

**The Temperature Effect of Tri-Halo Methane (THM) in Tap Water
and Wastewater of Perak Tengah Regions**

by:

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Dissertation submitted in partial fulfillment of

the requirements for the

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Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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Universiti Teknologi PETRONAS
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(CHEMICAL ENGINEERING)

Approved by,

(Dr. Asna MD Zain)

UNIVERSITI TEKNOLOGI PETRONAS
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May 2015

CERTIFICATION OF ORRIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NORA BINTI MOHD NOR

ABSTRACTS

In 1979 the United States Environmental Protection Agency (USEPA) state that the maximum of the concentration for the tri halo methane is 1 µg/L of potable water. But the 80mg/L is the maximum level of the contaminant. There are several method that can measure the tri halo methane such as High Performance Liquid Chromatography (HPLC) and gas-chromatography with electron capture detection (ECD), static headspace system and dynamic headspace (purge and trap) with ECD, electrolytic conductivity and mass-spectrometry and gas chromatography flame ionization detector (FID). The most popular method that are used in Europe is purge and trap method. After identify the component in the water the different of temperature contact with THMs will give effect would be identify. Based on the several sample are taken such in Perak Tengah was measured such as institute area, houses area, refinery area and industries area. These source can shows the different level of THMs with different level of temperature and concentration. THMs formation is accelerate by high temperature of 60°C and 90°C. The THMs found in waste water from industrial site using spike chlorine sample at 5ppm dosage is 4.46 ppm at 90°C.

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CHAPTER 1

INTRODUCTION

1.1 Background

In daily life water are uses in many ways for example for the dinking, washing, production and daily life. The tap water are using worldwide due to the important of water. For example in our earth water it is consist of 70% while for the land only 30%. Water can give effect in long term effect. Since water is very common there are several of causes why water becoming dangerous to our life or environment. If the water react with the other thing that will make the water become more reactive. For example the tri halo methane is the one of the contaminant that have in tap water. This contaminant will give effect to our body if did not take any pre caution to avoid this issues.

The common name of tri halo methane are bromoform, dibromochloromethane, bromodichloromethane and chloroform. The THMs will more produce than the low organic content that have higher organic content. There are several water source that have high organic content include lakes, reservoirs, rivers and streams. Chlorine are added to the water to reduce the organic content react to form the THMs. THMs and organic content getting lower towards the groundwater.

There a lot of water source contain a lot of microorganism such as bacteria, viruses, protozoa and others. Due to a lot microorganism in water contain so need kill the microorganism to avoid the health effect. Chlorine is the common disinfectant to kill the microorganism. The others advantages to add the chlorine is to reduce the number of water bone disease outbreaks, low cost and easy to use. The pre concentration step is the analytical method to determine the amount of the halogenated hydrocarbon in water.

However the chromatography is the one suitable method that are available in UTP to determine it.

To calculate the tri halo methane amount there are standard equation (1). Figure 1.1 shows that the molecular structure each of the components in the THMs. While the Figure 1.2 shows the general formula for the halogenated group that become main component in THMs.

THMs standard equation:

$$\frac{C_{\text{bromoform}}}{GV_{\text{bromoform}}} + \frac{C_{\text{dibromochloromethane}}}{GV_{\text{dibromochloromethane}}} + \frac{C_{\text{bromodichloromethane}}}{GV_{\text{bromodichloromethane}}} + \frac{C_{\text{chloroform}}}{GV_{\text{chloroform}}} \leq 1 \quad (1)$$

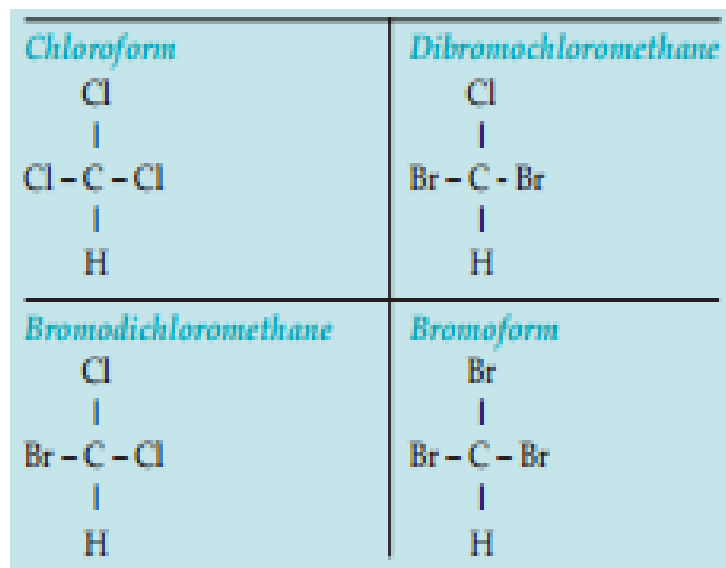


FIGURE 1.1 General Formula of Each THMs

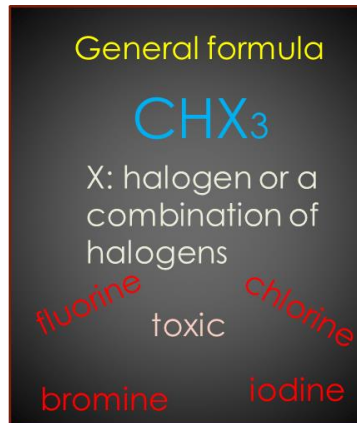



FIGURE 1.2. General Formula of THMs



Parameter	Group	RECOMMENDED RAW WATER QUALITY	DRINKING WATER QUALITY STANDARDS
		Acceptable Value (mg/litre (unless otherwise stated))	Maximum Acceptable Value (mg/litre (unless otherwise stated))
Chloroform	3	-	0.2
Bromoform	3	-	0.1
Dibromoklorometana	3	-	0.1
Bromodiklorometana	3	-	0.06
Trihalomethanes - Total	3	-	1.00

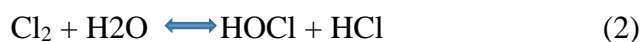
Chlorine is present in most disinfected drinking-water at concentrations of 0.2–1 mg/litre (WHO MALAYSIA)

FIGURE 1.3. The standard for the drinking water in Malaysia

Reff: World Health Organization (WHO) and Guidelines for Drinking-Water Quality

1.2 Problem Statement

There are a lot of step to measure each of the contaminant that have in THMs. To identify the level chlorine in water there are standard concentration of chlorine is concentrations of 0.2–1 mg/litre. The function of the chlorine is to kill the all the microorganism that can causes several disease that from water supply such as reservoirs, water mains and storage tanks. Hypochlorous acid (HOCl), and hydrochloric acid (HCl) will produce when dissolved in water together chlorine:



Disinfection by product (DBPs) is when the organic compounds will react with the chlorine. This is shows that chlorine is main causes the formation of THMs. The most common DBPs are tri-halo methane (THMs) and halo acetic acids (HAAs). The other problem is to identify the effect of tri halo methane if contact with temperature. Tri-halo methane such as bromoform and dibromochloromethane that have the health hazards.

The goal of this part established an accurate, sensitive and reproducible method for THMs analysis. Gas chromatography (GC) is the best method due to it can enter by the water. Since GC is the equipment that are available in University Teknologi Petronas (UTP). The sample will be detected by GC. There are several samples to differentiate the content of the contaminant. Samples are collecting in different place together with the different of source and waste come out from the source after used.

1.3 Objectives

Perak Tengah is the suitable region to identify the concentration of chlorine and tri-halo methane due to the uses of water is wide. The location are chosen based on the variety of activities such as there are houses, institutes, refinery and industries. Location are decided between:

- 1] Tap water of institute
- 2] Waste water from institute
- 3] Tap water from houses
- 4] Waste water from industries

The objective:

- 1- To identify the Temperature Effect of Tri-Halo Methane (THM) in Tap Water of Perak Tengah Regions
- 2- To identify the level of chlorine and level of each of the component of THMs to identify the formation of tri-halo methane.
- 3- The standard level of chlorine and THMs in tap water.

1.4 Scope of Study

As this project was involved experiment laboratory work, the study will focus to identify the temperature effect of tri halo methane contact with tap water in different places. The sample of water will be extracted using heptane and analysis the extraction solvent using the HPLC. This method is very suitable for the halogen group identification. With the different of concentration and different of temperature were identify.

CHAPTER 2

LITERATURE REVIEW

2.1 Chlorine Residual

Chlorine is the things that are added to the water to kill the microorganism but chlorine residual is the sufficient of the amount of chlorine that in the water. The chlorine residual will be react with the microorganism that can cause the disease. Chlorine residual can cause a lot of effect to human and environment.

There several characteristic of chlorine such as electron affinity, third highest electronegativity and oxidizing agent. Chlorine was added in tap water that is called by water chlorination. Due to the chlorine is very toxic so the function of chlorine to kill the certain bacteria and other microbe in tap water. The total chlorine is the remaining chlorine concentration after demand is counted. There divided into:

- 1) The unavailable disinfection will react with the chlorine to form contaminant.
- 2) The free residual chlorine is the chlorine available to inactivate disease-causing organisms, and measure to determine the portability of water. Mostly are available at the tap water
- 3) While combined residual chlorine are mostly are available at the wastewater. This type of chlorine is less effective than the free residual chlorine.

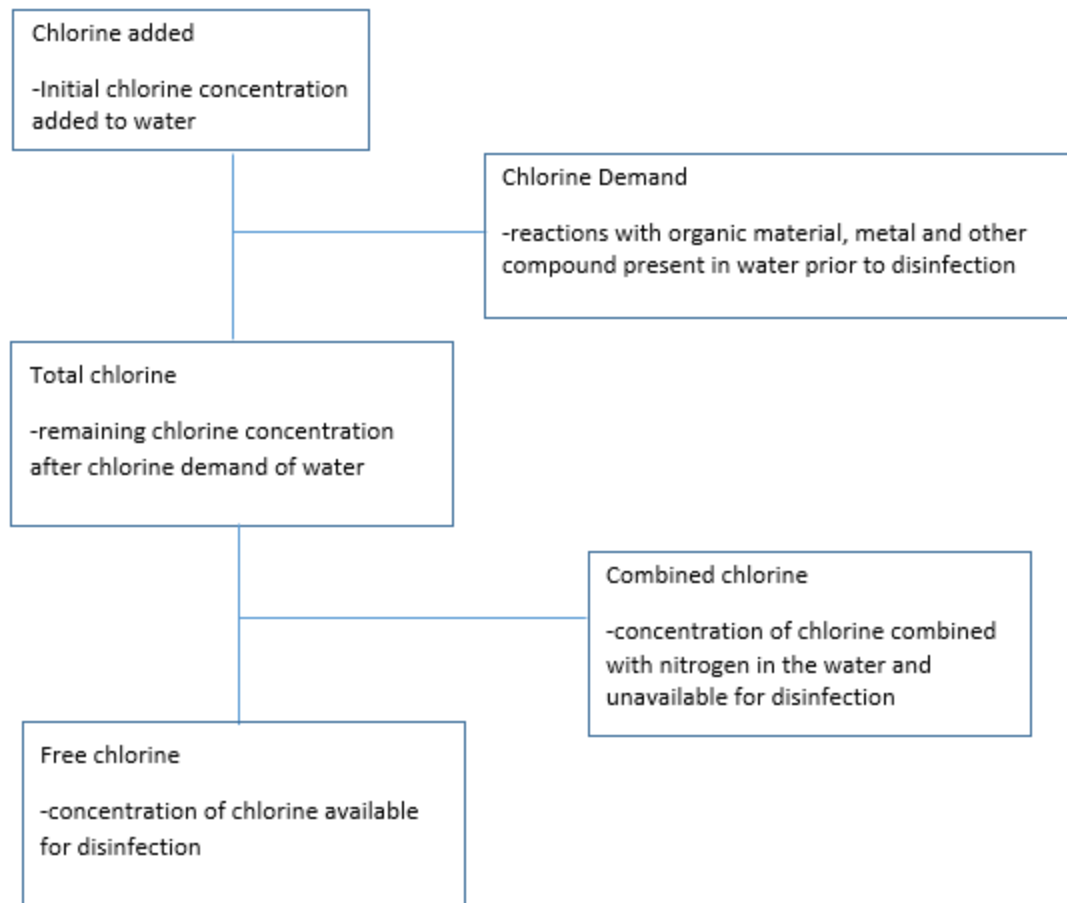


FIGURE 2.1. Chlorine Addition Flow Chart

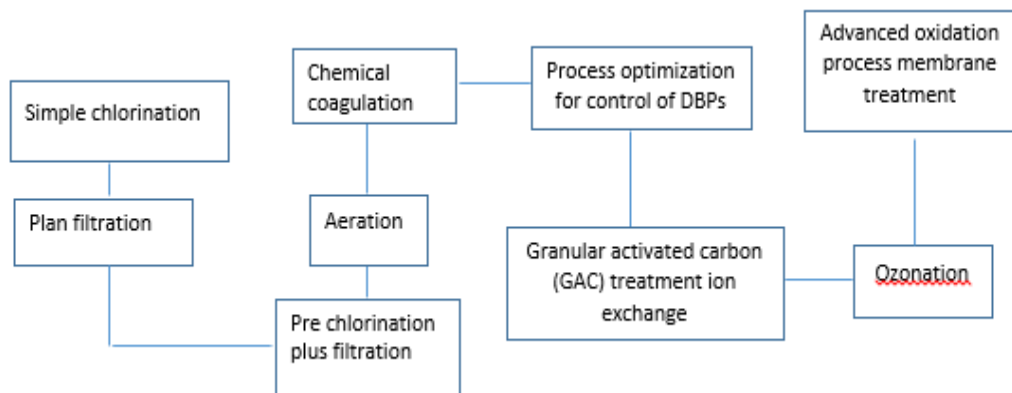


FIGURE 2.2. Water Treatment Process

2.2 Chlorine Effect

There is a lot of microorganism that living in source water such as algae, river weeds and decaying leaves. Source water must be control by chlorine to reduce the total or microorganism in source water to avoid any health effect. Chlorine can be good for water but it can effect to our health if the total of chlorine more than the standards. Residual concentration of chlorine of about 0.6 mg/l or more may cause problems of acceptability for some consumer. The standards level of chlorine in tap water for the boiling point -34.6°C, melting point -101°C, density 3.214 g/L at 0°C and 101.3 kPa, vapor pressure 480 Pa at 0°C, water solubility 14.6 g/L at 0°C and minimum concentration 0.02 mg/L. Drinking water also have some chlorine to kill the microorganism but the range between 0.2-1 mg/L. This is the standards level for chlorine to avoid the production of Tri-halo methane (WHO, 2004). There are several waterborne diseases due to the content of chlorine in water such as cholera, dysentery, jaundice, and typhoid (Calderon, 2000).

Chlorine is a yellow green gas that is extremely toxic as well as corrosive in moist atmospheres. Chlorine is about two-and-a-half times as heavy as air. Chlorine is not flammable or explosive and will not freeze, even at the lowest temperatures. Chlorine will react readily with water, moisture or moist tissues. While dry chlorine gas will not attack iron, copper, lead and some other metals and alloys, moist chlorine readily attacks most metals. Thus, with moisture, chlorine must be handled in corrosion resisting materials such as silver, glass, rubber and certain plastics. Chlorine can be detected at very low levels and has a characteristic sharp odor. At moderately low levels chlorine can be penetrating and very irritating to mucous membranes. A very small percentage in air causes severe coughing. Heavy exposure can be fatal.

TABLE 2.1. Physiological Effect of Breathing Air Chlorine Mixtures

Effect of Exposure	Parts of Chlorine Gas Per Million of Air By Volume (ppm)
Slight symptoms after several hours exposure	1
Irritates throat	10 - 15
Causes Coughing	30
Dangerous in 30 minutes	40 - 60
Fatal in a few breaths	1000 ppm

Mild exposure to chlorine produces no cumulative effects and complete recovery usually occurs. Inhalation of chlorine gas will cause an initial restlessness, anxiety, a severe irritation of the throat, and the production of excessive saliva. These symptoms are followed by coughing, retching, vomiting and difficulty in breathing. Individuals suffering from asthma and certain types of chronic bronchitis are particularly affected. Exposure of the skin to liquid chlorine will result in severe irritation and blisters.

2.3 Tri- Halo Methane (THMs)

Tri-halo methane (THMs) is the chemical compound that have one carbon and for hydrogen atom that are replaced by halogen atom such as chlorine, bromine, iodine and fluorine. All this atom in group 17 only in periodic table. The function of chlorine is to kill all the microorganism that have in water. While in other hand if have exceed chlorine in water it will produce tri-halo methane that can cause a lot effect to health. The common name for the tri-halo methane is chloroform. In organic chemistry chloroform is the one of the common chemical. The chloroform is less polar than water and easily to dissolve in many compounds.

There are some disadvantages of the chloroform due to it is more harmful than the carbon tetrachloride but the chloroform is cheaper and cleaner. Chloroform is an disinfection by product in drinking water that identified by (Rook, 1974) in the Netherlands and (Bellar *et al.*, 1974) in the United States. All the THMs are identified based on the concentration in drinking water from the 27 large cities by the National Organic Reconnaissance, (Symons *et al.*, 1975). They trace all the component of the

THMs such as chloroform, bromodichloromethanes, dibromochloromethanes, and bromoform.

There are several condition that The United States Environmental Protection Agency requirement. The limit for the THM concentration not exceed 100µg/L at the consumer's tap. Each of the counties have different limit for their level of THMs. There are mathematical model to predict of the concentration, temperature, pH and total organic carbon (Clark, 1998) and (Montgomery Watson, 1993). Bromide ion concentration is the one of the factor that are studied by the several research. (Bellar *et al.*, 1974) and (Clark, 1996) shows that THMs concentration increases with increasing bromide ion concentration. Other researchers studied the effect of other factors on THMs formation.

2.4 Method to Identify the Level of Chlorine

There are several method to measure the chlorine in water. This is because chlorine can give big effect if contact with other microorganism. Based on (Marianne R. Metzger, 2007) there three step to measure the chlorine. Firstly, test strips this method is very simple and an inexpensive between the others method. The test strips is the simple system that did not need any of maintenance. The test strips are dipped to the water and the color will change based on the change of the color at test strips. This is the characteristic the type of color if the strips in dark color there is less light will pass through so the result is the level of chlorine is low while the light color there is high light will pass through so the result will have high level of chlorine. This method very simple to predict but there are some errors occur during the test. The human error is the main error if using this method. Each human read in different way to measure the color of the strips. The range of the chlorine to measure to use this method is 0 -3.5 mg/L or 0 - 3.5 ppm.

The second method to measure the chlorine is calorimeter this method is continuous testing with instantaneous results. The method that can minimize the error of human and accuracy is calorimeter that using the visual analysis. The range of the chlorine to measure to use this method is 0 -4 mg/L or 0- 4 ppm. WHO,2004 state that the level of accuracy is dependent on other criteria including a constant supply of clean

water for taking samples, perfect operations of components such as pumps and tubing and large quantities of chemical reagents.

The third method is the amperometric is the measurement by sensor probe that is containing the electrolyte such as potassium chloride. The step begin from the bottom that the chlorine in water will across the membrane and react with the potassium chloride to generate electric current. The result if can get generate more of the electric current so the higher the level of chlorine. This method more accurate and expensive than the others two method. This method need to titrate and it is voltammetry analysis. There are two type in this method such as quantitative and quantitative. This method also can detect ion pressure.

Other than that UV Vis are using to identify the chlorine and this equipment are available in UTP. The absorption of UV or visible radiation corresponds to the excitation of outer electrons. There are three types of electronic transition which can be considered; Transitions involving p, s, and n electrons, transitions involving charge-transfer electrons, transitions involving d and f electrons.

When an atom or molecule absorbs energy, electrons are promoted from their ground state to an excited state. In a molecule, the atoms can rotate and vibrate with respect to each other. These vibrations and rotations also have discrete energy levels, which can be considered as being packed on top of each electronic level. Many molecules absorb ultraviolet or visible light. The absorbance of a solution increases as attenuation of the beam increases. Absorbance is directly proportional to the path length, b , and the concentration, c , of the absorbing species. Beer's Law states that

$$A = e b c \quad (3)$$

Where,

e is a constant of proportionality, called the absorptivity. Different molecules absorb radiation of different wavelengths. An absorption spectrum will show a number of absorption bands corresponding to structural groups within the molecule.

Wastewater treatment plant operators should be constantly alert for any chlorine leaks as well as thoroughly familiar with the properties of chlorine, the proper ways to handle it and protective as well as first aid measures associated with emergencies. Individuals working with chlorine should be trained in the use of self-contained breathing apparatus. While several types of gas masks should be available at the plant, it should be noted that the usual industrial canister type gas mask is not effective when chlorine in the air exceeds 1%. Hence, they are not recommended in dealing with chlorine gas. The plant should be supplied with a chlorine gas mask of a design approved by the Bureau of Mines.

When the oxygen content is limited (below 16%) a self-contained "supplied air" or oxygen supply type breathing apparatus is recommended. The masks should be located in readily accessible points, away from any areas that are likely to be contaminated by chlorine gas. Masks should be checked regularly. However, it is to be emphasized that whenever a room must be entered that may contain chlorine gas, great care must be taken. When approaching this situation the door must be carefully opened and left ajar to check for the smell of chlorine gas. An individual should *never* enter a room containing harmful levels of chlorine without:

1. A self-contained air supply
2. Protection to the eyes
3. Protective clothing
4. Help standing by, and
5. Notifying proper authorities

2.5 Method to Identify the Level of THMs

Tri- halo methane also have several method to measure the level of tri-halo methane in water. There are several method such as the purge and trap method (EPA method 501.1), liquid-liquid extraction (EPA method 501.2), gas chromatography, mass spectrometry and selected ion monitoring (EPA method 501.3).

There are several methods to determine four tri-halo methane such as chloroform, dichlorobromomethane, dibromochloromethane and bromoform for example EPA method (501.1). The gas chromatographic column and detector employed is actual detection limit. The range of the concentration is between 0.5 to 1500 micrograms per liter. The analysis more than 100 different of water supplies method 501.1 is very suitable rather than 501.2. Inert gasses are used to extract THMs through aqueous sample. The tri-halo methane with the other organic are low water solubility and vapor pressure than water that are efficiently transfer from the aqueous phase to the gaseous phase. After a predetermined period of time, the trapped components are thermally desorbed and back flushed onto the head of a gas chromatographic column and separated under programmed conditions. Dissimilar column is used for confirmation while aqueous standards and unknown is analyzed for extraction losses. The total analysis is approximately 35 minutes per sample.

EPA method (501.2) is to determine only of four tri-halo methane such as chloroform, dichlorobromomethane, dibromochloromethane and bromoform in drinking or tap water in Perak Tengah region. Gas Chromatography/Mass Spectrometry (GC/MS) is precision and accuracy data on actual sample and provide qualitative confirmation of results accurately. The range of the concentration is approximately 0.5 to 200 µg/L. The actual detection limit depend on the chromatographic system used. The liquid-liquid extraction technique efficiently extracts a wide boiling range of non-polar organic compounds. The semi specific electron capture detector and chromatographic columns which have relatively poor resolving power (low µg/L). In gas chromatography it have the temperature programming that interfaced to the mass spectrometry with all glass enrichment device and all glass transfer line.

This method 501.3 is provides procedures to identification and measurement tri-halo methanes (chloroform, bromoform, bromodichloromethane, and chlorodibromomethane) in several way such as finished drinking water, raw source water, or drinking water in any treatment stage. As the step above are mention involve gas chromatographic separation, identification, and measurement of these specific tri-halo methane. Different type of method have different to identify the tri halo methane. Method

501.2 is an extraction procedure; Methods 501.1 and 501.3 involve removal of tri-halo methane with purge and trap procedures. In Method 501.3, selected ion monitoring with a mass spectrometer is substituted for the halide-specific gas chromatographic detector specified in Method 501.1. It is used to analyze drinking water for these four tri-halo methane.

The best method to identify the tri halo methane is gas chromatography. This analyze list includes 12 commonly observed chlorination disinfection byproducts and six commonly used chlorinated organic solvents - carbon 3,4 tetrachloride, 1,2-dibromo-3-chloropropane (DBCP), 1,2-dibromoethane (EDB), tetrachloroethylene, 1,1,1-trichloroethane and trichloroethylene. This method is intended as a stand-alone procedure for the analysis of only the tri-halo methane (THMs) or as a procedure for the total analyze list. The six solvents may be analyzed in the THM mode, since the same de chlorination reagents may be employed.

The methodology to carry out the experiment the container that contain of tap water and waste water in different type of water must be air tight like Tupper ware and keep the container in cold condition to avoid the reaction between the chlorine that contain in tap water with remaining microorganism. There are several treatment to reduce the microorganism in tap water such as coagulation, sedimentation, filtration and disinfection. Coagulation is the process to remove all the dirt and other particle in water. While the sedimentation is to remove the heavy particle settle to the bottom and clear water to filtration. Addition for the filtration is the water passes through filters, some made of layers of sand, gravel and charcoal that can remove the smaller particles. Disinfection is when the small amount of chlorine is added or some other disinfection to kill any bacteria or organisms.

CHAPTER 3

METHODOLOGY

3.1 Introduction of Methodology

There are several method that can identify the tri-halo methane. Total tri-halo methane are bromoform, bromodichloromethane, chlorodibromomethanes and chloroform. The best method to identify all the type of tri-halo methane is liquid-liquid extraction gas chromatographic method.

TABLE 3.1. Type of detector

Type of detector	Applicable samples	Detection limit
Mass spectrometer (MS)	Tunable for any sample	23-100 pg
Flame Ionization (FID)	Hydrocarbon	1 pg/s
Thermal Conductivity (TCD)	universal	500 pg/ml
Electron Capture (ECD)	Halogenated hydrocarbon	5 fg/s

Determination of tri-halo methane by means of liquid-liquid extraction gas chromatographic electron captured detector method.

3.2 Apparatus for chlorine and THMs Determination

There are several of apparatus are using to identify the level of chlorine and also tri-halo methane. The apparatus consist of:

- a) Extraction vessel- 15 mL total volume glass vessel .

- b) Sampling container- 40 mL Micro syringes- 10, 100 μ L. Micro syringe- 25 μ L
- c) Syringes- 10 mL ,Syringes valve- 2 way with luer ends (2 ends).
- d) Pipette- 2.0 mL transfer.
- e) Glass stopped volumetric flask- 10-100 mL.
- f) Gas chromatography (GC)
- g) The column are using is column A, 0.32 mm ID x 30 m that have fused silica capillary with chemically bonded methyl polysiloxane phase. The linear velocity of the helium carrier at 23 cm/sec at 35°C. for the oven is programmed to hold at 35°C for nine minutes, to increase to 40°C at 1°C/min, and held for three minutes, to increase to 120°C at 6°C/min and held at 120° until all expected compounds have eluted. A temperature of 150°C is then maintained for five minutes. Injector temperature: 200°C.
- h) While for the column is column B -- 0.32 mm ID x 30 m with chemically bonded 50% trifluoropropyl phase. The linear velocity of the helium carrier gas is established at 27 cm/sec. The column temperature to hold at 30°C for 11 minutes, to increase to 120°C 551-7 at 10°C/min and held at 120°C until all expected compounds have eluted. A temperature of 150°C is then maintained for five minutes.
- i) Detector temperature: 290°C
- j) Salt scoops for sodium sulfate.
- k) Pipetting dispenser.
- l) Diazomethane generator.

3.3 Chemical and Reagents

There are several of chemical and reagent that are using to analysis the THMs

- 1) Pentane if do not have alternative way is using hexane, methyl cyclohexane or 2,2,4-tri methyl pentane. The chosen of pentane due to it can be eluted on all of the column before any of the tri halo methane. The condition of the design and condition of the gas chromatography is depend on the degree of difficulty such as when concentrations of the tri halo methane are in excess of 5 ug/L.

- 2) Methyl alcohol
- 3) Free and combined chlorine reducing agents - Sodium thiosulfate ACS Reagent Grade. Water are boiled for 15 minute to prepare the organic-free water at temperature 90°C, bubble a contaminant free inert gas through the water at 100 mL/minute for one hour. Standard:
 - bromoform 96%, bromodichloromethane 97%, chlorodibromomethane, chloroform 99%

3.4 Standard Stock Solution

- 1) The volumetric are filled 9.8 ml of methyl alcohol. To make alcohol all wet surface dry it need about 10 minutes to stand unstopped.
- 2) Weigh the unstopped flask to the nearest 0.1 mg. using a 100 µL syringe, add 2 to 3 drops of the reference standard to the flask, then reweigh. Be sure that the reference standard falls directly into the alcohol without contacting the neck of the flask. Dilute to volume, stopper, then mix by inverting the flask several times.
- 3) Use the 15 ml bottle to transfer the standard solution. Because of the toxicity of tri halo methane, it is necessary to prepare primary dilutions in a hood. During handle high concentration must wear the toxic gas respirator that recommended by NIOSH/MESA. Calculate the concentration in micrograms per microliter from the net gain in weight. Store the solution at 4°C. *Calibration standards.

3.5 Sample Collection and Handling

- 1) Use the 15 ml of the container to collect the sample.
- 2) Wash all sample bottles, rinse with tap water and finally with distilled water. Allow the bottles and seals to air dry, then place in a 105°C oven for 1 hour, then allow to cool in an area known to be free of organics.
- 3) For the sample stabilization

3.6 Calibration

1) Preparation of Calibration Standards

- a) Samples prepared at concentrations of 0.2 µg/L, 1.0 µg/L, and 2.0 µg/L.
- b) To prepare a calibration standard, add an appropriate volume of a primary dilution standard to a 35-mL of reagent water in a 40 mL. Use a 25 µL micro syringe and rapidly inject the standard into the middle point of the water volume.. Mix by inverting the sample vial three times without shaking. Aqueous standards must be prepared fresh daily and extracted immediately after preparation.
- c) Alternatively, add an appropriate volume of primary dilution standard and internal standard solution to reagent water in a 100 mL volumetric flask and fill to the mark. Mix by inverting three times. Weigh a 35 mL aliquot of this standard into a pre calibrated 40 mL vial.

2) External Standard Calibration Procedure

The peak are tabulated from the extraction and analyze versus concentration of the standard. If the ratio of response to concentration (response factor) is constant over the working range ($\leq 10\%$ relative standard deviation, [RSD]), linearity to the origin can be assumed, and the average ratio or response factor can be used in place of a calibration curve.

- 3) Extract and analyze each calibration standard. Tabulate peak height or area responses against concentration for each compound and internal standard. Calculate response factor (RF) for each compound using Equation 1.

$$RF = \frac{(As)(Cis)}{(Ais)(Cs)} \quad (4)$$

Where,

As = Response for the analyte to be measured.

Ais = Response for the internal standard.

Cis = Concentration of the internal standard ($\mu\text{g/L}$).

Cs = Concentration of the analyte to be measured ($\mu\text{g/L}$).

If RF value over the working range is constant ($<10\%$ RSD) the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response versus analyte ratios, A_s/A_{is} vs C_s/C_{is} .

- 4) The working calibration curve, calibration factor, or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any analyte varies from the predicted response by more than $\pm 20\%$, the test must be repeated using fresh calibration standard. If the fresh calibration standard also deviates by more $\pm 20\%$, a new calibration curve must be prepared for that compound.
- 5) Daily calibration requirements using the external standard calibration procedure are a minimum of two calibration check standards, one at the beginning and one at the end of the analysis day. These check standards should be at two different concentration levels to verify the calibration curve. For extended periods of analysis (greater than eight hours), it is strongly recommended that check standards be 551-14 interspersed with samples at regular intervals during the course of the analysis.

3.7 Quality Control

- 1) Each laboratory that uses this method is required to operate a formal quality control (QC) program. Minimum QC requirements are initial demonstration of laboratory capability, monitoring internal standard peak area or height in each sample and blank, analysis of laboratory reagent blanks, laboratory fortified blanks, laboratory fortified sample matrices, and QC samples. Additional quality control practices are recommended.
- 2) Initial Demonstration of Capability

Select a representative fortified concentration for each of the target analyses. Concentrations near analyze levels are recommended. Prepare a laboratory control (LC) sample concentrate in acetone or methanol 1000 times more concentrated than the selected concentration. The LC sample concentrate must be prepared independently from the standards used to prepare the calibration curve.

3.8 Extraction and Analysis

- 1) Remove the plungers from two 10-mL syringes and attach a closed syringe valve to each. Open the sample bottle (or standard) and carefully pour the sample into one of the syringe barrels until it overflows. Replace the plunger and compress the sample. Open the syringe valve and vent any residue air while adjusting the sample volume to 10 mL. Close the valve. Fill the second syringe in an identical manner from the same bottle. This syringe is reserved for a replicate analysis. If for any reason the chemical reducing agent has not been added to sample, then it must be added just prior to analyses at the rate of 3 mg/40 mL or by adding 1 mg directly to the sample in the extraction.



FIGURE 3.1. Preparatory funnel

- 2) Pipette 2.0 mL of extraction solvent into a clean extraction flask. Carefully inject the contents of the syringe into the extraction flask. Seal with a Teflon faced septum. Shake vigorously for 1 minute. Let stand until the phase's separate (approx. 60

seconds). If the phases do not separate on standing then centrifugation can be used to facilitate separation.

- 3) After the extraction has been completed, the extract is dried by passing it through anhydrous sodium. Removing water from the dichloromethane with sodium sulfate before the extract is concentrated to final volume. Dichloromethane can hold approximately 1 mL of water per 100 mL of solvent. If water remains in the extract, it will partition out of the extract when the volume is reduced. If this occurs, either the dichloromethane will evaporate first, leaving only water in the collection vessel, or a two-layer extract will form. In either event, the recoveries of the target compounds will be lower than desired, and the presence of water will interfere with gas chromatographic analysis. The best way to remove the water is to filter the dichloromethane extract through granular sodium sulfate held in a funnel with a high-quality grade (Whatman® 541) filter paper or glass wool.



FIGURE 3.2. Drying the Sample Extract with Sodium Sulfate

- 4) Approximately 30 g of sodium sulfate is sufficient for most samples. After drying the sample, thoroughly rinse the sodium sulfate to ensure that the entire sample is transferred to the collection vessel. Avoid using powdered sodium sulfate since some compounds can be adsorbed onto the smaller particles. Use only a 10-60 mesh granular sodium sulfate for best results. It also is important that this material be free from organic contaminants.

- 5) Analyze the sample by injecting 3.0 µL (solvent flush technique), of the upper (organic) phase into the gas chromatograph.

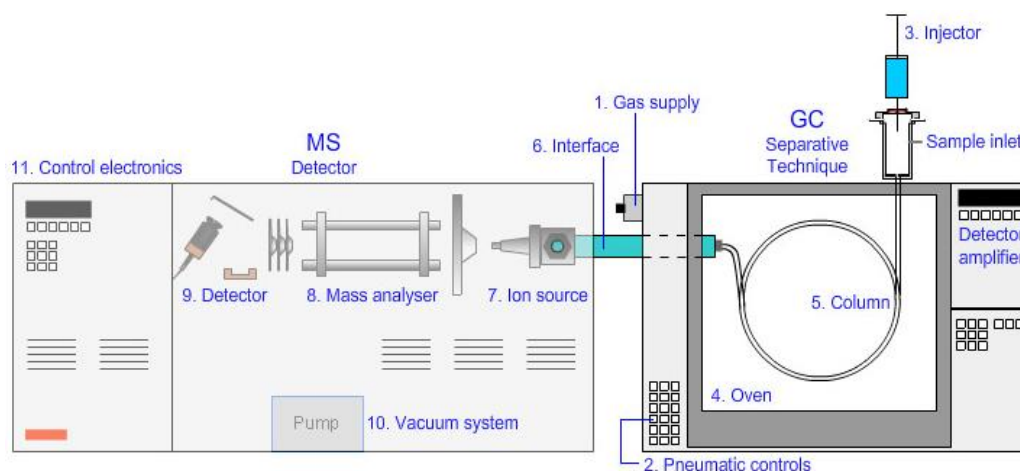


FIGURE 3.3. Schematic of Gas chromatography mass spectrometry

- 6) Analytical Quality Control: A 2 µg/L quality check standard should be extracted and analyzed each day before any samples are analyzed. Instrument status checks and lower limit of detection estimations based upon response factor calculations at 5 times the noise level are obtained from these data. In addition, the data obtained from the quality check standard can be used to estimate the concentration of the unknowns. From this information the appropriate standards can be determined. Analyze the sample blank and the raw source water to monitor for potential interferences.
- 7) Calculate using this formula:

$$\text{Concentration (ug/L)} = \frac{\text{sample peak area}}{\text{standard peak area}} * \text{std conc. (ug/L)} \quad (4)$$

$$\text{TTHM (ug/L)} = (\text{conc. CHCl}_3) + (\text{conc. CHBrCl}_2) + (\text{conc. CHBr}_2\text{Cl}) + (\text{conc. CHBr}_3)$$

3.9 Project Process Flow

This is the process flow for the project activity that must be followed in order to achieve the objective of the study:

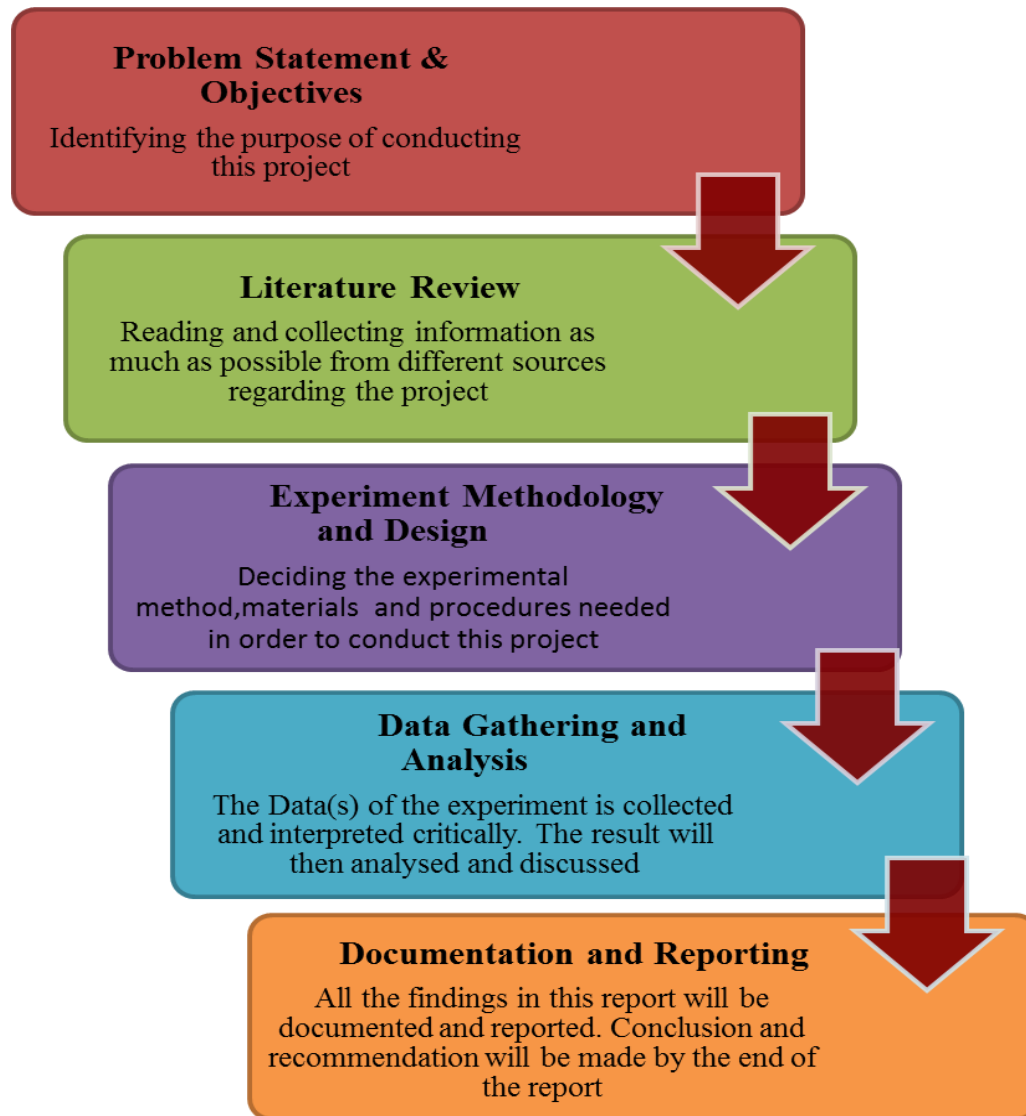


FIGURE 3.4. Process Flow of the project

3.10 GANTT CHART

3.10.1 FYP I

No	FYP Details/ week no	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Sample collection														
2	Selection of equipment														
	a) identify the suitable equipment														
	b) equipment that are available in UTP														
3	Procedure of the experiment														
4	Progress report														
	Project work continues														
5	a) methodology screening														
	b)finalize the methodology														
	c) project write up														
6	submission of interim draft report														
7	submission of interim report														

FIGURE 3.5. Gantt chart FYP I (Planning)

3.10.1 LIST OF MILESTONE

- ❖ Literature review (researched about the project)
 - ✚ Learn and understand more detail (27 Feb)
 - ✚ Consult the with the supervisor

- ❖ Analysis of the procedure
 - ✚ Identify the detail the level of THMs and chlorine (27 Feb)
 - ✚ Consult with technician to find the equipment available in UTP

- ❖ Methodology screening
 - ✚ Identify the step more detail from the extraction until the analysis to GC-ECD (4 Mac)

- ❖ Project write up
 - ✚ Write the report (get the confirmation about the detail of the project)

3.10.2 FYP II

No	FYP Details/ week no	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Sample collection														
2	Selection of equipment														
	a) identify the suitable equipment														
	b) equipment that are available in UTP														
3	Procedure of the experiment														
4	Progress report														
5	Pre-SEDEX Presentation														
	Submission of Draft Report														
	Submission of Dissertation (Soft bound)														
	submission of Technical Paper														
6	Oral presentation														
7	Submission of Project Dissertation (Hard Bound)														

FIGURE 3.6. Gantt chart FYP II (Planning)

3.10.2 LIST OF MILESTONE

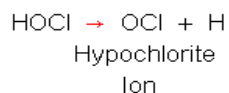
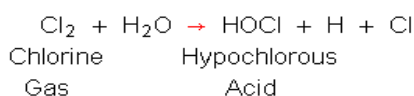
- ✚ 9 JULY 2015- the submission of the progress report. Still the lab work in progress due to the delay of the chemical delivery. Waiting the chemical delivery.
- ✚ 29 JULY 2015- The pre SEDEX competition. Project work still continues.
- ✚ 3 august 2015 - the submission of the draft report to the supervisor. To make sure all the format for the report.
- ✚ 10 august 2015 - submission the dissertation in soft copy and before to send checked the format.
- ✚ 14 august 2015- submission of the technical paper to the coordinator.
- ✚ 24/25 august the oral presentation for FYP II. Explain the detail of the project and come out the result. The experimental still in going due to the viability of equipment. Using GCMS from block 20. Interpret the data are given.
- ✚ 15 September 2015 - submission of hard copy of the project dissertation.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Chlorination

Chlorine are using for many type of function. Tap water using the chlorine to kill the microorganism in the source water to avoid any microorganism enter to human body. While for the wastewater chlorine are added for a number of different purpose and chlorine dosages and management will vary with the specific purpose. Chlorine are added before any treatment are applied. Chlorine is effective disinfecting agent to reducing the number of bacterial in waste water effluents. In wastewater treatment neither primary nor secondary methods of wastewater treatment can completely eliminate any of pathogenic bacteria that are always present. When wastewaters or treated effluents are discharged to bodies of water which are, or may be used as a source of public water supply, or for recreational purposes, treatment or disinfection for the destruction of pathogenic organisms is required to minimize the health hazards of pollution to these receiving waters.



(6)

In December 1974, independently (Rook and Bellar, *et al.* 1974) reported the formation of chloroform and other chlorine and bromine substituted tri halo methane

during drinking water treatment as direct result of the chlorination disinfection practice. Partly because of these discoveries, the United States Environmental Protection Agency (USEPA) undertook a survey to measure the concentration of halogenated compound. There is effect to tri halo methane if contact with temperature. A corresponding seasonal variation is noticed at a water utility using the same source and has been shown to be largely a temperature effect.

(Clark, 1998), (Bellar *et al.*, 1974), (MonotogomeryWatson, 1993), (Tarek Elmitwalli *et al.*, 2008) show that the factors of THMs formation include PH, temperature, contact time and chlorine concentration. Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. There are several tester to identify the contaminant inside the water. UV Vis is the one of the method to identify chlorine. Compared with the other method of spectrometry, UV Vis more adaptable and versatile. A small portion of residual chlorine results from this process, so water must be accurately monitored to ensure that it is safe for human consumption. Two main forms of residual chlorine exist, commonly referred to as 'free chlorine' or 'combine chlorine' residuals. UV-VIS spectroscopy offers an effective method for differentiating between the two. This identification is important because free residual chlorine is often considered a more effect disinfectant and can be used more effectively when properly detected in drinking water. From the figure below shows the schematic diagram of UV-Vis.

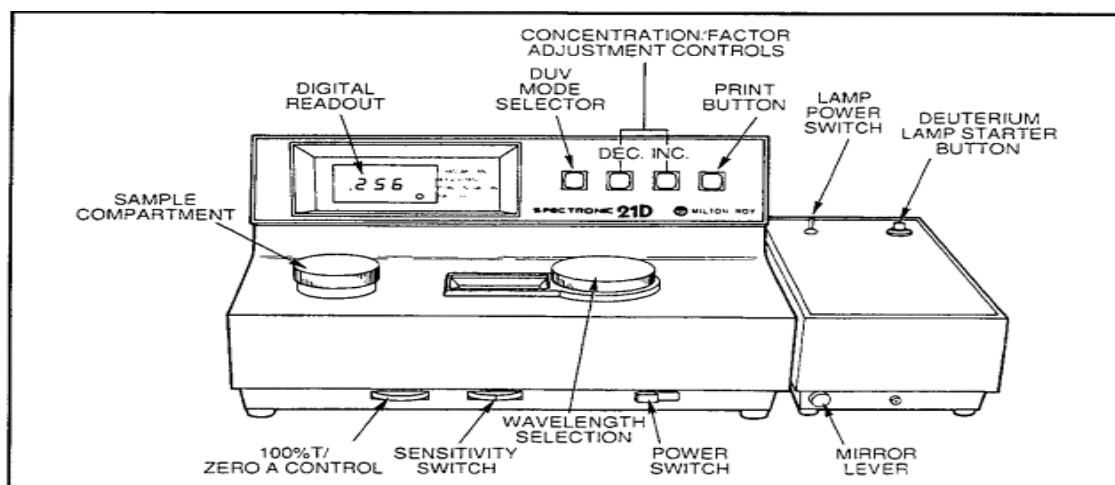


FIGURE 4.1 Schematic diagram of UV-Vis

The benefits of spectrophotometers are especially applicable in the world of environmental science. These light measurement tools are highly adaptable to meet specific needs and offer a durable method of analysis that is both portable and instantaneous. The chlorine are identified based on different of place. From the 4 of sample are extracted to the different of concentration, the chlorine are identified. Based on the graph below the chlorine content at different of the sample place. The sample are test using the UV-Vis.

Chlorination for disinfection requires that essentially all of the pathogens in the wastewater plant effluent be destroyed. At the same time it should be noted that many but not all of the nonpathogenic microorganisms are also destroyed. As noted, no attempt is made to sterilize waste water and this is not only unnecessary but impractical. In some instances sterilization might be detrimental where other treatment dependent upon microbial activity may follow chlorination. Fortunately pathogenic microorganisms are less resistant to chlorine than most non-pathogens so that disinfection can be effected without sterilization. Chlorination as commonly practiced in wastewater treatment is insufficient to inactivate all of the enteric (intestinal) viruses which may be present in wastewater.

Chlorine generally reacts in a prescribed order, first with inorganic reducing compounds. If enough chlorine is added to react with these substances, then the addition of more chlorine will result in reactions of chlorine with the organic matter that is present. This forms chloroorganic compounds, which have little or no disinfecting action. Again, if enough chlorine is added to react with all the reducing compounds and all the organic matter, then the addition of a little more chlorine will react with ammonia or other nitrogenous compounds to produce chloramines or other combined forms of chlorine which also have disinfecting action but are not as effective as free chlorine.

Beer-Lambert Law is the formula to find the concentration each of the sample.

$$A = \epsilon l c \quad (7)$$

Where, A = absorbance

ϵ = molar absorptivity

l = solution in a cell of length

TABLE 4.1. The concentration of chlorine using Beer Lambert Law

Absorbance	Molar absorptivity	concentration
2304	11000	0.21
5898	12000	0.49
9986	12500	0.79
18000	12000	1.5

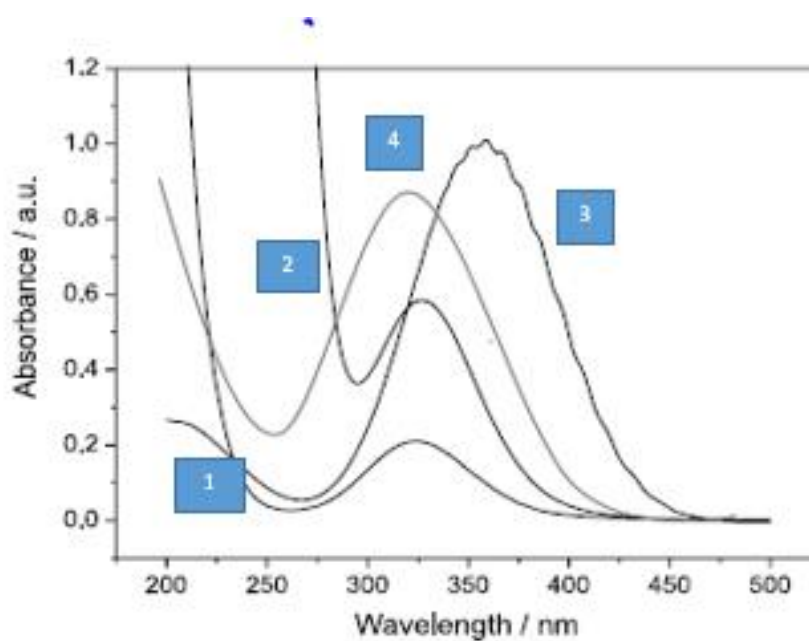


FIGURE 4.2. Concentration of chlorine using UV Vis

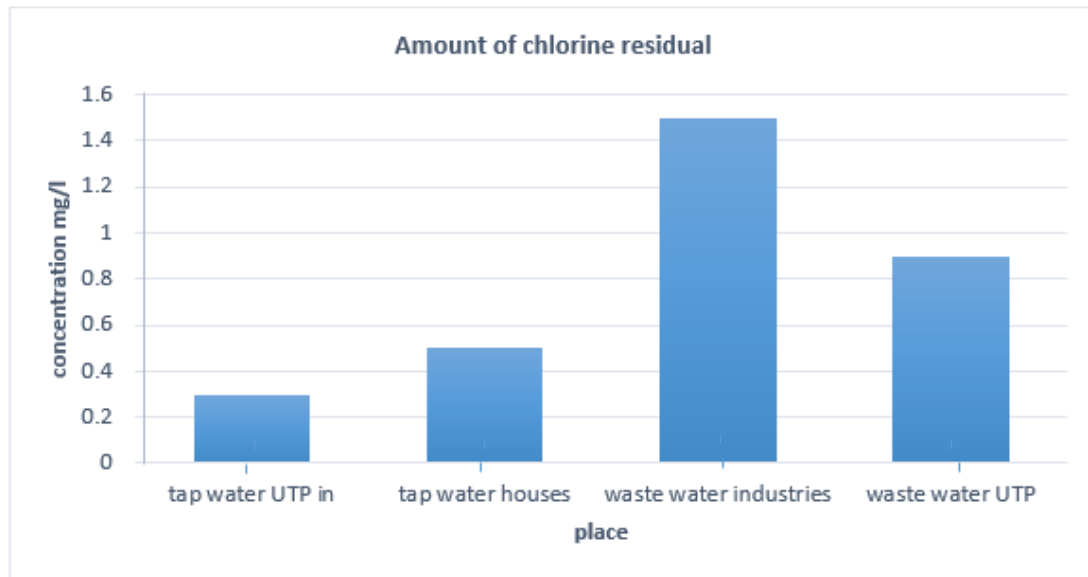


FIGURE 4.3. Concentration of chlorine

If continued the addition of the chlorine, it will become the destruction of chloramines and formation of free chlorine. In the wastewater treatment, the addition in sufficient dosages where is the free chlorine are formed is called breakpoint chlorination. There are several factor the effectiveness formation of the chlorine. In "pure" systems bacterial kill at a particular chlorine dosage is directly related to the number of bacteria present when the chlorine is first added. Moreover pH is the one of the factor formation of THMs, it will give effect the forma of chlorine present and at neutral pH's hypochlorous acid, chlorine will become more effective. While for the temperature it will speed up the chemical reaction, this is shows that the THMs will be increase if the temperature increase. However, chlorine is capable of undergoing a wide variety of reactions and probably reacts with the microbial cell at several levels.

4.2 Extraction of sample

Extraction is the one of the step to remove the water using the solvent. Extraction is liquid-liquid extraction is a method to separate compounds based on their relative solubility in two different immiscible liquids, usually water and an organic solvent. It is an extraction of a substance from one liquid into another liquid phase.

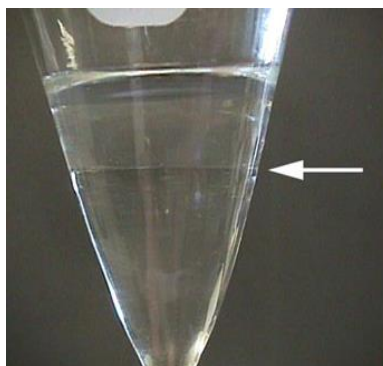


FIGURE 4.4. Two Phase of Layer

Before run with the chromatography each of the sample must be extract the THMs in solvent. The solvent are used is pentane. The pentane will extract the THMs. 10 ml of the sample will mixed with the solvent. Shake the mixture vigorously and the 2 phase will appear within 60 second. This method is to ensure the THMs are trap in the solvent.



FIGURE 4.5. The 2 phase are appear within 60second.

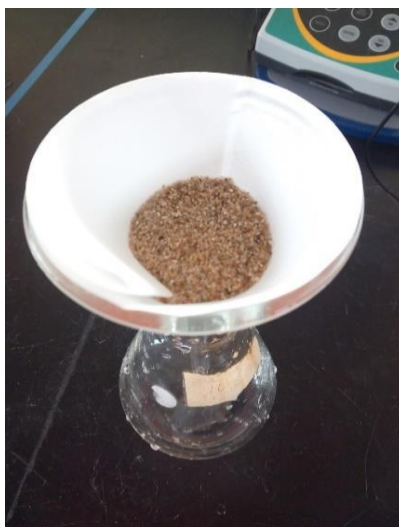


FIGURE 4.6. The 2 phase are appear within 60second. Then the solvent that have THMs are filter using the anhydrous sodium sulfate.

Based on the figure 4.6 the mixture will be filter in anhydrous sodium sulfate. This part is very important due to avoid any of water content in the solvent. After the preparatory shows the 2 phase the mixture will be filter using 30 mg of the anhydrous sodium sulfate. This is because the water content will be absorb by the anhydrous sodium sulfate.



FIGURE 4.7. The solvent are ready run with the chromatography with different source.

Based on the figure 4.7, all the sample are ready to test with chromatography from the different sources. Sample A is the tap water of institute. Sample B is the water flow out from the industry in Perak Tengah. While sample C the tap water from the houses and sample D is waste water of institute. All the sample are identify by the chromatography. Based on the different concentration of standard the sample are run using the gas chromatography mass spectrometry (GCMS). Each of the sample are run together with standards and the area of correction area.

4.3 Testing with GCMS

GCMS are using to identify each of the element. Condition of the GCMS as shown in figure 4.8 below.

GC-MS conditions	
Parameter	Condition
Column type	VF,5ms, 30 x 0.25 mm, 0.25 μ m
Injector	Splitless, 3 min sample exposure
Injector temperature	200°C
Oven temperature	35°C (hold for 4 min) @ 9°C /min and 120°C (hold for 3 min)
Ionisation	Electron impact
Carrier gas	Helium
Flow rate	1 mL/min
Detector	Mass spectrometer (ion trap)
Mode	Full Scan (m/z = 40-650)

FIGURE 4.8. Condition of GCMS

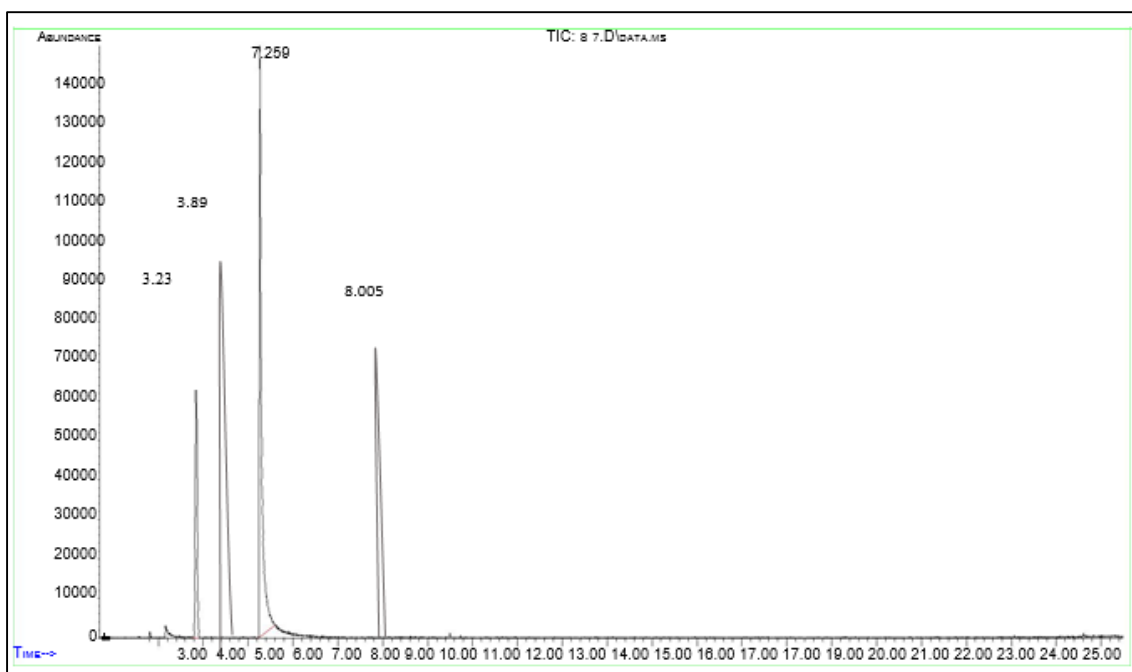


FIGURE 4.9. Result Based on all Sample of GCMS

```

Data Path : D:\MassHunter\GCMS\1\data\Nora\
Data File : s 7.D
Acq On    : 21 Aug 2015    18:33
Operator  :
Sample    : sample
Sample    : spike         5ppm
Misc      :
ALS Vial  : 10    Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method    : D:\MassHunter\GCMS\1\methods\THM (Nora).M
Title     :

Signal     : TIC: s 7.D\data.ms

```

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	8.014	366	377	389	BB 2	87030	74567	43.86%	30.489%
2	3.249	620	624	685	BB	148876	65438	100.00%	69.511%
3.	3.893	765	458	553	BB	65454	92354	80.00%	67.00%
Sum of corrected areas:								232359	

THM (Nora).M Mon Aug 24 12:59:25 2015

FIGURE.4.10 Data of the sample in GCMS

Based on the figure above, the GCMS show that the contaminant are present in sample. The contaminant are identified are chloroform, bromodichloromethane and bromoform. From the graph above the abundance vs time are measure. Each of the element are identified from the different time. For chloroform it is appear at 3.24 minute while bromodichloromethane at 3.89 and lastly bromoform are appear at 8.01 minute.

The sample are collected from the different of source. Each of the sample taken from the Perak Tengah to identify the level of contaminant THMs in water with different places. THMs are can be in any type of water. The main objective of the experiment to identify the contaminant level if contact with temperature. The water are extract by using the pentane before enter into the GCMS. Chloroform has the highest concentration in all samples. The role of the chlorine ion in the formation of THMs is critical. Tap water of institute and tap water houses show the low of formation of THMs due to level of chlorine also low.

After extraction the important method that have to be followed the sample that already extract by the solvent have to filter using the filter paper through the anhydrous sodium sulfate. This is to make sure the water content is zero in the solvent that could be damaged the column of the GC-FID or any GC. The formation of THMs varies with different water treatment processes. THMs compounds were detected in all water samples, after chlorination and ozonation point were collected from the treatment plants and from the consumption sites. No trihalomethanes were detected in raw water samples.

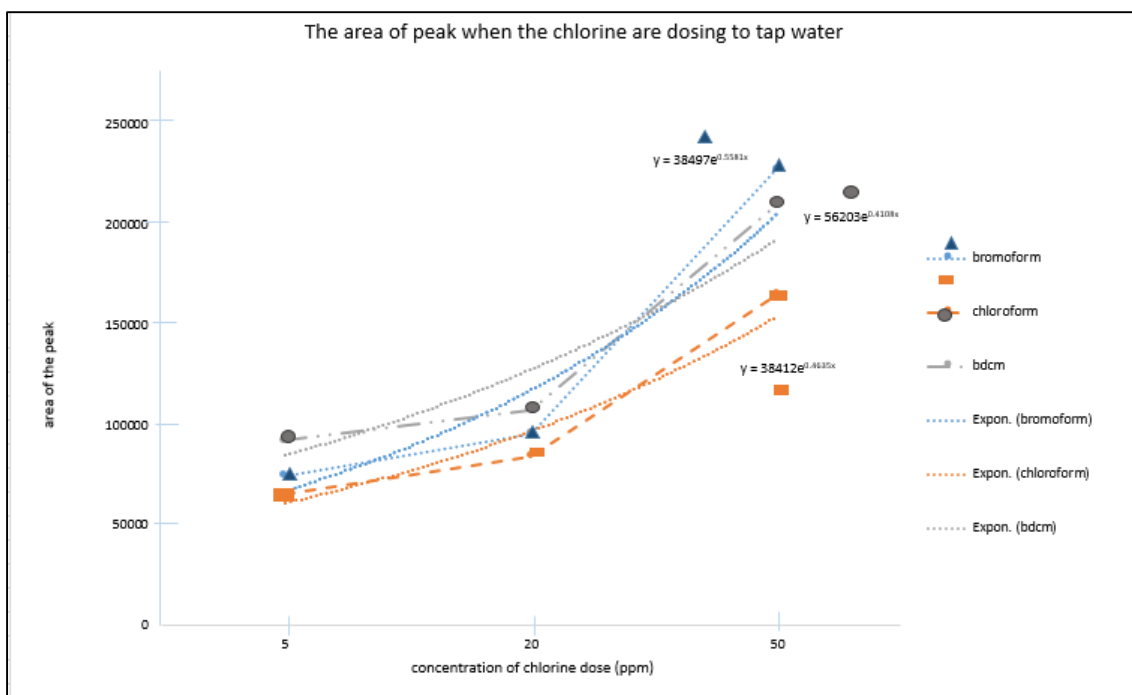


FIGURE 4.11 calibration curve of THMs

There are several factor formation of the THMs such as chlorine dose, time and temperature. Tap water are exposed to the different of chlorine dose. The concentration are 5ppm, 20ppm and 50ppm. The calibration curve are shown as in figure 4.11. GCMS are using to identify the area of the peak each of the THMs element. Based on the several factor the sample are exposed to the 3 factor. The exponential equation are using to calculate the concentration of chlorine for table 2.

4.4 Contact with same time but different of chlorine dose.

Based on the table below the sample are store in refrigerator in 15 hour before analyze using the GCMS. Using the exponential equation from the calibration curve the concentration each of the sample are identify. Using the equation 8 to identify the concentration of THMs. For the chlorine dose the concentration of THMs are produce are shown in table 4.2 below:

TABLE.4.2 The effect of THMs contact with different of chlorine dose.

		tap water	waste water institute	waste water industries
Time (minute)		900	900	900
Area of the peak	chloroform	35653	789907	455678
	bromoform	0	4566	654445
	BDCM	20045	378976	345656
TOTAL		55698	1173449	109776
concentration of chlorine ppm		0	15	16
THMs (µg/L)		0.00	96.51	99.1

$$\text{THMs} = (6.9102) (\text{cl dose})^{0.416} (\text{time})^{0.222} \quad (8)$$

The calculation as shown below

$$\text{THMs} = (6.9102) (15)^{0.416} (900)^{0.222} = 96.51 \mu\text{g/L}$$

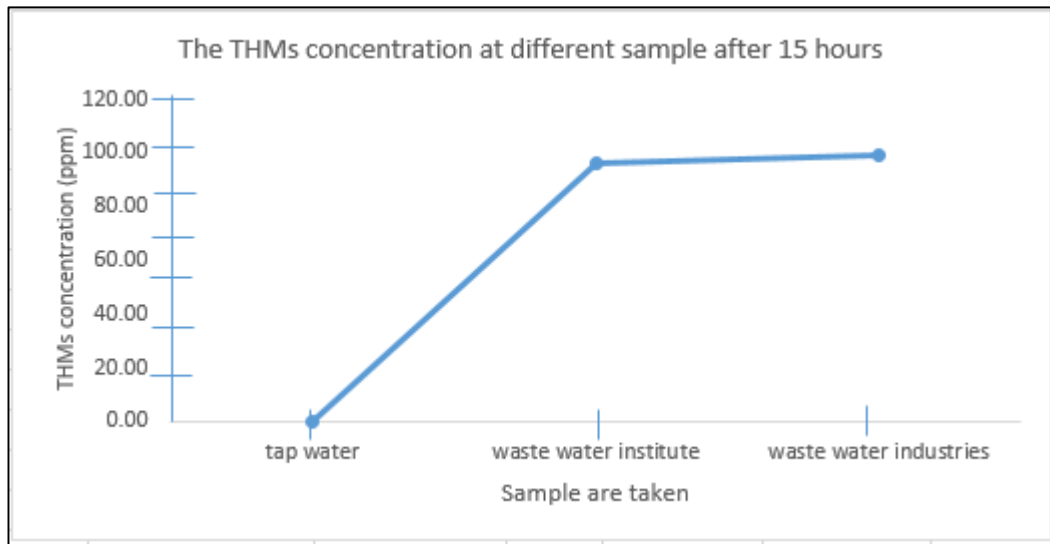


FIGURE 4.12. Effect THMs based on the chlorine dose at 5ppm

The figure 4.12 shown the different of chlorine are exposed. From the equation 8 from the (Mohamed Basiouny 2004) the THMs concentration are calculated in table 4.2. The

time are using is 900 minute chlorine are added to the sample. Using the tap water as the medium to identify THMs with the different of chlorine dose. At the high concentration the massive oxidation are takes place and membranes of all organic component are effected. In wastewater treatment the mechanism of chlorine is less important due to it is effect as a disinfecting agent. Chlorine demand is the chlorine used by organic and inorganic reducing substances. The chlorine are detected at between wavelengths (nm) 250 to 400. The total of the absorbance of the chlorine are observe. This is relate to the THMs. If the chlorine increase so the production of the THMs will be increase. From the experiment the waste water from the industries shows the higher concentration of THMs directly proportional to the chlorine dose. From the graph show the content of THMs in has higher concentration at 99.1 $\mu\text{g/L}$

4.5 Identify the concentration of THMs Contact with different of time

TABLE.4.3 The total of THMs contact with time at room temperature

time (minute)		30	60	120
tap water	chloroform	0	454	0
	BDCM	0	165	0
	bromoform	0	245	875
total THMs(area)		0	864	875
THMs in tap water (5ppm)($\mu\text{g/L}$)		0	0.019	0.019
waste water institute	chloroform	5346	5785	25447
	BDCM	0	0	0
	bromoform	0	678	5789
total THMs		5346	6463	31236
THMs in waste water institute (5ppm)($\mu\text{g/L}$)		0.12	0.14	0.67
waste water industries	chloroform	25345	34668	34789
	BDCM	0	0	1674
	bromoform	17667	768	25468
total THMs		43012	35436	61931
THMs in waste water industries (5ppm)($\mu\text{g/L}$)		0.93	0.76	1.33

TABLE 4.4 The area of standard are measured based on different concentration

concentration	standard peak area		
	5	20	50
chloroform	65438	84500	165345
BDCM	92354	107654	210034
bromoform	74567	95647	227657
total	232359	287801	603036

Based on the equation (4) the concentration waste water industries are calculated.

$$\begin{aligned} \text{Concentration of THMs } (\mu\text{g/L}) &= \frac{\text{sample peak area (61931)}}{\text{standard peak area (232359)}} \times \text{concentration of standard (5)} \\ &= 1.33 (\mu\text{g/L}) \end{aligned} \quad (9)$$

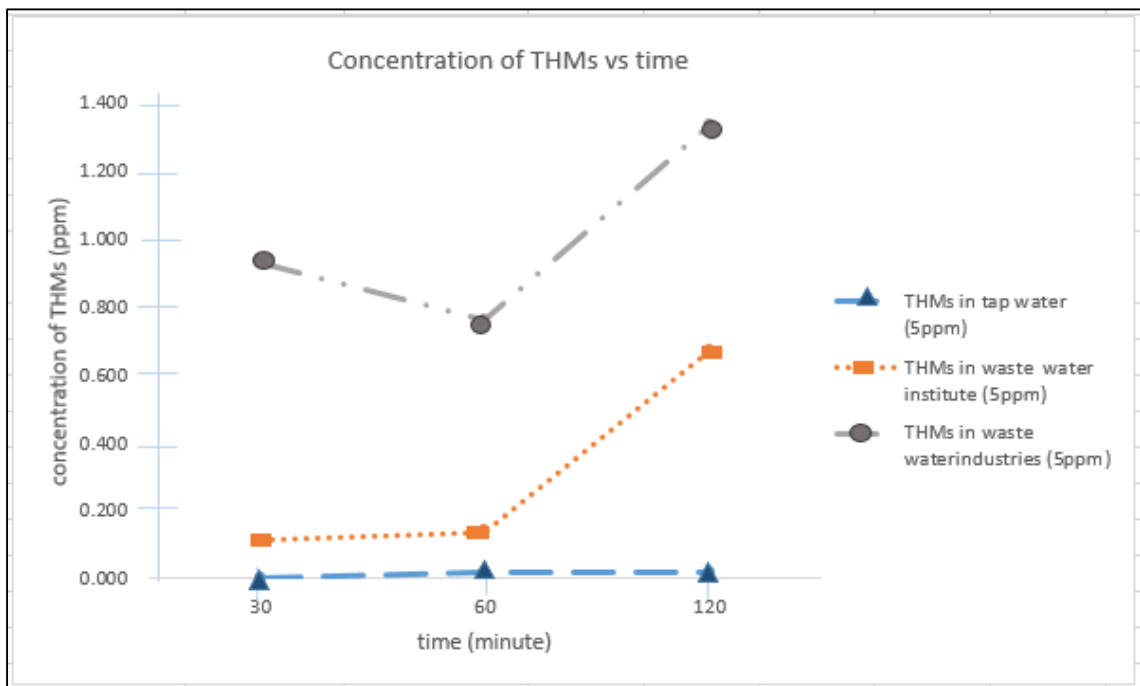


FIGURE 4.13. The concentration of THMs contact with time

Table 4.13 show the sample are exposed to the different of time. Using equation 4 to calculate the total concentration THMs are present. From the graph the total of THMs are measured are lower than the other sample such as waste water institute and waste water industries. The higher concentration is 1.33 $\mu\text{g/L}$ from the waste water industries that exceed the standard limit due to chlorine much higher due to treatment

process so the total of THMs are produces also increase. The 5ppm of chlorine are identify but the different of time are measured. The standard in drinking water the concentration of tap water are allowed is less than 1.00 mg/L. The standard concentration are using is 5 instead using 20 ppm and 50 ppm because the 5 ppm is the lowest concentration from the standard limit.

The concentrations of THMs compounds varied among the treatment plant. Levels of THMs are generally higher in treated water originating from surface water rather than groundwater because of the higher organic matter in the former. Levels of THMs can increase as the chlorinated water moves from the water treatment plant through the distribution system, because of the continued presences of a chlorine residual. During the treatment process the chlorine will react with the other component to form THMs.

4.6 Identify the concentration of THMs with the different temperature

THMs are exposed to the different of temperature. For the 30 minute the THMs are produce lower than the 60 minute and 120 minutes. The reaction between chlorine will take several time to produce THMs. Using the equation 4 to calculate the concentration of THMs.

TABLE 4.5 The THMs effect contact with different temperature

temperature, C		30	60	90
tap water	Chloroform	0	875	12674
	BDCM	0	457	456
	bromoform	0	1040	543
	total	0	2372	13673
THMs total		0	0.05	0.29
waste water institute	Chloroform	0	0	18956
	BDCM	0	21658	6548
	bromoform	0	5886	22682
	total	0	27544	48186
THMs total		0	1	1
waste water insdustries	Chloroform	0	967	14879
	BDCM	7637	87345	4867
	bromoform	0	16766	187534
	total	7637	105078	207280
THMs total		0.164	2.261	4.460

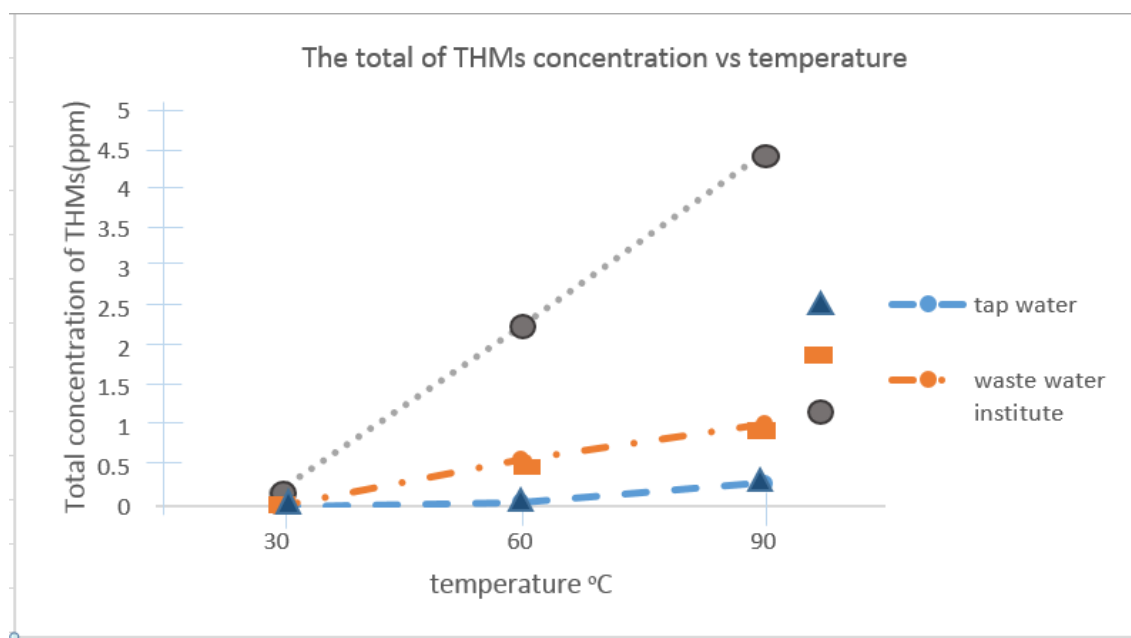


FIGURE 4.14. The concentration of THMs contact with different of temperature.

From the graph 4.14 show the THMs directly proportional to temperature increases. Each of the sample after 1 hour are exposed to the different temperature are analyze using the GCMS. The result shows that the sample of waste water industries the THMs concentration increases (4.46 $\mu\text{g/L}$) with temperature. Bromoform and chloroform, are easily absorbed by both the body and the environment. They typically enter the environment through disposal of the disinfected water, or as vapor because of their volatility. Vapors can remain in the air with a half-life of one to two months.

At the surface of the water, the halo forms decompose slowly due to the greater availability of oxygen. Under anaerobic conditions, commonly found in underground water sources, degradation of these molecules occurs more rapidly. Although these compounds are mobile in soil and seep into ground water, there is no evidence of their bioaccumulation in fish. Likewise, it is easily enter the human system through inhalation, absorption, and ingestion, but 50-90% is removed within eight hours. The tri halo methane may occur at the warm temperature. This is can mitigate DBP formation unless chlorine dosages are increased to maintain high residuals. The activity of microbial is lower and DBP formation reaction getting slower at the lower temperature. Since the boiling of THMs is greater than the boiling of water, so THMs will not eliminate due to the temperature.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

As for the conclusion, the objective for this project is to identify the temperature effect of THMs Contact of Tap Water in Perak Tengah Regions. Liquid- liquid extraction of gas chromatography is the method that can be used to measure contain of chlorine and THMs. There are several concentration and temperature of tri-halo methane to identify the characteristic each type of THMs. To avoid the formation of THMs all the precaution of formation such pH, concentration, time, chlorine dosing.

The chlorine dosing and time is the major factor of THMs formation. The rate of formation of THMs increases with the increasing of the temperature. The higher concentration are measure at waste water industries 4.46 $\mu\text{g/L}$. So the THMs may occur at the warm temperature. This is can mitigate DBP formation unless chlorine dosages are increased to maintain high residuals. The activity of microbial is lower and DBP formation reaction getting slower at the lower temperature.

As conclusion the result shows the tap water under the standard regulation for the drinking water. This can show that the tap water are save to use. While for the waste water institute shows still under the standards regulation due to the total chlorine present is low. Waste water industries shows the highest concentration from the standard regulation. So to avoid the health issues the waste water must be treat to kill the THMs. This is to ensure no THMs will be exposed to the environment.

5.2 Recommendations

During the experiment are conducted be careful with the sample preparation and have to extract cleanup, proper injection technique, and suitable analytical columns and standards will improve the results. When problems occur, using proper troubleshooting and maintenance techniques can quickly re-establish system integrity. The viability of chemical and equipment need to be improvement to avoid any problem during the period of the project.

Every causes can be to avoid using some precaution. Anyone drinking tap water should use some form of carbon filtration designed to reduce exposures to tri halo methane, halo acetic acids and other water treatment contaminants. This is to ensure that can reduce the causes for the several effect due to the contaminant. Carbon filtration systems come in various forms, including pitchers, faucet-mounted attachments and larger systems installed on or under countertops. Prices vary. They may be deceiving, because different systems require filter replacement periodically.

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