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USE OF THMFP, TOC AND CHLORINE DEMAND AS
CONTROL PARAMETERS FOR MONITORING THE
PERFORMANCE OF AN OZONATION/FBT SYSTEM

presented by

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Susan J. Masten
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# USE OF THMFP, TOC AND CHLORINE DEMAND AS CONTROL PARAMETERS FOR MONITORING THE PERFORMANCE OF AN OZONATION /FBT SYSTEM

By

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# ABSTRACT

## USE OF THMFP, TOC AND CHLORINE DEMAND AS CONTROL PARAMETERS FOR MONITORING THE PERFORMANCE OF AN OZONATION /FBT SYSTEM

By

**Ajay N. Kasarabada**

The presence of humic substances in drinking water is problematic due to the formation of trihalomethanes ie., chloroform, bromoform, bromodichloromethane, and dibromochloromethane and other by-products during disinfection with chlorine. Most of these disinfection by-products (DBPs) are either carcinogenic or potentially carcinogenic. Since conventional processes, such as coagulation, may not meet proposed U.S. EPA requirements on DBPs, alternate treatment technologies must be investigated.

The purpose of this work was to study the ozonation/ fluidized bed treatment system for the removal of trihalomethane precursors. The performance of this system was monitored by studying THMFP, TOC and chlorine demand and investigating if there exists any correlation between them. Analytical procedures to measure these parameters were also studied.

# ACKNOWLEDGMENTS

This happens to be a day when a dream turned into reality. I would like to take this opportunity to thank all those who helped me make this dream come true. I am most grateful to Alex Yavich without whom this work wouldn't have materialized. He was my guiding light. I am also grateful to my major advisor Dr. Susan Masten for her helpful ideas and suggestions during the course of this research work. From Thanksgiving Dinner to WERC projects, she made me feel at home and school at the same time. Thanks Dr. Masten for providing me funding for this research work and shaping me up to become a good environmental engineer.

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I would like to thank my parents for providing me all the tools to take on the "real world" and to be successful. I am grateful for your encouragement. Armed with your blessings, I am sure I will do well in my future endeavors. Thanks a lot Amma and Nannagaru.

***"A Winner Never Quits***
***A Quitter Never Wins"***

Ajay Kasarabada
August 20, 1997.

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# KEY TO SYMBOLS

| | |
|---|---|
| USEPA | UNITED STATES ENVIRONMENTAL PROTECTION AGENCY |
| SDWA | NEW SAFE DRINKING WATER ACT |
| DBP | DISNINFECTION BY-PRODUCTS |
| THM | TRIHALOMETHANES |
| THMFP | TRIHALOMETHANE FORMATION POTENTIAL |
| TOC | TOTAL ORGANIC CARBON |
| GC | GAS CHROMATOGRAPH(Y) |
| ECD | ELECTRON CAPTURE DETECTOR |
| ELCD | ELOCTROLYTIC CONDUCTIVITY DETECTOR |
| LLE | LIQUID LIQUID EXTRACTION |
| ICV | INSTRUMENTATION CALIBRATION VERIFICATION |
| QC | QUALITY CONTROL |
| HPLC | HIGH PRESSURE LIQUID CHROMATOGRAPH(Y) |
| PFBOA | PENTA FLUORO BENZOYL HYDROXYL AMINE |
| FBT | FLUIDIZED BED TREATMENT |
| FBR | FLUIDIZED BED REACTOR |
| HS | HEAD SPACE |

| | |
|---|---|
| C.I. | CONFIDENCE INTERVAL |
| EBCT | EMPTY BED CONTACT TIME |
| GC HS | HEAD SPACE GAS CHROMATOGRAPHY |
| GCECD | GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTOR |
| GCELCD | GAS CHROMATOGRAPHY WITH ELECTROLYTIC CONDUCTIVITY DETECTOR |
| HAA | HALO ACETIC ACID |
| LOQ | LIMIT OF QUANTITATION |
| DL | DETECTION LIMIT |
| RT | RETENTION TIME |
| PPB | PARTS PER BILLION |
| RD | RESIDUAL CHLORINE |
| $RD_0$ | RESIDUAL CHLORINE (INITIAL) |
| CD | CHLORINE DEMAND |
| $S_t$ | STRENGTH OF CHLORINE SOLUTION |
| $S_D$ | STRENGTH OF CHLORINE DOSING SOLUTION |
| DCA | DI-CHLORO ACETIC ACID |
| TCA | TRI-CHLORO ACETIC ACID |

# CHAPTER 1

# INTRODUCTION

The presence of humic substances in drinking water is problematic due to the formation of trihalomethanes ie., chloroform, bromoform, bromodichloromethane, and dibromochloromethane, and other by-products during disinfection with chlorine. Most of these disinfection by-products (DBPs) are either carcinogenic or potentially carcinogenic. This is a considerable cause for concern and therefore these by-products are increasingly regulated by the U.S. Environmental Protection Agency (U.S. EPA). A significant portion of the water treatment industry will face technical and fiscal hurdles in meeting the DBPs (disinfection by-products) requirements in the New Safe Drinking Water Act (SDWA) reauthorization (US. EPA, 1993). Since conventional processes, such as coagulation, may not meet proposed U.S. EPA requirements on DBPs, alternate treatment technologies must be investigated.

In the United States, chlorination is used as the principal technology for the disinfection of drinking water because of residual chlorine requirements. Concern relating to the formation of trihalomethanes (THMs) and other DBPs has generated increasing interest for using ozone as a primary disinfectant. In Europe ozone has been used for treatment of drinking water for approximately 100 years. The ability of ozone to disinfect polluted surface waters resulted in the first full scale application of the technology for treatment of drinking water in 1893 at Oudshoorn in Netherlands (Brink, Langlais, and Reckhow, 1991). Since that time, ozonation has become a major treatment technology for the disinfection of drinking water throughout Europe.

Lately there has been an increased interest in the United States in the use of ozone as a drinking water disinfectant. In 1990, some 40 drinking water plants in the US were using ozone for primary disinfection and chlorination to provide protection in the distribution system (Brink, Langlais, and Reckhow, 1991). Because of its oxidizing powers, ozone is not only a strong disinfectant but is also able to oxidize natural organic matter which serves as a precursor in the formation of DBPs. Some decrease in the formation of halogenated DBPs has been observed when ozonation precedes chlorination (Shukiary and Summers, 1992). However, ozonation creates by-products of its own, which not only carry with them a new set of health concerns, but which increase bacterial growth in drinking water distribution systems. These nutrients increase the potential of microbial regrowth in the distribution system. It often becomes necessary to stabilize the water by allowing some bioactivity which biodegrades these ozonated by-products. (Van Der Kooij et al., 1982).

This research work is part of a larger project in which an ozonation/biodegradation recirculation treatment process is being investigated for the removal of THMs and other DBP precursors from drinking water. The ultimate goal of the whole project is to develop a reliable cost effective process which can be used in both small and large drinking water treatment facilities.

The specific objectives of this study are:

1. To investigate analytical methods to estimate trihalomethane formation potential in drinking water. The analytical methods that were studied for measuring THMFP were headspace gas chromatography with electron capture/electrolytic conductivity detectors and liquid liquid extraction with pentane.
2. To compare headspace and liquid liquid extraction methods for THM analysis and investigate whether heating during the headspace analysis contributes to the formation of THMs.
3. To monitor the performance of an ozonation/fluidized bed treatment system by studying chlorine demand, THMFP, TOC and ozone dosage and to explore the possibility of a correlation between them

# CHAPTER 2

# THEORY OF THM FORMATION, CHLORINE AND OZONE INTERACTIONS

## LIERATURE REVIEW

Inspite of its great diversity, the organic matrix of surface waters is composed mostly of fulvic and humic substances whose structures, although still not clearly defined, have been represented by a general idealized formula (Doré, et al ., 1987).

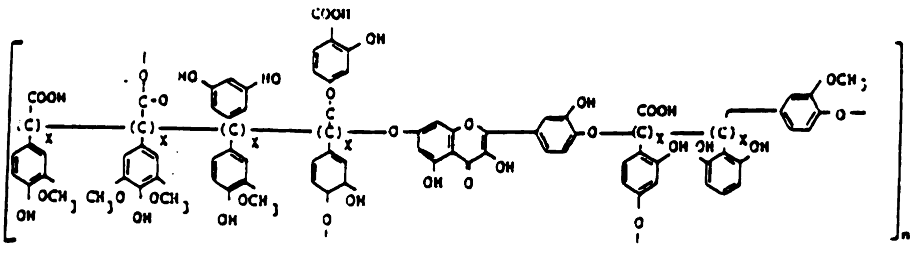


Figure. 1 Structure of Humic Acid

It is generally admitted that this type of structure can lead to the formation of THMs and non-volatile organochlorinated compounds during the chlorination of surface waters. It has been found that DBPs can be formed as a result of two phenomena (Doré, et al ., 1987):

1. An oxidizing action connected with the oxidation reduction potential of the HOCl/Cl$^-$ couple or ;
2. Addition or substitution reactions leading to the organochlorinated compounds:

The direct action of addition and substitution reactions by chlorine proceeds partly through electrophilic attack by oxidizing agents on sites having strong densities of electronic charges. As shown in Figure 2 and Figure 3, the main reactions that are believed to occur during the course of chlorination are: substitution reactions on the ring or on the aliphatic parts of the organic molecule; oxidation reactions which can be coupled to substitution; hydroxylation reactions and decarboxylation reactions.

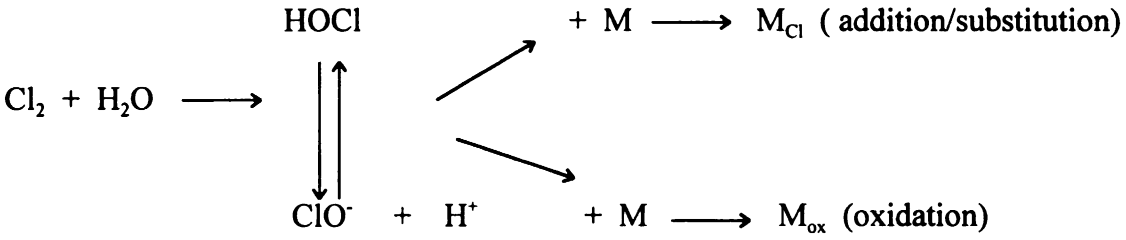


Figure 2. Reactions of chlorine in drinking water.

All the above reactions can lead to the formation of non-chlorinated compounds and aromatic and aliphatic chlorinated compounds characterized as total organic chlorine. The aliphatic organochlorinated compounds that are normally formed are THMs and haloacetic acids (HAAs). Non-volatile organochlorinated compounds include dichloro- and tri-chloroacetic acids (DCA and TCA). It has also been found that the modes of initial attack of chlorine and ozone on humic substance molecule are similar except for two fundamental differences (Doré., et al. 1987): the first being the substitution reactions lead in one case to hydroxylation and in the other case to chlorination; the second difference being the degradation of the humic substance molecule in terms of

TOC has been found to be much more significant with ozonation than with chlorine. The following figures shows the importance of the reactions that lead to the formation of THMs (Doré et al. 1987).

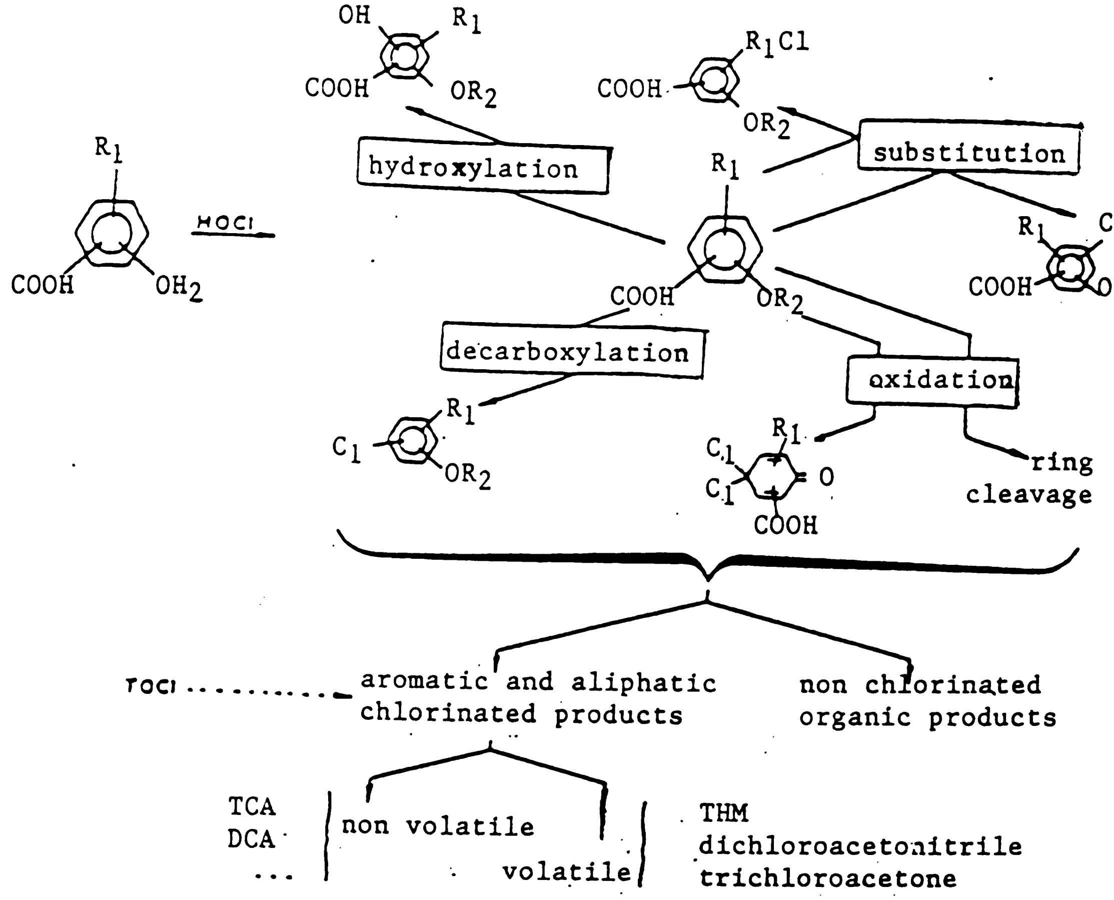


Figure 3 Summary of possible reactions of chlorine with aromatic compounds.

Doré et al. (1987) have found that over a 72 hour period contact time, the slopes of the curves of THMs' concentrations vs. chlorine dose are low for low chlorine doses (in particular for chloroform) and higher for higher chlorine doses. Doré et al. (1987) also showed that production of chloroform is very fast during the first few minutes of reaction followed by a much slower rate of formation of chloroform. They also showed that formation of THMs continued to increase even after 400 hours. This phenomenon is believed to result from the existence of at least two different types of reaction sites for chlorine: one very reactive and the other less reactive.

As a consequence of these phenomena the definition of chlorine demand becomes hypothetical. According to the Standard Methods for Examination of Water and Wastewater (1995), chlorine demand is an empirical quantity defined as:

$CD = RD_0 - RD$, where, $RD_0$ is initial residual chlorine concentration ( ~ 100 mg/L) and RD is residual chlorine in the sample after at least four hours of storage. In most water supplies, THMFP is expected to be related to chlorine demand because chlorine demand is due to the presence of organic compounds which when they react with chlorine they form THMs. Therefore, a very wide fluctuation in THMFP can be expected depending on the nature of the source water.

Although bromate formation is not relevant to this research work, it is necessary to understand the theory of bromate formation since the source water used in this project is the Huron River, Ann Arbor, MI, which contains considerable amounts of the bromide ion. Since in this research work, ozonated water is being chlorinated to measure THMFP, it is necessary to study the effect of ozonation on the formation of organohalogenated compounds. It is well known that ozone is very reactive with bromide ions (Hoigñe and Haag, 1983). It has been shown that the first phase of the reaction of ozone with bromide ions leads to the formation of hypobromous acid or hypobromite ion, depending on the pH of the medium: ( Figure 4)

$$2Br^- \xrightarrow{O_3} Br_2$$

$$Br_2 + H_2O \longleftrightarrow HOBr + Br^-$$

$$HOBR + H_2O \longleftrightarrow BrO^- + H_3O^+$$

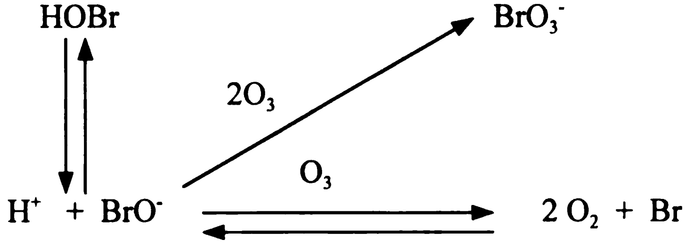


Figure 4. Reaction of ozone with aqueous bromine species.

In the presence of excess ozone, hypobromite ions react with ozone to form bromate or bromide ions, whose rate constants were established by Haag and Hoigñe ( 1983 ). Parallel to the action of ozone on bromide ions and on the various brominated species, ozone reacts with organic matter, and in particular on THM precursors as shown in the Figure 5.

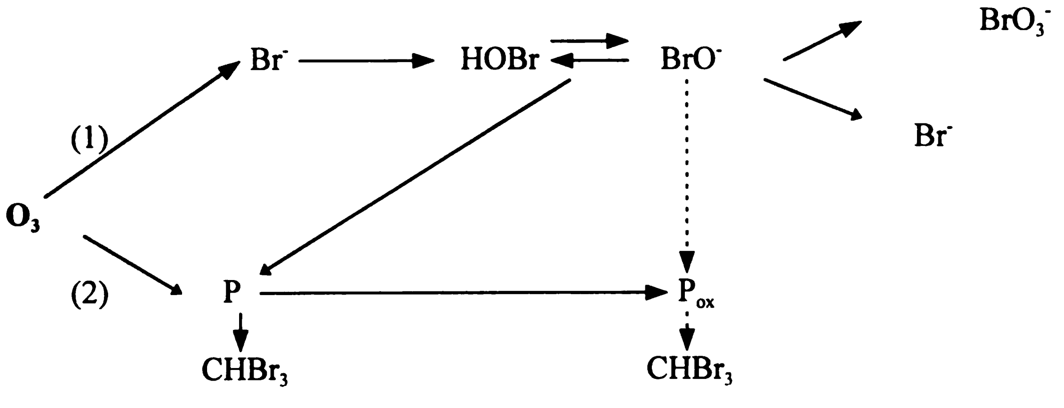


Figure 5. Reaction of Ozone with bromide ions and THM precursors.

If the rate of reaction 2 (precursor oxidation) is fast compared to the formation rates of hypobromous acid or of bromoform, the precursors will be degraded rapidly by ozone, and bromoform formation in the medium will not occur. On the contrary, if the rate of precursor degradation is slow, bromoform formation will occur during ozonation.

# CHAPTER 3

# MATERIALS AND METHODS

## 3.1 ESTIMATION OF CHLORINE DEMAND FOR DETERMINING THMFP

The description of this method provides the conditions and amount of chemicals and volumes of aqueous samples required for measuring chlorine demand. The samples are then dosed with 20 % excess chlorine so as to measure THMFP.

### 3.1.1 REAGENTS AND CHEMICALS

**Volumetric Standard.** A 0.1N sodium thiosulfate volumetric standard was procured from Supelco Inc (Bellefonte, PA). A titration standard of 0.01N was made from the volumetric standard by diluting it with ultrapure water.

**Reagents.** .A hypochlorite standard solution was procured from Supelco Inc. Potassium iodide crystals were obtained from Baxter Corporation (Muskegon, MI). Phosphate buffer (pH. 7.0) was obtained from Supelco Inc (Bellefonte PA).

**Reagent Water.** Ultrapure water was prepared in-house by employing the ultra-pure water system (Technic Central Systems, Seattle WN). Ultrapure water was used as chlorine demand free water.

## 3.1.2. APPARATUS

**Glassware.** Sampling bottles (125 mL) with Teflon® lined screw caps, volumetric standard flasks (250 mL), glass pipettes (10 mL), and Erlenmeyer flasks (125 mL) were used.

## 3.1.3. PROCEDURE: STANDARD IODIDE METHOD

**Summary**. The procedure involved two steps. A chlorine dosing solution ( 5 mg/mL) was prepared in the first step. Aqueous samples (125 mL) were then dosed with 20 % excess chlorine and incubated for 4 hours. The residual chlorine was determined in the second step.

**Details.** Two milliliters of sodium hypochlorite solution were diluted to 25mL with ultrapure water. This sample was then acidified with 2.5 mL of acetic acid and approximately 1g of KI was added. The solution turned brown. This solution was titrated against the 0.1 N sodium thiosulfate volumetric standard and when it turned light yellow a few drops of starch solution were added. The solution would then change to dark brown in color. Titration was continued until the solution turned colorless. The strength of the chlorine solution mg/mL is determined as : $S_t$ = (1)

$$\frac{(\text{Vol. of Sodium thiosulfate}) \times 35.45 \times (\text{Strength of sodium thiosulfate})}{2}$$

**Preparation of Chlorine Dosing Solution.** The chlorine dosing solution of 5 mg/mL ( Strength $S_D$ ) was prepared by diluting 1250/($S_t$) mL, to 250 mL in a standard flask. This dosing solution was refrigerated and used for a maximum of three weeks.

**Residual Chlorine Estimation.** A volume of 2.5 mL of chlorine dosing solution was transferred into a 125 mL bottle. It was filled up to the neck with ultra-pure water and closed with a screw cap. The bottle was shaken vigorously and then filled to the brim with water. An aliquot (50 mL) of sample was removed and was immediately analyzed for chlorine residual using the standard iodide method by titrating against 0.01N thiosulfate. The chlorine residual was around 100 mg/L is referred to as $RD_0$.

A volume of 2.5 mL of the chlorine dosing solution was then transferred into a 125 mL sampling bottle. A volume (2.5) mL of phosphate buffer was added. The bottle was filled to the neck with aqueous sample and capped. Its was then shaken vigorously. The bottle was then completely filled with the sample and left in a dark place for 4 hours at room temperature.

After 4 hours, the residual chlorine was determined by titrating 50 mL of sample with 0.01 N sodium thiosulfate by the standard iodide method. The residual chlorine (RD) in mg/L was then determined using equation 2:

$$\frac{(\text{Vol. of Thiosulfate}) \text{ x } 35.45 \text{ x } (\text{Strength of Thiosulfate}) \text{ x } 1000}{50} \qquad (2)$$

Chlorine demand (CD) in mg/L was then determined as:

$$CD = RD_0 - RD \qquad (3)$$

**Determination of THMFP.** The appropriate dosages of the chlorine dosing solution are determined for each sample. The chlorine dose in mL was then calculated as:

$$\frac{1.2 \times CD}{8 \times S_D}$$

This volume of the chlorine dosing solution was transferred into a 125 mL sample bottle and 2.5 mL of phosphate buffer (pH 7.0) was added. The bottle was then filled with the sample until the water level reached the base of the neck of the bottle. It was then shaken vigorously and sample water was added until there was no headspace in the bottle. The sample was kept in the dark at room temperature for 7 days. After seven days the sample was analyzed for THMs using the headspace GC method.

## 3.2. TRIHALOMETHANES (CHLORINATED VOLATILE ORGANICS) BY STATIC HEADSPACE SAMPLING AND GAS CHROMATOGRAPHY.

This method has been used to quantitatively analyze for the following compounds in aqueous samples: a) chloroform b) bromodichloromethane c) dibromochloromethane d) bromoform.

### 3.2.1 REAGENTS

A trihalomethane standard solution mix (100 mg/L) was obtained from Supelco Inc (Bellefonte PA). Ultrapure water was obtained from the Lab Five Ultrapure Water

System (Technic Central Systems, Seattle WA). Huron River water was taken from the inflow to the water treatment facility at Ann Arbor, Michigan. The water was filtered to remove suspended matter and stored at 5 °C. Tap water was collected from the East Lansing Municipal Water Treatment Plant.

### 3.2.2 APPARATUS

Two HS 40 automated head space samplers (Perkin Elmer Corporation, Norwalk, CT) interfaced with a Model 8700 Autosystem gas chromatographs (Perkin Elmer Corp. Norwalk, CT) were used. One of the gas chromatographs was equipped with a $^{63}$Ni electron capture detector (ECD) while the other was equipped with the Model 1000, Perkin Elmer electrolytic conductivity detector ( ELCD or Hall detector). The separation and operating conditions for the two methods are given below:

**HS40-GC-ECD:** During the initial phases of the project the column used was a DB 624 (J. W. Scientific Co., Folsom CA). The column used later was a 105 m, 0.53 mm I.D. MXT-502.2 column (Restek Corp. Bellefonte, PA) with a film thickness of 3µm df . The liquid phase was cross bonded phenylmethyl polysiloxane. Nitrogen was used as the carrier gas.

The head space auto sampler conditions were: Sample Temperature: 90° C; Needle Temperature: 120 °C; Transfer Line Temperature: 120 °C; GC Cycle Time: 20 min; Thermostat Time: 17 min; Pressurization time: 1.0 min; Inject time: 0.20 min.; Withdrawal time: 0.2 min; Carrier Gas Pressure: 300 kPa; Sample volume: 5 mL.

The GC conditions were: Instrument: AutoSys B; Detector B: ECD; Detector Temperature: 350 °C; Oven Equilibration time: 2.00 min; Maximum. oven temp: 350 °C , Cryogenic focusing off; Injector temperature: 200 °C; Column Head Pressure: 16 psi; Column temperature program: 80 °C hold 0 min, 10 °C /min 165 °C hold 0 min. ECD Attenuation: 0; ECD Range: 1 Auto Zero: ON ; Carrier Flow: 10 mL/min
Sampling Rate: 1.5625/min, offset: 5.0.

**HS40-GC-ELCD**: The auto sampler, GC oven and data acquisition conditions were identical to the GCECD. The differences between the two procedures were:

A column 30 m x 0.53 mm DB-624 column (J & W Scientific, Folsom, CA) was used. The temperature program was 90 °C , 10 °C/min to 180 °C (held for 0 minutes). Carrier gas used was nitrogen (10 mL/min). Injector: the sample temperature was 90 °C, the needle temperature was 120 °C, transfer line temperature was 120 °C ; Detector temperature was 350 °C .

Standard 22 mL head space vials (Alltech Company, Milwaukee,WI), TFE lined silicone septa (National Scientific Company, Lawrenceville, GA) and Hamilton syringes (25μL, 100μL, and 250μL) were used.

### 3.2.3 STANDARDS AND SAMPLES

Standards of 50, 100, 150, 200, 300, 400, 500 μg/L of total THMs were prepared in ultrapure water. The ultrapure water did not contain any measurable quantities of THMs. The calibration standard used was an EPA approved THM calibration standard prepared in methanol (Supelco Inc; Bellefonte PA). The standard was refrigerated and kept for no more than two weeks. All analyses were conducted in triplicate. The standard solutions were prepared by spiking THM-free water with THM calibration standard.

The accuracy and precision of the calibration data was assessed by running instrument calibration verification standards (ICV). The samples were also spiked with 20 μg/L and 80 μg/L of THMs to investigate the presence of any matrix interference in the samples.

**Sample Introduction**. Samples were introduced into the column via a heated capillary transfer line from a static head space auto sampler. The auto sampler was equipped with a forty sample carousel and samples were held at ambient temperature.

**Sample collection, preservation and handling.** Water samples from the pilot plant (Chapter 4 describes the pilot plant and the apparatus used in the facility) were chlorinated and kept in dark at 25° C for seven days in headspace-free 125 mL bottles. After the seven day period the samples were transferred into 20 mL headspace vials and immediately prepared for analysis using the headspace GC-ECD method. Four drops of sodium sulfite solution (1N) were added to destroy any excess chlorine. During the initial phase of the experiments the sample volumes used were 10 mL. The sample volume used in the latter phase of the project was 5 mL.

**Data Acquisition and Analysis.** A Windows® based chromatographic data acquisition system, PE-Nelson Turbochrom 4.1® was used. The system was interfaced to the GC via a Perkin Elmer 900-series interface A/D link box, to provide for the continuous storage of raw chromatograms in a personal computer, for subsequent off-line batch analysis.

**Calibration.** Five standards containing the four THM compounds were used in generating the calibration curves. The concentrations of the standards ranged from 10 μg/L to 200 μg/L. Linear regression techniques with the regression line forced through the origin were used to calculate the slope of the calibration curves.

### 3.2.4 QUALITY ASSURANCE AND QUALITY CONTROL

Laboratory blanks were analyzed at the beginning of each run, followed by two calibration check standards to ensure the accuracy/precision of the GC system. Headspace vials with 5 mL of reagent water were used for blank analysis. QC acceptance criteria ( ± 20%) were established for the response of check standards. If acceptance criteria were not met, a new calibration plot was generated.

## 3.3 TRIHALOMETHANES BY LIQUID-LIQUID EXTRACTION GAS CHROMATOGRAPHIC METHOD

This method has been used to quantitatively analyze for the following compounds in aqueous samples: a) chloroform b) bromodichloromethane c) dibromochloromethane d) bromoform.

### 3.3.1 REAGENTS

A trihalomethane standard solution mix (100 mg/L) was obtained from Supelco Inc (Bellefonte PA). Ultrapure water was obtained from the Lab Five Ultrapure Water System (Technic Central Systems, Seattle WA). Huron River water was taken from the inflow to the water treatment facility at Ann Arbor, Michigan. The water was filtered to remove suspended matter and stored at 5 °C. Tap water was collected from the East Lansing Municipal Water Treatment Plant. Pentane was obtained from Baxter Inc., (Muskegon, MI).

### 3.3.2 APPARATUS

A Hewlett Packard 5890A gas chromatograph equipped with a $^{63}$Ni electron capture detector (ECD) was used. The separation and operating conditions were:

**HP 5890A-GC-ECD:** A 30m, 0.53 mm I.D. DB-624 (J and W Scientific, Folsom California) column was used.

The GC conditions were: Detector B: ECD ; detector temperature was 350 °C; oven equilibration time was 2.00 min; maximum oven temperature was 350 °C , Cryo off; Injector B temperature was 200 °C; column head pressure was 16 psi; carrier gas used was nitrogen; column temperature program: 90 °C hold 0 min, 10 °C /min 120 °C hold 0 min. carrier flow: 10 mL/min.

### 3.3.3 STANDARDS AND SAMPLES

Standards of 50, 100, 150, 200, 300, 400, 500 µg/L of total THMs were prepared in ultrapure wate and in pentane. The ultrapure water did not contain any THMs. The calibration standard used was an EPA approved THM calibration standard in methanol. It was refrigerated and kept for no more than two weeks. All analyses were conducted in triplicate. The standard solutions were prepared by spiking THM-free water with the THM calibration standard.

The accuracy and precision of the calibration data was assessed by running instrument calibration verification standards (ICV). The samples were also spiked with 20 µg/L and 80 µg/L of THMs to investigate the presence of any interference in the samples.

**Sample Introduction**. Samples were manually injected into the GC column. A modified syringe with a plunger support was used to facilitate accurate injection.

**Sample collection, preservation and handling.** Water samples from the pilot plant were chlorinated and kept in dark at 25° C for seven days in headspace-free 125 mL bottles. After the seven day period the samples were transferred into 40 mL screw cap vials and immediately taken for liquid extraction with pentane. Four drops of 1N sodium sulfite solution were added to destroy excess chlorine. A sample volume of 5 mL was used.

**Data Acquisition and Analysis.** A Hewlett Packard Integrator was used for acquiring data from the run.

**Calibration.** Four standards containing the four THM compounds were used to generate the calibration curves. The concentration of the standards ranged from 10µg/L to 200µg/L. Response/ng was plotted against concentration to generate a linear regression fit.

### 3.3.4 PROCEDURE

Chlorinated volatile organics in the aqueous phase can easily be extracted using pentane as an extraction solvent. Aliquots (5mL) of samples were pipetted into a 40 mL screw cap vial. Four drops of 1N sodium sulfite solution were added to destroy any residual chlorine. Two (2) mL of pentane were then transferred to each vial. The vials were then shaken vigorously and allowed to stand for 5 minutes to facilitate phase separation. The pentane extract was removed using a Pasteur pipette and transferred to a 1.8 mL vial. Three (3) µL of extract was manually injected into the column. In order to determine the percentage recovery of each of the THMs, identical masses of THMs were injected into the GC by both direct injection (standards prepared in pentane) and pentane extraction (aqueous standards). The standards were first made in DI water, and THMs extracted using pentane. The mass of THMs in 2 mL of pentane extract was then determined and samples were prepared in pentane directly so that identical amounts of THMs are injected into the GC.

### 3.3.5 QUALITY ASSURANCE AND QUALITY CONTROL

Laboratory blanks were analyzed at the beginning of each run, followed by two levels of standards to ensure the integrity of the GC system. Vials with 5 mL reagent water were used for blank analysis. QC acceptance criteria ( ± 20%) were established for the response of check standards. If acceptance criteria were not met, a new calibration plot was generated.

## 3.4 ALDEHYDES IN AQUEOUS SAMPLES BY- LIQUID EXTRACTION GCECD ANALYSIS

This method has been used to quantitatively analyze for formaldehyde and methyl glyoxal in aqueous samples.

### 3.4.1 REAGENTS

**3.4.2 Stock Standards.** Methanolic stock solutions are procured from Supelco Inc, Bellefonte, PA.

**Aqueous Calibration Standards.** These are prepared in HPLC grade water ( J.T Baker Inc., Phillipsburgh, NJ) on the day of analysis.

**Reagent Water.** HPLC grade water was used as reagent water.

### 3.4.1. APPARATUS AND MATERIALS

**Gas Chromatograph.** A Perkin Elmer Autosystem GC with a Ni-63 Electron capture detector was used for this analysis.

**Column.** A 60 m, 0.53 mm I.D. DB-5 column ( JW Scientific, Folsom CA) and 3um df was used.

The GC conditions were: Instrument: AutoSys B; detector A: ECD; detector temperature was 300 °C; oven equilibration time was 2.00 min; maximum oven temp was 350 °C , Cryogenic focusing off; injector A temperature was 180 ° C; column head pressure was 14 psi; injection volume was 3μL. Column temperature program: 50 ° C hold 1 min, 4 ° C /min to 220 °C hold 0 min. and 20 °C/min to 250 °C, hold for 0 min; ECD Attenuation: 0; ECD Range: 1 Auto Zero: ON ; Carrier Flow: 2 mL/min Sampling Rate: 1.5625/min, offset: 5.0.

**Sample Introduction**. Samples were kept in a carousel on the GC and held at ambient temperature. An automated injection needle directly injected the sample into the column.

**Glassware.** 1.8 mL crimp top sampler vials with Teflon® coated septa were used.

**Microsyringes.** Gas tight Hamilton 10, 25, 50, 100 and 250 μL syringes were used.

**Sample collection, preservation and handling**. Water samples from the pilot plant were collected in 40 mL vials and were analyzed for aldehydes on the same day.

### 3.4.2 PROCEDURE

Aldehydes in aqueous samples cannot be determined by a direct injection. Therefore a derivitization technique was used ( Harumi Yamada, et al. 1989). PFBOA, O-2,3,4,5,6-pentafluorobenzyl hydroxylamine, was used as a derivitization agent. Ten (10) mL of aqueous samples were taken in 40 mL vials. A PFBOA solution of 1 mg/mL strength was made up and 1 mL was added to each of the sample vials. The vials were shaken well and kept for two hours for the derivatization reactions to occur. After two hours the derivatization was stopped by adding three drops of 18 N sulfuric acid. The derivitized aldehydes were then extracted using hexane (2 mL) as the extraction solvent. The vials were shaken vigorously and allowed to stand for five minutes to facilitate phase separation. The hexane layer was then transferred using a Pasteur pipette to a 1.8 mL vial and taken for GCECD analysis.

**Data Acquisition and Analysis.** A Windows® based chromatographic data acquisition system, PE-Nelson Turbochrom 4.1® was used. The system was interfaced to the GC via a 900-series interface A/D link box, to provide for the continuous storage of raw chromatograms in a personal computer, for subsequent off-line batch analysis.

## PREPARATION OF CLEAN GLASSWARE

All chlorine demand and organic free glassware were prepared by soaking the glassware overnight in a cleaning solution (soap). The glassware was rinsed 3 times with deionized water and 3 times with ultrapure water. The glassware was then placed in a 105 °C oven for 12 hours. Blank samples were run regularly to check for contamination.

# CHAPTER 4

## EXPERIMENTAL SYSTEM

### OZONATION/FBT SYSTEM.

A schematic of the experimental ozonation/FBT system is shown in Figure 5. The column sizes and operating conditions are summarized in Table 1. The system included an ozone generator, a mass flow controller, an ozone destruction unit, an ozone contactor, a retention tank, and a FBT column.

Ozone was generated from pure, dry oxygen using an Ozotech Model OZ1PCS/V ozone generator (Ozotech, Inc., Yreka, Ca). The gas flow rate to the reactor was controlled by a Sierra Instrument Model 900 mass flow controller which was installed between the ozone generator and the ozone contactor. A check valve was installed downstream of the flow controller to prevent water in the ozone contactor from cycling back into the flow controller and the ozone generator. Influent and effluent ozone gas concentrations were measured spectrophotometrically at 254 nm in 0.2-cm flow-through quartz cells with the Milton Roy Spectronic Genesys-5 spectrophotometer and amperimetrically with the Orbisphere MOCA ozone analyzer (Orbisphere Laboratories, Geneva, Switzerland). The aqueous ozone concentration was measured amperimetrically with the Orbisphere ozone analyzer.

The water was pumped by a peristaltic pump from a holding tank into the ozone contactor. The ozone contactor is a downflow injector-type bubble contactor that efficiently absorbs ozone. The contactor consists of a downflow vertical tube and an expanding cross section hood, as shown in Figure 5. Water and gas enter at the top of the contactor and flow concurrently downward through the tube into the expanding hood, and exit at the bottom of the contactor. The contactor was designed so that the inlet velocity is greater and the exit velocity is lower than the buoyant velocity of the bubbles. Thus, the bubbles are trapped inside the hood. At the bottom of the downward tube, the velocity changes rapidly creating significant swirling and turbulence at the top of hood. This results in a high gas-liquid interfacial area and a high gas transfer rate.

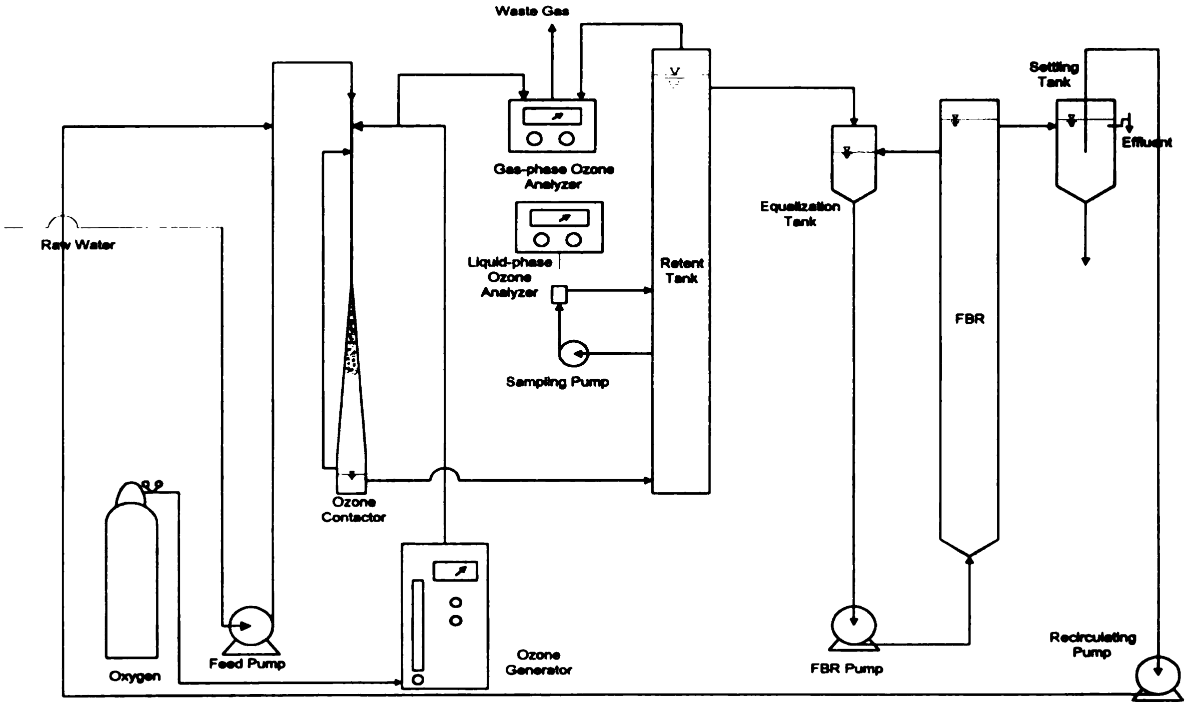


Figure 5. Schematic of Ozonation/FBT System

Table 1. Pilot plant parameters.

| **Equipment and control parameters** | Values |
|---|---|
| Ozone dose/concentration | 0-2 mg/mg C |
| Retention tank size | 2075 mL |
| Fluidized bed column volume | 1800 mL |
| Empty bed contact time (EBCT) | 180 min. |
| Flow rate | 10 mL/min |
| Recycle rate ( when used) | 10 mL/min |

A retention tank was installed downstream of the ozone contactor. The pressure head that develops in the hood of the contactor moves water out of the contactor into the retention tank. The retention time in the retention tank was sufficient for the complete decomposition of dissolved ozone. Samples of ozonated water were taken from the faucet in the side of the tank. Periodically, gas, which accumulated in the contactor, was released through the retention tank. This gas was analyzed for ozone and then passed through a potassium iodide trap to destroy any residual ozone prior to the discharge of the gas.

From the retention tank, water flowed by gravity into a small recirculation (equalization) tank from where it was recirculated through the FBT column with a peristaltic pump at a rate sufficient to fluidize the bed. The FBT column was a glass column 5 cm in diameter and 152.4 cm height. The height of the fluidized bed was maintained at 101.6 cm.

The research work presented in this thesis is part of a larger project in which we are currently investigating an ozonation/biodegradation recirculation treatment process for the removal of THMs and other DBP precursors from drinking water. The specific objectives of the whole project are:

1. To develop a predictive model to describe the kinetic behavior of humic substances during ozonation. This model will be based on the measurement of the concentration of humic substances. The total organic carbon (TOC), total solids, and UV absorption of treated and untreated solutions are being measured to determine the concentration of humic substances.
2. To determine the kinetics of the reaction of ozone with selected primary products formed from the ozonation of humic substances.
3. To determine the optimal operation parameters which will allow us to maximize biodegradability of humic substances.
4. To assess the ability of using ozonation as a pretreatment step before biological treatment for reducing the formation of THM precursors. The trihalomethane formation potential (THMFP) and chlorine demand would be monitored for untreated, ozonated and ozonated bio-treated water samples.
5. To develop a basis for the design of a new process to eliminate humic substances and their by-products from drinking water and to minimize bacterial regrowth problems in the distribution system.

# CHAPTER 5

# RESULTS AND DISCUSSION

This chapter discusses the data and results associated with each of the objectives of my research work. This includes: (1) the development and comparison of the analytical procedures for quantifying THMs in water and validation of experimental procedures; (2) the analysis of THMFP, chlorine demand, TOC and other parameters related to the pilot system; (3) the investigation to determine a correlation exists between these parameters.

## LIQUID-LIQUID EXTRACTION (LLE) vs HEAD SPACE (GC HS)

Liquid-liquid extraction is an EPA approved method for determining THMs in aqueous samples. Pentane is used as an extraction solvent. Static head space method is a dynamic method in which, depending on the temperature and pressure inside the vial, phase separation takes place and the volatile organics (VOCs) are volatilized from the solution. The headspace air is sampled and analyzed for the VOCs. Liquid-liquid extraction is more time consuming than head space techniques because of the time spent extracting the analyte(s). The analysis of the THMs was performed using both the methods mentioned above and statistical analysis was performed to compare accuracy, precision and detection limits of the two methods. Samples were also run to determine if the head space analysis contributed to an increase in THMFP due to the thermal decomposition of higher molecular weight chlorinated compounds.

Table A-1 shows the statistical analysis performed on the responses for the analysis of THMs using GC ECD for direct injection and liquid-liquid extraction (with 2 mL pentane). Figures 7a - 7d show the plotted results for each of the THMs.

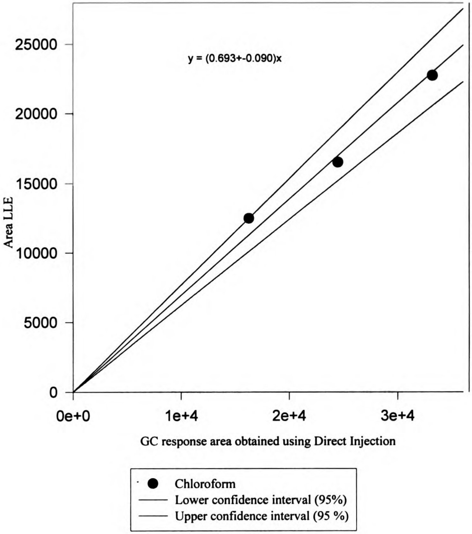


Figure 7a. Percentage recovery of chloroform using liquid-liquid extraction method

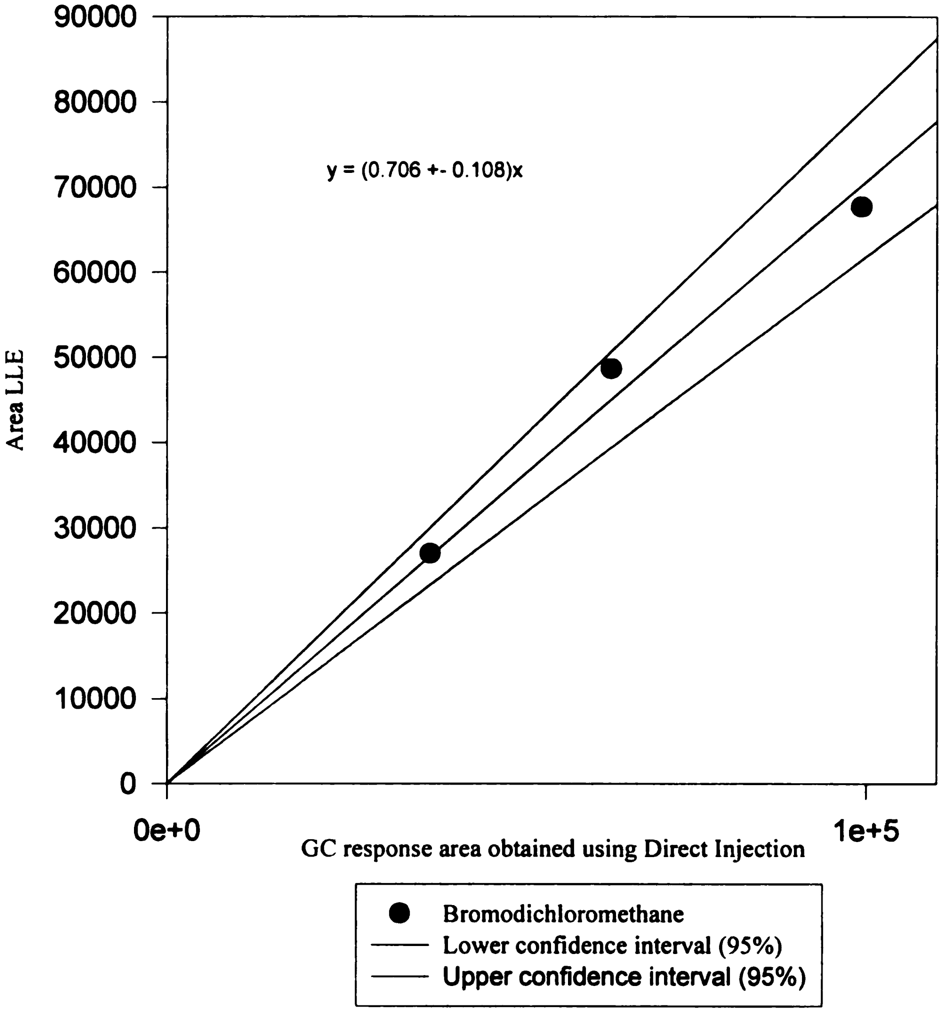


Figure 7b Percentage recovery of bromodichloromethane using liquid-liquid extraction method

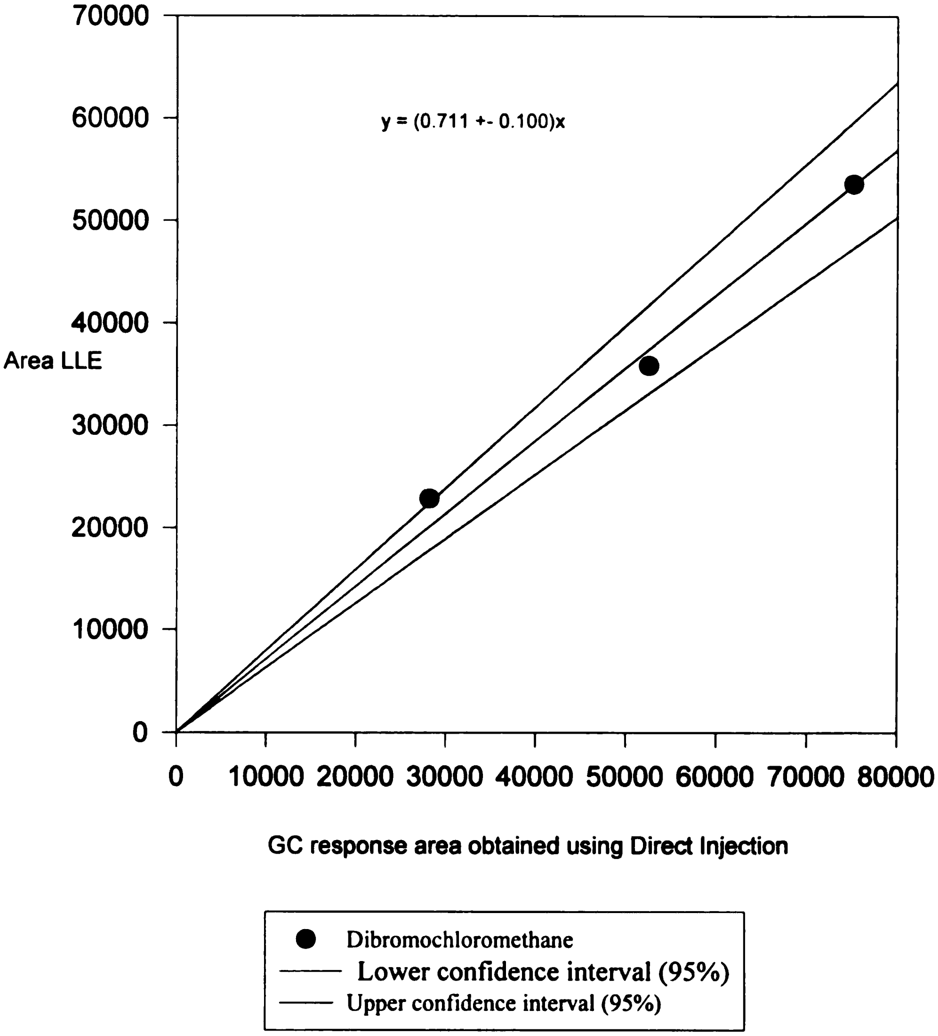


Figure 7c Percentage recovery of dibromochloromethane using liquid-liquid extraction method

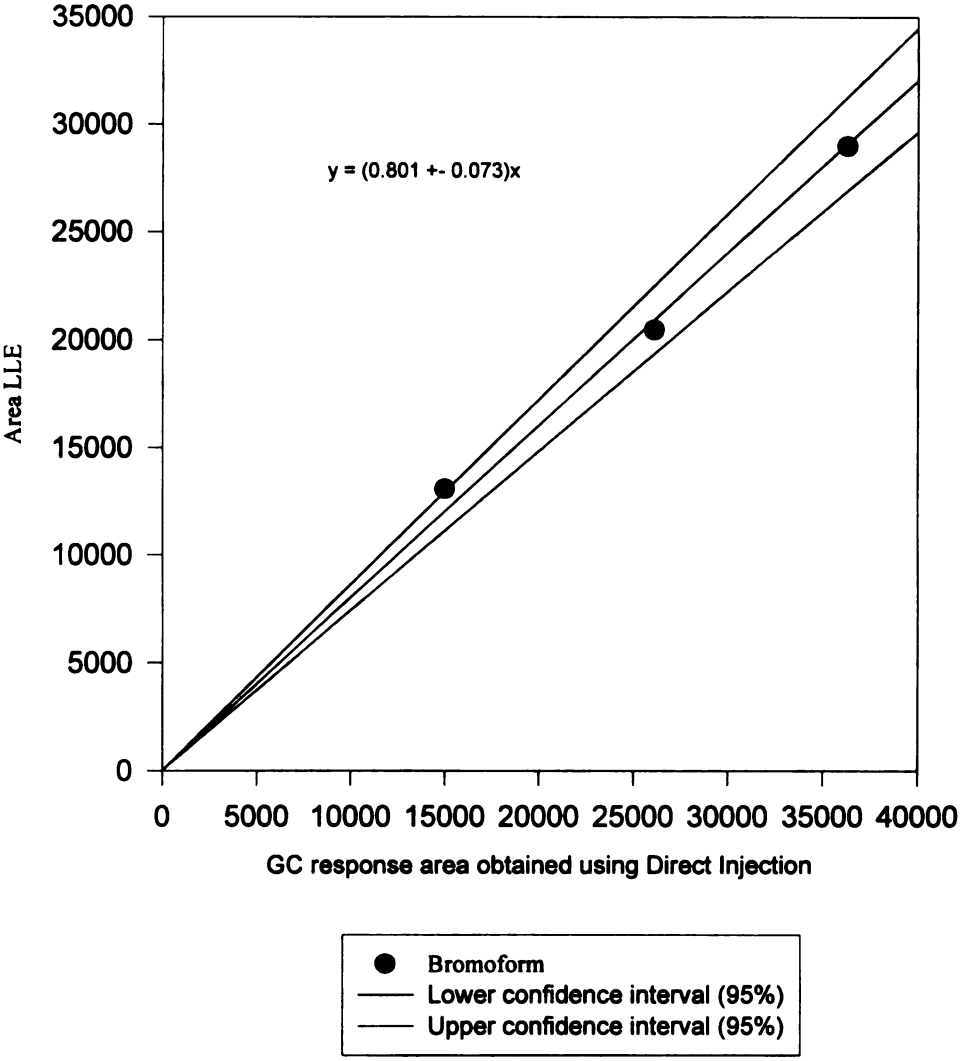


Figure 7d Percentage recovery of bromoform using liquid-liquid extraction method.

The percentage recovery for the THMs were:

Chloroform : 69.3 % ± 9 % Bromodichloromethane: 70.6 % ± 10.8 %

Bromoform: 80.1 % ± 7.3 % Dibromochloromethane : 71.1 % ± 10 %

Recovery studies were not conducted on the GS headspace technique since the headspace sampler did not employ a fixed sample loop for injection, and therefore sample volume injected into the GC could not be accurately determined.

Seven sets of identical samples were analyzed by LLE and GC-HS procedures. The results were compared by using the method of comparison of two dependent averages as outlined by Anderson (1987). The results of the statistical analysis is shown in Table 2.

**Table 2. Comparison of two dependent averages (paired data)**

| Sample | LLE (ppb) | HS (ppb) | d | $d^2$ | | |
|---|---|---|---|---|---|---|
| 1 | 305.00 | 303.00 | 2.00 | 4.00 | | |
| 2 | 156.00 | 154.00 | 2.00 | 4.00 | $s_d$ = | 24.59 |
| 3 | 387.00 | 350.00 | 37.00 | 1369.00 | | |
| 4 | 413.00 | 446.00 | 33.00 | 1089.00 | t= | 1.80 |
| 5 | 454.00 | 457.00 | 3.00 | 9.00 | | |
| 6 | 117.00 | 123.00 | 6.00 | 36.00 | $t_{0.05/2,6}$= | 2.45 |
| 7 | 159.00 | 125.00 | 34.00 | 1156.00 | | |
| | | **Sum** | 117.00 | 3667.00 | | |
| | | **Mean** | 16.71 | | | |

Since the t critical value was not exceeded, the null hypothesis was rejected and both the methods were found to be statistically equivalent with respect to accuracy/ precision. The equivalence of the accuracy and precision of the two methods as indicated by the above statistical analysis has great importance. In headspace analysis, the sample vials are thermostated at 90 °C for 20 minutes. Although residual chlorine in the system was destroyed before placing the samples in the auto sampler, it was not clear whether chlorine was still present in the sorbed phase. If chlorine was present in the sorbed phase, there is a possibility that it would be desorbed during the thermostating process and thereby facilitating THM formation. Since this problem is not encountered by the LLE method, the equivalency of the accuracy and precision of the two methods indicates that THMs were not forming during the headspace analysis. The LLE technique with pentane is an EPA approved method for THM quantification. Since in this study the LLE technique was found to be equivalent to the headspace technique with respect to its accuracy and precision, the use of GCHS is validated.

### GC-ECD vs GC-ELCD

The accuracy and precision of the calibration curves for GCECD and GCELCD were determined at the 95 % confidence level. Linear regression analysis was performed and the confidence intervals for the slopes were determined. The detection limits, retention times and the limits of quantitation for THM's using GC- ECD and ELCD have been summarized in Table 3. The detection limits were calculated using the procedure outlined in Skoog and West (1992). The calibration curves obtained for each of the THMs on the ECD and ELCD are shown in Figures B-1 and B-2. Concentrations of THMs that were detected in the sample runs are listed in Table 4.

**Table 3. Detection limits (DL), Limit of Quantitation (LOQ) in ug/L and Retention Times (RT) in minutes**

| Analytical System | | $CHCl_3$ | $CHBrCl_2$ | $CHBr_2Cl$ | $CHBr_3$ |
|---|---|---|---|---|---|
| **ELCD** | DL | 0.026 | 0.03 | 0.0588 | 0.1956 |
| | LOQ | 0.0868 | 0.1 | 0.1961 | 0.652 |
| | RT | 1.11 | 1.51 | 2.17 | 3.18 |
| **ECD** | DL | 0.0034 | 0.0007 | 0.0016 | 0.0088 |
| | LOQ | 0.0115 | 0.0019 | 0.004 | 0.0209 |
| | RT | 1.68 | 2.44 | 3.55 | 4.97 |

**Discussion:** From the limits of detection and quantitation (Table 3) it is apparent that much lower levels of detection were achieved by using automated head space gas chromatography coupled with electron capture detection. The response factors by themselves indicated a twenty times better sensitivity. The very low detection limits for bromodichloromethane and bromoform using the ECD made this method of detection feasible for the analysis of brominated volatile organics. Errors and deviations in injecting were eliminated by the use of auto sampling with programmed injection temperatures.

The instrument calibration verification standards were run to obtain the confidence interval for the calibration curves. A THM solution mix (80 µg/L) was used as an ICV. 8 µL of stock standard was added to 10 mL of water to obtain a 80 µg/ L ICV standard (shown in Table 4).

**Table 4** **Detector Response for Sample Run**

**HS40-GC-ECD**

**E.Lansing Drinking water**

| **Sample** | **$CHCl_3$** | | **$CHBrCl_2$** | | **$CHBr_2Cl$** | | **$CHBr_3$** | |
|---|---|---|---|---|---|---|---|---|
| | **response** | **conc** | **response** | **conc** | **response** | **conc** | **response** | **conc** |
| | **uV.s** | **ppb** | **uV.s** | **ppb** | **uV.s** | **ppb** | **uV.s** | **ppb** |
| | 85322 | 34 | 133306 | 9 | 47730 | 7 | 2737 | 2 |

**Spike in pure water** **THMs**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 20ppb | 64452 | 24 | 237968 | 15 | 129071 | 19 | 36692 | 22 |
| 80ppb | 202932 | 76 | 907887 | 59 | 461104 | 68 | 126309 | 76 |
| | | | | | | | | |
| **Spike in Huron river water** | | | | | | | | |
| 20ppb | 60702 | 23 | 124269 | 8 | 71638 | 11 | 26117 | 16 |
| 80ppb | 191223 | 72 | 848051 | 55 | 452482 | 67 | 131482 | 79 |

**HS40-GC-ELCD** **THMs**

**Spike in pure water**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **20ppb** | 2310 | 17 | 1586 | 13 | 680 | 11 | 166 | 9 |
| **80ppb** | 11208 | 83 | 7891 | 67 | 3071 | 51 | 673 | 37 |
| | | | | | | | | |
| **Spike in Huron river water** | | | | | | | | |
| **20ppb** | 2048 | 15 | 1307 | 11 | 588 | 10 | 177 | 10 |

Response factors indicate twenty times better sensitivity. As seen from the Table 5 the relative standard deviations for the GC-ECD are much smaller than for the GC-ELCD.

The calibration curves obtained using both detectors yielded a good fit ($r^2$>0.98) for all the THMs. The calibrations for the ECD were performed in the range of 0 μg/L to 200 μg/L where as the calibrations for the ELCD were performed in the range of 0 μg/L to 400 μg/L. This was because the ELCD was not very sensitive below 100 μg/L. Significantly lower detection limits were achieved by automated GC ECD. The detection limits have been compared in Table 6.

**Table 5. Statistical Analysis for ECD and ELCD**

ECD

ICV 80 ppb

| | **$CHCl_3$** | **$CHCl_2Br$** | **$CHClBr_2$** | **$CHBr_3$** |
|---|---|---|---|---|
| avgerage concentration (ppb) | 84.86 | 69.14 | 80.41 | 87.40 |

| | **$CHCl_3$** | **$CHCl_2Br$** | **$CHClBr_2$** | **$CHBr_3$** |
|---|---|---|---|---|
| Confidence Interval (95%) | 5.17 | 3.24 | 3.24 | 2.53 |
| standard. deviation | 0.77 | 1.31 | 1.84 | 1.35 |
| variance | 0.60 | 1.71 | 3.39 | 1.82 |
| relative standard .deviation. % | 0.91 | 1.89 | 2.29 | 1.54 |

ELCD

ICV 80 ppb

| | **$CHCl_3$** | **$CHCl_2Br$** | **$CHClBr_2$** | **$CHBr_3$** |
|---|---|---|---|---|
| average concentration (ppb) | 84.78 | 66.82 | 55.04 | 39.78 |

| | **$CHCl_3$** | **$CHCl_2Br$** | **$CHClBr_2$** | **$CHBr_3$** |
|---|---|---|---|---|
| Confidence interval(95.0%) | 12.77 | 13.07 | 15.11 | 19.67 |
| standard. deviation | 5.14 | 5.26 | 6.08 | 7.92 |
| variance | 26.45 | 27.68 | 36.99 | 62.69 |
| relative standard deviation %. | 6.07 | 7.87 | 11.05 | 19.90 |

**Table 6. Comparison of detection limits (DL) in μg/L of this work and Otson et al.(1979)**

| Analytical System | | $CHCl_3$ | $CHBrCl_2$ | $CHBr_2Cl$ | $CHBr_3$ |
|---|---|---|---|---|---|
| **ELCD** | **DL** | 0.026 | 0.03 | 0.0588 | 0.1956 |
| | **DL(Otson)** | 10 | 2 | 4 | 8 |
| **ECD** | **DL** | 0.0034 | 0.0007 | 0.0016 | 0.0088 |
| | **DL(Otson)** | <0.5 | 1 | 2 | 3 |

A two tailed t- test was performed to determine whether the precision of the two methods were statistically (at 95% C.I.) equivalent at low concentrations of THMs. The two methods were statistically different when the individual THMs were in the range of 20 μg/L. Since the concentration cannot exceed the USEPA limit of 80 μg/L total THMs in drinking water, and assuming about 20 μg/L of each of the four THMs, we could therefore conclude that the static GC-ECD approach would lead to accurate analysis of finished drinking water. The results obtained are considerably different to those obtained by Otson et al., (1979) (see Table 6). Superior accuracy and precision have been achieved as a consequence of automation and good quality columns. Accurate temperature programming has also helped in achieving good quantification.

## RESULTS FROM THE PILOT PLANT

**Chlorine Demand, THMFP and TOC.** Chlorine demand and TOC are used as surrogate parameters for THMs in drinking water. Since THMFP is empirical in nature, there is no means by which it can be exactly evaluated. Experiments using the ozonation recirculation system were conducted to evaluate the performance of the proposed process to control DBPs in water. Huron River water was used as the source of raw water.

Ozone dose, chlorine demand, THMFP (in this research work) and, TOC, UV-254 absorbance, molecular weight distribution , empty bed contact time (EBCT) and flow rate were monitored as part of the overall project . The control parameters that determined the operating conditions were ozone dose and EBCT/flow rate. Experiments were conducted with ozone doses varying from 0 to 2mg/mg C. The system was operated at a flow rate of 10 mL/min, which led to an EBCT in the biodegradation treatment column (FBT) of 180 minutes. The data collected during the period from Jan 1997 to April 1997 are summarized in Tables A-2 - A-4 ( Appendix A) and Figures 12-18.b.

Figure 9 shows the contribution of ozonation, FBT, and combined ozonation/FBT to the removal of TOC from Huron River water. It is interesting to note that the FBT was able to remove about 18 % of organic carbon from the untreated (non ozonated) Huron River water. Moreover ozonation at a dose of 0.5 mg/mg C did not increase the biodegradability of natural organic matter (NOM) but on the contrary there was a decrease in the bioremoval of organic carbon. This occurrence is also indicated by the

THMFP and chlorine demand reduction plots in Figure 8. These results substantiate the conclusion that ozone removed some organic matter that otherwise could have been degraded biologically. The contribution of ozone to the removal of organic carbon continued to increase with the ozone dose up to a dose of 1 mg/mg C and then it reached a plateau. As seen in Figure 8, chlorine demand and THMFP removals too, behave similarly. Further increase in ozone dose resulted in an increase in the bioremoval efficiency of the FBT. These trends seem to indicate a correlation between the TOC removal and chlorine demand and THMFP removal. Figures 10 and 11 are the plots of the percentage reduction in THMFP and chlorine demand versus percentage removal of TOC, respectively for Huron River water sample after ozonation/FBT. As seen from the figures the data seem to correlate excellently with a second order fit at 95 % confidence interval. (Data were fit by using Sigmaplot, a graphing and statistical software).

The influent, effluent and ozonated samples were compared to determine the extent to which chlorine demand and THMFP were reduced at any given ozone dose. As can be seen from the tables, correlations could exist between chlorine demand and THMFP at a particular ozone dose. Figure 12-18b. show the effect of ozone dose and combined ozonation and FBT on chlorine demand and THMFP on Huron River water, and the correlation between chlorine demand and THMFP. However, it has to be noted that the correlation between THMFP and chlorine demand is specific to type of water and the type of treatment employed; that is untreated, ozonated and ozonated/bio-treated. Also there is a variation in influent water characteristics depending on weather and other

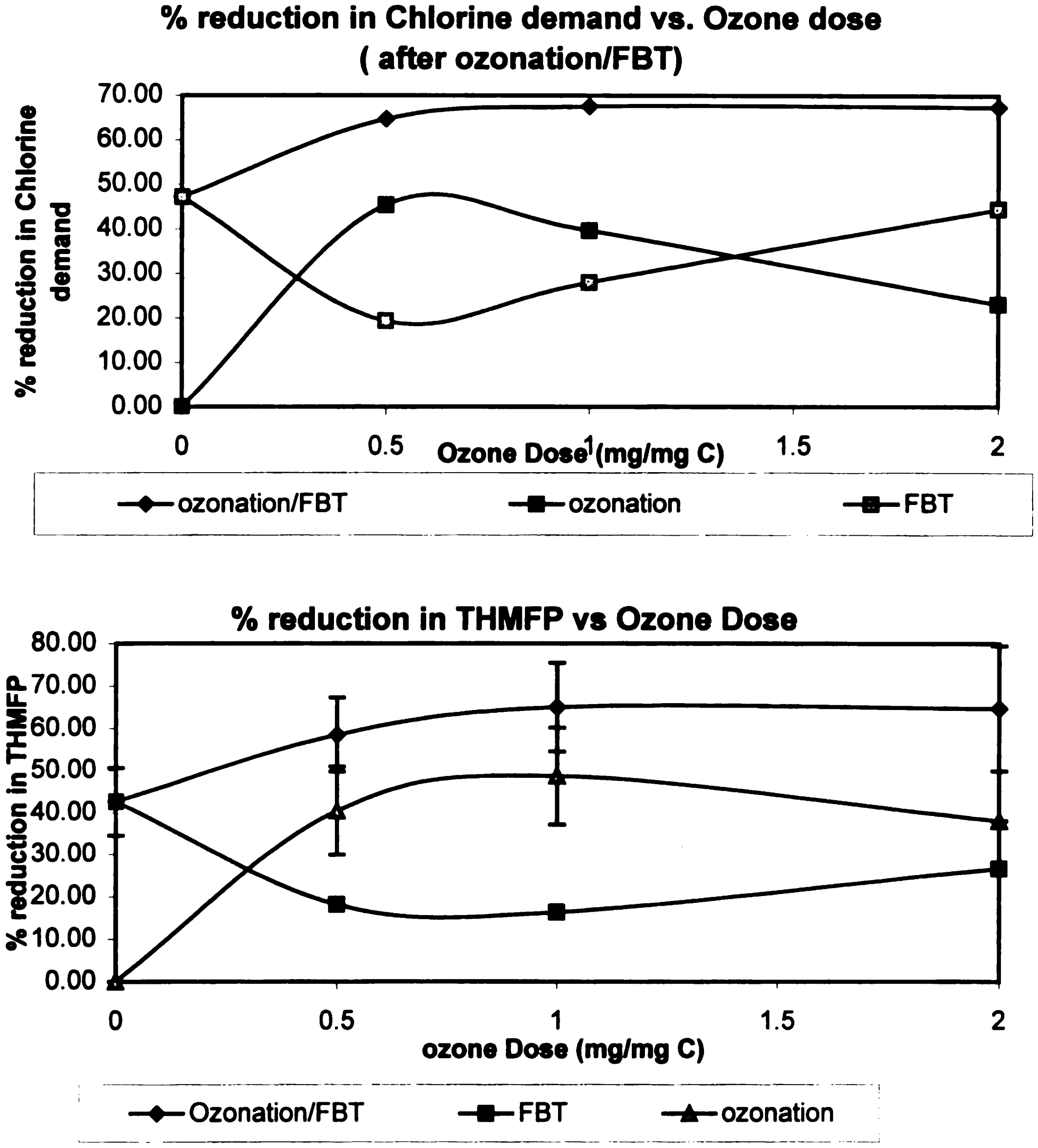


Figure 8 Effect of ozone dose on THMFP and Chlorine demand removal.

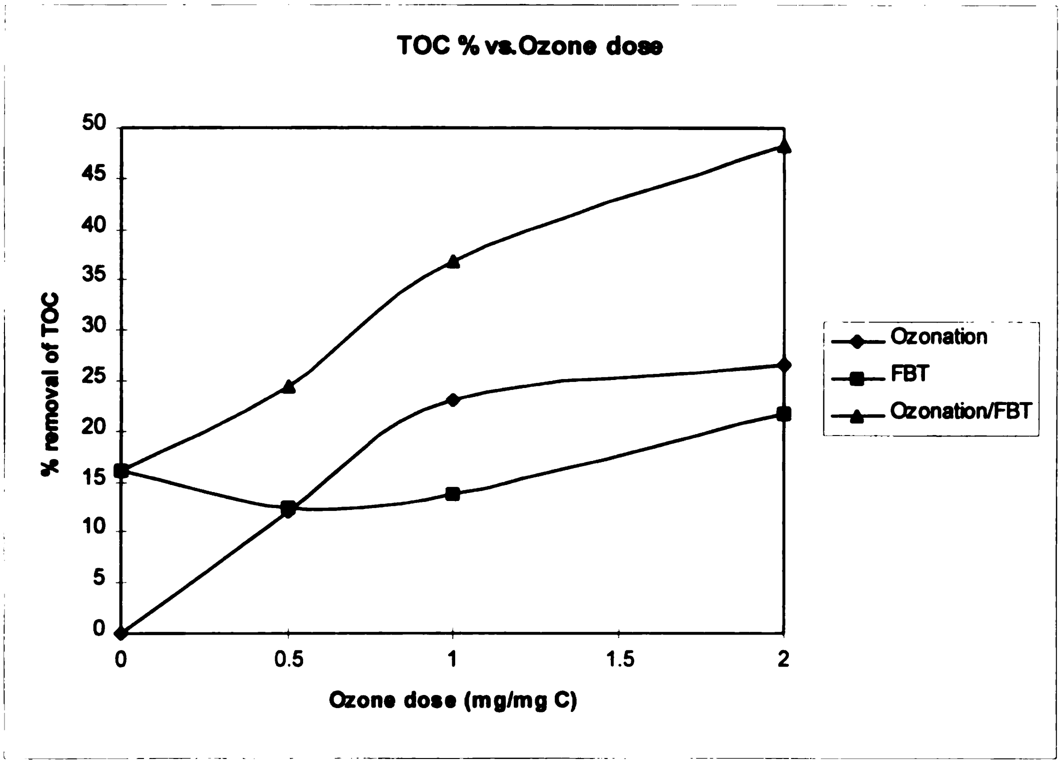


Figure 9 Effect of Ozone on TOC removal. (Courtesy: Alex Yavich)

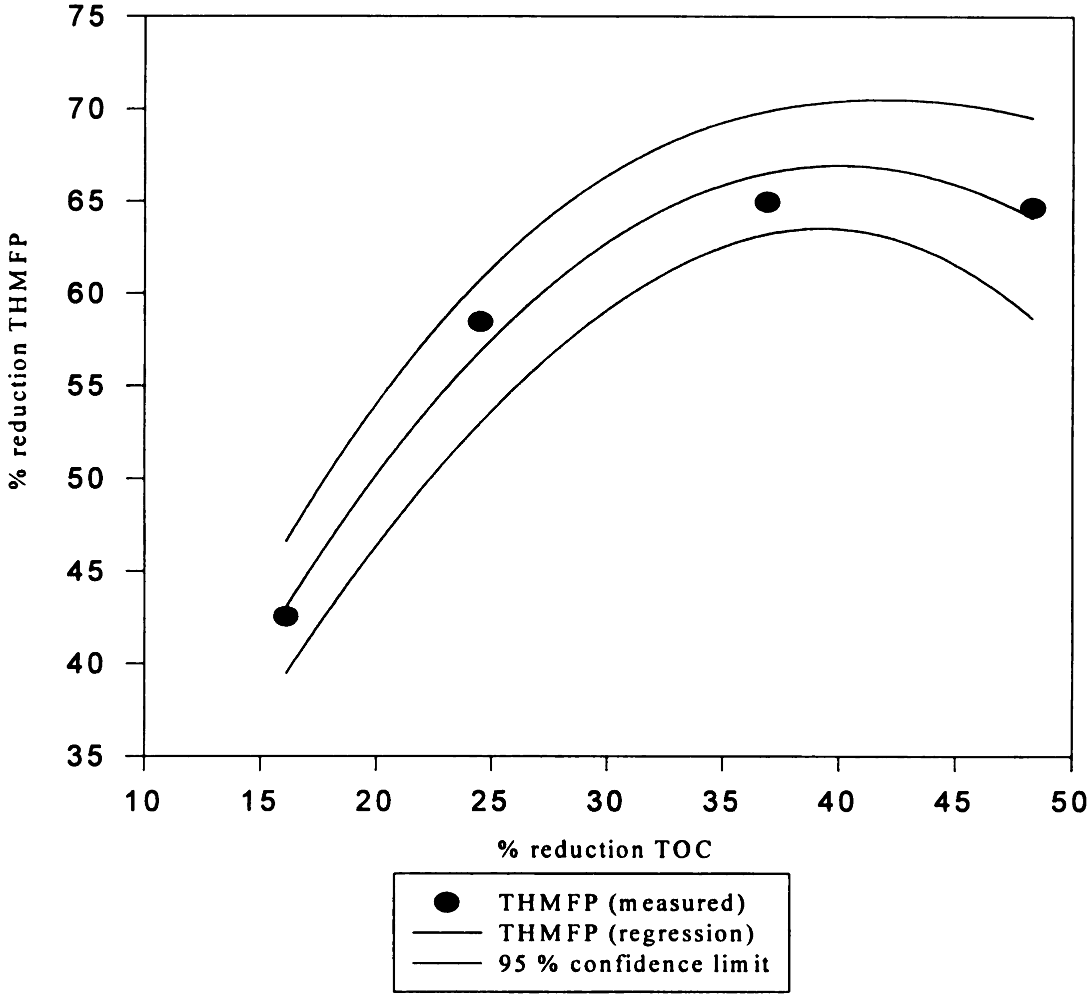


Figure 10 Correlation between TOC removal % and THMFP reduction %

conditions. Therefore different curves were plotted for ozonated samples and ozonated/FBT samples. As seen from the Figure 8, the chlorine demand is reduced by about 70 % for samples which were ozonated (1 mg/mg C) and treated biologically. There was a 40 % decrease in chlorine demand with ozonation alone. THMFP too, behaved similarly as chlorine demand and the percentage reductions achieved in the combined $O_3$/FBR system plateaued after 0.5 mg/mg C ozone dosage.

It is also interesting to note that when the system was operated without the addition of ozone, removal efficiencies of up to 45 % of chlorine demand and THMFP were achieved.

The total organic carbon (TOC) data has to be investigated to give a clearer picture of the nature of treatment. Table 7. shows the TOC % removal data for the system.

**Table 7. Percentage removals achieved in the pilot plant**

| Ozone dose | % removal | % removal | % removal |
|---|---|---|---|
| mg/mg C | ozonation | ozonation/FBT | FBT |
| 0 | 0 | 16.1 | 16.1 |
| 0.5 | 12 | 12.5 | 24.5 |
| 1 | 23 | 13.7 | 36.9 |
| 2 | 26.5 | 21.8 | 48.3 |

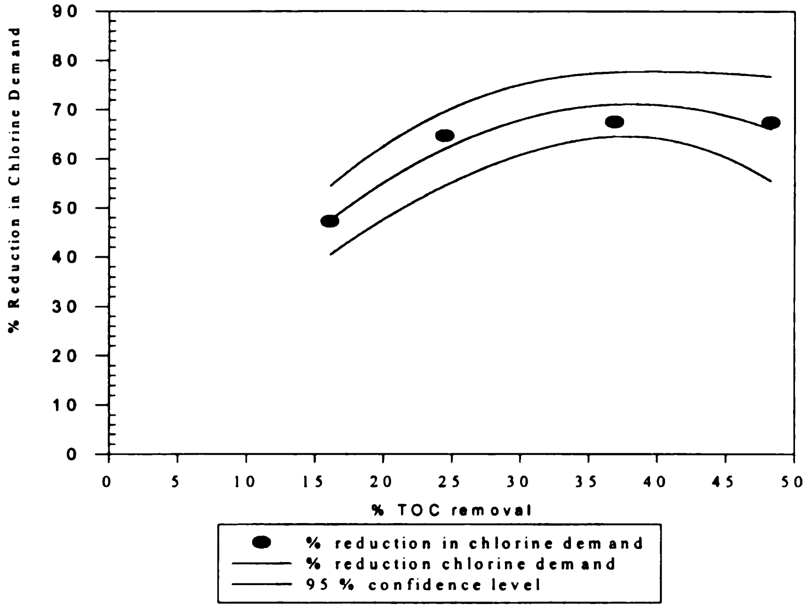


Figure 11 Correlation between % TOC removal and % reduction in chlorine demand.

**Evaluation of individual THMFP data.** Figures 16a-18a indicate that chloroform is the major component of THMFP. The concentrations of the brominated THMs were relatively constant for all chlorine doses. The formation of constant amounts of brominated THMs indicates that all the bromide in the effluent. Post ozonation effluent and post ozonation/FBR effluent has been consumed. Ozonated samples were analyzed (pre-chlorination) for the presence of bromoform since it is known that ozonating waters containing bromide leads to formation of bromoform. No measurable bromoform was found during the head space analysis of ozonated Huron River water. As such, either the concentration of bromide in raw water is not high enough to drive the reaction leading to

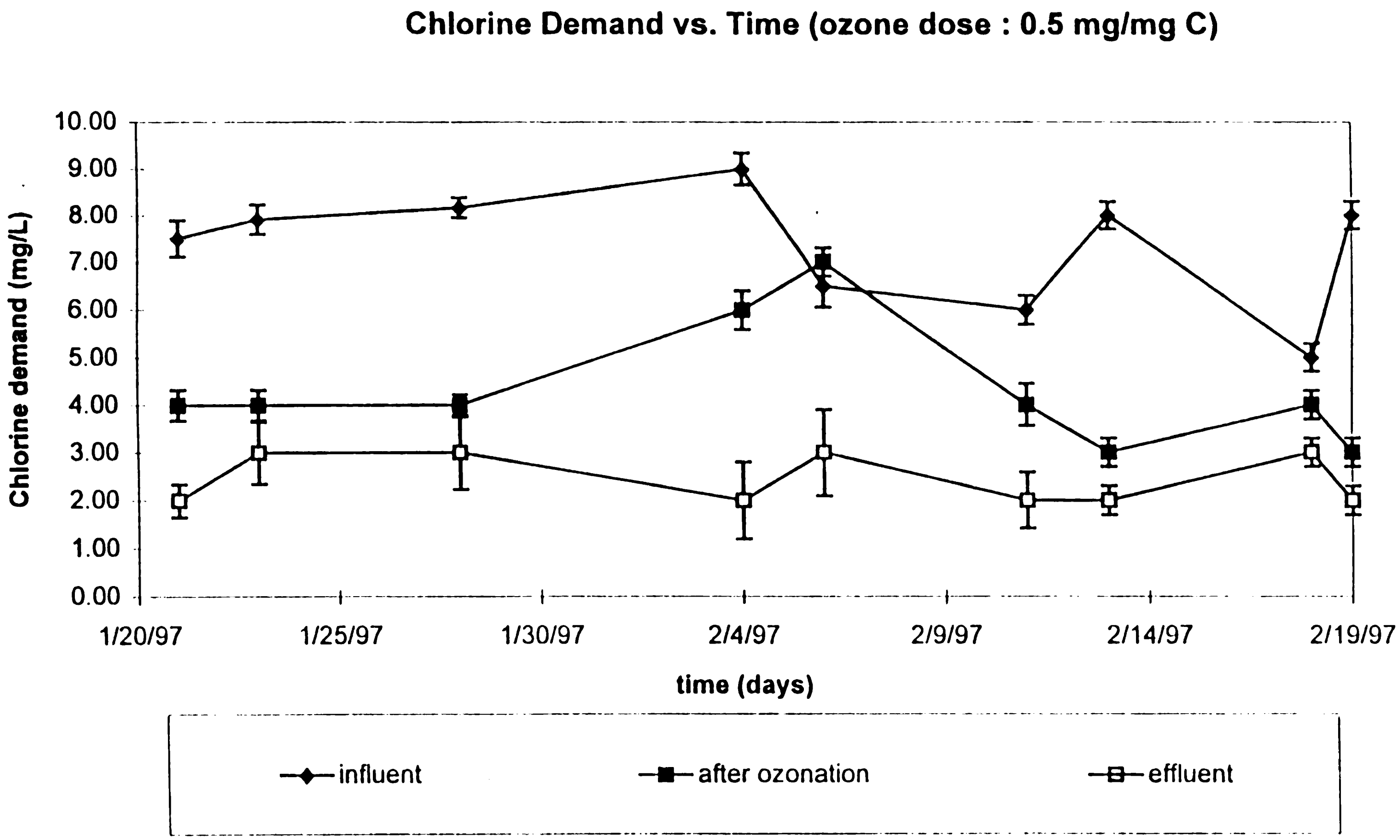


Figure 12 Variation of chlorine demand with time for ozone dose of 0.5 mg/mg C

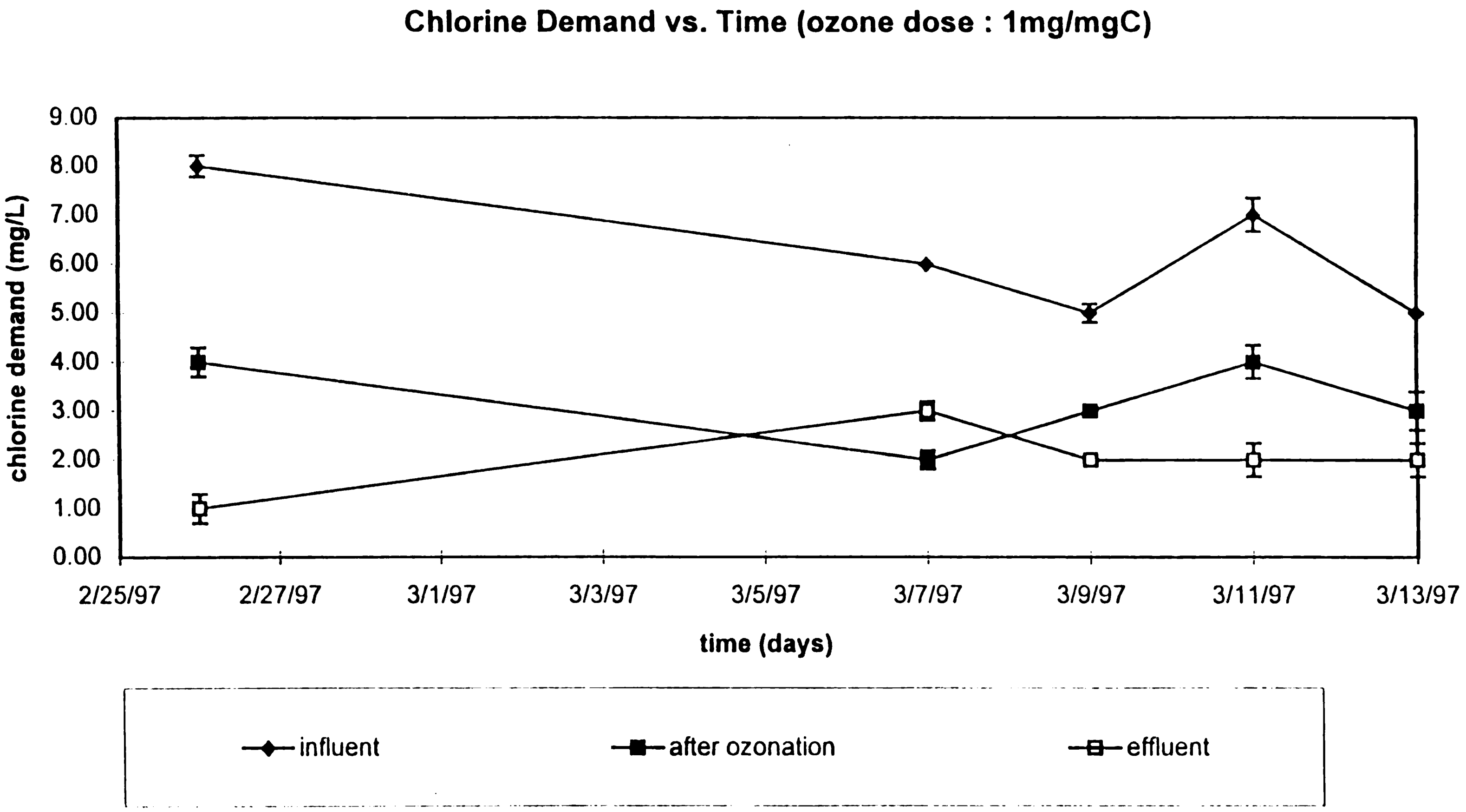


Figure 13 Variation of chlorine demand with time for ozone dose of 1mg/mg C

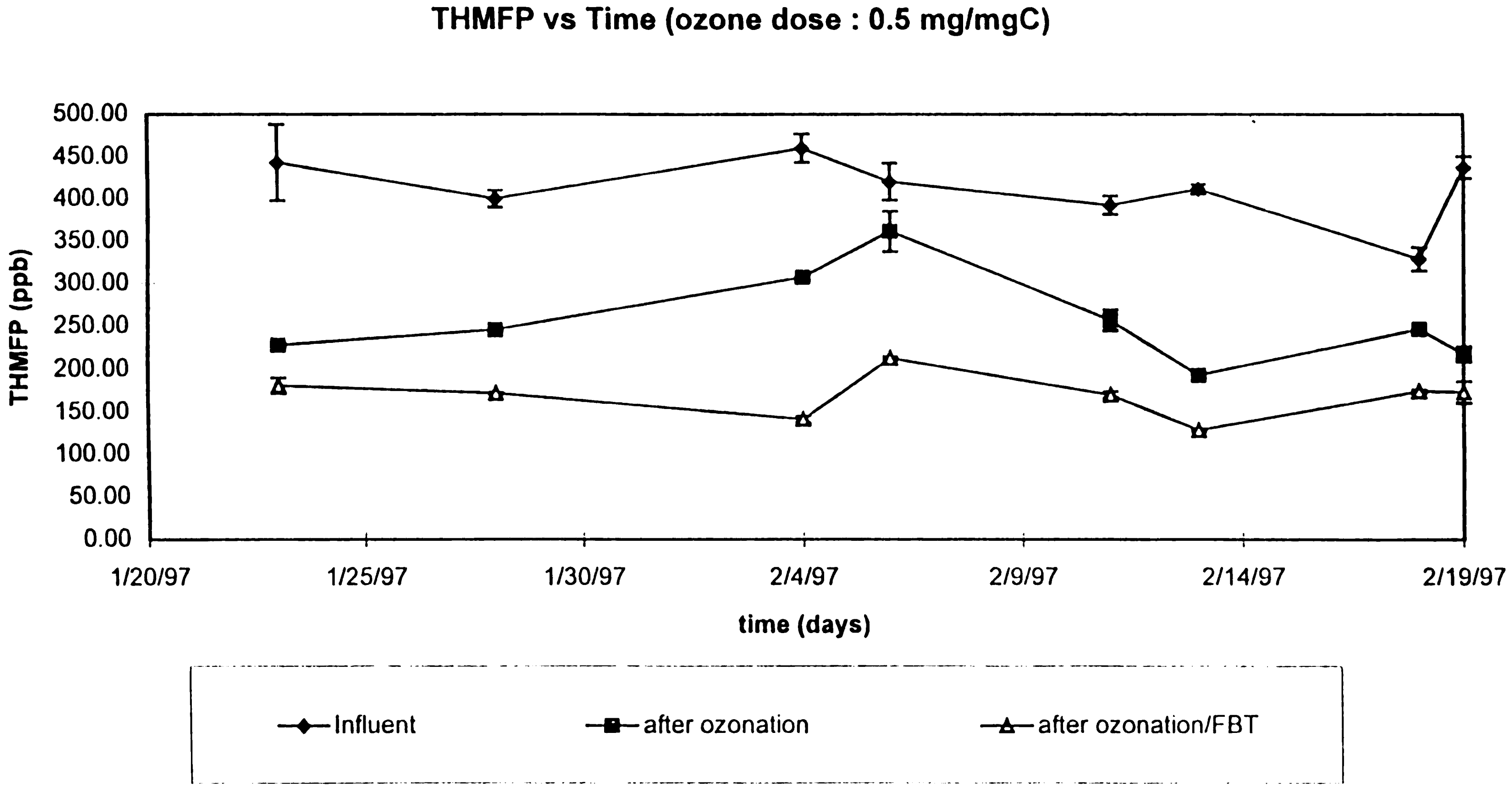


Figure 14 Variation of THMFP vs. Time for ozone dose of 0.5 mg/mg C

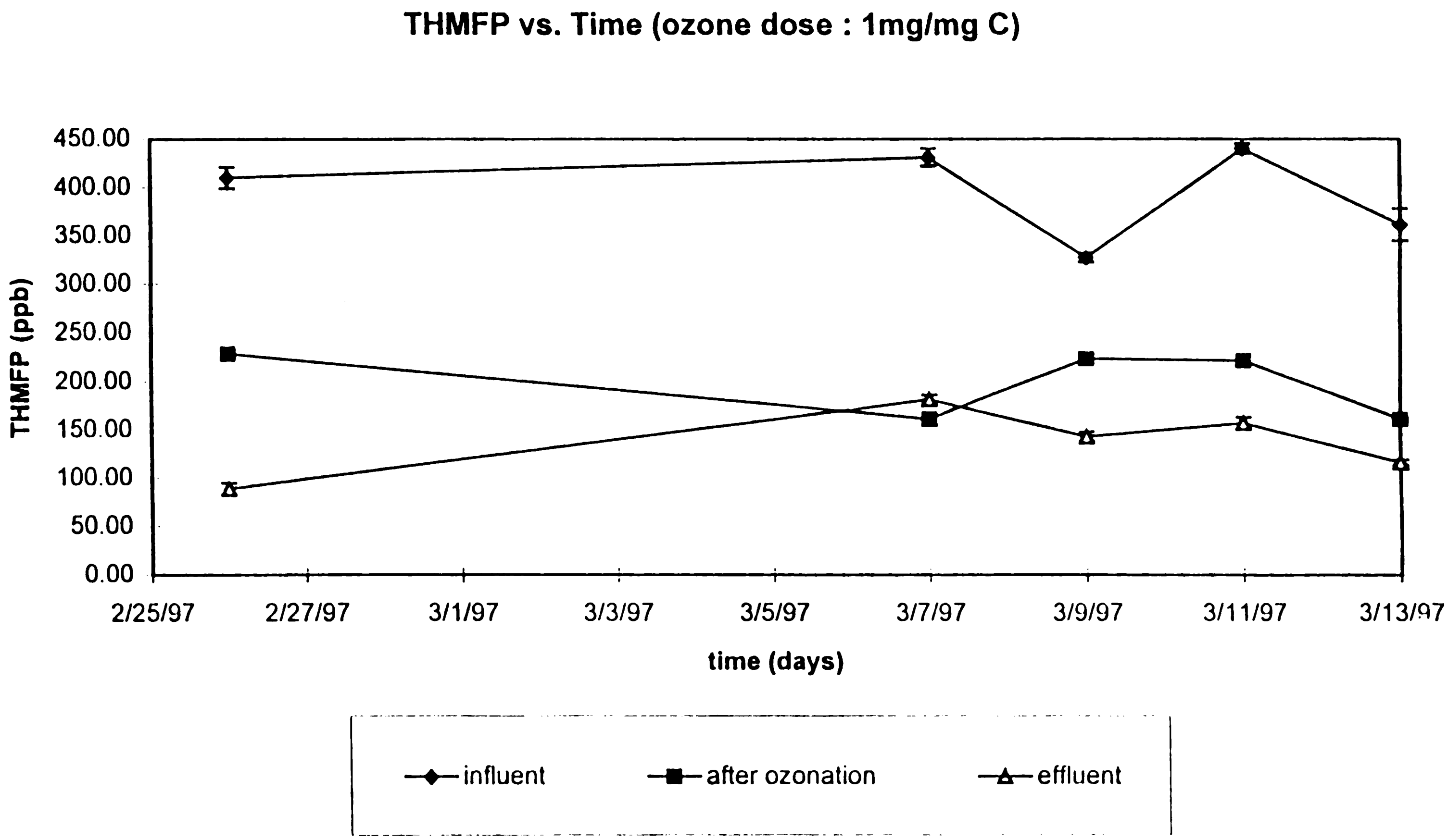


Figure 15 Variation of THMFP with time for ozone dose of 1mg/mg C

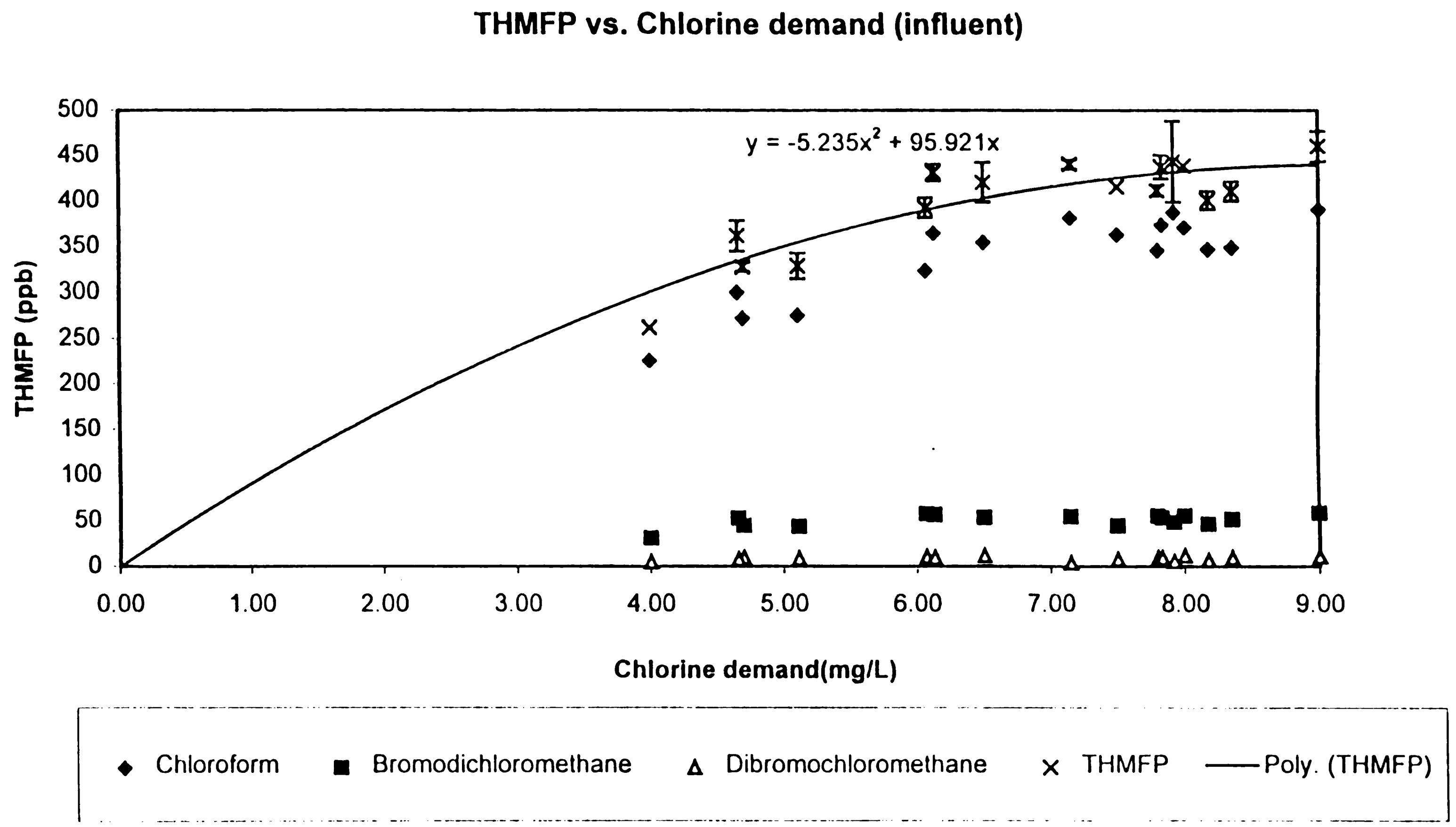


Figure 16a Correlation between THMFP and Chlorine demand for influent water.

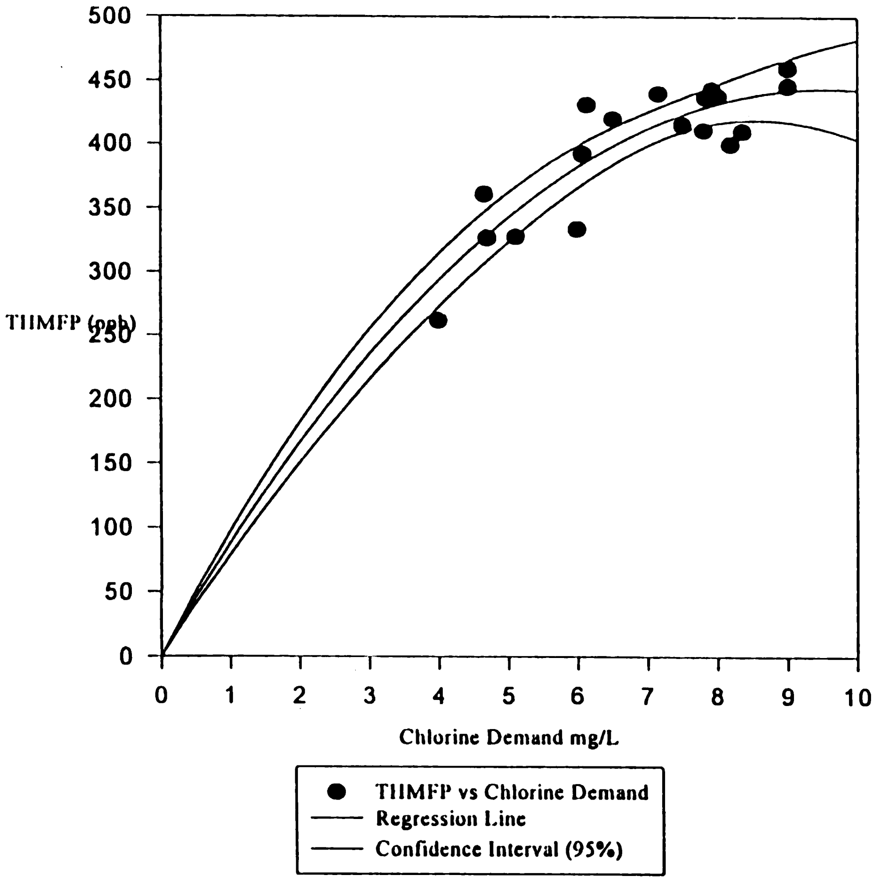


Figure 16b Correlation between THMFP and Chlorine demand for influent water

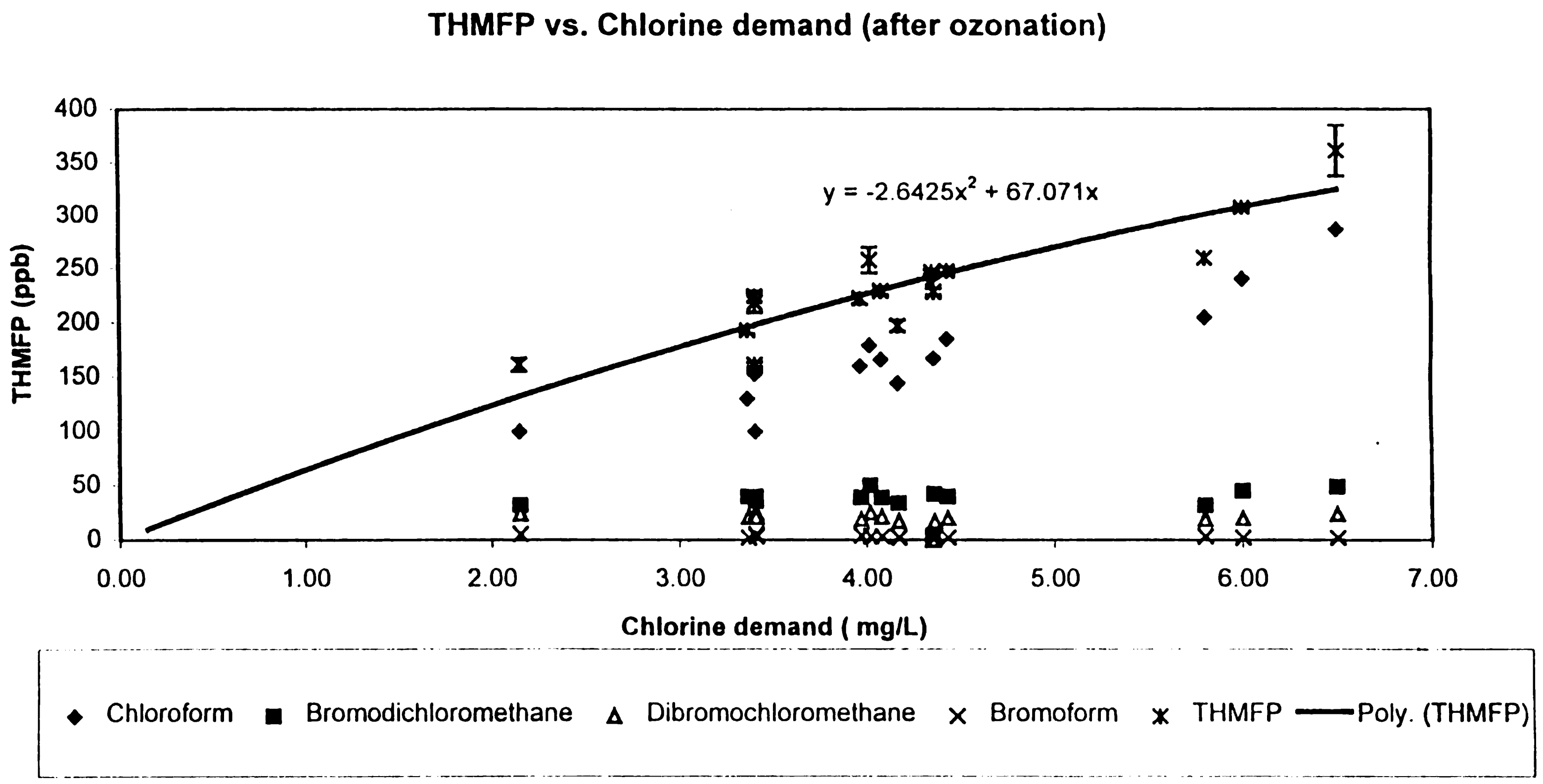


Figure 17a Correlation between THMFP and Chlorine demand for raw water after ozonation.

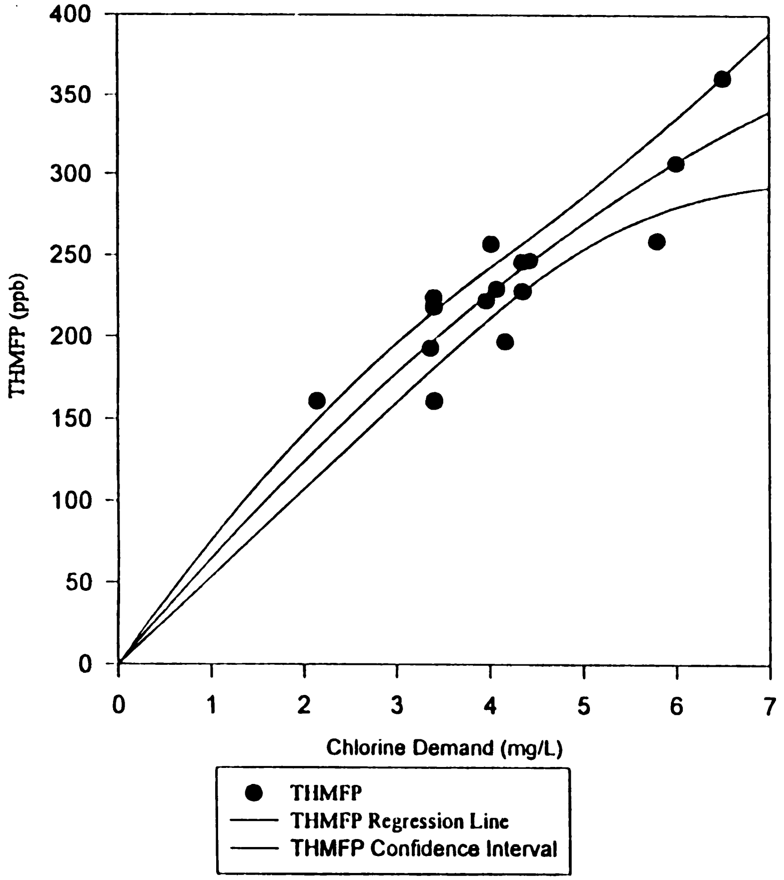


Figure 17b Correlation between THMFP and Chlorine Demand for post ozonation effluent

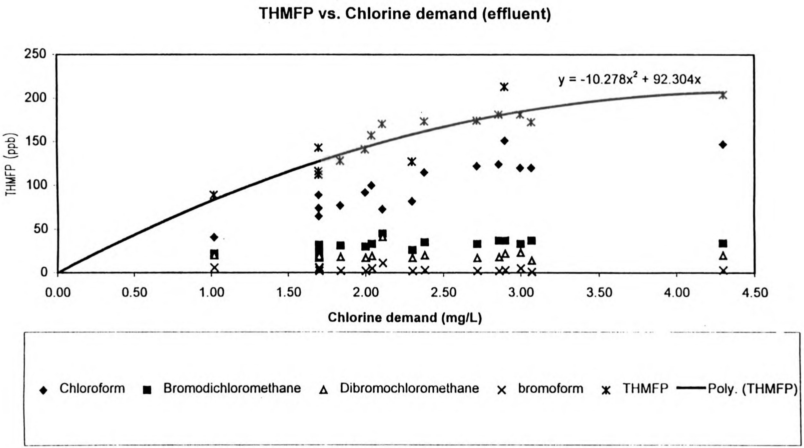


Figure 18a THMFP vs. chlorine demand for raw water after ozonation FBT

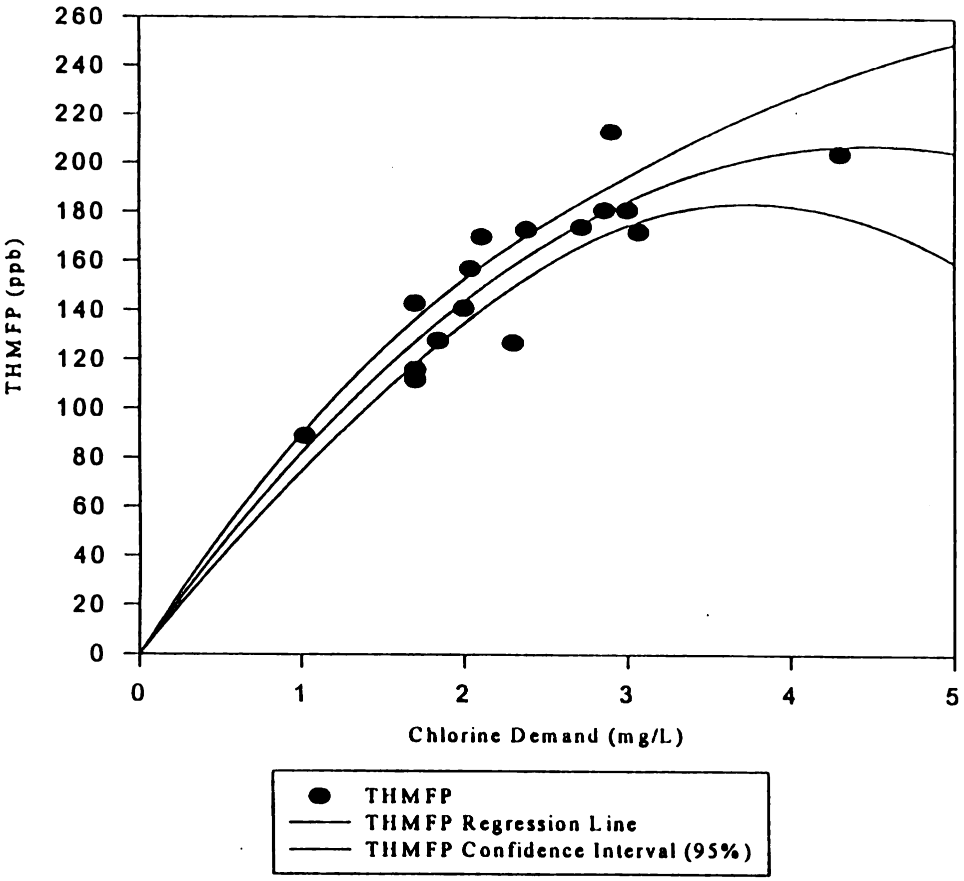


Figure 18b Correlation between THMFP and Chlorine Demand for Post Ozonation/FBT Effluent.

the formation of bromoform or the rate of reaction of oxidation of precursors is higher than rate of reaction of formation of bromoform. The presence of constant amounts of brominated THMs at all chlorine doses indicates that the concentration of bromide in raw water is not high enough to drive the reaction leading to formation of bromoform.

**Recycle mode of operation.** The results discussed previously seem to indicate that ozone is not being utilized efficiently in the combined ozonation/biodegradation treatment system. Ozone seems to oxidize organics that could have been biodegraded. One way to increase the efficiency of combined ozonation/biodegradation treatment is to operate the system in a cyclic mode, in which water alternately passes through ozonation and biodegradation steps. In this way ozonation is expected to degrade only those compounds that are not biodegradable. A summary of the experiments in which a portion of the system effluent was recycled back to the ozone contactor is presented in Table 8.

**Table 8 Comparison of recycle and non-recycle mode of operation.**

| Parameter | Raw water | Recycle mode (Recycle flow 10 mL/min Ozone dose 1mg/mg C) | Without Recycle |
|---|---|---|---|
| | | Effluent | Effluent |
| TOC mg/L | 5.86 | 3.43±0.03 | 3.67± 0.07 |
| Chlorine Demand, (mg/L) | 7.75±0.6 | 0.96 | 1.53±0.5 |
| THMFP (ppb) | 425±15 | 75 | 120±34 |

The influent and the recycle flow rates were 10 mL/min and the ozone dose was 1mg/mg C. These initial experiments support the idea that the recycle mode is able to increase the efficiency of the ozonation/FBT process.

# CHAPTER 6

# CONCLUSIONS

**The following conclusions can be drawn:**

Analytical experiments conducted during the method development stage validated the head space GC-ECD method for analyzing THMs. The LLE and HS methods were found to be statistically equivalent with respect to accuracy and precision.

Studies were conducted to evaluate the performance of the ozonation biodegradation treatment system to remove THM precursors from drinking water. The studies using a small pilot ozonation/FBT system were conducted with Huron River water, which is a source water for the Ann Arbor Water Treatment Plant. Ozone doses ranged from 0 to 2 mg $O_3$/mg TOC. Up to 70 % THMFP and chlorine demand were removed and 50 % of TOC was removed. Good correlations were observed between TOC, THMFP and chlorine demand. It was also shown that the correlations vary for ozonation, FBT and combined ozonation/FBT systems and also depend on the influent water characteristics, e.g., TOC and chlorine demand while complete conclusions cannot be drawn yet since the study is still in progress. But the trends do indicate that TOC, THMFP and chlorine demand can be used to evaluate process performance.

The studies have also shown that biodegradation efficiency of the FBR relative to the ozone consumption could be significantly increased by recycling a portion of system effluent to the ozone contactor.

## Future Work

Raw water quality is variable according to climatic and other conditions. Therefore, work has to be done to generalize the data for not only the variations in a single source of raw water but also to multiple sources. Data generalization can be achieved by modeling the process used in this study as two mixed flow reactors in series, and using TOC, THMFP and chlorine demand as concentration terms.

# APPENDICES

# APPENDIX A

Table A-1. Statistical analysis to get confidence limits for slopes for the

% recovery study

| Direct Injection(D.I.) (X) |  | LLE (Y) |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
| $CHCl_3$ |  |  |  |  |  |  | Recovery |  |
| Mass (ng) | Response D.I | Response LLE | X.Y | $X^2$ | $Y^2$ | $S_{yx}$ | (Slope) | 95% C.I |
| 0.38 | 16280.67 | 12482.00 | 2.03E+08 | 2.65E+08 | 1.56E+08 | 926.00 |  |  |
| 0.75 | 24507.67 | 16517.00 | 4.05E+08 | 6.01E+08 | 2.73E+08 |  | 0.69 | 0.09 |
| 1.13 | 33199.67 | 22766.00 | 7.56E+08 | 1.1E+09 | 5.18E+08 |  |  |  |
|  |  | Sum | 1.36E+09 | 1.97E+09 | 9.47E+08 |  |  |  |
| $CHCl_2Br$ |  |  |  |  |  |  |  |  |
| Mass (ng) | Response | Response |  |  |  |  |  |  |
| 0.38 | 37726.33 | 27007.00 | 1.02E+09 | 1.42E+09 | 7.29E+08 | 3128.17 |  |  |
| 0.75 | 63699.00 | 48654.00 | 3.1E+09 | 4.06E+09 | 2.37E+09 |  | 0.71 | 0.11 |
| 1.13 | 99354.00 | 67720.00 | 6.73E+09 | 9.87E+09 | 4.59E+09 |  |  |  |
|  |  | Sum | 1.08E+10 | 1.54E+10 | 7.68E+09 |  |  |  |

Table A-1 (Cont'd).

| $CHClBr_2$ | | | X.Y | $X^2$ | $Y^2$ | $S_{yx}$ | | C.I |
|---|---|---|---|---|---|---|---|---|
| **Mass (ng)** | **Response** | **Response** | | | | | | |
| 0.38 | 28227.00 | 22838.00 | 6.45E+08 | 7.97E+08 | 5.22E+08 | 2251.52 | | |
| 0.75 | 52612.33 | 35839.00 | 1.89E+09 | 2.77E+09 | 1.28E+09 | | 0.71 | 0.10 |
| 1.13 | 75171.33 | 53577.00 | 4.03E+09 | 5.65E+09 | 2.87E+09 | | | |
| | | **Sum** | 6.56E+09 | 9.22E+09 | 4.68E+09 | | | |
| **$CHBr_3$** | | | | | | | | |
| **Mass (ng)** | **Response** | **Response** | | | | | | |
| 0.38 | 14993.00 | 13050.00 | 1.96E+08 | 2.25E+08 | 1.7E+08 | 808.47 | | |
| 0.75 | 26111.33 | 20449.00 | 5.34E+08 | 6.82E+08 | 4.18E+08 | | 0.80 | 0.07 |
| 1.13 | 36297.67 | 28990.00 | 1.05E+09 | 1.32E+09 | 8.4E+08 | | | |
| | | **Sum** | 1.78E+09 | 2.22E+09 | 1.43E+09 | | | |

**Table A-2 Influent ( Huron River Water)**

| | DAY | Chl Dem | $CHCl_3$ | $CHCl_2Br$ | $CHClBr_2$ | $CHBr_3$ | THMFP |
|---|---|---|---|---|---|---|---|
| | | in mg/l | ppb | ppb | ppb | ppb | ppb |
| | | | | | | | |
| ✓ | 1/23/97 | 7.92 | 387 | 49 | 6 | 1 | 443 |
| ✓ | 1/28/97 | 8.18 | 346 | 47 | 7 | 0 | 400 |
| ✓ | 2/4/97 | 9.00 | 390 | 59 | 11 | 0 | 460 |
| ✓ | 2/6/97 | 6.50 | 354 | 54 | 12 | 0 | 420 |
| ✓ | 2/11/97 | 6.07 | 323 | 58 | 11 | 0 | 392 |
| ✓ | 2/13/97 | 7.80 | 345 | 56 | 10 | 0 | 411 |
| ✓ | 2/18/97 | 5.11 | 275 | 44 | 9 | 0 | 328 |
| ✓ | 2/19/97 | 7.83 | 373 | 54 | 10 | 0 | 437 |
| ✓ | 2/26/97 | 8.35 | 348 | 52 | 10 | 0 | 410 |
| ✓ | 3/7/97 | 6.13 | 364 | 57 | 10 | 0 | 431 |
| ✓ | 3/9/97 | 4.70 | 272 | 45 | 10 | 0 | 327 |
| ✓ | 3/11/97 | 7.15 | 381 | 55 | 4 | 0 | 440 |
| ✓ | 3/13/97 | 4.66 | 300 | 53 | 8 | 0 | 361 |
| ✓ | 3/18/97 | 7.50 | 362 | 45 | 8 | 0 | 415 |
| | 3/25/97 | 8.00 | 370 | 56 | 12 | 0 | 438 |
| | 3/27/97 | 4.00 | 226 | 31 | 5 | 0 | 262 |
| | 4/1/97 | 9.00 | 415 | 27 | 4 | 0 | 446 |
| | 4/8/97 | 6.00 | 304 | 26 | 4 | 0 | 334 |

## Table A-3 After Ozonation

| DAY | Ozone dose | Chl Dem. | $CHCl_3$ | $CHCl_2Br$ | $CHClBr_2$ | $CHBr_3$ | THMP | % red THMFP | % red. Chl dem |
|---|---|---|---|---|---|---|---|---|---|
| | mg/mg C | mg/l | ppb | ppb | ppb | ppb | ppb | | |
| 1/21/97 | 0.50 | 4.17 | 144 | 34 | 17 | 2 | 197 | | |
| 1/23/97 | 0.50 | 4.36 | 167 | 42 | 17 | 2 | 228 | 48.53 | 44.95 |
| 1/28/97 | 0.50 | 4.35 | 241 | 4 | 0 | 1 | 246 | 38.50 | 46.80 |
| 2/4/97 | 0.50 | 6.00 | 240 | 45 | 20 | 2 | 307 | 33.26 | 33.33 |
| 2/6/97 | 0.50 | 6.50 | 286 | 49 | 24 | 2 | 361 | 14.05 | 0.00 |
| 2/11/97 | 0.50 | 4.02 | 179 | 50 | 25 | 3 | 257 | 34.44 | 33.77 |
| 2/13/97 | 0.50 | 3.37 | 130 | 40 | 21 | 2 | 193 | 53.04 | 56.79 |
| 2/18/97 | 0.50 | 4.43 | 185 | 40 | 20 | 2 | 247 | 24.70 | 13.31 |
| 2/19/97 | 0.50 | 3.41 | 153 | 40 | 22 | 3 | 218 | 50.11 | 56.45 |
| 2/26/97 | 1.00 | 4.08 | 166 | 39 | 21 | 3 | 229 | 44.15 | 51.14 |
| 3/7/97 | 1.00 | 2.15 | 100 | 32 | 24 | 5 | 161 | 62.65 | 64.94 |
| 3/9/97 | 1.00 | 3.41 | 156 | 38 | 25 | 5 | 224 | 31.50 | 27.45 |
| 3/11/97 | 1.00 | 3.97 | 160 | 39 | 19 | 4 | 222 | 49.55 | 44.48 |
| 3/13/97 | 1.00 | 3.41 | 100 | 36 | 21 | 4 | 161 | 55.40 | 26.82 |
| 3/18/97 | 1.90 | 5.80 | 205 | 32 | 19 | 3 | 259 | 37.59 | 22.67 |

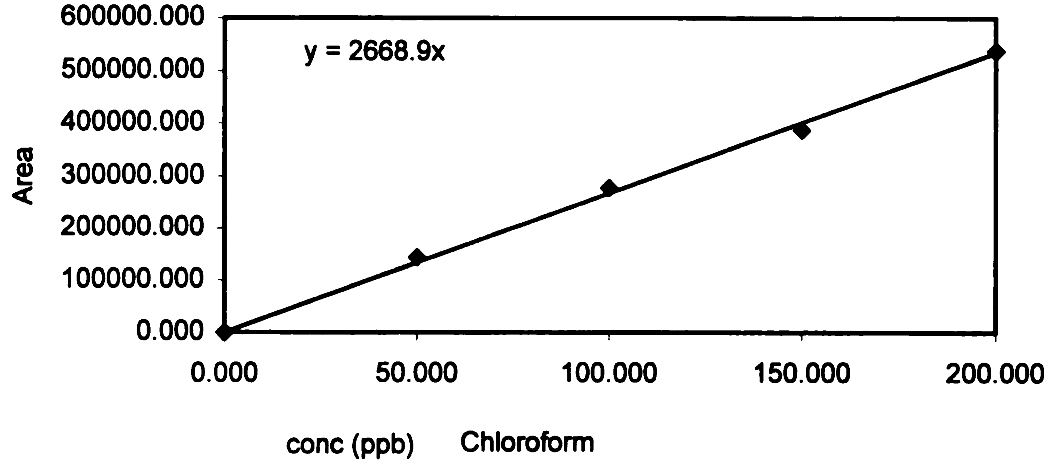
Note : % reduction in THMFP and chlorine demand is with respect to influent water sample ( initial THMFP and chlorine demand)

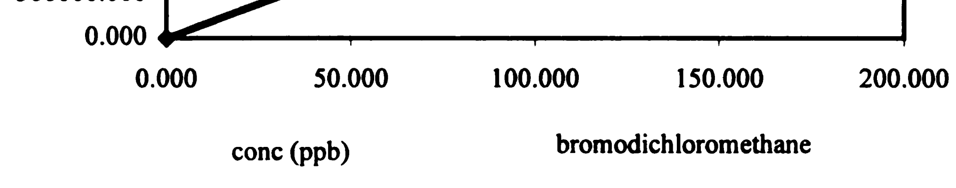
## Table A-4 Effluent from the system (after ozonation/FBT)

| DAY | Ozone dose | Chl Dem. | $CHCl_3$ | $CHCl_2Br$ | $CHClBr_2$ | $CHBr_3$ | THM FP | %red THM FP | %red. Chl dem |
|---|---|---|---|---|---|---|---|---|---|
| | mg/mg C | | | | | | | | |
| 1/21/97 | 0.50 | 2.30 | 82 | 26 | 17 | 2 | 127 | | |
| 1/23/97 | 0.50 | 2.86 | 124 | 37 | 18 | 2 | 181 | 59.14 | 63.89 |
| 1/28/97 | 0.50 | 3.07 | 120 | 37 | 14 | 1 | 172 | 57.00 | 62.45 |
| 2/4/97 | 0.50 | 2.00 | 92 | 30 | 17 | 2 | 141 | 69.35 | 77.78 |
| 2/6/97 | 0.50 | 2.90 | 151 | 37 | 22 | 3 | 213 | 49.29 | 55.38 |
| 2/11/97 | 0.50 | 2.11 | 73 | 45 | 41 | 11 | 170 | 56.63 | 65.24 |
| 2/13/97 | 0.50 | 1.84 | 77 | 31 | 18 | 2 | 128 | 68.86 | 76.41 |
| 2/18/97 | 0.50 | 2.72 | 122 | 33 | 17 | 2 | 174 | 46.95 | 46.77 |
| 2/19/97 | 0.50 | 2.38 | 115 | 35 | 20 | 3 | 173 | 60.41 | 69.60 |
| 2/26/97 | 1.00 | 1.02 | 41 | 22 | 20 | 6 | 89 | 78.29 | 87.78 |
| 3/7/97 | 1.00 | 3.00 | 120 | 33 | 23 | 5 | 181 | 58.00 | 51.08 |
| 3/9/97 | 1.00 | 1.70 | 89 | 27 | 21 | 6 | 143 | 56.27 | 63.83 |
| 3/11/97 | 1.00 | 2.04 | 100 | 33 | 19 | 5 | 157 | 64.32 | 71.47 |
| 3/13/97 | 1.00 | 1.70 | 65 | 32 | 17 | 2 | 116 | 67.87 | 63.52 |
| 3/18/97 | 2.00 | 1.70 | 74 | 20 | 17 | 5 | 116 | 72.05 | 77.33 |
| 3/25/97 | 0.00 | 4.30 | 147 | 34 | 20 | 3 | 204 | 53.42 | 46.25 |
| 3/27/97 | 2.00 | 1.70 | 65 | 23 | 19 | 5 | 112 | 57.25 | 57.50 |
| 4/1/97 | 0 | 5 | 276 | 23 | 4 | 0 | 303 | 32.06 | 44.44 |
| 4/8/97 | 0 | 3 | 126 | 21 | 10 | 0 | 157 | 52.99 | 50.00 |

Note : % reduction in THMFP and chlorine demand is with respect to influent water sample (initial THMFP) and chlorine demand.

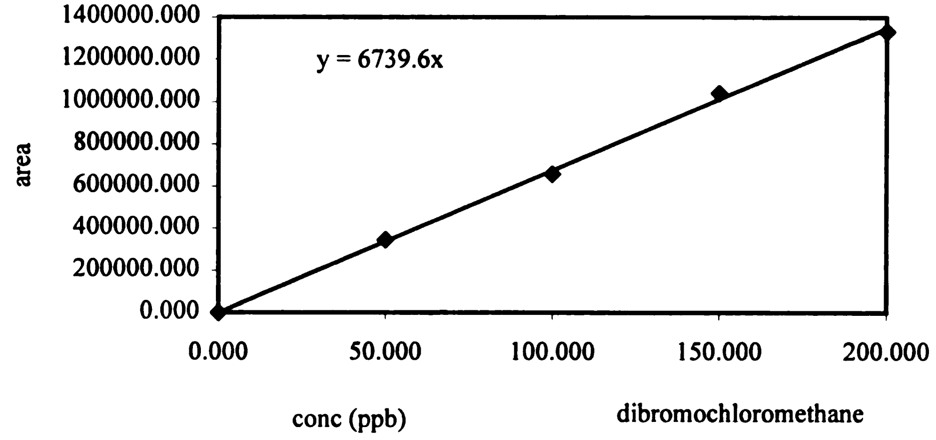
# APPENDIX B

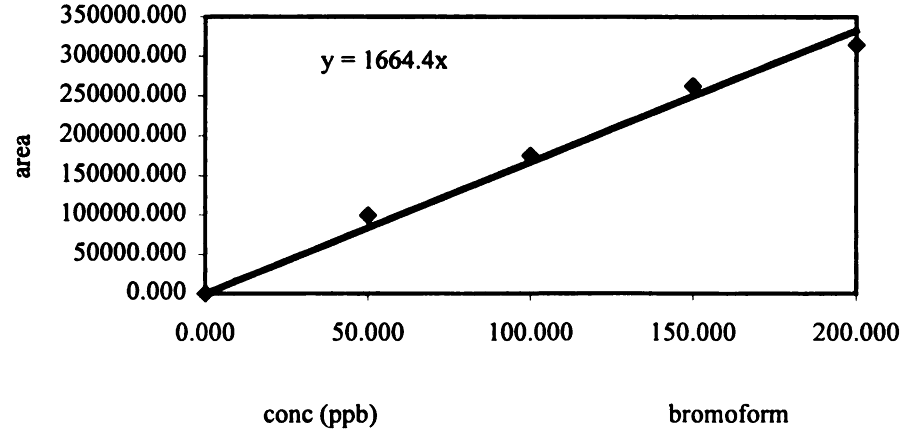




Note : Area is response area

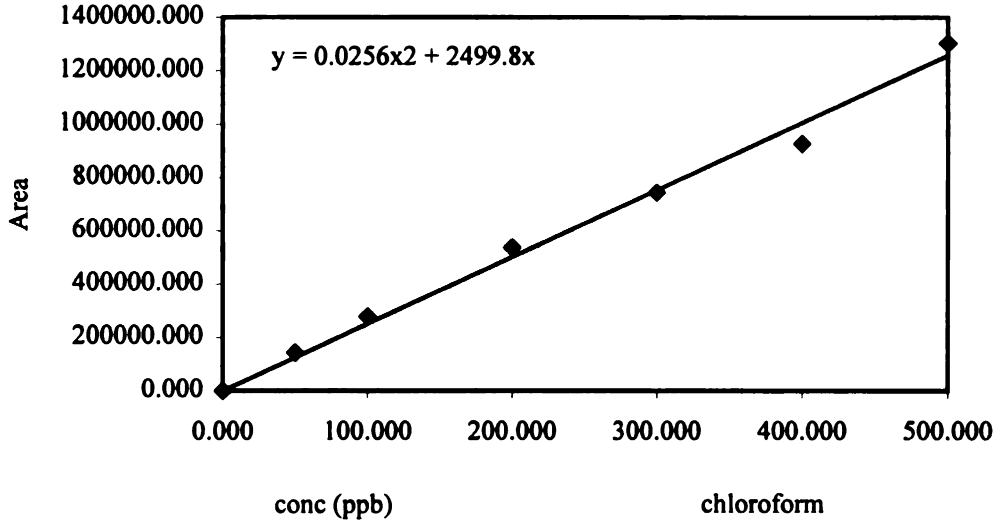
Figure B-1. Calibration curves for THMs by GCECD Head space Analysis

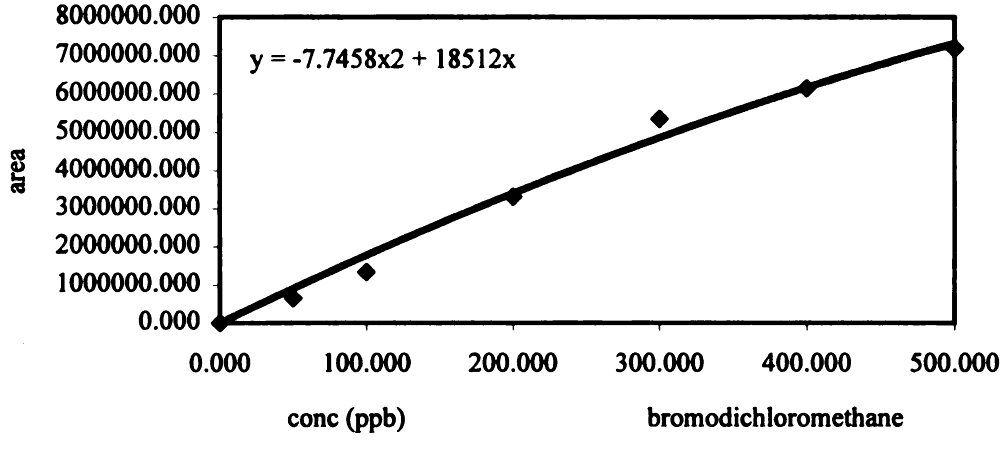




Note : Area is response area

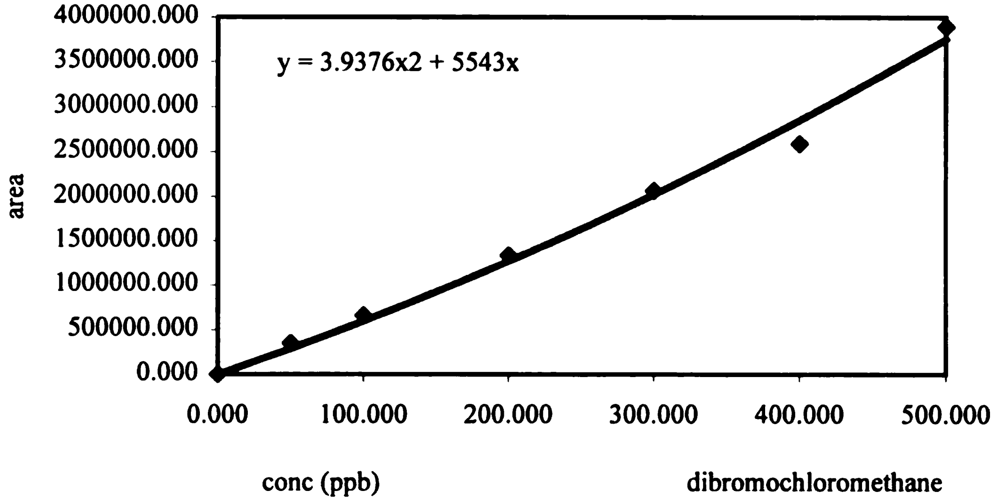
Figure B-1(cont'd). Calibration curves for THMs by GC ECD

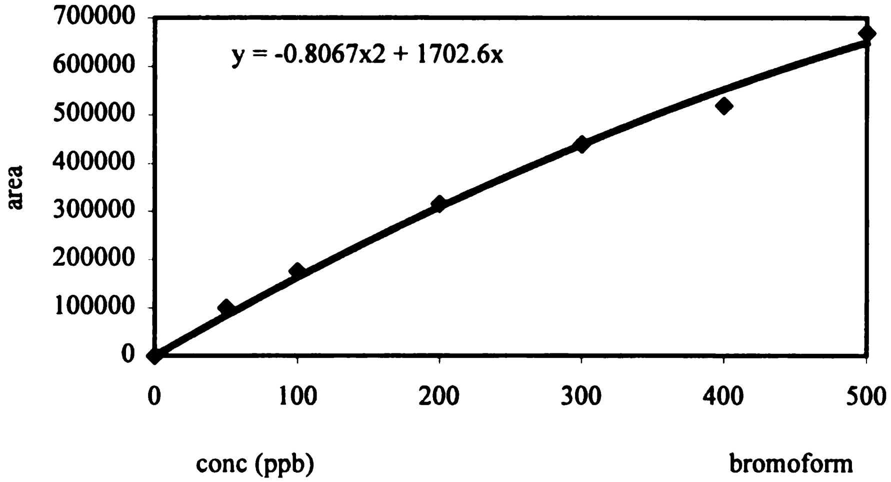




Note : area is response area

Figure B-2. Calibration curves for THMs by GCELCD





Note : area is response area

Figure B-2 (cont'd). Calibration curves for THMs on GCELCD.

# APPENDIX C

Experiments were conducted on East Lansing Drinking Water (tap water) to detect THMs. Using the GC-ECD, a total THM concentration of about 60 μg/L was observed in the East Lansing drinking water samples. All the THMs were detected. The GC-ELCD was not sufficiently sensitive enough for accurate analysis of tap water samples.

# LIST OF REFERENCES

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1. Anderson, R.L. *Practical Statistics for Analytical Chemists*, Van Nostrand Reinhold, New York, (1987)
2. Badawy, M.I. Evaluation of Headspace Technique for the Determination of Trihalomethanes in Water. *Bull.Environ.Contam.Toxicol. 48:630-34* (1992).
3. Castello, G. and T.C.Gerbino. Sensitivity and Linearity of Headspace and Liquid-Liquid extraction Techniques Gas Chromatographic Analysis of Halocarbons in Water. *J.Chromatography. 351:165- 75* (1986).
4. Doré. M; N. Merlet; B. Legube and J.Ph. Croue. Interactions Between Ozone, Halogens and Organic Compounds, *Ozone Science and Engineering 10:153-172* (1987).
5. Haag, W. and J. Hoigñe, Ozonation of Bromide Containing Waters: Kinetics of Formation of hypobromous Acid and Bromate. *Env. Sci. Tech. 17: 261-67* (1983)
6. Kolb, B; M. Auer, and P. Pospisil, Methods for the Quantitative Analysis of Volatile Halocarbons from Aqueous Samples by Equilibrium Headspace Gas Chromatography with Capillary Columns *J. Chromatography. 279: 341-48* (1983).
7. Langlais B.R; D.A. Reckhow and D.R. Brink, Editors, *Ozone in Water Treatment: Application and Engineering*, Lewis Publishers, Chelsea, MI (1991).

8. Nicholson. A.A; O. Meresz; B Lemyk, *Anal Chem., 49: 814-19* (1977).

9. Otson, R; D.T. Williams, and P.D. Bothwell. A Comparison of Dynamic and Static Headspace and Solvent Extraction Techniques for the Determination of Trihalomethanes in Water, *Environ. Sci.Technol. 13:936-39* (1979).

10. Pontius F.W., An Update of the Federal Drinking Water Regulations. *J.AWWA, 87:2:48* (1995).

11. Rajan, R.V; A.A. Yavich; J.L. Cook; R.F Hickey and S.J. Masten. Combination of Ozonation with Biological Fluidized Bed Treatment for Drinking Water Purification. *13th Ozone World Congress of International Ozone Association*, October 25-31, 1997, Kyoto, Japan.

12. Schnable, J.G; B. Dussert, and I.H. Suffet. Comparison of Quarter-hourly On-line Dynamic Headspace analysis to Purge and Trap Analysis of Varying Volatile Organic Compounds in Drinking Water Sources. *J.Chromatography. 513: 47-54* (1990).

13. Shukiary, H.M. and R.S.Summers. The Impact of Preozonation and Biodegradation on Disinfection By-product Formation. *Water Res.,26:9:1217* (1992).

14. Skoog, D.A. and J.J. Leary., *Principles of Instrumental Analysis*, Harcourt Brace College Publishers (1992).

15. Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, and WPCF, Washington D.C., 19th Edition (1995).

16. US Environmental Protection Agency. *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater. EPA-600/4-82-057* (1982).

17. US Environmental Protection Agency. *Methods for the Determination of Organic Compounds in Drinking Water. EPA-600/4-88-039* (1988).

18. Van Der Kooij, D.; A. Visser and W.A.M. Hijnen. Determining the Concentration of Easily Assimilable Organic Carbon in Drinking Water. *J.AWWA*, *74:10:540*, (1987).

19. Wang, H.; S.M. Simmons and A.R. Deininger. Application of Dynamic Headspace Analysis for Determination of Trihalomethanes in Flowing Water. *J. Chromatogr.Sci . 33:109-115* (1995).

20. Yamada, H. and I. Somiya. The Determination of Carbonyl Compounds in Ozonated Water by the PFBOA Method, *Ozone Science and Engineering*, *11:127-141* (1988).

21. Yavich A.A; A.N. Kasarabada; R.V. Rajan; R.F. Hickey, and S.J. Masten. The Use of Surrogate Parameters to Model the Kinetics of Ozone Reactions in Water . Submitted for presentation at *13th Ozone World Congress of International Ozone Association*, October 25-31, 1997, Kyoto, Japan.

22. Yavich A.A; R.V. Rajan; R.F. Hickey; J.L. Cook, A.N. Kasarabada and S.J. Masten. Control of Disinfection By-products in Drinking Water Using the Ozonation/FBR Process. 1997 AWWA Annual Conference, June 15-20, 1997.