

VALIDATION OF THE INFLUENCE OF CHLORINE DOSAGE IN LABORATORY-BASED MODEL FOR THE PRODUCTION OF CHLORINE DISINFECTANT BY-PRODUCTS IN DISTRIBUTION PIPES

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Abstract:

The need for safe and potable water is a basic need for every living entity and is now a global concern, necessitating an examination of the occurrence of Trihalomethanes (THMs) and Trihaloacetic acids (THAAs), two significant chlorination disinfectant byproducts (DBPs) in high-density polyethylene (HDPE) and G.I water distribution systems. This study entailed the identification and quantification of these disinfection byproducts (DBPs), thereafter addressing the occurrence of two prominent DBPs i.e. Trihaloacetic acids and Trihalomethanes in a controlled chlorine attempt in laboratory controlled prototype model. This prototype model matches and represents the original field-based water distribution network on the ground. This study sought to evaluate and compare the occurrence of chlorine DBPs considering the differences in production based on chlorine dosage and the properties of pipe materials. Gas chromatography-mass spectrometry (GCMS(ECD)) was utilized for the study of DBP, and laboratory-based distribution models were implemented. This study provides significant insights into the dynamics of THMs and THAAs in water distribution networks, presenting strategies for minimizing these DBPs and so enhancing the objective of delivering safer drinking water in these systems.

Keywords: Chlorination Disinfectant Products (DBPs), Laboratory-based prototype model, Chlorine Controlled Dosages, Trihalomethanes, Trihaloacetic acids.

1. Introduction:

Clean water is a basic need of life[1] and is fundamental for sustaining life, and a sufficient, safe, and accessible supply must be made universally available [2]. The distribution of global freshwater is inequitable, impacting two billion individuals in water-scarce nations[3]. The World Health Organization (WHO) characterizes "safe drinking water" as water that presents no substantial health hazards during a person's lifetime of consumption[4]. The WHO reports that in developing nations, 80% of all human diseases are linked to biological or chemical water contamination[4]. Approximately 2.3 billion individuals globally are at risk of waterborne diseases due to insufficient access to appropriately managed drinking water supplies and poor sanitation infrastructure[3]. The UNICEF Joint

Monitoring Program (2000-2017) indicates minimal global advancement in water quality, with merely a 10% increase in access to safe drinking water and a 16% rise in managed sanitation services[5]. Urgent research is essential for a thorough understanding of exposure and health effects from contaminant mixtures in drinking water[6]. Global attention has been devoted to the importance of safe potable water, whereas DBP has gained attention worldwide as a serious issue.[7]. In Pakistan, around 30% of illnesses and 40% of fatalities are ascribed to inadequate water quality. Literature suggests that waterborne infections constitute between 0.6-1.44% of the nation's Gross Domestic Product (GDP) loss according to[8]. Although chlorination is the most prevalent method for purifying water, it has notable drawbacks; prolonged exposure can lead to cancer owing to the formation of disinfection byproducts (DBPs), which adversely affect the kidneys, liver, and other bodily functions[9]. The principal factors contributing to the formation of disinfection byproducts (DBPs) include anthropogenic contaminants, algal organic matter, and natural organic matter.[10].

Chlorine and chloramine are extensively utilized for the disinfection of drinking water owing to their efficacy in combating waterborne infections[11]. Nonetheless, apprehensions stem from the emergence of disinfection byproducts (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs), recognized as possible hazards due to their teratogenic, carcinogenic, and mutagenic characteristics since their identification in 1974[12]. The creation of chlorine disinfection byproducts (DBPs) mostly results from the presence of natural organic matter, algal organic matter, and anthropogenic pollutants[10]. To ascertain chlorine residual, which significantly influences the formation of disinfection byproducts (DBP). Trihalomethanes and haloacetic acids are the principal categories of CDBPs; other groupings include halogenated nitrites, halo ketones, and chloropicrin. The potable water distribution system often employs ductile iron (DI), polyethylene (PE), and stainless steel[13]. Chlorine dioxide (ClO₂) is increasingly preferred due to its diminished formation of THMs and THAAs, and new research indicates a reduction in developmental toxicity relative to chlorine, suggesting its viability as an environmentally sustainable water treatment disinfectant[14]. The average concentrations of THM range among various countries, spanning from zero to 1000 mg/L[15]. Permissible limitations have been established in several places globally due to potential health risks. In Nigeria, the concentrations in treated water samples have been recorded to vary from zero to 95 mg/L[15]. In the United States, research indicated that finished water included amounts of up to 18 mg/L of disinfection byproducts (DBPs), whereas distribution systems demonstrated values of up to 22 mg/L of DBPs in distribution networks[16]. The average concentrations of THMs and THAAs in China throughout the treatment period were 19.9 mg/L and 3.4 mg/L, respectively[17]. This indicates that the concentrations of THMs and THAAs in the water distribution system demonstrate regional variability[18]. The U.S. EPA regulates chlorination concerning disinfection byproducts (DBPs) such as THMs and THAAs. A survey of 500 significant U.S. drinking water facilities revealed midpart per billion concentrations of trihalomethanes (THMs) and trihaloacetic acids (THAAs) in chlorinated water[19]. In the last forty years, many chemical and inorganic substances, both halogenated and nonhalogenated, have been recognized as disinfection byproducts in addition to THMs and THAAs.

China's standards (GB5749-2006) establish different maximum contaminant levels for trihalomethanes (THMs) and trihaloacetic acids (THAAs)[20]. The potable water quality in the twin metropolis cities of Rawalpindi and Islamabad, Pakistan, is deemed inadequate for human consumption[21]. The study determined that merely 25% of the population has access to potable water nationwide. A significant portion of the region experiences unregulated chlorination by unqualified personnel, potentially resulting in the excessive generation of THMs in chlorinated potable water[21]. Nevertheless, as indicated by[21], there is now an absence of a thorough literature review or study assessing the occurrence of THMs in the drinking water sources of the twin towns of Rawalpindi and Islamabad. The absence of study may impede the formation of a robust basis for further inquiries. The study conducted by[21] reveals that Islamabad has elevated levels of total THMs in comparison to Rawalpindi. Although essential for eliminating infections, chlorination results in unwanted disinfection byproducts (DBPs) due to chemical interactions with organic substances in water[22]. [23] the investigation found that the degradation parameters of chlorine walls in cement-lined cast iron pipes initially diminish and subsequently grow over time. This indicates that iron corrosion escalates with age, resulting in increased consumption. Nevertheless, the paper lacked any experimental work or a credible model to substantiate this result. This concept contrasted the findings of the study conducted by [24], which established that the walls of newly produced PVC pipes do not significantly affect chlorine consumption. Plastic pipes have become the dominant material for various supply networks due to their remarkable flexibility, corrosion resistance, and jointing capabilities. Nonetheless, it is crucial to acknowledge that these pipe materials substantially influence the production of disinfection byproducts (DBPs)[25]. The features of source water, shaped by geological factors, watersheds, and bromide concentration, affect the generation of disinfection byproducts (DBPs). Various disinfectants yield different types of disinfection byproducts (DBPs), with chlorine producing carbonaceous DBPs

(C-DBPs) and chloramine resulting in nitrogenous DBPs (NDBPs)[26]. The research conducted by [27] and [28] both noted a substantial reduction in the concentrations of free and total chlorine residual in water distribution systems as the residence time rose. A total of 350 pipe sections were analyzed in the study done by [23] for experimental purposes. The selection of these pipes was based on their age, encompassing both newly installed and older pipes of diverse ages. The water supply employed in this investigation was obtained from desalination facilities. The research [23] indicates that the reduction of chlorine in a pipe is due to two factors: the transfer of mass from the bulk to the pipe wall surface and the chemical reaction with the pipe wall surface. A study revealed that THMs were primarily found in GI pipes[29]. The formation of THAAs was not influenced by the materials employed in the pipes. The investigation also revealed the existence of undesirable nitrogenous disinfection byproducts (DBPs). One study[30] indicated that the concentration of THAAs in the four pipe loop systems was arranged in the following order: HDPE surpasses PP, which in turn exceeds PVC and GS, owing to multiple influencing factors. Another study identified by [31] indicates that disinfection byproducts (DBPs) escalate with the growing width of the pipe. Pipe materials significantly impact the formation of disinfection byproducts (DBPs) and biofilms. The diverse composition of biofilms results in differences in their physical characteristics, including thickness, surface roughness, and porosity. These disparities may influence the transfer and infiltration of disinfectants[32]. Diverse techniques, such as gas chromatography (GC), liquid chromatography (LC), and ion exchange chromatography, are employed to identify disinfection byproducts (DBPs) in water. Gas chromatography, utilizing detectors such as electron capture detectors or mass spectrometry, is appropriate for recognized disinfection byproducts, however liquid chromatography coupled with mass spectrometry is proficient for polar and high-molecular-weight disinfection byproducts. Total organic halide (TOX) study measures both identified and unidentified disinfection byproducts (DBPs)[33]. An independent analysis demonstrated that the formation of various DBPs depends on numerous significant factors [34]. The dosage of chlorine is 1. 2. Temperature 3. pH 4. Contact duration 5. Organic matter content 6. Composition of water. Identifying geographical and temporal differences in the formation of THMs and THAAs under different chlorine dosages is crucial due to their potential effects on water quality[35]. Various pipe materials can affect the generation of disinfection byproducts (DBPs) in drinking water distribution systems[36]. Biofilms on pipe walls primarily comprise bacteria, corrosion byproducts, and inorganic deposits. Research demonstrates that biofilms on pipe walls, cultivated in filtered water, possess a greater capacity for the formation of THMs than filtered water alone after 48 hours of exposure to a chlorine concentration of 4 mg/L[36]. Biofilms on pipe walls affect the delivery and reactivity of disinfectants, hence impacting the generation of disinfection byproducts (DBPs)[37]. Research indicates elevated levels of trihalomethanes (THMs) in simulated pipelines compared to glass bottles, suggesting the presence of THM precursor components on the inside surfaces of the pipes. Initial findings indicated no substantial change in total haloacetic acids (THAAs); however, a recent study implies potential HAA development inside biofilms on tube walls. Pipelines enveloped in biofilm demonstrate increased chlorine utilization and THM generation, highlighting the necessity to mitigate DBP hazards stemming from biofilm on pipe walls. Comprehending the geographical and temporal variations of THMs and THAAs aids in adjusting chlorine dosages to reduce DBP production. By analyzing these changes, water treatment facilities can customize disinfection methods to certain pipe attributes, hence minimizing the likelihood of increased DBP levels[38].

This targeted approach contributes to ensuring compliance with water quality standards and minimizing potential health risks associated with DBPs in the water supply[39]. [40] study on ductile iron pipes revealed higher THMs and THAAs formation linked to DBP precursor matter on the pipe wall. According to [41], an investigation was conducted to examine the seasonal and regional fluctuations in the production of THM and THAAs across three distinct water distributions, and this experiment was done to assess the seasonal and regional changes in the production of THM and THAAs across three unique water distributions. Five sampling sites were designated for sample collection. Two locations were selected following filtration and chlorination, whereas three locations were selected subsequent to the distribution line flow. Gas chromatography with an electron capture detector (GC-ECD) was utilized to quantify THM, adhering to the U.S. Environmental Protection Agency Method 551.1 with several alterations.

The study area, which includes the Mardan region, provides a foundation for a comprehensive examination of the presence of disinfection byproducts (DBPs) in water distribution systems. This discovery is significant due to the potential health dangers linked to disinfection byproducts (DBPs), especially their carcinogenic properties. This study approach encompasses three primary domains: identification, quantification, and the development of validation understanding. The study was conducted in District Mardan, situated at the geographical coordinates of 34°05' N to 34°32' N and 71°48' E to 72°25' E. District Mardan is acknowledged as a core district in the Khyber Pakhtunkhwa province of Pakistan. The research area is divided into three distinct zones based on groundwater hydrology: the

urbanized/industrial zone, which includes Shergarh and Takhtbhai, and the non-industrial zone, known as the Surkhabi control region. The district is divided into three separate zones: Zone 1, Zone 2, and Zone 3, as illustrated in Figure 1. The industrial zones predominantly comprise industrial operations, including car wash facilities, commercial markets, and other manufacturing processes. Conversely, restricted or nonindustrial zones include human activities unrelated to industrial or commercial operations.

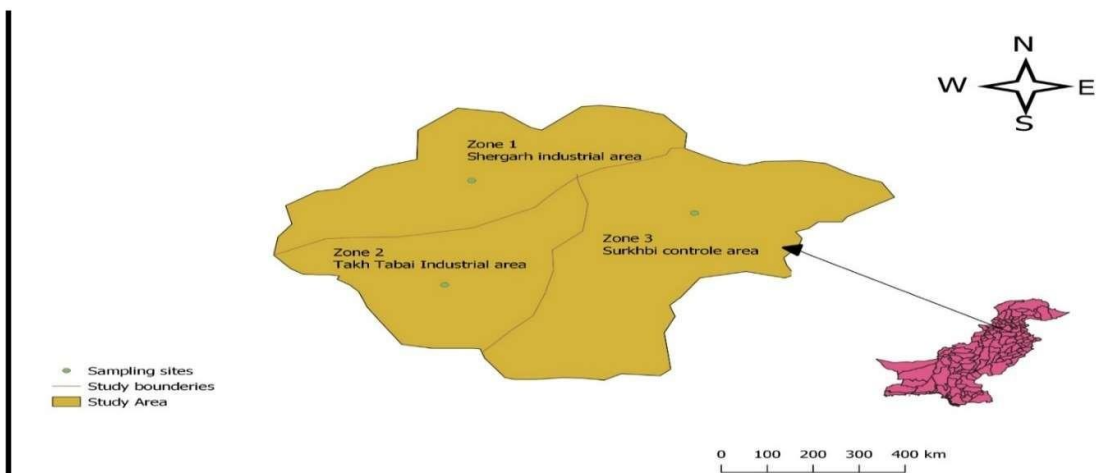


Figure 1 Study Area Division

For identification and quantification, a total of three samples were chosen from each of the three zones under the district jurisdiction. The investigation of each sample was conducted using controlled amounts of chlorine. To simulate the continuous flow of water in distribution pipes under regulated conditions, a laboratory-based model was constructed to duplicate the flow of a large water supply network in HDPE-type cum G.I. nature pipes. The measurement of trihalomethanes and trihaloacetic acids was conducted under headspace conditions. The experimental setup involved the utilization of (GC-ECD) while maintaining regulated settings.

2. Methodology

2.1 Materials

Calcium hypochlorite, in granular powder form, was obtained from the water quality laboratories of the Public Health Engineering Department in Khyber Pakhtunkhwa, Pakistan. THMs and THAAs, two standardizing chemicals for DBPs, were obtained from Standard Sales in Pakistan. Ethyl acetate, a liquid-liquid separator, was obtained from the Public Health Engineering Department KP for the purpose of separating solute and solvent. The distilled water was obtained from the water quality laboratory of the Public Health Engineering Department in Khyber Pakhtunkhwa, Pakistan, for the purpose of cleaning pipe networks.

2.2 Sampling Zone

A multi-staged random sampling technique is employed to provide coherent sampling over all three zones of District Mardan Region, which is the second-largest district in Pakistan's KP Province. To detect and quantify the production of Chlorination DBPs, primary sampling units (PSU) were chosen for each of the three regions, specifically two from industrial areas and one from regulated zones. Water from the ground source was chosen for distribution in these three district zones, with which elevated head tanks or overhead reservoirs were employed to provide head elevation and deliver it to the consumers. The intake source for all inputs was groundwater, sometimes known as tubewell. Nearly all groundwater sources exhibited a groundwater potential below 300-400ft, with a static water level ranging from 60-100ft. The mean yield of the tubewell ranged from 20 to 25 feet, whereas the mean flow rate of each groundwater source was around 0.00315 m³/s to 0.00526 m³/s. To conduct the sample analysis, it was necessary to have tubewell water that was at least 10 years old and had a distribution network spanning at least 5 kilometers. Additionally, all water samples were obtained at terminal or end-user points.

2.3 Setup

A considerable quantity of glassware was employed during the study for all sampling objectives. The unique sampling medium was purified with detergents, rinsed with tap and ultrapure water, and subsequently placed in an oven at 150°C for 1-2 hours. The sampling procedure involved the collection of samples in 100ml amber glass vials equipped with polypropylene screw tops and TFE-faced septa. Furthermore, to facilitate a comprehensive examination, the vials were carefully filled to avert the inclusion of air bubbles.

A pilot-scale laboratory model of a water distribution system was developed to facilitate adjusting chlorine dosages, as illustrated in Figure 2. This system integrates loops made of HDPE with supporting galvanized iron pipes. Each loop was around 5 to 10 feet in length, with a pipe diameter of 1 inch. The loops were fitted with ball valves, elbows, unions, and sockets to analyze the properties of water and control water pressure and velocity. Furthermore, they have been utilized to channel the water flow in the intended direction. The water's velocity was controlled between 0.2 m/s and 1.8 m/s. A centrifugal pump with a power output of 0.3 HP was employed to maintain a continuous water flow. A reservoir holding 50 gallons of water is promptly supplied with samples from the site within the distribution network. The Public Health Engineering Department KP employed a mobile water quality testing laboratory to gather water samples from several zones for the assessment of temperature and sunlight exposure. Before the introduction of the water sample into the pilot-scale laboratory distribution system, an extensive purging of the system was performed with ultrapure water for 30 minutes to eradicate any remaining pollutants. The distribution network methodology comprises four elements: flushing, parameter correction, chlorination dosing, and sampling. After the purification process with uncontaminated water, the samples were placed into a 50-gallon reservoir and subjected to suction via pumping mechanisms. The water flow from each loop demonstrated consistency and uninterrupted velocity, hence guaranteeing equal opportunities for particle mixing with the incorporation of chlorine doses. After achieving a stable flow, chlorine dosages of 0.2 mg/L, 1.8 mg/L, and 2.4 mg/L were administered for each trial. Zone 1 exhibited a concentration of 0.2 mg/L, zone 2 recorded 1.8 mg/L, and zone 3 measured 2.4 mg/L. THMs and THAAs were effectively recognized and measured at different chlorine concentrations.

The determination of the minimum velocity is established by the Reynolds number (Remin), and as stated in the U.S. EPA/CR guidance, the suggested range for Re min is between 0.5 and 1.0 [42]. Before determining the produced DBPs, a slight modification was done in EPA method 551.1 [43], which includes liquid-liquid extraction (LLE) with Ethyl Acetate instead of MTBE due to environmental concerns as mentioned in [43]. The consequences of MTBE prevail in the environment and specifically in drinking water [44]. The separation occurred after the sample completed the distribution/rotation in the prepared water distribution model pipes in the laboratory. To do (LLE), a separating funnel was employed, adhering to the procedural specifications of a 1:2 ratio between the solute and solvents. In this instance, the solutes consisted of THMs and THAAs. The ethyl acetate solvent was used to separate the solute and solvent. The separation process began by placing the solute and solvent partially and mixing/shaking for 5 minutes. Then, 10 ml of solvent (separator) was added, followed by constant shaking for 5 minutes. This process was repeated 5 times, resulting in a 100 ml sample separation. 50 ml of solvent (separator) was added with 5-minute shaking intervals. The LLE technique was employed to separate the funnel into two distinct layers. Subsequently, water was extracted from the solute using a funnel dropper, leaving behind the solute as the residual.

Gas Chromatography-Mass Spectrometry (GCMS-5977B AGILENT TECHNOLOGIES USA) Analytical conditions as shown in Table 1, were employed to identify THMs and THAAs, as per the guidelines set forth by the Environmental Protection Agency (EPA) in 55.1. The column consisted of fused silica capillary DB-1 with dimensions of 30m ± 0.32 mm i.d. and a film thickness of 0.25µm. Helium (99.99% pure) was employed as the carrier gas, while nitrogen (99.99%) served as the makeup gas as shown in Figure 3.



Figure 2 Prototype Model Setup

Table 1 Analytical Conditions of Gas chromatographic-mass Spectrometric Determination of DBPs

S.no	Nomenclature	Details	S.no	Nomenclature	Details
1	Run Time	36 mins	16	Total Flow	On 24mL/min
2	Post Run Time	0 mins	17	Septum Purge	On 3mL/min
3	Oven Temperature	70°C	18	Gas Saver	Off
4	Hold Time	3 mins	19	Split Ratio	20:1
5	Post Run	50°C	20	Split Flow	20mL/min
6	Temperature Rate	10°C/min	21	Thermal annex(initial)	280°C
7	Equilibrium Time	2 mins	22	Post Run	0°C
8	Max Temp	300°C	23	Column 1 Flow	On
9	Slow Fan	Disabled	24	Initial (Post Run)	1mL/min
10	Mode	Split	25	Column	DB-1
11	Heater	On 250°C	26	Length	25mX0.250mmx0.25um
12	Pressure	On 8.805 psi	27	Gas Used	Helium
13	Jet Cleaning	No Clean	28	Scan Low Mass	30
14	Solvent Delay	2 mins	29	Scan High Mass	650
15	Scanning	Norma	30	Threshold	150



Figure 3 GC-MS used for qualification and quantification of chlorine DBPs

3. Results

To obtain occurrence results of Chlorine DBPs [40] made a sequence-wise batch supply of chlorine dosage for the water distribution network model and observed the production weightage/variations accordingly against chlorine-controlled dosages supplied. The proportion of detected DBPs varied among the water samples from zone 1, zone 2, and zone 3. The identification of essential parameters for the production of DBPs was conducted for each water sample, average range of parameters is presented in Table 2. The study was performed sequentially, starting with a concentration of 0.2mg/L, then 1.8mg/L, and finally 2.4mg/L. Initially, for chlorine dosage of 0.2 mg/L, no focused elements DBPs i.e. Trihalo acetic acids and Trihalomethanes were traced rather than any other of their family derivatives. Water Sample Parameters for Zone 1 including pH, DO, Turbidity, TOM, and Temperature were traced out separately.

Table 2 Water Parameter Range for All Samples Taken

S. No	Parameters	Range	S. No	Parameters	Range
1	pH	7.2-7.8	5	Temperature	30-38 °C
2	DO	5-5.7 mg/L	6	Hardness	Soft water
3	Turbidity	1-3 NTU	7	Total Organic Matter	1.8-2.2mg/L
4	Taste	Fair			

For zone 2 with enhancement in chlorine dosage to 1.8mg/L sample, for searching of chlorine DBPs the sample was investigated under GC.MS (ECD) for about 5-6 hours and it couldn't be discovering any halogenated Chlorine DBPs but rather any of their family members. This non-tracing of none of any members of THMs or THAAs in even the second sample from zone 2 diverts our results towards the lesser amount of Chlorine DBPs production in the HDPE cum G.I nature pipe medium due to a lesser amount of reaction between pipe material and water sample in presence of organic matter this no identification of DBPs family elements also diverts our attention towards the issue of lesser contact time of pipe nature reaction with chlorine and precursors due to smooth surface this make the sense of lower production.

The zone 3 water sample with 2.8 mg/L chlorine dosage with, focused halogens family members including trichloroacetic acid and trichloronitromethane was traced with peak number 2 at 4.340 mins. The other elements traced at peak number 3 were carbon tetra chloride, at peak number 4 phthalic anhydride, at peak number 5 hexadecanoic acid, at peak number 6 hexadecanoic acid, at peak number 7 octadecanoic acid, at peak number 8 methyl stearate, at peak number 9 Bis phthalate were identified. The identification of both chlorine DBPs trichloroacetic acid and trihalomethanes or their family members for zone 3 under GC.MS (ECD) were traced for zone 3 majority due to increased dosage of chlorine content under known water

parameters as shown in Figure 4. However, it has been found that for chlorine dosage of 2.8mg/L about 0.2mg/L THAAs were quantified as a result and about 0.167 mg/L THMs were found after running under a controlled environment and HDPE pipe medium as shown in Figure 5.

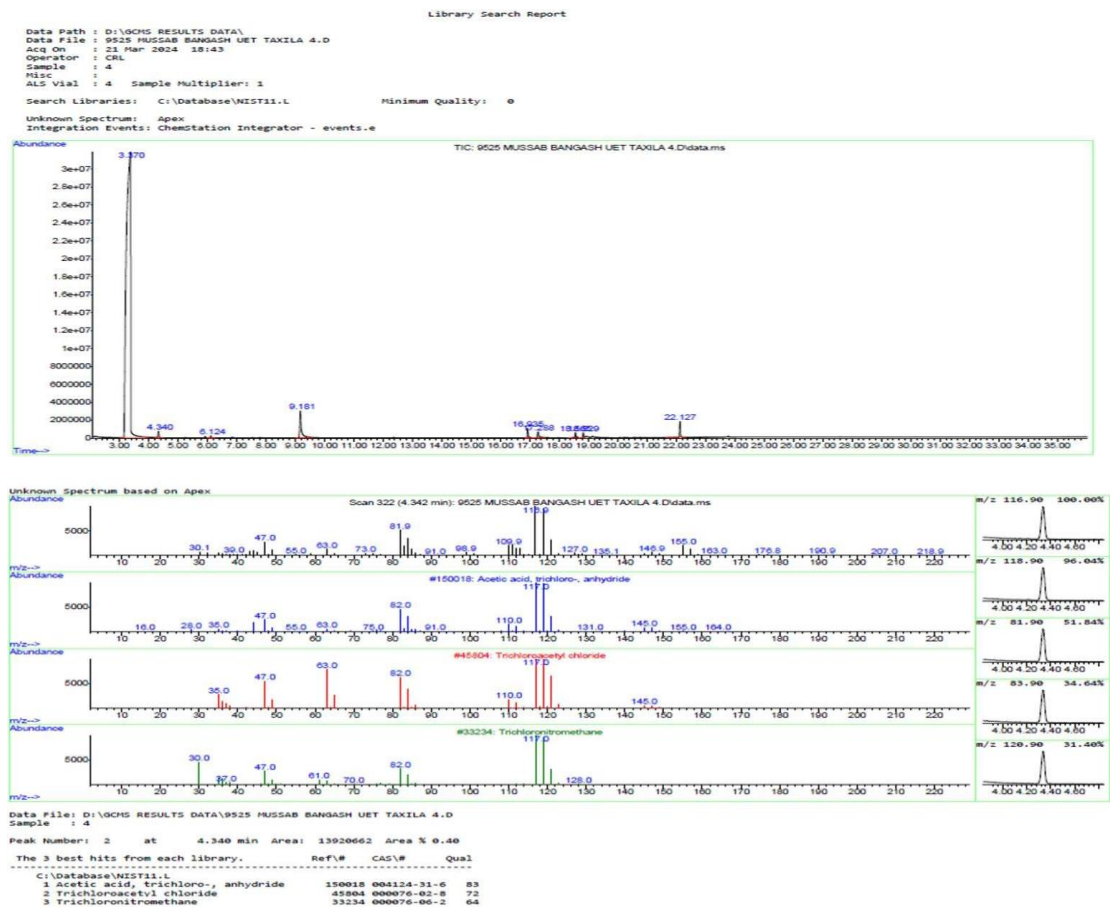


Figure 4 (a) Obtained Chromatogram for Zone 3 Water Sample (b) Obtained Mass Spectrometry for traced DBPs for Zone 3 Water Sample.

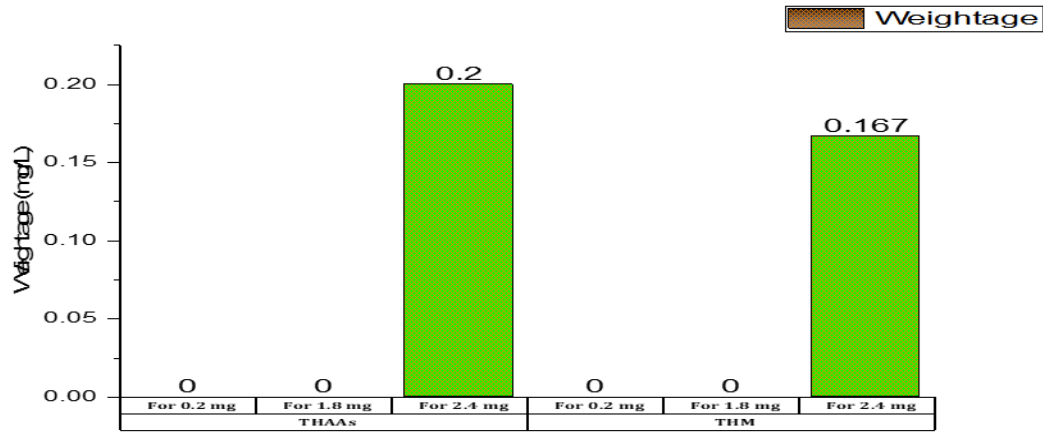


Figure 5 Founded THAAs and THMs for Different Chlorine Dosages

The quantification of prominent DBPs capacity was assessed and compared using eq.1. The traced element eq.3 was generated by using based on eq.2.

$$TTHMs + THAAs = \text{prominent chlorine DBPs} \quad (1)$$

$$\text{Chromatogram Peak Height} \propto \text{Chromatogram Peak Area} \quad (2)$$

$$TE \text{ Peak Height (TE mg/l)} =$$

$$\frac{SR \text{ Element Area} \times TE \text{ Peak Height}}{SR \text{ Element Peak Height}} \quad (3)$$

4. Conclusion

Examining various regulated chlorine dosages reveals a tendency to increase chlorine quantities, which correlates with a more pronounced detection of chlorine disinfection byproducts (DBPs) and a proportional boost in quantification, particularly observed at dosages of 0.2 mg/L, 1.8 mg/L, and 2.8 mg/L. The behaviors of identification and non-identification varied based on the characteristics of the pipe media and other significant water quality factors, including pH, hardness, dissolved oxygen, turbidity, discharge, and flow duration. It has been determined that enhancing chlorine dose about pipe characteristics exhibits intricate natural behavior, resulting in fluctuations in production following the addition of chlorine. The detection of significant THMs and THAAs further supports their abundant presence, attributable to their notable characteristics and generation potential when oxidizing agents such as chlorine interact with other organic elements in water samples.

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