

FACTORS AFFECTING THE FORMATION OF TRIHALOMETHANES DURING
WATER CHLORINATION: A BENCH-SCALED STUDY

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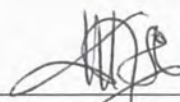
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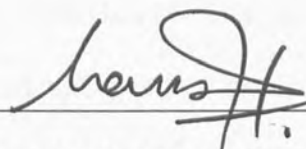
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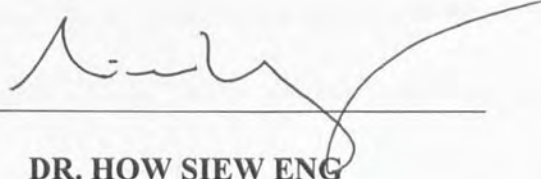
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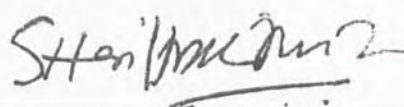
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ABSTRACT

This study aimed to evaluate the role of chlorine dose, temperature and contact time on the formation of THMs as a result of chlorination of swamp water. All samples were extracted using purge-and-trap (PAT) technique followed by determination of trihalomethanes by gas chromatography-electrolytic conductivity detectors (GC-ELCD). Pearson correlation was applied during data analysis. Concentration of trihalomethanes increased progressively as chlorine dose increased from 2 mg/L to 8 mg/L with strong relationship between them. The relationship between temperature and trihalomethanes was weak. The reaction rate of trihalomethanes formation increased as temperature increased from 4 °C to 35 °C but showed a decreased at 25 °C. Increase in contact time from 4 hours to 12 hours showed strong relationship with trihalomethanes except bromodichloromethane. This result indicated that presence of trihalomethanes in water was exclusively due to chlorination.



**FAKTOR MENYEBABKAN PEMBENTUKKAN TRIHALOMETANA SEMASA
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ABSTRAK

Kajian ini bertujuan untuk menilai peranan dos klorin, suhu dan tempoh tindak balas dalam pembentukan trihalometana semasa hasil daripada pengklorinan air paya. Kesemua sampel diekstrak dengan menggunakan teknik purge-and-trap (PAT) diikuti dengan penentuan trihalometana dengan kromatografi gas dengan penunjuk electrolytic conductivity (GC-ELCD). Korelasi Pearson digunakan dalam analisis data. Peningkatan kepekatan trihalometana adalah berkadar langsung dengan peningkatan dos klorin dari 2 mg/L ke 8 mg/L dengan hubungan yang kuat antara mereka. Hubungan antara suhu dan trihalometana adalah lemah. Kadar tindak balas pembentukan trihalometana meningkat dengan peningkatan suhu dari 4 °C hingga 8 °C tetapi menunjuk penurunan pada suhu 25 °C. Peningkatan tempoh tindak balas dari 4 jam ke 8 jam menunjukkan hubungan yang kuat dengan trihalometana kecuali bromodiklorometana. Keputusan ini menunjukkan bahawa kehadiran trihalometana dalam air adalah berpunca daripada pengklorinan.



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LIST OF SYMBOLS

$\mu\text{g/L}$	Microgram per litre
Mg/L	Miligram per litre
kPa	kilopascal
$^{\circ}\text{C}$	Degree Celsius
%	Percentage
mL	Millilitre
L	Litre
cm	Centimetre
km	Kilometre
mg	Milligram
h	hour
$\mu\text{S/cm}$	Microsiemens per centimetre
NTU	Nephelometric Turbidity Unit
+/-	Plus or minus
w/v	Weight over volume
mg/L	Miligram per litre
N	Normality
ID	Internal diameter
TFE	Teflon faced silicone septa
DBPs	Disinfection by-products
THMs	Trihalomethanes

CHCl ₃	Chloroform
CHCl ₂ Br	Bromodichloromethane
CHClBr ₂	Chlorodibromomethane
CHBr ₃	Bromoform
TTHMs	Total trihalomethanes
EPA	US Environmental Protection Agency
WHO	World Health Organization
TOC	Total organic carbon
UV	Ultra-violet
NOM	Natural organic matter
THM-Br	Brominated trihalomethanes
GC	Gas chromatography
HPLC	High performance liquid chromatography
CE	Capillary electrophoresis
LLE	Liquid-liquid extraction
HS	Headspace
PTI	Purge and trap injection
PAT	Purge-and-trap
LPME	Liquid phase micro extraction
GC-ELCD	Gas chromatography-electrolytic conductivity detectors
VCHCs	Volatile halogenated hydrocarbons
HAAs	Haloacetic acids
EU	European Union



THMFP	Trihalomethanes total potential
IARC	International Agency for Research on Cancer
NaOCl	Sodium Hypochlorite
NaOH	Sodium Hydroxide
H ₂ O	Water molecule
HOCl	Hypochlorous acid
H ⁺	Hydrogen ion
OCl ⁻	Hypochlorite ion
HOBr	Hypobromite
NaOBr	Sodium Hypobromite
IPCS	International Programme of Chemical Safety
T_c	Critical Temperature



CHAPTER 1

INTRODUCTION

1.1 Research Background

Chlorination is a widely used method of disinfection where pathogenic or micro organisms in drinking water are deactivated by application of chlorine in order to ensure the residual concentration in drinking water distribution systems is harmless. In another word, it protects the regrowth of pathogenic or micro organism in drinking water. Disinfection is the most important stage in the treatment of drinking water in water treatment plant. Pathogenic or micro organisms are responsible for water borne diseases such as typhoid fever, cholera and dysentery. Chlorine is used for decades in disinfection as disinfection agent due to its proven effectiveness and inexpensive. Indeed, chlorination is used for most municipal water supply system in Malaysia for disinfection (Md Pauzi Abdullah *et al.*, 2003).

Although chlorination is cheap and effectively deactivate pathogenic or micro organisms, but its cause formation of disinfection by-products (DBPs) as side product. Among DBPs formed, trihalomethanes (THMs) are toxic and carcinogenic. Four main



trihalomethanes that responsible for the carcinogens risk are chloroform (CHCl_3), bromodichloromethane (CHCl_2Br), chlorodibromomethane (CHClBr_2) and bromoform (CHBr_3). Various researches are done on the THMs in drinking water by many scientists. Many countries have set the maximum contamination level for total trihalomethanes (TTHMs) in drinking water. US Environmental Protection Agency (EPA) has set $80 \mu\text{g/L}$ as TTHMs concentration in drinking water. On the other hand, European Union Legislation has set $150 \mu\text{g/L}$ until December 2008 and $100 \mu\text{g/L}$ thereafter as TTHMs concentration (Nikolaou *et al.*, 2004).

During chlorination, chlorine reacted with organic matters that naturally presence in water and cause formation of THMs by addition and substitution reactions. Humic and fulvic acid are the organic matter, the main precursor that usually measured with non-specific parameters like total organic carbon (TOC) or UV absorbance. Formation of THMs depend on few primary factors, that is raw water quality, type and concentration of natural organic matter (NOM), bromide ion concentration, chlorine form and dose, contact time, pH, alkalinity, temperature, and organic nitrogen concentration. Chlorinated THMs will continue to form as there is residual of chlorine in the water distribution system with the presence of organic matter until all the free chlorine is consumed. While for brominated THMs, its formation happened when presence of bromide due to oxidation by hypochlorous acid to yield hypobromous acid with residual hypochlorous acid. Its reacts with precursor organic compound which result in mixed chloro-bromosubstitution products. THMs also increase with the increase of temperature and pH. Formation of THMs decrease with decrease of ammonia concentration. Chlorinated and



brominated speciation THMs are mainly influenced by organic matter and bromide concentration in drinking water. For example, brominated THMs (THM-Br) increase with the ratio of bromide and TOC. On the other hand, formations of chloroform increase with TOC but decrease with bromide, while formations of CHBr_3 show the opposite behavior. CHCl_2Br and CHClBr_2 show the similar behaviors but they increase very quickly with bromide and slowly with organic matter. (Solini and Collivignarelli, 2004; Zoccolillo *et al.*, 2005; Juan *et al.*, 2006)

The determination of THMs is generally performed by chromatographic methods. The most used method are gas chromatography (GC), followed by high performance liquid chromatography (HPLC) and capillary electrophoresis (CE). There are number of techniques have been reported for analyze THMs in water, such as direct injection, liquid-liquid extraction (LLE), static headspace technique, dynamic headspace (HS) technique or purge and trap injection (PAT), solid phase micro extraction (SPME) technique and liquid phase micro extraction (LPME) technique (Nikolaou *et al.*, 2002).

All the technique has different recoveries, detection limit and effectiveness in determination of THMs in drinking water. For direct injection, although it is an attractive technique, but there is problem with column stability and critical temperatures for both column and injector. While PAT technique showed good result, but it is more time consuming. On the other hand, purge and PAT have relatively high detection limits from 0.1 to 0.04 $\mu\text{g/L}$ due to the low recoveries of analytes when cartridges are used as trap and this method is not specific for THMs determination. HS techniques is relatively less



sensitive compared LLE and headspace method only suitable to analyze sample with high concentration due to high detection limits from 0.05 to 0.2 $\mu\text{g/L}$. HS technique also have low recoveries (Nikolaou *et al.*, 2002).

The technique used in this study is purge and trap for gas chromatography-electrolytic conductivity detectors (GC-ELCD). GC-ELCD is an element-detective selection method for compounds containing halogen, nitrogen and sulphur. The high selectivity for halogen makes the detector suitable for analysis of halogen compounds in complex samples matrices such as environmental sample. PAT-GC-ELCD is a technique with lowest detection limit, ranging from 0.01 to 3 $\mu\text{g/L}$ and applicable concentration range of this method is also compound and instrument dependent and is approximately 0.02 to 200 $\mu\text{g/L}$ (Mu *et al.*, 1999, USEPA, 1995).

1.2 Objectives of Study

The objectives of this study were:

- a. to determine the extent of THMs presence in chlorinated swamp water
- b. to study the effect of chlorine dose, temperature and contact time on formation of trihalomethanes of chlorinated natural water by bench-scaled study



1.3 Scope of Study

Due to the diversity of this field, the scope of this study was to determine THMs only, and not the whole variety of DBPs. Out of the so many types of THMs, only four main trihalomethanes were studied, namely CHCl_3 , CHCl_2Br , CHClBr_2 and CHBr_3 . Compounds in these four main THMs are known as carcinogenic compounds in drinking water. Water samples are taken from swamp at Likas, Sabah as natural water. A bench-scaled chlorination experiment was conducted using swamp water from Likas, Sabah in order to investigate the effect of different factors on the formation of THMs. These factors were contact time, chlorine dose and temperature.



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