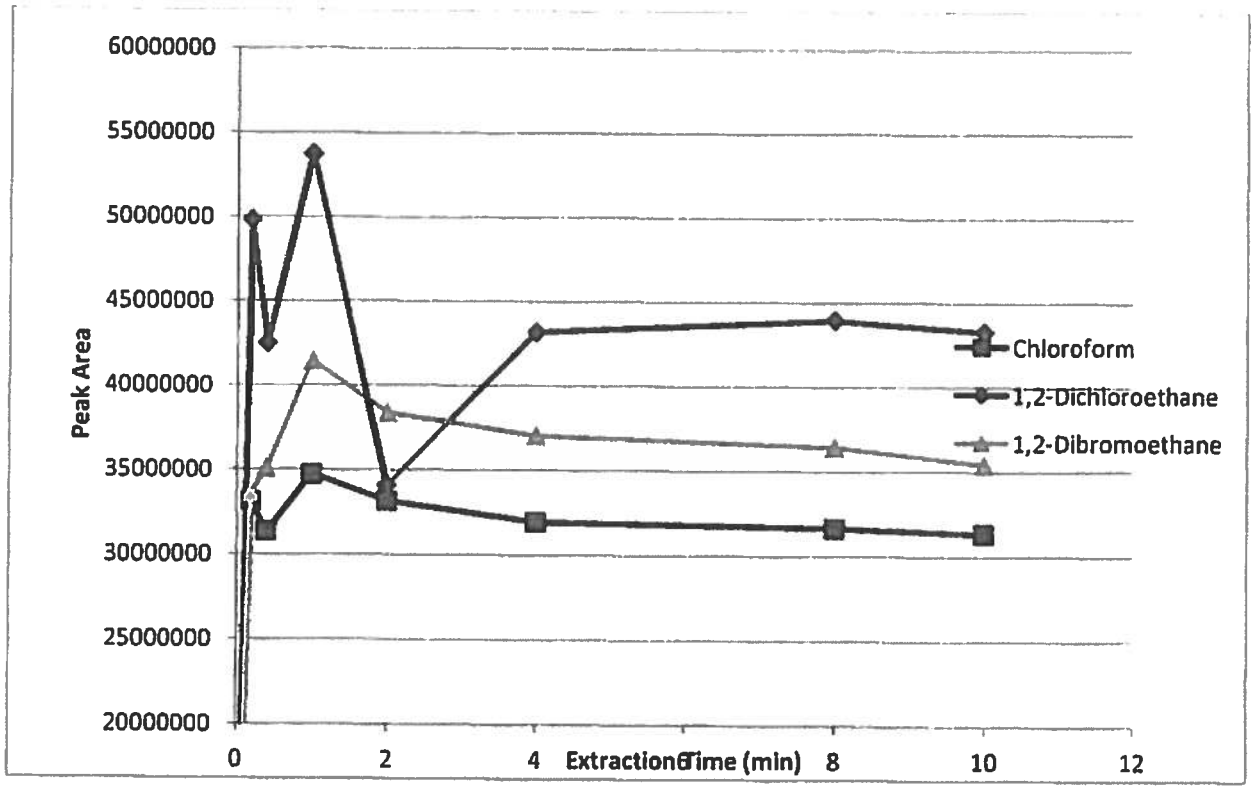

Figure 3.3 Extraction profile for headspace analysis of a spiked THM standard using 60 µm PDMS/DVB fiber.

Peaks at the 1 minute extraction time are artifacts which may be present through sampling errors. The artifact is illustrated by the 1,2-dibromoethane temperature profile. The rapid rise in peaks at extraction times of 20 and 40 seconds corresponds to extraction from the gas phase,[28] followed by slow increase related to the mass transfer of sample from water though the headspace to the fiber.[27] The normal shape of the curve should be a slow decrease in slope until zero-slope conditions is achieved. Figure 3.4 illustrates the normal shape of the curve for extraction from a gas phase (3).

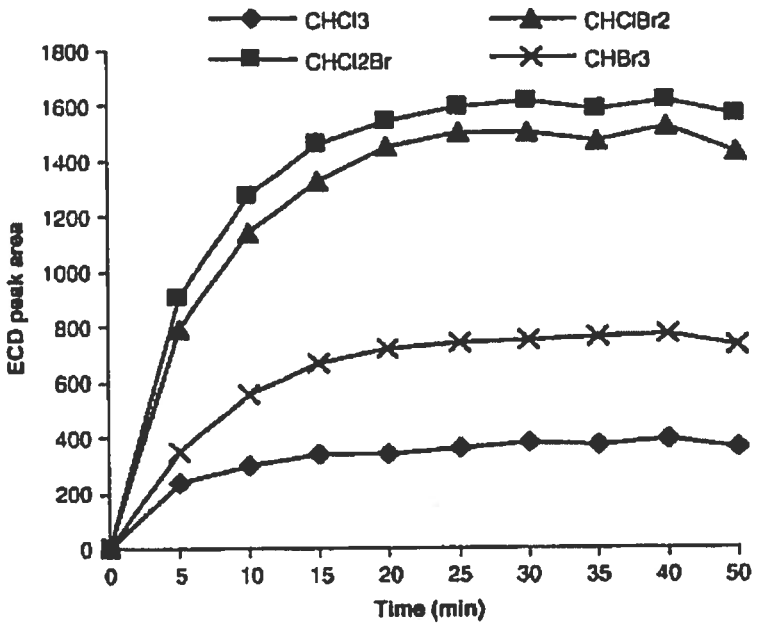

Figure 3.4 Normal curve associated with SPME extraction from sample headspace.

However at 1 minute, there is a sharp increase in peak area for all 3 THM components. The 1,2-dibromoethane peak at 1 minute deviates from the typical decrease in slope, giving an indication of an error in the peak area. The chloroform and 1,2-dichloroethane peaks illustrate a sharp increase in peak area at 20 seconds, and a large drop in peak area is shown after the initial 20 second extraction time. The peak area then slowly increases until equilibrium is reached at 4 minutes. Such deviations may in part be explained by volatility. As mentioned earlier, 1,2-dibromoethane (K_H = 0.066) has a plot characteristic to that of SPME extraction from a gas phase. However both chloroform and 1,2-dichloroethane have larger Henry's Law constants (0.43 and 0.14 respectively) than 1,2-dibromoethane. Therefore chloroform and 1,2-dichloroethane are more easily distributed into the gas phase than 1,2-dibromoethane. This explanation is illustrated by the peak areas at a 20 second extraction time, where both chloroform and 1,2-dichloroethane have their largest relevant peak areas in their respective profiles and 1,2-

dibromoethane has the lowest peak area in its extraction profile. THM component peaks are not in equilibrium with the SPME fiber before 4 minutes, giving rise to noise in the data peaks.

3.1.3 Determination of Optimized Spin Rate

The spin rate, of the Teflon coated stir bar, theoretically decreases the time to reach equilibration between the sample headspace and aqueous layer. Equilibration times for the analysis of volatile samples are fast and are frequently limited by the diffusion of analytes in the coating.[29] Therefore the total equilibrium time will depend mostly on the partition of the analyte between the gaseous and aqueous matrices. The results obtained in Figure 3.5 illustrates that the spin rate had little effect on the concentration of analyte extracted.

Table 3.2 GC/MS peak area and spin rate for headspace analysis of a 10% methanol/water sample spiked with THMs using 60μm PDMS/DVB fiber

Spin rate	Peak Area (± 5.2%)		
(rpm)	Chloroform	1,2-dichloroethane	1,2-dibromoethane
500	30496817	39862959	35258010
700	28780316	38445421	34413529
900	29721730	40473603	34931312
1100	28789901	39000882	34915198

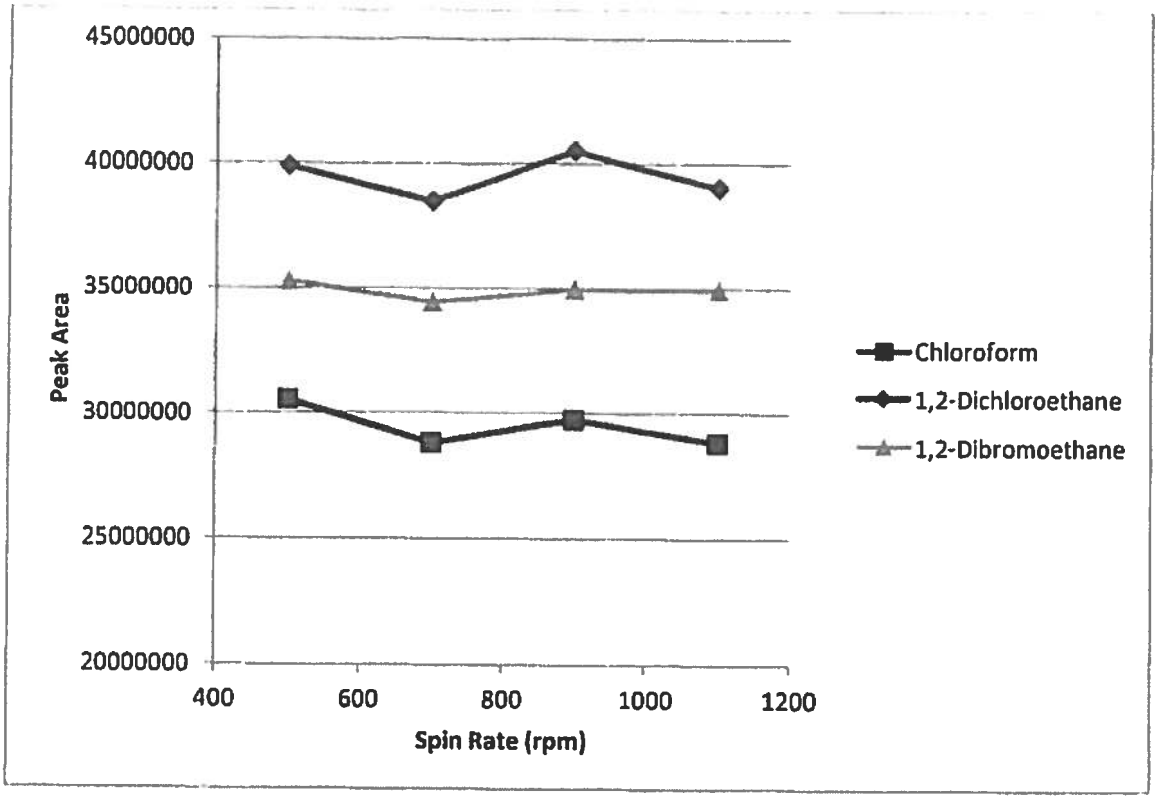

Figure 3.5 Spin rate profile for headspace analysis of a spiked THM standard using 60 µm PDMS/DVB fiber.

Any small changes in peak areas are caused by experimental error (±5%). The relative invariance of the peak areas can be explained by the equilibration time. During analysis of spin rates an extraction time of 4 minutes was used, as determined by the extraction time profile. The THM components will have already reached equilibrium by the time the 4 minute extraction is completed. Variation in spin rate will not have an effect on peak areas once the equilibrium is reached, as agitation only serves to decrease the initial equilibration time.[29] If an extraction were to be completed in a shorter time span than 4 minutes, then diminished peak heights would occur.

Time is required to reach that initial equilibrium between the aqueous phase and the headspace before the SPME fiber can be introduced to the sample headspace.

Agitation will reduce the time required for this initial equilibrium, and therefore reduce the time in between replicate analysis.

Results show that spin rate can be selected anywhere between 500 and 1100 rpm due to the relative invariance of the peak areas. 900 rpm was selected for two reasons. The first reason is that the initial equilibrium time can be decreased relative to 500 and 700 rpm, since increasing spin rate decreases equilibration time.[29] The second reason is that using 900 rpm prevents splashing of the water onto the SPME fiber and this rate could be accurately controlled by the heater stirrer mantle that was used. At higher spin rate, for example 1100 rpm, the increased agitation resulted in the splashing of water inside of the headspace vial which gives a systematic error.

3.1.4 Determination of Optimized Extraction Temperature (°C)

Increasing the extraction temperature theoretically decreases the time required to reach equilibrium. However, data points shown in Figure 3.6 illustrate a decrease in peak area as the temperature is increased. Increasing the extraction temperature decreases the sample-headspace distribution constant (K_{hs}) and thus decreases the concentration of analyte adsorbed onto the fiber.[29] The relation between K_{hs} and temperature is shown in equation (13).[29]

$$K_{hs} = K_H / RT \qquad (13)$$

K_H is Henry's Law constant, R is the gas constant and T is the temperature. The equation illustrates that temperature is inversely related to the sample-headspace distribution coefficient. A decreased K_{hs} will affect the fiber-headspace distribution coefficient (K_{fs}) by equation (14),[29]

$$K_{fs} = [n(K_{hs}V_h + V_s)] / [V_f(C_0V_s - n)] \qquad (14)$$

K_{hs} is directly correlated with K_{fs}. A decrease in K_{fs} lowers the mass of analyte (n) which can be adsorbed to the fiber.

Table 3.3 GC/MS peak area and spin rate for headspace analysis of a 10% methanol/water sample spiked with THMs using 60µm PDMS/DVB fiber

Temperature (°C) (± 0.5°C)	Peak Area (± 5.2%) Chloroform	1,2-dichloroethane	1,2-dibromoethane
20	29963194	41876318	33549914
25	28187853	39667428	32838354
30	28591532	38897843	32540786
35	28491732	38599406	31645136
40	27851511	32131574	31193131
45	28399811	29686659	29349922

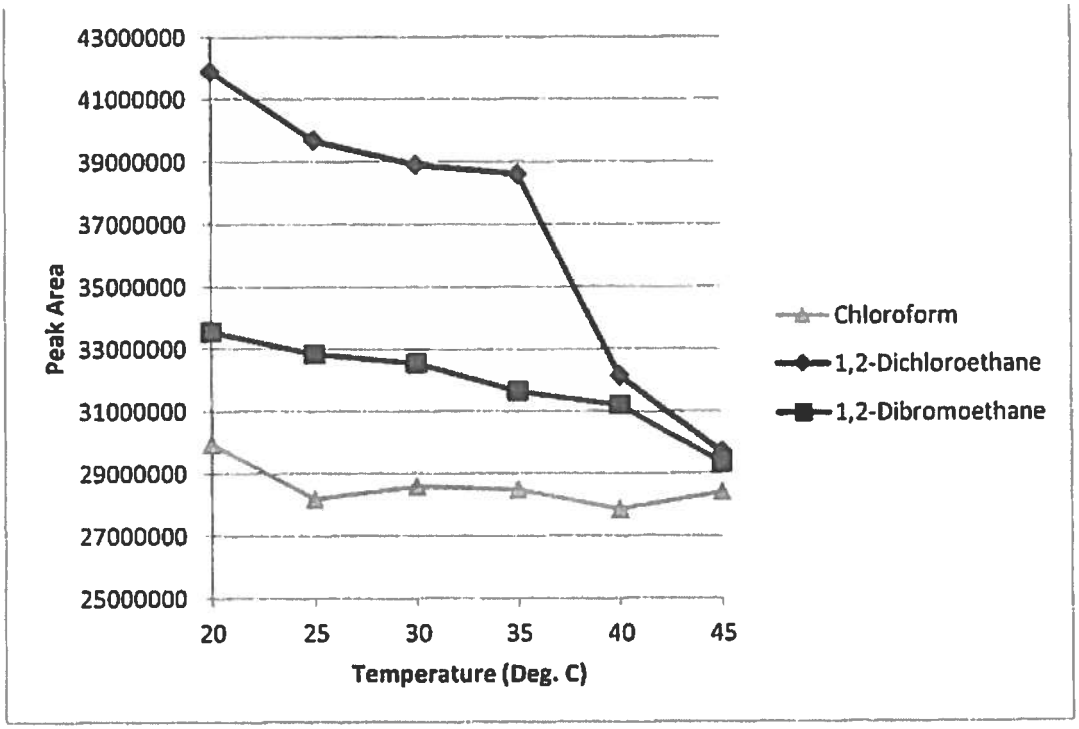

Figure 3.6: Extraction temperature profile for headspace analysis of a spiked THM standard using 60 µm PDMS/DVB fiber.

Since THM concentrations are low in natural waters (≤100 ppb),[4] the highest concentration possible must be extracted. The highest concentrations are extracted at 20^0C, as illustrated in Figure 3.6. However, an ice bath is required to reach 20°C. Temperatures moderated by an ice bath could not be held stable for long periods of time for a number of samples. Therefore an optimized extraction temperature of 25°C was utilized. A 25°C temperature is around the laboratory room temperature and is easily held constant with the use of a hotplate, allowing for reproducible analyses.

3.1.5 Determination of Fiber Type For THM Analysis

The affinity of the analyte towards a specific fiber will affect the concentration of analyte extracted. Therefore it is important to select the proper fiber type based upon the analyte. Three fibers (PDMS/DVB, Carbowax/DVB, and polyacrylate) were tested toward their ability to extract THMs. Carbowax/DVB fibers are known to be able to extract alcohols and polar compounds while polyacrylate fibers are better suited for polar semi-volatile compounds and PDMS/DVB fibers have been used in the literature[28] to extract volatile components. Results showed (Table 3.4 and Figure 3.7) that the PDMS/DVB fiber gave the highest extraction rates of the three fibers tested and hence this fiber was used throughout for this research.

Table 3.4 GC/MS peak area and fiber selection for headspace analysis of a 10% methanol/water sample spiked with THMs.

	Peak area (± 5.2%)		
Component	PDMS/DVB (60 μm)	Carbowax/DVB (70 μm)	Polyacrylate (85 μm)
Chloroform	30573280	22596207	14578888
1,2-dichloroethane	44577267	22659909	13211724
1,2-dibromoethane	26874857	14957521	8295135

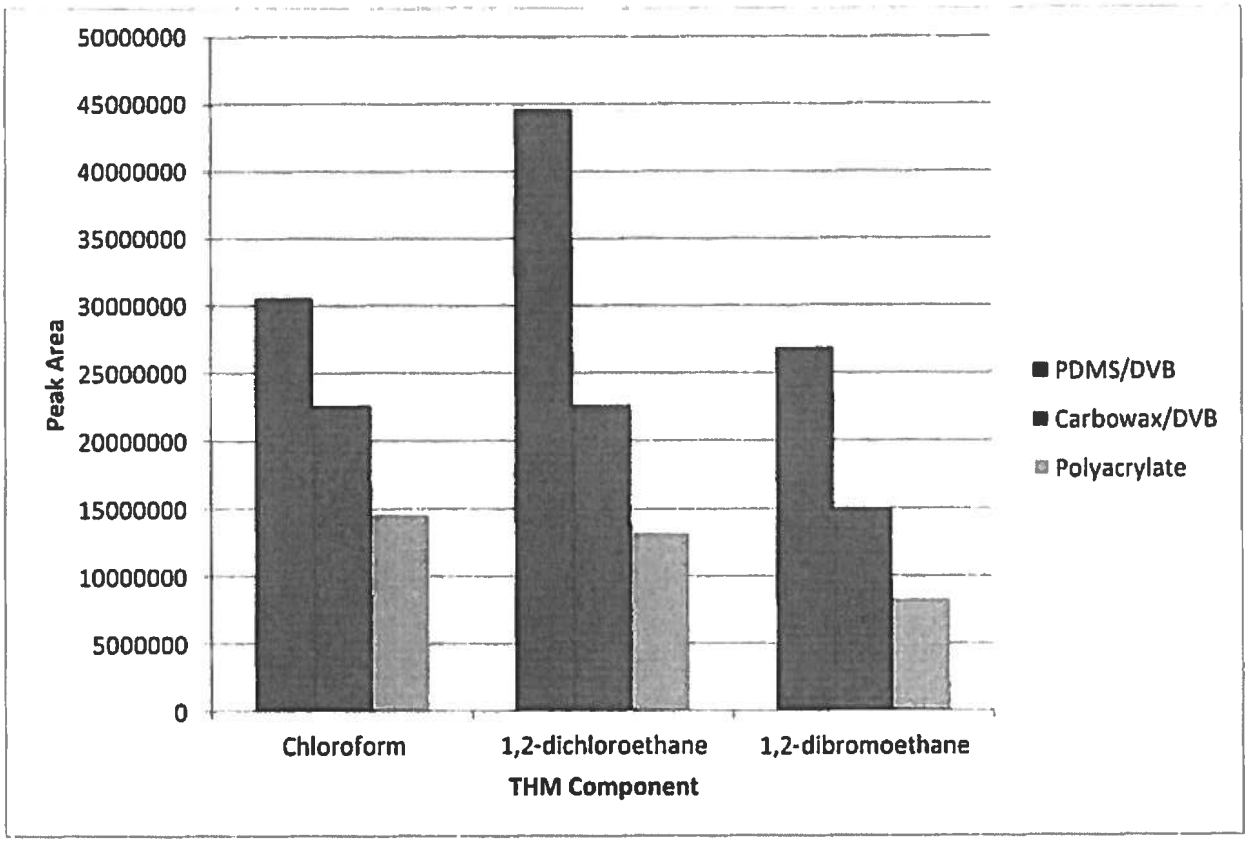

Figure 3.7 Fiber selection profile for headspace analysis of a spiked THM standard.

3.2 THM Calibration Curves

Figures 3.8-3.12 show calibration curves that were created from: chloroform, 1,2-dichloroethane, bromodichloromethane, chlorodibromomethane, and 1,2-dibromoethane via serial dilution in sealed vials. These were used to determine the concentration of

THMs in the natural water samples as a comparative study against standard addition plots. Calibration curves are plotted from a range of 10-1 ppm. Therefore any Q-test results will pertain to that data range.

Table 3.5 GC/MS chloroform peak areas using 60 µm PDMS/DVB

Concentration (ppm)	Peak Area (± ppm%)	RSD (%)	Q-test (90%)
200 ± 3.58%	4190215	6.34	pass
100 ± 5.68%	2065144	8.97	pass
50.0 ± 7.78%	930511	9.54	pass
25.0 ± 9.88%	513212	5.60	pass
10.0 ± 12.18%	164280	8.29	fail
5.00 ± 14.28%	41418	21.2	pass
2.00 ± 16.58%	11139	13.9	pass
1.00 ± 18.68%	3492	22.4	pass

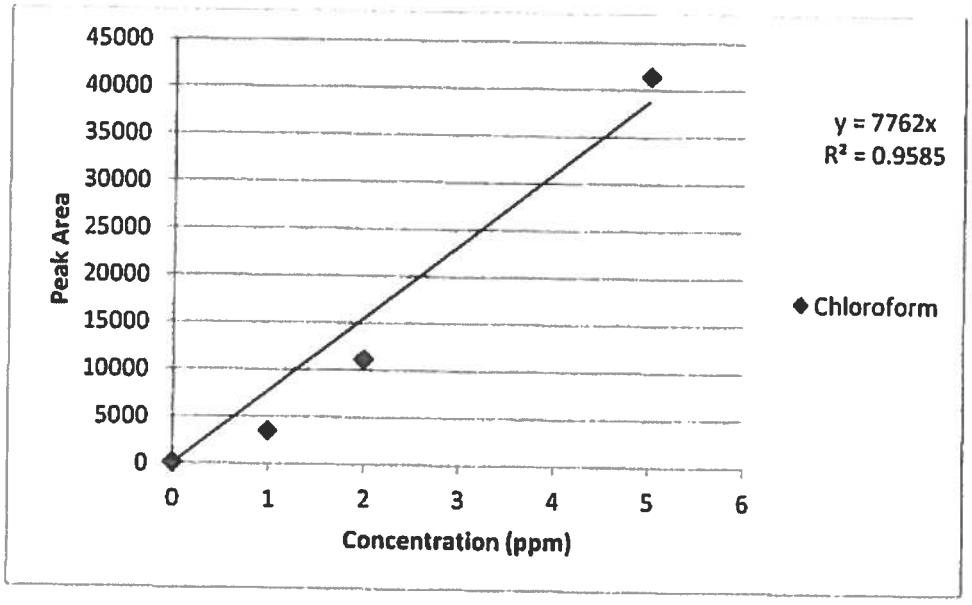

Figure 3.8 Chloroform calibration curve at a concentration range of 5-1 ppm.

Table 3.6 GC/MS 1,2-dichloroethane peak areas using 60 µm PDMS/DVB

Concentration (ppm)	Peak Area (± ppm%)	RSD (%)	Q-test (90%)
200 ± 3.58%	4264940	8.38	pass
100 ± 5.68%	1797339	7.16	pass
50.0 ± 7.78%	750845	5.05	pass
25.0 ± 9.88%	439689	9.38	pass
10.0 ± 12.18%	133287	7.35	pass
5.00 ± 14.28%	29829	22.9	pass
2.00 ± 16.58%	7190	25.9	pass
1.00 ± 18.68%	5464	42.7	pass

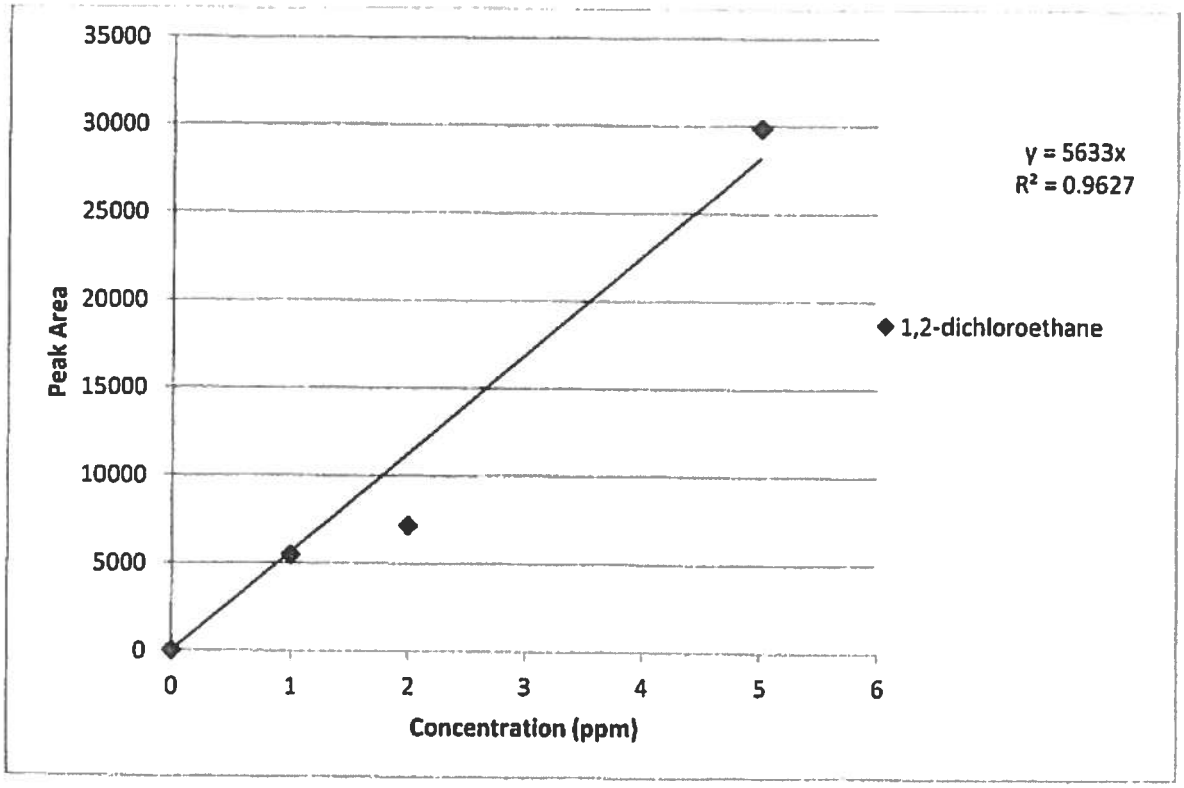

Figure 3.9 1,2-dichloroethane calibration curve at a concentration range of 5-1 ppm.

Table 3.7 GC/MS bromodichloromethane peak areas using 60 μm PDMS/DVB

Concentration (ppm)	Peak Area (± ppm%)	RSD (%)	Q-test (90%)
200 ± 3.58%	4846816	7.72	pass
100 ± 5.68%	1965501	7.90	pass
50.0 ± 7.78%	911200	2.59	pass
25.0 ± 9.88%	530294	6.25	pass
10.0 ± 12.18%	154240	5.26	pass
5.00 ± 14.28%	48450	64.9	pass
2.00 ± 16.58%	6584	16.5	fail
1.00 ± 18.68%	8814	38.0	pass

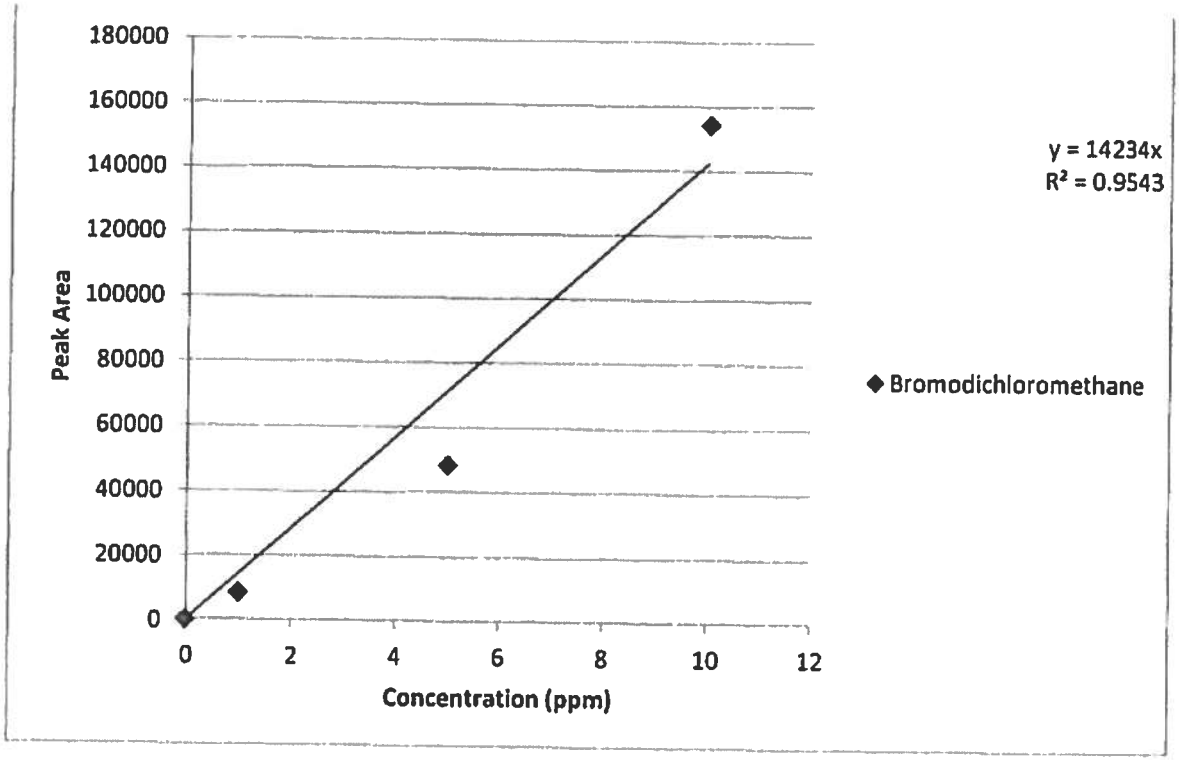

Figure 3.10 Bromodichloromethane calibration curve at a concentration range of 10-1 ppm.

Table 3.8 GC/MS chlorodibromomethane peak areas using 60 µm PDMS/DVB

Concentration (ppm)	Peak Area (± ppm%)	RSD (%)	Q-test (90%)
200 ± 3.58%	3111040	8.04	pass
100 ± 5.68%	1357871	4.04	pass
50.0 ± 7.78%	630615	2.38	pass
25.0 ± 9.88%	414714	10.4	pass
10.0 ± 12.18%	102325	4.13	pass
5.00 ± 14.28%	58411	13.5	pass
2.00 ± 16.58%	22516	3.07	pass
1.00 ± 18.68%	11352	3.13	pass

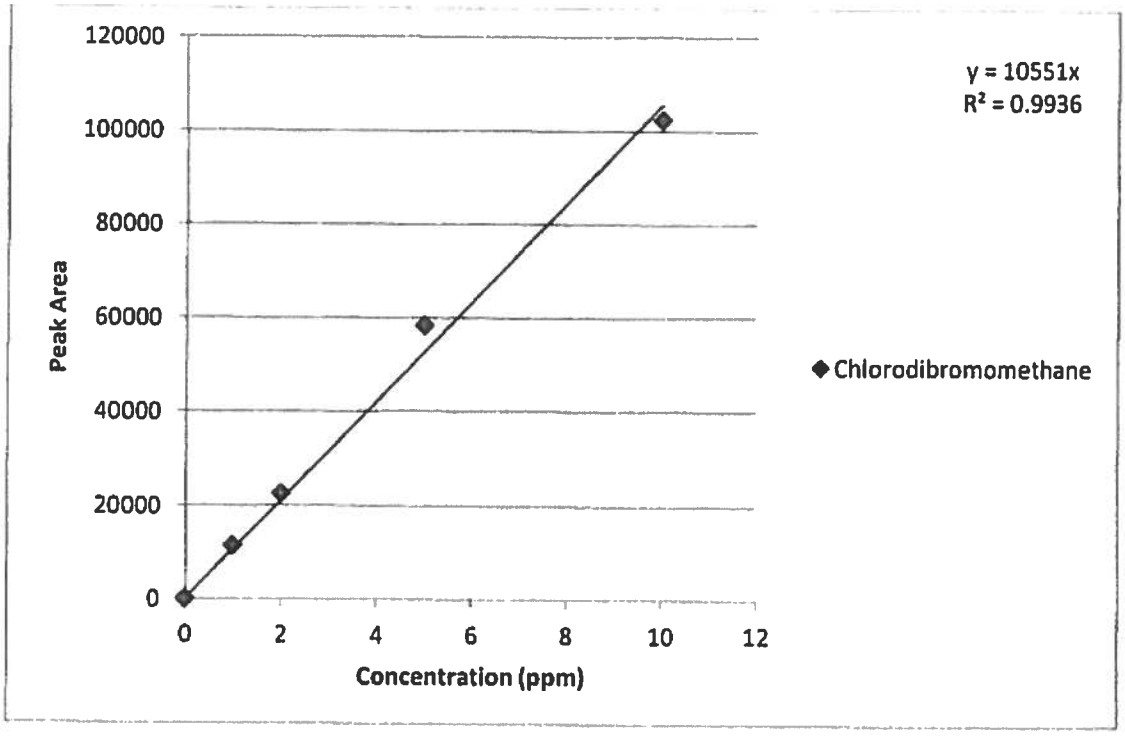

Figure 3.11 Chlorodibromomethane calibration curve at a concentration range of 10-1 ppm.

Table 3.9 GC/MS 1,2-dibromoethane peak areas using 60 µm PDMS/DVB

Concentration (ppm)	Peak Area (± ppm%)	RSD (%)	Q-test (90%)
200 ± 3.58%	4190342	4.04	pass
100 ± 5.68%	1654005	3.36	pass
50.0 ± 7.78%	752601	1.25	pass
25.0 ± 9.88%	402888	8.46	pass
10.0 ± 12.18%	111992	7.23	pass
5.00 ± 14.28%	53369	9.31	pass
2.00 ± 16.58%	23571	1.41	pass
1.00 ± 18.68%	12756	1.25	pass

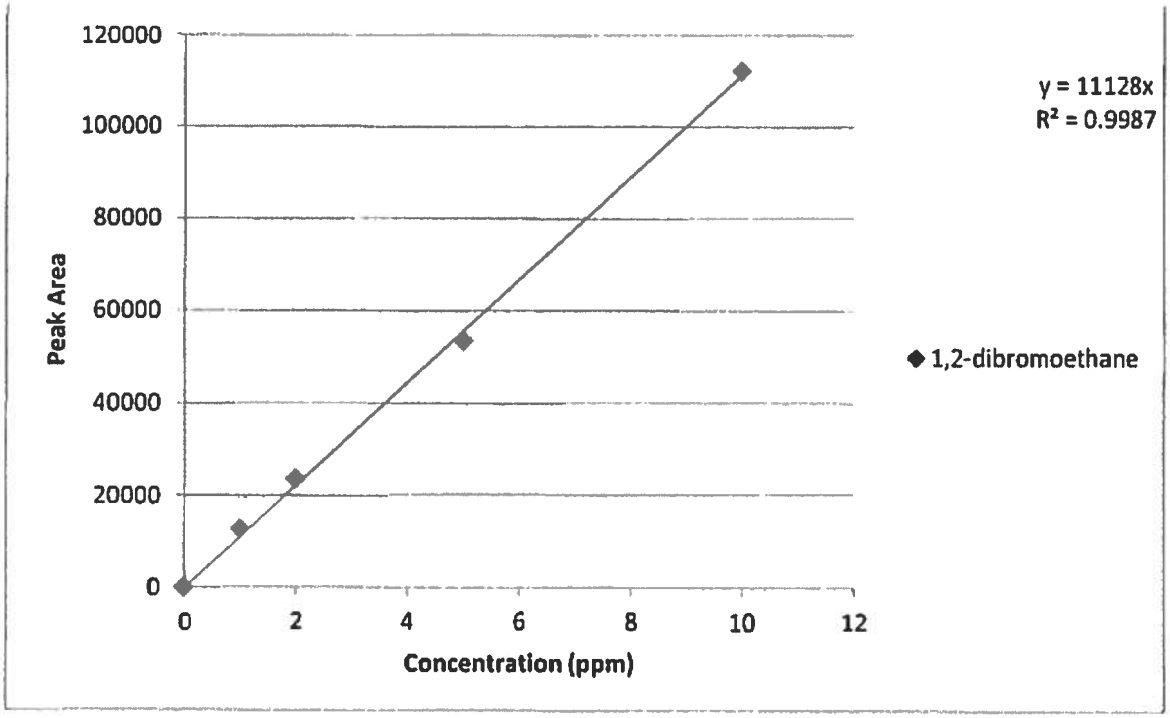

Figure 3.12 1,2-dibromoethane calibration curve at a concentration range of 10-1 ppm.

Table 3.10 Summary of calibration curves with equations of lines and R^2 values

Component	Line Equation	R^2	Detection Limit (ppm)
Chloroform	y = 7762x	0.9585	0.413
1,2-dichloroethane	y = 5929.5x	0.9627	0.285
Bromodichloromethane	y = 16746x	0.9543	0.939
Chlorodibromomethane	y = 13189x	0.9936	0.161
1,2-dibromoethane	y = 12365x	0.9987	0.0456

The calibration curves were all linear with a correlation coefficient ranging from 0.9543 to 0.9987. The intercept was set at (0,0) because there is no signal at zero concentration. Detection limits were found to be 0.413, 0.285, 0.939, 0.161, and 0.0456 ppm for chloroform, 1,2-dichloroethane, bromodichloromethane, chlorodibromomethane, and 1,2-dibromoethane respectively. Data taken from the Newfoundland Government THM survey of natural waters show total THM concentrations in Trout Pond and Three Mile Pond at 158.15 ppb and 117.07 ppb respectively. The concentrations are well below the detection limits found for the chloroform, 1,2-dichloroethane, and bromodichloromethane calibration curves. However, the detection limit for the 1,2-dibromoethane calibration curve is below the THM concentrations found in both Trout Pond and Three Mile Pond, while the detection limit for chlorodibromomethane was just above the THM concentrations.

The linear working range for each calibration curve was found at a concentration range of 10-1 ppm with agreeable correlation coefficients. A full concentration range of 200-1 ppm was not used due to the loss in linearity which can be explained using the beer lambert law in section 1.8. The molar absorbtivity is linear at low concentrations, allowing for a linear relationship between the instrument response and concentration. However, at high concentrations (>50 ppm) the molar absorbtivity is no longer constant, resulting in a non-linear relationship between instrument response and concentration.

Accurate results cannot be determined from the calibration curves. First, percent uncertainties are too high for the lower concentration range of the calibration curve. The 1ppm standards have an 18.7% uncertainty associated with them and as a result, any concentrations obtained from the calibration curve would not be representative of the actual THM concentrations in the water samples. The high percent errors are due to the method used for serial dilution in standard preparation. All standards were prepared in sealed 100 mL flasks then transferred to 40 mL headspace vials for analysis using a 10 mL and 500 µL syringe. Transfer to and from the 100 mL flasks also has an associated percent error. Preparation of the 200 ppm standard alone has a 3.6% uncertainty associated with it. As with all serial dilutions, the percent error increases as more and more standards are made. Standards were not produced in volumetric flasks due to loss of THM from transfer of sample between flasks. The use of volumetric flasks would have reduced the percent error substantially.

The second reason that the calibration curves cannot be used to obtain accurate results is that the detection limits, with the exception of 1,2-dibromoethane, are above the recorded THM values for Three Mile Pond and Trout Pond. A detection limit is the lowest quantity of substance that can be distinguished from the baseline noise. Anything below that detection limit cannot be accurately determined.

3.3 Standard Addition Plots

Natural water samples were analyzed by use of the standard addition method. Each water sample was spiked with a known concentration of THM then run in triplicate. Standard addition plots for each water sample are illustrated in Figures 3.13-3.17. Tables 3.12-16 give the average peak areas for each sample spike. Chemical parameters, including

dissolved solids, pH, temperature, and conductivity were measured before analysis to assess the chemical properties of the water. The chemical parameters will not be used in the quantitative analysis of THMs. Results are listed in Table 3.11.

Table 3.11 Parameters for natural water samples taken from Three Mile Pond and Trout Pond

Trout Pond Samples	Conductivity (μS/cm) ± 0.1 μS/cm	pH ± 0.02	Temperature (°C) ± 0.5°C	Dissolved Solids (mg/L) ± 1 mg/L
1	47.9	6.01	6.90	118
2	46.1	6.34	6.50	21
3	45.0	6.39	4.70	20
4	62.7	6.40	6.80	29
5	65.1	6.47	8.30	30
6	65.4	6.53	7.90	29
7	66.7	6.62	9.50	31
8	45.8	6.26	9.40	28
Three Mile Pond				
1	65.9	6.35	10.00	31
2	66.2	6.60	9.20	30
3	65.5	6.67	9.20	30
4	66.8	6.78	10.20	30
5	64.6	6.84	10.40	29
6	65.2	6.88	9.90	30
7	64.9	6.89	11.30	29

Table 3.12 Three Mile Pond Sample 2 THM peak areas

Concentration (ppm)	Component Peak Area Chloroform	RSD	1,2-dichloroethane	RSD	Bromodichloromethane	RSD
0	35343 ± 1%	7.92%	6387 ± 1%	4.39%	1260 ± 1%	5.71%
1.2	232812 ± 1.8%	10.0%	1257289 ± 1.8%	2.98%	98847 ± 1.8%	5.92%
2.4	307755 ± 2.6%	15.1%	3107030 ± 2.6%	12.2%	2863473 ± 2.6%	4.54%
6	10378394 ± 3.2%	3.66%	6669961 ± 3.2%	1.47%	19814193 ± 3.2%	4.14%
12	15810445 ± 3.4%	2.50%	11287165 ± 3.4%	5.71%	27874688 ± 3.4%	4.04%

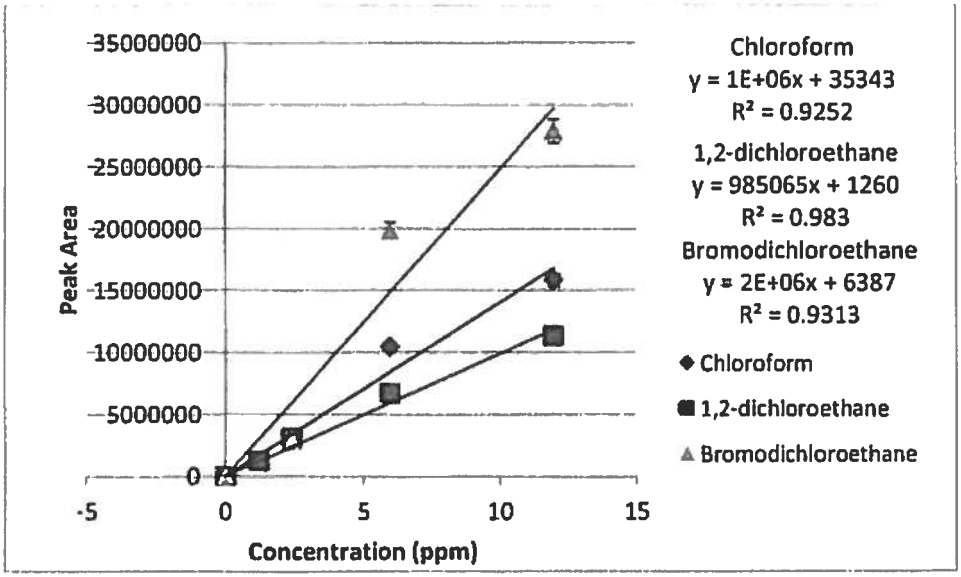

Figure 3.13 Three Mile Pond sample 2 standard addition plot

Table 3.13 Summary of standard addition plots for 3P#2 with equations of lines and R^2 values

Component	Line Equation	R^2	Detection Limit (ppm)
Chloroform	y = 1E+06x + 35343	0.9252	0.441
1,2-dichloroethane	y = 985065x + 1260	0.9830	0.390
Bromodichloromethane	y = 2E+06x + 6387	0.9313	0.534

The standard addition plots for Three Mile Pond sample 2 were found to be linear with a correlation coefficient ranging from 0.9252 to 0.9830. Detection limits of 0.441, 0.390, and 0.534 ppm were measured for chloroform, 1,2-dichloroethane, and bromodichloromethane respectively. Each of the detection limits are above the total THM concentrations measured in Three Mile Pond. Therefore accurate results cannot be quantified from this sample. Peak areas measured at 1.2 and 2.4 ppm for chloroform and 1.2 ppm for bromodichloromethane failed the Q-test at 95% confidence. These points were not added to the standard addition plot.

Table 3.14 Three Mile Pond sample 3 THM peak areas

Concentration (ppm)	Component Peak Area Chloroform	RSD
0	15044 ± 1%	9.09%
1.2	212724 ± 1.8%	2.68%
2.4	2039258 ± 2.6%	8.52%
6	10189967 ± 3.2%	3.29%
12	14675128 ± 3.4%	3.55%

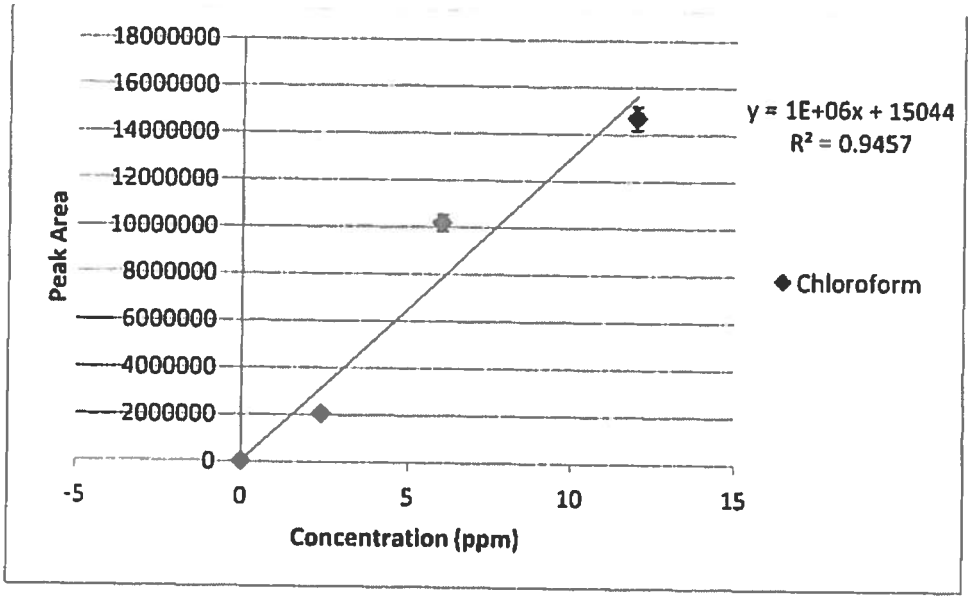

Figure 3.14 Three Mile Pond sample 3 standard addition plot

Table 3.15 Summary of standard addition plots for 3P#3 with equations of lines and R^2 values

Component	Line Equation	R^2	Detection Limit (ppm)
Chloroform	y = 1E+06x + 15044	0.9457	0.138

The standard addition plot for Three Mile Pond sample 3 was found to be linear with a correlation coefficient of 0.9457. A detection limit of 0.138 ppm was measured for chloroform. The detection limit is greater than the total THM concentrations measured in Three Mile Pond. Therefore accurate results regarding chloroform concentrations cannot be quantified. Peak area measured at a concentration of 1.2 ppm failed the Q-test at 95% confidence and was therefore not included on the standard addition plot.

Table 3.16 Three Mile Pond sample 6 THM peak areas

Concentration (ppm)	Component Peak Area Chloroform	RSD	Bromodichloromethane	RSD
0	17606 ± 1%	4.17%	877 ± 1%	45.1%
1.2	35706 ± 1.8%	3.52%	6603601 ± 1.8%	1.15%
2.4	57968 ± 2.6%	16.7%	5853300 ± 2.6%	2.60%
6	7160703 ± 3.2%	12.9%	16936646 ± 3.2%	0.639%
12	13418432 ± 3.4%	5.20%	25124992 ± 3.4%	1.00%

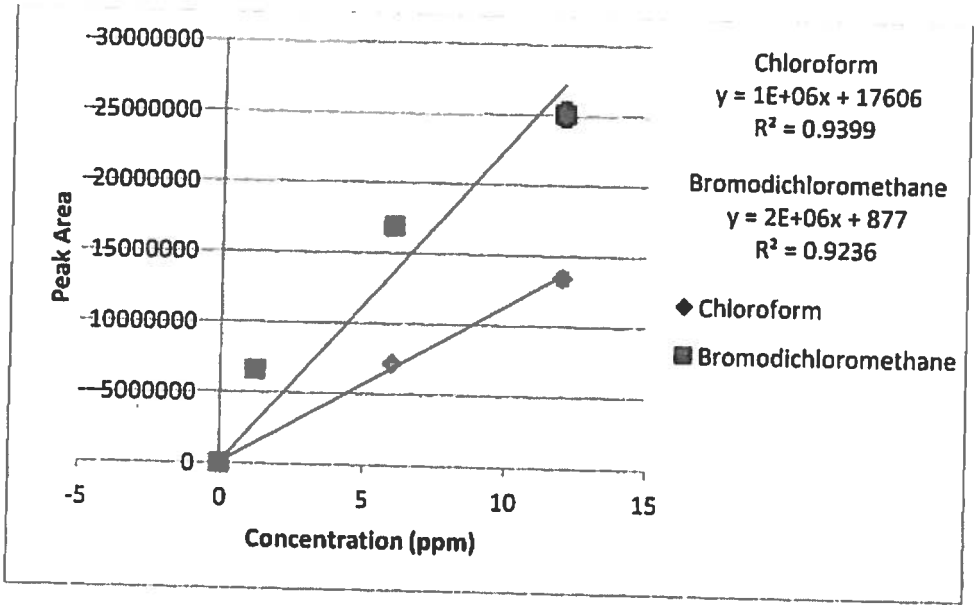

Figure 3.15 Three Mile Pond sample 6 standard addition plot

Table 3.17 Summary of standard addition plots for 3P#6 with equations of lines and R^2 values

Component	Line Equation	R^2	Detection Limit (ppm)
Chloroform	y = 1E+06x + 17606	0.9399	0.139
Bromodichloromethane	y = 2E+06x + 877	0.9236	1.04

The standard addition plots for Three Mile Pond sample 6 was found to be linear with correlation coefficients ranging from 0.9236 to 0.9399. Detection limits were measured at 0.139 and 1.04 ppm for chloroform and bromodichloromethane respectively. Total THM concentration for Three Mile Pond is below the detection limits. Therefore accurate results regarding component concentrations cannot be quantified. Peak areas

measured at 1.2 and 2.4 ppm for chloroform and 2.4 ppm for bromodichloromethane failed the Q-test at 95% confidence. These points were not included on the standard addition plot.

Table 3.18 Trout Pond sample 4 THM peak areas

Concentration (ppm)	Component Peak Area Chloroform	RSD	1,2-dichloroethane	RSD
0	1757 ± 1%	4.62%	2728 ± 1%	8.36%
1.2	30970 ± 1.8%	6.07%	1467501 ± 1.8%	8.33%
2.4	49231 ± 2.6%	0.72%	1203910 ± 2.6%	3.08%
6	3254469 ± 3.2%	1.21%	4326336 ± 3.2%	6.89%
12	7984852 ± 3.4%	1.66%	7338956 ± 3.4%	6.14%
	1,2-dibromoethane	RSD	Bromodichloromethane	RSD
0	3320 ± 1%	7.59%	1580 ± 1%	30.2%
1.2	5783656 ± 1.8%	2.38%	4850286 ± 1.8%	2.91%
2.4	4878477 ± 2.6%	4.04%	9518200 ± 2.6%	2.81%
6	8494887 ± 3.2%	1.60%	16542231 ± 3.2%	2.91%
12	14039419 ± 3.4%	2.20%	19736280 ± 3.4%	2.57%

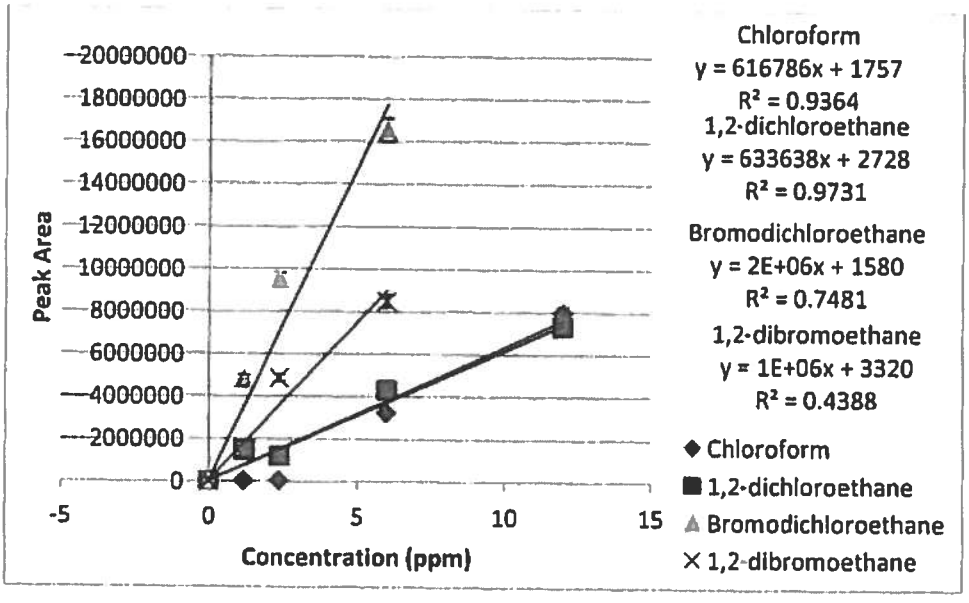

Figure 3.16 Trout Pond sample 4 standard addition plot

Table 3.19 Summary of standard addition plots for TP#4 with equations of lines and R^2 values

Component	Line Equation	R^2	Detection Limit (ppm)
Chloroform	y = 616786x + 1757	0.9364	1.23
1,2-dichloroethane	y = 633638x + 2728	0.9731	0.321
Bromodichloromethane	y = 2E+06x + 1580	0.7481	0.389
1,2-dibromoethane	1E+06x + 3320	0.4388	0.608

Standard addition plots for chloroform and 1,2-dichloroethane in Trout Pond sample 4 were found to be linear with correlation coefficients of 0.9364 and 0.9731 respectively. However standard addition plots for bromodichloromethane and 1,2-dibromomethane were not found to be sufficiently linear with correlation coefficients of 0.7481 and 0.4388. Detection limits were measured at 1.23, 0.321, 0.389, and 0.608 ppm for chloroform, 1,2-dichloroethane, bromodichloroethane, and 1,2-dibromoethane respectively. Total THM concentration for Trout Pond is below all of the detection limits. Therefore accurate analysis of THM concentrations cannot be quantified. Peak areas measured at 10 ppm for chloroform and 1,2-dibromoethane were not included in the standard addition plot due to errors resulting from ion-capture detector saturation.

Table 3.20 Trout pond sample 8 THM peak areas

Concentration (ppm)	Component Peak Area Chloroform	RSD	Bromodichloromethane	RSD
0	15541 ± 1%	8.41%	538 ± 1%	30.6%
1.2	28007 ± 1.8%	11.2%	7104976 ± 1.8%	3.67%
2.4	39370 ± 2.6%	2.40%	11435513 ± 2.6%	5.96%
6	5409776 ± 3.2%	6.25%	19803095 ± 3.2%	6.24%
12	11089953 ± 3.4%	3.96%	22789997 ± 3.4%	2.41%

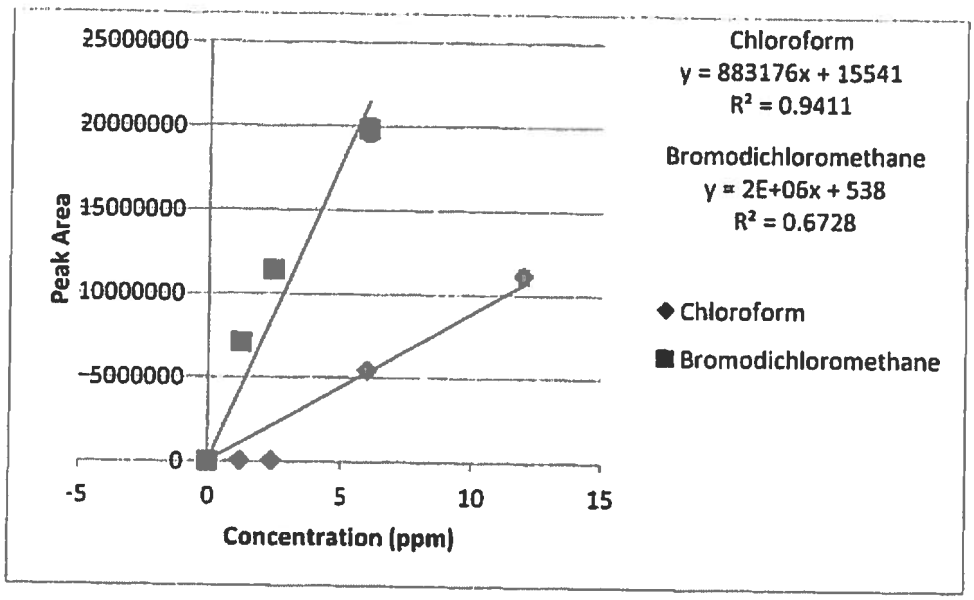

Figure 3.17 Trout Pond sample 8 standard addition plot

Table 3.21 Summary of standard addition plots for TP#8 with equations of lines and R^2 values

Component	Line Equation	R^2	Detection Limit (ppm)
Chloroform	y = 883176x + 15541	0.9411	1.11
Bromodichloromethane	y = 2E+06x + 538	0.6728	0.523

The standard addition plot for chloroform in the Trout Pond sample 8 was found to be linear with a correlation coefficient of 0.9411. However, the standard addition plot for bromodichloromethane was not found to be sufficiently linear with a correlation coefficient of 0.6728. Detection limits were measured at 1.11 and 0.523 ppm for chloroform and bromodichloromethane respectively. Total THM concentration measured from Trout Pond is below the detection limits found from the calibration curves. Therefore an accurate analysis for quantification of THM concentrations cannot be done. The peak area measured at 10 ppm for bromodichloromethane was not included in the standard addition plot due to errors resulting from oversaturation of the ion capture detector.

3.4 THM Concentrations in Natural Water Samples

THM concentrations measured from the water samples collected from Trout Pond and Three Mile Pond are listed in Tables 3.22 and 3.23. Concentrations were measured using both the calibration curves prepared *via* serial dilution and the standard addition plots prepared *via* sample spikes.

Table 3.22 Concentrations of THMs in original water samples taken from Trout pond and Three Mile Pond using the standard calibration curves

Sample	Component	Peak Area (± 1%)	Concentration (ppm)	Total THM (ppm)
3P#2	Chloroform	35343	4.42	6.76
	1,2-dichloroethane	6387	1.32	
	Bromodichloromethane	1260	1.02	
3P#3	Chloroform	15044	2.12	2.12
3P#6	Chloroform	17606	2.41	3.40
	Bromodichloromethane	877	0.993	
TP#8	Chloroform	15541	2.17	
	Bromodichloromethane	538	0.972	
TP#4	Chloroform	1757	0.612	2.63
	1,2-dichloroethane	2728	0.725	
	Bromodichloromethane	1580	1.04	
	1,2-dibromoethane	3320	0.254	

All concentrations measured using the THM calibration curves are not representative of the estimated THMs present in Three Mile Pond and Third Pond. Concentrations were measured in the ppm range instead of the literature ppb values.[25] However, the estimated THM concentrations were measured from samples collected in the winter season. The concentrations in table 3.22 may be representative of the THM concentrations in the fall season, where a high volume of natural organic material is degraded.

Table 3.23 Concentrations of THMs in original water samples taken from Trout Pond and Three Mile Pond using the standard addition plots

Sample	Component	Peak Area (± 1%)	Concentration (ppb)	Total THM (ppb)
3P#2	Chloroform	35343	35.3	39.8
	1,2-dichloroethane	6387	1.28	
	Bromodichloromethane	1260	3.19	
3P#3	Chloroform	15044	15.0	15.0
3P#6	Chloroform	17606	17.6	17.9
	Bromodichloromethane	877	0.439	
TP#8	Chloroform	15541	17.6	17.9
	Bromodichloromethane	538	0.269	
TP#4	Chloroform	1757	28.5	36.9
	1,2-dichloroethane	2728	4.31	
	Bromodichloromethane	1580	0.790	
	1,2-dibromoethane	3320	3.32	

THM concentrations measured by analysis of standard addition plots are not representative of the total THM concentrations present in Three Mile Pond and Trout Pond. Total THM concentrations were measured in the ppb range, which correlates to the THM concentration range in each of the ponds. Measured total concentrations range from 15.0-39.8 ppb, which are markedly less than 158.15 and 117.07 ppb for Trout Pond and Three Mile Pond respectively. This observation makes sense since samples were analyzed about 4 months after sample collection. However, the analysis is not accurate since concentrations are blow the detection limits of the standard addition plots. In addition, not all standard addition plots had good R^2 values. While some standard addition plots had R^2 values as high as 0.9830, other standard addition plots, such as 1,2-dibromoethane in the TP#4 sample, had R^2 values as low as 0.4388. Because total THM measured as the sum of all the THMs in the sample, one bad correlation coefficient will give inaccurate results for the entire sample. At best, only a rough estimate of the THM concentrations in the samples can be determined. Unfortunately, the GC/MS broke down

during the semester, resulting on the loss of valuable analysis weeks. Hence there was not enough time to correct or redo calibration data.

3.5 Validation of Results by GC/MS

Identification and validation of THMs in natural water samples require information on component retention times in addition to peak identification. All THM standards and water samples were analyzed with a GC/MS. The gas chromatogram measured THM component retention times and the mass spectrometer identified each of the component peaks by their molar masses and peak fragments, as described in section 1.5. According to the chromatographic data, chloroform passed through the column first (retention time of 1.77 minutes), followed by 1,2-dichloroethane (2.04 mins), then bromodichloromethane (2.92 mins), then chlorodibromomethane (5.67 mins) and finally 1,2-dibromooethane (5.93 mins). Elution order may be explained by bromine substitution. Retention time increases as more bromines are substituted on the molecule, which is consistent with data found in the literature.[6,7] A possible explanation is that the bromines are lower in the Periodic Table group of halogens than chlorine, indicating a bulkier and a higher weight molecule, which normally has an increased retention time in a chromatographic column.

Retention times were used to identify THM peaks in the water samples that were too small to give an accurate mass spectrum. Spiking the water samples with a known concentration of THM gave rise to a component peak with a retention time matching that of the original unknown peak in the sample, further validated the identity of the component peaks in the original sample.

Coupling the GC with a MS allowed for immediate peak identification by analyzing the mass to charge ratios of the molecular and fragmentation peaks. Molecular peaks and their identifying fragments for each THM component is listed in Table 3.24.

Table 3.24 Molecular and fragmentation ion peaks for the THM components

Component	Molecular peak (m/z)	Fragmentation peaks (m/z)
Chloroform	119	84, 49
1,2-dichloroethane	98	63
1,2-dibromoethane	187	108
chlorodibromomethane	207	172, 128, 93, 49
bromodichloromethane	163	128, 93, 84, 49

Unfortunately, peak areas in the un-spiked samples were too small and gave a baseline mass spectrum instead of the component mass spectrum. Other peaks were present in the water sample which did not correspond to the five THM standards utilized in the laboratory. In order to identify unknown peaks to check for additional THMs, a corresponding standard for the suspected unknown would need to be utilized. THMs which were detected in the natural water samples were bromodichloromethane, chloroform, 1,2-dibromoethane, and 1,2-dichloroethane. No concentrations were found for chlorodibromoethane.

3.6 Validity of THM standards and calibration curves

THM components were intentionally set to have the same concentrations; however these concentrations did not always correspond to the peak areas obtained. The variation in peak areas could be a result of the differing Henry's Law constants, which ultimately has an effect on the distribution coefficient. Differing distribution coefficients will vary the concentration of each component in the headspace, giving rise to a variation in the peaks during analysis. Because SPME is primarily an equilibrium process, the

mass of analyte adsorbed depends primarily on the distribution coefficients, as illustrated in equation (7).

$$n = (K_{fh}K_{hs}V_fC_0V_s) / (K_{fh}K_{hs}V_f + K_{hs}V_h + V_s) \quad (7)$$

The distribution coefficients describe the properties of the fiber and its selectivity towards the analyte versus other matrix components.[29]

THM components may have differing affinities towards the PDMS/DVB fiber; however this difference should be minimal due to the similarity in structure between the THMs. Percent differences for peak areas ranged upwards of 50%. Such a large variation in peak area can only be explained by percent uncertainty. While a contribution from THM structural differences is present, a large portion of the error is associated with the concentration values of the THM standards. These percent errors can result in a differentiation of the concentration added, and therefore differentiate peak areas.

The calibration curves created from the series of standards could not be used in the accurate determination of THM concentrations in the water samples. The primary reason is because of the linear working range chosen for the calibration curves. A minimum concentration of 1 ppm was chosen for the standards, which is set above the maximum THM concentration found in either Three Mile Pond or Trout Pond. The linear working range of 10-1 ppm does not correspond to the concentrations found in the water samples since natural THM concentrations are on the order of ppb. Therefore concentrations cannot be accurately determined. Creating a series of standards with a linear working range within the range of the natural THM concentrations would yield much better results.

3.7 Validity of the Standard Addition Plots

The standard addition plots created from spiking the water samples with known volumes of THM standards could not be used in the accurate determination of natural THM concentrations. Spiking the samples gave rise to a large variation in peak areas. Peak area variations between spikes are listed in Table 3.18 for the 2.4 and 6 ppm chloroform spikes. A peak difference of 6511% is associated between the 2.4 and 6 ppm spikes which is not representative of the actual peak areas associated with that concentration range. The maximum difference between the peak heights should be at 150%. The large variation in peak areas gave rise to the low R^2 values associated with some of the standard addition plots and resulted in the variation of the slope between the calibration lines. Accurate THM concentrations cannot be determined with such a large variation in the peak area.

Peak areas did not correspond to peaks measured from the serial dilution calibration curves when comparing similar concentrations. The 10 ppm standard for bromodichloromethane had an associated peak area of 154240. However, the 10 ppm spike of bromodichloromethane in Trout Pond sample 8 corresponded to a peak area of 11089953. The difference in peak areas is over 7000%. There are matrix effects associated with the use of methanol as a solvent for THM standard preparation. However, these matrix effects would not change the peak area on the order of 7000%. Similar observations are made with every water sample.

The large variability can be associated with the small volumes of THM spiked into the water samples. Achieving a 1 ppm spike in a 30 mL sample requires volumes on the order of 0.03 μL. Any additional volume added to the sample will result

contamination, resulting in a major increase in peak area. Although great care was taken to keep the injection volumes constant, contamination of the samples was not completely prevented according to the major increases in peak areas. A low percent error (~3.4%) is associated with the spiked concentrations. This uncertainty does not take sample contamination into account.

3.8 Validity of the SPME technique

Despite the low quantitative power of the resulting calibration curves, SPME remains a valid possibility for the extraction of THMs from natural waters. The average RSD values associated with each THM replicate analysis are shown in Table 3.25.

Table 3.25 Average relative standard deviation values for replicate analysis of THM components

Component	Replicate number	Average %RSD
Chloroform	32	7.62
1,2-dichloroethane	18	10.5
1,2-dibromoethane	13	4.17
bromodichloromethane	27	11.6
Chlorodibromomethane	8	6.09

Variation of the injection is not included as part of the tabulated RSD values. Injection into the GC/MS can have a RSD of about 5-8%. The use of an auto-injector can drop the RSD to about 0.5%. The RSD values were obtained from both the serial dilution calibration curves and the standard addition plot extraction data. The results are comparable because the sample preparation will not affect the RSD of the SPME extraction. Average peak areas and their standard deviations found through replicate analysis are determined solely by the reproducibility of the SPME extraction. RSD values as high as 60% was measured. The high RSD values correlate with errors in the

extraction, such as extractions while not at equilibrium or not having the SPME fiber in the same position within the headspace. The average RSD values for SPME extraction of chloroform, bromodichloromethane, and chlorodibromomethane are comparable to the RSDs measured from the EPA technique of liquid-liquid extraction.[5]

4.0 Conclusion

The newly developed method for the determination of THM concentrations in natural waters can be validated if the proper concentration range is chosen for the standards and can be quantitated by the technique. Results and conclusions made in this study are based on the comparison to concentrations measured by the Goernment of Newfoundland and Labrador. However, their samples were collected in the winter. THM samples for this analysis were collected in the fall season. The increased organic degradation in the fall season may contribute to an increased THM load on a natural water system, giving concentrations greater than those collected by the Newfoundland Government. As a result, quantification of THMs collected in the fall season can be quantitated while THM samples collected in the winter seasons cannot be quantitated by this study.

Volatility associated with THMs accounts for the loss in concentration between the fall months and the winter months. This loss in concentration is illustrated by the decreased THM concentrations obtained from the standard addition plots. Good correlation coefficients of the calibration curves and the good %RSD values of the SPME extraction technique were obtained which suggests that quantitative studies could be completed with a linear working range of 10-1ppm. A range that could encompass 20ppb

to 1 ppm analysis of THM concentration values could be used to discern samples found in Three Mile Pond and Trout Pond in the winter months. The good %RSD values obtained for all THM extractions validates SPME as a potential extraction technique for THM analysis.

Problems with the GC/MS led to about a month delay in analyzing THM samples with standard addition methods. As a result, the concentrations of THMs in the old samples were greatly diminished, resulting in analysis problems. In this research it was found that the standard addition plot gave poor results for THM analysis at low concentration ranges for an accurate quantitative analysis. This was due to the low precision to deliver the small volumes required for each sample spike to attain the proper working range. Such micro techniques were not available to be utilized in this research. Any excess volumes added to the samples invalidated the data. As a result, only estimated concentrations could be measured using the standard addition plots. Standard addition plots would give better results if high precision equipment was utilized.

GC/MS proved to be an efficient technique for the separation and identification of THM components. THM separation requires a 9 minute run time. Coupled with a 4 minute extraction, a replicate can be ran and analyzed within 15 minutes with good reproducibility. THMs detected in the water samples include bromodichloromethane, chloroform, 1,2-dibromoethane, and 1,2-dichloroethane. Concentrations for each detected THM could not be analyzed accurately.

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Appendix A (Referenced from Department of Environment and Conservation.)

A-1

Newfoundland Labrador

Department of Environment and Conservation

THMs Summary for Public Water Supplies in Newfoundland and Labrador

Community Name	Serviced Area(s)	Source Name	THMs Average (µg/L)	Average Type	Total Samples Collected	Last Season Sampled
Anchor Point	Anchor Point	Well Cove Brook	137 68	Running	49	Summer 2013
Appleton	Appleton (+Glenwood)	Gander Lake (The Outflow)	55 00	Running	48	Summer 2013
Aquaforte	Aquaforte	Davies Pond	0 00	Running	39	Fall 2011
Arnold's Cove	Arnold's Cove	Steve's Pond (2 Intakes)	111 90	Running	61	Summer 2013
Avondale	Avondale	Lee's Pond	141 50	Running	29	Summer 2013
Badger	Badger	Well Field, 2 wells on standby	1 65	Simple	13	Spring 2013
Baie Verte	Baie Verte	Southern Arm Pond	106 00	Simple	2	Summer 2013
Baine Harbour	Baine Harbour	Baine Harbour Pond	19 08	Simple	8	Summer 2002
Barachois Brook	Barachois Brook	Drilled	0.00	Simple	2	Winter 2003
Bartletts Harbour	Bartletts Harbour	Long Pond (same as Castors River North)	0 35	Simple	2	Winter 2012
Bauline	Bauline	#1 Brook Path Well	63 85	Running	22	Summer 2013
Bay L'Argent	Bay L'Argent	Sugarloaf Hill Pond	66 07	Running	45	Summer 2013
Bay Roberts	Bay Roberts, Spaniard's Bay	Rocky Pond	34 72	Running	57	Summer 2013
Bay St. George South	Heatherton	#1 Well Heatherton (Home Hardware)	5 60	Simple	6	Spring 2013
Bay St. George South	Highlands	#3 Brian Pumphrey Well Highlands	2 20	Simple	1	Spring 2013
Bay St. George South	Jeffrey's	#1 Well Jeffery's (Joe Curnew)	0 00	Simple	4	Spring 2013
Bay St. George South	Jeffrey's	#2 Well Jeffery's (Calvin Madore)	0.00	Simple	4	Spring 2013
Bay St. George South	Jeffrey's	#3 Well Jeffery's (Sid Shears)	0 00	Simple	2	Spring 2013
Bay St. George South	Lock Leven	#5 Well Loch Leven (Jerry Quilty)	1.50	Simple	4	Spring 2013
Bay St. George South	McKay's	#2B Lions Club Well	0 00	Simple	4	Spring 2013
Bay St. George South	McKay's	#3 Woodworth Well McKay's	0 00	Simple	4	Spring 2013
Bay St. George South	McKay's	#7 Well McKay's (Gordon Hulan)	0.00	Simple	8	Spring 2013
Bay St. George South	Robinson's	#1 Well Robinson's (Louie MacDonald)	4 30	Simple	3	Spring 2013
Bay St. George South	St. Fintan's	#2 Well St. Fintan's (Louis King)	0 00	Simple	4	Spring 2013
Bay St. George South	St. Fintan's, St. David's	#1 Well St. Fintan's (The Y)	0.00	Simple	5	Spring 2013
Bay de Verde	Bay de Verde	Island Pond	10.03	Simple	52	Summer 2013
Beaches	Beaches	Grassey Pond Brook	45 17	Running	30	Summer 2013
Beachside	Beachside	Long Pond	36.00	Simple	43	Summer 2013
Bellburns	Bellburns	Bound Brook Tributary	90 68	Running	46	Summer 2013
Belleoram	Belleoram	Rabbits Pond	176 07	Running	11	Summer 2013
Bellevue	Bellevue	Big Pond	89 50	Running	31	Summer 2013
Bellevue Beach	Bellevue Beach	Unnamed Brook	0 00	Simple	9	Fall 2001
Benoit's Siding	Benoit's Siding (aka Bennett's Siding)	Drilled	3 70	Simple	2	Winter 2003
Benoit's Siding	Doyles	# 2 Well Doyles	6.00	Simple	2	Winter 2010
Benton	Benton	Little Pond	79 97	Running	56	Summer 2013
Birchy Bay	Birchy Bay	Jumper's Pond	219 00	Running	87	Summer 2013
Bird Cove	Bird Cove (+Brig Bay)	Inner Gilmour Pond	162 80	Running	42	Summer 2013
Biscay Bay	Biscay Bay	Unnamed Pond	0 00	Simple	1	Spring 2002
Bishop's Falls	Bishop's Falls	Northern Arm Lake	79 63	Running	52	Summer 2013

Newfoundland Labrador — Department of Environment and Conservation

THMs Summary for Public Water Supplies in Newfoundland and Labrador

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Community Name	Serviced Area(s)	Source Name	THMs Average (µg/L)	Average Type	Total Samples Collected	Last Season Sampled
Black Duck Cove	Black Duck Cove	Long Pond - Black Duck Cove Intake	0 00	Simple	1	Summer 2012
Black Tickle-Domino	Black Tickle-Domino - Outside Tap	Martin's Pond - Tap at Pumphouse	81 50	Simple	26	Summer 2013
Black Tickle-Domino	Black Tickle-Domino - PWDU	Martin's Pond - Tap at Pumphouse	10.17	Simple	15	Summer 2013
Blaketown	Blaketown	#2 Daphne Pincent Well	14 60	Simple	4	Fall 2012
Blaketown	Blaketown Centre	#3 Fred Osborne Well	36 50	Simple	10	Spring 2013
Blaketown	Blaketown North	#4 Hilda Barrett Well	3 45	Simple	4	Fall 2012
Blaketown	Blaketown South	#1 Selby Mercer Well	1 10	Simple	4	Fall 2012
Bonavista	Bonavista	Long Pond	200 75	Running	94	Summer 2013
Botwood	Botwood	Northern Arm Lake	76 35	Running	30	Summer 2013
Branch	Branch	Valley Pond	0 00	Running	4	Winter 2003
Brent's Cove	Brent's Cove	Paddy's Pond	0 00	Simple	13	Spring 2003
Brig Bay	Brig Bay	Inner Gilmour Pond	179 75	Running	41	Summer 2013
Brighton	Brighton	Hynes Cove Pond	385 50	Running	63	Summer 2013
Brigus	Brigus (+Cupids, +South River)	Brigus Long Pond (to Brigus)	64 63	Running	73	Summer 2013
Britannia	Britannia		13 70	Running	14	Fall 2001
Bryant's Cove	Bryant's Cove South Side	#1 Well - Bert James Well #2 Well - Baxter Bowering Well	0.00	Simple	3	Fall 2012
Buchans	Buchans	Buchans Lake aka Sandy Lake	72 60	Running	58	Summer 2013
Buchans	Buchans - PWDU	Buchans Lake aka Sandy Lake	0 00	Simple	8	Summer 2011
Buchans Junction	Buchans Junction	Lapland Pond	141 48	Running	47	Summer 2013
Bunyan's Cove	Bunyan's Cove	#1 Wellfield	16.00	Simple	14	Spring 2013
Bunyan's Cove	Bunyan's Cove	#2 Wellfield	14 55	Simple	4	Fall 2012
Burgeo	Burgeo	Long Pond	45 33	Running	62	Summer 2013
Burgoyne's Cove	Burgoyne's Cove	Lower Rocky Pond	30 13	Running	64	Summer 2013
Burin	Burin	Long Pond	61 95	Running	72	Summer 2013
Burin	Burin (+Lewin's Cove)	Big Pond	77 70	Running	74	Summer 2013
Burin	Port au Bras	Gripe Cove Pond	63 72	Running	64	Summer 2013
Burlington	Burlington	Eastern Island Pond	280 67	Running	43	Summer 2013
Burnt Islands	Burnt Islands	Long Lake	26 02	Running	52	Summer 2013
Burnt Islands	Burnt Islands - PWDU	Long Lake	1 17	Running	21	Summer 2013
Campbellton	Campbellton	Indian Arm Brook	191 50	Running	55	Summer 2013
Canning's Cove	Centre Canning's Cove	#3 Well - Glenda Penney	3 05	Simple	5	Fall 2012
Canning's Cove	Lower Canning's Cove	#1 Well - Pleman Pitts	6 25	Simple	5	Fall 2012
Canning's Cove	Upper Canning's Cove	#2 Well - Eugene Ellis	10 60	Simple	5	Fall 2012
Cape Freels North	Cape Freels North	Long Pond	77 53	Running	39	Summer 2013
Cape St George	Cape St. George, Red Brook, De-Grau, Marches Point	Rouzes Brook	29 98	Running	58	Summer 2013
Carbonear	Carbonear	Island Pond / Flings Long Pond	25 85	Running	83	Summer 2013
Carmanville	Carmanville	Grandfathers Pond	119 00	Running	70	Summer 2013
Cartwright	Cartwright	Burdett's Pond	402 00	Running	34	Summer 2013
Cavendish	Cavendish	Long Pond	78 45	Running	52	Summer 2013

Newfoundland Labrador

Department of Environment and Conservation

THMs Summary for Public Water Supplies in Newfoundland and Labrador

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Community Name	Serviced Area(s)	Source Name	THMs Average (µg/L)	Average Type	Total Samples Collected	Last Season Sampled
Cavendish	North Side Cavendish	#1 Well - Max Bishop	0 00	Simple	1	Summer 2004
Cavendish	North Side Cavendish	#2 Well - Tom Critch	0 00	Simple	1	Summer 2004
Centreville-Wareham-Trinity	Centreville-Wareham	Northwest Pond	126 75	Running	72	Summer 2013
Centreville-Wareham-Trinity	Trinity	Southwest Feeder Pond	235 50	Running	72	Summer 2013
Chance Cove	Back Cove Area	Olive Smith Well	4.20	Simple	5	Spring 2013
Chance Cove	Lower Cove East	Albert Rowe Well	24 80	Simple	11	Spring 2013
Chance Cove	Lower Cove Point	Eugene Smith Well	0 00	Simple	11	Spring 2013
Chance Cove	New Housing Area	New Housing Area Well	10 40	Simple	7	Spring 2013
Chance Cove	Upper Cove Centre	Angus Brace Well	1 90	Simple	7	Spring 2013
Chance Cove	Upper Cove South	Edgar Crann Well	9.70	Simple	7	Spring 2013
Chanceport	Chanceport	Bridger's Cove Pond	0.00	Simple	7	Summer 2004
Channel-Port aux Basques	Channel-Port Aux Basques	Gull Pond & Wilcox Pond	106 55	Running	108	Summer 2013
Charlottetown (Labrador)	Charlottetown (Labrador)	Middle Pond	71 05	Running	36	Summer 2013
Churchill Falls	Churchill Falls	Smallwood Reservoir	86 43	Running	34	Summer 2013
Clarenville	Clarenville, Shoal Harbour	Shoal Harbour River	55 80	Running	23	Summer 2013
Clarke's Beach	Clarkes Beach	Clarkes Pond	31 75	Running	64	Summer 2013
Colliers	Harbour Drive	#4 Well - Flynn's Well	3 50	Simple	1	Spring 2012
Colliers	Harbour Drive	#5 Well - Whalen's Well	3 30	Simple	4	Fall 2012
Colliers	Harbour Drive & Main Road	#3 Well - Griffin's Well	7 65	Simple	8	Fall 2012
Colliers	Main Road	#1 Well - Mahoney's Well	3 60	Simple	4	Fall 2012
Colliers	Merrigan's Lane + Main Rd	#2 Well - Merrigan's Well	3 20	Simple	4	Fall 2012
Come By Chance	Come By Chance	Butchers Brook	64 13	Running	84	Summer 2013
Comfort Cove-Newstead	Comfort Cove-Newstead	Steady Cove Pond	155 75	Running	75	Summer 2013
Conception Bay South	Conception Bay South	Bay Bulls Big Pond	42 42	Running	48	Summer 2013
Conception Harbour	Cemetery Road & Main Road	Cemetery Road Well	9.35	Simple	3	Fall 2012
Conception Harbour	Healey's Pond Rd, Old Rd & Main Rd	Healey's Pond Road Well	2 50	Simple	3	Fall 2012
Conception Harbour	Lower Bacon Cove	Lower Bacon Cove Well	15.80	Simple	8	Spring 2013
Conception Harbour	Upper Bacon Cove, Kitchuses	Upper Bacon Cove Well	10.70	Simple	4	Spring 2013
Conche	Conche	Martin's Brook	65.50	Simple	50	Summer 2013
Conne River	Conne River	Southwest Brook	115 07	Running	102	Summer 2013
Cook's Harbour	Cook's Harbour	Unnamed Pond	218 00	Running	42	Summer 2013
Corner Brook	Corner Brook (All of eastside, portion of westside) (+Massey Drive)	Trout Pond, Third Pond (2 intakes)	134 15	Running	82	Summer 2013
Corner Brook	Corner Brook (Curling) (+Mount Moriah)	Second Pond (Three Mile Pond)	104 50	Running	49	Summer 2013
Corner Brook	Corner Brook (Portion of westside)	Burnt Pond	137 50	Running	47	Summer 2013
Cottlesville	Cottlesville	Rushy Cove Pond	254 25	Running	48	Summer 2013
Cottrell's Cove	Cottrell's Cove	Cotrell's Pond	91 38	Running	53	Summer 2013
Cow Head	Cow Head	Short Cat Path Pond	198 00	Running	64	Summer 2013
Cox's Cove	Cox's Cove	Cox's Brook	55 38	Running	58	Summer 2013
Cox's Cove	Upper Area	Upper Area Wellfield	0 00	Simple	7	Fall 2012
Crow Head	Crow Head	Oars Pond	179 00	Running	31	Summer 2013

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Community Name	Serviced Area(s)	Source Name	THMs Average (µg/L)	Average Type	Total Samples Collected	Last Season Sampled
Cupids	Cupids	Brigus Long Pond (to Brigus)	80.03	Running	61	Summer 2013
Daniel's Harbour	Daniel's Harbour	Unnamed Spring & Brook	44.67	Running	55	Summer 2013
Deadman's Bay	Deadman's Bay	Deadman's Pond	50.40	Running	59	Summer 2013
Deep Bight	Deep Bight	Deep Bight Well Field	1.30	Simple	5	Fall 2001
Deer Lake	Deer Lake (+Reidville)	Humber Canal, Grand Lake	81.13	Running	84	Summer 2013
Dildo	Dildo, Broad Cove (+South Dildo)	Broad Cove Pond	95.97	Running	71	Summer 2013
Dover	Dover	Hare Bay Pond	171.00	Running	43	Summer 2013
Dunfield	Dunfield		3.00	Simple	1	Fall 2001
Eastport	Eastport (+Sandy Cove)	Dug	1.75	Simple	22	Fall 2012
Eddies Cove West	Eddies Cove West	Unnamed	0.00	Simple	1	Fall 2003
Elliston	Elliston	Big Pond	34.60	Running	61	Summer 2013
Embree	Embree (+Little Burnt Bay)	Troke's Cove Pond	131.75	Running	71	Summer 2013
Englee	Englee	Island Cove Pond	73.35	Running	83	Summer 2013
Fairbanks-Hillgrade	Fairbanks-Hillgrade	Saltine's Pond	182.50	Running	56	Summer 2013
Fermeuse	Fermeuse	Port Kirwan Road Well	2.10	Simple	3	Spring 2013
Fermeuse	Fermeuse, Kingman's	Merrymeeting Pond, Bear Cove Pond (2 intakes)	60.95	Running	75	Summer 2013
Ferryland	Ferryland	Deep Cove Pond	198.75	Running	60	Summer 2013
Flat Bay	Flat Bay (East)	#1 Well	0.00	Simple	2	Fall 2000
Flat Bay	Flat Bay (East)	#2 Well	7.45	Simple	3	Fall 2012
Flat Bay	Flat Bay (East)	#3 Well	1.65	Simple	5	Fall 2012
Flat Bay West	Flat Bay West - Federation of Indians	#3 Well	0.00	Simple	5	Fall 2012
Fleur de Lys	Fleur De Lys	First Pond, Narrow Pond	232.75	Running	49	Summer 2013
Flower's Cove	Flower's Cove (+Nameless Cove)	French Island Pond	174.50	Running	44	Summer 2013
Fogo Island	Fogo	Freeman's Pond	93.53	Simple	65	Summer 2013
Fogo Island	Joe Batt's Arm-Barr'd Islands-Shoal Bay	Long Pond	60.50	Simple	56	Summer 2013
Fogo Island	Seldom-Little Seldom	Bullock Cove Pond	249.83	Simple	57	Summer 2013
Fogo Island	Tilting	Sandy Cove Pond	340.00	Simple	71	Summer 2013
Forresters Point	Forresters Point	Rudges Pond	0.00	Simple	34	Summer 2013
Forteau	Forteau	Trout Brook	12.45	Running	36	Summer 2013
Fortune	Fortune (+Grand Bank)	Horsebrook	63.72	Running	60	Summer 2013
Fox Roost-Margaree	Fox Roost-Margaree	Drilled Well and Margaree Pond	149.63	Running	6	Summer 2013
Fox Roost-Margaree	Fox Roost-Margaree - PWDU	Drilled Well and Margaree Pond	58.78	Running	4	Summer 2013
Francois	Francois	Our Pond	0.00	Simple	1	Fall 2003
Frenchman's Cove	Frenchman's Cove	Dug Well	18.15	Simple	16	Spring 2013
Freshwater	Freshwater (Carbonear)	#2 Well - Covage's Lane Well	0.00	Simple	2	Winter 2004
Freshwater	Freshwater (Carbonear)	#3 Well - Wallace Snow Well	2.40	Simple	1	Summer 2003
Gallants	Gallants	Gallant's Brook	0.00	Simple	1	Fall 2003
Gambo	Gambo	Dark Cove Pond	43.35	Running	65	Summer 2013
Gander	Gander	Gander Lake	69.30	Running	134	Summer 2013
Gander Bay South	George's Point, Harris Point	Barry's Brook	88.32	Running	64	Summer 2013

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Community Name	Serviced Area(s)	Source Name	THMs Average (µg/L)	Average Type	Total Samples Collected	Last Season Sampled
Garden Cove	Garden Cove	Arch Cove Pond	139 25	Running	52	Summer 2013
Garnish	Garnish	Witchazel Pond	143 00	Running	71	Summer 2013
Gaskiers	Gaskiers-Point La Haye	Big Hare Hill Pond	75 85	Simple	58	Summer 2013
Gaultois	Gaultois	Piccaire Pond	3 00	Simple	41	Spring 2008
George's Brook-Milton	George's Brook	George's Brook	105 50	Running	65	Summer 2013
George's Brook-Milton	Milton	Lilly Pond	72 45	Running	47	Summer 2013
Georgetown	Georgetown	Drilled	3 10	Simple	2	Spring 2013
Gillams	Gillams	Masters Pond	85 47	Running	7	Summer 2013
Glenburnie-Birchy Head-Shoal Brook	Glenburnie-Birchy Head-Shoal Brook	Croucher's Brook	7 03	Simple	17	Summer 2013
Glenwood	Glenwood	Gander Lake (The Outflow)	62 47	Running	69	Summer 2013
Glovertown	Glovertown	Northwest Pond	83 10	Running	83	Summer 2013
Goobies	Goobies	Water Pond	111 32	Running	42	Summer 2013
Goose Cove East	Goose Cove East	Jack's Pond	116 30	Running	44	Summer 2013
Grand Bank	Grand Bank	Horsebrook	86 78	Running	18	Summer 2013
Grand Bank	Grand Bank (Backup Supply)	Grand Bank Brook (Backup Supply)	60 50	Running	76	Winter 2009
Grand Falls-Windsor	Grand Falls-Windsor (+Bishop's Falls, +Wooddale, +Botwood, +Peterview)	Northern Arm Lake	66 99	Running	130	Summer 2013
Grand Le Pierre	Grand Le Pierre	Nip Nose Pond	0.00	Simple	3	Fall 1998
Grates Cove	Grates Cove Centre	#1 Cyril Meadus Well	0 00	Simple	1	Summer 2004
Grates Cove	Grates Cove North End	#3 Frank Janes Well	7 05	Simple	2	Fall 2012
Grates Cove	Grates Cove South End	#4 Stoyles Hill Well	0.00	Simple	1	Summer 2004
Great Brehat	Great Brehat	Little Steady Pond	3 53	Simple	36	Summer 2013
Great Codroy	Great Codroy East	#1 Well	0 00	Simple	6	Spring 2012
Great Codroy	Great Codroy West	#2 Well	2 75	Simple	4	Spring 2012
Green Island Brook	Green Island Brook	Green Island Brook	73 00	Simple	40	Summer 2013
Greenspond	Greenspond	Shambler's Cove Pond	50 72	Running	63	Summer 2013
Hampden	Hampden	Elliot Brook	118 22	Running	52	Summer 2013
Hant's Harbour	Hant's Harbour	Eastern Pond (Halfway Brook)	51 83	Running	64	Summer 2013
Happy Adventure	Happy Adventure	Goose Neck Pond	104 95	Running	65	Summer 2013
Happy Valley-Goose Bay	Happy Valley-Goose Bay	Spring Gulch	54 97	Running	48	Summer 2013
Happy Valley-Goose Bay	Happy Valley-Goose Bay	Well Field (connect summer 2002)	91 63	Running	33	Summer 2013
Harbour Breton	Harbour Breton	Connaigre Pond, Hutchings Pond	147 50	Running	114	Summer 2013
Harbour Grace	Harbour Grace South	Southside Wellfield	0 00	Simple	3	Spring 2013
Harbour Grace	Harbour Grace, Harbour Grace South (+Riverhead)	Bannerman Lake	35 00	Running	80	Summer 2013
Harbour Grace	Riverhead	Mercer's Rd. Well	0.00	Simple	2	Spring 2013
Harbour Grace	Thickett	#1 Thicket Susie Galway Well	0 00	Simple	2	Spring 2013
Harbour Grace	Thickett	#2 Thicket New Well	1 50	Simple	2	Spring 2013
Harbour Main-Chapel's Cove-Lakeview	Harbour Main, Chapel's Cove, Lakeview	Flynn's Hill Well	0 00	Simple	4	Spring 2013
Harbour Main-Chapel's Cove-Lakeview	Harbour Main, Chapel's Cove, Lakeview	Holden's Road Well	0 00	Simple	4	Spring 2013
Harbour Main-Chapel's Cove-Lakeview	Harbour Main, Chapel's Cove, Lakeview	Maloney's River	121 10	Running	62	Summer 2013

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Community Name	Serviced Area(s)	Source Name	THMs Average (µg/L)	Average Type	Total Samples Collected	Last Season Sampled
Hare Bay	Hare Bay (+Dover)	Hare Bay Pond	129 07	Running	64	Summer 2013
Harry's Harbour	Harry's Harbour	#1 Well - Northeast Well	6.15	Simple	6	Fall 2012
Harry's Harbour	Harry's Harbour	#2 Well - Northwest Hill / Country Road	4 85	Simple	5	Spring 2013
Harry's Harbour	Harry's Harbour	#3 Well - South Well	14.05	Simple	5	Fall 2012
Hawke's Bay	Hawke's Bay	Torrent River	173 00	Running	56	Summer 2013
Heart's Content	Heart's Content	Southern Cove Pond	81.95	Running	62	Summer 2013
Heart's Delight-Islington	Heart's Delight-Islington	Long Pond	80 75	Running	86	Summer 2013
Heart's Desire	Heart's Desire	Terrence Pond	26 80	Running	59	Summer 2013
Hermitage	Hermitage-Sandyville	Granter's Pond	318 75	Running	67	Summer 2013
Herring Neck	Herring Neck, Hatchet Harbour, Salt Harbour, Shoal Cove, Sunnyside	Gut Pond	147 75	Running	56	Summer 2013
Hickman's Harbour-Robinson Bight	Hickman's Harbour-Robinson Bight	Big Loss Pound Pond	47.45	Running	61	Summer 2013
Hodge's Cove	Hodge's Cove	Drilled	0 00	Simple	5	Spring 2013
Holyrood	Holyrood	Main Line	28.17	Simple	24	Summer 2013
Holyrood	Holyrood	O'Connell's Well	84 70	Simple	19	Summer 2013
Holyrood	Holyrood	Woodford Station - Healey's Well and Quinlan's Well	4.70	Simple	3	Spring 2013
Hopeall	Gilberts Hill	Gilberts Hill Well	1.10	Simple	2	Winter 2005
Hopeall	Hopeall	Charles Cumby Well	0 00	Simple	1	Summer 2004
Hopedale	Hopedale	American Pond	75.95	Running	32	Summer 2013
Howley	Howley	Sandy Lake	0 00	Running	56	Summer 2013
Howley	Howley - PWDU	Sandy Lake	5.72	Running	20	Summer 2013
Hughes Brook	Hughes Brook	Reservoir	28 88	Running	43	Summer 2013
Humber Arm South	Frenchman's Cove Area	Gurges Pond	67 25	Running	9	Summer 2013
Humber Arm South	Halfway Point, Benoit's Cove, John's Beach	Dormody's Brook	47 60	Running	58	Summer 2013
Indian Bay	Indian Bay	Indian Bay Brook	45 92	Running	61	Summer 2013
Irishtown-Summerside	Irishtown	Irishtown Brook	196 50	Running	56	Summer 2013
Irishtown-Summerside	Summerside	Pynn's Pond	122 10	Running	61	Summer 2013
Isle aux Morts	Isle aux Morts	Burnt Ground Pond	197 48	Running	52	Summer 2013
Isle aux Morts	Isle aux Morts - PWDU	Burnt Ground Pond	55 13	Running	4	Summer 2013
Jackson's Arm	Jackson's Arm	Unnamed Brook	117 10	Running	44	Summer 2013
Jackson's Cove-Langdon's Cove-Silverdale	Langdon's Cove	#3 Well Langdon's Cove Well	5 00	Simple	8	Spring 2013
Jackson's Cove-Langdon's Cove-Silverdale	Silverdale, Nickey's Nose Cove	Nickey's Nose Cove Pond	39 88	Running	54	Summer 2013
Jean de Baie	Jean de Baie	#1 Well	1 15	Simple	3	Winter 2004
Keels	Keels	Boland's Pond	427 50	Running	59	Summer 2013
King's Point	King's Point	Bulley's Pond	47 42	Running	50	Summer 2013
Kingston	Kingston		18 08	Simple	6	Fall 2001
Kippens	Kippens	Well Field	2 50	Simple	20	Fall 2012
L'Anse au Clair	L'Anse au Clair	Park Pond	1 67	Running	36	Summer 2013
L'Anse au Loup	L'Anse au Loup	L'anse Au Loup River	31 77	Running	34	Summer 2013
La Poile	La Poile	Black Duck Pond	0 00	Simple	2	Summer 2003
Labrador City	Labrador City	Beverly Lake	47 55	Running	56	Summer 2013

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Community Name	Serviced Area(s)	Source Name	THMs Average (µg/L)	Average Type	Total Samples Collected	Last Season Sampled
Lamaline	Lamaline	Upper Hodges Pond	284 98	Running	53	Fall 2011
Lawn	Lawn	Brazil Pond	0 00	Simple	64	Summer 2013
Lawn	Lawn - PWDU	Brazil Pond	0 00	Simple	2	Summer 2013
Leading Tickles	Leading Tickles	Cook's Pond	162 00	Running	65	Summer 2013
Leading Tickles	Leading Tickles - PWDU	Cook's Pond	60 63	Simple	4	Spring 2013
Lewin's Cove	Lewin's Cove	Big Pond	87 05	Running	52	Summer 2013
Lewisporte	Lewisporte	Stanhope Pond	170 75	Running	89	Summer 2013
Little Bay	Little Bay	First Pond	55 38	Running	40	Summer 2013
Little Bay	Little Bay	Mine Pond	141 75	Running	43	Summer 2013
Little Bay Islands	Little Bay Islands	Jones' Pond & Gull Pond	360 00	Simple	52	Spring 2013
Little Burnt Bay	Little Burnt Bay	Troke's Cove Pond	156 75	Running	51	Summer 2013
Little St. Lawrence	Little St. Lawrence	Butler's Brook (2 Intakes)	0 00	Running	36	Winter 2009
Long Harbour-Mount Arlington Heights	Long Harbour-Mount Arlington Heights	Shingle Pond and/or Trout Pond (2 Intakes)	76 93	Running	68	Summer 2013
Loon Bay	Loon Bay	Southeast Pond	92 63	Running	52	Summer 2013
Lourdes	Lourdes (+West Bay)	Victor's Brook	193 57	Running	75	Summer 2013
Lower Lance Cove	Lower Lance Cove	Big Long Pond	38 63	Running	59	Summer 2013
Lumsden	Lumsden	Gull Pond	109 40	Running	67	Summer 2013
Lushes Bight-Beaumont-Beaumont North	Lushes Bight, Beaumont	Milkboy's Pond/Gull Pond	120 00	Running	45	Summer 2013
Main Brook	Main Brook	Joe Burt's Pond	0.00	Simple	31	Summer 2013
Mainland	Mainland	Caribou Brook	41 97	Simple	44	Spring 2013
Makinsons	Hodgewater Line East & Juniper Stump	Taylor's Wells	57.83	Simple	10	Summer 2013
Makinsons	Turkswater & Hodgewater Line West	Country Path Wells	5.40	Simple	3	Spring 2013
Makkovik	Makkovik	Ranger Bight Pond	149 25	Running	36	Summer 2013
Mary's Harbour	Mary's Harbour	St. Mary's River	212 50	Running	37	Summer 2013
Mary's Harbour	Mary's Harbour - PWDU	St. Mary's River	41.00	Simple	3	Summer 2013
Marystown	Marystown	Fox Hill Reservoir / Clam Pond	66 18	Running	103	Summer 2013
Marysvale	Marysvale, Long Pond	Drilled	2 50	Simple	3	Spring 2013
Massey Drive	Massey Drive	Trout Pond, Third Pond (2 intakes)	144 50	Running	43	Summer 2013
Mattis Point	Mattis Point	Drilled	0 00	Simple	2	Fall 2000
McCallum	McCallum	Drilled	373 33	Simple	45	Summer 2013
McIvers	McIvers	McIvers Brook	114 05	Running	54	Summer 2013
Meadows	Meadows, Summerside West	Masters Pond	97.33	Simple	54	Summer 2013
Merritt's Harbour	Merritt's Harbour	Jimmy's Pond	191 75	Running	56	Summer 2013
Middle Arm	Middle Arm	Dam Pond Brook	5 70	Running	40	Summer 2013
Miles Cove	Miles Cove	Paddock's Pond	143 50	Running	53	Summer 2013
Millertown	Millertown	Water Pond	124 55	Running	59	Summer 2013
Milltown-Head of Bay D'Espoir	Milltown, Head of Bay D'Espoir	Jersey Pond	192 27	Running	88	Summer 2013
Ming's Bight	Ming's Bight	Middle Brook Pond	105 45	Running	30	Summer 2013
Morrisville	Morrisville	Morrisville Pond	9 80	Running	34	Summer 2013
Mount Moriah	Mount Moriah	Second Pond (Three Mile Pond)	123 95	Running	43	Summer 2013

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Community Name	Serviced Area(s)	Source Name	THMs Average (µg/L)	Average Type	Total Samples Collected	Last Season Sampled
Mount Pearl	Mount Pearl	Bay Bulls Big Pond	44 25	Running	50	Summer 2013
Musgrave Harbour	Musgrave Harbour	Rocky Pond	155 38	Running	63	Summer 2013
Nain	Nain	Nain Brook and Anainik's Pond	41 63	Running	41	Summer 2013
Nameless Cove	Nameless Cove / Flower Cove	French Island Pond	173 75	Running	41	Summer 2013
Natuashish	Natuashish (Sango Bay)	Sango Brook and Wellfield	54 58	Running	8	Summer 2013
New Chelsea-New Melbourne-Brownsdale-Sibley 's Cove-Lead Cove	Sibley's Cove, Lead Cove	Sibley's Cove Pond	28 13	Running	55	Summer 2013
New Perlican	New Perlican	New Perlican River	73 90	Running	62	Summer 2013
New-Wes-Valley	Newtown-Templeton	Carter's Pond	171 05	Running	68	Summer 2013
New-Wes-Valley	Wesleyville-Badger's Quay-Pool's Island, Brookfield-Poundcove	Little Northwest Pond	187 75	Running	65	Summer 2013
Newman's Cove	Newman's Cove	Heale Pond Brook	16 55	Running	56	Summer 2013
Nippers Harbour	Nippers Harbour	Blackhead Pond Brook	1 35	Running	49	Summer 2013
Norman's Cove-Long Cove	Norman's Cove-Long Cove	John Newhooks Pond	146 75	Running	29	Summer 2013
Norris Arm	Norris Arm (south)	Mill Lake	128 75	Running	81	Summer 2013
Norris Point	Norris Point	Neddy Harbour Pond	104 40	Running	62	Summer 2013
North Harbour	North Harbour	Grandfather's Pond	10 65	Simple	2	Summer 2013
North West River	North West River	Wellfield (#1 & #3 Well) + #2 Well	1 75	Simple	9	Fall 2012
Northern Arm	Northern Arm	Muddy Hole Pond	89 50	Running	64	Summer 2013
O'Donnells	O'Donnell's	Well Field	0 00	Simple	13	Spring 2013
O'Regans	O'Regan's West		0 00	Simple	3	Winter 2001
O'Regans East	O'Regan's East	Drilled	0 75	Simple	4	Fall 2012
Old Perlican	Old Perlican	Bell Pond	35 83	Running	90	Summer 2013
Pacquet	Pacquet	Big Brook	7 55	Running	48	Summer 2013
Paradise	Paradise	Bay Bulls Big Pond	43 40	Running	50	Summer 2013
Parkers Cove	Parkers Cove	Unnamed brook	106 78	Running	48	Summer 2013
Parson's Pond	Parson's Pond	Cold Brook	38 22	Running	54	Summer 2013
Pasadena	Pasadena	Blue Gulch Pond	173 75	Running	9	Summer 2013
Pasadena	Pasadena (inactive)	Transmission Pond	66 30	Simple	42	Spring 2010
Peterview	Peterview	Northern Arm Lake	90 00	Running	30	Summer 2013
Petit Forte	Petit Forte	Reddy's Pond	0 00	Simple	3	Fall 2009
Petley	Petley	Drilled	0 00	Simple	3	Fall 2001
Petty Harbour-Maddox Cove	Petty Harbour-Maddox Cove	Western Barrens Pond	108 85	Running	29	Summer 2013
Phillips Head	Phillips Head	Dogberry Brook	86 15	Running	43	Summer 2013
Piccadilly Head	Piccadilly Head (+West Bay)	Unnamed Brook	0 00	Simple	41	Winter 2013
Piccadilly Slant-Abraham's Cove	Abraham's Cove	#2 Well - Abraham's Cove	0 00	Simple	5	Winter 2012
Piccadilly Slant-Abraham's Cove	Piccadilly Slant	#1 Well - Piccadilly Slant	2 70	Simple	5	Winter 2011
Pidgeon Cove-St. Barbe	Pigeon Cove - St. Barbe	Long Pond	0 00	Simple	1	Fall 2002
Pilley's Island	Pilley's Island	Loadabats Pond	64 80	Running	58	Summer 2013
Placentia	Dunville	Wyses Pond	67 65	Running	114	Summer 2013
Placentia	Freshwater, Argentia site	Clarkes Pond	135 48	Running	82	Summer 2013

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Community Name	Serviced Area(s)	Source Name	THMs Average (µg/L)	Average Type	Total Samples Collected	Last Season Sampled
Placentia	Placentia, Jerseyside, SE Placentia	Larkins Pond	163 25	Running	113	Summer 2013
Plate Cove East	Plate Cove East		0 85	Simple	2	Fall 1986
Pleasantview	Pleasantview	Little Arm Pond	150 05	Running	57	Summer 2013
Plum Point	Plum Point	Grand Pond	93 15	Running	31	Summer 2013
Point Leamington	Point Leamington	Little Pond	119 10	Running	69	Summer 2013
Point May	Point May	Short's Pond	358 80	Running	59	Summer 2013
Point May	Point May - PWDU	Short's Pond	6 00	Simple	1	Spring 2013
Point of Bay	Point of Bay	Indian Cove Pond	165 25	Running	45	Summer 2013
Pollards Point	Pollards Point East	George Ricks Pond	153.00	Simple	2	Summer 2012
Pollards Point	Pollards Point, Country Cove	Country Cove Pond	0 00	Simple	1	Fall 2003
Pool's Cove	Pool's Cove	Widgeon Pond	165 98	Running	59	Summer 2013
Port Albert	Port Albert	Beaverton Pond	150 45	Running	51	Summer 2013
Port Anson	Port Anson	Anchor Pond	182 05	Running	51	Summer 2013
Port Blandford	Port Blandford	Noseworthy's Pond	189 25	Running	71	Summer 2013
Port Hope Simpson	Port Hope Simpson	Arnold's Brook and Pond	323 25	Running	34	Summer 2013
Port Kirwan	North Side	Dug Well / Drilled Well	1 90	Simple	3	Spring 2013
Port Kirwan	Port Kirwan	Developed Spring	2.70	Simple	6	Spring 2013
Port Saunders	Port Saunders	Tom Taylor's Pond	191 00	Running	61	Summer 2013
Port au Choix	Port au Choix	Well Field	133 30	Running	29	Summer 2013
Port au Choix	Port au Choix	Winterhouse Pond	113.30	Simple	71	Summer 2013
Port au Port East	Port au Port East	Drilled Well - 75-80% Berry Head Watershed - 20-25%	32 65	Simple	30	Spring 2013
Port au Port West-Aguathuna-Felix Cove	Felix Cove	#4-Goose Pond Road Well	13.10	Simple	11	Spring 2013
Port au Port West-Aguathuna-Felix Cove	Felix Cove	#5 Ocean View Drive Well	0.00	Simple	3	Spring 2013
Port au Port West-Aguathuna-Felix Cove	Port au Port West	Jim Rowe's Brook	185.00	Simple	34	Fall 2008
Port au Port West-Aguathuna-Felix Cove	Port au Port West, Aguathuna	#1 & #3 & #6 FatherJoy's Well	82 35	Running	24	Summer 2013
Portland Creek	Portland Creek	Unnamed Streams	38 92	Running	49	Summer 2013
Portugal Cove South	Portugal Cove South	Wrights Brook	0 00	Simple	24	Fall 2011
Portugal Cove-St. Phillips	Portugal Cove-St. Phillips	Bay Bulls Big Pond	44 40	Running	36	Summer 2013
Postville	Postville	Big Pond	208 50	Running	34	Summer 2013
Pouch Cove	Pouch Cove	North Three Island Pond	173 95	Running	66	Summer 2013
Purcell's Harbour	Purcell's Harbour	Purcell's Harbour Pond	319 00	Running	66	Summer 2013
Pynn's Brook	Pynn's Brook	Pynn's Brook	28 00	Simple	41	Summer 2013
Raleigh	Raleigh	#4 Well	2 70	Running	11	Winter 2012
Ramea	Ramea	Northwest Pond	183 50	Running	70	Summer 2013
Ramea	Ramea - PWDU	Northwest Pond	26 77	Running	21	Summer 2013
Random Sound West	North West Brook, Ivany Cove	#1 Well - Cabot Road South Well	0 00	Simple	2	Winter 2003
Random Sound West	North West Brook, Ivany Cove	#2 Well	4 25	Simple	2	Winter 2003
Random Sound West	North West Brook, Ivany Cove	#3 Well - Harbour Well	27 60	Simple	10	Spring 2013
Random Sound West	Queen's Cove	Reservoir	150 25	Running	68	Summer 2013
Rattling Brook	Rattling Brook	Mark's Pond Brook	200 25	Running	43	Summer 2013

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THMs Summary for Public Water Supplies in Newfoundland and Labrador

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Community Name	Serviced Area(s)	Source Name	THMs Average (µg/L)	Average Type	Total Samples Collected	Last Season Sampled
Red Bay	Red Bay	Northern Brook	16 30	Running	37	Summer 2013
Red Harbour	Red Harbour	Drilled	2 67	Simple	3	Fall 2001
Reidville	Reidville	Humber Canal, Grand Lake	98 00	Running	43	Summer 2013
Renews-Cappahayden	Cappahayden	#1 Dinn's Well	19 30	Simple	13	Spring 2013
Rigolet	Rigolet	Rigolet Pond	223 00	Simple	34	Summer 2013
River of Ponds	River of Ponds	Burnt Head Ponds	57 40	Running	49	Summer 2013
Riverhead	Riverhead (St. Mary's Bay)	Well Field	0 00	Simple	1	Fall 2006
Robert's Arm	Robert's Arm	Young's Pond / Dam Pond	104 97	Running	57	Summer 2013
Rocky Harbour	Rocky Harbour	Gull Pond	203 00	Running	60	Summer 2013
Roddickton-Bide Arm	Bide Arm	First Clay Cove Pond	123 65	Running	43	Summer 2013
Roddickton-Bide Arm	Roddickton	East Brook Pond	126 50	Running	65	Summer 2013
Rose Blanche-Harbour Le Cou	Rose Blanche-Harbour Le Cou	Rose Blanche Brook	27 33	Running	64	Summer 2013
Rushoon	Rushoon	Big Pond Brook	23 15	Running	53	Summer 2013
Salmon Cove	Salmon Cove	Rocky Pond	32 13	Running	50	Summer 2013
Salvage	Salvage	Wild Cove Pond	343.75	Running	60	Summer 2013
Sandringham	Sandringham	Drilled	0 00	Simple	4	Fall 2012
Sandy Cove	Sandy Cove	Dug	1 90	Simple	23	Fall 2012
Seal Cove (FB)	Seal Cove, F B.	Big Black Duck Pond	0 00	Simple	16	Fall 2007
Seal Cove (WB)	Seal Cove, W B.	Seal Cove Brook & Long Pond	122 15	Running	53	Summer 2013
Sheaves Cove	Sheaves Cove	Drilled	1 50	Running	6	Winter 2010
Sheaves Cove	Sheaves Cove	Unnamed Brook	0.73	Running	38	Winter 2013
Sheppardville	Sheppardville	Drilled	31 00	Simple	21	Summer 2013
Sheshatsheits	Sheshasheits - Indian Band Council	Wells 1, 2 & 3	72 40	Simple	18	Fall 2012
Ship Cove-Lower Cove-Jerry's Nose	Lower Cove	#6 Well - Lower Cove Well	0 00	Simple	3	Spring 2013
Ship Cove-Lower Cove-Jerry's Nose	Ship Cove East	#3 Well - Bernard Brake Well	0 00	Simple	3	Spring 2013
Ship Cove-Lower Cove-Jerry's Nose	Ship Cove, Jerry's Nose	#1 Well - PJ's Variety Well	0 00	Simple	9	Fall 2012
Ship Cove-Lower Cove-Jerry's Nose	Ship Cove, Jerry's Nose	#2 Well - Howard & Rodney Jesso Well	0 00	Simple	2	Spring 2013
Ship Cove-Lower Cove-Jerry's Nose	Ship Cove, Jerry's Nose	#4 Well - Nancy Rowe Well	0 00	Simple	3	Spring 2013
Ship Cove-Lower Cove-Jerry's Nose	Ship Cove, Jerry's Nose	#5 Well - Murdock Wheeler Well	4 80	Simple	3	Spring 2013
Shoe Cove	Shoe Cove	Second Pond	0 00	Running	14	Summer 2013
Small Point-Adam's Cove-Blackhead-Broad Cove	Adam's Cove	#1 Well - Reg Bursey Well	3.90	Simple	1	Spring 2013
Small Point-Adam's Cove-Blackhead-Broad Cove	Broad Cove	#6 Well - Herb Trickett Well	103 00	Simple	1	Spring 2013
Small Point-Adam's Cove-Blackhead-Broad Cove	Broad Cove	#7 Well - Gin Badcock Well	18 50	Simple	1	Spring 2013
Small Point-Adam's Cove-Blackhead-Broad Cove	Small Point	#8 Well - Effie Flight Wells	3 00	Simple	1	Spring 2013
Smith's Harbour	Smith's Harbour	Fleshetts Brook	0 00	Running	54	Summer 2013
Smith's Sound	Harcourt-Monroe-Waterville	Developed Spring	0 00	Simple	6	Spring 2013
Sop's Arm	Sop's Arm	Little Tickle Pond	0 00	Running	4	Winter 2006
South Brook	South Brook	Next to Brook	9 02	Running	48	Summer 2013
South Dildo	South Dildo	#5 Well - Calvin Reid Well	0 00	Simple	2	Winter 2005
South Dildo	South Dildo	Broad Cove Pond	99 93	Running	51	Summer 2013

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THMs Summary for Public Water Supplies in Newfoundland and Labrador

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Community Name	Serviced Area(s)	Source Name	THMs Average (µg/L)	Average Type	Total Samples Collected	Last Season Sampled
South River	South River	Brigus Long Pond (to Brigus)	99 78	Running	29	Summer 2013
Southern Harbour	Southern Harbour	Brigades Pond	111 60	Running	83	Summer 2013
Southport	Southport		0 00	Simple	3	Spring 2001
Spaniard's Bay	Spaniard's Bay (+Upper Island Cove)	Kelly's Pond (Spider's Pond)	44 20	Running	62	Summer 2013
Springdale	Springdale	Sullivan's Pond (2 Intakes)	72 40	Running	73	Summer 2013
Springdale	Springdale Industrial Park	Well	0 00	Simple	7	Spring 2013
St. Alban's	St. Alban's	Well Field	0.00	Simple	10	Spring 2013
St. Andrews	Air Strip Road	#4 Well Strip Road Well	0 00	Simple	4	Spring 2013
St. Andrews	St. Andrew's	#1 Well	1 90	Simple	3	Fall 2012
St. Andrews	St. Andrew's	#2 Well	0.00	Simple	3	Fall 2012
St. Andrews	St. Andrew's East	#3 Well	1 80	Simple	3	Fall 2012
St. Anthony	St. Anthony	St. Anthony Pond	130 25	Running	71	Summer 2013
St. Anthony Bight	St. Anthony Bight	Cabbox Pond	0 00	Running	45	Summer 2013
St. Bernard's-Jacques Fontaine	St. Bernard's-Jacques Fontaine	Rattle Brook	0 00	Running	60	Summer 2013
St. Bride's	St. Bride's	North Side Brook	0 00	Running	4	Winter 2003
St. Bride's	St. Bride's	South Side Brook	0 00	Running	4	Winter 2003
St. George's	St. George's	Dribble Brook (Backup Supply)	409 00	Running	46	Fall 2009
St. George's	St. George's	Wellfield	9 35	Simple	12	Spring 2013
St. John's	St. John's	Windsor Lake	53 75	Running	73	Summer 2013
St. John's	St. John's (+Mt. Pearl, +Paradise, +Portugal Cove-St. Phillips, +CBS)	Bay Bulls Big Pond	42 00	Running	86	Summer 2013
St. John's	St. John's Mixing Zone	St. John's Mixing Zone	75 70	Running	6	Summer 2013
St. John's	St. John's, Kilbride	Petty Harbour Long Pond (inactive)	60 33	Simple	27	Fall 2002
St. Judes	St. Judes	Chute Brook	0 00	Simple	3	Summer 2005
St. Judes	St. Judes	Uncle Arthur Brook	0 00	Simple	3	Summer 2005
St. Lawrence	St Lawrence	St. Lawrence River	38 63	Running	73	Summer 2013
St. Lawrence	St. Lawrence - PWDU	St. Lawrence River	12 93	Simple	21	Summer 2013
St. Lewis	St. Lewis	Tub Harbour Pond	211 00	Running	39	Summer 2013
St. Lunaire-Griquet	Gunners Cove	Lookout Brook	210 50	Running	33	Summer 2013
St. Lunaire-Griquet	St. Lunaire-Griquet	Drilled	18 30	Simple	11	Spring 2013
St. Lunaire-Griquet	St. Lunaire-Griquet	Joe's Pond	125 37	Simple	49	Summer 2013
St. Mary's	St. Mary's	Wellfield	4 50	Simple	4	Spring 2013
St. Pauls	St Pauls	Two Mile Pond	363 75	Running	63	Summer 2013
St. Shott's	St. Shott's	Unnamed Pond	77 45	Running	59	Summer 2013
Steady Brook	Steady Brook	Steady Brook	132 07	Running	60	Summer 2013
Stephenville	Stephenville	Well Field	13 68	Running	39	Summer 2013
Stephenville Crossing	Stephenville Crossing	Well Fields 1 & 2	1 37	Simple	6	Fall 2012
Stoneville	Stoneville	Dog Bay Pond Brook	99 45	Running	51	Summer 2013
Straitsview	Straitsview	Saddle Hill Pond	95 95	Running	46	Summer 2013
Summerford	Summerford (+Cottlesville)	Rushy Cove Pond	279 50	Running	73	Summer 2013
Sunnyside (T.B)	Sunnyside	Center Cove River	303 00	Running	42	Summer 2013

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THMs Summary for Public Water Supplies in Newfoundland and Labrador

Community Name	Serviced Area(s)	Source Name	THMs Average (µg/L)	Average Type	Total Samples Collected	Last Season Sampled
Terrenceville	Terrenceville	Big Brook	165 25	Running	70	Summer 2013
Thornlea	Thornlea	Big Bakeapple Pond	0 00	Running	40	Summer 2013
Tizzard's Harbour	Tizzard's Harbour	Rocky Pond	50 15	Running	58	Summer 2013
Tompkins	Tompkins	Greg Wall Well	0.00	Simple	2	Winter 2003
Torbay	Torbay	North Pond	132 38	Running	70	Summer 2013
Trepassey	Trepassey	Broom Cove Pond	48 65	Running	26	Summer 2013
Trepassey	Trepassey	Miller's Pond	11 57	Running	79	Summer 2013
Trinity	Trinity, T B.	Indian Pond	215 75	Running	31	Summer 2013
Trinity Bay North	Little Catalina	Whirl Pond	225 00	Running	78	Summer 2013
Trinity Bay North	Melrose	Whirl Pond	227 75	Running	75	Spring 2013
Trinity Bay North	Port Union, Catalina (+Little Catalina)	Whirl Pond	176 07	Running	79	Summer 2013
Triton	Triton, Jim's Cove, Card's Harbour	Triton Pond	189 00	Running	72	Summer 2013
Trout River	Trout River	Feeder Brook	36 75	Running	59	Summer 2013
Twillingate	Twillingate	Wild Cove Pond	121 88	Running	86	Summer 2013
Upper Amherst Cove	Upper Amherst Cove	Drilled	12 50	Simple	14	Spring 2013
Upper Ferry	Upper Ferry	#4 Well - Angus MacNeil Well	0.00	Simple	1	Spring 2005
Upper Ferry	Upper Ferry - Lower	#1 Well - Gerard Brownigg Well	1 60	Simple	2	Winter 2003
Upper Ferry	Upper Ferry - Middle	#2 Well - Hughie Macissac Well	3 85	Simple	2	Winter 2003
Upper Ferry	Upper Ferry - Upper	#3 Well - Marshall Devoe Well	0 00	Simple	2	Winter 2003
Upper Island Cove	Upper Island Cove	Kelly's Pond (Spider's Pond)	60 45	Running	72	Summer 2013
Victoria	Victoria (+Salmon Cove)	Rocky Pond	29 17	Running	58	Summer 2013
Virgin Arm-Carter's Cove	Virgin Arm-Carter's Cove		9 57	Simple	7	Winter 2001
Wabana	Wabana	#3 Yard West Mines Road	20.00	Simple	12	Spring 2013
Wabana	Wabana	#4-West Mines Road	16 65	Simple	11	Spring 2013
Wabana	Wabana	Middleton Ave	5 60	Simple	3	Spring 2013
Wabana	Wabana	Mixed Supplies	35 00	Simple	21	Spring 2013
Wabana	Wabana	Normore Crescent East #1	0.00	Simple	3	Spring 2013
Wabana	Wabana	Quigley's Line	2.35	Simple	13	Spring 2013
Wabana	Wabana	Scotia #1	25 80	Simple	5	Spring 2013
Wabana	Wabana	St. Edward's Memorial St.	2 20	Simple	3	Spring 2013
Wabush	Wabush	Wahnahnish Lake	86 00	Running	48	Summer 2013
West Bay	West Bay	Unnamed Brook	1 07	Simple	37	Winter 2013
West Bay	West Bay	Victor's Brook	114 85	Running	41	Summer 2013
West St. Modeste	West St. Modeste	Well Field	88 18	Running	35	Summer 2013
Westport	Westport	Western Brook Pond	0 00	Simple	46	Spring 2013
Whitbourne	Whitbourne	Hodges River	95 38	Running	66	Summer 2013
Whiteway	Whiteway (+Cavendish)	Long Pond	124 85	Running	66	Summer 2013
Whiteway	Whiteway - PWDU	Long Pond	38 25	Running	5	Summer 2013
Wild Cove	Wild Cove	Hedderson's Pond Brook	0 00	Simple	14	Winter 2008
Winterland	Winterland	Well Field	5 50	Simple	3	Fall 2012
Winterton	Winterton	Western Pond	32 95	Running	66	Summer 2013

Appendix B (Referenced from HACH Technologies)[7] B-1

Trihalomethanes

DOC316.53.01143

THM Plus™ Method **Method 10132**

(10 to 600 ppb as Chloroform) **Water Bath Method**

Scope and Application: For screening THMs in drinking water samples and Formation Potential tests.

Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 411 Instrument-specific information

Instrument	Sample cell	Cell orientation
DR 6000	2427606 and 2495402	Sample cell faces right
DR 5000	2427606 and 2495402	Sample cell faces user
DR 3900	2427606 and 2495402	Sample cell faces user
DR 3800, DR 2800, DR 2700	2427606 and 2495402	Sample cell faces right

Before starting the test:

Analyze the samples immediately after collection or refrigerate the samples until the analysis is complete.

If the samples were refrigerated after collection, do not warm the samples to room temperature prior to analyzing. This will minimize volatilization of the disinfection by-products (DBPs). If refrigerated samples are analyzed, heat the samples for an additional two minutes (total of seven minutes) in step 12 of the procedure.

If analyzing more than four samples, use 450 mL of water in the water bath.

THM Plus Reagent 2 **must** be at room temperature before use.

A bottle-top dispenser may be used in place of the TenSette® Pipet.

Trihalomethane compounds are extremely volatile. Immediately cap sample cells after filling with sample.

Reagent blank is stable for 1–2 hours and need not be prepared for each test.

Do not mark below the 10 mL fill line.

Collect the following items:

Description	Quantity
THM Plus Reagent Set	varies
Beaker, 600-mL	1
Cell Holder Assembly, TTHM	1
Evaporating Dish, 125 mm x 65 mm	2
Hot Plate, 7 x 7 inch	1
Pipet, TenSette®, 0.1–1.0 mL and tips	1
Pipet, TenSette®, 1–10 mL and tips	1
Sample Cells, 10-mL (see the *Instrument-specific information* table)	2
Wipers, disposable	varies
Ice[1]	varies

See *Consumables and replacement items* for reorder information.

[1] Depending on the temperature of the tap water, ice may be needed for the cooling baths used in steps 14 and 17.

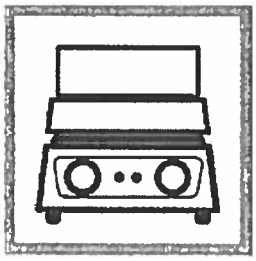
THM Plus Method

***Important Note:** Perform steps 4–9 rapidly to avoid loss of THMs from the sample. When testing more than one sample, complete steps 4–9 for one sample before going on to another. If dispensing sample with a pipette, the pipette must dispense quickly without causing aeration or back pressure.*

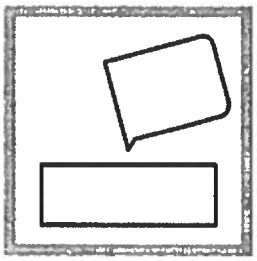
1. Select the test.

Insert an adapter if required (see the *Instrument-specific information* table).

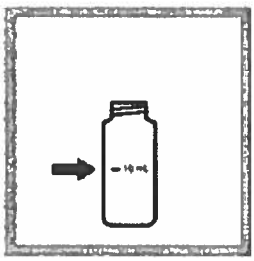
Refer to the user manual for orientation.



2. Prepare a hot water bath by adding 500 mL of water to an evaporating dish. Put the dish on a hot plate and turn the heater on high.



3. Prepare a cooling bath by adding 500 mL of cold (18–25 °C) tap water to a second evaporating dish. Maintain the temperature in this range.

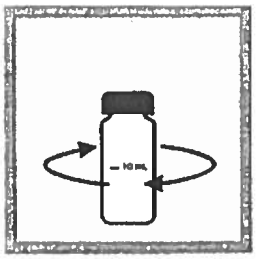


4. **Prepared Sample:** Fill one round sample cell to the 10-mL mark with sample. Cap and label as "sample".

THM Plus Method (continued)

5. Blank Preparation: Fill the second sample cell with deionized water. Cap and label as "blank".

6. Add three drops of THM Plus Reagent 1 to each cell.

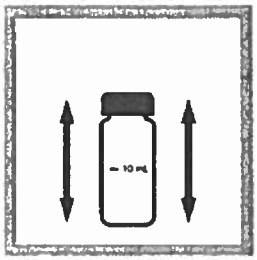


7. Cap tightly and mix gently by swirling each cell three times.

Vigorous shaking can cause loss of THMs into the sample cell headspace.

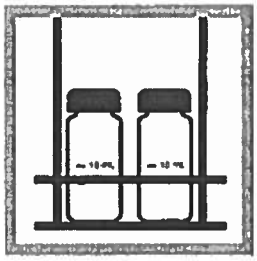
8. Use a TenSette® Pipet to add 3 mL of THM Plus Reagent 2 to each cell. Avoid excess agitation of the sample when dispensing the reagent.

The reagent is viscous and a small amount may remain on the tip after dispensing. This will not affect the results.



9. Cap tightly and mix by shaking.

Thorough mixing makes sure that all of the THM goes into the liquid and does not accumulate in the air above the sample.



10. Place the sample cells in the cell holder assembly.

11. Place the assembly in the hot water bath when the water is boiling rapidly.

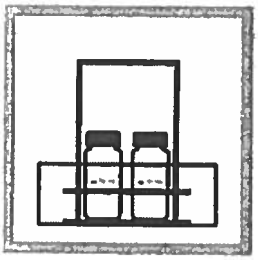
Do not allow the water to rise above the white "diamond" near the top of the sample cells.

12. Start the instrument timer.

A five-minute reaction period will begin.

Heat for 7 minutes if refrigerated samples are being analyzed.

THM Plus Method (continued)



13. When the timer expires, remove the assembly and sample cells from the hot water bath. Place in the cooling bath.

Use ice to cool the tap water if necessary.

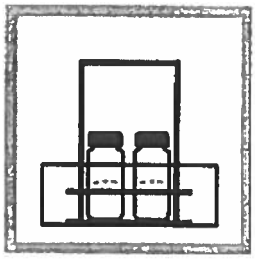
14. Start the instrument timer.

A three-minute cooling period will begin.

When the timer expires, remove the cells from the cooling bath.

Invert each cell a few times to make sure that a uniform temperature of the sample is maintained.

15. Use a TenSette Pipet to add 1 mL of THM Plus Reagent 3 to each cell. The sample and blank will become warm.



16. Replace the cooling water with fresh, cold tap water. Place the assembly that contains the sample and blank cells into the cooling bath.

Use ice to cool the tap water if necessary.

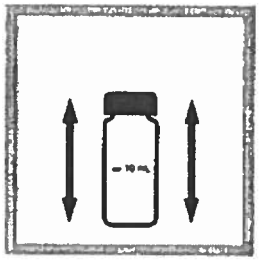
17. Start the instrument timer.

A three-minute cooling period will begin.

When the timer expires, remove the cells from the cooling bath.

The temperature of the sample should be 15–25 °C.

18. Add the contents of one THM Plus Reagent 4 Powder Pillow to the sample cell and one to the blank.



19. Cap each cell tightly and mix by shaking until all the powder dissolves.

The powder dissolves slowly. Intermittent shaking during the first five minutes of the color development period will help dissolve the reagent powder.

20. Start the instrument timer.

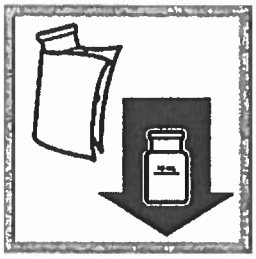
A 15-minute development time will begin.

The color is stable for at least 30 minutes after the 15-minute development time.

THM Plus Method (continued)

21. After the timer expires, pour the prepared sample and prepared blank into two square sample cells.

Allow the solution to settle in the square cells for 30 seconds to enable any turbidity that may be present to settle.



22. When the timer expires, wipe the blank and insert it into the cell holder.

23. ZERO the instrument.

The display will show:

0 ppb $CHCl_3$

24. Wipe the prepared sample and insert it into the cell holder.

READ the results in ppb chloroform ($CHCl_3$).

Interferences

Table 412 Interfering substances[1]

Interfering substance	Interference level
Chlorine	10 mg/L
Copper	1000 mg/L
Hardness, Ca	1000 mg/L as $CaCO_3$ May have some turbidity until Reagent 3 is added
Hardness, Mg	4000 mg/L as $CaCO_3$ May have some turbidity until Reagent 3 is added
Iron	10 mg/L
Lead	2 mg/L
Mercury	10 mg/L
Monochloramine	20 mg/L
Nickel	10 mg/L
Sodium Bisulfite	100 mg/L
EDTA	Interferes negatively at all levels

[1] The substances in the *Interfering substances* table have been tested and found to cause no interference up to the indicated levels.

Table 413 Additional disinfection by-products (DBPs) that are included in results

Compound	Effect
1,1,1-trichloro-2-propanone	Interferes positively
1,1,1-tricholoacetonitrile	Interferes positively
Chloral hydrate	Interferes positively
Dibromochloroacetic acid	Interferes positively

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Table 413 Additional disinfection by-products (DBPs) that are included in results

Compound	Effect
Dichlorobromoacetic acid	Interferes positively
Tribromoacetic acid	Interferes positively
Trichloroacetic acid	Interferes positively

Sample collection, preservation and storage

- Collect samples in 40-mL glass bottles sealed with Teflon®-lined septa caps.
- Fill the bottles slowly to overflowing so that no air is included with the sample.
- Seal the bottles tightly and invert to check that no air has been trapped.
- Because trihalomethane compounds (THMs) are extremely volatile, immediate analysis yields the greatest accuracy. If the samples cannot be analyzed immediately, cool samples to 4 °C. This will slow the formation of any additional THM compounds in chlorinated samples.
- Store the samples at 4 °C in an atmosphere free of organic vapors. Samples should not be held more than 14 days. 0.1 N Sodium Thiosulfate can be used to dechlorinate samples for longer storage.
- Add 1 drop of 0.1 N Sodium Thiosulfate to dechlorinate a finished or distribution system sample collected in a 125 mL bottle.

Accuracy check

Required for accuracy check:

- THM Standard Ampule, 10 mg/L as chloroform
- Ampule breaker
- Wiretrol™ Pipet

Note: Make sure that the chloroform is not lost to volatilization when attempting to add the chloroform to the solution. Make sure that the chloroform ampule is kept cold (can use a small ice-bath).

Standard additions method (sample spike)

1. Open a THM Standard Ampule, 10 ppm as chloroform.
2. Use a Wiretrol Pipet to transfer 0.100 mL (100 µL) of the chloroform standard into a fresh 10 mL portion of sample.
3. Immerse the end of the pipet tip under the water and slowly dispense the chloroform.
4. Cap the sample cell immediately and swirl three times to mix.

Note: The accuracy check methods require careful attention to technique, for it is very easy to lose the chloroform to volatilization when attempting to add it to the solution. Make sure the chloroform ampule is kept cold (may wish to use a small ice-bath)

5. Immediately start steps 6–24 of the procedure to analyze the spiked sample.
6. The value of the spiked sample should increase 100 +/- 20 ppb over the value obtained on the original unspiked sample.
7. Calculate the % Recovery:

$$\% \text{ Recovery} = \frac{\text{ppb THMs Spiked Sample} - \text{ppb THMs Unspiked Sample}}{\text{100 ppb THM Added}} \times 100$$

Standard solution method

1. Prepare a 99 ppb chloroform standard by pipetting 10.0 mL of organic-free water into a sample cell. Open a THM Standard Ampule, 10 ppm as chloroform. Use a Wiretrol Pipet to transfer 0.100 mL (100 µL) of the chloroform standard into the organic-free water. When adding the standard into the sample, discharge the pipet slowly at or near the bottom of the sample cell with a slight swirling motion.

   Note: If the aliquot of the standard is discharged too quickly, the solution will form a single bubble which will rise to the top of the solution and volatilize, without being absorbed in the solution.

2. Cap the sample cell immediately and swirl three times to mix.
3. Immediately start steps 6–24 of the procedure. Do not make up the standard in advance. Use the standard immediately upon preparation.
4. To adjust the calibration curve using the reading obtained with the 99 ppb Standard Solution, navigate to Standard Adjust in the software: **OPTIONS>MORE>STANDARD ADJUST**
5. Turn on the Standard Adjust feature and accept the displayed concentration. If an alternate concentration is used, enter the concentration and adjust the curve to that value.

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Method performance

Program	Standard	Precision 95% Confidence Limits of Distribution	Sensitivity Concentration change per 0.010 Abs change
725	66 ppb $CHCl_3$	53–79 ppb $CHCl_3$	19 ppb $CHCl_3$

Summary of method

The THM Plus method reacts with the trihalogenated disinfection by-products formed as the result of the disinfection of drinking water with chlorine in the presence of naturally occurring organic materials. These disinfection by-products (DBPs) may be produced in the treatment plant or the distribution system as long as the water is in contact with free chlorine residual. The formation of the DBPs is influenced by chlorine contact time, chlorine dose and residual, temperature, pH, precursor concentration, and bromide concentration.

The predominant DBPs formed by the chlorination of drinking water are the trihalomethanes or THMs. The four trihalogenated compounds that form are chloroform, bromoform, dichlorobromomethane, and dibromochloromethane. These four compounds comprise the Total Trihalomethanes (TTHMs) group which is regulated under the Safe Drinking Water Act. The combined concentration of the TTHMs, is regulated in drinking water samples. Other DBPs that may be present and react under the conditions of the THM Plus method are listed in Interferences.

In the THM Plus method, THM compounds present in the sample react with N, N,-diethylnicotinamide under heated alkaline conditions to form a dialdehyde intermediate. The sample is then cooled and acidified to pH 2.5. The dialdehyde intermediate formed is then reacted with 7-amino-1,3 napthalene disulfonic acid to form a colored Schiff base. The color formed is directly proportional to the total amount of THM compounds present in the sample. Test results are measured at 515 nm and reported as ppb chloroform.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Reagent Set (50 tests[1]), includes:			2790800
THM Plus™ Reagent 1	6 drops	15 mL	2753929
THM Plus™ Reagent 2	6 mL	330 mL	2754048
THM Plus™ Reagent 3	2 mL	110 mL	2754142
THM Plus™ Reagent 4	2 pillows	100 pillows	2756699

[1] Fifty tests equals 25 samples and 25 individual blanks. Additional tests can be obtained when multiple samples are run using a single blank.

Required apparatus

Description	Quantity	Unit	Catalog number
Beaker, 600-mL	1	each	50052
Cell Holder Assembly, TTHM	1	each	4788000
Evaporating Dish, 125 mm x 65 mm	2	each	2764700
Hot Plate, 7 x 7 in., 115 VAC, digital	1	each	2881600
Hot Plate, 7 x 7 in., 230 VAC, digital	1	each	2881602
Pipet, TenSette®, 0.1–1.0 mL	1	each	1970001

Required apparatus

Description	Quantity	Unit	Catalog number
Pipet Tips for TenSette Pipet 19700-01	varies	50/pkg	2185696
Pipet, TenSette®, 1–10 mL	1	each	1970010
Pipet Tips, for TenSette Pipet 19700-10	varies	50/pkg	2556996
Wipers, disposable	varies	280/pkg	2097000

Recommended standards

Description	Unit	Catalog number
Chloroform, 10-ppm ampule	7/pkg	2756707
Water, Reagent, Organic-free	500 mL	2641549

Optional reagents and apparatus

Description	Unit	Catalog number
Pipet, filler, safety bulb	each	1465100
Pipet, volumetric, class A, 10 mL	each	1451538
Pipettes, Wiretrol™, 50–100 µL	250/pkg	2568905
Vials, glass, 40-mL, with Septa cap	5/pkg	2794005
Sodium thiosulfate standard solution, 0.1 N	100 mL	323-32

Appendix C – UV/VIS Data

Table A-1 Absorbencies at a common wavelength for a spiked 10% methanol/water sample

Concentration (V/V)	Absorbance 207 nm	214 nm
4 drops in quartz cell	No absorbance	No absorbance

Table A-2 Absorbencies at a common wavelength for a 1/100 THM/methanol sample

Concentration (V/V)	Absorbance 207 nm	214 nm
1/100	0.1552	0.1375

Table A-3 Absorbencies at a common wavelength for the THM standards in methanol

Concentration (PPM)	Absorbance at 207 and 214 nm unless otherwise stated 207 nm	214 nm
200	4.500	4.500
100	1.6765 (203nm)	1.8835 (213 nm)
50	No Absorbance	1.1638 (213 nm)
25	0.7842 (206 nm)	0.8010 (212 nm)
10	No Absorbance	0.3433 (210 nm)
5	0.1511 (205 nm)	0.1510 (211 nm)
2	No Absorbance	No Absorbance
1	No Absorbance	No Absorbance

Note: No absorbance = closest wavelength which holds an absorbance value is $\geq \pm 5$ nm from 207 and 214 nm.