Appendix D

THM Sampling Protocol and Field Sheet

REVISION DATE: JULY, 1998 **METHOD NUMBER:M230.01**

TRIHALOMETHANES IN WATER

1. Introduction

1.1 This method employs solid phase micro-extraction/ capillary column gas chromatography/mass spectrometer detector (SPME/GC/MS) for the qualitative and quantitative determination of trihalomethanes in water.

1.2 The method detection limit is 5 ug/L of the trihalomethanes.

1.3 The operating range is 1-500 ug/L.

2. Summary of Method

2.1 The water sample is extracted onto a SPME fiber. The desorbed material from the fiber is analyzed using GC/MS.

3. Interferences

3.1 Interferences may be caused by contaminants in the air such as solvents. A distilled water blank must be routinely demonstrated to be free from interferences by running procedural blanks.

4. Sample Collection, Preservation, and Handling

4.1 Samples must be collected in precleaned glass vials with teflon lined covers. 2 mL of sample is required for this analysis.

4.2 Samples should be analyzed within 14 days of collection.

5. Safety

5.1 The toxicity of the reagents have not been precisely defined so exposure to these chemicals should be reduced to the lowest possible level.

5.2 MSDS are available for all chemicals required for this analysis and should be consulted prior to use.

6. Apparatus and Materials

6.1 Glassware:

6.1.1 20 mL amber or clear glass bottles fitted with screw caps and teflon liners.

6.1.2 2 mL vials fitted with crimp caps and teflon liners.

6.1.3 Volumetric flasks (A grade).

6.2 Equipment:

6.2.1 Hamilton 1710 100 µL gas tight syringe.

6.2.2 Hamilton 1001 1000 µL gas tight syringe.

6.2.3 Hamilton 701N 10 µL gas tight syringe.

6.2.4 100 µm Polydimethylsiloxane Solid Phase Microextraction fiber.

6.2.5 Varian 8200 AutoSampler equipped with SPME accessory.

6.2.6 Varian 3400 Gas Chromatograph equipped with a Saturn II Mass Spectrometer.

6.2.7 Dell 166 Gxi Computer and Printer installed with Varian GC/MS software.

6.3 Reagents:

6.3.1 Methanol - pesticide grade.

6.3.2 19 Mohm deionized water.

6.3.3 Supelco EPA 524 Internal Standard Mix. Catalog No.:4-8948. 2000 µg/mL of Fluorobenzene and 1,2-Dichlorobenzene-d_4 in Methanol.

6.3.4 Supelco Trihalomethanes Calibration Mix. Catalog No.: 4-8140. 200 µg/mL of Bromodichloromethane, Dibromochloromethane, Chloroform, and Bromoform.

6.3.5 Sodium sulfate - TRACEPUR, anhydrous, oven dried at 400°C for 4 h.

7. Standards Preparation

7.1 See standard operating procedure SOP 04.1. Fill a stock solution preparation log form for each standard prepared.

7.2 Internal Standard Preparation:

7.2.1 Pipette 1.0 mL of the Supelco EPA 524 Internal Standard Mix spiking solution into a precleaned 50 mL volumetric flask using the Hamilton 1001 1000 µL gas tight syringe. Make to the mark with Methanol.

7.2.2 Dilute this solution 1 mL in 10 mL for the working Internal Standard solution. This provides a spiking solution of the following composition:
4.0 µg/mL Fluorobenzene
4.0 µg/mL 1,2-Dichlorobenzene-d_4

7.2.3 Solution should be stored at 4°C

7.2.4 Solution should be replaced after one month.

7.3 Standard Solutions Preparation:

7.3.1 Pipette 1.0 mL of the 200 µg/mL Supelco Trihalomethanes Calibration Mix solution into a precleaned 5 mL volumetric flask using the Hamilton 1001 1000µL gas tight syringe. Make up to mark with Methanol.

7.3.2 This provides a standard solution of the following composition:
40.0 µg/mL Bromodichloromethane
40.0 µg/mL Dibromochloromethane
40.0 µg/mL Chloroform
40.0 µg/mL Bromoform

7.3.3 Pipette 1.0 mL of this 40.0 µg/mL standard solution into a precleaned 10 mL volumetric flask using the Hamilton 1001 1000 µL gas tight syringe. Make up to the mark with Methanol.

7.3.4 This provides a standard solution of the following composition:
4.0 µg/mL Bromodichloromethane
4.0 µg/mL Dibromochloromethane
4.0 µg/mL Chloroform
4.0 µg/mL Bromoform

7.3.5 New standards should be checked against standard reference materials.

7.3.6 Standard solutions should be stored at 4°C.

7.3.7 Standards should be replaced after six months.

8. Sample Preparation

8.1 Weigh out several portions of approximately 0.28 g of sodium sulfate (one portion is required for each sample vial).

8.2 Place 1.2 mL of sample in a vial using a disposable glass pipette.The 1.2 mL are measured against other vials that have exactly 1.20 mL of water (measured using the Hamilton 1001 1000µL gas tight syringe). Pipette 10 µL of internal standard below the water level using the Hamilton 1710 100µL gas tight syringe. Add approximately 0.28 g of sodium sulfate and cap vial.

8.3 For the standard solutions, place 1.2 mL of water in a vial. Pipette the appropriate volume of 40.0µg/mL or 4.0 µg/mL standard solution below the water level using the Hamilton 701N 10µL gas tight syringe. Pipette 10 µL of internal standard below the water level using the Hamilton 1710 100µL gas tight syringe. Add approximately 0.28 g of sodium sulfate and cap vial.

9. Sample Clean-up

9.1 There is no sample cleanup required for this method.

10. Gas Chromatography

10.1 GC Operating Conditions:
(also see attached Saturn GC/MS method SATURN.MTH)

Column	DB-5 fused silica capillary column, 30m x 0.25mm, 0.25 µm film-thickness
Carrier gas	Helium at an inlet pressure of 20 psi with a flow rate of 1.05 mL/min at 35°C.
Injector temperature	250°C.
Transfer Line temperature	250°C.
Temperature program	Initial temperature 35°C, hold for 5 min increase at 5°C/min to 85°C, hold for 5 min

10.2 MS Operating Conditions
(see also attached Saturn GC/MS method SATURN.MTH)

Mass Range	50 to 300 m/z
Scan Time	1.000 s
Segment Length	19.80 min
Fil/Mul Delay	1.00 min

Peak Threshold	1 count
Mass Defect	100 mu/ 100u
Background Mass	45 m/z
Ion Mode	EI
Ion Preparation	None
Ion Control	Auto
Cal Gas	Off

Instrument is tuned as described in the Instrument Instruction Manual.

10.3 Calibrate the system prior to analysis.

10.4 The calibration standards must bracket the analyte concentrations found in the samples.

10.5 Instrument Setup

10.5.1 Check Air/Water Levels.
From the **Exec Page** in SATURN, Click on **Instr Control.** When Instrument Control display appears, click and hold on **Setup** in the menu bar and select **Check For Air/Water**. Continue with setup if both air and water levels are OK.

10.5.2 Create Analysis List.
From the **Exec Page,** click on **Analysis** to display the Analysis Program. Clear the old Analysis List of all but one entry by clicking on the **Del** box at the bottom of the screen.

Specify a new path for your new Analysis List. This indicates the disk drive and directory in which the datafile is stored. The path specified for THM analysis is C:\SATURN\THM2*date*\. To edit, highlight the first entry below the Datafile heading, and click and hold on **Util** in the menu bar and select **Change Entry Paths.**

Create a new Analysis List. For each entry in the Analysis List a unique data file name must be specified and sample information can be entered. Click in the first space below the Datafile heading in the lower half of the display. Then click on the **Edit** box to enter sample information and a data file name. To add more entries, click on the **Add** box at the bottom of the screen. Highlight each entry individually to edit sample information as previously done.

Create GC and MS Methods. The GC and MS methods have already been created. Verify that TEST_DB5 and DB5_TEST are displayed below the GC Method and MS Method headings, respectively.

Check Entries. Once the Analysis List is complete, you can determine whether your entry list is valid by clicking and holding on **Util** and selecting **Check All Entries**. An ERROR or WARNING message will appear if one or more entries are not valid (for example, if two entries have the same datafile name). If all entries in the Analysis List are OK, save it by clicking and holding on **File** in the menu bar and selecting **Save Analysis List**.

Data Acquisition. The Analysis Program is used to set up the instrument automatically for acquiring data. When the acquisition begins, the data files are acquired in order from the lowest to the highest selected entry.To initiate the acquisition sequence, highlight the first entry below the Datafile heading then pull down the **Control** menu in the Analysis Program and select **Start Autosampler Run**. A dialog box appears. Verify that the first and last entry correspond to the first and last entry in your Analysis List. Then click **OK** to start the Autosampler Run.

During this process, you will receive the following messages:
DOWNLOADING TO GC
(GC EQUILIBRATING)
(GC STABILIZING)
(GC EQUILIBRATED)
DOWNLOADING TO SATURN
PRESS SPACE BAR OR START GC TO BEGIN AQUISITION

After you receive the final message, go on to setup the AutoSampler system. Return to Windows by pressing the Windows button located on the keyboard. Then double click on the **Systems Control** icon.

10.5.3 Systems Control

Click and hold on **Instrument** in the menu bar. A display of four modules will appear. When the first module becomes highlighted, select **Varian 8200 #1**.When the AutoSampler is READY, click and hold on **File** in the menu bar and select **Method File** and **Open**. Select the **hs48_20.mth** method file. In the Method Editor, **Sections** is highlighted. Click on **1 8200 Stand-Alone AutoSampler-Module 28**. The following box will appear:

Carrousel Type: 48 vials
GC cycle time 30.00 min
SPME Mode
Absorb time 20.00 min
Desorb time 2.00 min
√ Sample Headspace

Exit from this and click and hold on **File** in the menu bar and select **Sample List File** and **Open**. Select the **thm_2mL.smp** sample list file. Delete the old Sample List by highlighting the entire list and clicking on the **Delete** box. To create a new Sample List, click on the **Carrousel** box and then on **Append**. Save the Sample List by clicking and holding on **File** and select **Save**. Close the Sample List box.

Click and hold on **File** in the menu bar and select **Method File** and **Activate**. Select the **hs48_20.mth** method file. Choose **Inject** samples, and **Reactivate** method. Close the activation box.

Click and hold on **File** in the menu bar and select **Sample List File** and **Activate**. Select the **thm_2mL.smp** sample list file. To start, click on the **Begin** box and then click on **OK** to verify the method (hs48_20.mth).

System Control will now inject all samples using the method chosen. To view modules, click and hold on **Windows** in the menu bar and select **Show Modules**.

11. Data Retrieval

11.1 From the **Exec Page** in SATURN, click on **File Manager**. Search for the appropriate path (C:\SATURN\THM2*date*\) and file using the ↑↓ and ← → arrow keys. To view the chromatogram of the selected (highlighted) file, press **ENTER** and **F2**. An option to change the chromatogram scan range (1-1187) will appear. Press **ENTER** after each choice.

11.2 To Set Chromatogram Display press **D**. This sets the scan range (1 - 1187) and selects a number of ions to view. Keep the scan range between 1 and 1187 by pressing **ENTER** twice. Then you have a choice of the # Chromatograms to Display. Press **4** (four groups of ions to view) and **ENTER**. A Chromatogram Plot Selection window will appear; enter the appropiate ions for analysis:

In the first block, press **S** and **ENTER**. This sums a group of ions. Type 85 and **ENTER**, then 87 and **ENTER** as the first set of ions to view. Press **ENTER** once again to move to the following block. Repeat for each set of ions.

Chromatogram #1

For CHLOROFORM and BROMODICHLOROMETHANE, the ions of interest are the Sum of ions **85 + 87**. The peak for Chloroform appears at scan number 105, while that of Bromodichloromethane shows up at scan number 165.

Chromatogram #2
For CHLORODIBROMOMETHANE, the ions of interest are the Sum of ions **127+129**. The peak for Chlorodibromomethane appears at scan number 308.

Chromatogram #3
For BROMOFORM, the ions of interest are the Sum of ions **171 + 173 + 175**. The peak for Bromoform appears at scan number 522.

Chromatogram #4
For DICHLOROBENZENE (Internal Standard), the ions of interest are the Sum of ions **150 + 152**. The peak for Dichlorobenzene appears at scan number 840.

11.3 Once the four chromatograms appear, press **F4** to normalize the plots. To switch between chromatograms press **END**. To integrate the peaks in each plot press **F8**; three numbers will be shown with each integrated peak - the first is the scan number, the second is the peak height, and the third is the peak area. Of most concern is peak area.
A manual integration may also be done by pressing **Q**. Select Quantitation Mode: **Manual/Automatic Peak Integration Routines**, and Integration Mode: **M-Manual Integration**. Move cursor to left side of peak and press space bar, then move cursor to right side of peak and press space bar to select points of integration.

11.4 Record all peak areas in the THM log book.

12. Calculations

12.1 Calibration curves are plotted for each trihalomethane using spreadsheet (Lotus 123; file: IS_REGRE.WK3). Each calibration standard is plotted as A_S/A_{IS} vs. M_S/M_{IS} where
A_S = Area of the standard
A_{IS} = Area of the internal standard
M_S = Mass of the standard
M_S = Mass of the internal standard = 1

The plot is a straight line with a correlation coefficient of at least 0.99. Five standards are used (in duplicate) to prepare the calibration curves, with the lowest standard of a value within ten times the detection limit.

12.2 The area of the internal standard is considered in the calculation to account for the percent recovery.

12.3 The output from the calibration is the mass (in ng) of the respective trihalomethane corrected for percent recovery.

12.4 The trihalomethane concentration in the water sample is then determined from the following equation:

$$\text{Concentration } (\mu g/L) = M_{(ng)} / V_{(mL)}$$

Where: $M_{(ng)}$ is the mass of the respective trihalomethane (in ng).
$V_{(mL)}$ is the total volume of the sample = 1.2 mL

12.5 Record all sample concentrations in the THM log book.

13. Quality Assurance/ Quality Control

13.1 A **procedural blank** is performed daily using deionized water. Results are rejected if the blank is greater than the detection limit.

13.2 A **standard reference material** is analyzed (in duplicate) with each run. ERA THM Reference 3221 is used. The concentration of reference material is determined from the calibration curve and results are rejected if the concentration does not fall within Performance Acceptance Limits.

13.3 A **duplicate analysis** should be performed at least once in every ten samples. Results are rejected (and analysis is repeated) if two numbers vary by greater than twenty percent.

14. References

14.1 "Determination of a Wide Range of Organic Impurities in Water with Automated Solid Phase Microextraction," Penton, Z., Varian GC Advantage Note 3.

14.2 "Standard Methods for the Examination of Water and Wastewater," Eaton, A.D., Clesceri, L.S., Greenberg, A.E.,19th ed., 1995.

WATER SAMPLING PROTOCOL
for
DISINFECTION BY-PRODUCTS (DBPs)

1. **Sampling kit requirements:**

1.1 - **thermometer**

1.2 - **portable pH meter**. (Optional)
[The meter should be freshly pre-calibrated; **DO NOT USE** pH strips, they have been found to be inaccurate in certain types of water]

1.3 - **portable colorimeter**. (If required - for Chlorine determination)

1.4 - **DPD pouches.** (for Chlorine [Free and Total] determination)

1.5 - **200 mL (tall type) glass beaker**

1.6 - **Ascorbic Acid Solution** (0.114M; 0.500mg/25mL purified water]

1.7 - **calibrated dropper**.
We have used a 2 mL disposable pipet (contains 0.01 calibration marks) cut & flame polished @ the ca 0.5 mL mark and a pipet Helper™ [Brinkmann]

1.8 - **Teflon wash bottle with purified water**

1.9 - **Laboratory paper tissue / towel**

1.10 - **Return Label**

1.11 - **Field data sheet**

1.12 - **Questionnaire**

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2. **Sampling Bottles / Vials**

2.1 - **DBPs** (semi-volatile DBPs, including THMs); 60 mL amber bottles/ white caps containing 1 mL of Buffer solution (pH 4.1).

2.2 - **HAAs** ; 25 mL amber vial containing sodium thiosulfate.

2.3 - **Aquapak** ; 250 mL polycarbonate bottles

2.4 - **TOC** ; 100 mL glass amber bottles

2.5 - **Bromide ion** ; 65 mL glass amber bottles/ black caps.

2.6 - **Xtra** ; 120 mL glass amber bottles (for in-house pH adjustment re HAAs/DBPs analysis).

3. SAMPLING PROTOCOL

3.1 RAW WATER [R] (Record sampling location)

3.1.1 - Allow water to be sampled to run freely into the supplied beaker until it has reached a constant temperature. Record temperature on field data sheet.

3.1.2 - If pH meter is available, determine pH of water and record on field data sheet.

3.1.3 - Add 0.2 mL Ascorbic Acid solution (0.114M) to the target **DBP** sampling bottles *[60 mL glass amber bottles containing 1mL buffer solution]*. Use the calibrated pipet and pipet Helper.

3.1.4 - Fill required (see **3.1.8**) sampling bottles/vials labelled **DBPs, HAAs, Aquapak and TOC** by running a **gentle stream** of water against the inside of the tilted bottle/vial **<u>just to overflow</u>** to prevent any headspace and/or dilution of the preservatives. Cap with Teflon-lined screw cap and mix. (Teflon side must face water sample; do not allow any air pocket)

3.1.5 - Fill Label information (see label example below for DBPs) as required, i.e., circle appropriate information. Do not fill in ID line (reserved for LAB). Use waterproof ink or cover label with transparent tape.

ID:▒▒▒▒▒▒ Date:_____

Site:_____ _____

Type: R T D1 D2 D3
Replicate: A B Anal: <u>DBPs</u>

3.1.6 - For bottles labelled **Xtra** and **Bromide ion**, fill bottles, discard and refill. (Requires rinsing prior to sampling)

3.1.8 - the required replicate are:

- **Semi-volatile DBPs (DBPs); 2X**
- **HaloAcetic Acids (HAAs); 3X**
- **Xtra ; 2X**
- **Aquapak series (AQPK); 2X**
- **Total organic carbon (TOC); 2X**
- **Bromide ion (BRI); 2X**

3.1.9 - As soon as possible after collection, store in cooler containing frozen ice-packs for shipment to Health Canada laboratories where the samples will be stored in a cold room.

3.2 TREATED WATER (@ plant)

3.2.1 - Repeat sampling requirements as described above (3.1) for water to be sampled for plant effluent treated **[T]** water.

3.2.2 - Determine the **residual chlorine (free and total)** and record on the data sheet.

3.2.3 - Fill, **in required replicates**, sampling bottles with **well flushed plant treated water** as above for raw water for all required parameters:

T

- **DBPs; 2x**
- **HAAs; 3X**
- **Xtra ; 2X**
- **Aquapak series; 2X**
- **TOC; 2X**
- **Bromide (BRI); 2X**

3.3 DISTRIBUTION SYSTEM WATER [D]

3.3.1 - With assistance of plant personnel, select and record on the DATA SHEET the distribution system sampling sites along a typical distribution line representing sites close to the treatment facility [D1; ca 1-2 km], mid - system [D2] and far - system site [D3; do not use a location known to be a dead-end]. Also record the approximate water residence time and/or distance from facility. ***[A repeat of the survey will be conducted for the cold water months, i.e., January - March 2000]***

3.3.2 - At each distribution system sampling sites **[D1; D2 and D3]** repeat sampling requirements as described for plant effluent treated **[T]** water. (Determination of residual chlorine required)

3.3.3 - Determine the **residual chlorine (free and total)** and record on the data sheet.

3.3.4 - Fill, **in required replicates**, sampling bottles with **well flushed distribution system water** as above for treated water for all required parameters:

D1, D2, D3	**- DBPs;**	**2x**
	- HAAs;	**3X**

4. SHIPPING PROTOCOL

4.1 Pack shipping cooler as required to prevent bottle breakage / leakage and to maintain cool conditions:

4.1.1 - void space should be filled with packing / adsorbent paper

4.1.2 - insert sample boxes into supplied zip-lok bag and seal to prevent water damage

4.1.3 - make sure cold packs are completely frozen (If thawed, ice bags may be used but must be double plastic bagged to prevent water leakage; will supply bags)

4.2 - Ship the water samples the same day as collected [overnight express - PUROLATOR/FEDEX] to Health Canada for analysis.

The sample kit should reach the laboratory within 48 hours of sampling.

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DO NOT ALLOW SAMPLES to FREEZE during transport [WINTER]

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Water Disinfection By-Products (DBPs) DATA SHEET

SAMPLE ID: _____ DATE: _____

SITE: _____

SAMPLING LOCATIONS:

Raw [R] _____

Treated [T] _____

Distribution [D1] _____

Distribution [D2] _____

Distribution [D3] _____

Water Type	R	T	D1	D2	D3
Temp. (°C)					
pH					
Chlorine (free)					
Chlorine (total)					
Distance (km)					

COMMENTS / OBSERVATION:

Limited Survey of Chlorinated Disinfection By-Products (CDBPs) in Drinking Water from Canadian towns using Small Systems.

As part of continuing studies on disinfection by-products in Canadian drinking water, Health Canada is conducting a survey of CDBPs in water from towns using small systems. The study will target mainly areas where data gap has been identified as part a CDBP task group - water quality issues data gathering on Canadian water treatment facilities and on DBPs data, particularly the trihalomethanes (THMs). A previous Health Canada DBP survey (1993) targetted larger facilities. The parameters monitored in the 1993 survey will be monitored in this study. This will include the THMs, HAAs, HANs, haloketones, chloral hydrate, etc. in addition to auxiliary parameters (TOC, bromide ion, alkalinity, residual chlorine, etc.). The THMs will be analysed as part of a liquid-liquid extraction technique modified to include cyanogen chloride and chloral hydrate in addition to the other semi-volatile DBPs including THMs, HANs, haloketones and chloropicrin. The survey will be conducted during the warm water season (August - September 1999) and cold water season (January- March 2000). The water samples will be collected from five locations (Raw [R], treatment plant [T], near [D1], mid-system [D2] and end-of-line [D3]). The study will provide comprehensive DBP data in water from small facilities.

Sampling protocol for Disinfection By-products (DBPs) and other auxiliary parameters

The sampling of water samples for the analysis of DBPs requires specific protocols in order to obtain quality data. Each group of DBPs will require a specific set of preservative / additive targetted to the analytical protocol. For this study, in order to facilitate the sampling requirements, the pH adjustment of water samples for analysis of semi-volatile DBPs will be done by addition of a buffer solution. Also, field determination of residual chlorine (free and total) will be required.

Since the samples need to be delivered to Health Canada's laboratory (Ottawa) within 48 hours of sampling, access to shipping locations should be considered for the selection of target sites. Also, sampling should be done during the early part of the week (Monday - Wednesday) to allow delivery of samples and analysis of DBP target analytes in a timely manner (same week).

THM SAMPLING

(FIELD SHEET)

TOWN _____

SITE #1

LOCATION _____

DATE _____ TIME _____

TEMP _____ FREE CHLORINE _____

REMARKS _____

SITE #2

LOCATION _____

DATE _____ TIME _____

TEMP _____ FREE CHLORINE _____

REMARKS _____

SITE #3

LOCATION _____

DATE _____ TIME _____

TEMP _____ FREE CHLORINE _____

REMARKS _____