FORMATION AND MODELING OF DISINFECTION BY-PRODUCTS IN NEWFOUNDLAND COMMUNITIES

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By

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Abstract

For the past few years, the presence of disinfection by-products (DBPs) especially chlorinated DBPs has become a health concern. This will be an important and particular concern at the water utilities. As standards are becoming very strict, water utilities have to adjust their operation strategies to comply with the new regulations while maintaining residual chlorine, which should ensure an acceptable microbiological quality. This study was aimed at finding the parameters affecting the formation of these DBPs, studying the kinetics of DBPs formation during the chlorination of raw water and developing models to predict the formation of DBPs. Gas chromatograph with an ECD detector was used for the analysis of the samples. Four compounds of trihalomethanes(THMs) Chloroform, dibromochloromethane, bromodichloromethane, bromoform, four compounds of Haloacetonitriles (HANs) dichloroacetonitrile, trichloroacetonitrile, bromochloroacetonitrile, dibromoactonitrile along with two compounds of Haloketones (HKs) 1,1 - dichloropropanone and 1,1,1- trichloropropanone were analysed. Chloroform, dichloroactonitrile and 1,1,1- trichloropropanone dominated among the DBPs. TOC, pH, chlorine dosage and reaction time were the important parameters which where affecting the formation of these DBPs. The models to predict the formation of THMs, HANs and HKs were developed with coefficient of correlations of 0.77, 0.685 and 0.681 respectively. Data fit software was used to develop these models.

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Table of Contents

List of Tables

List of Figures

List of Acronyms

BCAN: Bromochloroacetonitrile

BDCM: Bromodichloromethane

CAN: Chloroacetonitrile

CBPs: Chlorinated by-products

$CHBr_3$: Bromoform

$CHBrCl_2$: Bromodichloromethane

$CHCl_3$: Chloroform

$CHClBr_2$: Chlorodibromomethane

CT: Product of chlorine residual and time required

DBA: Dibromoacetic acid

DBAC: Dibromoacetone

DBAN: Dibromoacetonitrile

DBCM: Dibromochloromethane

DBPs: Disinfection By-Products

DCA: Dichloroacetic acid

DCAN: Dichloroacetonitrile

DOC: Dissolved organic Carbon

DPD: Diethyl-p-Phenylene Diamine

ECD: Electron Capture Detector

EPA: Environmental Protection Agency

GAC: Granular Activated Carbon

GC: Gas Chromatograph

HAAs: Haloacetic Acids

HKs: Haloketones

HANs: Haloacetonitriles

IARC: International Agency for Research on cancer

ISTD: Internal Standard

LOAEL: Lowest observed adverse effect level

MBA: Monobromoacetic acid

MTBE: Methyl tert butyl ether

NOAEL: No observed adverse effect level

NOM: Natural Organic Matter

NPOC: Non-purgeable organic carbon

RSD: Residual Standard Deviation

SGA: Small for gestational age

TCA: Trichloroacetic Acid

TCAN: Trichloroacetonitrile

TCP: 1,1,1 trichloropropanone

TDI: Tolerable daily intake

TFE: Tetraflouroethylene

THMs: Trihalomethanes

TOC: Total Organic Carbon

TOX: Total Organic Halogen

TTHMFP: Total Trihalomethanes Formation Potential

TTHMs: Total trihalomethanes

UV: Ultra Violet

U.S. EPA: United States Environmental protection Agency

WHO: World health organization

Chapter 1

Introduction

1.1 Back-ground Information

The purpose of disinfecting water supplies is to reduce the density of pathogenic micro organisms and thus diminish the risk of water borne diseases transmission which otherwise can cause serious illnesses and deaths. These pathogenic micro organisms include viruses, bacteria and protozoa. Though disinfection can be accomplished by a number of physicochemical water treatment processes, such as coagulation, sedimentation, filtration, lime-soda softening and adsorption, a specific chemical is usually added into surface water treatment process called disinfectants to prevent the transmission of waterborne diseases(Health Canada, 2000). Disinfectants may be used early in the treatment process as an oxidant and/or to provide initial disinfection. Typically disinfectant is applied in the final stage of treatment. This disinfectant addition must achieve an adequate inactivation of microorganisms before the treated water reaches the first consumer and be large enough to ensure an adequate residual at the periphery of the distribution system to inhibit microbial re-growth. The economy and effectiveness of chlorine in killing water borne micro organisms has made chlorination a tremendous public health success world wide.

In the 19th century, major outbreaks of waterborne diseases were common in Canada, the United States and other developed countries. Beginning in the early 20th century, the provision of chlorinated drinking water virtually eliminated typhoid fever,

cholera and other waterborne diseases, representing one of the great achievements of public health (Donald, 2000).

Chlorine was discovered in 1774 by the Swedish chemist Karl Wilhelm Scheele and confirmed to be an element in 1810 by Sir Humphry Davy (White GC, 1992). Use of chlorine as a disinfectant was first introduced by Semmelweis on the maternity ward of the Vienna General Hospital in 1846 to clean the hands of medical staff and prevent puerperal fever. In 1881 Koch showed that pure cultures of bacteria were destroyed by hypochlorites (White GC, 1992).

The first continuous usage of chlorination in the US began in 1908 for the water supply to Jersey City, New Jersey, and at a site that served the Chicago Stockyards to control sickness in livestock caused by sewage-contaminated water (White GC, 1992). In Canada, the earliest use of chlorination was in Peterborough, Ontario, in 1916 (Peterborough Utilities Commission, 1998). Chlorination has been the main method of disinfecting in drinking water for several decades and has proven effective against most waterborne pathogens.

Chlorination has positioned itself as a major offensive against most waterborne pathogens. Microorganisms that can cause disease are named as microbial pathogens. They can be harmful to those who become injected. Pathogens associated with the water borne diseases mostly belong to the group of microbial agents like the bacteria, viruses and protozoa. Theoretically, to remove these pathogens from the drinking water is not an easy job. We can just add the disinfectants, provide a sufficient contact time to ensure that the disease causing capabilities of the microbes have been completely destroyed and then the disinfected water is released for the distribution. In practical applications the

process is not so simple because of the facts that parameters like residual chlorine, temperature, pH come into the picture.

The physical characteristics of the water such as dissolved and suspended solids have the ability to affect the process of disinfection. The chemical parameters like the naturally occurring organic matters and matters produced by human activities can influence the normal chemical reactions expected to take place during treatment and the disinfecting process. The pathogens, which are associated with the higher organisms like the algae, rotifers and worms, may survive the effect of disinfectants. The aforesaid impediments are eliminated in the actual drinking water processes that are comprised of screening, coagulation, flocculation, sedimentation, filtration, disinfection, clear water reservoir storage and pumping into the main distribution system. After the impurities are removed from the untreated water, a sufficient quantity of disinfectants is added to the water. This renders the pathogens harmless. It is imperative to maintain a residual level of disinfectant along the water distribution systems. This is to prevent any recurrence of the microbial growth or invasion of harmful microorganisms into the distribution pipes.

1.2 Disinfection of drinking water

Disinfection of drinking water is defined as a treatment process for the purpose of the destruction or inactivation of human pathogens, up to a given level of safety that should be maintained throughout water storage and distribution. The process depends on the type and concentration of the disinfectant, type and concentration of the microorganisms, and the physical and chemical properties of the source water. The disinfection process should balance the ability to kill or inactivate a wide variety of

microbial pathogens, maintain a residual and minimize the formation of harmful by-products. Combinations of primary and secondary disinfectants have been used recently in an attempt to minimize the formation of harmful by-products.

There are a variety of disinfection methods utilized worldwide for the treatment of water. The most commonly used disinfectants are:

- Chlorine
- Chloramination
- Chlorine dioxide
- Ozone
- Ultraviolet radiation
- Mixed Oxidants
- Iodine

Various disinfectants, their potential health effects from ingestion of water, and their source of contamination is given in Table1.1.

Table 1.1 Disinfectants

Contaminant	Potential Health Effects from Ingestion of Water	Sources of Contaminant in Drinking Water
Chloramines as (Cl_2)	Eye/nose irritation; stomach discomfort, anemia	Water additive used to control microbes
Chlorine as (Cl_2)	Eye/nose irritation; stomach discomfort	Water additive used to control microbes
Chlorinedioxide as(ClO_2)	Anemia; infants & young children: nervous system effects	Water additive used to control microbes

Source: US EPA, 2002

Throughout North America, chlorination is the most widely used method of disinfection. Chlorine is used mainly because:

- It is effective against a broad range of pathogens including bacteria, viruses and protozoa
- It provides residual protection by preventing microbial growth after the treated water enters the distribution system and
- The technology associated with chlorine disinfection is simpler than other disinfection technologies and can be utilized in treatment plants of all sizes.

Chlorine can be administered to a water system in both gaseous and liquid forms.

All forms of chlorine invariably react with the water to form hypochlorous acid, which acts as the effective disinfectant. The hypochlorous acid, in turn, dissociates into the hypochlorite ion depending on pH and temperature.

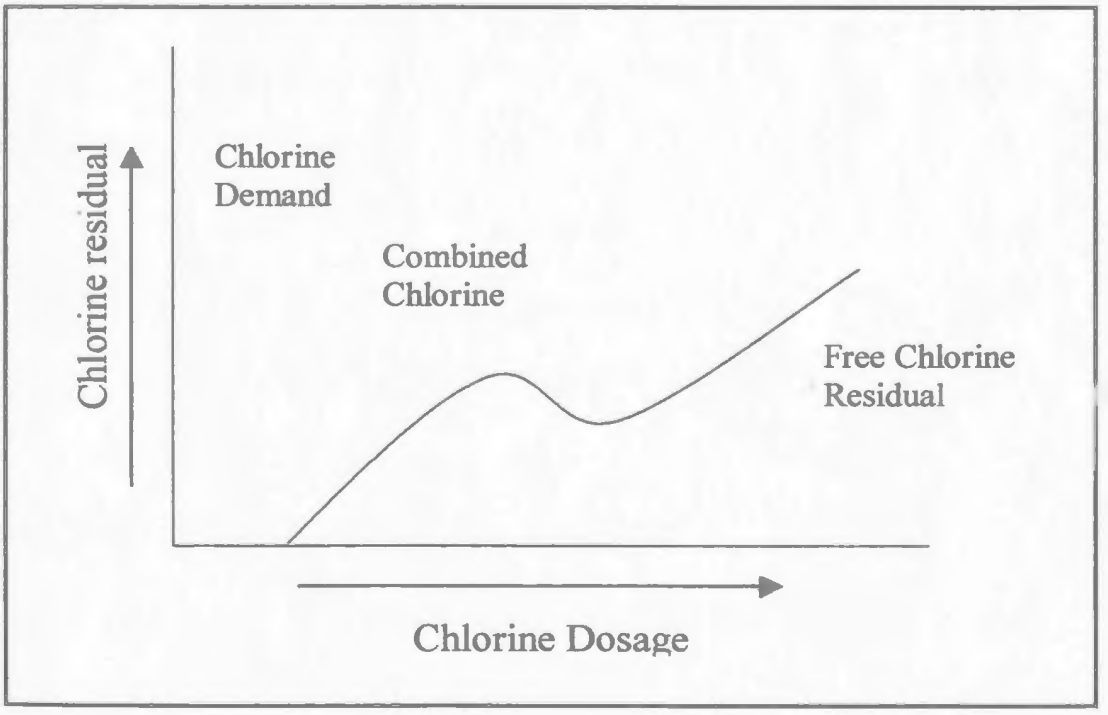
$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^- \qquad \text{Equation (1.1)}$$

$$HOCl \longrightarrow H^+ + OCl^- \qquad \text{Equation (1.2)}$$

Hypochlorous acid ⟶ Hydrogen ion + Hypochlorite ion

The chlorine dosage is the amount of chlorine added to the water. As shown above, hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) develop in water treated with chemicals for chlorination. The amount of hypochlorous acid and hypochlorite ion in water is defined as free available chlorine.

Figure1.2: Chlorine dosage, Demand and Residual



Source: Dept. of Environment, NL

The chlorine residual is the amount of chlorine measured in the water when it is analyzed. When chlorine is added to raw water, chemicals present in the raw water begin to react with or use up the chlorine, exerting a demand for the chlorine. The difference between the chlorine dosage and the chlorine residual that would be expected by analysis is called the chlorine demand. Chlorine existing in combined chemical forms with ammonia or organic nitrogen compounds is referred to as combined available chlorine or combined residual chlorine. When all of the ammonia has been consumed and all of the combined chlorine has been oxidized, the chlorine added becomes equal to the chlorine residual. This chlorine dosage is called the breakpoint. Beyond the breakpoint, the chlorine is in the form of free available chlorine. The explanation can be shown in graphical format as in figure 1.2 above.

1.3 Disinfection By-products

Chlorine's oxidizing power causes it to react with naturally occurring organic material in raw water to produce hundreds of chlorinated organic compounds, referred as chlorination disinfection by-products (CBPs) including Trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), chloral hydrate and 3-chloro-4-(dichloromethyl)-5- hydroxy-2(5H)-furanone, or MX. The order of dominance (formation potential) is generally THMs > HAAs > HANs (WHO, 2000). Chlorinated THMs, HAAs and HANs species usually dominate over brominated species, except in waters with high bromide levels.

The concentration levels of these by-products are the function of many parameters including the level of the organic material in the source water. As a result, the water

supplies that use the surface waters (lakes, rivers, and reservoirs) as their intake source produce the higher level of by-products than the water supplies that use the ground waters (wells, springs) as their intake source.

Chlorine Dioxide:

Chlorine dioxide forms chlorite ion (ClO_2^-) and chlorate ion (ClO_3^-) by-products; organic halogen DBPs are not directly formed. Unlike the other disinfectants, the major chlorine dioxides DBPs are derived from decomposition of the disinfectant as opposed to reaction with precursors.

Chlorite is the predominant species formed. Formation of chlorite can be estimated by a simple percentage (50–70%) of the applied chlorine dioxide dose. The toxic damage of chlorite is primarily in the form of oxidative damage to red blood cells at doses as low as 10-mg/kg-body weight. There are also indications of mild neurobehavioural effects in rat pups and conflicting data on genotoxicity (Health Canada, 2000).

Ozone:

Ozone can react directly or indirectly with bromide to form brominated ozone DBPs, including bromate ion (BrO_3^-). In the presence of natural organic matter, non-halogenated organic DBPs such as aldehydes (e.g., formaldehyde), ketoacids and carboxylic acids are formed during ozonation. If both natural organic matter and bromide are present, ozonation forms HOBr, which, in turn, leads to the formation of brominated organohalogen compounds (e.g., bromoform).

Bromide concentration and ozone doses are the best predictors of bromate formation during ozonation, with about 50% conversion of bromide to bromate; brominated organic DBPs formed on ozonation generally occur at low levels (Health Canada, 2000).

Table 1.2 Disinfectant by-products present in disinfected waters

Disinfectant	Significant organo-halogen products	Significant inorganic non-halogenated products	Significant organic/non-halogenated products
Chlorine/Hypochlorous acid	THMs, HAAs, HANs, chloral hydrate, chloropicrin, chlorophenols, N-chloramines, halofuranones, bromohydrins	chlorine, chlorate (mostly from hypochlorite use)	aldehydes, cyanoalkanoic acids, alkanoic acids, benzene, carboxylic acids
Chlorine dioxide		chlorite, chlorate	unknown
Chloramine	HANs, cyanogen chloride, organic chloramines, chloramino acids, chloral hydrate, haloketones	nitrate, nitrite, chlorate, hydrazine	aldehydes, ketones
Ozone	bromoform, MBA(Monobromo acetic acid, DBA(Dibromoaceti c acid), DBAC(Dibromoacet one), cyanogen bromide	chlorate, iodate, bromate, hydrogen peroxide, hypobromous acid, epoxides, ozonates	aldehydes, ketoacids, ketones, carboxylic acids

Source: (IPCS, EHC 216)

1.4 Purpose of the study

The purpose of the present study is to find the parameters affecting the formation of DBPs in Newfoundland communities and to develop models to predict their formation based on their water quality parameters. Laboratory experiments are performed by chlorinating the raw water samples and finding the amount of THMs, HANs and Haloketones (HKs) at different reaction times and at different dosages.

1.5 Significance of the study

When the water is subjected to chlorination in an attempt to eliminate the disease causing microorganisms, the chlorine comes in contact with the naturally occurring organic matter. As a result of this reaction, the CBPs are formed.

Considerable research has been conducted to examine the association between the exposure to DBPs in drinking water and the potential increase in risk of various cancers. Recently there has been a shift of interest from cancer to reproductive outcomes such as spontaneous abortion, stillbirth, preterm delivery, low birth weight etc (Nieuwenhuijsen et al., 2000).

The study is aimed at reviewing the health effects of DBPs and the various techniques to control them.

The main objective was aimed at finding the different DBPs in water, their formation and the factors that are contributing to their formation in the Newfoundland communities so that attempts can be made to find new treatment techniques or modify the present ones to decrease the formation.

1.6 Outline of Thesis

The review on various types of DBPs, their formation and mechanism, drinking water guidelines of DBPs given by various organizations, toxicological information and health risk of DBPs are presented briefly in the literature review of chapter 2.

Chapter 3 focuses on the sample collection, preservation, various pieces of equipment and methods used in determining the water quality parameters. It also describes the procedure of chlorination, calibration of the DBPs standards looking at, its accuracy and the methods used in analyzing the samples. Results of the laboratory analyses are also listed in this chapter.

Chapter 4 presents the correlation between the DBPs and the various parameters affecting their formation as well as those highly effective in their formation. Various models fitted for each type based on the parameters affecting their formation along with their accuracy are also discussed briefly in this section. Datafit and Minitab are the software used in this statistical analysis. The conclusions and recommendations are presented in the chapter 5 and 6.

Chapter 2

Literature Review

2.1 Disinfection By-products in Drinking water

DBPs are formed upon the reaction of chemical disinfectants with DBP precursors. Natural organic matter (NOM), commonly measured by total organic carbon (TOC), serves as the organic precursor, whereas the bromide ion (Br^-) serves as the inorganic precursor. DBP formation is influenced by water quality (e.g., TOC, bromide, pH, temperature, ammonia, carbonate alkalinity) and treatment conditions (e.g., disinfectant dose, contact time and removal of NOM before the point of disinfectant application, prior to addition of disinfectant).

DBPs occur in complex mixtures are a function of the chemical disinfectant used, water quality conditions and treatment conditions and other factors including the combination/sequential use of multiple disinfectants/oxidants. Moreover, the composition of these mixtures may change seasonally. Clearly, potential chemically related health effects would be a function of exposure to DBP mixtures. (WHO, 2000)

THMs were the first category of DBPs to be detected in drinking water (Bellar et al., 1974; Rook, 1974), followed by HAAs (Quimby et al., 1980; Christman et al., 1983; Miller and Uden, 1983; Reckow and Singer, 1984; Krasner et al., 1989) and HANs, HKs and chloropicrin at lower concentrations (Trehy and Bieber, 1980; Krasner et al., 1989; Williams et al., 1997)

Mass balance on halogenated DBPs (based on TOX, total organic halogen) suggests that less than half of total halogenated organics have been identified. No mass

balance is possible to account for the quantity of non-halogenated DBPs that remain unidentified. New analytical approaches are necessary to assess the full spectrum of possible DBPs. The recent and emerging DBPs are halogenated furanones like MX (3-chloro-4(dichloromethyl)-5-hydroxy-2(5H)-furanone), haloacids like 3,3,dichloropropenoic acid, halonitromethanes like dibromonitromethane, halomethanes like bromochloroiodomethane, dichloroiodomethane, nitrosamines like nitrosodimethylamine(NDMA) etc.,

2.1.1 Types of DBPs

Trihalomethanes:

THMs are the most commonly occurring groups of CBPs. They were first identified at higher concentrations in chlorinated drinking water than in natural raw water by Rook (1974) and by Bellar et al., (1974). THMs are small organic compounds similar in structure to methane, but they have three hydrogen atoms substituted with chlorine or bromine. They are formed in water when disinfectants such as the chlorine used in water treatment plants react with the organic water; e.g. humic acids, which are found in the source water, especially in case of surface waters. Disinfectants reduce the levels of microbes in the water supply; however, as the use of disinfectants in water increases, the risk of THMs formation increases. Thus, THMs can be found in most disinfected drinking water supplies.

THMs levels in drinking water also suggest the seasonal variations. In winter months the concentrations are found to be lower (Otson, 1987; Williams et al., 1980).

During winter, by reducing the quantity of applied chlorine, the THM levels can be reduced significantly at that time of the year (Kar and Husain, 1999). Since the concentrations of the natural organic matter are lower in winter, the quantity of chlorine required to disinfect is much less in the winter than in the summer.

The most important THMs in disinfected water are:

- Trichloromethane (Chloroform) $CHCl_3$
- Dibromochloromethane $CHClBr_2$
- Bromodichloromethane $CHCl_2Br$
- Tribromomethane (Bromoform) $CHBr_3$

Chloroform:

Chloroform is one of the THMs, which is detected most frequently and at highest concentration in drinking water. It is a clear, colourless, non-flammable liquid having a characteristic heavy, pleasant and sweet taste with crisp odour. It dissolves in acetone and dissolves slightly in water (0.8g/g of water at 20°C). The vapour pressure at 25°C is 23.33kPa with a log octanol-water partition coefficient of 1.97 (NAS, 1987).

Dibromochloromethane:

Dibromochloromethane(DBCM) is a heavy, colorless to pale yellow liquid used as a chemical intermediate in the manufacture of fire extinguishing agents, aerosol propellants, refrigerants, and pesticides. Its boiling point is about 118°C; its specific gravity is 2.38 and it has a density of 2451 kg/m^3 at 20°C. It is soluble in alcohol, ether, acetone, benzene, and organic solvents (NAS, 1987).

Bromodichloromethane:

Bromodichloromethane(BDCM) is a colorless liquid that boils at 90.1°C. It is soluble in water (4,500 mg/L), alcohol, ether, acetone, benzene, and chloroform. BDCM is not readily flammable (IARC, 1991). The vapour pressure at 20°C is 2.0 kPa with a log Octanol-water partition coefficient of 2.09. BDCM is used in the synthesis of organic chemicals and as a reagent in laboratory research. It has also been used to separate minerals and salts, as a flame retardant, and in fire extinguishers.

Bromoform:

It is a colourless-yellow liquid with a boiling point of 149.5°C. The vapour pressure at 25°C is 0.7 kPa with a log octanol-water partition coefficient of 2.30. Bromoform was used in the late 19th and early 20th centuries as a sedative for children with whooping cough.

Haloacetic acids:

Haloacetic acids (HAAs) are a type of CBPs that are formed when the chlorine used to disinfect drinking water reacts with naturally occurring organic matter (NOM) in water. HAAs are relatively new disinfection by-products.

HAAs are collections of several different compounds. The sum of bromodichloroacetic Acid ($BrCl_2AA$), dibromochloroacetic Acid (Br_2ClAA), and tribromoacetic Acid (Br_3AA) concentrations is known as HAA_3. The sum of monochloroacetic Acid (ClAA), monobromoacetic Acid (BrAA), dichloroacetic Acid (Cl_2AA), trichloroacetic Acid (Cl_3AA), and dibromoacetic Acid (Br_2AA) concentrations are known as HAA_5. HAA_6 refers to the sum of HAA_5 and bromochloroacetic Acid

(BrClAA) concentrations. HAA_6 and HAA_3 together make up HAA_9 (Roberts et al., 2002). Dichloroacetic acid (DCA) and Trichloroacetic acid (TCA) are the first and second most dominant species.

Dichloroacetic acid:

DCA is a colourless liquid with a pungent odour. It boils at 193-194°C and has a density of 1563 kg/m^3. It is soluble in water. Its two crystalline forms melt at 9.7°C and –4°C (Windholz et al., 1983). DCA is used as a chemical intermediate and in pharmaceuticals and medicine (Hawley, 1981). This compound exists in drinking water as the salt, despite the fact that it is widely referred to as DCA. DCA has a kp_a of 1.48 at 25°C. As a consequence, it occurs almost exclusively in the ionized form at the pHs found in drinking water (a pH range of 5-10) (WHO, 2000).

Trichloroacetic acid:

TCA takes the form of non-flammable, deliquescent colorless crystals, also having a sharp pungent odour. The crystals melt at 57.5°C and boil at 197.5°C. At 25°C, 1.2 kg of TCA crystals is soluble in 1 litre of water. The compound is used in organic synthesis, as a reagent for detection of albumin, in medicine for the removal of warts and as an astringent, in pharmacy and in herbicides (NAS, 1987).

Haloacetonitriles:

The four compounds that constitute the Haloacetonitriles (HANs) are dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN). The HANs are colorless to yellow, volatile liquids. The chlorinated acetonitriles are used as insecticides and fungicides. A summary of their chemical and physical properties is show below in Table 2.1

Table 2.1 Chemical and Physical properties of Haloacetonitriles

	Dichloro-acetonitrile $CHCl_2CN$	**Trichloro-acetonitrile CCl_3CN**	**Bromochloro-acetonitrile CHBrClCN**	**Dibromo-acetonitrile $CHBr_2CN$**
Molecular weight	109.94	144.39	154.4	198.9
Appearance	Liquid	Colorless, volatile liquid	Liquid	Liquid
Density (kg/m^3)	1370	1440	1680	2300
Melting point (°C)	NA	-42	NA	NA
Boiling point (°C)	112.3	85.7	125-130	67-69

Source: NAS, 1987

Chloropicrin:

Chloropicrin (CCl_3NO_2) is a slightly oily, colorless, refractive liquid that is relatively stable and nonflammable. It has a boiling point of 112°C and a freezing point of –69.2°C; its specific gravity is 1.692 at 0°C; and it is soluble in alcohol, benzene, ether, and carbondisulfide and slightly soluble in water (0.17g/100g water at 18°C). A strong irritant that is toxic when ingested or inhaled, it is used in organic synthesis, dyestuffs, fumigants, fungicides, insecticides and tear-gas (NAS, 1987).

1,1dichloro-propanone:

It has a molecular weight of 127 with a boiling point of 120°C. Its specific gravity is 1.31 and it is soluble in water and ether (NAS, 1987).

1,1,1 trichloro-propanone (TCP):

TCP has a molecular weight of 161 with a boiling point of 149°C. Its specific gravity is 1.44 and it is soluble in water and ether (NAS, 1987).

3-chloro-4- (dichloromethyl)-5- hydroxy –2(5H) –furanone (MX):

It is a by-product of chlorination that is typically found at very low concentrations (approximately <0.000067 mg/L) in drinking water. The weight of evidence indicates that MX is a direct-acting genotoxicant in mammals, with the ability to induce tumors in multiple sites .The primary sites for tumor formation are thyroid and liver (U.S., EPA, 2002)

N-nitrosodimethylamine (NDMA):

Health effects data indicate that NDMA is a probable human carcinogen, as described in (IRIS, 1991). Risk assessments have estimated that the 10^{-6} lifetime cancer risk level is 0.000007 mg/L based on induction of tumor at multiple sites. Short-term studies have shown that NDMA is moderately toxic to wildlife and laboratory and domestic animals. Long-term studies have shown that NDMA primarily affects the liver (Health Canada, 2002).

2.1.2 Formation of DBPs

DBPs formation begins at the first point of chlorination and continues for days as the water passes through the distribution system. DBPs levels at any point in the system vary as a function of time from the point of chlorination.

The formation of one of the DBPs chloroform can be represented as follows:

$$\text{Free } Cl_2 + \text{NOM} \longrightarrow CHCl_3 + \text{Other DBPs}$$

In the presence of bromide ions, free chlorine readily oxidizes the bromide ion to hypobromous acid (HOBr), which can subsequently react with natural; organic material to produce bromoform:

$$\text{Free } Cl_2 + Br \longrightarrow HOBr + Cl$$

$$HOBr + \text{NOM} \longrightarrow CHBr_3 + \text{Other Disinfection By-products}$$

The combined action of both chlorine and hypobromous acid leads to the formation of the mixed chloro-/bromo-THMs species and other mixed halogenated by-products (Rook, 1977; Cooper et al., 1985; Singer and Chang, 1989).

It is generally accepted that the reaction between chlorine and humic substances, a major component of NOM (natural organic matter), is responsible for the production of organochlorine compounds during drinking-water treatment. Humic and fulvic acids show a high reactivity towards chlorine and constitute 50-90% of the total DOC (dissolved organic carbon) in river and lake waters (Thurman, 1985). Other fractions of the DOC comprise the hydrophilic acids (up to 30%), carbohydrates (10%), simple carboxylic acids (5%) and proteins/amino acids (5%). The reactivity of carbohydrates and carboxylic acids towards chlorine is low, and they are not expected to contribute to the

production of organochlorine compounds. However, hydrophilic acids such as citric acid and amino acids will react with chlorine to produce chloroform and other products and may contribute towards total organochlorine production (Larson & Rockwell, 1979). Free chlorine reacts with water constituents by three general pathways: oxidation, addition and substitution (Johnson & Jensen, 1986). Chlorine can undergo an addition reaction if the organic compound has a double bond. For many compounds with double bonds, this reaction is too slow to be of importance in water treatment. The oxidation reactions with water constituents such as carbohydrates or fatty acids (e.g., oleic acid) are generally slow. Most chlorine DBPs are formed through oxidation and substitution reactions. THMs have the general formula CHX_3, where X can be Cl or Br. Chloroform may be produced through a series of reactions with functional groups of humic substances. The major functional groups of humic substances include acetyl, carboxyl, phenol, alcohol, carbonyl and methoxyl. The reactions proceed much more rapidly at high pH than at low pH. Rook (1977) proposed resorcinol (meta 1,3 isomer) structures to be the major precursor structure in humic material for chloroform formation. In accordance with this hypothesis in the chlorination of terrestrial and aquatic humic substances, a series of intermediates were detected that contained a trichloromethyl group and that could be converted to chloroform by further oxidation or substitution reactions (Stevens et al., 1976).

However, the production of chlorinated compounds such as dichloropropanedoic acid, 2,2-dichlorobutanedoic acid, cyanogen chloride (CNCl), HANs or the cyano-substituted acids cannot be explained on the basis of resorcinol structures, and possible production pathways require protein-type precursors (De Leer et al., 1986). The reaction

pathway for amino acids involves initial rapid formation of the monochloramine and dichloramine, which can react further to form aldehyde or HANs, respectively. Trehy et al. (1986) demonstrated the formation of chloral hydrate along with HANs after chlorination of amino acids by substitution reactions, and aldehydes were shown to be the oxidation products.

2.1.3 General Mechanism

DBPs are formed in the water supplies when the natural organic matters (NOM) present in the untreated water react with the chlorine during treatment. Natural organic matter is characterized by the various natural processes such as the soil chemistry, hydrology, climatic conditions and the sources of the organic materials. It represents the complex matrix of the organic material found in the natural waters. Untreated waters contain the NOM in the form of the suspended organic matter particles and dissolved organic carbon (DOC) and can be categorized into the humic and non-humic portions. The humic portion is more hydrophobic in character and contains mostly the humic and fulvic acids where as the non-humic portion is less hydrophobic and essentially consists of the hydrophilic acids, proteins, amino acids, and carbohydrates.

The most significant factor of THMs formation is the precursor itself, the constituent that causes THMs formation when reacted with either chlorine or bromine. Both type and concentration of precursor material are important considerations (Stevens and Symons, 1977; Rook et al., 1982). Humic substances are considered to be the main precursors in THMs formation. Because an exact structure cannot be written for humic

substances, these substances cannot be measured directly. Consequently, they are normally characterized by non-specific parameters such as based on their ability to absorb UV light, i.e., UVA at 254nm, by their organic carbon composition, i.e., DOC, or by their potential to form THMs (Aiken et al., 1985).

Aquatic humic substances, constituting most of the naturally occurring organic matter in water supplies, account for approximately 30 to 50% of the DOC in most natural waters and have been shown to be the most important precursors in THMs formation (Rook, 1976; Stevens et al., 1976; Thurman, 1985). Humic substances in natural waters are complex mixtures of organic matter. They are described as a general category of naturally-occurring, biogenic, heterogeneous organic substances that can generally be characterized as being yellow to black in color, of high molecular size, and refractory (stable) (Aiken et al., 1985). The nature of aquatic humic substances and their complex character vary seasonally and with geographic location. This can be an important factor in influencing the performance of the THMs upon chlorination.

2.1.4 Factors Affecting DBPs Formation

The factors that effect the formation of the THMs are:

- pH
- Temperature
- Reaction time
- Chlorine dose and chlorine demand
- Bromide ion concentration
- Nature and concentration of the precursor

pH:

A number of studies have found pH to be a very important parameter in determining THMs formation. The increase in THMs formation when pH was increased from 7 to 11 was found to be 40% and 50%, depending on the organic source and chlorination condition (Oliver, 1978 and Oliver and Lawrence, 1979) respectively. Stevens et. al., (1976) reported that the THMs formation from humic acid increases from 5.2 to 9.2, and that at pH of 3.4, THMs formation was virtually the same as at a pH of 5.2. Oliver (1980) and Peters et al. (1980) found an increase in THMs production when pH was elevated after chlorination was terminated.

But with increasing pH, HAAs formation decreases. At high pH values, hydrolysis of many halogenated DBPs occurs (Krasner et al., 1989). As a result, total organic halide (TOX) concentration is lower at pH>8 (Singer, 1994).

Temperature:

DBPs formation has been found to be strongly dependent on temperature. High temperature results in high DBPs yield. Temperature has been suggested by many researchers as one of the causes of the significant differences observed in THMs values between summer and winter (Stevens et al., 1976; Schnoor et al., 1979;). The increase in THMs formation per 10°C rise in temperature has been estimated to be about 35- 50% (Engerholm and Amy, 1983).

Chlorine Demand:

The relationship between chlorine dose and THMs formation is complicated. THMs production has been found to increase with an increased chlorine dose (Stevens et al., 1976; Symons et al., 1993). With increasing chlorine dose and residual, formation of HAAs becomes greater than THMs formation. Also more trihalogenated than mono- and di-halogenated species and more chlorinated than brominated species are formed. Depletion of the free chlorine residual ceases THMs and HAAs formation. However, limited formation of some other DBPs continues due to hydrolysis reactions (Nikolaou et al., 1999).

Bromide ions:

Aqueous chlorine is capable of oxidizing low levels of bromide ions present in natural waters to hypobromous acid (HOBr). The resulting HOBr is then available for initiating bromine addition and substitution reactions, which are often faster than their analogous chlorinating reactions. As a result numerous researchers have found that in waters with high bromide levels the brominated species –bromoform, dibromoaceticacid etc may be the major species formed. Luong et al., (1982) also found that chlorine acts preferentially as an oxidant while bromine acts as a substituting agent.

Reaction Time:

With increasing contact time, THMs and HAAs formation increases, Whereas DBPs such as haloacetonitriles and haloketones, which where initially formed, decay as a result of hydrolysis and reactions with residual chlorine (Nikolaou et al., 1999).

2.2 Toxicological Information of DBPs

Trihalomethanes:

Chloroform:

It was recognised as a liver toxin many years ago but interest in the carcinogenicity of chloroform was sparked by the completion of a carcinogenicity study by the National Cancer Institute in the United states, which showed increases in mouse liver tumours, and an increase in Kidney tumours in male rats. The NOAEL (No observed adverse effect level) for cytoethality (death of a cell) and regenerative hyperplasia (abnormal increase in the number of cells) in mice was 10 mg/kg of body weight/day after administration of chloroform in corn oil for 3 weeks. Based on the mode of action evidence for chloroform carcinogenicity, a TDI (Tolerable daily intake) of 10 μg/kg of body weight was derived. There is also a significant body of evidence, which continues to increase, that chloroform promotes the formation of tumours by causing cell death and reparative cell proliferation (ILSI, 1997). Chloroform has been classified in Group II– probable carcinogenic to the humans.

The most widely used system for classifying comes from the International Agency for Research on Cancer(IARC), which is a part of the World Health Organization(WHO). The IARC has evaluated the cancer causing potential of about 900 likely candidates in the last 30 years, placing them into one of the following groups.

Group 1: Carcinogenic to humans

Group 2A: Probably carcinigenic to humans

Group 2B: Possibly carcinogenic to humans

Group 3: Unclassifiable as to carcinogenicity in humans

Group 4: Probably not carcinogenic to humans.

Dibromochlromethane:

Produces liver and kidney damage in both mice and rats. Induces tumours of the liver in mice. A TDI for DBCM of 30 mg/kg of body weight was derived based on the NOAEL for liver toxicity of 30 mg/kg of body weight/day. IARC (International agency for research on cancer) has evaluated the carcinogenicity of DBCM and concluded that there is inadequate evidence for its carcinogenicity in humans and limited evidence for its carcinogenicity in experimental animals. The compound was assigned to Group III: DBCM is not classifiable as to its carcinogenicity to humans (IARC 1991, 1999).

Bromodichloromethane :

BDCM administered in corn oil by gavage for 14 consecutive days to 10 male CD-1 mice at 148 mg/kg per day caused liver and kidney damage (NTP, 1987). BDCM has been shown to reduce sperm motility in rats consuming 39 mg/kg of body weight per day in drinking water. BDCM induces tumours at lower doses than the other THMs. BDCM is also considered to be a weak mutagen. Mutagen is a chemical, which acts as an agent that can induce or increase the frequency of mutation in an organism.

Table 2.2 Toxic doses of BDCM in animals

Male ICR mice	Oral	LD_{50}	450 mg/kg
Female ICR mice	Oral	LD_{50}	900mg/kg
Male Sprague Dauley rats	Oral	LD_{50}	916 mg/kg
Male CD-1 mice	Oral	LD_{50}	450 mg/kg
Female CD-1 mice	Oral	LD_{50}	900 mg/kg
Female Sprague Dawley rats	Oral	LD_{50}	969 mg/kg

Adapted from NTP, 1987

BDCM is reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity in experimental animals (NTP 1987, IARC 1991, 1999). IARC has evaluated the carcinogenicity of BDCM and concluded that there is sufficient evidence for its carcinogenicity in experimental animals and inadequate evidence for its carcinogenicity in humans. On this basis, BDCM was assigned to Group IIB: the agent is possibly carcinogenic to humans (IARC, 1991, 1999). Among the four THMs commonly found in drinking water, BDCM appears to be the most potent rodent carcinogen. BDCM caused cancer at lower doses and at more target sites than for any of the other THMs.

Bromoform:

Bromoform caused low incidence of intestinal tumours in rats. It is also a weak mutagen. A TDI for bromoform of 25 μg/kg of body weight of body weight per day (WHO, 2000). Bromoform was used in the late 19th and early 20th centuries as a sedative for children with whooping cough. Patients were typically given doses of one drop (approximately 180 mg) 3-6 times per day (Burton-Fanning, 1901), which usually resulted in mild sedation in the children. A few rare instances of death or near-death were reported but were believed to be due to accidental overdoses (Dwelle, 1993). These clinical observations have been used to estimate a lethal dose for a 10- to 20-kg child to be about 300 mg/kg of body weight and an approximate minimal dose for sedation to be 50 mg/kg of body weight per day (US EPA, 1994b).

IARC has evaluated the carcinogenicity of bromoform and concluded that there is inadequate evidence for its carcinogenicity in humans and limited evidence for its carcinogenicity in experimental animals. The compound was assigned to Group III: bromoform is not classifiable as to its carcinogenicity to humans (IARC, 1991 and 1999).

Haloacetic acids:

Dichloroacetic acid:

A TDI of 40 μg/kg of body weight for DCA is based on a NOAEL of 40 mg/kg of body weight per day. DCA induces liver tumours in mice at high doses (WHO, 2000).

Trichloroacetic acid:

TCA induces liver tumours in mice at high doses (Cancho et al., 1999). A TDI of 40 μg/kg of body weight for TCA based on a NOAEL of 40 mg/kg of body weight per day for hepatic toxicity in a long-term study was found in mice.

Dibromoacetic acid:

There are a significant number of data on the effects of DBA on male reproduction. A TDI of 20 μg/kg of body weight was determined based on NOAEL of 2 mg/kg of body weight per day (WHO, 2000). DCA produces neurological, reproductive and ocular effects. The neurological effects are seen in both the central and peripheral nervous systems. Reproductive effects are seen in the testes, and ocular effects are mainly changes in the lenticular tissue.

Haloacetonitriles:

Concentrations of the various HANs compounds range from 1 to 40 μg/L; however, HANs are also formed in vivo following ingestion of chlorinated water. Bull et al. (1985) tested the ability HANs such as CAN, DCAN, TCAN, BCAN and DBAN to induce point mutations in the Salmonella/microsome assay, to induce SCEs (Sister Chromatid Exchanges) in CHO (Chinese Hamster Ovary) cells *in vitro,* to produce micronuclei in polychromatic erythrocytes in CD-1 mice and to act as tumour initiators in

the skin of Sencar mice. There are no long-term toxicity studies for DCAN and DBAN; however, these DBPs, together with TCAN, are associated with developmental health effects. TCAN is a teratogen in rats and dichloroacetonitrile is a weak bacterial mutagen (Cancho et al., 1999).

Dichloroacetonitrile:

Table 2.3 Toxic doses of DCAN in animals

Male CD-1 mice	Oral	270 mg/kg
Femal CD-1 mice	Oral	279 mg/kg
Male charles River CD rats	Oral	339 mg/kg
Female charles River CD rats	Oral	330 mg/kg

Adapted from NTP, 1987

A TDI of 15 μg/kg of body weight for DCAN based on a NOAEL of 15 mg/kg of body weight/day in a reproductive toxicity study was found in rats (WHO, 2000).

Dibromoacetonitrile:

Table 2.4 Toxic doses of DBAN in animals

Male CD-1 mice	Oral	289 mg/kg
Femal CD-1 mice	Oral	303 mg/kg
Male charles River CD rats	Oral	245 mg/kg
Female charles River CD rats	Oral	361 mg/kg

Adapted from NTP, 1987

A TDI of 23 μg/kg of body weight was calculated for DBAN based on the NOAEL of 23 mg/kg of body weight per day in the 90-day study in rats (WHO, 2000).

Trichloroacetonitrile:

LOAELs for TCAN of 7.5 mg/kg of body weight per day for embryotoxicity and 15 mg/kg of body weight per day for developmental effects were identified.

Haloketones: Exposure of mice to 1,1- dichloropropanone results in liver toxicity. The toxicological effects of the halopropanones provide evidence that some of the representatives of this class are highly toxic, with acute lethal doses being as low as 25 mg/kg of body weight. The gastrointestinal tract and liver appear to be key target organs (WHO, 2000).

2.3 Drinking water Guidelines

Various regulatory agencies have established guidelines for THMS, HAAs, HANs and other DBPs. The guidelines provided by the U.S EPA, WHO and Health Canada are listed in Table 2.5.

The U.S EPA maximum contaminant level (MCL) for TTHMs (Total trihalomethanes) was established at 0.1 mg/L. However, the EPA federal Register on "Disinfectants and Disinfectant By-products: Proposed Rule" (1994) reports the proposed MCL for TTHMs as 0.08 mg/L. It also reports the sum of five HAAs (HAA_5) as 0.06 mg/L. Health Canada has set the interim maximum acceptable concentration (IMAC) of THMs as 0.1 mg/L.

There are no Canadian guidelines for DBPs other than THMs. Recently Health Canada has been considering one for HAAs. The Maximum Contaminant Level (MCL) is

the maximum permissible level of a contaminant in water, which is delivered to any user of a public water system. The Maximum Contaminant Goal (MCLG) is the maximum level of a contaminant in drinking water at which no known or anticipated adverse effect on the health of persons would occur and which allows for an adequate margin of safety.

Table 2.5: DBPs Guidelines

DBPs	U.S. EPA Proposed MCLG or MCL (mg/L)	WHO (mg/L)	Health Canada IMAC (mg/L)
Total Trihalomethanes	0.08	-	0.1
Chloroform	0	0.2	-
Dibromochloromethane	0	0.1	-
Bromodichloromethane	0	0.06	-
Bromoform	0	0.1	-
Haloacetic acids (HAA5)	0.06	-	-
Dichloroacetic acid	0	0.05	-
Trichloroacetic acid	0.3	0.1	-
Dichloroacetonitrile	-	0.09	-
Dibromoacetonitrile	-	0.1	-
Trichloroacetonitrile	-	0.001	-

The list of various DBPs, their MCLs, potential health effects and source of contamination as promulgated by EPA are given in Table 2.6

Table 2.6: Disinfection by-products and health effects

Contaminant	MCLG (mg/L)	MCL or TT (mg/L)	Potential Health Effects from Ingestion of Water	Sources of Contaminant in Drinking Water
Bromate	Zero	0.010	Increased Risk Of Cancer	By-product of drinking water disinfection
Chlorite	0.8	1.0	Anaemia; infants & young children: nervous system effects	By-product of drinking water disinfection
Haloacetic Acids (HAA5)	N/a	0.06	Increased risk of cancer	By-product of drinking water disinfection
Total Trihalomethanes	None	0.10	Liver, kidney or central nervous system problems; increased risk of cancer	By-product of drinking water disinfection

Source: U.S EPA, 2002

U.S. EPA also has proposed the following maximum disinfectant residual level goals (MRDLGs) and maximum residual disinfectant levels (MRDLs). MRDLG is the level of disinfectant below which there is no known or expected risk to health. MRDL is the highest level of disinfectant allowed in drinking water. These are listed in Table 2.7.

Table 2.7: U.S. EPA Proposed MRDLGs and MRDLs for disinfectants

Disinfectant Residual	MRDLG (mg/L)	MRDL (mg/L)
Chlorine	4 (as Cl_2)	4 (as Cl_2)
Chloramines	4 (as Cl_2)	4 (as Cl_2)
Chlorinedioxide	0.8 (as ClO_2)	0.8 (as ClO_2)

Source: U.S EPA, 2002

2.3.1 DBPs in Newfoundland Drinking water Supply

The Department of Environment in partnership with municipal governments is monitoring the THMs in drinking water on a regular basis. The distribution of THMs levels in various water supplies of Newfoundland and Labrador until March 31, 2004 as given by the "The Government of Newfoundland and Labrador, Department of Environment and Conservation "is shown in Figure 2.1. As can be seen from the statistics of Figure 2.1 around 85 communities are exceeding the Canadian regulatory THMs limit of 100μg/L.

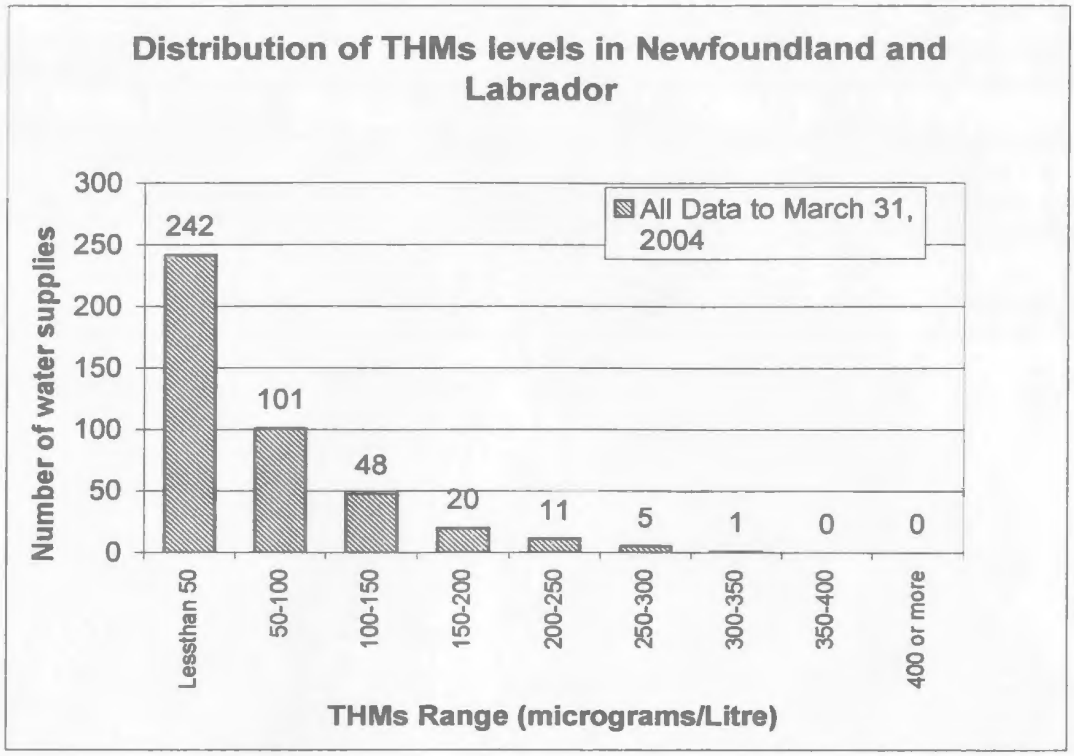
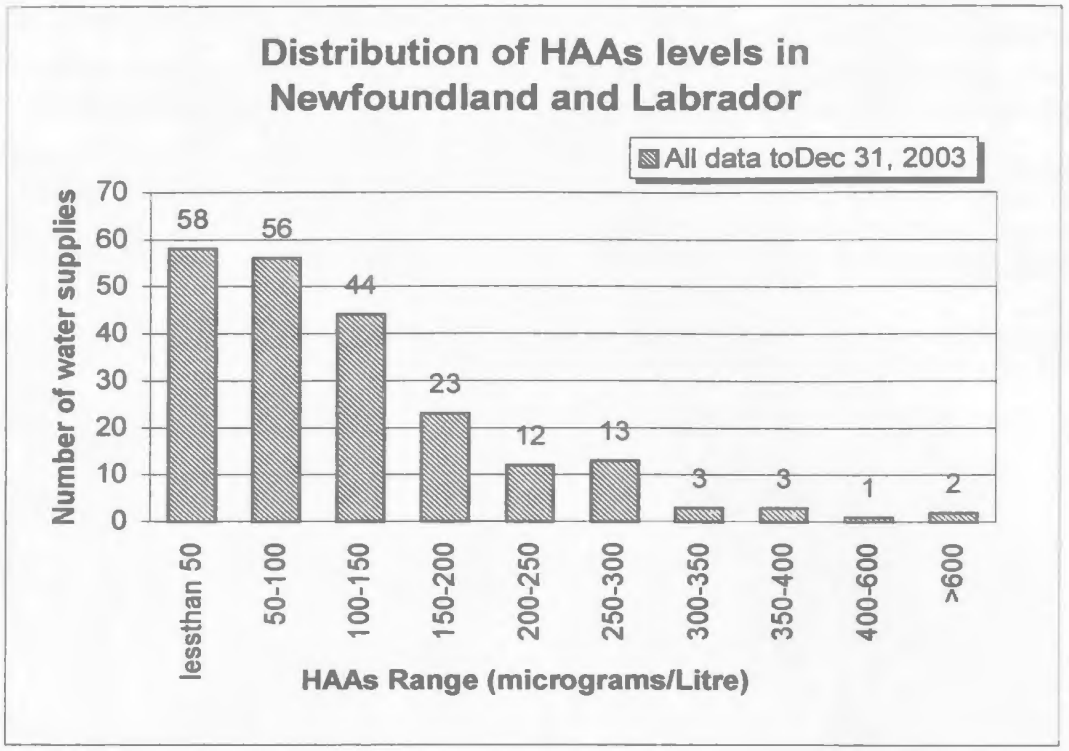


Fig 2.1: THMs levels in Newfoundland and Labrador

Source: Dept. of Environment, NL

The reported HAA values refer to the sum of the concentration of six haloacetic acid compounds which include monochloroacetic acid, dichloroacetic acid, and trichloroacetic acids, monobromoacetic acid, dibromoacetic acid and bromochloroacetic acid.

The distribution of HAAs levels in various water supplies of Newfoundland and Labrador until Dec 31, 2003 as given by the "The Government of Newfoundland and Labrador, Department of Environment and Conservation" is shown in Figure 2.2. As we can see from the statistics of Figure 2.2 around 135 communities are exceeding the EPA regulatory HAAs limit of 60μg/L.



Source: Dept. of Environment, NL

Figure 2.2: HAAs Levels in Newfoundland and Labrador

2.4 Health Risk of DBPs

2.4.1 Reproductive and Developmental Epidemiology

DBPs in drinking water have received considerable interest because of their possible association with cancers especially with bladder and rectal cancers. Recently there has been a shift of interest from cancer to reproductive outcomes such as spontaneous abortion, stillbirth, neural tube defect, preterm delivery, low birth weight etc. But very little is known about the potential adverse reproductive effects of the DBPs. Among the DBPs, the THMs are generally the most prevalent and are measured routinely. The adverse effects due to by-products in drinking water are difficult to establish as they

exist in low concentrations and in conjunction with many other chemicals. Obtaining estimates of a person's exposure in utero to such agents is dependent mainly on the type of disinfection process of the mother's residential water source. It also further depends on the person's consumption of tap water, the level of toxicants present in the water supply during the critical exposure period and exposure through pathways other than ingestion such as inhalation of and dermal contact with and uptake of by-products while showering, bathing and swimming.

The evaluated associations mostly between the DBPs exposure and outcomes grouped has effects on

1. Fetal Growth: Low birth weight (<2500g); very low birth weight (<1500g); Preterm delivery (<37 weeks of gestation) and intrauterine growth retardation (or small for gestational age).

2. Fetal Viability: Spontaneous abortion and stillbirth.

3. Fetal Malformations: All malformations or all cleft defects, major cardiac defects, neural tube defects, and chromosomal abnormalities.

Reproductive and developmental effects of exposure to DBPs in drinking water:

1. Fetal Growth:

Though the studies that evaluated small for gestational age (SGA) have several limitations, three studies (Kramer et al., 1992, Bove et al., 1995 and Gallaghar et al., 1998) provided moderate evidence for a causal relationship between a narrow definition of SGA and TTHMs levels that could be found currently in some U.S. public water systems. The other study by Gallaghar et al., (1998) concluded that with the best exposure

assessment there is a strong association between SGA and TTHMs exposure. Dodds et al., (1999) found a very weak association in his study. Table 2.8 lists comprehensive information about epidemiological studies ascertaining the risk of fetal growth as a result of DBPs exposure. The Table 2.8 also reports various relative risks. Relative risks are interpreted as "statistically significant" if their associated 95% confidence intervals (CI) do not include 1.0 and "not statistically significant" if they do so. A result greater than 1.0 is interpreted as a positive risk and less than 1.0 as a negative risk.

Table 2.8 Low birth weight, growth retardation (SGA), Preterm delivery and exposure to chlorinated by-products: Epidemiologic studies

Outcome measure/ Author (year)	Exposure Measure	Relative risk (95% Confidence interval)
Low birth weight		
Gallagher et al.,(1998)	THMs ≥ 61μg/L	2.1(1.0-4.8)
Kanitz et al., (1996)	Sodium hypochlorite	6.0(0.6-12.6)
Savitz et al., (1995)	THMs > 83 μg/L	1.3(0.8-2.1)
Bove et al., (1992)	THMs > 80 μg/L	1.3(1.1-1.5)
Kramer et al., (1992)	Specific THMs	1.3(0.8-2.2)
Growth Retardation		
Bove et al., (1995)	THMs > 100 μg/L	1.5(1.2-1.9)[a]
Kramer (1992)	Chloroform ≥ 10 μg/L	1.8(1.1-2.9)
Preterm Delivery		
Kanitz et al., (1996)	Chlorine dioxide	1.8(0.7-4.7)
	Sodium hypochlorite	1.1(0.3-3.7)
Savitz et al., (1995)	THMs > 83 μg/L	0.9(0.6-1.5)
Bove et al., (1992)	THMs > 80 μg/L	1.0(0.9-1.1)
Kramer et al., (1992)	Specific THMs	1.1(0.7-1.6)

[a] 90% confidence interval

2. Fetal Viability:

There were some inconsistencies in the epidemiological evidence for the association between DBPs exposure and fetal viability. The study by Waller et al., (1998) found an apparent dose-dependent increase in rates of spontaneous abortions associated with TTHMs in California. Savitz et al., (1995) found little evidence of association using either the concentration of TTHMs >81μg/L or a dose estimate based on the amount of tap water consumed. An increased risk of stillbirth was reported for women in Nova Scotia by Dodds et al., (1999). Table 2.9 lists comprehensive information about epidemiological studies ascertaining the risk of fetal viability as a result of DBPs exposure.

Table 2.9 Spontaneous abortion, Stillbirth and exposure to chlorinated by-products: Epidemiologic studies

Outcome measure/ Author (year)	**Exposure measure**	**Relative risk (95% confidence interval)**
Spontaneous abortion		
Waller et al., (1998)	TTHMs (≥ 5 glasses/day + ≥ 75 μg/L)	1.8(1.1-3.0)
	BDCM (≥ 5 glasses/day + ≥ 18 μg/L)	3.0(1.4-6.6)
Savitz et al., (1995)	THMs> 80 μg/L	1.2(0.6-2.4)
Stillbirth		
Dodds et al., (1999)	THMs > 100 μg/L	1.66(1.09-2.52)
Aschengrau et al., (1993)	Chlorinated surface water	2.6(0.9-7.5)
Bove et al., (1992)	THMs > 80 μg/L	0.7(0.4-1.2)

In New Jersey Bove et al., (1992, 1995) found little evidence of an association with TTHMs at 80μg/l, but did report a weak association between stillbirth and use of surface water systems.

3. Fetal Malformations:

Bove et al (2002) found consistency among the studies in the findings for neural tube defects and oral cleft defects but not for cardiac defects (Bove et al., 1995, Dodds et al., 1999, Klotz et al., 1999). Bove et al., (1995) found an association between cardiac defects and TTHMs. An association between chlorination and urinary tract defects was found in three studies that evaluated that end point (Kallen and Robert (2000), Magnus et al., 1999, Aschengraun et al., 1989). Table 2.10 lists comprehensive information about epidemiological studies ascertaining the risk of fetal malformations as a result of DBPs exposure.

Table 2.10 Birth defects and exposure to chlorination by-products: Epidemiologic studies

Outcome measure/ Author (year)	**Exposure measure**	**Relative risk (95% confidence interval)**
Major malformations		
Aschengrau et al., (1993)	Chlorinated surface water	1.5(0.7-2.1)
Bove et al., (1992)	THMs > 80 μg/L	1.6(1.2-2.0)[a]
Neural tube defects		
Dodds et al., (1999)	THMs > 100 μg/L	1.18(0.67-2.10)
Klotz and Pyrch (1999)	THMs > 40 μg/L	2.1(1.1-4.0)
Magnus et al., (1999)	Chlorination	1.26(0.61-2.62)
Bove et al., (1995)	THMs > 80 μg/L	3.0(1.3-6.6)[a]
Oral cleft defects		
Bove et al., (1995)	THMs > 100 μg/L	3.2(1.2-7.3)[a]
Cardiac defects		
Magnus et al., (1999)	Chlorination	1.05(0.76-1.46)
Bove et al., (1995)	THMs > 80 μg/L	1.8(1.0-3.3)
[a] 90% confidence interval		

2.4.2 Reproductive and Developmental Toxicology

The reproductive effects in females have been principally embryolethality and fetal resorptions associated with the haloacetonitriles (TCAN, DCAN, BCAN, DBAN) and halo acetates, while DCAA and DBAA have both been associated with adverse effect on male reproduction (WHO, 2000). The adverse developmental effects from embryo culture tests on the developing heart, neural tube, eye, pharyngeal arch, and somites tended to be associated with haloacetic acids tested at high doses (Hunter et al., 1996, Smith et al., 1989).

Cardivascular effects were also observed in vivo for TCAA and DCAA from developmental segmnet II toxicity studies at high doses (Smith et al., 1988 and 1990). Whole litter resorption likened to miscarriage or spontaneous abortion was also observed at high doses in vivo for a range of DBPs as indicated in Table 2.11 below (Murrray et al., 1979, Smith et al., 1990, Bielmeier et al., 2001). Fetal toxic effects such as reduced fetal body weights and increased variation were observed at high doses in vivo for chloroform, BDCM, DBCM, DCAA, TCAA, DCAN, TCAN, DBAN, BCAN (Murray et al., 1979, Ruddick et al., 1983, Smith et al., 1990). Male reproductive effects such as inhibited spermiation, reduced epididymus, sperm number and motility, increased abnormal sperm, testicular damage and inhibited invitro fertilization were reported for DCAA, DBAA, TCAA and BDCM (Toth et al., 1992, Linder et al., 1997).

Tyl (2000) conducted a comprehensive review of the reproductive and developmental toxicological literature on DBPs representing over thirty-five studies. He concluded that, "The screening studies, performed for a number of DBPs, are adequate and sufficient only to detect potent reproductive/ developmental toxicants for hazard

identification". The database identifying certain DBPs with potential reproductive or developmental effects is listed in the Table 2.11.

Table 2.11 Potential Hazards of DBPs for reproductive and Developmental Effects

Type of Hazard	Disinfection by-products
Developmental defects	TCAA, DCAA, MCAA and chlorite
Whole litter resorption	Chloroform, bromoform, BDCM, DBCM, DCAA, TCAA, DCAN, and TCAN
Fetotoxicity (reduced fetal body weights, increased variations)	Chloroform, BDCM, DBCM, DCAA, TCAA, DCAN, TCAN, DBAN, BCAN, and MCAN.
Male reproductive effects (spermatotoxic)	DCAA, DBAA, BDCM

Source: Tyl, 2000

From these studies it can be seen that the reproductive and developmental epidemiological database for exposure to CBPs in drinking water shows association and moderate evidence for association between DBPs exposure and SGA, neural tube defects, spontaneous abortions, still births and birth defects. Although the evidence for these associations is weaker, its gaining weight and the measures aimed at reducing the concentrations of by-products could have a positive impact on public health.

2.4.3 Cancer Epidemiology

Bladder cancer and CBPs exposure has historically been the most strongly supported association of all the possible cancers, based on human evidence. A positive association between the consumption of chlorinated water and bladder cancer was found by Yang et al., (1998). There was also evidence of increases risk as a function of

increasing DBPs exposure duration (Koivusalo et al., 1998). Long exposure duration ≥ 45 years were associated with about a two fold increase in risk. Recently the new publication by C.M.Villanueva et al., (2003) on DBPs meta-analysis of case control and cohort studies using which EPA found support for an association between exposure to chlorinated surface water and bladder cancer. In the recent two new human epidemiology studies Yang et al., (1998) did not identify an association between consumption of chlorinated drinking water and colon cancer where as King et al., (2000b) study found evidence of a DBPs association with colon cancer among males, but no association was observed among females.

Further the evidence for an association between DBPs and rectal cancer is stronger than for colon cancer. Yang et al., (1998) and Hildesheim et al., (1998) both found associations between chlorinated drinking water exposure and rectal cancer. The association also had a similar magnitude in both sexes. Hildesheim et al., (1998) also found an association in both sexes with lifetime average THMs concentration.

To date the EPA has established lifetime cancer risk levels for four DBPs which are bromoform, BDCM, bromate and DCA and they are classified as probable carcinogens. The slope factor is a measure of the potency of a carcinogen while the 10^{-6} lifetime cancer risk concentration provides an estimate of the concentration of a contaminant in drinking water that is associated with an estimated excess lifetime cancer of one in a million. ED_{10} is the Maximum likelihood estimate of the dose-produced effects in 10 percent of the animals. LED_{10} is the lower 95 percent confidence bound. Table 2.12 lists the quantification of cancer risk

Table 2.12: Quantification of Cancer Risk

	Risk factors from LED_{10}		Risk factors from ED_{10}	
DBPs	Slope factor $(mg/kg/day)^{-1}$	10^{-6} Risk conc. (mg/L)	Slope factor $(mg/kg/day)^{-1}$	10^{-6} Risk conc. (mg/L)
Bromodichloromethane	0.034	0.001	0.022	0.002
Bromoform	0.0045	0.008	0.0034	0.01
Dibromochloromethane	0.04	0.0009	0.017	0.002
Dichloroaceticacid	0.048	0.0007	0.014	0.003

Source: IPCS, EHC 216

2.5 Control of Disinfection by-products

Control of DBPs in drinking water can be achieved by the options like source control, precursor control, alternative disinfectants and DBPs removal. Precursor removal refers to strategies aimed at lowering the concentration of NOM. The alternative oxidants and disinfectants category involves supplementing or replacing the use of chlorine; some of these alternatives serve only a limited function, e.g. as an alternative primary or secondary disinfectant, and must still be used in conjunction with chlorine or other alternatives discussed in this section. Although these alternative oxidants and disinfectants may assist in the control of halogenated DBPs, some of them produce other non-halogenated DBPs that may also be of concern. The air stripping option consists of eliminating the volatile THMs species after they are formed. Because this technology addresses only DBPs that are volatile (e.g. the THMs), it cannot be used to control the

other halogenated DBPs that are of public health concern, most of which are non-volatile, and therefore air stripping is not recommended as a desirable treatment strategy. The applicability and limitations of each is discussed further below.

2.5.1 Source Control

It has been demonstrated by a number of researchers (Oliver and Shindler, 1980, Hoehn et al., 1980, Wachter and Andelman 1984, Karimi and Singer 1991) that algal growth leads to the production of DBPs precursors.

Control of nutrient inputs:

One approach to controlling DBPs formation is to control nutrient inputs to waters that are used as drinking-water sources, in order to limit the algal growth potential of these waters. Management strategies for controlling nutrient enrichment of waters include structural controls such as storm-water detention basins to trap nutrients, and nonstructural controls such as land-use controls, e.g. limiting development on watersheds used for water supply. To more effectively establish and assess the impact of such controls, relationships need to be developed between nutrient inputs (nutrient loading) and the production of DBPs precursors. Similarly, models need to be developed that link DBPs formation potential of the water to land-use practices in the watershed.

Algal control strategy:

Algal control strategy is the control of nutrient cycling in reservoirs and impoundments. Installation of hypolimnetic aeration systems and harvesting programs for aquatic growths are two examples of nutrient control strategies.

Source-control strategy:

Source control strategy is aimed at controlling bromide levels. It is the control of saltwater or brine intrusion into the water source. Because bromide drives the rate and extent of halogenated DBP formation to a greater degree and shifts DBP speciation to forms that are believed to be more harmful, the development of barriers (structural or hydrodynamic) to saltwater intrusion may have significant benefits.

Aquifer storage and recovery (ASR):

Aquifer storage and recovery can markedly reduce halogenated DBPs concentrations in finished drinking water. By drawing raw water from the water source during seasons when the quality of the raw water is best, storing the water after treatment in controlled storage aquifers, and then recovering the stored water for distribution to consumers, THMs and HAAs formed during treatment can be eliminated (Singer et al., 1993).

2.5.2 Precursor Removal

The major technologies for the removal of DBPs precursors are enhanced coagulation, granular activated carbon (GAC) adsorption, and membrane filtration. Aluminium and ferric salts have been shown to readily coagulate NOM (Kavanaugh, 1978; Babcock and Singer 1979; Reckhow and Singer 1984). For alums, the optimal pH tends to be 5.5 to 6.0.

Hydrophobic organic carbon, e.g. humic material, is more susceptible to coagulation than hydrophilic organic carbon (Collins et al. 1986; Semmens and Staples 1986; Singer and Harrington 1993). The hydrophobic/hydrophilic distribution is not

generally known for most water supplies, but the hydrophobic fraction is believed to constitute about 30-70% of the TOC content of most natural waters used for municipal water supply (Singer and Harrington 1993). Accordingly, the effectiveness of TOC (NOM) removal by coagulation depends on the TOC content and alkalinity of the raw water, the hydrophobic/hydrophilic distribution of the TOC, and the pH of coagulation. TOC removals greater than 50% have been demonstrated, with even greater removals of HAAs and THMs precursors.

Enhanced Coagulation:

TOC concentration and alkalinity of the water affect the effectiveness of this technique. When the alkalinity is low, low alum addition may be needed in order to lower the pH and achieve more effective coagulation of NOM. When alkalinity is high, an excessive amount of alum is demanded or an acid (sulfuric) may be needed. The hydrophobic/hydrophilic distribution of TOC plays an important role, because hydrophobic organic carbon is more susceptible to coagulation than hydrophobic organic carbon (Singer and Harrington, 1993)

Granular activated carbon adsorption:

Granular activated carbon is a relatively expensive process. In most cases separate post filtration beds are needed. Empty-bed contact times above 15 min are required and regeneration frequencies are between three and six months. Decreasing pH of water or increasing alum dosages during pre-treatment increase effectiveness of the method (Semmens et al., 1986).

Membrane filtration:

Membrane filtration is a relatively expensive process. To achieve TOC removals in excess of 75%, membrane filtration generally requires the use of nanofilters, with membranes having molecular weight cutoffs of 200-500 daltons (Taylor et al., 1987; Amy et al., 1990; Laine et al., 1993). For most applications, pretreatment is required to prevent fouling of the membranes. The technology is relatively expensive, but costs appear to be coming down as new technological developments take place. A significant limitation in the use of nano-filtration at this time is disposal or processing of the waste brine that is generated.

Powder activated carbon adsorption:

Dosage and contact time are the main factors affecting the efficiency of the method. An increase beyond 60 min in contact time or beyond 30mg/l in dosage is not convenient (Sandrucci et al., 1995).

Use of activated carbon adsorption and membrane filtration, especially when control of pesticide contamination is needed as well, has been reported in the Netherlands (Premazzi et al., 1997). Preozonation on the basis of low doses in order to enhance flocculation is a new technique being developed (Premazzi et al., 1997).

2.5.3 Alternative Oxidants and Disinfectants

Monochloramine:

Monochloramine (NH_2Cl) does not produce appreciable amounts of any known DBPs, although some DCA can be formed from monochloramine, and cyanogen chloride formation is greater than with free chorine (Jacangelo et al., 1989; Smith et al., 1993;

Cowman and Singer 1994). It has much higher CT (product of residual chlorine and time required) values than free chlorine and is therefore a poor primary disinfectant for use within the treatment plant. Additionally, it is a poor oxidant and is not effective for taste and odor control or for oxidation of reduced iron and manganese. However, because of its persistence it is an attractive secondary disinfectant for maintenance of a stable disinfectant residual in the distribution system. Care must be exercised in selecting the proper ammonia-to-chlorine ratio so that nitrification problems do not occur in the distribution system; (Wolfe et al., 1990; Lieu et al., 1993). Some utilities using monochloramine as a secondary disinfectant switch back to free chlorine for a few weeks each year in order to eliminate biological growths that may have colonized the distribution system.

Chlorine dioxide (ClO_2):

It is a good disinfectant (relatively low CT values) and an effective oxidant for taste and odor control and iron and manganese oxidation. If the raw water contains ammonia, it does not exert a chlorine dioxide demand. Chlorine dioxide does not produce halogenated DBPs to any significant degree, except for chlorite (ClO_2^-); 50-70% of the chlorine dioxide consumed gets reduced to chlorite (Rav Acha et al., 1984; Werdehoff and Singer, 1987). Chlorine dioxide reacts with NOM to produce oxidation by-products that are most likely similar to those produced by ozone (Richardson et. al., 1994). The oxidation by-products of chlorine dioxide treatment have not been studied extensively, and therefore the public-health impact of chlorine dioxide treatment, except for chlorite, is largely unknown.

Ozone (O_3):

Ozone is the most effective oxidant and disinfectant used in water-treatment practice. It has the lowest CT values, but disinfection credit is based on residual molecular ozone, i.e. the molecular ozone remaining after overcoming the ozone demand of the water. Molecular ozone is unstable and does not produce a persistent disinfectant residual. Therefore, although ozone is a good alternative primary disinfectant to free chlorine, it must be used in conjunction with a persistent secondary disinfectant, e.g. monochloramine. The combination of ozone and monochloramine as primary and secondary disinfectants respectively appears to be an attractive combination for minimizing halogenated DBPs formation while achieving effective disinfection.

Permanganate (MnO_4^-):

Permanganate is an effective oxidant for taste and odor control and for oxidation of reduced iron and manganese. However, it is a poor disinfectant and is not approved for this purpose. Permanganate consumption leads to the formation of insoluble manganese dioxide [$MnO_2(s)$], which may create operational problems in the treatment plant and distribution system if not properly controlled.

Ultraviolet (UV) light:

Ultraviolet light is an effective disinfectant for viruses and bacteria (Wolfe 1990) but it requires low-turbidity feed water with a low concentration of UV-absorbing substances to allow for penetration of the radiation through the water and to prevent fouling of the lamps. UV light does not appear to generate DBPs, but little research has been done on the subject. UV light does not provide a disinfectant residual and therefore can only be used as a primary disinfectant. The application of UV light and

monochloramine as primary and secondary disinfectants, respectively, can achieve effective disinfection with little formation of known halogenated DBPs. UV light is not a reliable disinfectant for Giardia and Cryptosporidium cysts and therefore its application is limited to ground waters and well-filtered surface waters.

2.5.4 DBP Removal

Air Stripping:

DBPs, which have already been formed, can be removed with the methods of packed column air stripping (Packed towers) or diffused air stripping (compressed air). Application of air stripping in Italy has been reported (Premazzi et al., 1997). Air contamination or residual disinfectant removal could be the main negative points of these techniques.

Reverse Osmosis:

This method can remove 85-90% of all organic compounds. As membrane technology improves and cost decreases, the procedure seems more attractive for DBP removal (Premazzi et al., 1997).

Granulated activated carbon:

With this technique many categories of organic compounds can be removed. However, regular maintenance is necessary and microbiological contamination might take place (Premazzi et al., 1997).

2.6 Modeling

The modelling of DBPs consists of establishing empirical or mechanistic relationships between DBPs levels in treated water, and the parameters of water quality and of operational control, which can be linked to their formation. Past research has shown that the most important factors for DBPs formation are: the levels of organic matter in water (generally designed by total or dissolved organic carbon and by 254-nm UV-absorbance); the applied chlorine dose; the pH of water; water temperature; and the reaction time of residual chlorine in water. The concentrations of bromides are also usually considered because of their influence on the distribution of the four trihalomethane compounds. The chlorination of waters with low bromide concentrations generally leads to higher proportions of chloroform in comparison with other three trihalomethane compounds.

An overview of the THMs models proposed by various authors is discussed in this section.

a. Amy (1987):

A standard trihalomethane formation potential was conducted for raw waters from different utilities across the US under the following conditions. 20°C, pH 7, a chlorine to NPOC (non-purgeable organic carbon) ratio of 3.0 and a reaction time of 168 hr. Each of the natural waters was studied in a series of experiments that encompassed the following parameters and ranges of conditions. Temperature of 10, 20 and 30 °C; pH were ambient, ambient +1.5, and amb. –1.5; bromide level were ambient, amb. + 0.25 mg/L, amb. +0.5 mg/l, and amb +1.0 mg/L; chlorine to NPOC levels of 0.5, 1.0, 3.0 and

5.0 (mass basis) and reaction times of 0.1, 0.5, 1, 2, 4, 8, 24, 48, 96 and 168 hrs. The following terms were assigned to various parameters.

TTHM = molar basis total THMs concentration (μ mol/L)

RXNTM = reaction time (h),

CLDose = applied chlorine dose (mg as Cl_2/L),

TEMP = temperature (°C)

PH = pH level (pH units)

BR= bromide concentration. (mg/L)

UVABS = uv absorbance (cm^{-1})

PH = (pH – 2.6) with 2.6 represented a statistically determined minimum pH at which THMs formation commences.

Data with chlorine dose adequate to maintain a positive residual were only chosen for the model.

$$TTHM = 0.031\ (UV\ ABS^{*}\ TOC)^{0.440} * (CLDose)^{0.409} * (RXNTM)^{0.265} * (Temp)^{1.06} * (pH-2.6)^{0.715} * (BR+1)^{0.0358} \quad \textbf{(2.1)}$$

R^2= 0.903

b. Golfinopoulos (1998):

To determine the level of THMs in Athens water supply system, a survey was conducted over a period of time. A multiple regression model for THM formation was generated for predicting THMs in the finished water leaving the plant using the field sampling of the Galatsi Treatment Plant (GTP) of Athens with respect to temperature(T), pH, chlorine dose(D), bromide(Br) and chlorophyll(chla).

$$TTHM = 13.5\ln(Chla) - 14.5(pH) + 230(Br) - 140(Br)^2 - 25.3(S) + 11.06(Sp) - 6.6(T*Sp) + 1.48(T*D) \quad (2.2)$$

S: dummy variable indicating summer season;

Sp: dummy variable indicating spring season;

TOC was not included in this model as the results obtained were not reliable as suggested by author.

Table 2.13: Overview of different THMs models

Author	Source of data	Data generation approach for THM	Model equation	r^2
Arizona State university (Amy et al., 1987)	Raw waters from different utilities across the US	Laboratory scale with variable chlorine dose, temperature and contact time	$TTHM^{**} = 0.031\ (UV * TOC)^{0.440} * (D)^{0.409} * (t)^{0.265} * (T)^{1.06} * (pH-2.6)^{0.715} * (Br+1)^{0.0358}$	0.90
Lou & Chiang (1994)	Water from the Taipei (Taiwan) distribution system	Eighteen points sampled twice over a 6 month period	$TTHM = (TTHMo) + 7.01\ (pH-2.3)^{0.11} (NVTOC)^{1.06} (t)^{0.748} (D)^{0.764} (\beta)$	NP
Ibarluzea et al., (1994)	Water from the treatment plant of Sebastian (Spain)	Sampling at the treatment plant and the finished water	$CHCl_3 = 10.8 + 0.04(Flu) + 1.16(ph) + 0.12(T) + 1.91\ (Co)$	0.98
US Geological Survey (Rathbun 1996)	Waters collected at different locations along the Mississippi river and two affluents	Laboratory scale with variable chlorine doses, pH and contact time. Temperature kept constant	$TTHM = 14.69\ (pH-3.8)^{1.01} (D)^{0.206} (UV)^{0.849} (t)^{0.306}$	0.94
Chang et al., (1996)	Water samples from raw water at a utility in Taiwan	Laboratory scale with variable chlorine dose and contact time	$TTHM = 12.7\ (TOC)^{0.291} (t)^{0.271} (D)^{-0.072}$	0.82
Clark & Sivaganesan (1998)	Prepared synthetic waters with solution of humic acid	Laboratory scale with variable chlorine dose, temperature, pH and contact time	$TTHM = A\left(C_1 - \left(\frac{C_1(1-K)}{1-Ke^{ut}}\right)\right)$	0.71 & 0.78 for A & K
Golfinopoulos et al., (1998)	Water from the utility of Athens (Greece)	Sampling at four points in the treatment plant (one at the finished water outlet)	$TTHM = 13.5\ln(Chla) - 14.5(pH) + 230(Br) - 140(Br)^2 - 25.3(S) + 11.06(Sp) - 6.6(T*Sp) + 1.48(T*D)$	0.98
Rodriguez et al., 2000		Laboratory	$TTHM = 0.044(DOC)^{1.030} (t)^{0.262} (pH)^{1.149} (D)^{0.277} (T)^{0.968}$	0.9

NP: value not presented by authors; **in µmol/L

Nomenclature: TTHM: total trihalomethanes(µg/l); TTHMo: TTHM at the finished water before chlorination(µg/l); UV: absorbance at 254nm(cm^{-1}); TOC: total organic carbon(mg/l); NVTOC: non-volatile TOC(mg/l);Br: bromide((µg/l); Chla: chlorophyll a(mg/m^3);T: water temperature(°C); Flu: fluorescence of the raw water(%); d :chlorine dose(mg/l);t: contact time(h);Co: residual chlorine at the treatment plant after chlorination(mg/l); C_1initial residual chlorine(mg/l);β: parameter depending on water dispersion within distribution system; e: random error; K: dimensionless parameter; u: reaction rate constant(min);S: dummy variable indicating summer season; Sp: dummy variable indicating spring season;

c. Rodriguez et al., (2000):

The author used the three databases developed by Amy et al., (1987); Rathbun, (1996) and Montgomery Watson, (1991) in the development of his model. The result of data combination was a unique database, which considers wider ranges of water quality and operational parameters. However to take into account the specific water quality conditions of Quebec water utilities which use chlorination as the unique treatment process, only observations corresponding to concentrations of dissolved organic carbon (DOC) between 1.0 and 8.0 mg/l were considered. A multivariate regression model for THMs formation was created. The method consists of first classifying the predictor variables according to their statistical significance and then including one variable at a time at different steps. To assess the quality of data used for analysis, the database was randomly separated into two data sets. One data set was used to estimate the statistical parameters of the model, while the other served to evaluate the model's prediction performance.

$$TTHM = 0.044(DOC)^{1.030}\,(t)^{0.262}\,(pH)^{1.149}\,(D)^{0.277}\,(T)^{0.968} \qquad \textbf{(2.3)}$$

Where DOC is expressed in mg/l and t, D, and T denote respectively contact time (h), chlorine dose (mg/l) and water temperature (°C).

The analysis of exponential coefficiens in models suggests that the effects of chlorine dose and contact time on TTHM formation are more non-linear than the effect of DOC, pH and water temperature.

In this chapter, various types of DBPs, toxicity, formation, factors influencing the formation, drinking water guidelines of DBPs, health risks of DBPs, control technologies and literature review of various models were discussed. In the next chapter the experimental methodology used to find the DBPs and the parameters influencing their formation will be presented.

Chapter 3

Experimental Methodology

DBPs are formed upon the reaction of chemical disinfectants with organic precursors like NOM measured by TOC. The formation of DBPs is influenced by water quality parameters like TOC, pH, temperature, alkalinity, turbidity etc and treatment conditions like disinfectant dose, reaction time and removal of NOM before applying the disinfectant.

The objective of this study is to analyze both the tap water and raw water samples from selected communities of Newfoundland to find the DBPs concentration and correlate with the level of TOC, DOC and pH. The raw water samples were chlorinated with different doses with controlled and uncontrolled pH at constant temperature and to study the effect of formation of the DBPs. The use of raw water samples is mainly to know the effect of formation of DBPs with time at other controlled parameters, where as the use of tap water samples is to know at the consumer point the parameters like TOC, DOC affecting DBPs formation.

Five communities in the Atlantic province were initially selected for this analysis. The tap water and raw water samples were collected from five communities and they were Keels, Clarenville, Ferryland, Bonavista, Burin, and St.John's. Clarenville has a population of 5104, Ferryland 607, Bonavista 4021, Burin 2470, Keels 85 and St.John's 99,182 according to the 2001 census by Government of Newfoundland.

The raw water samples of Clarenville were collected from the water treatment plant before treatment from Lower Shoal Harbour river and the tap water samples from residence 0.5km from the treatment plant. The treatment features for the tap water samples in Clarenville were conventional water treatment plant, coagulation, filtration with chlorine disinfection. The raw water samples from Ferry land were collected from Deepcove Pond and the tap water samples from Avlon building. The treatment features for the tap water samples in Ferry land was just chlorination. The raw water samples of Bonavista were collected from wet well screen house located approximately 200 feet from the intake of the long pond and the tap water samples from the town hall. The treatment features for the tap water samples in Bonavista included gas chlorination and pH adjustment. The raw water samples of Keels were collected from Boland's pond and the tap water samples from the consumer one km from the plant. The treatment features in tap water samples was liquid chlorination. The tap water samples for St.Johns were collected from the S.J.Carew Building and the treatment features were pH adjustment and chlorination(and are in the process of installing a membrane filtration plant). Because of limited resources available, it was difficult to obtain and analyze equal numbers of samples from all the communities.

3.1 Sample collection and Storage

The raw water samples were collected in 2 - litre plastic bottles. The tap water samples, which were chlorinated previously, were collected in 60 ml glass vials with duplicates, with minimum turbulence and the bottles were filled headspace free. After the vials were filled they were kept in a portable ice cooler. Between the period of time of

sample collection and transportation to Memorial University the samples were kept in a cooler to maintain a temperature of 4°C. The samples after collecting at university were again preserved in refrigerator at a constant temperature of 4°C. All the collected samples were analyzed in the environmental laboratory in the faculty of Engineering within 14 days of sample collection. The samples were dechlorinated by the addition of ammonium chloride to the empty vials. All the glassware including sample vials prior to use were cleaned with detergent and tap water and then thoroughly rinsed with distilled water. The vials were then allowed to dry at room temperature and then placed in oven and heated to 400°C for 30 minutes. After removing from the furnace they were allowed to cool in the desiccators.

3.2 Sample characterization

pH:

The pH was measured with a Model 3000 VWR scientific pH Meter. The pH meter was calibrated daily using the standard buffer solutions. A two point calibration was used employing either a pH of 4 and 7 (for pH below 7) or 7 and 10 (for pH above 7).

Turbidity:

Turbidity was measured with a DRT-15CE Portable Turbidimeter, which was calibrated and checked with a reference standard every time before taking a reading.

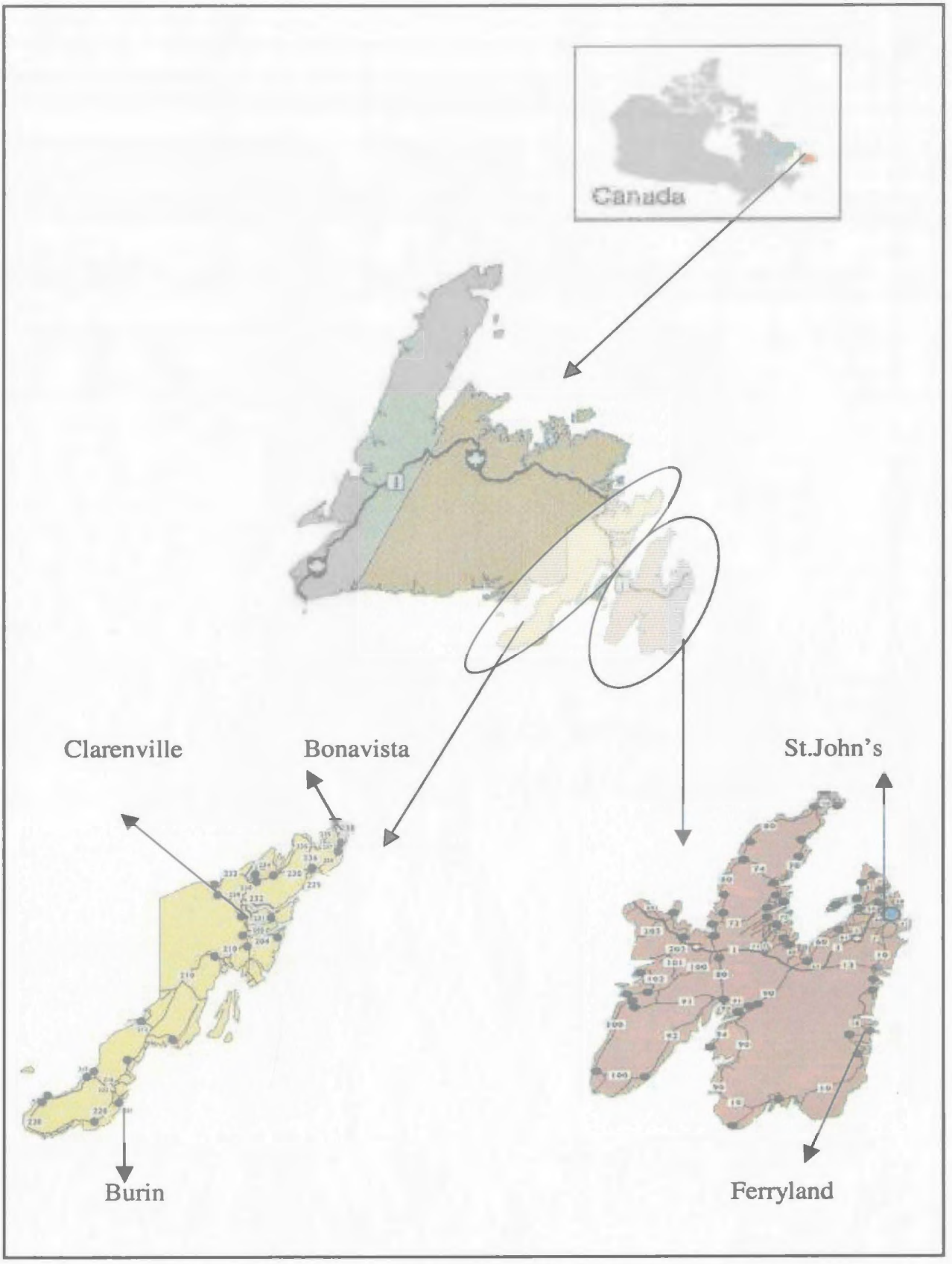


Fig: 3.1 Location of Newfoundland communities where samples were collected.

Ultraviolet Absorbency:

UV254 analysis was conducted with an HP 8453 Spectrometer with a 1-cm quartz cell. A blank with deionized water was run prior to sample analysis. Duplicate analyses were performed on each sample and the average was reported. If the difference between the two values was greater than 0.001/cm, a third analysis was performed and the average of all three values was reported. The specific ultraviolet absorbency (SUVA) was calculated as UVA* 100/DOC (unit of L/mg-m).

Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC):

The TOC and DOC concentrations were measured using a Shimadzu TOC 5000A analyzer. The CO_2 detector was a linearized non-dispersive infrared detector (NDIR). Potassium hydrogen phthalate was used as an external standard. The instrument was calibrated with a series of standards in the ranges of 15, 25, 30 50 mg/L. The organic carbon determination was made by injection mode with two injections; one for determining the Total carbon and the other to find the inorganic carbon. The organic carbon was then calculated by the difference between the total carbon and inorganic carbon.

To find the DOC the samples were filtered with 0.45 μm membrane filters and then were used to calculate the dissolved organic carbon. The instrument provided reliable, accurate and reproducible data with a minimum detection limit of 4ppb.

3.3 Determination of DBP formation

Chlorination was carried out for raw water samples at both controlled buffer of pH 8.0±0.2 and at uncontrolled buffer. For samples at controlled buffer, before dosing samples were buffered to pH of 8.0 with approximately 2ml/L borate buffer (1.0M boric acid) and 0.26M Sodium Hydroxide in deionized water (Summers et al., 1996). An appropriate amount from a sodium hypochlorite dosing solution 5mg/ml was then added to the raw water to obtain the desired disinfectant dose.

The sodium hypochlorite dosing solution was made from 5% active chlorine (Sodium hypochlorite) stock solution. Prior chlorination, the strength of the dosing solution was measured 3 times to ensure accuracy. The average of the three analyses was used to calculate the dosing solution volume required to obtain the desired chlorine dose. The same amount of deionized water was chlorinated under the same conditions as the samples. This blank was used as a reference to establish the initial chlorine concentration.

It is difficult to compare the kinetic behavior between water samples because the rate of decay of chlorine is dependent on chlorine concentration (initial and residual) (Isabel et al., 2000; Fang et al., 1999). In order to overcome this difficulty, the chlorine dose was selected to yield a 120 hr residual of 1 ± 0.4mg/L free chlorine.

All samples were chlorinated in 300ml-chlorine demand free, glass stoppered BOD bottles and stored headspace free at 23° C in the dark. After contact periods of 1, 3, 7, 24 and 120 hrs chlorine residual, THMs and HANs were measured at different times for each bottle. A separate bottle was used for each reaction time investigated.

3.3.1 Chlorine Demand

The Chlorine concentration of the 5% aqueous sodium hypochlorite solution is measured by titrating to starch iodide end point using the 0.025N sodium-thiosulphate titrant. From this the volume of stock hypochlorite solution required to produce a chlorine concentration of 5 mg Cl_2/ml of 250ml is calculated using

$$\text{Hypochlorite solution required} = \frac{1250}{\text{stock hypo - chlorite solution conc. in mg } Cl_2/\text{ml}} \quad (3.1)$$

The amount of stock hypochlorite solution required was then diluted in a 250ml volumetric flask and then filled with chlorine demand free water up to the mark. The solution was then mixed and transferred to an amber bottle sealed with a TFE (Tetrafluoroethylene)-lined screw cap and refrigerated and stored.

To find the chlorine demand of the water sample, 5ml of phosphate buffer and 5 ml chlorine dosing solution was added into a 250- ml bottle and completely filled with water and sealed with a TFE-lined screw cap. It was stored in the dark for at least 4 hrs at 25°C. After storage time, the chlorine residual was determined. The chlorine demand is determined by the difference in the initial chlorine dosage concentration and the chlorine residual at the end of 4 hrs.

3.3.2 Free Residual Chlorine

Chlorine concentration was measured by the DPD (Diethyl-p-Phenylene Diamine) powder pillows photometric method (USEPA-approved HACH 8021 method) using a spectrophotometer. Samples were dispersed into a 25-ml spectrophotometer cell and mixed with a free chlorine powder pillow and the absorbence of the solution was

measured at 530nm. This method can measure chlorine concentration up to 2.0 mg/L. The detection limit of the method is 0.01 mg/L. If the chlorine residual concentration was more than 2 mg/L, the samples were diluted with deionized water to the range of 0 to 2 mg/L, then the concentration was measured and corrected for dilution. Duplicate analyses were performed on each sample and the average was reported. If the difference between the two values was greater than 0.04mg/L, a third analysis was performed and the average of all three values was reported.

3.3.3 THM analysis

Gas chromatography is used to separate a sample containing a mixture of compounds into isolated fractions. The gas chromatograph (GC) is a highly versatile tool for environmental analyses. Ideally, each compound is separated from the sample into a portion of the carrier gas stream and then detected as it exits the column.

The two main demands on chromatography for effective analytical use are:

1. Analyte of interest needs to be separated from other parts of the sample in a reproducible way. Each time a standard or sample is run, the same retention time and signal strength at each peak should be obtained.
2. Standards and unknowns run in different matrices and different levels should give a scalar response, that is the peak area response at a given retention time should be directly proportional to concentration.

Working with GC commonly requires a high level of analytical intuition, instrumental knowledge, time and practice preparing samples. In the GC, a gaseous transport medium (mobile phase) carries the compound after it has been vaporized

through a column, which contains a stationary phase. GC requires that the components are or will become gaseous during the analysis.

The mobile phase or carrier gas e.g. helium (He) flows through the separation column and the single compounds are adsorbed on the surface of the solid stationary phase. This will depend upon the chemical properties of the solute and the solvents (Stationary phase). It is this partitioning of the solute between the two phases that is responsible for the separation of the individual components or solutes. The quality of chromatographic separation known as resolution is high only if the components are found frequently in the stationary phase. For good separations of high resolution it is important that the different species undergo a selective interaction with the stationary phase. This interaction depends on the molecular structure and especially on the type of functional group and geometry of the molecules of the solutes and the stationary phase. The solvent (stationary phase) selectively retards the sample components according to their distribution coefficient. These components bands leave the column in the gas stream (solvent) and are recorded as a function of line by a detector and a computer data system.

One more factor, which is important, is temperature. High temperatures, in general lead to faster chromatography. For a run with many compounds with a wide range of column affinity, it is of general practice to start the run at a low temperature such that only the most mobile compounds elute. Then the column temperature is increased in succession and this method is called temperature gradient. The baseline commonly changes in GC during gradient due to changes in detector sensitivity for the carrier gas. If the subtle differences in column affinity between two compounds can be accentuated at lower temperature, the less mobile compound may lag further behind. However once

separation is established, it may be good to rise the column temperature to get the less mobile compound to move faster. Thus sensitive temperature control and thermal stability of the column are usually crucial factors for reproducible chromatography.

The detector that was used in GC to find the by-products was μ-ECD, also called the micro electron capture detector. The μ-ECD contains a cell plated with ^{63}Ni, a radioactive isotope. The ^{63}Ni releases β particles that collide with carrier gas molecules to produce low energy electrons - each β particle produces approximately 100 electrons. The free electrons produce a small current called the reference or standing current that is collected and measured in a pulsed circuit. When a sample component molecule comes into contact with the free electrons, the electrons may be captured by the sample molecules to create negatively charged ions. The voltage across the cell electrodes is pulsed to collect the remaining free electrons while the heavier ions are relatively unaffected and swept out the vent with the carrier gas flow. Cell current is measured and compared to a reference current. The pulse rate is adjusted to maintain a constant cell current. The more free electrons, the lower the pulse frequency required to match the reference current. When a compound that captures electrons passes through the cell, the pulse rate rises. This pulse rate is then converted to a voltage and recorded.

The main characteristics of an ECD detector are:

1. Very sensitive to halogens to 0.1pg
2. Very sensitive to carrier gas flow
3. Linear over a limited range
4. Detector is damaged/deteriorated by water, oxygen and sulfur

5. Safety issues because of radioactive
6. A selective detector.

The methods used in the determination of various DBPs are listed in Tables 3.1 and 3.2.

Table 3.1 Approved methods for DBP analysis

DBPs	MCL	U.S.EPA approved methods
THMs	80 μg/L	U.S. EPA methods 502.2, 524.2, and 551.1
HAA5	60 μg/L	U.S. EPA methods 552.1 and 552.2
Chlorite	1 mg/L	U.S. EPA methods 300.0 and 300.1
Bromate	10 μg/L	U.S. EPA methods 300.1

Table 3.2 Suggested analytical methods for DBPs

DBPs	Analytical Methods
Haloacetonitriles	U.S.EPA Method 551.1
Chloral hydrate	U.S.EPA Method 551.1
Chloropicrin	U.S.EPA Method 551.1
Chloropropanones	U.S.EPA Method 551.1
Aldehydes	U.S.EPA Method 556

The analysis of THMs consisting of chloroform, DBCM, BDCM and bromoform were only done initially for both the raw water and tap water samples. The equipment used were a gas chromatography system capable of temperature programming and equipped with a linearized micro electron capture detector (μ-ECD), and a fused silica capillary column 0.25mm ID*30m fused capillary with chemically bonded methyl polysiloxane phase of 1μm film thickness. Other accessories included a splitless injector, Hamilton gas tight syringes, disposable pasteur pipets, 60ml vials with PTFE(polytetraflouroethylene) faced septa caps, 2ml vials with teflon faced septa, and 30 ml vials for storage of standard solutions.

The column oven was temperature programmed as follows:

1. Held at 35°c for 22 minutes
2. Increased to 145°C at 10°C/min and held at 145°C for two minutes
3. Increased to 225°C at 20°C/min and held at 225°C for 15 minutes
4. Increased to 260°C at 10°C/min and held at 260°C for 30 minutes

Injector temperature: 200°C

Detector temperature: 300°C

Carrier gas: Helium

Purity of the gas: Ultra high purity grade of 99.999%

Linear velocity of Helium gas = 25 cm/sec at 35°C

Makeup flow gas: Nitrogen

Velocity of Nitrogen gas = 60 ml/min

Reagents and standards used were:

1. MTBE(Methyl-tert-butyl-ether)-high purity grade
2. Acetone –high purity
3. Methanol
4. Phosphate buffer
5. Ammonium chloride
6. Pure standards of chloroform, DBCM, BDCM and bromoform of 200 µg/L in MeOH (Methyl Alcohol)
7. Internal standard, bromoflourobenzene of 1000 µg/L in acetone.

3.3.3.1 Calibration

Calibration curves for the four THMs compounds chloroform, DBCM, BDCM and bromoform were prepared by analyzing five different concentrations of THMs prepared from a certified company, Sigma Chemicals. Each standard solution was then spiked with 60µg/L of internal standard solution. The standard solutions were analyzed using the same procedure that was used to analyze the samples.

The internal standard method was used to calibrate and quantify the concentrations of THMs in the samples. An internal standard (ISTD) is a pure compound added to a sample (standard or water sample) in known amounts and used to calibrate concentration measurements of other compounds in the sample. A solution of bromoflourobenzene was used as an ISTD and was added to all the samples.

Five calibration standards of 5, 10, 20, 40, and 80µg/L were prepared. As a means of eliminating any matrix effects due to the use of the phosphate buffer and dechlorinating agent, the procedural calibration standards were also prepared in reagent water, which has been buffered to pH 4.8 - 5.5 and dechlorinated with ammonium chloride. To prepare this buffer/dechlorinating reagent water, 8.3g of phosphate buffer/ammonium chloride were added to 500ml of reagent water. Then 50 ml of buffer/ ammonium chloride reagent water was measured into a 60-ml vial to which 25µl of the desired concentration of primary dilution standard was injected into the middle point of the water volume. Next 300 µl of the internal primary dilution standard was added to it. The vial was then capped and the sample was agitated by carefully inverting the sample vial two times with minimal sample agitation. Soon after mixing exactly 3ml of MTBE was added to the sample vial. The vial was then recapped and was vigorously and consistently shaken by hand for four minutes to extract the MTBE/Sample mixture. The vial was kept aside and allowed for the water and MTBE phases to separate for about 2 to 3 minutes. Then by using a disposable pasteur pipet, a portion of the solvent phase was transferred into a 2ml vial. In this manner all the five calibration standard extracts of 50, 10, 20, 40 and 80µg/L were prepared and injected into the GC/ECD for calibration.

The measurements of THMs were quantified by calculating the ECD detector response to each compound relative to the internal standard. Chromatogram for 10 µg/L concentration of standard solution of THMs is shown in the figure 3.2.

The response factor (RF) was calculated with the equipment's computer software using the equation:

$$RF = Rs^* Ci/Ri^*Cs \qquad (3.2)$$

Rs = Response for calibration standard

Ri = response for the ISTD

Ci = Concentration of ISTD

Cs = Concentration of the calibration standard

The equations used to calculate the actual amount of a calibrated component are:

Response Ratio = Response x / Response ISTD **(3.3)**

x is the calibration standard

Actual amount of x= (Response Ratio * RFx)*(Actual amount of ISTD) * M* D **(3.4)**

where RFx is the response factor for compound x= Amount ratio/Response ratio

M is the multiplier (M is assumed as 1)

D is the dilution factor (D is assumed as 1)

Relative amount of x =(Actual amount of x) *100/Sample amount **(3.5)**

The equation used to calculate the amount of unknown samples is:

Actual amount of x= RF_X (Response Ratio) x* Amount ISTD* M*D **(3.6)**

Response ratio=Response x/Response ISTD **(3.7)**

The precision of the analyses of the analytes during the calibration process is shown in Table 3.3 below. The correlation coefficient r^2 ranged from 0.9954 to 0.99868 and %RSD (Residual standard deviation) from 0.22382 to 1.62845, where RSD is useful for comparing the uncertainty between different measurements of varying magnitude. The RSD is calculated from the standard deviation and is expressed as

%RSD = (Standard Deviation/Mean) * 100 **(3.8)**

Table 3.3: Precision of analyses during calibration

Analyte	Correlation Coefficient, r^2	%RSD
Chloroform	0.995	0.261
Dibromochloromethane	0.997	1.160
Bromodichloromethane	0.997	1.628
Bromoform	0.998	0.223

The repeatability of the method was investigated by analyzing buffered/dechlorinated reagent water with standard solutions of 10, 20, 40 and 80 µg/L concentrations. The repeatability of analyses for different THMs at different concentrations using the relative standard method is shown in Table 3.4.

Table 3.4: Repeatability of analysis at different trihalomethanes concentrations using relative standard deviation method

Conc. (µg /L)	Chloroform (%RSD)	Dibromochloro methane (%RSD)	Bromodichloro-methane (%RSD)	Bromoform (%RSD)
10	1.135	2.41	2.59	0.17
20	0.765	0.9	0.86	0.46
40	3.07	1.25	0.962	5.81
80	0.78	0.6	0.44	1.98

The accuracy of the method and experimental work was calculated by preparing different concentrations of 5, 20 and 30µg/L, which were not used in the calibration.

These standard solutions were injected into the equipment using the same method for calibration assuming them as samples and the percent recovery of each concentration was found. Only one injection was performed for each concentration and it was found that at lower concentrations the percent recovery was high. The percent recovery of the analytes for each concentration is shown in Table 3.5.

Table 3.5: Accuracy of THMs results

Analyte	**Fortified Conc. (µg/L)**	**Measured Conc. (µg/L)**	**Percent Recovery**
Chloroform	5	9.36	187
	20	25.81	129
	30	32.55	108
Dibromochloromethane	5	7.97	159
	20	21.38	106.9
	30	30.7	102
Bromodichloromethane	5	7.3	146
	20	20.24	101.2
	30	30.99	103
Bromoform	5	7.07	141
	20	21.12	105.6
	30	31.99	106.6

3.3.3.2 Analysis of sample

A 50ml sample aliquot is extracted with 3 ml of MTBE. One μL of the extract was then injected into a GC equipped with a fused silica capillary column and linearized electron capture detector for separation and analysis. Procedural standard calibration was used to quantitate method analytes. Procedural standard calibration is a calibration method where aqueous calibration standards are prepared and processed in exactly the same manner as a sample. All steps in the process from addition of sampling preservatives through instrumental analyses are included in the calibration. Using this calibration compensates for any inefficiency in the processing procedure. Standard laboratory safety measures were practiced to minimise exposure to the chemicals and reagents. This was important, as the toxicity and carcinogenicity of chemicals used in this method have not been precisely defined. Material Safety Data Sheets (MSDS) of all chemicals used were readily made available for reference.

The following steps were involved in the preparation of the sample and are summarized here again:

a. The samples (tap and raw water) were removed from storage and allowed them to equilibrate to room temperature.
b. A 50ml of sample was then transferred into a clean glass vial.
c. Then 300μl of internal standard was injected into the sample.
d. The sample was mixed slowly and carefully by inverting the sample vial 2 times with minimal agitation

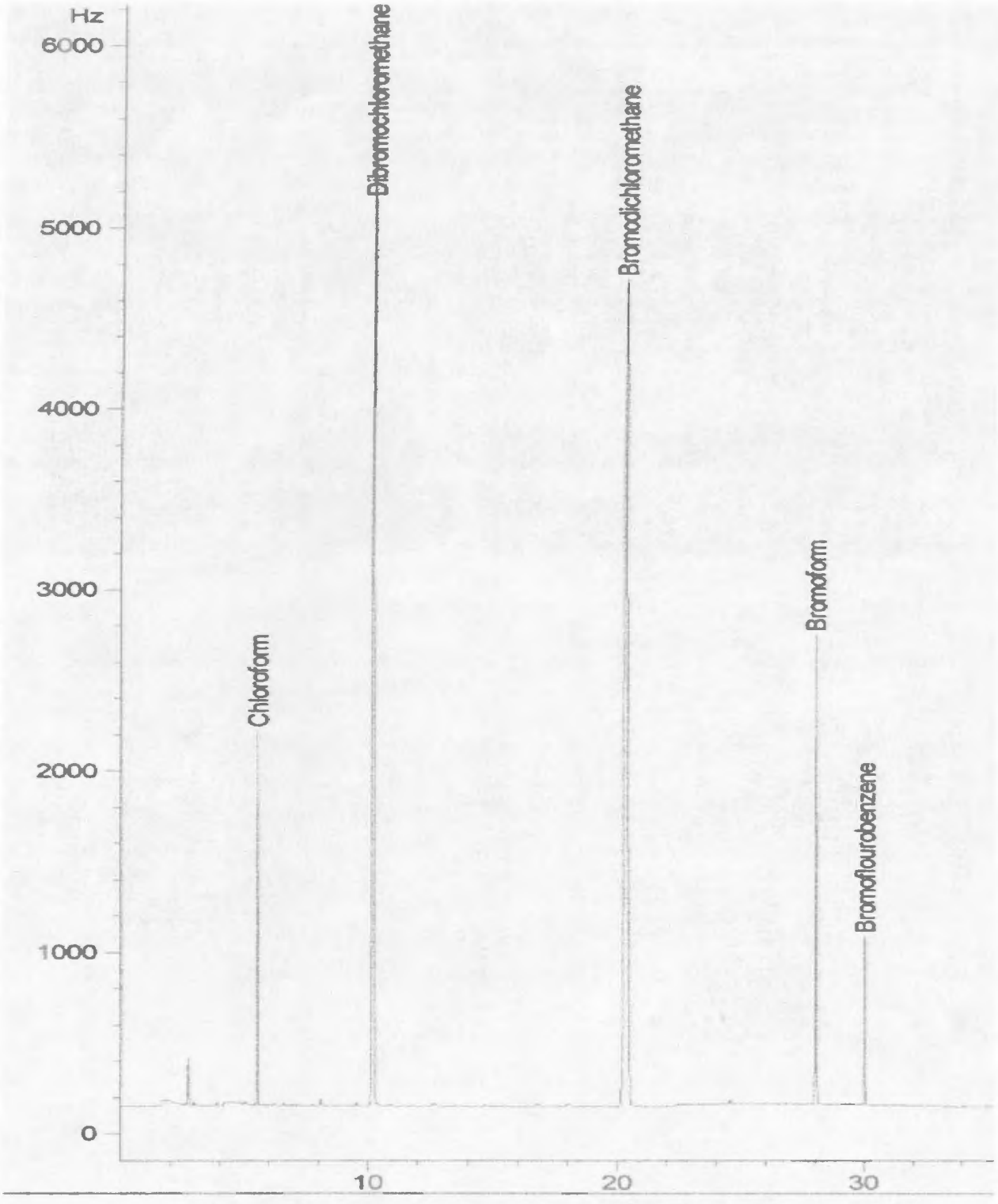


Fig 3.2 Chromatogram of 10 μg/L concentration of standard solution of THMs

e. Exactly 3 ml of MTBE was then added to sample

f. Water and MTBE phases were allowed to separate for about 2 minutes.

g. Then by using a disposable pasteur pipet a portion of the solvent phase from the 60ml vial was transferred into a 2ml vial.

h. The sample extracted was then stored in a freezer or analysed immediately. If stored the sample was analysed before 14 days after extraction.

i. 1µl of the sample extract was injected into the GC and the resulting peak response was recorded.

j. Chromatogram with four THM compounds present in the Bonavista tap water sample is shown in the figure 3.3.

3.3.4 THMs, HANs and other DBPs analyses

As a next step, both the raw water and tap water samples were analyzed for THMs, HANs and HKs. THMs included chloroform, BDCM, DBCM and bromoform. HANs included DCAN, TCAN, BCAN and DBAN. HKs include

1,1-dibromopropanone and TCP.

The list of reagents and standards included are:

1. MTBE-high purity grade
2. Acetone –high purity
3. Methanol

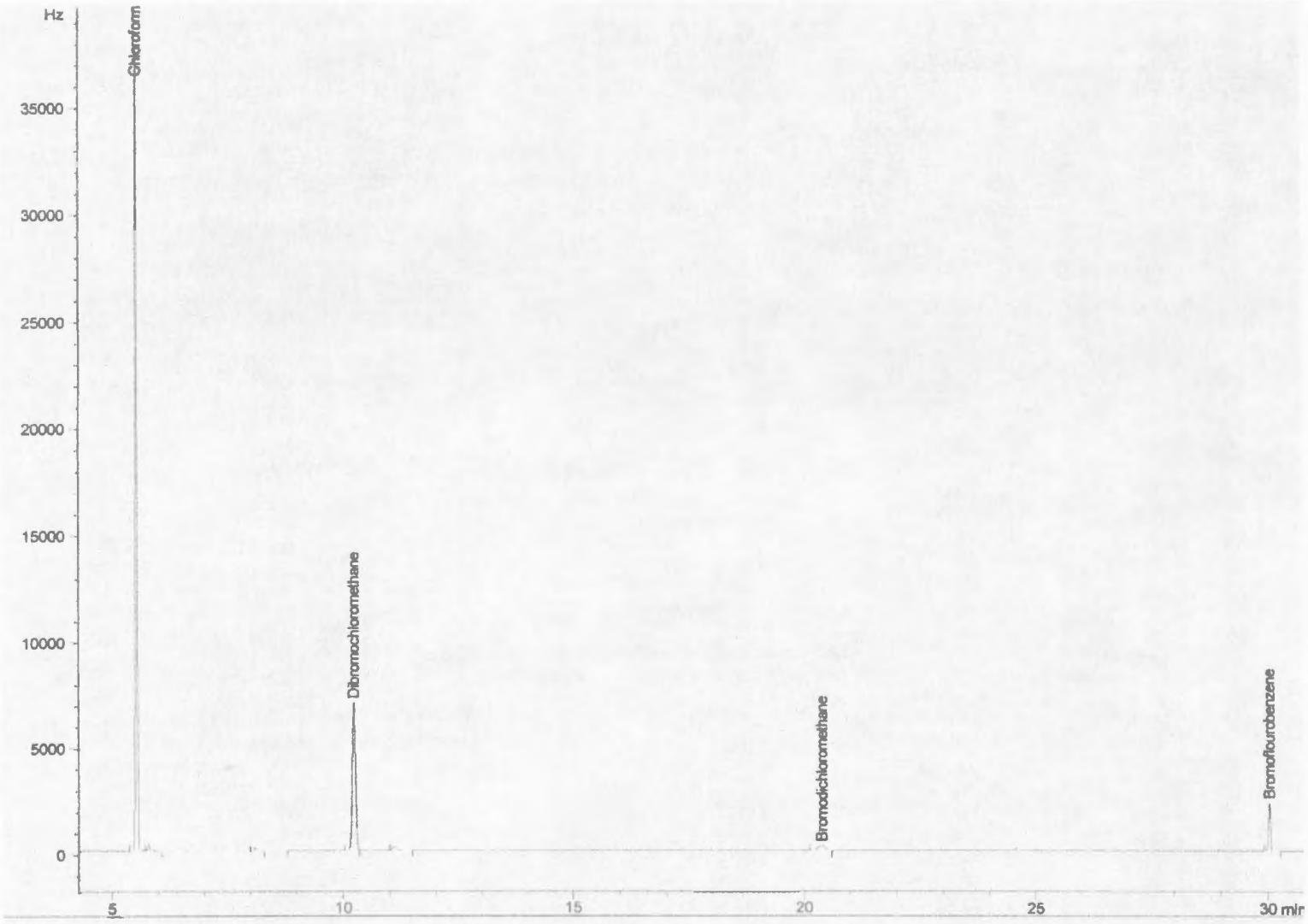


Fig 3.3: Chromatogram of Bonavista tap water sample containing four THM compounds

4. Sodium sulphate Na_2SO_4-oven dried in furnace at 400°C for 30 minutes and stored in a capped glass bottle
5. Phosphate buffer
6. Ammonium chloride
7. Standard solution mixture of HCM-551D DBPs mixture purchased from Ultrasceintific
8. Surrogate standard solution of IST-152 Decaflourobiphenyl - 1000 µg/L in acetone from Ultrasceintific

Surrogate Primary dilution standard: The primary dilution standards were prepared such that at least 25µl of the primary dilution standard should be required to be added to the sample to get the desired required dose of 10µg/L. So the 100 µl of the surrogate stock solution was diluted to volume with 10 ml of acetone. This yielded a primary dilution standard of 10µg/L. Now addition of this 50 µl of primary dilution surrogate standard to 50ml of sample would finally give a required concentration as 10µg/L.

3.3.4.1 Calibration

Four calibration standards of 10, 25, 50 and 80µg/L were prepared. As a means of eliminating any matrix effects due to the use of the phosphate buffer and dechlorinating agent, the procedural calibration standards were also prepared in reagent water, which had been buffered to pH 4.8-5.5 and dechlorinated with ammonium chloride. To prepare this buffer/dechlorinating reagent water, 8.3g of phosphate buffer/ammonium chloride were added to 500ml of reagent water. Then 50 ml of buffer/ ammonium chloride reagent

water was measured into a 60-ml vial to which 25µl of the desired concentration of primary dilution standard was injected into the middle point of the water volume. Next 50 µl of the surrogate primary dilution standard was added to it. The vial was then capped and the sample was mixed by carefully inverting the sample vial two times with minimal sample agitation. Soon after mixing exactly 3ml of MTBE was added to the sample immediately followed by the addition of 20g of sodium sulfate to the sample vial. The vial was then recapped and was vigorously and consistently shaken by hand for four minute to extract the Na_2SO_4/MTBE/Sample mixture. Water and MTBE phases were allowed to separate for about 2 to 3 minutes. Then by using a disposable pasteur pipet, a portion of the solvent phase was transferred into a 2ml vial. In the same manner all the four-calibration standard extracts of 10, 25, 50 and 80µg/L were prepared and injected into the GC/ECD for calibration. The chromatogram of the 10µg/L concentration of DBPs is shown in the figure 3.4.

The precision of the analyses of all the eleven analytes during the calibration process is shown in Table 3.6. The standard solutions of each concentration 10, 25, 50 and 80µg/L were injected three times and the average reading was used for the calibration. The linear least square correlation r^2 ranged from 0.954 to 0.977 and the %RSD from 0.873 to 9.667.

Table 3.6: Precision of analyses during DBPs calibration

Analyte	Correlation	%RSD
Chloroform	0.954	0.873
Trichloroacetonitrile	0.954	9.668
Dichloroacetonitrile	0.966	4.689
Dibromochloromethane	0.957	3.910
1,1, dichloropropanone	0.967	2.248
Chloropicrin	0.956	5.075
Bromodichloromethane	0.960	2.842
Bromochloroacetonitrile	0.964	3.206
1,1,1 trichloropropanone	0.977	2.628
Bromoform	0.967	0.886
Dibromoacetonitrile	0.978	2.778

The precision and accuracy of the method and experimental work was calculated by preparing a concentration of 10µg/L again as used in the calibration. This standard solution was injected into the equipment using the same method for calibration and the percent recovery of the concentration was found. Only one injection was performed for the concentration. The percent recovery of the analytes for 10µg/L concentrations is shown in Table 3.7.

Table 3.7: Accuracy of DBPs results

Analyte	Fortified Conc. (µg/l)	Measured Conc. (µg/l)	Percent Recovery
Chloroform	10	15.08	150.8
Trichloroacetonitrile	10	12.09	120.9
Dichloroacetonitrile	10	11.56	115.6
Dibromochloromethane	10	12.55	125.5
1,1, dichloropropanone	10	11.22	112.2
Chloropicrin	10	12.03	120.3
Bromodichloromethane	10	12.42	124.2
Bromochloroacetonitrile	10	11.97	119.7
1,1,1 trichloropropanone	10	10.36	103.6
bromoform	10	12.18	121.8
Dibromoacetonitrile	10	11.17	111.7

3.3.4.2 Analysis of sample

The experimental procedure followed was in accordance with the EPA method 551.1 prepared by the National Exposure Research Laboratory, U.S.E.P.A, titled "Determination of Chlorination disinfection by-products, chlorinated solvents and halogenated pesticides/herbicides in drinking water by liquid-liquid extraction and gas

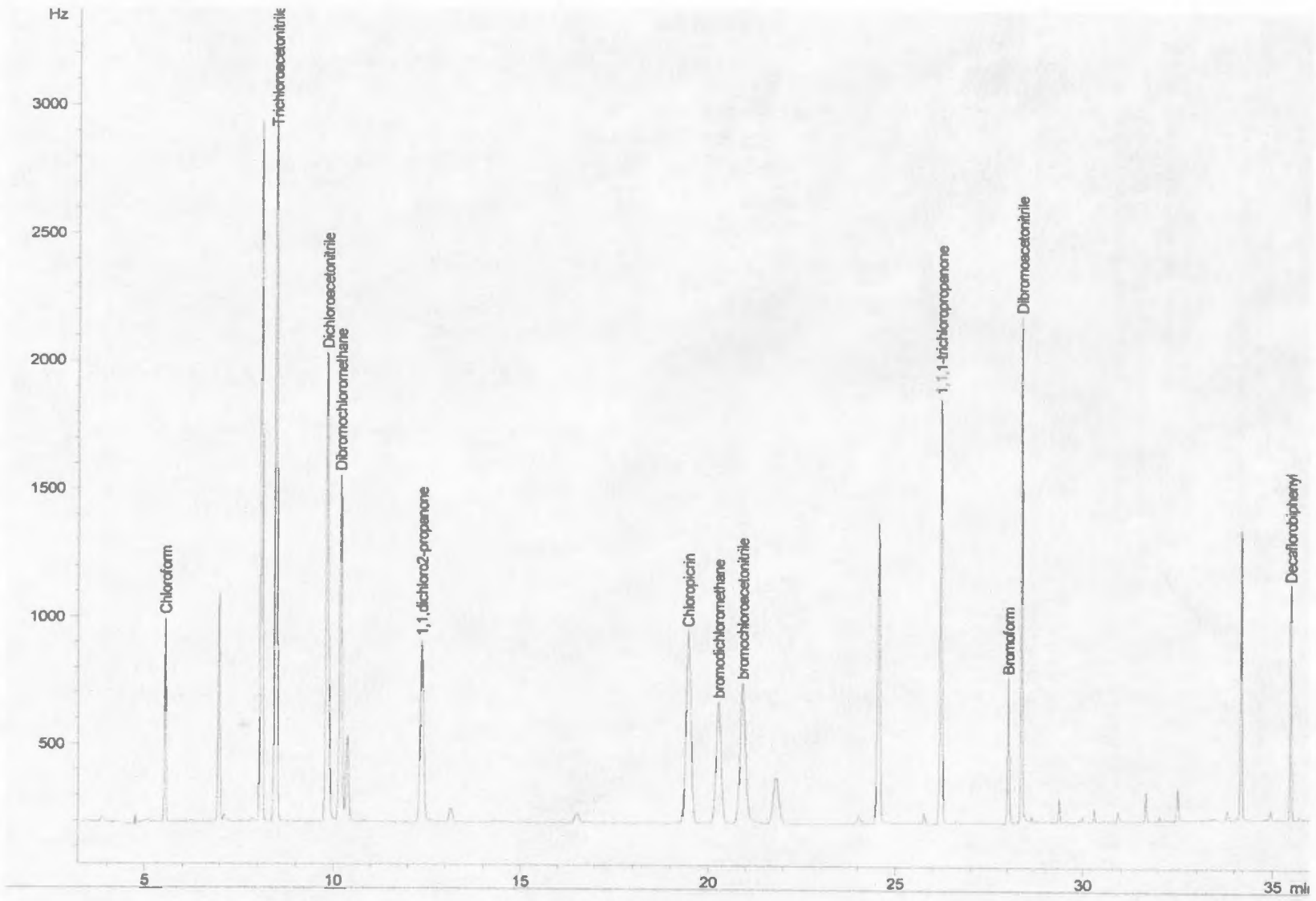


Fig 3.4: Chromatogram of 10μg/L standard concentration solution of DBPs mixture of THMs, HANs and HK's

chromatography with electron capture detection". The procedure used was described briefly in the following section.

A 50ml sample aliquot is extracted with 3 ml of MTBE. One µL of the extract was then injected into a GC equipped with a fused silica capillary column and linearized electron capture detector for separation and analysis. Procedural standard calibration was used to quantitate method analytes.

The steps involved in the preparation of the sample are summarized as follows:

a. The samples were removed from storage and allowed them to equilibrate to room temperature.
b. A 50ml of sample was then transferred into a clean glass vial.
c. Then 50µl of surrogate standard was injected into the sample.
d. The sample was mixed slowly and carefully by inverting the sample vial 2 times with minimal agitation
e. Exactly 3 ml of MTBE was then added to sample
f. 20g of Na_2SO_4 was added to the sample vial which was immediately capped and vigorously shaken consistently by hand for 4 minutes to extract the sample. Otherwise if not done immediately Na_2SO_4 solidifies at the bottom of vial and will not dissolve during extraction
g. Water and MTBE phases were allowed to separate for about 2 minutes.
h. Then by using a disposable pasteur pipet a portion of the solvent phase from 60ml vial was transferred into a 2ml vial.

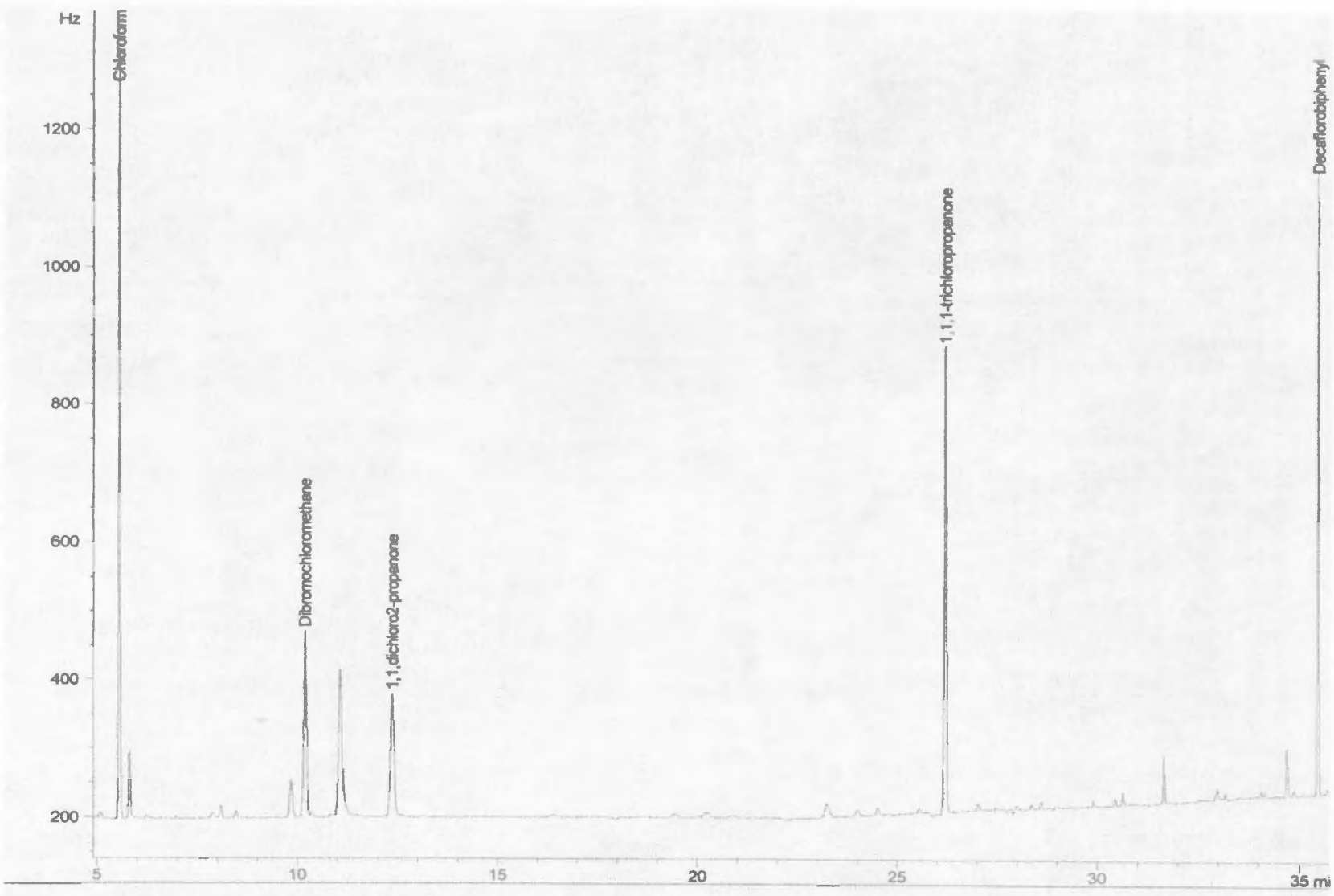


Fig3.5: Chromatogram of Ferryland tap water sample for the THMs, Hans and HKs

i. The sample extracted was then stored in a freezer or analysed immediately. If stored the sample was analysed before 14 days after extraction.

j. 1μL of the sample extract was injected into the GC and the resulting peak response was recorded.

k. Chromatogram with DBPs present in the Ferryland tap water sample is shown in the Figure 3.5.

Few chromatograms of the calibration standards, raw water and tap water samples for some communities are shown in the appendix.

3.4 Experimental Data

The data obtained from the laboratory analysis are presented in the following section. The data are categorized into 3 stages:

1. Tap water sample data
2. Chlorination of raw water to find the formation of THMs at different contact times and doses.
3. Chlorination of raw water to find the formation of THMs, HANs and HKs at different contact times and doses.

1. Tap water sample Data:

For each tap water sample collected in a 60-ml vial a minimum of two duplicate samples were also collected and analyzed. During analyses of the extract of the sample all the extracts were injected 3 times for accuracy. Finally the average of all these readings was taken as the final reading of the water sample. The THMs concentration was determined

by summing the concentration level of chloroform, DBCM, BDCM and bromoform. Concentration levels less than 1μg/L were ignored in the estimation because of precision error of the instrument. Such values were shown in the table as <1 μg/L.

Table 3.8: Summary statistics of tap water data

	TTHM	pH	TOC	DOC	Turbidity	Alkalinity
Number of samples	10	10	10	10	10	10
Mean	132.9	5.62	5.76	4.95	0.41	11.26
Median	138.9	5.56	5.82	5.17	0.43	9.0
Q1	48.5	5.29	2.63	2.53	0.29	7.65
Q3	189.2	6.11	7.91	6.41	0.5	12.5
Minimum	35.4	4.88	2.32	2.02	0.2	6.0
Maximum	290.0	6.23	12.41	10.4	0.63	28.0
Standard Deviation	84.1	0.48	3.39	2.63	0.12	6.4

2. Raw water data for THMs:

The concentration of THMs at both controlled and uncontrolled pHs, with constant temperature of 23°C, with varying doses is shown in Table 3.10 for communities selected.

Table 3.9: Tap water data for various locations in Newfoundland

		Chloroform µg/L	$CHClBr_2$ µg/L	$CHBrCl_2$ µg/L	$CHBr_3$ µg/L	TTHM µg/L	pH	Turbidity (NTU)	Alkalinity mg $CaCO_3$	TOC	DOC	UV254nm
February	Keels	283.1	7.2	<1	<1	290.3	4.88	0.49	6	12.41	10.4	0.308
	Clarenville	47.84	4.5	<1	<1	52.3	5.54	0.28	14	2.34	2.27	0.023
	Ferryland	173.7	11.6	<1	<1	185.4	5.59	0.54	12	6.62	6.14	0.185
	Bonavista	176.9	11.5	<1	<1	188.5	6.23	0.63	28	9.40	5.28	0.130
	Burin	116.6	11.1	<1	<1	127.8	4.95	0.2	8	5.21	5.05	0.139
March	Clarenville	66.2	3.9	<1	<1	70.1	5.48	0.3	8	2.32	2.02	0.027
	Ferryland	141.8	8.1	<1	<1	150.0	5.93	0.44	10	6.41	6.31	0.198
June	St.Johns-1	19.4	10.0	5.9	<1	35.4	6.19	0.42	8	2.77	2.68	0.019
	St.Johns-2	20.0	10.6	6.1	<1	36.8	6.09	0.45	6.6	2.72	2.61	0.015
	Ferry	166.26	18.61.	<1	<1	191.1	5.410	0.37	12	7.41	6.71	0.201

Table 3.10: Concentration of four THM compounds and parameter values of TOC, DOC, UV254nm

	Chlorine Dosage (mg Cl_2/L)	Reaction time (hr)	Residual Chlorine (mg Cl_2/L)	$CHCl_3$ (µg/L)	$CHClBr_2$ (µg/L)	$CHBrCl_2$ (µg/L)	$CHBr_3$ (µg/L)	pH	TOC (mg/L)	DOC (mg/L)	UV254 nm (cm^{-1})	Turbidity (NTU)	Alkalinity mg caco3/L
Keels, Feb 4th	Raw Water							3.95	14.17	8.84	0.292	0.64	8
	31.25 mg Cl_2/L at pH=9												
		3	12	751.53	27.66	1.19	<1						
		7	11	810.06	30.52	1.35	<1						
		24	5.5	813.93	28.91	1.19	<1						
		48	4	1015.66	35.86	1.34	<1						
		120	1.48	1309.50	41.92	1.39	<1						
	30 mg Cl_2/L with buffer at pH=8												
		3	8	785.38	26.95	1.13	<1		12.60				
		7	4.67	1175.78	37.79	1.28	<1		12.39				
		24	1	891.12	29.78	1.15	<1		12.14				
		48	0.8	1189.01	38.25	1.27	<1		13.08				
		120	0.63	1566.98	44.89	1.30	<1		13.04				
	30mg Cl_2/L at pH=9	1	22	2213.30	53.75	<1	<1	9.03	12.47				
		3	14.67	1028.35	25.49	<1	<1	9.08	11.82				
		7	10	1261.00	30.83	<1	<1	9.07	11.59				
		24	10.5	1241.86	29.67	<1	<1	8.7	11.35				

	Chlorine Dosage (mg Cl_2/L)	Reaction time (hr)	Residual Chlorine (mg Cl_2/L)	$CHCl_3$ (µg/L)	$CHClBr_2$ (µg/L)	$CHBrCl_2$ (µg/L)	$CHBr_3$ (µg/L)	pH	TOC (mg/L)	DOC (mg/L)	UV254 nm (cm^{-1})	Turbidity (NTU)	Alkalinity mg caco3/L
		120	0.3	812.42	19.99	<1	<1	9.0	11.59				
Clarenville Feb4th	Raw water							5.69	9.04	8.23	0.33	0.3	12
	30 mg Cl_2/L at ph 8	1	37.5	693.56	9.91	<1	<1	8.64	9.42				
		3	16.5	979.61	11.47	<1	<1	7.38	9.33				
		7	12.75	1007.13	12.08	<1	<1	8.3	9.15				
		24	11.33	1099.64	13.56	<1	<1	6.91	9.13				
		48	10.80	1300.83	13.76	<1	<1	7.2	8.79				
		120	3.16	985.58	11.43	<1	<1	7.6	8.49				
	30 mg Cl_2/L, no buffer	1	30	397.76	7.29	<1	<1	5.68	8.50				
		3	15	798.83	9.56	<1	<1	5.73	9.29				
		7	10.87	500.14	7.11	<1	<1	5.64	9.44				
		24	10.00	728.73	9.05	<1	<1	5.62	9.16				
		48	8.40	709.59	10.96	<1	<1	6.42	8.86				
		120	4.50	800.41	8.97	<1	<1	5.7	8.42				
	27 mg Cl_2/L, no buffer	1	12	332.07	7.20	<1	<1	5.55	9.79				

		3	10	946.86	8.74	<1	<1	5.22	9.42				
	Chlorine Dosage (mg Cl_2/L)	**Reaction time (hr)**	**Residual Chlorine (mg Cl_2/L)**	**$CHCl_3$ (µg/L)**	**$CHClBr_2$ (µg/L)**	**$CHBrCl_2$ (µg/L)**	**$CHBr_3$ (µg/L)**	**pH**	**TOC (mg/L)**	**DOC (mg/L)**	**UV254 nm (cm^{-1})**	**Turbidity (NTU)**	**Alkalinity mg caco3/L**
		7	9.15	760.72	6.93	<1	<1	5.24	9.57				
		24	8.3	1225.29	9.16	<1	<1	5.2	8.86				
		48	6.8	863.36	9.39	<1	<1	5.32	8.46				
		120	4.5	876.79	9.79	<1	<1	5.28	8.12				
	27mg Cl_2/l , pH 8	1	13	573.33	6.57	<1	<1	7.64	9.10				
		3	11.5	674.16	8.12	<1	<1	7.15	9.34				
		7	9	942.98	10.94	<1	<1	7.53	9.77				
		24	5.6	1074.52	14.30	<1	<1	7.82	10.8				
		48	4.4	972.07	13.52	<1	<1	7.48	10.48				
		120	1.5	1361.23	13.23	<1	<1	7.75	9.9				
Bonavista Feb4th	Raw water							4.99	6.28	6.21	0.137	0.67	
	ph 8, 26mg/L cl2	1	16	200.43	14.06	<1	<1	7.37	5.72	5.73	0.198	0.22	
		3	14.3	309.51	17.29	<1	<1	7.39	5.64	6.01	0.205	0.19	
		7	11.5	313.09	20.12	1.06	<1	7.64	5.67	4.65	0.028	0.24	
		24	10.5	377.64	24.39	1.26	<1	7.64	6.27	5.18	0.031	0.15	
		48	8	1088.97	45.38	<1	<1	7.74	6.25	4.81	0.022	0.17	
		120	6.2	723.69	29.70	<1	2.49	7.72	5.99	4.48	0.030	0.14	

	Chlorine Dosage (mg Cl_2/L)	Reaction time (hr)	Residual Chlorine (mg Cl_2/L)	$CHCl_3$ (µg/L)	$CHClBr_2$ (µg/L)	$CHBrCl_2$ (µg/L)	$CHBr_3$ (µg/L)	pH	TOC (mg/L)	DOC (mg/L)	UV254 nm (cm^{-1})	Turbidity (NTU)	
Ferry-land Feb4th	Raw water							5.27	9.30	7.42	0.182	0.4	
	buffer ph 8 , 23.4 mg/L Cl_2	1	16.5	294.96	18.44	<1	<1	7.88	27	10.88	0.138	0.44	
		3	12	514.61	24.81	<1	<1	7.88	10.26	7.95	0.138	0.28	
		7	10	403.73	21.50	<1	<1	7.94	6.64	6.28	0.118	0.2	
		24	7.6	835.58	32.10	<1	<1	7.73	8.99	8.09	0.117	0.19	
		48	5.2	748.97	31.16	1.11		6.76	6.29	5.94	0.094	0.2	
		120	3.9	1024.83	35.40	<1	1.03	7.26	6.52	4.01	0.017	0.09	
Burin, Feb 25th	Raw water							5.43	7.33	7.22	0.202	3.7	
	22.36 mg/L cl2 buffer ph 8,	1	8	269.85	18.76	<1	<1	7.97	6.67	6.51	0.164	1.77	
		3	7.4	383.20	21.5	1.07	<1	7.97	5.58	6.91	0.146	1.71	
		7	6.8	629.87	32.87	1.2	<1	8.02	9.96	8.11	0.143	1.68	
		24	4.8	943.39	42.40	1.38	<1	8.02	5.95	5.36	0.134	1.55	
		48	3.25	1341.58	50.17	<1	<1	7.82	7.58	7.04	0.116	1.48	
		120	1.6	1681.42	53.69	<1	<1	7.99	7.46	5.30	0.089	1.38	

3. Chlorination of raw water to find the formation of THMs, HANs and HKs at different contact times and doses:

The raw water samples from communities of Ferryland and Clarenville were dosed with different amounts of chlorine at controlled and uncontrolled pH with temperature being maintained constant at 23±1°C. The concentrations of the four THMs compounds (chloroform, DBCM, BDCM and bromoform), the four haloacetonitriles (DCAN, TCAN, DBAN and BCAN) and the two haloketones (1,1-dichloropropanone and TCP) were found at different reaction times of 1, 3, 7, 24, 48 and 120 hrs respectively. At the same time the different parameters which influenced the formation like TOC, DOC, UV254nm, turbidity were measured at different contact times. All these DBPs concentrations and the parameters are listed in Table 3.11

Table 3.11: Raw water data of THMs, HANs, and HKs

Ferry	Chlorine Dosage	21.33mgCl_2/L, no buffer						Raw water
	Reaction time (hr)	1	3	7	24	48	120	
	Residual Chlorine	6.6	4.58	4.25	2.167	1.48	0.34	
	$CHCl_3$ (µg/L)	93.03	123.49	118.01	132.86	186.75	119.73	
	$CHClBr_2$ (µg/L)	9.35	11.01	10.55	11.16	13.76	10.66	
	DCAN (µg/L)	6.53	8.13	7.53	11.46	12.60	14.08	
	TCAN (µg/L)	-	-	--	-	-	-	
	1,1DCP (µg/L)	4.48	4.18	4.09	4.31	4.59		
	1,1,1TCP (µg/L)	10.73	12.0	10.22	13.25	17.50	16.92	
	pH	5.72	5.65	5.73	5.77	5.78	5.77	5.41
	TOC (mg/L)	7.99	7.32	6.94	7.28	7.29	7.80	8.06
	DOC (mg/L)	8.36	7.27	6.92	7.23	7.22	7.63	7.82
	UV254nm (cm^{-1})	0.092	0.078	0.067	0.072	0.071	0.084	0.087
	Turbidity (NTU)	0.5	0.46	0.65	0.6	0.54	0.58	0.68
Ferry	Chlorine Dosage	22.5 mgCl_2/L, with buffer						
	Reaction time	1	3	7	24	48	120	
	Residual Chlorine	9	6.6	5.34	3.16	2.16	0.48	
	$CHCl_3$ (µg/L)	126.55	201.92	285.36	332.2	328.62	245.25	
	$CHClBr_2$ (µg/L)	11.76	14.60	17.54	19.45	19.28	15.66	
	DCAN (µg/L)	6.65	8.63	7.16	7.34	6.22	5.25	
	TCAN (µg/L)	--	-	-	-	-	-	
	1,1DCP (µg/L)	3.86	4.17		4.00	3.18		
	1,1,1TCP (µg/L)	10.67	8.19	3.51	3.47	6.01	3.03	
	pH	7.6	7.42	7.35	7.52	7.37	7.72	
	TOC (mg/L)	6.73	6.98	6.82	8.31	7.15	6.37	
	DOC (mg/L)	6.26	6.15	5.09	5.29	5.8	5.56	
	UV254nm (cm^{-1})	0.097	0.097	0.121	0.085	0.103	0.080	
	Turbidity	0.4	0.2	0.24	0.28	0.54	0.22	

Clarenville	Chlorine Dosage	27.5mgCl_2/L, with buffer						
	Reaction time (hr)	1	3	7	24	48	120	
	Residual Chlorine	9	5	3.75	1.33	0.57	0.03	
	$CHCl_3$ (µg/L)	208.06	342.03	444.74	626.34	749.27	779.16	
	CHClBr2 (µg/L)	6.96	8.00	8.46	9.14	10.43	10.25	
	DCAN (µg/L)	6.87	8.35	9.2261	8.012	6.916	4.56	
	TCAN (µg/L)	-	-	-	-	-	-	
	1,1DCP (µg/L)	4.03	4.10	4.18	3.71		4.39	
	1,1,1TCP (µg/L)	15.99	13.05	8.21	3.46	3.17		
	pH	7.58	7.52	7.74	7.73	7.84	7.8	
	TOC (mg/L)	10.55	8.58	8.87	8.18	8.02	7.14	
	DOC (mg/L)	7.73	7.48	7.15	8.18	7.92	6.57	
	UV254nm (cm^{-1})	0.167	0.168	0.155	0.172	0.169	0.141	
	Turbidity (NTU)	0.32	0.32	0.41	0.39	0.33	0.35	
Clarenville	Chlorine Dosage	27.5mgCl_2/L, no buffer						
	Reaction time (hr)	1	3	7	24	48	120	
	Residual Chlorine	6.94	5.7	4.75	1.95	0.6	0.13	
	CHCl3 (µg/L)	74.55	112.61	254.85	419.56	274.79	355.7	
	CHClBr2 (µg/L)	5.56	7.44	8.29	9.04	7.55	8.510	
	DCAN (µg/L)	5.93	7.21	10.21	14.39	12.71	17.18	
	TCAN (µg/L)	-	-	-	-	-	-	
	1,1DCP (µg/L)	-	-	-	-	-	-	
	1,1,1TCP (µg/L)	10.16	11.54	20.06	37.69	27.32	32.44	
	pH	6.38	6.28	6.23	6.27	6.37	6.08	6.07
	TOC (mg/L)	11.41	10.73	7.61	7.69	7.20	7.38	7.65
	DOC (mg/L)	10.18	10.01	7.09	7.25	6.23	5.85	7.07
	UV254nm (cm^{-1})	0.163	0.165	0.153	0.170	0.144	0.128	0.295
	Turbidity (NTU)	0.59	0.48	0.42	0.49	0.69	0.64	0.35

Chapter 4

Modeling of DBPs Formation

4.1 Characteristics and benefits of models

The modeling of DBPs consists of establishing empirical or mechanistic relationships between DBPs levels in treated water, and the parameters of water quality and of operational control, which can be linked to their formation. Past research has shown that the most important factors for DBPs formation are: the levels of organic matter in water generally designed by total or dissolved organic carbon and by 254-nm UV-absorbance; the applied chlorine dose; the pH of water; water temperature; and the reaction time of residual chlorine in water. The concentrations of bromides are also usually considered because of their influence on the distribution of the four THMs compounds. The chlorination of waters with low bromide concentrations generally leads to higher proportions of chloroform in comparison with other three THMs compounds.

Models for DBPs may be useful in different ways. They can be used routinely by utility operators to control their operational parameters (for example, pH and chlorine dose) or in plot trials to evaluate the effects of upgrading physico-chemical treatment (to increase organic matter removal) on DBPs levels. Models can also be used by environmental health researchers to undertake epidemiological studies by generating, from operational and water quality predictors, past data about DBPs in water utilities. Finally, models can be used by regulatory agencies to estimate, on a national or a

regional basis, requirements for infrastructures updating at utilities complying with proposed regulations.

4.2 Modeling methodology

Models for DBPs can be developed from data generated through different approaches. On one hand, data may be generated from field sampling at the treatment plant and along distribution systems. In this case, the measured DBPs can be related to water quality and operational data corresponding to actual treatment operations at the utility. On the other hand, DBPs data may be generated at laboratory- scale by carrying out batch chlorination tests of raw or treated water samples. This approach is currently used to evaluate TTHMFP tests (APHA, AWWA 1992). The advantages with models developed from laboratory-scale data are that operational conditions can be controlled, and that the effect of contact time on DBPs levels can be assessed. The main draw back of this approach to data generation is that the effects of the distribution system on residual chlorine depletion and on DBPs formation cannot be quantified. DBPs models from data generated through sampling at representative points of the distribution system have the advantage that DBPs concentrations are close to those to which humans are actually exposed in their tap water. However, the difficulty of estimating travel times of water within the system is generally a major limitation of models developed with this type of data.

Both approaches to data generation have been used for developing THMs predictive models, most of them empirical. An overview of the structure and results of these models suggests that prediction capabilities are significantly higher for models generated from bench scale data. This is mainly due to the difficulty of adequately estimating the time water take to travel along the distribution system when developing models from field-scale data. For the same reason, and because the effects of biofilm and pipe material are not considered, the applicability of models from bench-scale data in predicting DBPs in real distribution systems is difficult to assess. As for field-scale data models, their applicability is sometimes limited to the specific system from which the data is gathered.

As a result of the complex nature of DBPs precursor compounds and their corresponding reactions with disinfectants, models for quantification of DBPs have largely been developed using empirical approaches (Westerhoff et al, 2000).

Several statistical equations used to model THMs formation (Westerhoff et al, 2000; Lyn & Taylor, 1993; Malcolm Pirnie Inc., 1992; Singer & Chang, 1989; Amy et al., 1987; Morrow & Minear, 1987; Engerholm & Amy, 1983; Engerholm & Amy, 1981) have the generalized form shown in the following equation:

$$TTHM = k*(DOC)^{a}*(pH-b)^{c}* T^{d}*(Cl_2)^{e}*(UVA)_{254}{}^{f} *(Br)^{g}* t^{h} \quad (4.1)$$

In which k, a, b, c, d, e, f, g and h are fitting constants. DOC, pH, T, Cl_2, UVA, Br and t represent dissolved organic carbon (DOC), pH of sample, temperature, chlorine dose, ultraviolet absorbency at 254nm, bromide concentration, and reaction time respectively.

4.3 Modeling of THMs

Two compounds of THMs were detected in the majority of samples. Only chloroform and DBCM could be quantified in all these samples. Chloroform constituted the major component in THMs. The relationship between the formation of THMs and the independent variables like pH, TOC, Chlorine dosage, Residual chlorine, time is shown in Table 4.1. Pearson r is a standardized measure of the relationship between two continuous variables. Its value can range from –1 to +1, with r = -1 indicating a negative relationship, r = 1 indicating a perfect positive relationship between the two variables.

$$r = \frac{\Sigma Z_X Z_Y}{N} \qquad (4.2)$$

Z_x = Z score for variable X

Z_y = Z score for variable Y

N = number of pairs of scores

The p-value of a statistical significance test represents the probability of obtaining values of the test statistic that are equal to or greater in magnitude than the observed test statistic.

A low p-value less than 0.05 means that there is a statistically significant relationship between the two variables.

Table: 4.1 Relationship between formation of dependent variable THM with independent variables

THM formation with independent variables	Pearson r	p
pH	0.558	0.000
TOC	0.174	0.304
Chlorine Dose	0.112	0.509
Residual Chlorine	-0.382	0.019
Time	0.441	0.006

Effect of TOC:

Using the Pearson correlation method, a low but definite with small relationship (r=0.174) was obtained between THMs formation and TOC as shown in Table 4.1. A relationship of (r = 0.64) was obtained between the DOC and TOC. So only one of TOC and DOC can be taken into account to obtain a good model. Most investigations have found that THMs formation increased with increasing soluble humic material. The rate of THMs formation is equal to that of the TOC consumption. Higher TOC will provide more THMs if enough residual chlorine is available.

Effect of pH:

Simple regression analysis was used to examine the correlation of THMs concentration with respect to pH measured. The results are shown in Table 4.1. The Pearson method of correlation was applied and a good correlation (r=0.558), definite with

small relationship was obtained between THMs formation and pH. In general it was shown that the rate of THMs production increases with pH. It can be seen from Figure 4.1 that for the communities of Ferryland and Clarenville the formation of THMs increased with increase in the pH.

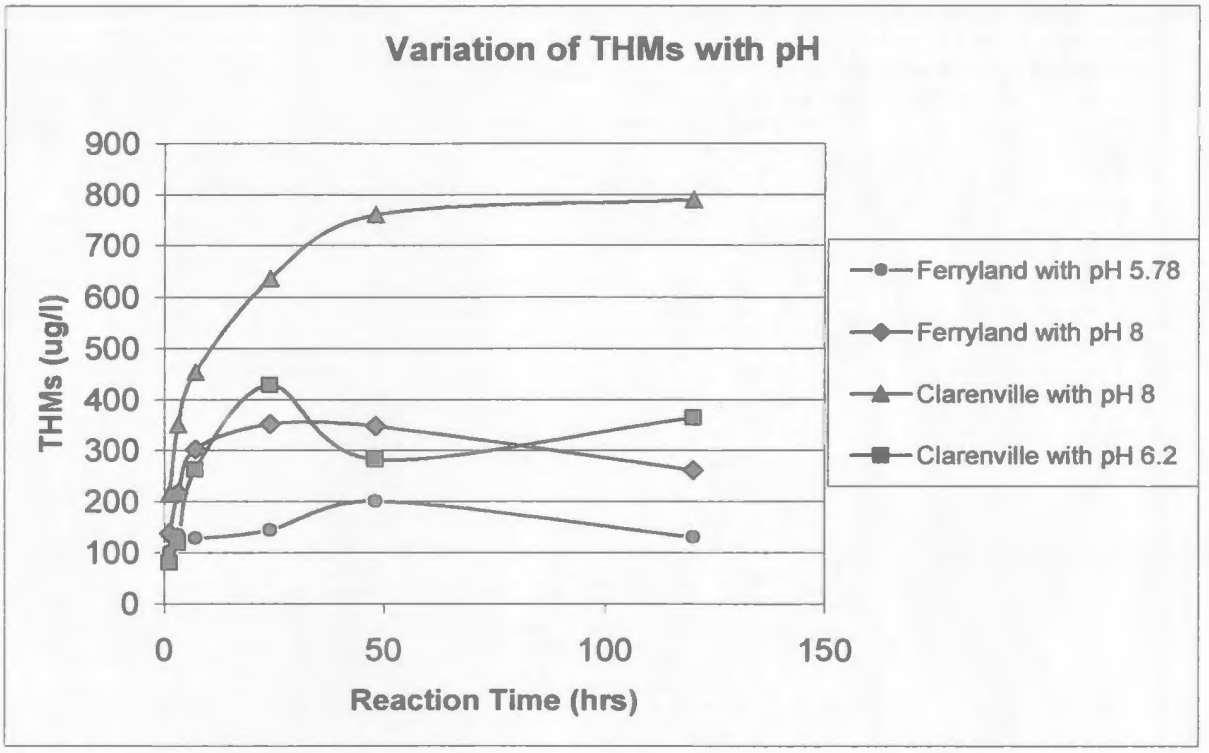


Fig 4.1: Variation of THMs with pH

Effect of Chlorine dosage:

To find the effect of chlorine dosage on the formation of THMs, samples were dosed with different dosages of chlorine. Using the Pearson correlation method, a low but definite small relationship (r=0.112) was obtained between the THMs formation and chlorine dosage. The increase in the formation of THMs with the increase in the chlorine dosage at constant pH for the community of Ferry land is shown in Figure 4.2.

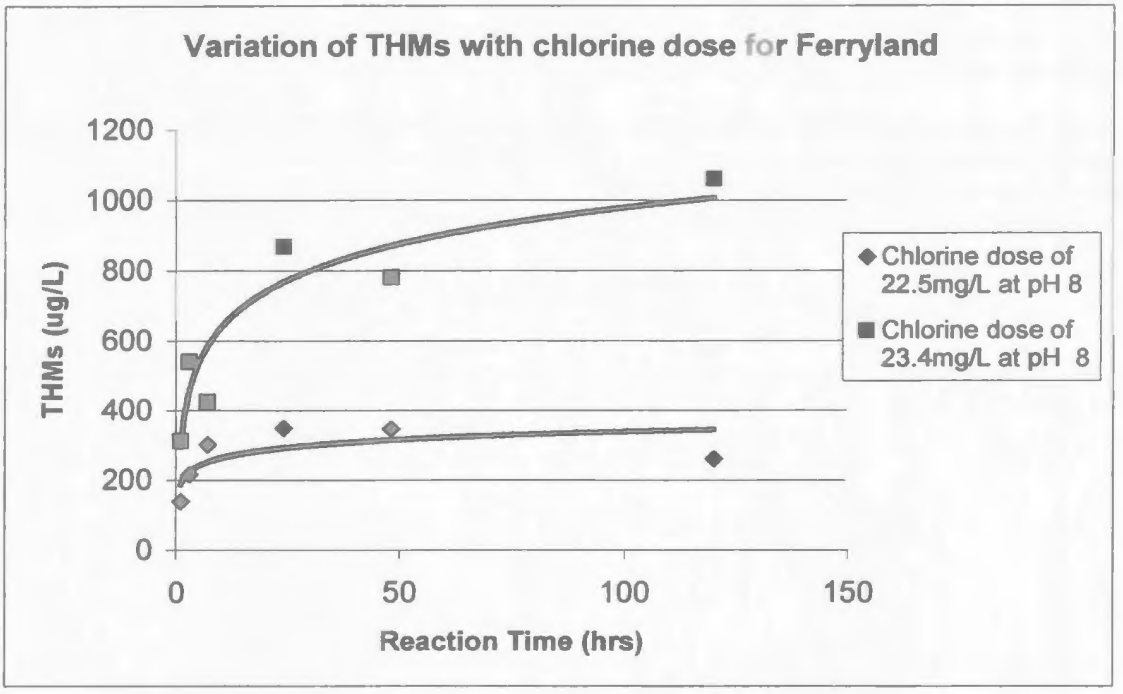


Fig 4.2 Variation of THMs with chlorine dose

Effect of residual chlorine:

The residual chlorine at different reaction times was used to find its significance on THMs formation. Using the Pearson correlation method, a moderate correlation with small relationship (r= -0.382) was obtained between THMs formation and residual chlorine. The significant relationship between the residual chlorine and formation of THMs is shown in Figure 4.3.

Effect of temperature:

There was no observable correlation between the temperature and THMs formation as the chlorination of all the raw water samples was carried out at a temperature of 23°C.

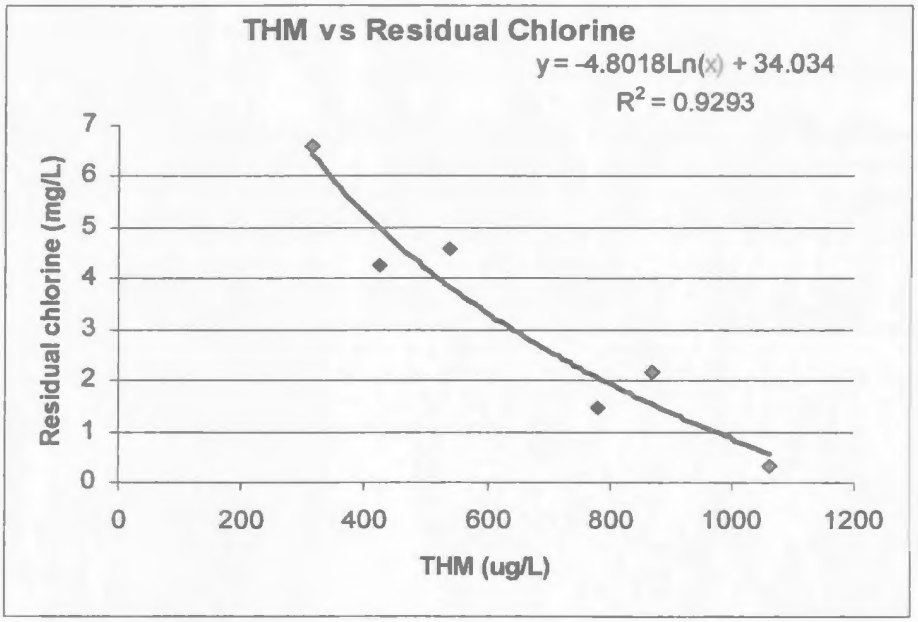


Fig 4.3 THMs vs. Residual Chlorine

Suggested Model:

Using the Datafit and Minitab software, models for THMs were developed. The regression model obtained for the raw water for the formation of THMs is generalized as follows:

$$THMs = a\,(D)^{b}(pH)^{c}\,(TOC)^{d}\,(t)^{e} \qquad \textbf{(4.3)}$$

Where D is the chlorine dose in mg/L

TOC is the total organic carbon expressed in mg/L

t the contact time expressed in hrs

and a, b, c, d the estimated values of statistical coefficients.

The model parameters and tested accuracy are shown in Table 4.2.

Table 4.2: Results of statistical regression for THMs Model

Results	Non-linear model
Coefficient of correlation (r^2)	0.77
Model Significance	p <0.0001
Statistical Coefficients	
a	0.0001
b	3.14
c	1.56
d	0.69
e	0.175

The model was found to be statistically significant to all four variables, where the coefficient of correlation represents the proportion of the variance in one variable that can be determined on the basis of the variability in the second variable. A low p-value less than 0.05 means that the model is significant at 95% confidence interval.

The variance analysis of the model is shown in Table 4.3. Degrees of Freedom (DF) are equal to the number of observations in a sample minus the number of estimated parameters. The degrees of freedom represent the remaining amount of information in a sample of data that can be used for other purposes such as hypothesis testing. Here in this model, the total number of observations used was 51 and the number of estimated

parameters were 5, so the degrees of freedom = 51-5 = 46. F-ratio is the ratio of two independent estimates of the variance of a normal distribution and is calculated as the mean square regression/the mean square error. The larger the ratio is, the more significant the parameter in the regression model. Prob (F) tests the hypothesis that all coefficients to the independent variable are simultaneously equal to zero. It tests for the statistical significance of the regression as a whole.

Table 4.3: Variance Analyses for THMs Model

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob(F)
Regression	4	4399363	1099840	38.17	0
Error	46	1325401	28813		
Total	50	5724764			

The measured values from the experiments and the predicted values from the model are listed in Appendix Table 1. The first observation of measured value 703.47 in the Appendix Table 1 is found for Ferry land sample for a chlorine dosage of 30 mg/L, at a pH of 8 with TOC of 9.42mg/L after 1hr of chlorination. The predicted value 633.63 was obtained by plugging in the values of chlorine dose, pH, TOC and contact time in the model for THMs of equation 4.1. The same procedure was followed in calculating the measured and predicted values for the other models described in the further part of this section. Figure 4.4 shows the measured and predicted values plot.

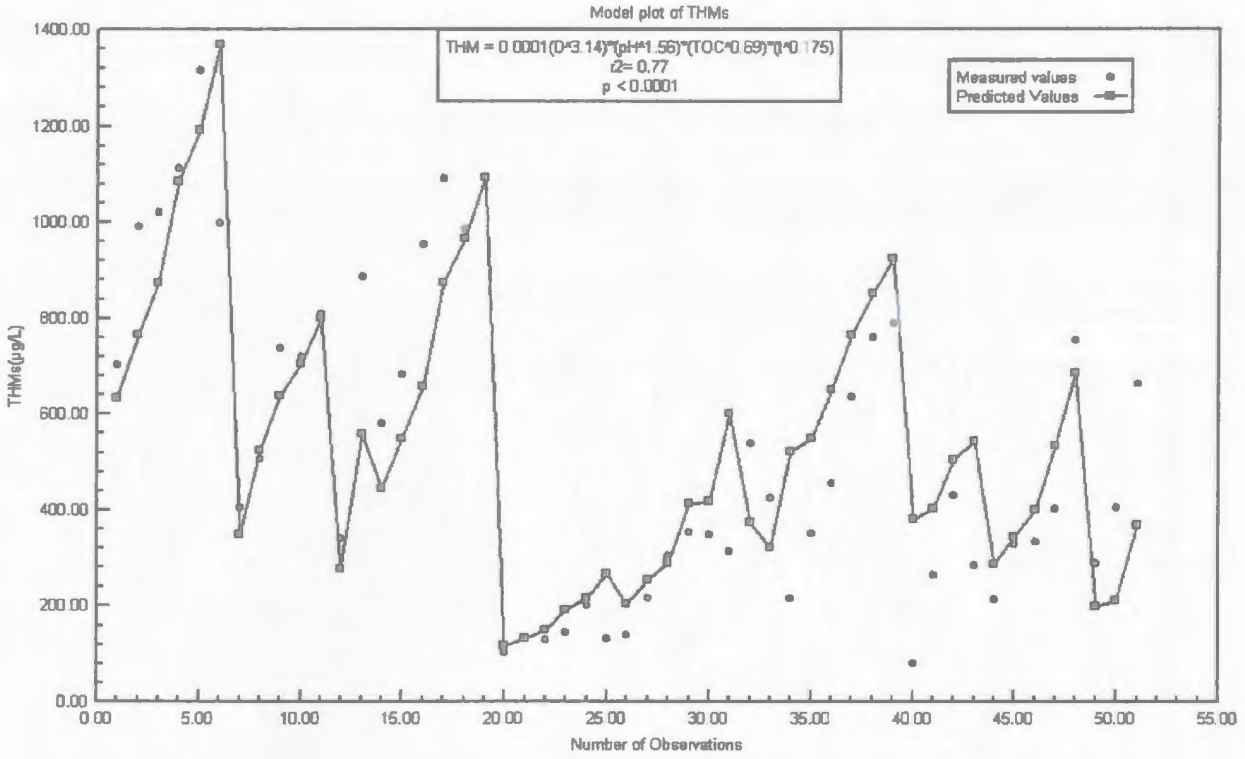


Fig 4.4: Model plot for THMs

The measured vs predicted values plot is shown in Figure 4.5.

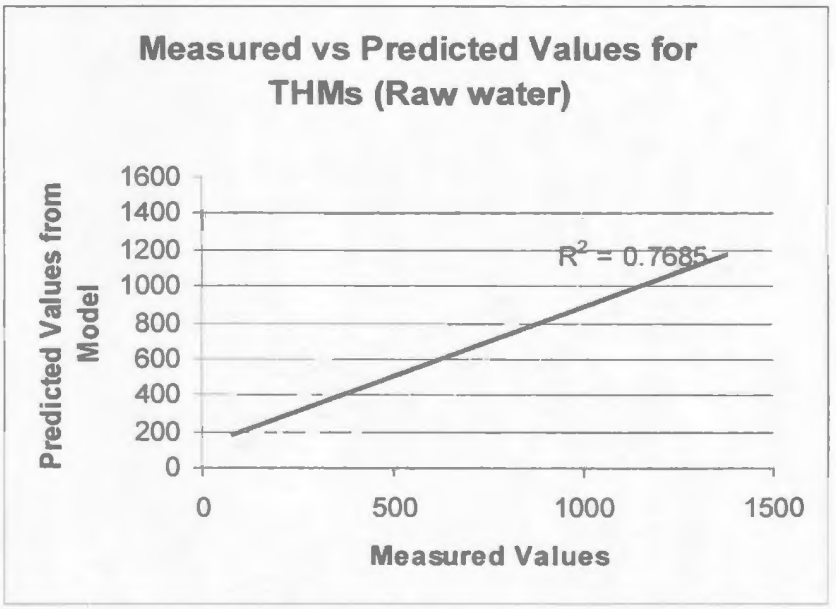


Fig 4.5: Measured vs predicted values plot for raw water THMs

The normality of residuals is satisfied as seen in the normal probability plot (Figure 4.6) with p-value 0.817. It can also be inferred from the figure that residuals are randomly scattered and there exists no trend between the residuals. The goodness of fit looks to be satisfactory from the normal probability plot of residuals as shown in Figure 4.7.

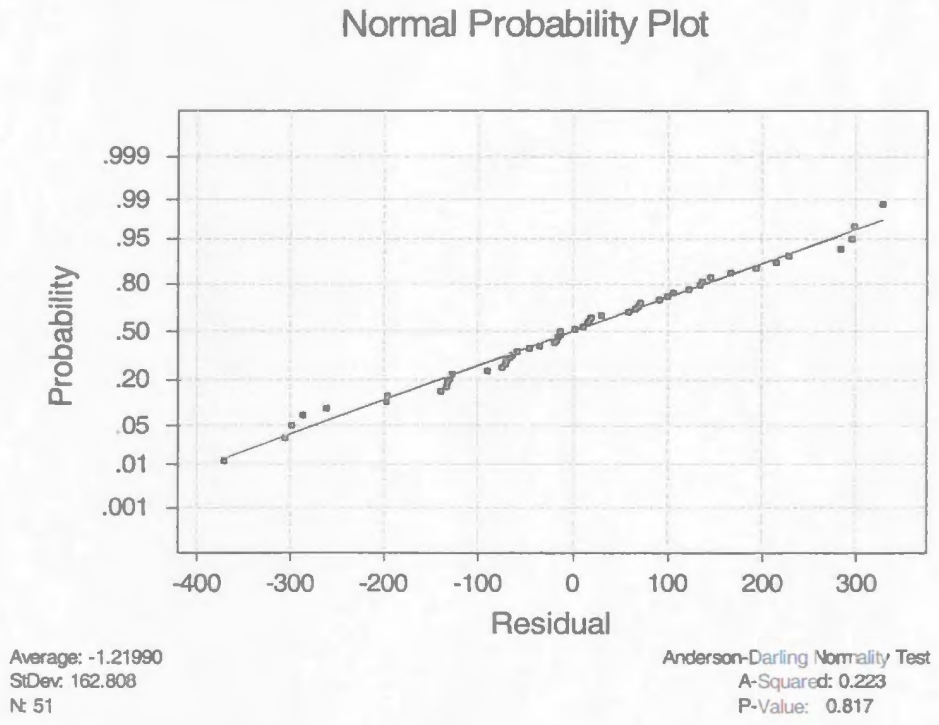


Fig 4.6: Normal Probability Plot for Equation 4.1

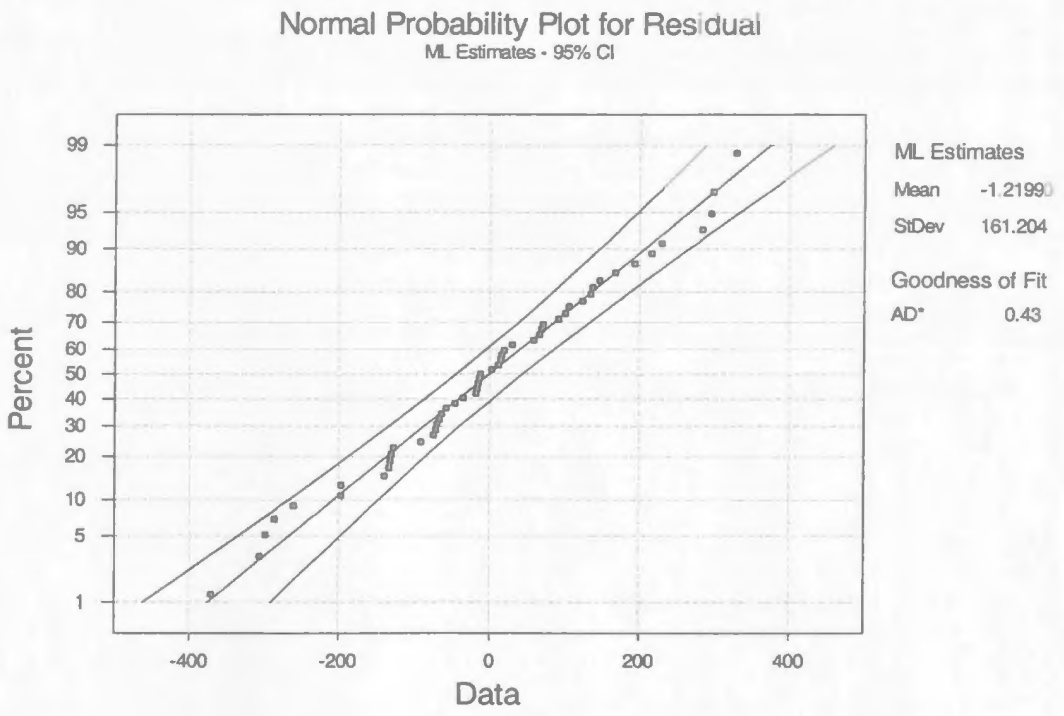


Fig 4.7: Normal Probability Plot for Residuals for Equation 4.1

4.4 Modeling of HANs

One compound of HANs i.e. DCAN was detected in the majority of samples. DCAN constituted the major component in HANs. The relationship between the formation of DCAN and the independent variables like pH, TOC, chlorine dosage, residual chlorine, time etc is shown in Table 4.4.

Table 4.4: Relationship between formation of dependent variable DCAN with independent variables

DCAN formation with independent variables	Pearson r	p
PH	-0.537	0.007
TOC	-0.131	0.542
Chlorine Dose	0.077	0.719
Residual Chlorine	-0.416	0.043
Time	0.288	0.173

Effect of pH: Simple regression analysis was used to examine the correlation of DCAN with respect to pH measured. The results are shown in Table 4.4. The Pearson method of correlation was applied and a high correlation but negative, definite with small relationship r= -0.537 was obtained between DCAN formation and pH.

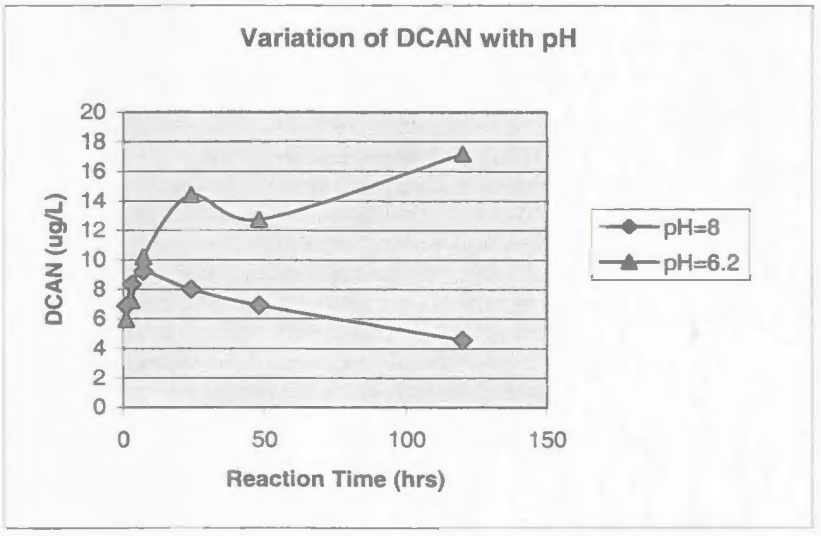


Fig 4.8: Variation of DCAN with pH

Effect of Chlorine dosage:

To find the effect of chlorine dosage on the formation of DCAN, the samples were dosed with different dosages of chlorine. Using the Pearson correlation method, a low but definite small relationship (r = 0.077) was obtained between the DCAN formation and chlorine dosage.

Effect of residual chlorine:

The residual chlorine at different contact times was found to find the effect of residual chlorine on DCAN formation. Using the Pearson correlation method, a negative moderate but definite with small relationship r = -0.416 was obtained between DCAN formation and residue chlorine.

Effect of temperature:

There was no correlation between the temperature and DCAN formation as the chlorination of all the raw water samples was carried out at a temperature of 23°C.

Suggested Model:

Using the Datafit and Minitab software, models for DCAN were developed. The regression model obtained for the raw water for the formation of DCAN is generalized as follows:

$$DCAN = a\,(pH)^{b}\,(D)^{c}\,(t)^{d}(R)^{e} \qquad \textbf{(4.4)}$$

Where D is the Chlorine dose expressed in mg/L

t the reaction time expressed in hrs

R the residual chlorine at time t

and a, b, c, d, e the estimated values of statistical coefficients.

The model accuracy is shown in Table 4.5. The model was found to be statistically significant to all the five variables.

Table 4.5: Results of statistical regression for DCAN Model

Results	**Non-linear model**
Coefficient of correlation (r^2)	0.685
Model Significance	$p < 0.001$
Statistical Coefficients	
a	3.567
b	-1.64
c	1.03
d	0.234
e	0.18

The variance analysis of the model is shown in Table 4.6.

Table 4.6: Variance Analysis for DCAN Model

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob (F)
Regression	4	115.75	28.93	9.25	0.00037
Error	17	53.14	3.12		
Total	21	168.89			

The measured and predicted values for the DCAN are shown in Appendix Table 2.

The measured and predicted values plot is shown in Figure 4.9

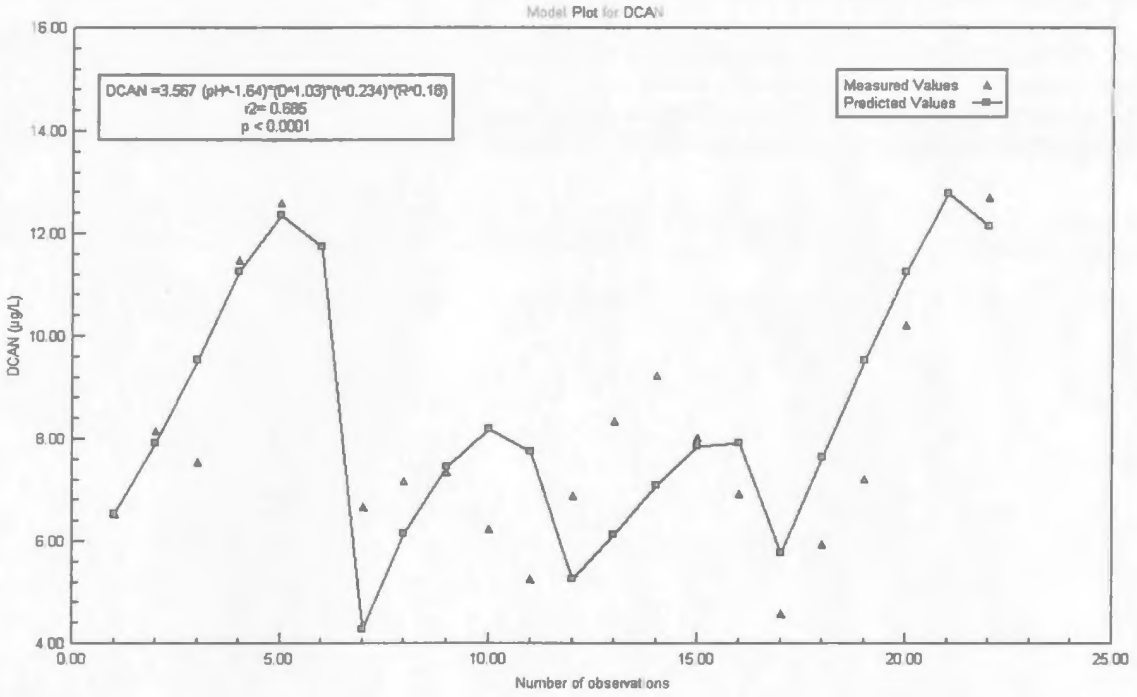


Fig 4.9: Model plot for DCAN

The measured vs predicted plot for DCAN is shown in the Figure 4.10.

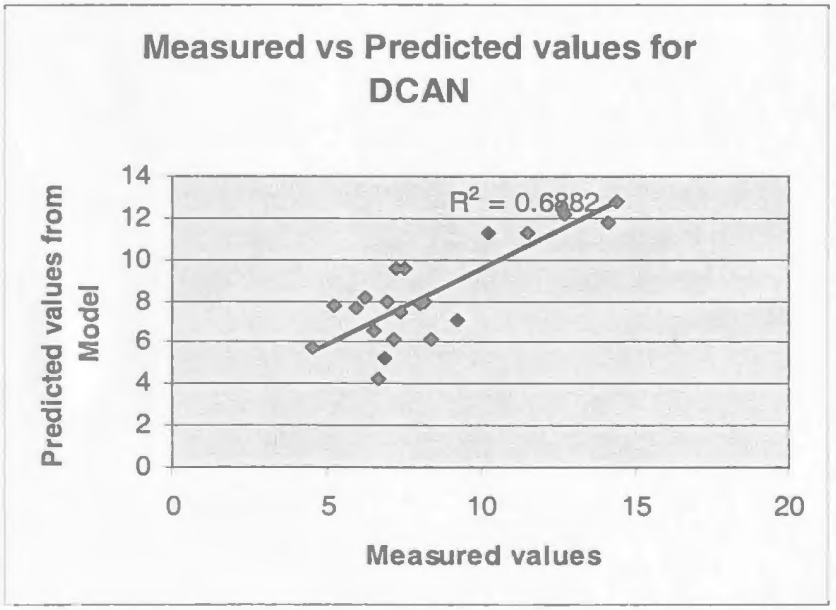


Fig 4.10: Measured vs Predicted values plot for DCAN

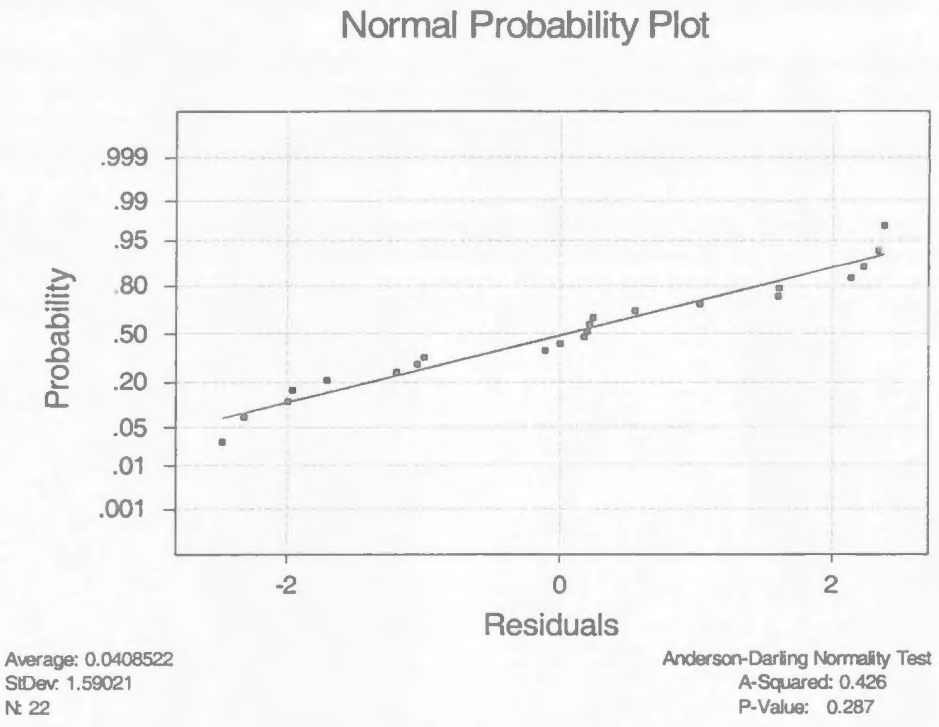


Fig 4.11: Normal probability plot for Equation 4.2

The normality of residuals is satisfied as seen in the normal probability plot (Figure 4.11) with p-value 0.287. It can also be inferred from the figure that residuals are randomly scattered and there exists no trend between the residuals. The goodness of fit looks to be satisfactory from the normal probability plot of residuals as shown in Figure 4.12

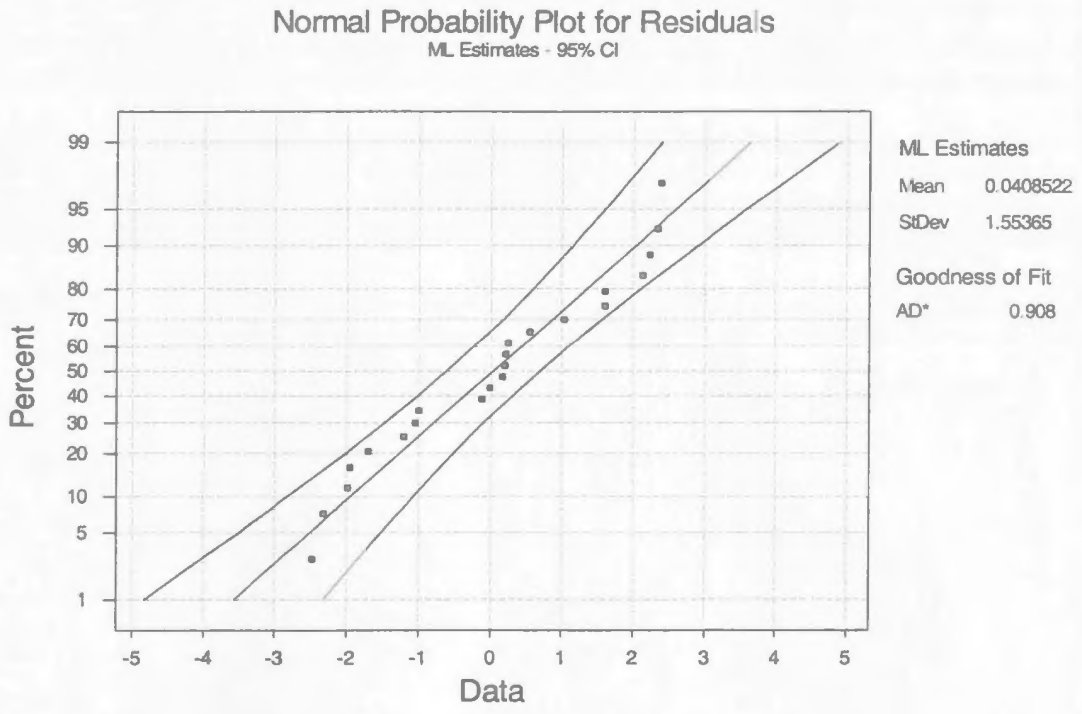


Fig 4.12: Normal Probability Plot for Residuals for Equation 4.2

4.5 Modeling of HKs

One compound of HK was detected in the majority of samples. Only TCP could be quantified in all these samples. TCP constituted the major component in HKs. The relationship between the formation of TCP and the independent variables like pH, TOC, chlorine dosage, residual chlorine, time etc is shown in Table 4.7.

Table 4.7: Relationship between formation of dependent variable TCP with independent variables

TCP formation with independent variables	Pearson r	p
PH	-0.575	0.003
TOC	-0.312	0.138
Chlorine Dose	0.265	0.210
Residual Chlorine	-0.127	0.554
Time	0.079	0.714

Effect of pH:

Simple regression analysis was used to examine the correlation of TCP with respect to pH measured. The results are shown in Table 4.7. The Pearson method of correlation was applied and a negative but high correlation, definite with small relationship r= -0.575 was obtained between TCP formation and pH. The formation of TCP with varying pH is shown in Figure 4.13.

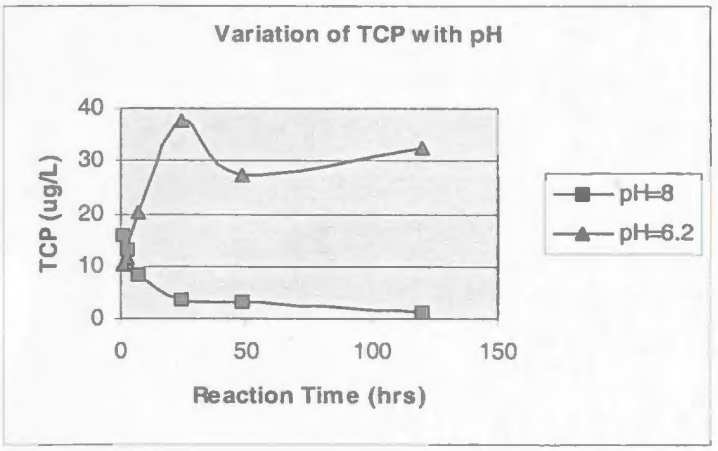


Fig 4.13: Variation of TCP with pH

It was also seen that there exists a moderate correlation between the formation of DCAN and TCP.

The estimation can be given by the equation

$$TCP = 2.426(DCAN) - 9.0569 \quad (4.5)$$

with $r^2 = 0.7019$ and can be interpreted from Figure 4.14

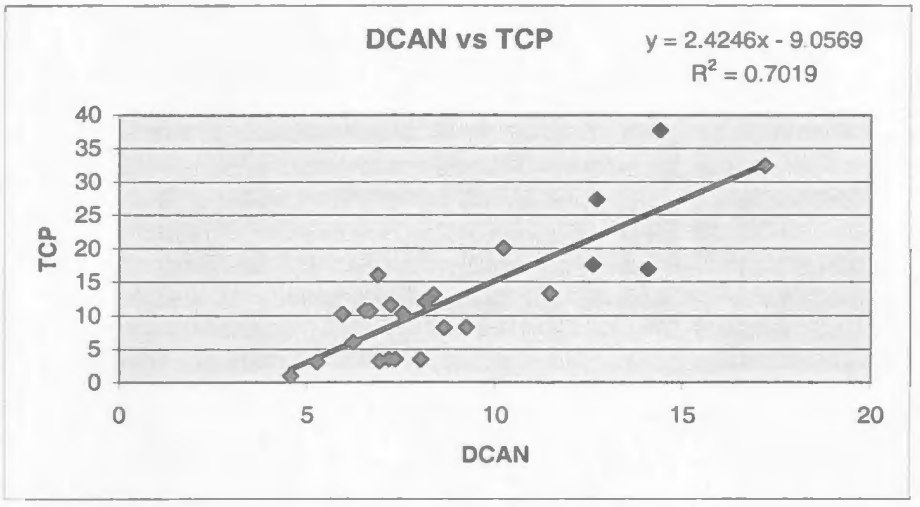


Fig 4.14: DCAN vs. TCP

Suggested Model:

Using the Datafit and Minitab software, models for TCP were developed. The regression model obtained for the raw water for the formation of TCP is generalized as follows:

$$TCP = a\,(pH)^{b}\,(D)^{c}\,(t)^{d} \quad (4.6)$$

Where D is the Chlorine dose expressed in mg/L

t the reaction time expressed in hrs

and a, b, c, d, the estimated values of statistical coefficients.

The model accuracy is shown in Table 4.8. The model was found to be statistically significant to all the four variables.

Table 4.8: Results of statistical regression for TCP

Results	**Non-linear model**
Coefficient of correlation (r)	0.681
Model Significance	p <0.0001
Statistical Coefficients	
a	0.785
b	-4.659
c	3.474
d	0.147

The variance analysis of the model is shown in Table 4.9.

Table 4.9: Variance Analysis for TCP

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob(F)
Regression	3	1344.21	448.07	14.25	3E-005
Error	20	628.85	31.44		
Total	23	1973.06			

The measured and predicted values for TCP Model are shown in Appendix Table 3.

The measured and predicted values plot of the model is shown in Figure 4.15.

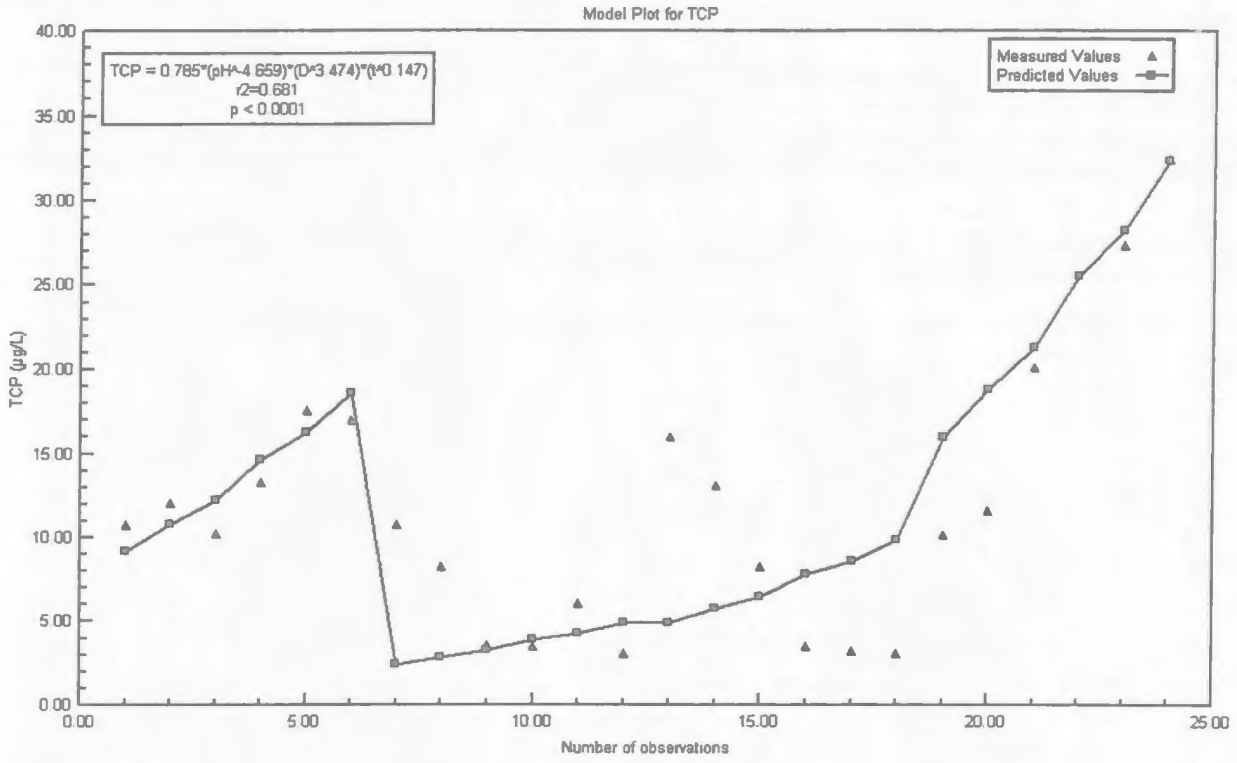


Fig 4.15: Model Plot for TCP

The measured vs predicted values plot for TCP is shown in the Figure 4.15.

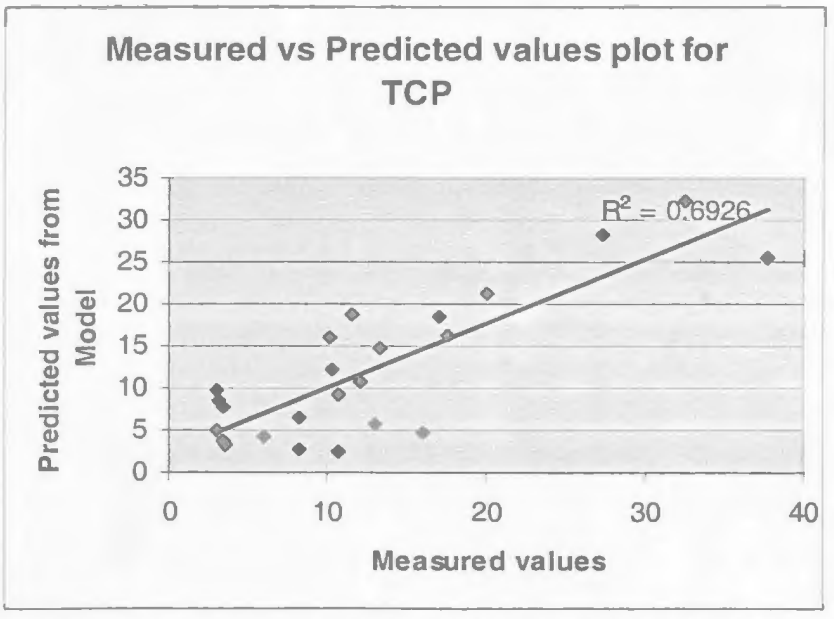


Fig: 4.16 Measured vs Predicted values for TCP

The normality of residuals is satisfied as seen in the normal probability plot (Figure 4.17) with p-value 0.087. It can also be inferred from the figure that residuals are randomly scattered and there exists no trend between the residuals. The goodness of fit looks to be satisfactory from the normal probability plot of residuals as shown in figure 4.18 as almost all the residual points lie with in the 95% confidence interval.

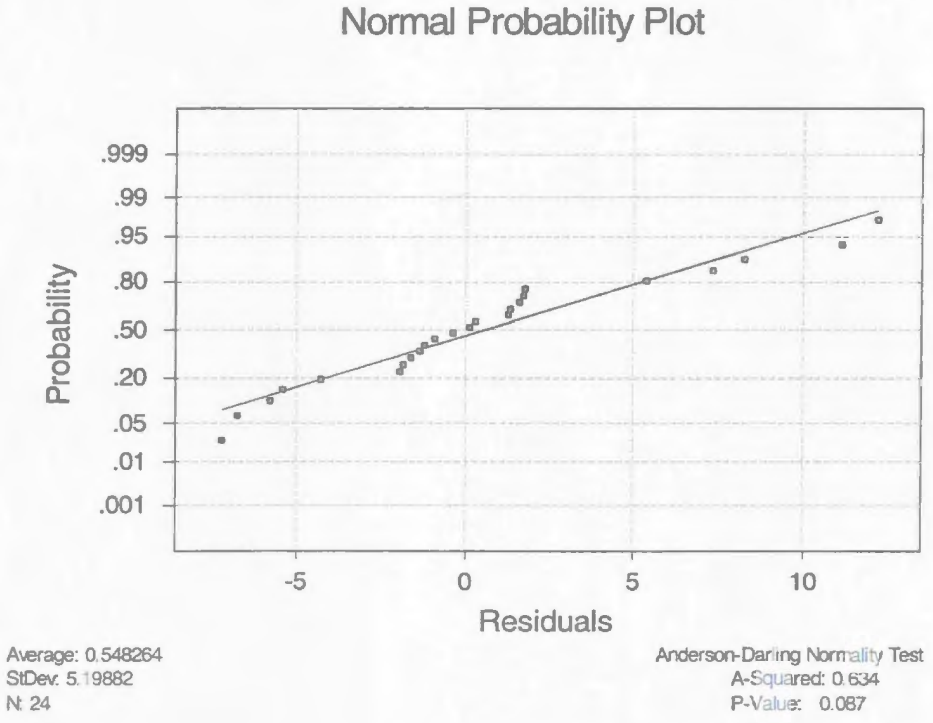


Fig: 4.17 Normal Probability Plot for Equation 4.14

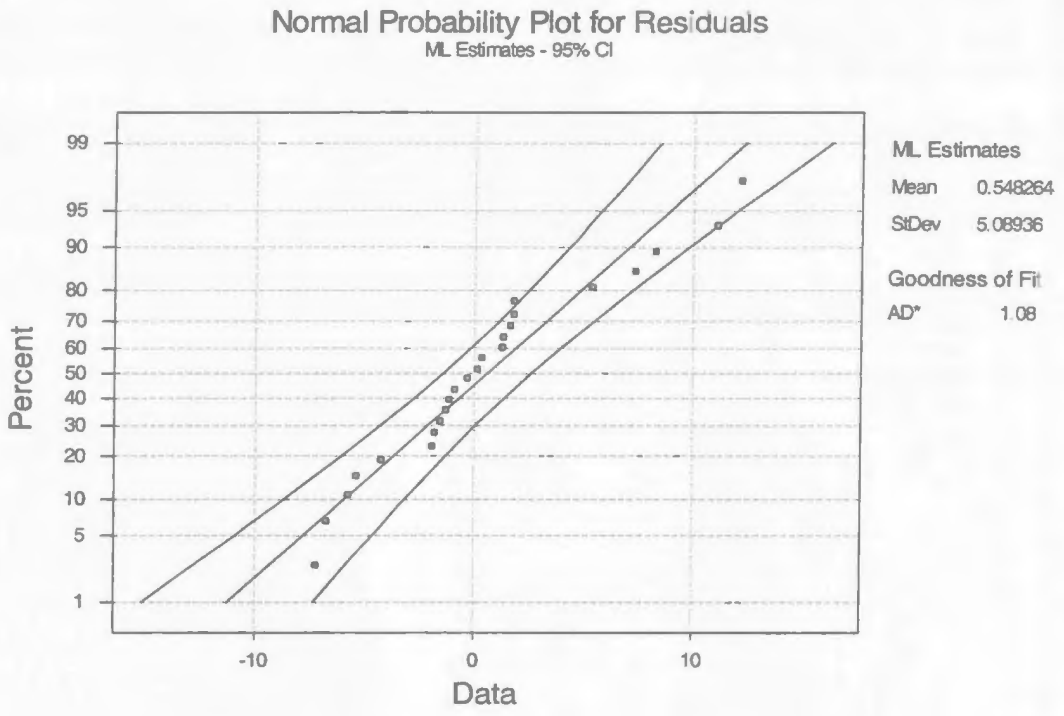


Fig 4.18 Normal Probability plot of residuals for Equation 4.4

4.6 Modeling for tap water THMs

Two compounds of THMs were detected in the majority of samples. Only chloroform and DBCM could be quantified in all these samples. Chloroform constituted the major component in THMs. The relationship between the formation of THMs and the independent variables like pH, TOC, chlorine dosage, residual chlorine, time etc is shown in Table 4.10.

Table 4.10: Relationship between formation of dependent variable tap water THMs with independent variables

THM formation with independent variables	Pearson r	p
PH	-0.476	0.164
TOC	0.967	0.000
DOC	0.958	0.000
Turbidity	0.448	0.194
Alkalinity	0.191	0.596

Effect of TOC:

Using the Pearson correlation method, a high but definite with relationship (r=0.967) was obtained between THM formation and TOC as shown in Table 4.13. A relationship of r = 0.937 was obtained between the DOC and TOC. So only one of TOC and DOC was taken into account to increase the model efficiency. Most investigations have found that THM formation rises with increasing soluble humic material. The rate of THMs formation is equal to that of the TOC consumption. Higher TOC will provide more THMs if enough residual chlorine is available. Figure 4.19 shows the relationship between the variation of THMs and TOC concentrations.

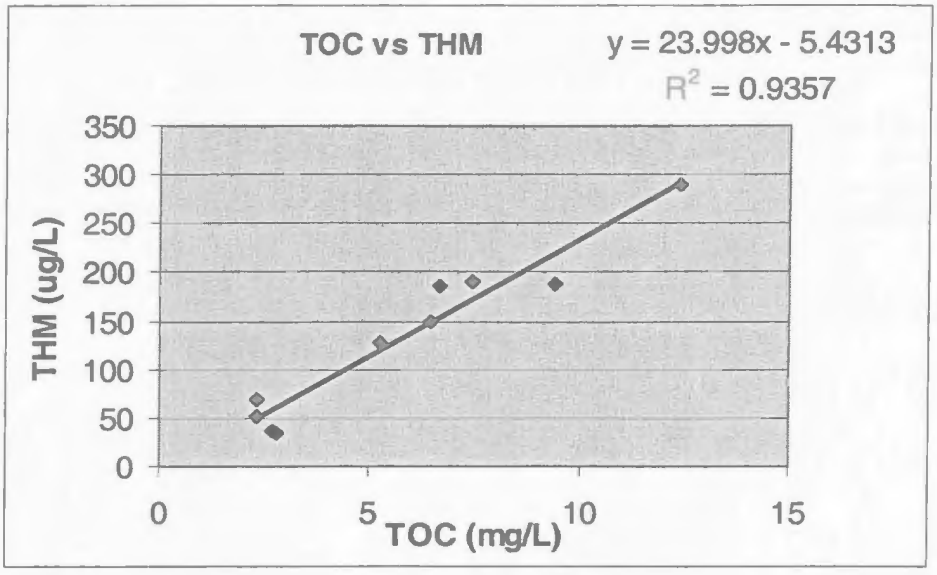


Fig 4.19: TOC vs. THMs

Effect of pH:

Simple regression analysis was used to examine the correlation of THMs concentration with respect to pH measured. The results are shown in Table 4.10. The Pearson method of correlation was applied and a moderate correlation but negative (r = -0.476), definite with small relationship was obtained between THMs formation and pH. In general it was shown that the rate of THMs production increased with pH. However, as the correlation between the TOC and THMs was very high, pH was shown to have a negative effect.

Effect of temperature:

There was no observable correlation between the temperature and THMs formation as the chlorination of all the raw water samples was carried at a temperature of 23°C.

Effect of Turbidity:

Simple regression analysis was used to examine the correlation of THMs formation with respect to turbidity measured. The results are shown in Table 4.10. The Pearson method of correlation was applied and a moderate correlation (r= 0.448), definite with small relationship was obtained between THMs formation and turbidity. Though turbidity was shown to have a moderate correlation in the formation of THMs, it was not taken into account in the modeling of THMs because of its correlation with TOC.

Effect of Alkalinity:

Simple regression analysis was used to examine the correlation of THMs concentration with respect to alkalinity measured. The results are shown in Table 4.10. The Pearson method of correlation was applied and a very low correlation (r = 0.191), definite with small relationship was obtained between THMs formation and alkalinity.

Suggested Model:

Using the Datafit and Minitab software, models for THMs formation were developed. The regression model obtained for the tap water for the formation of THMs is generalized as follows:

$$THMs = a + b*(pH) + c*(TOC) \quad (4.7)$$

Where TOC is the total organic carbon expressed in mg/L

and a, b, c the estimated values of statistical coefficients.

The model accuracy is shown in Table 4.11. The model was found to be statistically significant to all the three variables.

Table 4.11: Results of statistical regression for Tap water

Results	**Linear model**
Coefficient of correlation (r)	0.963
Model Significance	p <0.0001
Statistical Coefficients	
a	173.64
b	-30.31
c	22.53

The variance of analyses is shown in Table 4.12.

Table 4.12: Variance Analysis for Tap water

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob(F)
Regression	2	61184	30592	92.60	4E-005
Error	7	2312	330		

The measured and predicted values for THMs model are shown in Appendix Table 4.

The measured vs predicted values plot is shown in Figure 4.20.

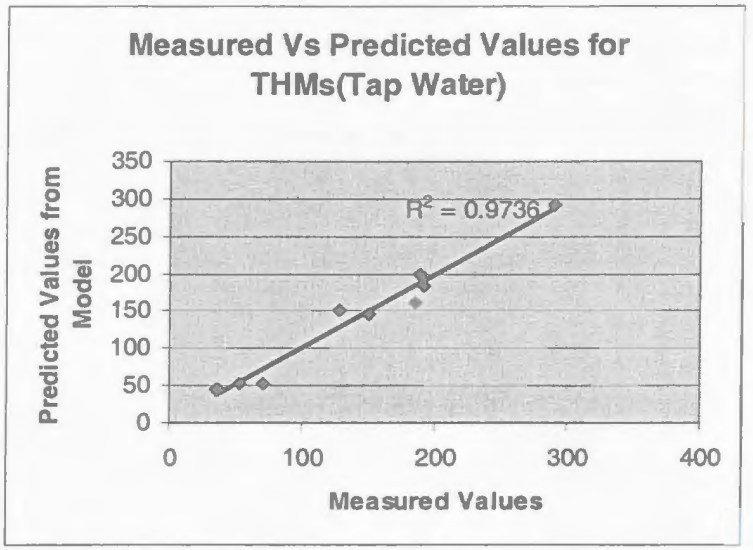


Fig 4.20: Measured vs Predicted values for Tap water THMs

The Normality of residuals is satisfied as seen in the normal probability plot (Figure 4.21) with p-value less than 0.005. It can also be inferred from the figure that residuals are randomly scattered and there exists no trend between the residuals. The goodness of fit looks to be satisfactory from the normal probability plot of residuals as shown in Figure 4.22.

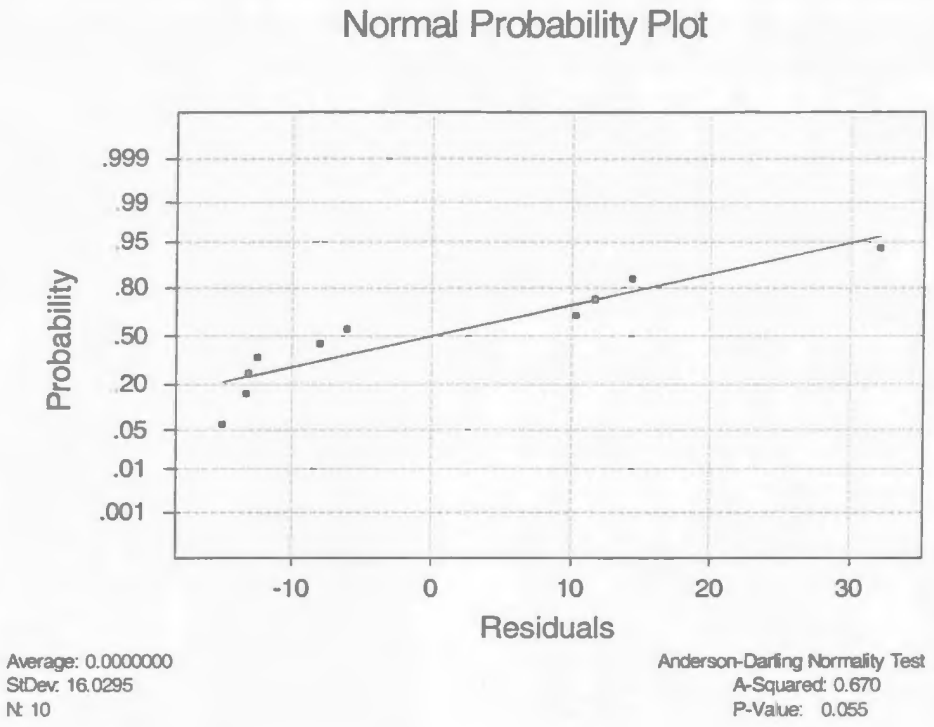


Fig 4.21: Normal probability Plot for Equation 4.5

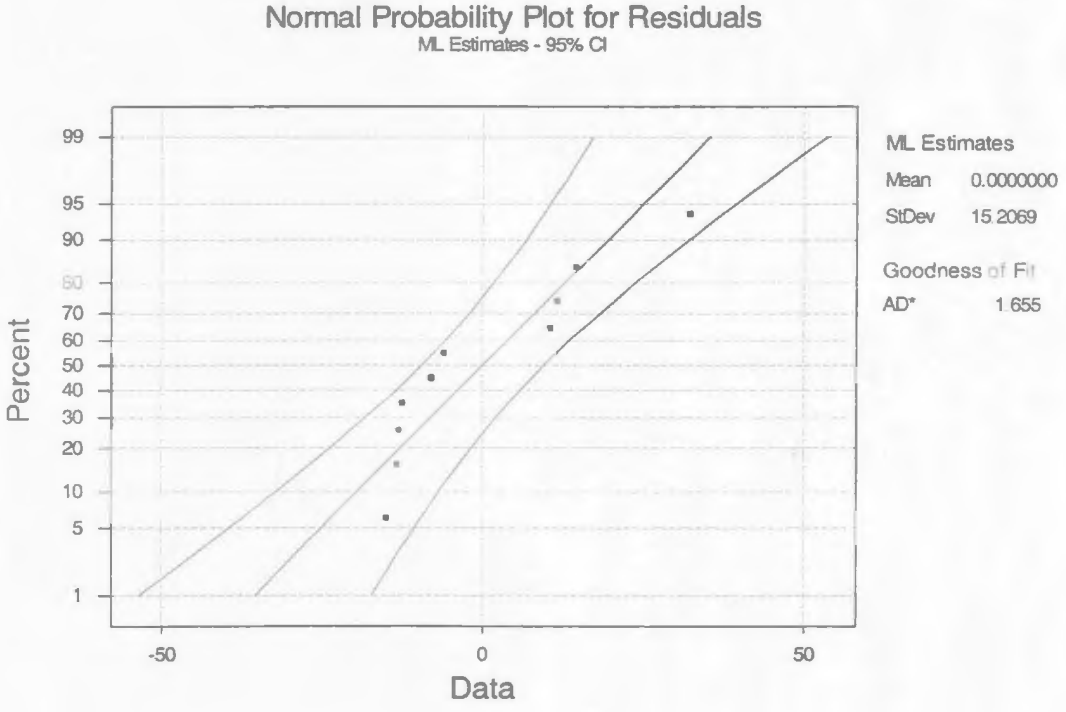


Fig 4.22: Normal probability Plot for Residuals for Equation 4.5

4.7 Fitting of various Models

The data obtained from the raw water chlorination for the formation of THMs was used to compare with the previous models proposed for different water utilities.

a. Amy et al., (1987):

Amy et al., (1987) has proposed the following model to predict the formation of THMs in raw water in different utilities of U.S. The reaction time used was until 168 hr with positive chlorine residual.

$$THM = 0.031\ (UV * TOC)^{0.440} * (D)^{0.409} * (t)^{0.265} * (T)^{1.06} * (pH-2.6)^{0.715} * (Br+1)^{0.0358}$$

The data when fitted into this model gave a least square regression correlation coefficient of $r^2 = 0.44$.

The low value of correlation may be due to the difference in the quality of the source water, the temperature was maintained constant at 23°C in the proposed model of THMs and bromine parameter was not considered in the model.

b. Amy et al., (1998):

In 1998 Amy et.al further revised his model with the inclusion of dissolved organic matter instead of total organic carbon and UV absorbance and considered the chlorine dose parameter.

$$THM = 0.00412(DOC)^{1.10}\ (D)^{0.152} * (Br)^{0.068}\ (T)^{0.61}\ (pH)^{1.60}\ (t)^{0.260}$$

The data when fitted into this model gave a least square regression correlation coefficient of $r^2 = 0.615$.

The low value of correlation may be due to the difference in the quality of the source water, the temperature was maintained constant at 23°C in the proposed model of THMs and bromine parameter was not considered in the model.

c. Rodriguez et al., (2000):

The model proposed by Rodriguez is based on the combination of three other databases and was modelled based on the water quality parameters of Quebec water utilities.

$$THM = 0.044\,(DOC)^{1.030}\,(t)^{0.262}\,(pH)^{1.149}\,(D)^{0.277}\,(T)^{0.968}$$

The present data when fitted into this model gave a least square regression correlation coefficient of $r^2 = 0.538$.

The low value of correlation may be due to the difference in the quality of the source water and the temperature was maintained constant at 23°C in the proposed model of THMs.

Thus it can be concluded from the above comparison that these models are very much site specific and purely depend on the quality of the water source.

Chapter 5

Conclusions

The following conclusions are drawn from this study:

1. Among all the THMs studied for the communities in the province of Newfoundland, chloroform had the significant presence and highest concentration in both the drinking water and chlorinated raw water samples. Chloroform constituted more than 90% of the total THMs and the second highest is dibromochloromethane. Dichloroacetonitrile (DCAN) among the Haloacetonitriles and 1,1,1-trichloropropanone among the haloketones had the most significant presence.
2. During the formation of THMs in chlorinated raw water samples increase in the pH of the water samples at constant chlorine dosage has shown increase in the formation of THMs and with the increase in the chlorine dose at constant pH, there was also an increase in the formation of THMs
3. The non-linear regression model developed with least square correlation coefficient of 0.77, can be used to estimate the THMs concentrations for different water quality parameters in water utilities where chlorination is the only treatment in the process.

   The non-linear regression model developed for THMs is

   $$THMs = 0.001(D)^{3.14}(pH)^{1.56}(TOC)^{0.69}(t)^{0.175}$$

   Where t is the reaction time in hrs; D the chlorine dosage in mg/L;

   TOC is the total organic carbon in mg/L

4. The relationship of formation of DCAN with pH was high but negative. With the decrease in the pH of the chlorinated raw water, the formation of DCAN increased with time, and with the increase in the pH of the water, the formation of DCAN decreased with time. The non-linear regression model developed for the formation of DCAN is

   $$DCAN = 3.567(pH)^{-1.64}(D)^{1.03}(t)^{0.234}(R)^{0.18}$$

   Where D is the chlorine dose in mg/L,

   t is the reaction time in hrs and

   R the residual chlorine in mg Cl_2/L

5. The relationship of formation of TCP with pH was also high but negative. With the decrease in the pH, the formation of TCP increased with time, where as with increase in the pH, the formation decreased with time.

   The non-linear regression model developed for the formation of TCP is

   $$TCP = 0.785(pH)^{-4.659}(D)^{3.474}(t)^{0.147}$$

   Where D is the chlorine dose in mg/L and

   t is the reaction time in hrs.

6. The linear regression equation between THMs and TOC was shown to have a least square correlation coefficient of 0.93. The linear regression model developed for the formation of tap water THMs is

   $$THMs = 173.64 - 30.31(pH) + 22.53(TOC)$$

   Where TOC is the total organic carbon in mg/L.

7. Although very little is known about the adverse reproductive effects of DBPs, there should be concern in Newfoundland because around 80 communities in the province are exceeding the 100μg/L limit.
8. The models developed purely depend on the quality of water source and are very much site specific.

Chapter 6

Recommendations

1. The samples that were used in the analysis and formation of models are limited, so additional samples should be obtained from each study location in order to obtain more conclusive results.
2. Since the sampling was performed mostly in winter, the seasonal effect was not considered in the modeling of DBPs. Therefore it is recommended to perform sampling in all the seasons of the year to take seasonal effect into account in the development of models.
3. Since the chlorination of the raw water samples was carried at constant temperature the effect of temperature is not included.
4. As the experiments were performed in the laboratory the effects of the distribution system on residual chlorine depletion and on DBPs formation cannot be quantified exactly by these models.
5. The analysis for the HAAs is not performed in this study. It would be useful in future to continue work on this DBPs due to their presence in treated Newfoundland waters.
6. Since the potential of health related risk associated with use of chlorinated water is high due to the formation of DBPs, further research is recommended in this direction to find the best available treatment technology for the small communities that is feasible at reasonable cost.

7. Case studies are further recommended in the province to see the effect of DBPs on the reproductive and developmental outcomes.
8. Further studies are recommended for the unidentified DBPs.

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APPENDIX

Table 1: Measured and predicted values for THMs model

Measured Values	Predicted Values from Model
703.47	633.632
991.08	763.474
1019.21	874.181
1113.2	1083.870
1314.59	1192.527
997.01	1367.598
405.05	346.716
507.25	524.820
737.78	638.253
720.55	704.502
809.38	798.913
339.27	274.422
886.58	559.198
579.9	444.038
682.28	548.388
953.92	656.571
1088.82	873.865
985.59	966.723
1374.46	1091.73
102.381	116.112
134.507	132.500
128.562	148.264
144.022	190.261
200.51	215.070
130.392	264.862
138.320	203.104

Continued....

Measured Values	Predicted Values from Model
216.524	252.574
302.902	288.664
351.651	410.848
347.903	417.998
313.415	600.788
539.422	373.001
425.248	320.410
215.029	521.131
350.030	547.847
453.200	650.601
635.489	763.844
759.707	851.071
789.417	922.481
80.1251	378.937
263.145	403.016
428.605	504.080
282.344	544.011
214.499	286.068
326.81429	343.791
333.21548	400.354
402.0477	532.888
753.4003	684.923
288.6151	197.841
404.70183	212.175
662.75082	367.541

Table 2: Measured and predicted values for DCAN

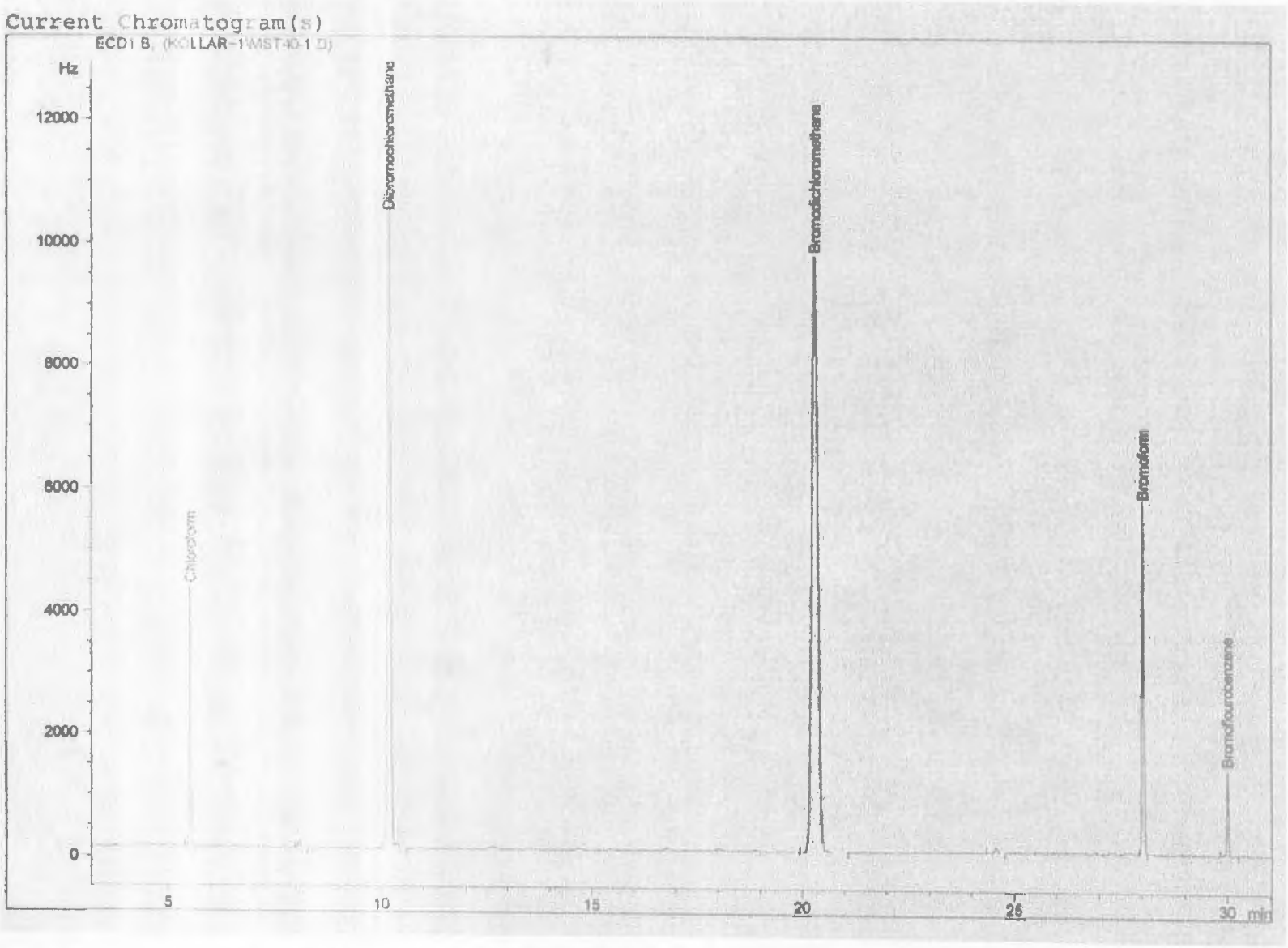
Measured DCAN values	Predicted DCAN Values from Model
6.539	6.540
8.139	7.920
7.535	9.528
11.461	11.259
12.606	12.363
14.08	11.747
6.66	4.279
7.168	6.142
7.343	7.456
6.229	8.188
5.259	7.734
6.873	5.262
8.351	6.121
9.226	7.087
8.012	7.843
6.916	7.916
4.566	5.764
5.935	7.641
7.217	9.538
10.211	11.255
14.396	12.789
12.71	12.158

Table 3: Measured and Predicted values of TCP model

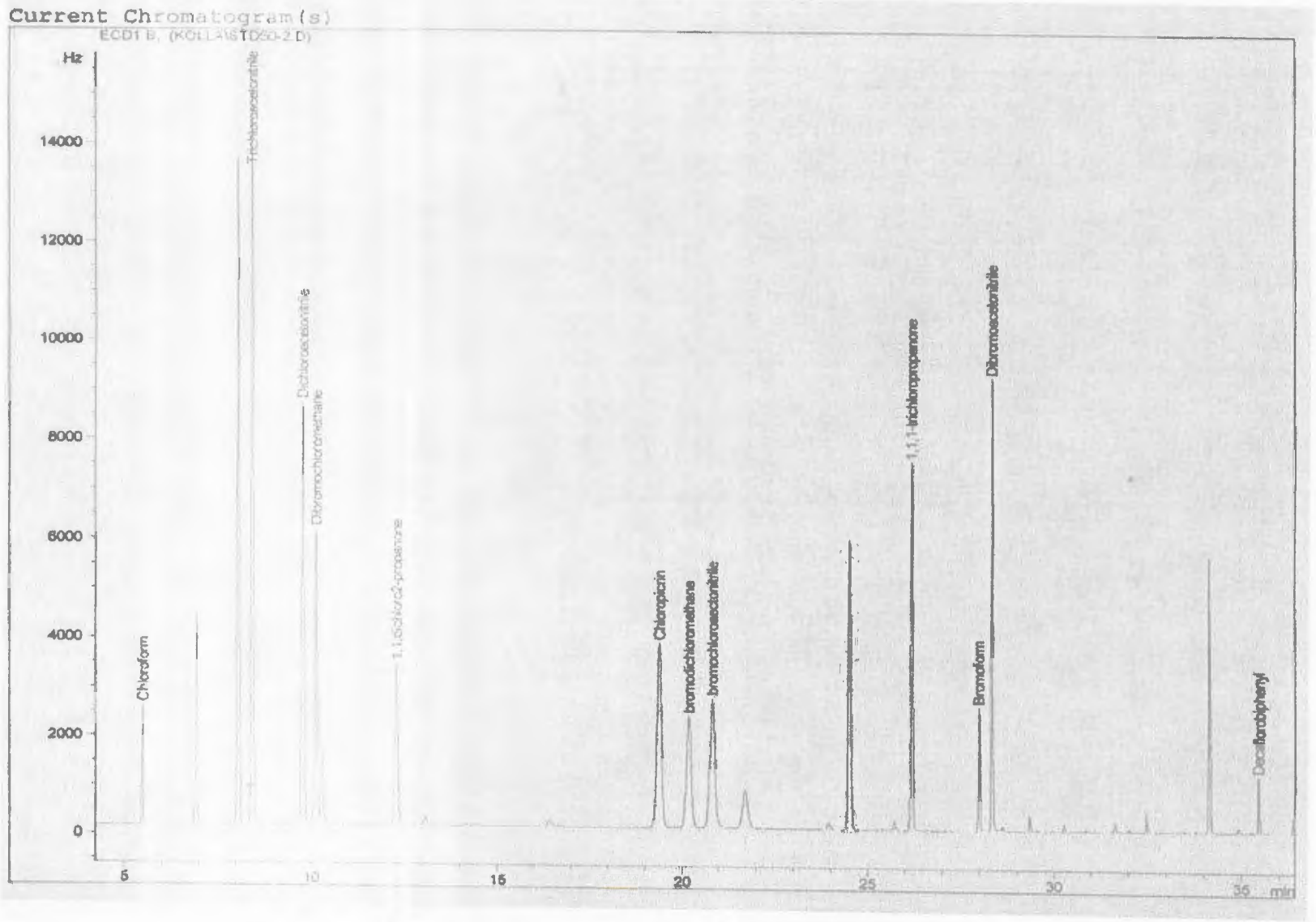
Measured TCP values	Predicted TCP values from Model
10.731	9.165
12.006	10.774
10.225	12.206
13.252	14.634
17.504	16.206
16.921	18.547
10.675	2.426
8.198	2.852
3.515	3.231
3.476	3.874
6.014	4.290
3.037	4.910
15.992	4.872
13.054	5.727
8.215	6.488
3.463	7.779
3.1728	8.615
3.079	9.860
10.167	15.978
11.547	18.784
20.064	21.280
37.692	25.514
27.328	28.255
32.44	32.337

Table 4: Measured and predicted values of tap water THMs model

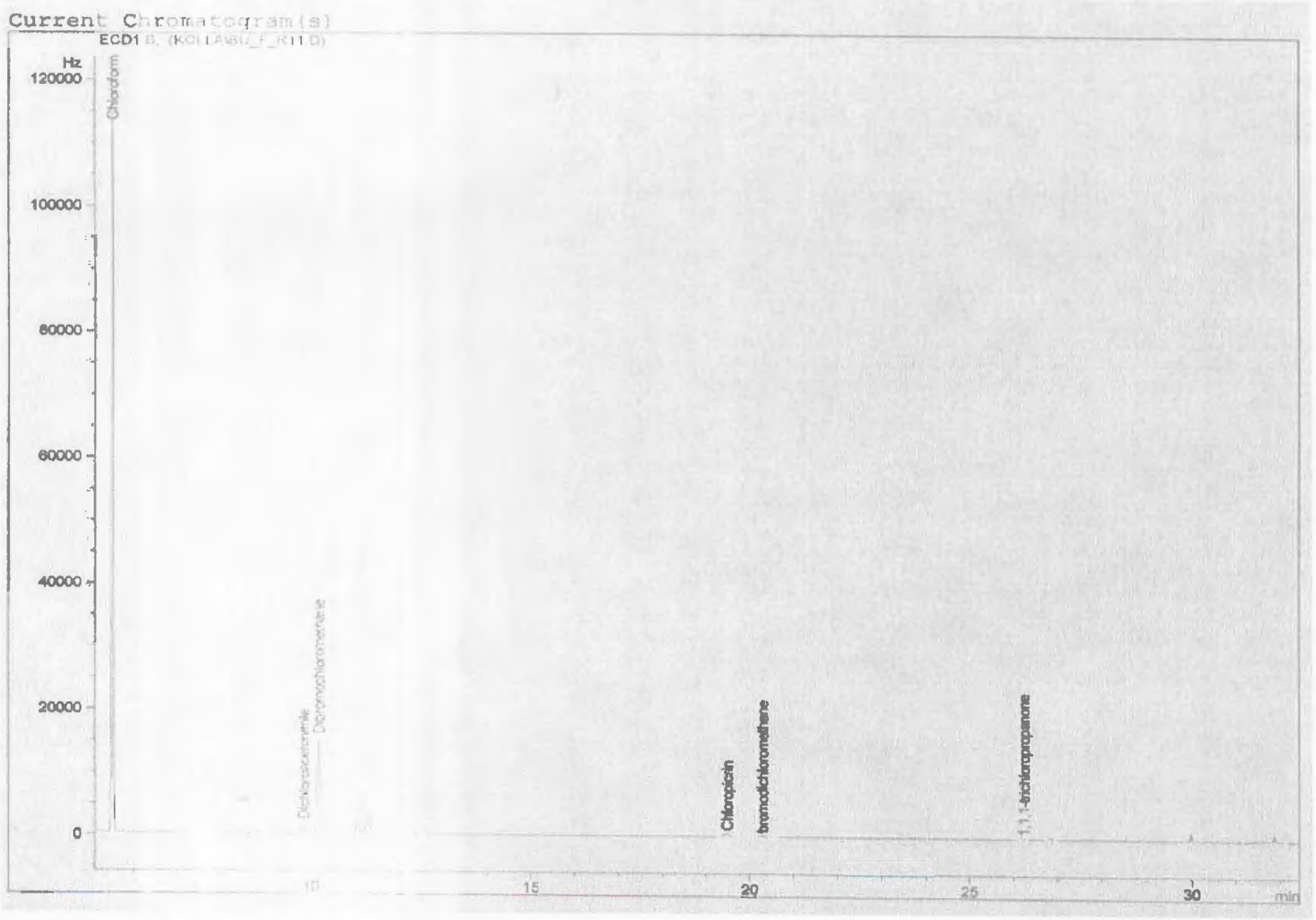
Measured THM values	Predicted THM values from Model
290.320	292.715
52.356	52.352
185.442	161.081
188.543	197.802
127.816	150.165
70.135	53.739
150.059	145.966
35.403	44.852
36.879	45.291
191.1	184.087



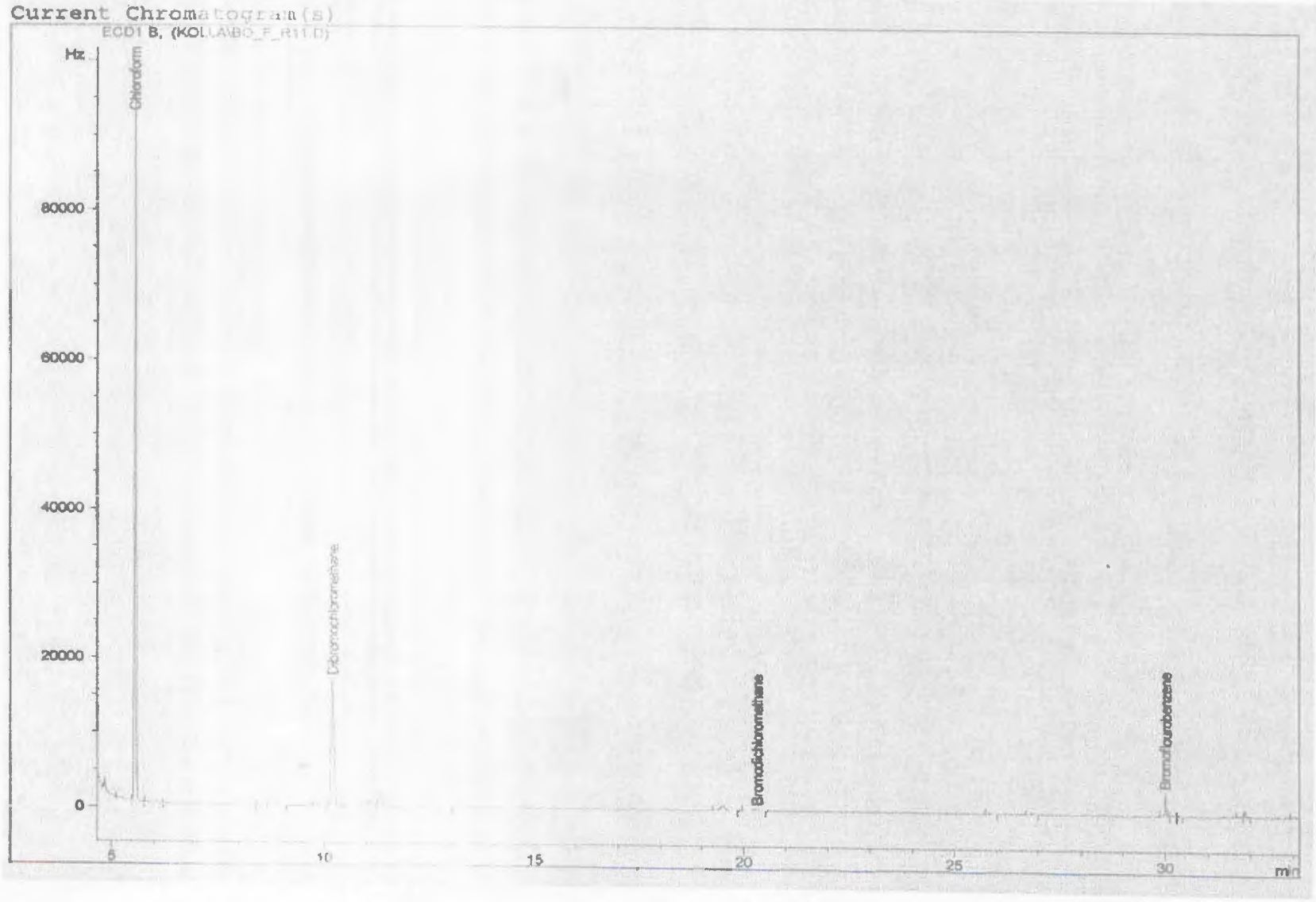
Chromatogram of standard 40µg/L containing four THM compounds



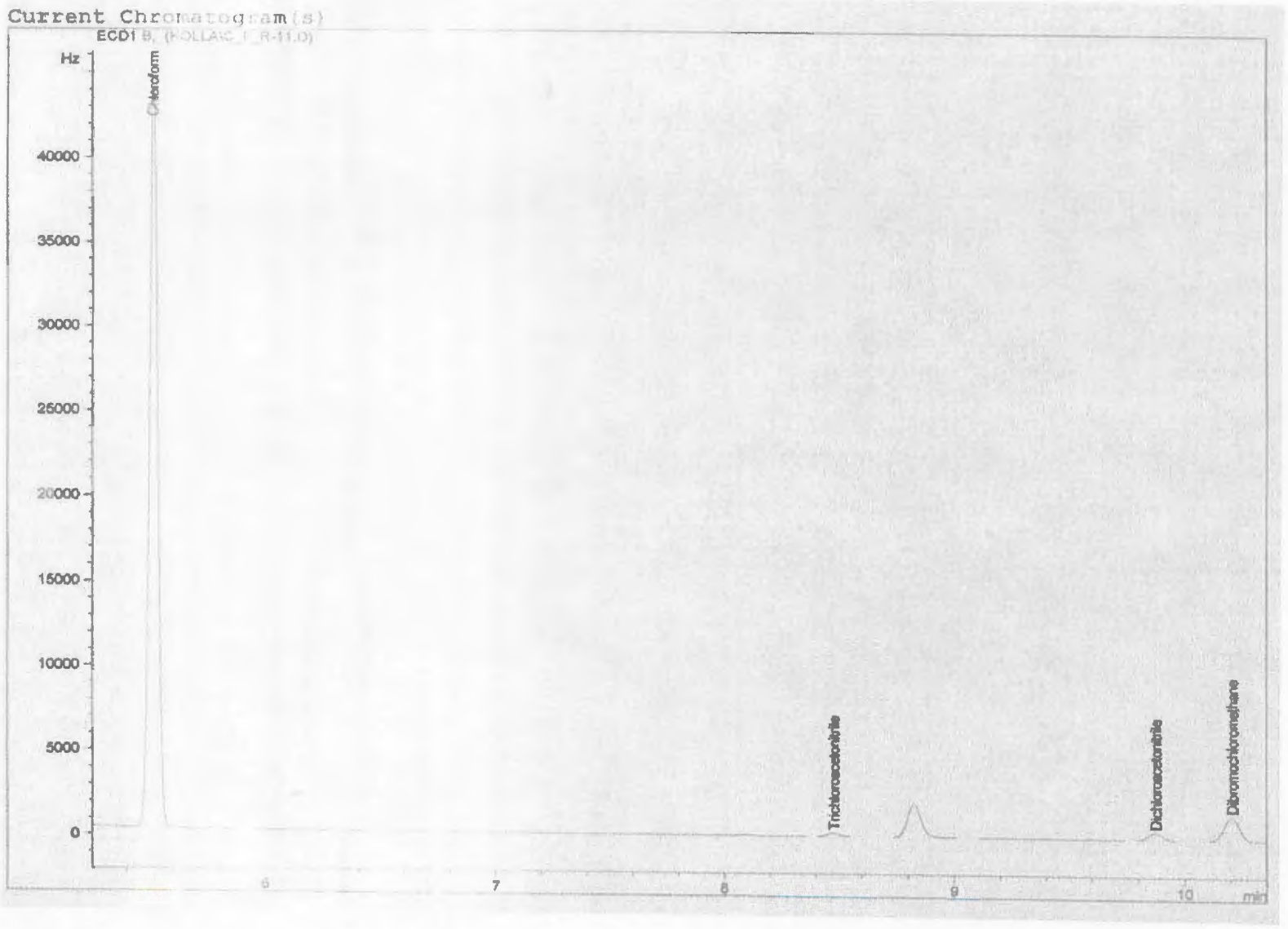
Chromatogram of standard 50µg/L containing THMs, HANs and HKs



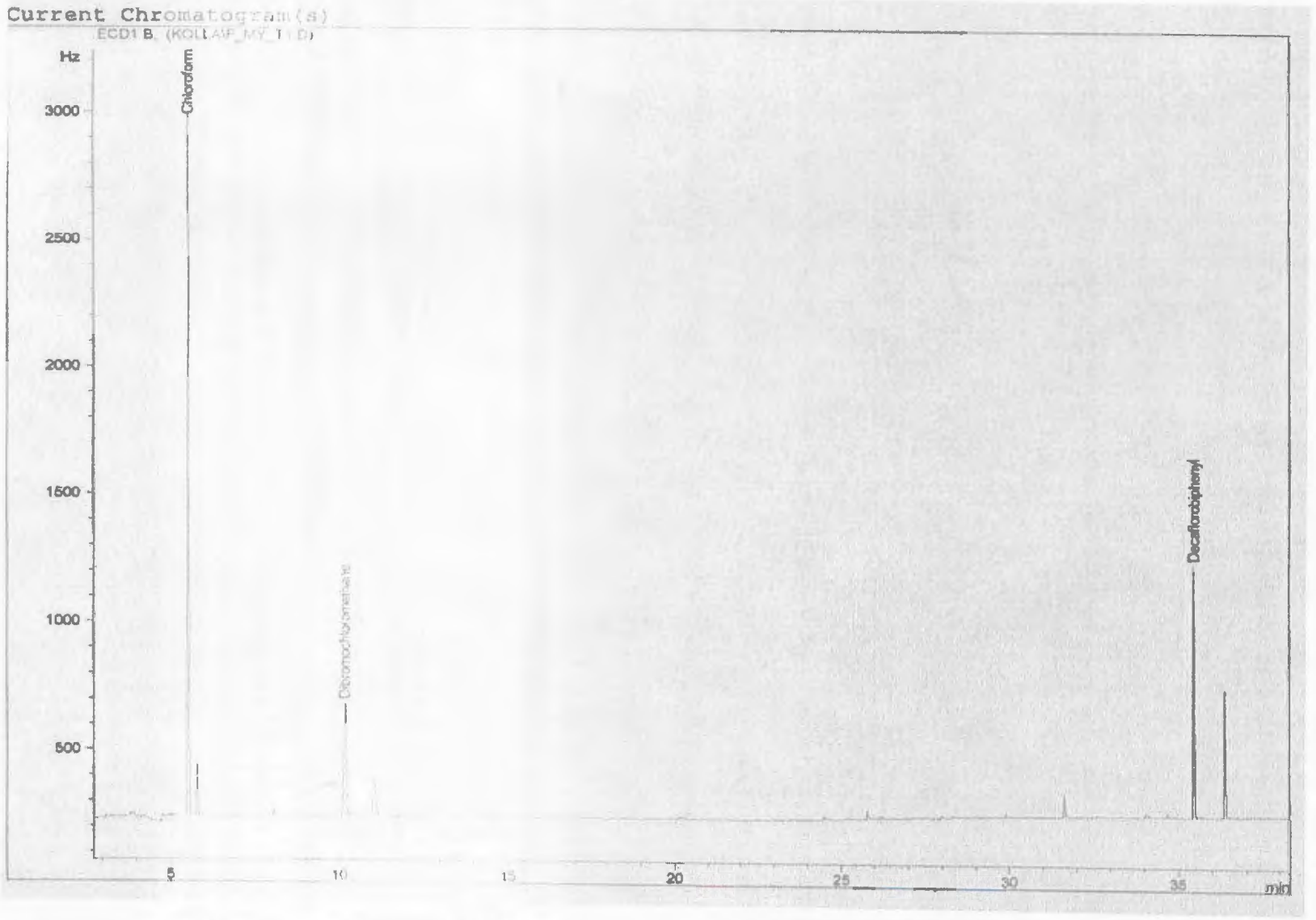
Chromatogram containing DBPs of Burin chlorinated water at 48 hrs contact time



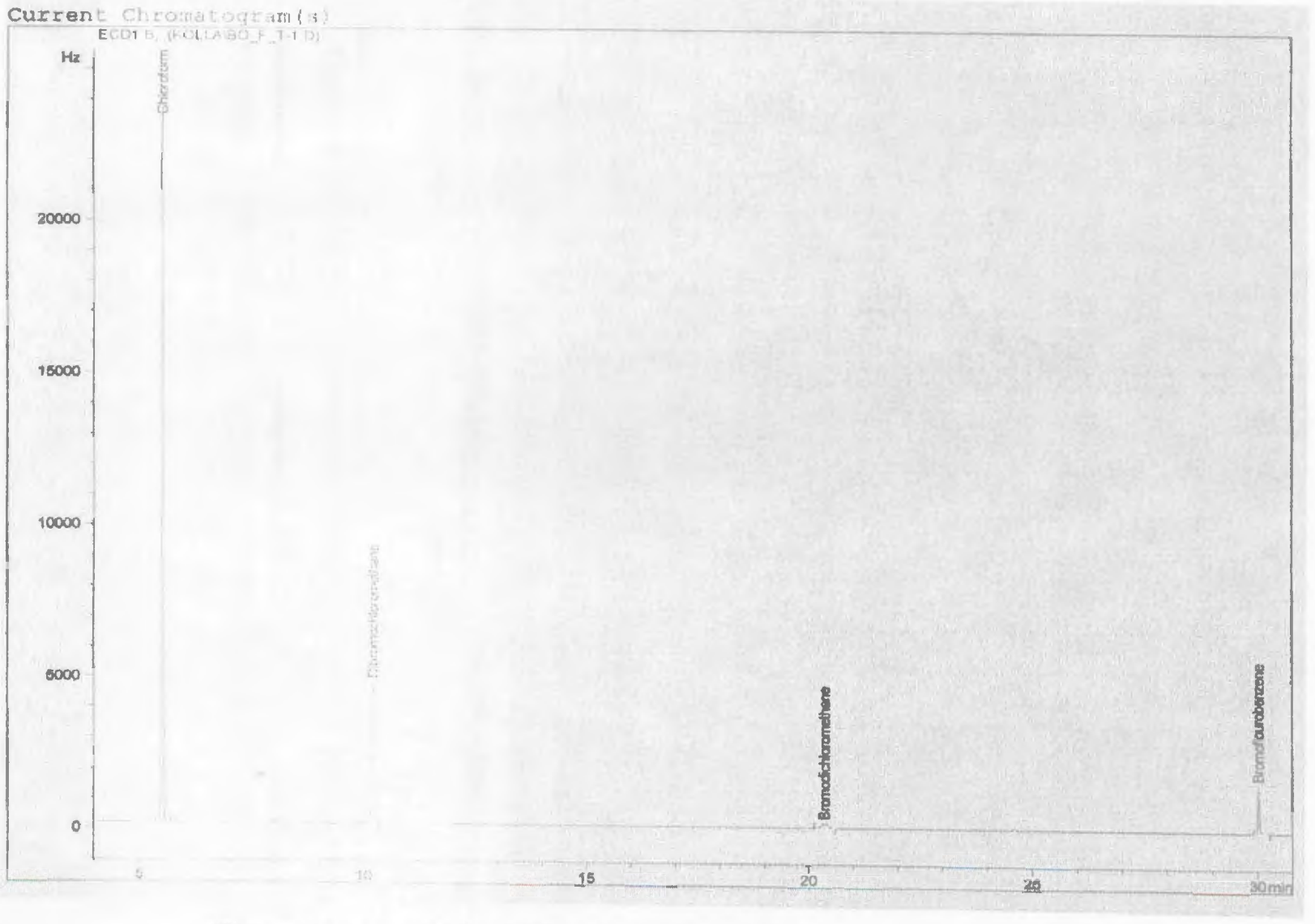
Chromatogram containing DBPs of Bonavista chlorinated water at 24 hrs contact time



Chromatogram containing DBPs of Clarenville chlorinated water at 24 hrs contact time



Chromatogram containing DBPs of Ferry Land tap water



Chromatogram containing DBPs of Bonavista tap water