

CHARACTERIZATION TREATMENT AND REMOVAL OF TRIHALOMETHANE
PRECURSORS IN BANGKOK
SOURCE WATER



Mr. Bunyarit Panyapinyopol

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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วิธีการดูดติดผิวโดยใช้เรซินสามชนิด คือ DAX-8 AG-MP-50 และ WA-10 ได้ถูกนำมาใช้ในการจำแนกลักษณะของน้ำดิบจากโรงผลิตน้ำประปายางเขนเป็นหกกลุ่ม พบว่าปริมาณอินทรีย์คาร์บอนละลายน้ำเรียงลำดับจากมากไปน้อย คือ ไฮโดรฟลิคที่เป็นกลาง ไฮโดรฟอบิกที่เป็นกรด ไฮโดรฟลิคที่เป็นกรด ไฮโดรฟอบิกที่เป็นกลาง ไฮโดรฟลิคที่เป็นด่าง และ ไฮโดรฟอบิกที่เป็นด่าง ตามลำดับ ซึ่งสารอินทรีย์กลุ่มไฮโดรฟลิคที่เป็นกลาง และไฮโดรฟอบิกที่เป็นกรดเป็นสารอินทรีย์ของกลุ่หลักที่ก่อให้เกิดการก่อตัวของสารไตรฮาโลมีเทน (THMFP) ในแหล่งน้ำดิบ ในขณะที่สารอินทรีย์กลุ่มไฮโดรฟอบิกที่เป็นด่าง และไฮโดรฟลิคที่เป็นด่างเป็นกลุ่มที่เกิดปฏิกิริยาได้มากที่สุด โดยที่ความสัมพันธ์ในลักษณะเป็นเส้นตรงระหว่างความเข้มข้นของสารอินทรีย์แต่ละกลุ่มกับ THMFP ซึ่งบ่งชี้ว่าปฏิกิริยาของสารอินทรีย์แต่ละกลุ่มกับคลอรีนเกิดขึ้นเป็นแบบแปรผันตรง

การจำแนกลักษณะสารอินทรีย์ส่งผลให้เกิดการเปลี่ยนแปลงความเข้มข้นของโบรไมด์ในสารอินทรีย์แต่ละกลุ่มเปลี่ยนไปจากความเข้มข้นในน้ำดิบ และยังมีผลต่อการเกิดสารไตรฮาโลมีเทนชนิดที่มีโบรไมด์เป็นองค์ประกอบ แต่ผลของการเปลี่ยนแปลงนี้ยังอยู่ในช่วงที่ยอมรับได้ ผลจากการศึกษาการเกิดปฏิกิริยาของสารอินทรีย์แต่ละกลุ่มกับคลอรีนส่งผลให้ระดับการเกิด THMFP สูงขึ้นกว่าในน้ำดิบและน้ำตัวอย่างที่ได้จากการผสมสารอินทรีย์แต่ละกลุ่มเข้าด้วยกัน ซึ่งแสดงให้เห็นว่าเกิดจากผลการยับยั้งในการเกิดปฏิกิริยาจากการอยู่ร่วมกันของสารอินทรีย์แต่ละกลุ่ม

การโคแอกกูเลชันโดยใช้สารส้มสามารถลดการเกิด THMFP ได้แต่ประสิทธิภาพยังไม่ดีเมื่อเทียบกับการใช้สารส้มร่วมกับโพลีเมอร์ โดยที่ประสิทธิภาพของโพลีเมอร์ DADMAC มีประสิทธิภาพสูงสุดในการลด THMFP รองลงมาคือ EpiDMA CatPAM และ AnPAM ตามลำดับ ซึ่งโพลีเมอร์แต่ละตัวมีผลกับการลดปริมาณสารอินทรีย์แต่ละกลุ่มได้ไม่เท่ากัน เช่น CatPAM เหมาะกับไฮโดรฟอบิกที่เป็นกลาง DADMAC เหมาะกับไฮโดรฟอบิกที่เป็นด่าง EpiDMA เหมาะกับไฮโดรฟลิคที่เป็นกลาง และสารส้มเหมาะกับไฮโดรฟอบิกที่เป็นกรด และไฮโดรฟลิคที่เป็นกรด

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Resin adsorption technique using three types of resin; DAX-8, AG-MP-50, and WA-10 was employed to characterize the raw water from the Bangkhen water treatment plant, Bangkok Thailand. The dissolved organic carbon (DOC) mass distribution sequences of the six organic fractions in the raw water from high to low were hydrophilic neutral (HPIN), hydrophobic acid (HPOA), hydrophilic acid (HPIA), hydrophobic neutral (HPON), hydrophilic base (HPIB), and hydrophobic base (HPOB). HPIN and HPOA were the two main precursors of THMFP in this water source, whereas HPOB and HPIB were the most active precursors. A linear dependency between each organic fraction concentration and THMFP indicated that the reactions of each organic fraction with chlorine were first-order.

The fractionation led to a deviation of bromide concentration in each organic fraction from the original concentration, and this affected the formation of brominated THM species. However, this effect was demonstrated to be within an acceptable range. The chlorination of an individual organic fraction resulted in a higher level of THMFP than that of the raw water and mixed fractions. This indicated that there existed an inhibitory effect between the organic species.

Coagulation by using alum was proven to be able to remove THMFP but not as effectively as that with alum combined with polymers. DADMAC was found to be the most effective polymer for the removal of THMFP, where the next most effectives were EpiDMA, CatPAM, and AnPAM, respectively. Each polymer showed different preferences in the removal of each organic fraction, i.e. CatPAM for HPON, DADMAC for HPOB, EpiDMA for HPIN, and alum alone for HPOA and HPIA.

Inter-department Environmental Management	Student's signature.....
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ABBREVIATIONS AND SYMBOLS

AC	Activated carbon
AMW	Apparent molecular weight
AnPAM	Anionic polyacrylamide
Br ⁻	Bromide ion
°C	Degree celsius
CatPAM	Cationic polyacrylamide
CHCl ₃	Chloroform
CH ₃ OH	Methanol
DADMAC	Polydiallyl dimethyl ammonium chloride
DPD	N, N-decethyl-p-phenylenediamine
DBPFP	Disinfection by-product formation potential
DBAA	Dibromoacetic acid
DBPs	Disinfection by-products
DCAA	Dichloroacetic acid
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
D/DBP rule	Disinfectant and disinfection by-product rule
EpiDMA	Epichlorohydrin dimethyl amine
ECD	Electron capture detector
FS	Fractionated samples
GAC	Granular activated carbon
GC	Gas chromatography
HAAs	Haloacetic acids
HANs	Haloacetonitriles
HCl	Hydrochloric acid
HOBr	Hypobromous acid
HOCl	Hypochlorite
HPIA	Hydrophilic acid
HPIB	Hydrophilic base
HPIN	Hydrophilic neutral
HPOA	Hydrophobic acid

HPOB	Hydrophobic base
HPON	Hydrophobic neutral
H ₂ SO ₄	Sulfuric acid
IESWTR	Interim Enhanced Surface Water Treatment Rule
KHP	Potassium hydrogen phthalate
MCL	Maximum contaminant level
mg/L	Milligram per liter
mL/min	Milliliter per minute
MBAA	Monobromoacetic acid
MCAA	Monochloroacetic acid
MS	Mixed sample
NaOH	Sodium hydroxide
NOM	Natural organic matter
nm	Nanometer
NTU	Nephelometric turbidity unit
OM	Organic matter
PAC	Powder activated carbon
PACl	Polyaluminium chloride
PAHS	Polyaluminum hydroxysulfate
POC	Particulate organic carbon
DADMAC	Polydiallyl dimethyl ammonium chloride
psi	Pound square per inch
RO	Reverse osmosis
rpm	Rotation per minute
RW	Raw water
SUVA	Specific ultraviolet absorbance
TCAA	Trichloroacetic acid
THM	Trihalomethane
THMFP	Trihalomethane formation potential
THMs	Trihalomethanes
TOC	Total organic carbon
TOXFP	Total organo-halide formation potential
USEPA	United States Environmental Protection Agency

UV	Ultraviolet
UVA	Ultraviolet absorbent
μm	Micro meter
$\mu\text{s/cm}$	Microsemen per centimeter
$\mu\text{g/L}$	Microgram per liter



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CHAPTER I

INTRODUCTION

1.1 Motivations

Often, surface water is reported to contain organic matter derived both from natural degradation of some organic substances within the ecological systems and from human activities. Organic contaminants in surface water are different from location to location due to the differences in the ecosystem and the activities of human beings at each specific location. This organic matter cannot easily be captured using conventional water treatment techniques (coagulation with alum, sedimentation, and filtration) and therefore it can enter municipal water treatment systems and get distributed through the water supply network. Moreover, during the disinfection process with chlorine or chlorinated compounds, which is a common treatment technique in municipal water supply facilities, the organic matter could potentially be converted to harmful disinfection by-products (DBPs) such as trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs). THMs are identified as potential adverse health agents for which U.S. Environmental Protection Agency (USEPA) proposed the drinking water standard under the Disinfectants/Disinfection By-Products (D/DBP) Rule with a THMs Maximum Contaminant Level (MCL) of 0.08 mg/L for Stage 1 and 0.04 mg/L for Stage 2.

Although conventional water treatment processes were often designed and operated for turbidity and color removal, and not targeted on the organic precursor removal, they were illustrated to have potential for the removal of some organic contaminants (Amy and Chadik, 1983; Krasner and Amy, 1995; Huang and Shiu, 1996; and Exall and Vanloon, 2000). Past reports demonstrated that enhanced coagulation, such as pH adjustment, adding polymer or overdose of alum, could be an effective method for organic matter removal (Cheng *et al.*, 1995; Dennett *et al.*, 1996; Vrijenhoek *et al.*, 1998; and Marhaba and Pipada, 2000). This technique has therefore been proposed as a best available technology of the stage 1 of the D/DBP Rule and is a valuable means of controlling DBP formation without requiring significant capital investments (Crozes *et al.*, 1995). Also, coagulation by combination of alum and

polymer technique could be employed to improve THM precursors removal (Bolto *et al.*, 1999; and Bolto *et al.*, 2002).

To better understand THM precursors and the formation kinetics of THMs, it is recommended that the organic matter be characterized. The differentiation between each organic species might not be practical and therefore several past researches focused on grouping the organic matters into several common groups according to the physical/chemical properties of organic species e.g. size, polarity, molecular weight, etc. Resin adsorption has lately been successfully employed as a fractionation technique for organic matters. Marhaba *et al.* (2003) modified the technique proposed by Leenheer (1981) by replacing one of the resins to reduce the contamination from the back elution of the organics. This allowed a more reliable result of the fractionation particularly for the water source that contained low level of TOC (less than 5 mg/L).

To accomplish THM precursors reduction, this work was designed to consist of two parts. The first part was to characterize organic constituents and to determine the kinetics of the chlorination reactions. The second part was to investigate the mechanism of the coagulation with polymers in controlling the generation of THMs in the chlorination process. The result can provide an insight into the use of alum and polymers in the removal of THM organic precursors. The organic polymers of interested in this work were cationic polyacrylamide (CatPAM), anionic polyacrylamide (AnPAM), polydiallyl dimethyl ammonium chloride (or commonly known as DADMAC), and epichlorohydrin dimethyl amine (EpiDMA) which were reported to be the most frequently used polymers in the USA (Fielding *et al.*, 1999). For both cationic polyacrylamide and anionic polyacrylamide are commonly used as coagulant aid in Thailand water treatment plant. The result would be useful for the operation and management of the water treatment facility in the control of THM formation.

1.2 Objectives

1. To determine the most problematic organic matter fraction in water source.

- Fractionation
 - Trihalomethane Formation Potential (THMFP) test
2. To determine a suitable coagulant treatment process to reduce the THM precursors.
 - Jar-test coagulation
 - THMFP test
 - Fractionation

1.3 Scope of Study

1. The characteristic and reactivity of Bangkok water treatment plant raw water were measured in terms of DOC, UV-254, and THMFP.
2. The organic fractionation method employed in this work followed that developed by Marhaba *et al.* (2003).
3. The determination of the dosage of alum and polymer for the maximum reduction of THM formation potential were achieved through the use of jar test.
4. Polymers used in this experiment were cationic polyacrylamide (Policat C-84EF, Kemwater), anionic polyacrylamide (Magnafloc 308, Kemwater), polydiallyl dimethyl ammonium chloride; DADMAC (C591, Cytec), and epichlorohydrin dimethyl amine; EpiDMA (C319, Polydyne).

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Organic Matters

The term “organics” refers to general chemical compounds that contain carbon (C) and one or more of the following elements; hydrogen (H), nitrogen (N), and oxygen (O). There are several major sources responsible for organic contaminants in watercourses, e.g. dissolution of naturally occurring organic materials, contaminants from municipal and industrial activities, etc. Nowadays, organic matters (OM) are derived mostly from chemical industry rather than naturally biological activities. These anthropogenic compounds may also contain atoms of sulfur (S), phosphorus (P), fluoride (F), chloride (Cl), bromide (Br) and iodine (I), etc.

Organic matter has generally been quantified by measurements of total organic carbon (TOC), particulate organic carbon (POC), and dissolved organic carbon (DOC), the last one is based on the filtration of the water sample through a 0.45 micrometer membrane filter. Measurement of OM in terms of TOC is the most comprehensive in presenting the amount of organic precursors. Generally, naturally-origin organic matter was found in varying TOC concentrations in natural water sources, for examples, it can be as low as 2.5 or as high as 22 mg/L (Leenheer, 1981; Amy *et al.*, 1990; Krasner *et al.*, 1996; Marhaba and Van, 2000; and Croue *et al.*, 2003). The variation of DOC levels in water sources depends on environment and activities of the surrounding area particularly human-being deeds such as agriculture and industry which always ends up with a high level of DOC contamination.

Organic matter in surface water is mainly comprised of humic substances 50-65% (Collin *et al.*, 1986; Leenheer and Croue, 2003) and non-humic substances. Humic or hydrophobic substances that precipitated at pH 1, was defined by Thurman and Malcolm in 1981 as polar, straw-colored, organic acids derived from soil humus and terrestrial/aquatic plants, which contributed from about 50% to more than 90% of organics in natural waters. Humic substances can be further categorized into humic acids, fulvic acids, and humin.

- Humic acids are not soluble in water under the pH of less than two. They can be extracted from soil by various reagents. They are dark brown to black in color. Humic acids are composed of complex aromatic macromolecules, such as amino sugars (Coelho *et al.*, 1997).
- Fulvic acids, light yellow to yellow-brown in color, are the fraction of humic substances that is soluble under all pH range. Fulvic acids are the remaining part in the solution after the removal of humic acids by acidification. They contain mostly acidic functional groups such as COOH (Leenheer *et al.*, 1995; and Chen *et al.*, 2002).
- Humic, black color, is a non-soluble part in any condition in the fraction of humic substances (Shih and Wu, 2002).

Non-humic or hydrophilic substances have no color and are composed of non-complicated structured compounds including carboxylic acids, carbohydrates, amino acids, amino sugars, proteins, nutrients (Marhaba and Van, 1999), polysaccharides, nucleic acids, and small molecules (Stevenson, 1982).

There are two approaches in identifying the complex nature of DOM. A simplified approach makes use of uncomplicated measurements, i.e. TOC, ultraviolet absorbance (UVA), specific ultraviolet absorbance (SUVA), and fluorescence. A more complicated approach includes the categorization based on molecular weight (MW) fraction, size, polarity, acid/basic and solubility properties.

TOC is one of the most applied measurements for quantifying DOM. In fact, TOC is the measure of all the organic substances presented in the water sample, including suspended fractions which could be simply removed by coagulation/sedimentation. The more frequently used parameter is therefore DOC which is the measure of similar quantity with TOC but without the suspended fraction. This could be achieved through the filtering through 0.45 μm membrane filter.

UV-visible has also been conventionally proposed to characterize dissolved organic matter in the watercourses. Most research has employed the measurement at the wavelength of 254 nm (or often referred to as UV-254) as the representative for the relative quantity of aromatic-humic organic substances (Leenheer and Croue, 2003). A perhaps more frequently used parameter is SUVA (specific ultraviolet absorbance) which is simply the ratio between UV-254 and DOC of the water sample. This parameter is often employed to refer to the aromatic nature of the water sample as it is based on the mass of total organic matter presented, where a higher SUVA indicated that the sample is more enriched with higher molecular weight, humic, hydrophobic, and aromatic character (Krasner *et al.*, 1996). For example, SUVA in the range of 4-5 L/mg-m means that the character of organics are more humic-like, higher molecular weight, more readily to be removed by coagulation and represents mainly humic substances. On the other hand, in the case of SUVA less than 3 L/mg-m, the organic matters in the water sample are likely to be those with lower molecular weight with non-humic nature (Edzwald and Van, 1990). Under this category, the USEPA proposed Disinfectant and Disinfection By-product (D/DBP) Rule at SUVA of 2 L/mg-m as criteria that triggers the usage of enhanced coagulation.

Fluorescence shows the fingerprint of the compounds that present in the water sample, which can apply to develop the treatment process. The resulting fingerprints have to be compared with some specific database to identify the organic species. Unfortunately, the lack of the database at the present time prevents the widespread use of this measurement technique.

Other complicated techniques based on properties such as molecular weights and sizes are generally applied in categorizing the organic matters, which is based on the use of membrane with different cutoff sizes. However, these techniques are purely physical which does not provide information on the property of the resulting organic fractions. This therefore might not be helpful in the design of treatment systems particularly those based on the chemical properties of the substances to be removed.

Among all the quantities mentioned above, DOC seems to be one of the most common parameters used to identify the level of organic contaminants in terms of

mass. However, one serious drawback from using DOC is that this quantity is often not sufficient for the design of the water treatment system. This is because DOC contains several organic compounds with very different nature, some are hydrophobic, some hydrophilic, or some can be quite acid, and some exhibit more base property, etc. And since the treatment often is designed based on the different physical/chemical properties of the contaminants, the knowledge on DOC alone is inadequate when it comes to select abatement system choices. Hence, it is important that more detail variables are employed as a measure of organic contaminants in the water source. Conventionally, this is achieved by using the fractionation method which allows the separation of the organic matter in the water sample to several fractions before the DOC test. Resin adsorption has been widely used as an effective fractionation method. In this method, the organic constituents will be separated into various fractions depending on their affinities with the various types of adsorption resins. Detail of such technique will be the focus of the next section.

2.2 Resin Fractionation

Fractionation of dissolved organic matter (DOM) has gained much interest in the past decade because of the need to find the reactivity of organic fraction in water with disinfectants that produces disinfection by-products (DBPs). Recently, resin adsorption fractionation has proven to have a potential in the identification of problematic organic fraction in source waters (Marhaba *et al.*, 2003).

2.2.1 Types of Resin

With a proper arrangement of a few adsorption resins, Leenheer (1981), one of the pioneers in the area of fractionation method, could separate DOMs into six organic fractions, i.e. hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), and hydrophilic acid (HPIA), hydrophilic base (HPIB), and hydrophilic neutral (HPIN). This technique was then employed for the characterization of other water sources (Korshin *et al.*, 1997; Marhaba and Van, 1999; and Marhaba and Pu, 2000). Table 2.1 shows some examples of water sources characteristics and fractionation methods available from literature. The resin adsorption procedure proposed by Leenheer (1981) was later modified by Marhaba *et al.*, 2003 by replacing one of the resins, from Duolite A7 to WA-10 for which they

claimed to be able to reduce the resin bleeding of organic mass during the back elution. Characteristics of each resin used in fractionation procedure are detailed as follows.

DAX resins are macroporous methacrylate copolymers which are nonionic and able to isolate different organic species depending on the pH level. Examples of DAX types are DAX-2, DAX-4, DAX-7 and DAX-8 as also indicated in Table 2.1. This resin was generally used to fractionate DOM into hydrophobic and hydrophilic fractions i.e. Thurman and Malcolm, 1981; Collins *et al.*, 1986; Krasner *et al.*, 1996; and Chang *et al.*, 2001; etc. The most common among the four is DAX-8, the resin with high affinity for hydrophobic organics. At neutral pH, DAX-8 adsorbs hydrophobic neutral fraction and therefore separating this fraction from the water sample. By adjusting the pH to basic range, the resin is then selective for the hydrophobic base fraction from the deprotonated sample. Similarly, at acidic range, the resin is suitable for the adsorption of hydrophobic acids. Hence, with a proper alternation of pH, all three hydrophobic organic fractions could then be separated from the water sample.

AG-MP-50, cationic resin, (strong acid, sulfonated, polystyrene macroporous resin) can be used for adsorption of Ca^{2+} , Mg^{2+} , Na^+ and antibiotics, and it is also used to isolate the hydrophilic base (HPIB) organic fraction. The separation occurs best at low pH (pH = 2) where HPIB will be retained in the resin.

Anion exchange resin WA-10 is a weak anionic resin with a slightly hydrophilic property (weak anionic, phenol-formaldehyde condensation macroporous resin). In fact, the earlier resin with this property is Duolite A7 (with a slightly stronger hydrophilic property) was employed to separate the hydrophilic acid by Leenheer (1981), but this resin was subsequently substituted with WA-10 by Marhaba *et al.* (2003) for the reason that WA-10 had stronger physical and chemical stability that could reduce the resin bleeding in fractionation procedure. WA-10 resin is often used as the final resin in isolating HPIA from HPIN (Bolto *et al.*, 1999).

2.2.2 Products from the Fractionation

The six organic fractions obtained from the fractionation method above have been analyzed for their organic constituents which can be briefly summarized below.

1. Hydrophobic acids (HPOA) – aliphatic carboxylic acids of five to nine carbons, one and two-ring aromatic, carboxylic acids, one and two-ring phenols, fulvic acid (Leenheer, 1979).
2. Hydrophobic bases (HPOB) – amino acids, sugars, polysaccharides (Bruchet *et al.*, 1990), one and two-ring aromatic amines except pyridine (Leenheer, 1979).
3. Hydrophobic neutrals (HPON) – hydrocarbon; aliphatic alcohols, alkyl alcohols, ethers, ketones, and aldehydes, more than five carbons; aliphatic carboxylic acids and aliphatic amines, more than nine carbons; aromatic carboxylic acids and aromatic amines of three rings and greater (Leenheer, 1979).
4. Hydrophilic acids (HPIA) – short fatty acid, glucuronic acids (Sonnenberg and Holmes, 1998), aliphatic acids of less than five carbons (Leenheer, 1979), hydroxyl acids, sugars acids (Imai *et al.*, 2003), polyfunctional carboxylic acids (Swietlik *et al.*, 2004).
5. Hydrophilic bases (HPIB) – aliphatic amines less than nine carbons, amino acids (Leenheer, 1979; and Sonnenberg and Holmes, 1998), pyridines (Leenheer, 1979), amino sugar, peptides, protein (Marhaba and Pu, 2000).
6. Hydrophilic neutrals (HPIN) – aliphatic amides, alcohols, aldehydes, esters, and ketones less than five carbons (Leenheer, 1979), polysaccharides (Tipson, 1968 cited in Marhaba and Van, 1999).

2.2.3 Limitations on the Use of Resin Fractionation Procedure

- Fractionation and isolation technique are time and labor consuming (Marhaba *et al.*, 2000; and Leenheer and Croue, 2003).
- The nature of the organic fraction is based on operational definition.

- Fractionation and isolation of organic matter only exhibited a good recovery of organic matter when the sample contained low level of inorganic salt particularly salinity. Desalting step before fractionation might be needed prior to the fractionation especially when the organic only presents in small quantity (Leenheer, 2000).

2.3 Disinfections and Disinfection By-Products (DBPs)

Disinfection is used to eliminate pathogenic microorganisms in drinking water and also sewage effluent. Pathogens presented in water supplies are extremely harmful and can cause disease in humans. For drinking water, disinfection is an important step to ensure that water is safe to drink, and the U.S. regulation (Environmental Protection Agency, EPA) stated that disinfection must provide a 99.9 percent inactivation of *Giardia lamblia* and enteric viruses to protect human health. Moreover, a certain level of disinfectant should remain in the finished water to prevent the re-growth of microorganisms in the distribution system.

2.3.1 Disinfectants

Disinfection can be achieved with many chemical disinfectants such as ozone, ultraviolet (UV) radiation, potassium permanganate, chlorine dioxide, and chlorine. Each method has its own advantages and disadvantages as briefly discussed below.

Ozone

Ozone is the most effective oxidant and disinfectant. It is formed by passing air through high voltage electrical discharge field where O_2 is converted to O_3 . As a very strong oxidant, ozone requires shorter contact time and lower dose than most other disinfectants. However, as ozone is unstable, it is required that ozone be generated on-site which means that every facility must have an ozone generator. In addition, ozone cannot remain long enough in the water distribution system and therefore this poses the problems on the re-growth of the microorganisms.

Ultraviolet radiation

Ultraviolet (UV) radiation is generated by a specific lamp. When the radiation penetrates the cell wall of an organism, the cell's genetic material is interrupted and

the cell is incapable of further reproducing. UV light is an effective disinfectant particularly in destroying bacteria and viruses. The efficiency depends on the contact time. However, it cannot provide a disinfecting role in the water distribution system. UV radiation is unsuitable for water with high levels of suspended solids, color, turbidity, or soluble organic matter because these materials can absorb and obstruct the UV radiation which leads to a lower disinfection performance.

Chlorine dioxide

Chlorine dioxide (ClO_2) is a very effective disinfectant for odor and taste control but it has to be generated onsite because chlorine dioxide is an unstable gas. This gas was reported to produce only few DBPs of concern (Richardson *et al.*, 1994) which are chlorite and chlorate (Marhaba and Washington, 1998). There is no significant formation of THMs and it does not react with bromide to form brominated by-products.

Chlorine

At atmospheric pressure, chlorine gas is toxic, yellow-green in color, and forms liquid at high pressure. Chlorine is most widely used in the disinfection process because it is very effective in removing almost all microbial pathogens. It is appropriate as both primary and secondary disinfectants. Moreover, the most important advantage that chlorine still commonly using is it can maintain as a residual disinfectant in the water supply distribution system.

2.3.2 Disinfection By-Products

Only some of disinfection by-products (DBPs) have been examined for their toxicological effects but most have been found to exhibit carcinogenic potential. The formation of DBPs depends on the type of precursors in the water and also on the types of disinfectants.

Ozone disinfection by-products

Ozone will not produce chlorinated by-products such as THMs, HAAs, and HANs but it may form a variety of oxidation by-products in the presence of organic matter (Marhaba and Washington, 1998). However, if the waters containing bromide

ion are ozonated, brominated species DBPs can form. A variety of ozone by-products is listed in Table 2.2.

Ultraviolet radiation disinfection by-products

It is possible to obtain oxidative by-products in the high pressure UV systems. UV DBPs may form due to the production of OH radicals when the water is in contact with UV radiation. However, conventional UV does not appear to form any DBPs of current concerns (Marhaba and Washington, 1998).

Chlorine disinfection by-products

Chlorine DBPs are formed when free chlorine (hypochlorous acid: HOCl) added to water reacts with the organic matter presented in water. Some of the major types of chlorine DBPs are listed in Table 2.3. THMs were often found to be the most dominant DBPs, followed by HAAs (Krasner *et al.*, 1989; Marhaba and Van, 1999; Owen *et al.*, 1995; and Grenier *et al.*, 1992). THMs and HAAs were identified as potential adverse health effect agents. The generalized equation describing the formation of chlorine halogenated DBPs is shown in Equation (2.1) (Marhaba and Washington, 1998):



2.3.3 Trihalomethanes (THMs)

THMs are organohalogen compounds which are the derivatives of methane when three out of the four hydrogen atoms are substituted by three halogen atoms such as chlorine, bromide, and iodine. THM species of concerns in drinking water are chloroform, bromodichloromethane, dibromochloromethane, and bromoform. The chemical structures of these THM species are shown in Figure 2.1.

2.3.4 THMs Toxicity

THMs were found in chlorinated drinking water since 1974 by Rook. THMs have been shown to potentially cause tumours in liver, kidney or large intestine in laboratory animals (Fawell, 2000).

Chloroform is often used as a representative of the THMs because it usually presents in the greatest concentration among the four THMs species. Chloroform is also commonly used in chemical and pharmaceutical industries. National Cancer Institute of the United States showed that chloroform increased mouse liver tumours and increased kidney tumours in rats (reported in Fawell, 2000). National Toxicity Program, Department of Health and Human Services of the United States reported that bromodichloromethane induced renal tumours in mice and rats, liver tumours in mice and intestinal tumours in rats whereas bromoform produced intestinal tumours in rats (reported in Singer, 1993).

2.4 Trihalomethane Precursors

The fractionation allows a thorough investigation of the formation of Trihalomethanes (THMs) from the organic matters in water source. For instance, hydrophobic fraction was often found to have higher THMs reactivity than the hydrophilic in the water sample from Canton, Springfield, Las Vegas, and Daytona, USA (Collins *et al.*, 1986). Korshin *et al.* (1997) tested total organo-halide formation potential (TOXFP) of water samples from Mt Wernon and Everett water source, USA and found that the hydrophobic acid fraction exhibited the highest level of TOXFP, and TOXFP decreased in the order from HPOA > HPIA > HPIN. Marhaba and Van (1999) and Marhaba and Pipada (2000) examined the water sample from Central New Jersey, USA and reported that hydrophobic base fraction was the most reactive in the formation of THMs followed by the hydrophilic acid fraction. Chang *et al.* (2001) demonstrated that 76% of DOC from Pan-Shin water works, Taiwan was the hydrophilic and hydrophobic acid fractions and it was the hydrophobic acid fraction that exhibited the greatest ability in the formation of THMs. The difference in the reported active species of organic fraction from location to location suggested that, although DOC was fractionated into various organic fractions, the THM formation mechanism still could not be generalized. The variation in the environment and the activities of human beings in each specific location might be the main reason for the

differences in the nature of the organic species presented in the water sources. Table 2.1 provides a concise review of previous works on trihalomethane formation potential (THMFP) from several water sources.

2.5 Factors Controlling THMs Formation

Many researches have reported that several environmental factors such as DOC, temperature, bromide concentrations, and operational factors (for chlorination) such as pH, chlorine dose, and reaction time could significantly affect the formation of THMs (Singer, 1994; Pourmoghaddas and Stevens, 1995; El-Shahat *et al.*, 2001; and Nikolaou, 2004). A brief discussion on this aspect follows.

2.5.1 Chlorine Dose

Literature revealed that higher dose of chlorine concentration resulted in an increase in THMs formation (Trussel and Umphres, 1978; and El-Shahat *et al.*, 2001). Since THMs was a chlorination by-product, the level of chlorine residual directly influenced the level of THM formation (Kawamura, 1991).

2.5.2 pH

The effect of pH on the formation of THMs has been widely investigated. Most have come to very similar conclusion that THMs formation increased with an increase in pH (Steven *et al.*, 1976; and Trussel and Umphres, 1978). For example, Trussel and Umphres in 1978 illustrated that reducing pH from 9 to 7 could reduce over 50% of THM formation. Kawamura (1991) stated that the changes in pH altered the functional groups of precursor molecules which resulted in the THM formation potential.

2.5.3 Reaction Time

Numerous investigators have reported that the increase in chlorine contact time resulted in increasing THMs formation (Trussell and Umphres, 1978; Recknow and Singer, 1984; and El-Shahat *et al.*, 2001). The initial rate of reaction between chlorine and organic matter was rapid and this rate decreased with reaction time.

2.5.4 Precursor Concentration

The level of THMs in the finished water was usually directly correlated to the level of total organic carbon (TOC) in raw water (Stevens, 1976; Trussell, 1978; Babcock, 1979; and USEPA, 1994). Chlorination of water without the organic precursors will not result in THM formation. Therefore, precursor concentration is one of the important factors affecting the THMs formation

2.5.5 Bromide

Bromide was generally reported to have effects on the formation of THMs (Trussell and Umphres, 1978; Richardson *et al.*, 1999; Chang *et al.*, 2001; Kampioti and Stephanou, 2002; and Myllykangas *et al.*, 2003). In the presence of chlorine and bromide, free chlorine (HOCl) was shown to rapidly oxidize bromide to hypobromous acid (HOBr), which was quickly reacting with precursors to form THMs. Then HOCl and HOBr reacted with organic matter to produce the mixed chloro-bromo DBPs (Marhaba and Washington, 1998). In addition, chlorination with the absence of bromide could only lead to the formation of chloroform species. On the other hand, if the water source contained high bromide concentration, chlorination would result in the formation of brominated THM species which, in turn, led to an increase in THMs formation

2.5.6 Temperature

Water temperature directly influences the rate of THM formation i.e. higher temperature encourages a faster THM formation rate. Stevens *et al.* (1976) studied chloroform production at pH 7 at three different temperature levels. The results indicated that the formation of chloroform increased with temperature. Annual variation in temperature was also found to have impact on THM formation where a lower THM levels was observed during the cold months and a higher THM levels during the warmer period (Otson *et al.*, 1981; and El-Shahat *et al.*, 2001). In many cases, THM levels during the summer months (average water temperature = 25°C) was nearly twice as great as THM levels during the winter season (average water temperature = 4°C) (Kawamura, 1991).

2.6 THM Precursors Removal

As the organic matter is the main precursor for chlorinated by-products. Controlling the THMs formation could then be accomplished by lowering the organic precursors in the water before chlorination. Several methods for the removal of organic compounds in the water sources were proposed and they are described below.

2.6.1 Adsorption with Activated Carbon

Several organic compounds could be well adsorbed on the surface of activated carbon (AC). Granular activated carbon (GAC) and powder activated carbon (PAC) are often used in drinking water treatment for the removal of organic, odor, taste, and color. Activated carbon can remove organic precursors effectively with an adequately long contact time provided the adsorption capacity is high.

2.6.2 Membranes

There are several types of membrane used for treating water supply treatment; microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). The pore sizes of the membranes could be ordered from large to small as follows; $MF > UF > NF > RO$. MF and UF are not very good in organic precursor removal because of their large pore size. Smaller pore membranes such as NF and RO can significantly remove most organic precursors.

2.6.3 Anion Exchange

Generally, organic matter in water at neutral to basic pH range is present as negatively ions so it can be removed by anion exchange resin (Kim and Symons, 1991; Collin *et al.*, 1996; and Bolto *et al.*, 2002). Bolto *et al.* (2002 and 2004) explored an anion exchange for the removal of natural organic matter and reported that ion exchange was an effective method for removing humic substances.

2.6.4 Coagulation and Sedimentation

Conventional water treatment facilities generally consist of coagulation, sedimentation, and filtration processes, which have been traditionally used to remove suspended solids for drinking water. These processes, although might not be effective, could also remove organic contaminants in the water. With a proper

control of coagulation conditions, several reports have shown that some specific THM precursors could be removed (see Table 2.4 for details). The removal of DBP precursors represents a valuable option for reducing the potential for chlorinated by-products formation without requiring significant capital investments (Chadik and Amy, 1983; and Crozes *et al.*, 1995). As coagulation is among the most economical means employed in the water treatment facilities, it has been received considerable attention as a method for removing THM precursors (Chadik and Amy, 1983; Hoehn *et al.*, 1984; Vrijenhoek *et al.*, 1998; Randtke and Hoehn, 1999; Cheng *et al.*, 1995; and Marhaba and Pipada, 2000) and has been proposed as the best available technology of the stage 1 of the D/DBP Rule. Note that enhanced coagulation included the proper usages of coagulant aids and the adjustment of the pH of raw water.

2.7 Mechanism of Organic Precursors Removal by Coagulation

2.7.1 Coagulation with Alum

Coagulation can effectively destabilize colloidal suspension which is subsequently removed by sedimentation but not so effective in removing organic components. Typically, coagulation exhibits preferential removal of humic substances (such as humic and fulvic acids) over non-humic substances (AWWARF, 1993). One possible mechanism for the removal of organic species is the interaction between the metal hydroxide and the function groups in the organic matters. The polar function groups of fulvic acids, such as $-\text{COOH}$, $-\text{OH}$, $-\text{C}=\text{O}$ etc., can donate electrons, and form complexation with aluminium hydroxide during the coagulation reaction (Zhang and Wang, 2000). Nevertheless, there are more than one potential mechanism responsible for the removal of DOM in water and these are delineated as followed: (Dempsey, 1984; and Randtke, 1988)

- 1) Colloid destabilization by four mechanisms: adsorption and charged neutralization, electrical double layer compression, adsorption and bridging, and enmeshment in a precipitate (sweep floc).
- 2) Precipitation, the conversion of a dissolved substance to a solid. Precipitation of DOM refers to the formation of a humate or fulvate with a lower solubility product that causes precipitation.

- 3) Coprecipitation, defined as the contamination of a precipitate by an impurity that is otherwise soluble under the conditions of precipitation. In coprecipitation, the soluble organic material is adsorbed onto the growing crystals of the aluminium hydroxide. Bonds involved in adsorption of DOM can include Van der Waals interactions, hydrogen bonding, hydrophobic bonding, ionic bonds, or dipole interactions.

Factors that affect the coagulation are:

- pH; For pH less than 5, the removal occurred by charge neutralization and for pH more than 7, removal was taken placed by direct adsorption onto a solid hydroxide precipitate (Krasner and Amy, 1995). Lower pH to the range of slightly acidic (5-6.5) was often reported to be more suitable for the DOC removal (Randtke, 1988; Cheng *et al.*, 1995; Dennett *et al.*, 1996; Huang and Shiu, 1996; Vrijenhoek *et al.*, 1998; Bell-Ajy *et al.*, 2000; and Duan and Gregory, 2003). This might be because the lower pH could reduce the charge density of DOC, which rendered organic species more hydrophobic and adsorbable as the aluminum salts hydrolysis products were more positively charged.

- Coagulant dose; higher coagulant dose could improve DOC removal because it provided more metal complex for floc formation or positively charged metal hydroxide for charged neutralization (Randtke, 1988; Dennett *et al.*, 1996; Huang and Shiu, 1996; Vrijenhoek *et al.*, 1998; and Duan and Gregory, 2003).

2.7.2 Coagulation with Polymer

Possible mechanisms for the removal of DOM by polymer coagulation are charged neutralization or adsorption, polymer bridging, precipitation and coprecipitation. Polymers may enlarge DOM removal by improving liquid-solid separation (Jacangelo *et al.*, 1995). The advantages of using polymer are, for example: (i) less dependence on pH, (ii) less sludge generated than inorganic coagulants, (iii) lower level of dissolved metal ion in the water, (iv) a longer filter run, and (v) no effect to water alkalinity, etc. (Mallevalle *et al.*, 1984; and Bolto *et al.*, 1999). In addition, a combination of alum and polymer is an attractive treatment option because it was proven that an improvement in the removal of DOM during enhanced

coagulation could be obtained (Bolto *et al.*, 2001; Walker and Kim, 2001; and Bolto *et al.*, 2002). However, Bolto *et al.* (2001) stated that water containing more hydrophobic compounds could be easier to treat than that with high hydrophilic contaminants.

There are concerns about the usages of organic polymers as coagulant or coagulant aid as polymers might have come with other organic contaminants which could also lead to THMs formation (Lee *et al.*, 1998). In addition, adding polymer has been proven to improve the removal of humic substances but may result in an equal or greater level of TOC in finished water. Lurie *et al.* (1997) reported that organic matter removal increased with increasing polymer dosage during coagulation, possibly due to electrostatic interaction between polymer and organic matter. Hence, the excess of polymer gave rise to the organic matter content in the treated water. Therefore it is important to determine appropriate polymer dosages for each specific water source.



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2.8 Tables and Figures

Table 2.1 Review of fractionation method

Name	Water source	Resin	Fraction	THMFP
Leenheer, 1981	South Platte River, USA. (DOC 7.5 mg/L)	DAX-8, AG-MP-50, and Duolite A7	HPOA 15.7%, HPOB 1%, HPON 35.8%, HPIA 19.9%, HPIB 22.6%, and HPIN 4.9%	-
Thurman and Malcolm, 1981	Suwanee River in southern Gorgia, Biscayne groundwater, and Fox Hills groundwater (USA)	XAD-8 and AG-MP-50	Humic acid, and fulvic acid	-
Miller and Uden, 1983	Hop Brook, Amherst, USA.	XAD-2 and XAD-8	Humic acids and fulvic acids	-
Joyce <i>et al.</i> , 1984	Massachusetts	XAD-2 and XAD-8	Humic acids and fulvic acids	-
Collin <i>et al.</i> , 1986	Canton, Springfield, Las Vegas, and Daytona (USA), TOC 2.5-8.3 mg/L	DAX-8 and UF membrane	HPO > HPI	HPO > HPI
Semmens and Staples, 1986	Mississippi River, USA (TOC 6.3 mg/L)	XAD-2 and XAD-8	HPIN 13.9%, HPIB 5.7%, HPIA+HPIN 54.5%, HPOA 25%, and HPOB 0.8% (HPO 60% and HPI 40%)	HPIA+HPIN > HPOA > HPIN > HPOB > HPIB (HPI > HPO)
Amy <i>et al.</i> , 1990	Sacramento River Delta, California, USA (DOC 2.1-22 mg/L)	XAD-8	Humic fraction 38-62% and nonhumic fractions	-
Amy <i>et al.</i> , 1992	10 wells ground water, USA (DOC 1.2-14 mg/L)	XAD-8	Humic 55-94% and nonhumic fractions	-

Name	Water source	Resin	Fraction	THMFP
Croue <i>et al.</i> , 1993	Apremont reservoir, France (DOC 7.3-11.5 mg/L)	XAD-4 and XAD-8	HPO 50-55% and HPIA 20-25%	HPO more reactive with chlorine than HPIA
Krasner <i>et al.</i> , 1996	USA and France (DOC 1.86-48.3 mg/L)	XAD-4 and XAD-8	HPO 46%, HPON 5%, HPI 25%, and HPIA 24%	-
Korshin <i>et al.</i> , 1997	Mt Vernon and Everett, USA (DOC 4 and 1.7mg/L)	DAX-8, AG-MP-50, and Duolite A7	HPOA 43-53%, HPOB 1-2%, HPON 0-8%, HPIA 37-40%, HPIB 1-3%, and HPIN 5-8%	TOXFP; HPOA > HPIA > HPIN
Martin-Mousset <i>et al.</i> , 1997	Reservoirs DOC 6.8-7.8 mg/L and from Rivers, DOC 2.8-5.3 mg/L	XAD-4 and XAD-8	HPO 41-62% and HPI 14-26%	-
Xu <i>et al.</i> , 1997	Taihu Lake, China (DOC 6.9 mg/L)	XAD-2, XAD-7, XAD-8, D001-CC, and D301	Fulvic acids 36%, HPON 18%, HPIA 16%, HPIB 13%, HPO weak acids 10%, humic acids 6%, and HPOB 1%	-
Yamada <i>et al.</i> , 1998	Katsura, Uji, Kidzu, and Yodo River	Acidified to pH 1 and centrifugation	Fulvic acids 0.5-3.2 mg/L and humic acids 0.025-0.2 mg/L	Humic acids > fulvic acids
Bolto <i>et al.</i> , 1999	Moorabool, Hope Valley, and Wanneroo (Australia)	XAD-4, DAX-8, and IRA-958	Very HPOA 34-80%, slightly HPOA 9-21%, HPI charged fraction 9-33%, and HPIN 1-15%	Moorabool, HPI charged > HPIN > very HPOA > slightly HPOA and Wanneroo, HPIN > slightly HPOA > HPI charged > very HPOA
Bremere <i>et al.</i> , 1999	Rhine River, Holland (TOC 8 mg/L)	XAD-4 and XAD-8	HPI > 90% and HPO > 10%	-
Galapate <i>et al.</i> , 1999	Treated industrial wastewater (DOC 2.5-85.4 mg/L)	XAD-8	HPI 1.2-22.3 mg/L and HPO 0.06-4.67 mg/L	HPO > HPI

Name	Water source	Resin	Fraction	THMFP
Marhaba and Van, 1999	Central New Jersey, USA (DOC 3.78 mg/L)	DAX-8, AG-MP-50, and Duolite A7	HPIA 44.2%, HPIN 19%, HPON 16.7%, HPOA 11.1%, HPOB 5.5%, and HPIB 3.5%	HPOB > HPIA > HPON > HPOA > HPIB > HPIN
Pomes <i>et al.</i> , 1999	Lake Maumelle and Winona, USA (DOC 2.8-3.7 mg/L)	XAD-8, AG-MP-5, acidified to pH 1 and centrifugation	Fulvic acids 85.1-93.3% and humic acids 6.7-14.9%	Fulvic acids > humic acids
Lin <i>et al.</i> , 2000	Commercial humic solution	DAX-8	HPO 85% and HPI 15%	HPO > HPI
Marhaba and Van, 2000	Northern New Jersey, USA. (DOC 3.8 mg/L)	DAX-8, AG-MP-50, and Duolite A7	HPIA 53%, HPIN 13%, HPOA 12%, HPON 10%, HPOB 7%, and HPIB 5%	HPIA 69%, HPON 18%, HPOA 6%, HPOB 4%, HPIB 2%, and HPIN 1%
Chang <i>et al.</i> , 2001a	Da Cha creek, Taichung, Taiwan (DOC 2 mg/L)	DAX-4 and DAX-7	HPO substance 43%, HPIA 41%, and non-acid hydrophilic 16%	-
Chang <i>et al.</i> , 2001b	Pan-Shin Water works, Taiwan (DOC 0.78 mg/L)	XAD-8 and UF membrane	HPOA > HPI > HPON > HPOB	HPOA > HPOB > HPON > HPI
Lee <i>et al.</i> , 2002	Nakdong River, Korea (DOC 3.71 mg/L)	XAD-4 and XAD-8	HPO, transphilic, and HPI	-
Marhaba <i>et al.</i> , 2003	New Jersey, USA. (DOC 4.92 mg/L)	DAX-8, AG-MP-50, and WA-10	HPON 38%, HPIA 32%, HPOA 13%, HPIN 8%, HPIB 6%, and HPOB 3%	-
Bengraïne and Marhaba, 2003	New Jersey, USA	DAX-8, AG-MP-50, and WA-10	HPOA, HPOB, HPON, HPIA, HPIB, and HPIN (HPI 38% and HPO 62%)	-
Croue <i>et al.</i> , 2003	South Platte River, Colorado, USA (DOC 2.6 mg/L)	XAD-4, XAD-8, and MSC-1H	HPOA, HPON, Transphilic acids, Transphilic neutral, and HPI	HPO 50-55% and HPIA 20-25%
Imai <i>et al.</i> , 2003	Lake Kasumigaura, Japan (DOC 2.94-4.42 mg/L)	XAD-8, AG-MP-50, and AG-MP-1	Aquatic humic substances 26-39.8%, HPON 0-19%, HPIA 39.4-61.3%, HPIB 3.7-13.8%, and HPIN 0-10.9%	HPI 57% and aquatic humic substances 35%

Name	Water source	Resin	Fraction	THMFP
Leenheer <i>et al.</i> , 2003	Suwannee River, Georgia, USA.	XAD-8	Fulvic acids	-
Swietlik <i>et al.</i> , 2004	Mosina Water Intake (TOC 3.8-6.5 mg/L)	XAD-4, XAD-8, AG-MP-50, and Duolite A7	Humic acids 19%, HPOA 54%, HPOB traces, HPON 12%, HPIA 7%, HPIB 5%, and HPIN 3%	-

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Table 2.2 Ozonated DBPs

Chemical Class	Chemical Compound
Aldehydes	Formaldehyde
	Acetaldehyde
	Glyoxal
	Methyl glyoxal
Aldo- and Ketoacids	Pyruvic acid
	Glyoxylic acid
	Ketomalonic acid
Carboxylic acids	Oxalic acid
	Succinic acid
	Formic acid
	Acetic acid
Peroxides	Hydrogen peroxide
Brominated by-products	Bromate
	Bromoform
	Brominated acetic acids
	Bromopicrin
	Brominated acetonitriles

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Table 2.3 Chlorinated DBPs (Marhaba and Washington, 1998)

Chlorinated DBPs	Chemical compound
Trihalomethanes (THMs)	Chloroform
	Bromodichloromethane
	Dibromochloromethane
	Bromoform
Haloacetic Acids (HAAs)	Monochloroacetic Acid (MCAA)
	Dichloroacetic Acid (DCAA)
	Trichloroacetic Acid (TCAA)
	Monobromoacetic Acid (MBAA)
	Dibromoacetic Acid (DBAA)
Haloacetonitriles (HANs)	Dichloroacetonitrile
	Trichloroacetonitrile
	Dibromoacetonitrile
	Bromochloroacetonitrile
Cyanogen Halides	Cyanogen Chloride
	Cyanogen Bromide

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Table 2.4 Review of coagulation condition

Name	Water source	Condition	%Removal
Amy and Chadik, 1983	Biscayne Aquifer, Edisto River, Mississippi River, Jame River, Ilwaco Reservoir, Daytona Beach Aquifer, and Scioto River (USA)	Four cationic polymers at 15-20 mg/L	27-65% THMFP reduction
Hubel and Edzwald, 1987	Grasse River	Alum with cationic copolymer, and nonionic PAM	32-66% TOC removal and 26-70% THMFP removal
Crozes <i>et al.</i> , 1995	Missouri River and Sacramento River	Alum, Ferric chloride 0-120 mg/L, and medium MW synthetic cationic polymer 0.1-0.3 mg/L	about 50% TOC removal
Lee <i>et al.</i> , 1998	Synthetic water	Polyaluminium chloride 60 mg/L with copolymer acrylamide/trimethylaminoethyl acrylate and nonionic polyacrylamide 0.5-1 mg/L	20% lindane removal, 65% <i>p,p</i> -DDT removal, more than 70% aldrin removal etc.
Bolto <i>et al.</i> , 1999	Moorabool river, Hope Valley (reservoir/long river), and Wanneroo (groundwater)	DADMAC 5-8 mg/L, CatPAM 7-8 mg/L, CPMA (cationic polymethacrylate) 7-8 mg/L, and alum 30-60 mg/L	%UV removal; 35-70%, 31-69%, 50-75%, and 69-88%, respectively
Chang <i>et al.</i> , 1999	Pan-Hsing water treatment plant (Taiwan) and humic acid	Optimum dose at 2 mg/L and 10 mg/L DADMAC, respectively	69% and 82% chloroform removal, respectively
Marhaba and Pipada, 2000	Raritan/Millstone and Canal Road water treatment plants, Central New Jersey	Maximum TOC removal condition for HPIA, HPIB, HPIN, and HPON at pH 6 and alum dosages 60 mg/L. For HPOA and HPOB fractions, occurred at pH 6 and alum dosages 40 mg/L	TOC removal of HPIA, HPIB, HPIN, HPOA, HPOB, and HPON were 51, 46, 44, 68, 71, and 52%, respectively

Name	Water source	Condition	%Removal
Freese <i>et al.</i> , 2001	Kwazulu-Natal, South Africa.	Ferric chloride 6-30 mg/L	40% THMFP and 50-75% organic carbon removal
Walker and Kim, 2001	Alum Creek (Delaware, OH) and Walborn Reservoir (Alliance, OH)	Ferric chloride 0.5 mg/L with <2.5 mg/L nonionic PAM, 10-20 and 30 mg/L for high and medium cationic charge density cationic diallyl dimethyl, respectively	Less than 50% UV removal for cationic charge density cationic diallyl dimethyl, the others were low efficiency
Bolto <i>et al.</i> , 2002	Bell Bay: Tasmania, Hope Valley: South Australia, and Wanneroo: Western Australia	DADMAC 5-8 mg/L, Cationic polymethacrylate 7-8 mg/L and alum 30-60 mg/L	>40%, > 50%, and >60% UV removal, respectively
Chang <i>et al.</i> , 2005	Synthetic source water (Humic acid)	- Alum 60 mg/L combine with 10 mg/L DADMAC - Alum 20-60 mg/L with CatPAM and NonionicPAM 2-10 mg/L	- 90% TOC removal of Humic acid - Less than 10% Humic acid removal

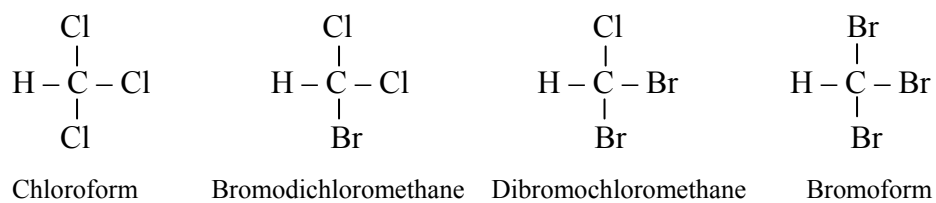


Figure 2.1 Chemical structures of THMs



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CHAPTER III

METHODOLOGY

3.1 Overview

Water samples were taken from the intake of the Bangkhen water treatment plant, the main water supply for Bangkok Metropolitan, Thailand. This water treatment plant was designed to supply water at approximately 3 million cubic meters per day. Experiments in this research could be separated into two main parts. The first part was the characterization of the water source which was accomplished by accomplished with the fractionation of the organic contents in the water sample and the THMFP tests of the resulting fractionates. The second part was the examination of the efficiency in THMFP reduction by coagulation with alum and polymer. Figure 3.1 illustrates how the two experiments were conducted.

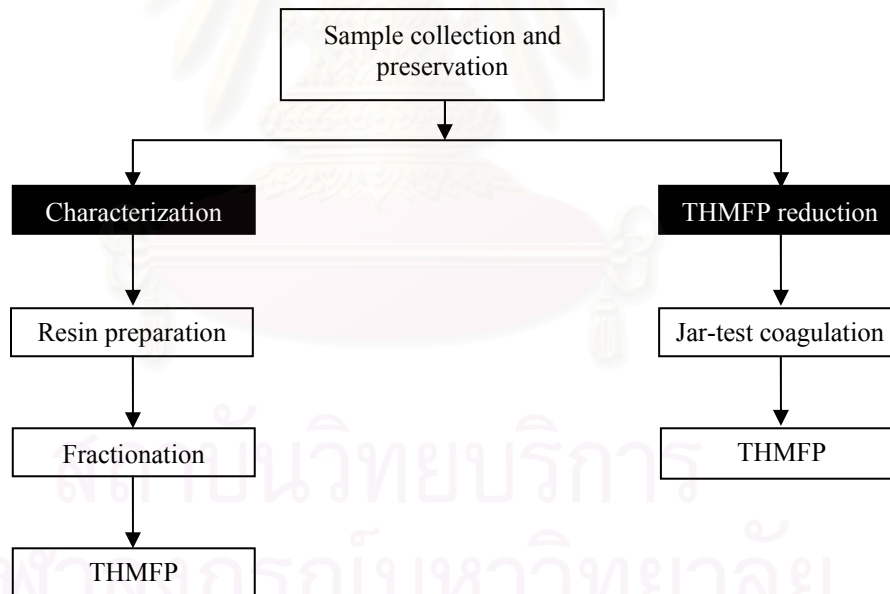


Figure 3.1 Experimental procedure

The first step of the experiment was to collect samples from the treatment plant with the sampling procedure as described in Section 3.2. Detailed procedure for the characterization part is given in Section 3.3 whereas coagulation experiment is

illustrated in Section 3.4. Note that, in the detail description below, all chemicals used in the experiment were analytical grade.

3.2 Sample Collection and Preservation

- Take sample from the intake of the treatment plant, the sampling point is shown in Figure 3.2
- Filtrate the sample through 0.45 μm cellulose nitrate membrane within 24 hours
- Store in a cold room with temperature controlled at 4°C before and after fractionation



Figure 3.2 Sampling point

3.3 Characterization of Organic Contents in Water Source

3.3.1 Resin Preparation

The resin adsorption procedure as proposed by Marhaba *et al.* (2003) was applied. With this method, the dissolved organic contents were fractionated into six fractions; hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), hydrophilic acid (HPIA), hydrophilic base (HPIB), and hydrophilic neutral (HPIN) using three types of resin, i.e. DAX-8, AG-MP-50, and WA-10. The preparation procedure for each resin is described below:

DAX-8, nonionic resin (Supelco)

- Soak in 0.1N NaOH for 24 hours
- Soxhlet extraction for 24 hours with acetone, apparatus as shown in Figure 3.3
- Soxhlet extraction for 24 hours with hexane
- Soak in methanol for 24 hours
- Transfer into three glass columns
- Rinse with 0.1N NaOH at 2.5 bed volumes
- Rinse with 0.1N HCl at 2.5 bed volumes
- Rinse with Mill-Q water until the conductivity and DOC of the effluent lower than $1 \mu\text{s}/\text{cm}$ and $0.2 \text{ mg}/\text{L}$, respectively



Figure 3.3 Soxhlet extraction apparatus

AG-MP-50, cationic resin (Bio-Rad)

- Soxhlet extraction for 24 hours with methanol
- Transfer into glass column
- Rinse with 1N NaOH at 2 bed volumes
- Rinse with 2N HCl at 4 bed volumes
- Rinse with Mill-Q water until the conductivity and DOC of the effluent lower than $1 \mu\text{s}/\text{cm}$ and $0.2 \text{ mg}/\text{L}$, respectively

WA-10, weak anionic resin (Supelco)

- Soak in methanol for 24 hours
- Transfer into glass column
- Rinse with 1N HCl at 2 bed volumes
- Rinse with 1N NaOH at 2.5 bed volumes
- Rinse with Mill-Q water until the conductivity and DOC of the effluent was lower than 1 $\mu\text{s}/\text{cm}$ and 0.2 mg/L, respectively

All resins were packed in a 2 cm diameter and 120 cm long glass column. The glasswool, initially cleaned by soxhlet extraction with methanol for 24 hours, was packed at the bottom of column as a support for the resins.

3.3.2 Fractionation Procedure

The resins were ready to use after the preparation as described above. The fractionation of organic contents in the water sample was performed according to the procedure below (see Figure 3.4 and 3.5 for a schematic of the fractionation procedure). Each resin was packed into the column as illustrated in Figure 3.6.

1. Adjust the sample to pH 7 and pass it through the first DAX-8 resin column at a flow rate of not more than 12 bed volumes per hour
2. As the sample flowed passed the column, rapidly replace the sample with Milli-Q water at 1 bed volume
3. Elute the hydrophobic neutral fraction from the column by methanol
4. Evaporate the hydrophobic neutral fraction from methanol solution by rotary evaporator
5. Adjust the sample effluent to pH 10 by 2N NaOH and pass to the second DAX-8 resin column at a flow rate of not more than 12 bed volumes per hour
6. As the sample flowed passed the column, rapidly replace the sample with Milli-Q water at 1 bed volume
7. Elute the hydrophobic base fraction from the resin with 0.1N HCl at 0.25 bed volume and 0.01N HCl at 1.5 bed volumes at a flow rate of not more than 0.2 bed volume per hour, respectively

8. Acidify the effluent to pH 2 with 6N H₂SO₄ before pump the solution through the last DAX-8 resin column at a flow rate of not more than 12 bed volumes per hour
9. As the sample flowed passed the column, rapidly replace the sample with Milli-Q water at 1 bed volume
10. Elute the hydrophobic acid fraction from resin with 0.1N NaOH at 0.25 bed volume and 0.01N NaOH at 1.25 bed volumes at a flow rate of not more than 0.2 bed volume per hour, respectively
11. Pass the effluent through the AG-MP-50 resin column at a flow rate of not more than 5 bed volumes per hour
12. As the sample flowed passed the column, rapidly replace the sample with Milli-Q water at 1 bed volume
13. Elute the hydrophilic base fraction from the resin with 1N NaOH at 1 bed volume at a flow rate of not more than 2 bed volume per hour
14. Pass the effluent through the WA-10 resin column at a flow rate of not more than 8 bed volumes per hour. The effluent contained hydrophilic neutral fraction.
15. Elute the hydrophilic acid fraction with 0.1N NaOH at 1.5 bed volumes and 0.01N NaOH at 1 bed volume at a flow rate of not more than 4 bed volumes per hour, respectively

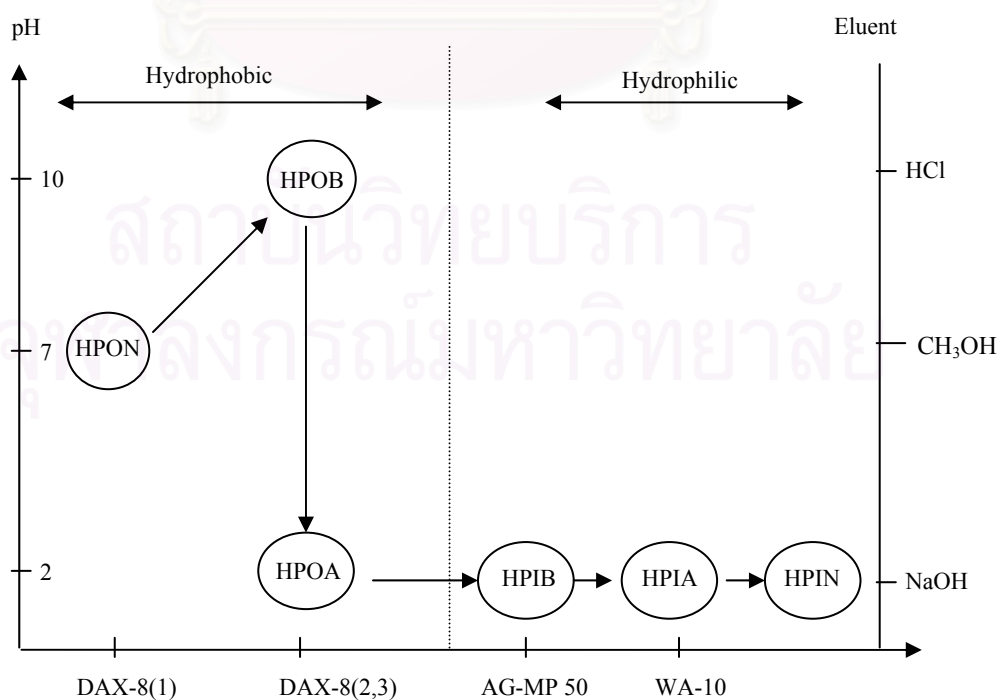


Figure 3.4 Fractionation procedure (Marhaba *et al.*, 2003)

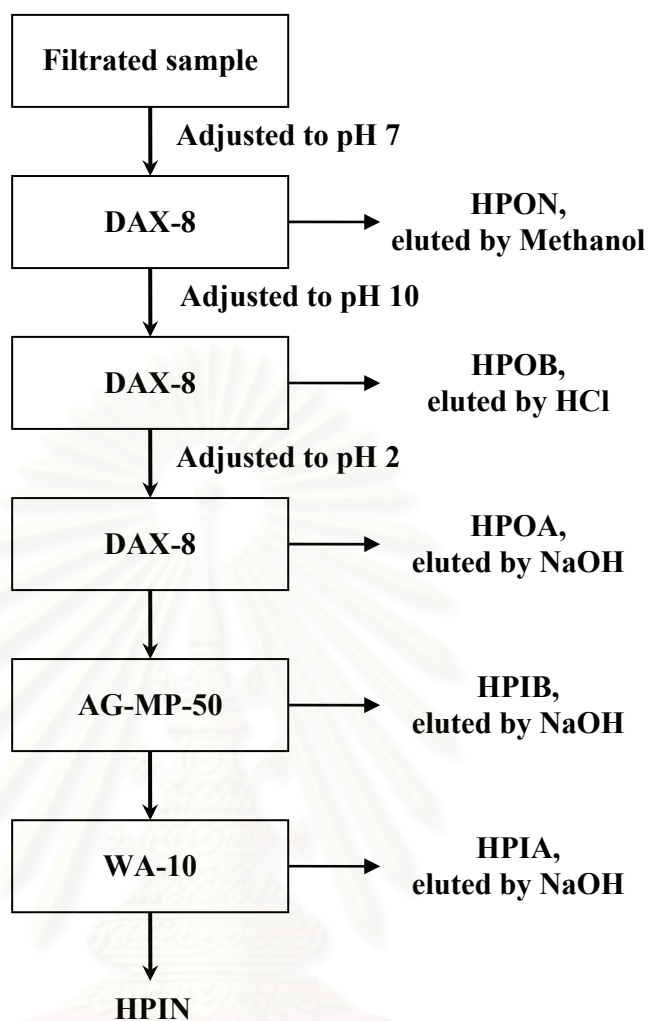


Figure 3.5 Fractionation schematic diagram (Marhaba *et al.*, 2003)



Figure 3.6 Fractionation columns

3.3.3 Trihalomethane Formation Potential (THMFP) test

THMFP tests for all samples (raw water, fractionated water, and coagulated water) were achieved following the Standard methods 5710B, 7 days chlorine test with sodium hypochlorite solution. Detailed procedure for this test follows:

- Adjust the pH of the samples to 7 ± 0.2 using H_2SO_4 and NaOH
- Add 1 ml phosphate buffer solution for each 50ml of sample.
- Incubate the samples at $25\pm 2^\circ C$ in amber bottles with PTFE liners for 7 days
- Test for the residue chlorine at the end of day 7. The samples must have a remaining free residue chlorine of between 3-5 mg/L.
- Extract THMs with pentane according to the procedure mentioned in the Standard Methods 6232B.
- Analyze THMs by the GC with ECD detector (Agilent 6890 series).

GC Condition for the determination of THMs are as follow.

Manufacture name/model	Agilent 6890
Column	DB 624, J&W Science
Detector	ECD
Injection temperature	225°C
Initial temperature	75°C
Temperature program	<ul style="list-style-type: none"> • 15°C/minute to 100°C holding time 1 minute • 15°C/minute to 130°C holding time 1 minute • 15°C/minute to 180°C holding time 1 minute
Final time duration	11 minutes

3.4 Coagulation Experiment

Jar-tests (Phipps and Bird), as shown in Figure 3.7, were conducted to determine the optimum concentration and pH for the coagulation of organic contents using alum and polymers. Four types of commercially available polymers were investigated in this

work, i.e. cationic polyacrylamide; CatPAM (Policat C-84EF, Kemwater), anionic polyacrylamide; AnPAM (Magnafloc 308, Ciba), polydiallyl dimethyl ammonium chloride; DADMAC (C591, Cytec), and epichlorohydrin dimethyl amine; EpiDMA (C319, Polydyne). The testing conditions included the doses of alum and polymers, types of polymers, and the level of pH as given in Table 3.1. The detailed coagulation combination of conditions is illustrated in Figure 3.8. The procedure for the coagulation experiment can be summarized as follows.



Figure 3.7 Jar-test apparatus

Procedure in coagulation experiment:

- Add NaOH or H₂SO₄ (to adjust pH)
- Add alum and rapid-mix at 100 rpm for 1 minute
- Add polymer and rapid-mix at 100 rpm for 1 minute
- Slow-mix at 30 rpm for 30 minutes
- Leave it to settle for 1 hour before collecting the supernatant sample
- Filtrate through 0.45 μm membrane filter paper
- Measure DOC, UV-254 and carry out THMFP test

The efficiency of coagulation process was measured by monitoring the changes in THMFP, DOC and UV-254 before and after the coagulation. As the optimum coagulation condition for each polymer was determined, the coagulated samples with the optimal condition were fractionated to examine for the remaining

organic fraction. Experiments with random samples were 10% duplicated for quality control purposes.

Table 3.1 Coagulation condition

Conditions	
Alum dose	15, 30, and 45 mg/L
Polymer type	Cationic polyacrylamide (A) Anionic polyacrylamide (B) Polydiallyl dimethyl ammonium chloride (C) Epichlorohydrin dimethyl amine (D)
Polymer dose	0.1, 0.5, and 1.0 mg/L
pH	5.5, 7.0, and 8.5

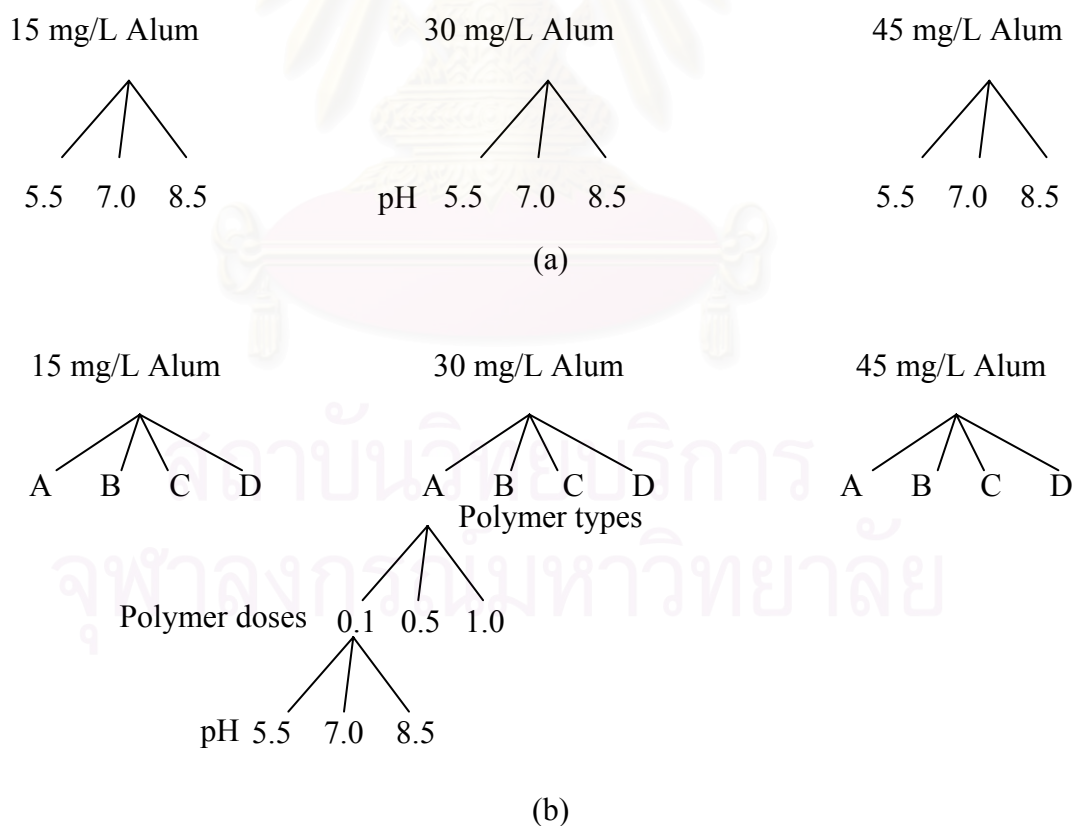


Figure 3.8 Coagulation conditions: (a) Coagulation with alum, (b) Coagulation with alum and polymer

3.5 Analytical Methods

3.5.1 DOC

The dissolved organic carbon (DOC) was measured from the filtered sample using the TOC analyzer (OI Analytical, Model 1010, 1051) followed the Standard Methods 5310C. Potassium hydrogen phthalate (KHP) was used to prepare standard for the calibration of the TOC instrument (prepared at concentration of 1000 mg/L). The calibration curve was done at five concentrations, i.e. 0, 1, 2.5, 5, and 10 mg/L. All samples were pH adjusted to 7 by NaOH or H₂SO₄ before measurement. At least three replications of each measurement were carried out and more replications were executed in the cases where the variation between each measurement exceeded 5%. Milli-Q water was run at every three samples to clean the system.

3.5.2 Free chlorine

Residual chlorine was measured in accordance with the procedure mentioned in the Standard Method 4500-Cl G i.e. N, N-dethyl-p-phenylenediamine (DPD) colorimetric method. The level of chlorine was then represented by the light absorbance at 515 nm using Genesys 10 UV thermo spectronic.

3.5.3 UV-254

The UV absorbance at a wavelength of 254 nm was reported to represent the aromatic character of organic matters as they imparted an ability to absorb light in the UV range. UV-254 was measured in compliance with the Standard Methods 5910B using Genesys 10 UV thermo-spectronic with a 1 cm quartz cell. All fractionated samples were adjusted to pH 7 by NaOH or H₂SO₄ prior to the measurement.

3.5.4 Turbidity

Turbidity of raw water was measured with HACH 2100N Turbidimeter. The turbidity of water was expressed in the unit of nephelometric turbidity unit (NTU).

3.5.5 pH

All samples were measured for their pH level with HACH EC 30 pH meter. Before each experiment, the instrument was calibrated at pH 4, 7, and 10 according to the procedure recommended by the supplier.

3.5.6 Alkalinity

Alkalinity of sample was determined by the titration with 0.02 N H₂SO₄ according to the Standard Methods 2320-B.

3.5.7 Bromide ion

Bromide content was measured by using an ion chromatography instrument (DIONEX, ICS-2500).

The summary of analytical methods and instruments involved in this work are shown in Table 3.2.

Table 3.2 Analytical method and instrument

Parameter	Analytical method	Instrument
TOC	Standard Method 5310 C	OI Analytical, Model 1010, 1051
UV	Standard Method 5910 B	Genesys 10 UV thermo spectronic
pH	-	Horiba pH meter
Turbidity	-	HACH, 2100 Turbidity meter
Alkalinity	Standard Method 2320 B	-
Free chlorine	Standard Method 4500-Cl G	Genesys 10 UV thermo spectronic
THMFP& THMs	Standard Method 5710 and 6232 B	Agilent 6890 series gas chromatography with ECD detector

Note that Milli-Q water (ELGA, Ultra Analytical) was used for all dilutions, samples and chemicals preparation, and final glassware cleansing in this work.

CHAPTER IV

CHARACTERIZATION OF ORGANIC FRACTIONS AND TRIHALOMETHANE PRECURSORS

4.1 Literature Reviews on the Identification of Disinfection By-Product Precursors

Organic matters consist of a large variety of organic compounds and in many cases these compounds are referred to as one quantity, i.e. dissolved organic carbon (DOC). This is to simplify the test method and to reduce the analysis time in characterizing the state of the water source. However, the wide variety of the physical/chemical properties of DOC prevents the thorough evaluation of the kinetics of reactions of DOC with other chemicals such as, in this case, chlorine. Hence, several investigations (as shown in Table 2.1) have introduced more detailed quantities to describe the organic matters, and this was commonly based on the chemical properties of the organic constituents such as hydrophobic and hydrophilic nature, and/or the acid/base disposition. To achieve this, fractionation methods by using resin adsorption are often employed. Several studies have reported source water characteristics from different source waters located in many countries using the fractionation method, and also evaluated the THMFP of each organic fraction, details as shown in Table 2.1 in Chapter 2.

4.2 Purposes of this Chapter

The main purpose of this chapter was twofold. Firstly, it was aimed to investigate the mass distribution of dissolved organic fraction of the water sample from Bangkok Water Treatment Plant. This was accomplished by using the resin adsorption technique as proposed by Marhaba *et al.* (2003). Next, the THMFP of each individual organic fraction was determined. The characterization of this water source would be useful in the future management of this water treatment facility, such as the development of suitable DBPs control methods, etc.

4.3 Materials and Methods

Experiment in this part follows the steps specified in Figure 4.1. In this work, the resin adsorption technique as proposed by Marhaba *et al.* (2003) was employed to

separate the dissolved organic matters in the water sample into six different fractions. Detailed procedure for the fractionation method and the experimental method on THM formation potential test (THMFP) are provided in Chapter 3 (Section 3.3). The relationships between the total DOC and DOC of each organic fraction with THMFP were examined by a simple linear regression analysis by the commercially available statistical program, SPSS version 11.5.

4.4 Results and Discussion

4.4.1 Characterization

The results from the analysis of the water samples and from the fractionation are illustrated in Figure 4.2. The DOC mass distribution sequences of the six organic fractions in raw water from high to low were HPIN, HPOA, HPIA, HPON, HPIB, and HPOB. It can be seen that the total weight of all organic fractions was about 9% more than the original weight in the water sample. This weight surplus may have come from resin bleeding during the elution process (Leenheer, 1981). This level of inaccuracy was considered acceptable as this fractionation technique was often reported to give as much as 10-15% tolerance of DOM recovery (Day *et al.*, 1991; and Marhaba and Pipada, 2000). Variation from 8-12% was also reported by Croue *et al.* (1993).

The results from Figure 4.2 revealed that hydrophilic neutral (HPIN) fraction was the major component in the water sample (45%) whilst the hydrophobic acid (HPOA) was the second (34%). These two fractions alone constituted as much as 79% of the total organic content. The remaining of the organic fractions were HPIA (18%) and HPON (6%) whereas the last two fractions (HPIB and HPOB) existed in slight quantity (each at 3%). Comparative evaluation of these results along with the reported data from literature was provided hereafter.

4.4.2 THMFP

Percentage distribution of THMFP of each organic fraction is shown in Figure 4.3. The first two main precursors of THMFP were found to be HPIN and HPOA with 32% and 21% by weight of THMFP obtained from these two fractions, respectively. HPIA, HPOB

and HPIB produced the same level of THMFP at around 13-15% by weight, whereas HPON was found to give the smallest quantity of THMFP. The THMFP results of each fraction were evaluated against the other reported data in the following subsections.

Figure 4.4 illustrates the comparison between the total THMFP and the specific THMFP from each organic fraction. The total THMFP was defined as the ratio between THMFP from each organic fraction and DOC of the water sample. This was to give an overall picture of how THMs were formed in the water sample. The specific THMFP, on the other hand, was the ratio between THMFP and DOC of each organic fraction. This facilitated the analysis of the reactivity of each organic fraction on the formation of THMs. The total THMFP was derived from each organic fraction with HPIN being the main source whereas HPOA the second. This finding was not surprising as these two fractions were the two main organic components (79%) in this water source. Other fractions could be ordered according to their capability in forming THMs from high to low as: HPIB, HPOB, HPIA, and HPON, respectively. It should be mentioned, however, that, although organic fractions with larger quantity could potentially lead to more THMs formed during the chlorination, the reactivity of such organic fractions might not follow the same trend. The results from the analysis revealed that the main precursors of THMs in this water source were not observed to be the most active THM precursor, and rather, they were among the most inactive as discussed further below.

4.4.2.1 HPOA and THMFP

The concentration of HPOA was found to be about 34% (DOC 1.62 mg/L) in raw water and this was capable of producing 21% by weight of THMs (see Figures 4.2 and 4.3). This level was found to be in the reported range of 8 – 68% in raw waters elsewhere (Day *et al.*, 1991; Korshin *et al.*, 1997a; and Marhaba and Van, 1999). In terms of the total THMFP, this fraction was the second most important source and it was the main source of THMFP among the hydrophobic species. However, according to its specific THMFP, this fraction was one of the least active sources (see Figure 4.4). This implied that HPOA was the major precursor of THMFP simply because it was presented in large quantity in raw water. This finding was found to be different from other reports. For instance, Chang *et al.* (2001) demonstrated that HPOA

fraction was the greatest precursor for disinfection by-products, particularly THMs. This might be due to the differences in the character of the organic species in the water samples.

4.4.2.2 HPOB and THMFP

This fraction was observed to give the highest specific THMFP at 619 $\mu\text{g}/\text{mg}$. This indicated that HPOB was highly reactive with chlorine in forming THMs. This corresponded well with the report of Marhaba and Van (1999). More importantly, Marhaba and Van (2000) reported that this fraction could not be effectively removed by coagulation from the raw water. For this reason, this fraction could be used as one of the warning signals of THMs in the treatment process. However, in this case, its relatively low total THMFP suggested that this fraction did not exist in large quantity with only 3% by weight of the DOC content in the raw water. This finding was similar to other reports which indicated that the range of HPOB in other water sources was in the range of 0-22% by weight (Day *et al.*, 1991; Korshin *et al.*, 1993; Marhaba and Van, 1999; and Marhaba and Van, 2000).

4.4.2.3 HPON and THMFP

HPON was the least problematic precursor to THMs in the water sample as its contribution to the total THMFP was the lowest among the six organic fractions, and it also was relatively inactive to the reaction with chlorine (low specific THMFP). Hence, this fraction was not considered as a problematic precursor for THMs in this water source. In addition, HPON in the water sample existed in a relatively lower quantity (only 6%). The reported data on the quantity of HPON in other water sources were quite variable with the smallest of 0% (Korshin *et al.*, 1997a) to the largest of 36% (Leenheer, 1981). Other reported data (Chang *et al.*, 2001; Marhaba and Van, 1999; and Marhaba and Van, 2000) indicated that this organic fraction did not exhibit high specific THMFP when compared to other organic fractions, which agreed well with the finding in this work.

4.4.2.4 HPIA and THMFP

Figure 4.4 illustrates that HPIA had a rather low specific THMFP compared to other organic constituents in this water sample (in the same level as HPOA and HPIN). This meant that HPIA was quite inactive in forming THMs in the chlorination process. However, the total THMFP from this fraction was quite high. This was because it existed in a large quantity in the water source (18% by weight). This result was quite different from other reports, i.e. Marhaba and Van in 1999 and 2000 illustrated that HPIA was among the most active organic fraction in the formation of THMs. This was possibly due to the differences in the nature of HPIA from the different water sources. Note, however, that the quantity of HPIA obtained from this work lied within the reported range of 8 – 53% from other water sources (Day *et al.*, 1991; Korshin *et al.*, 1997; Marhaba and Van, 1999; and Marhaba and Van, 2000). Nevertheless, the presence of such organic species was rather significant in terms of future management of the treatment plant, as previous investigation (Marhaba and Van, 1999) revealed that HPIA fraction was one of the most difficult components to be removed by coagulation. Therefore, with its high quantity presented in the water source, this organic species could then be considered a problematic THM precursor.

4.4.2.5 HPIB and THMFP

Although HPIB was only presented in small quantity in this water source, the results in Figure 4.4 demonstrate that the total THMFP from this fraction was relatively high. The same figure shows that HPIB was actually the most active precursor of THMs as its specific THMFP was the second highest among the six organic fractions, and the greatest among the three hydrophilic fractions. It is therefore a major concern for the operation of water treatment plant as an only tiny amount of HPIB could lead to a formation of THMs in large quantity. In addition, the coagulation/sedimentation or filtration was not an effective means in removing this organic fraction (Marhaba and Van, 2000).

HPIB was also found to be presented in small quantity in the water source reported in (Korshin *et al.*, 1997a; Marhaba and Van, 1999; and Marhaba and Van, 2000). However, the reactivity of this fraction was only found to be moderate by

Marhaba and Van (1999). This meant that HPIB from the two water sources might consist of different organic species.

4.4.2.6 HPIN and THMFP

Specific THMFP as illustrated in Figure 4.4 indicates that HPIN was one of the most inactive organic precursors of THMs. A similar result was reported by Marhaba and Van (1999). This was possible as Bruchet *et al.* in 1987 reported that this organic fraction was primarily composed of polysaccharides, which were not quite reactive with chlorine. However, an extremely high total THMFP was obtained from this organic fraction. This was because HPIN was the most dominant constituent among the six organic fractions in this water sample (45% DOC). This was the highest among the reported data which stated that HPIN was in the range from 5-19% of the total organic content (Leenheer, 1981; Korshin *et al.*, 1997a; Marhaba and Van, 1999; and Marhaba and Van, 2000; and Marhaba *et al.*, 2003). Hence, for this particular water source, this fraction should be considered as the major concern in this water treatment facility as the main cause of THMs.

4.4.3 SUVA and THMFP

Table 4.1 illustrates the level of SUVA obtained from each organic fraction compared with the specific THMFP. The numbers in the table represented the average values of the parameters. The standard deviation was also added to the column to indicate the level of scattering on the experimental results. As can be observed from the previous section, the base fractions, either hydrophobic or hydrophilic properties, seemed to be the most reactive organic species with chlorine. Interestingly, these two base fractions also provided relatively high SUVA values (greater than 2 L/mg-m). High SUVA was reported to imply high aromatic character (Korshin *et al.*, 1997b; and Thompson *et al.*, 1997) and therefore this result implied that the aromatic organic compounds were the active precursors of THMs. The HPON fraction, however, also exhibited high level of SUVA but its specific THMFP was rather low. This meant that only the aromatic content with base property that was active in the chlorination reaction and despite a high content of aromatics, the neutral property of the HPON fraction did not lead to a production of THMs.

4.4.4 THM Species Formation Potential

THMs evaluated for each sample were the sum of four species, i.e. chloroform (CHCl_3), bromodichloromethane (CHCl_2Br), dibromochloromethane (CHClBr_2), and bromoform (CHBr_3). The results from the evaluation of THMFP of each water sample revealed that only chloroform and bromodichloromethane were formed during the chlorination of each organic fraction. The two brominated species, i.e. dibromochloromethane and bromoform, were not detected from the method employed in this work.

Figure 4.5a displays the specific chloroform formation potential ($\text{CHCl}_3\text{-FP}$) and specific bromodichloromethane formation potential ($\text{CHCl}_2\text{Br-FP}$) obtained from each organic fraction. The trend of specific $\text{CHCl}_3\text{-FP}$ followed that of specific THMFP quite closely. In other words, specific $\text{CHCl}_3\text{-FP}$ was generated mostly from the HPOB fraction followed in order from high to low by HPIB, HPON, HPIN, HPIA, and HPOA. This was because most of the THMFP formed in the water sample was chloroform, and the bromo-species (only bromodichloromethane in this case) was only responsible for as small as 3% of the total THMFP. Figure 4.5b illustrates that most of the THMs species in the samples was chloroform species where the total $\text{CHCl}_3\text{-FP}$ had the same trend as that for total THMFP. In other words, HPIN was the main source of $\text{CHCl}_3\text{-FP}$, and HPOA was the second most important.

The specific $\text{CHCl}_2\text{Br-FP}$, however, did not quite follow the trend of the specific THMFP. The most active precursor for this THM species became the HPIB, followed by HPOB, HPIA and HPOA from high to low, respectively. HPON was found not to react with bromide at all. HPIN, however, was not found to give bromodichloromethane but the analysis for the bromide content in this organic fraction revealed an absence of bromide ion (see Table 4.2). Hence, it could not be concluded that bromide did not involve in the chlorination reaction of HPIN. Figure 4.5b shows that the bromo-THM species was only presented in small quantity when compared to that of chloroform. Hence, unlike the case of $\text{CHCl}_3\text{-FP}$, the contribution of $\text{CHCl}_2\text{Br-FP}$ on the total THMFP was not obvious.

It is interesting to note that each organic fraction contained different amount of bromide ion as indicated in Table 4.2. This means that the resins used in the fractionation had different capacity in retaining bromide ions and therefore the organic eluants from the back-elution of the organic fractions consisted of bromide ion at different levels. The different bromide ions in each organic fraction might affect the species of the THMs in each fraction of water sample. For instance, HPOA was found not to be active when compared with that of HPIA, but the level of bromide ions presented in HPOA fraction (0.002 mg/L) was also significantly lower than that in HPIA fraction (0.069 mg/L). Hence, it was difficult to conclude that HPIA was more active in forming bromodichloromethane than HPOA. On the other hand, it was clear that HPOB was significantly more active in reacting with bromide ions than other species as there was only a relatively small level of bromide ions in this organic fraction (0.016 mg/L). However, the amount of brominated THM species only accounted for as much as 12% of the total THMs, and our preliminary results (not shown here) also revealed that the influence of bromide concentration (in the range found in the work) on the formation of the various THM species was at most 12%. Hence, the effect of bromide ion concentration was not included in this discussion.

4.4.5 Relationship between DOC and THMFP

Further investigation was conducted to examine the relationship between the level of organic content and the THMFP from each organic fraction. Hence, each organic fraction was diluted to four concentration levels, each of which was tested for its THMFP. The results are displayed in Figure 4.6. Linear relationships were found in all cases with the correlations between THMFP and the DOC of each organic fraction as follows:

$$Y_1 = 27.955 X_1 + 74.644 \quad (R^2 = 0.966, N = 11) \quad \text{--(4.1)}$$

$$Y_2 = 405.85 X_2 + 31.363 \quad (R^2 = 0.998, N = 12) \quad \text{--(4.2)}$$

$$Y_3 = 76.502 X_3 + 17.845 \quad (R^2 = 0.996, N = 11) \quad \text{--(4.3)}$$

$$Y_4 = 56.865 X_4 + 38.193 \quad (R^2 = 0.993, N = 11) \quad \text{--(4.4)}$$

$$Y_5 = 379.04 X_5 + 33.665 \quad (R^2 = 0.986, N = 12) \quad \text{--(4.5)}$$

$$Y_6 = 75.675 X_6 + 31.535 \quad (N = 7) \quad \text{--(4.6)}$$

where Y_{1-6} are THMFP of HPOA, HPOB, HPON, HPIA, HPIB, and HPIN, respectively ($\mu\text{g/L}$), and X_{1-6} are DOC of HPOA, HPOB, HPON, HPIA, HPIB, and HPIN, respectively (mg/L).

The number of data points used to construct Equations (4.1)-(4.5) was equal to twelve as there were four concentration levels and the test at each level was triplicate. However, those out-of-range data points were removed in some circumstances and therefore the number of samples was some time reduced to eleven. In addition, the HPIN fraction could not be prepared in a highly concentrated form and therefore there were only two concentration levels available for the construction of such relationship with THMFP. This made the total sample number of six and with an extra set of experimental data conducted in the formulation of Equation (4.6), the total number of samples for this equation became 7. Overall, the linear dependency between the various organic species and THMFP indicated that the reactions between these organic fractions with chlorine were first-order, at least for the range of concentrations and source water reported in this work.

4.5 Concluding Remarks

The investigation illustrated the organic characteristics of the water from the Bangkhen Water Treatment Plant. The dominant organic fractions in this water source were HPIN and HPOA. THMFP obtained from these two fractions were also found to be in largest quantities when compared to other species. However, the results indicated that the most active precursors for THMFP were not the species that were present in large quantity, but were HPOB and HPIB. These two species were also found to be quite active in forming chloroform species but the brominated THM species was found to be derived mostly from HPIA and HPIB. In the next chapter, the formation kinetics of each THM species will be examined. The effect of fractionation method on the formation of THMs will also be scrutinized.

4.6 Tables and Figures

Table 4.1 SUVA and Specific THMFP of organic fractions

Source	SUVA (L/mg-m)	Specific THMFP ($\mu\text{g}/\text{mg}$)
Hydrophobic		
Acid	1.67	77.9 \pm 6.5
Base	2.31	619 \pm 2.3
Neutral	2.59	145 \pm 8.6
Hydrophilic		
Acid	0.71	95.6 \pm 15
Base	2.50	551 \pm 41
Neutral	0.94	90.6 \pm 2.8

Table 4.2 Bromide ion concentration in water samples

	Bromide (mg/L)
RW	1.002
HPOA	0.002
HPOB	0.016
HPON	0.007
HPIA	0.069
HPIB	0.004
HPIN	0.000

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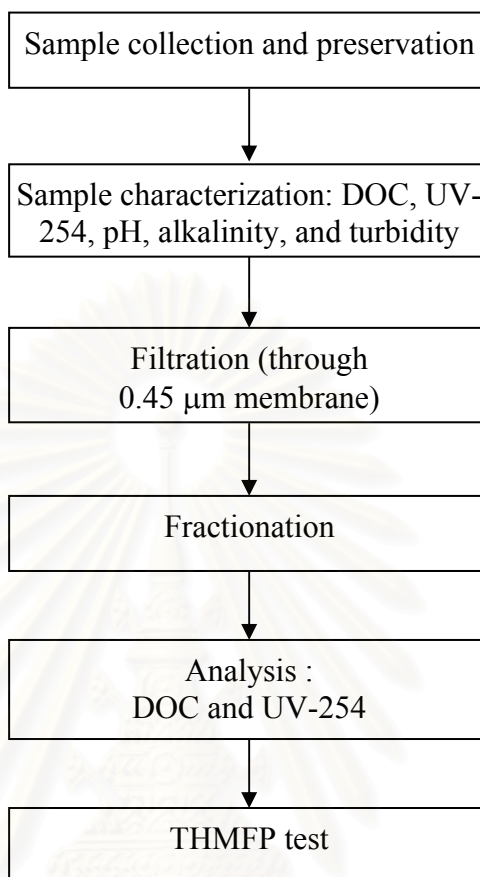


Figure 4.1 Experimental procedure

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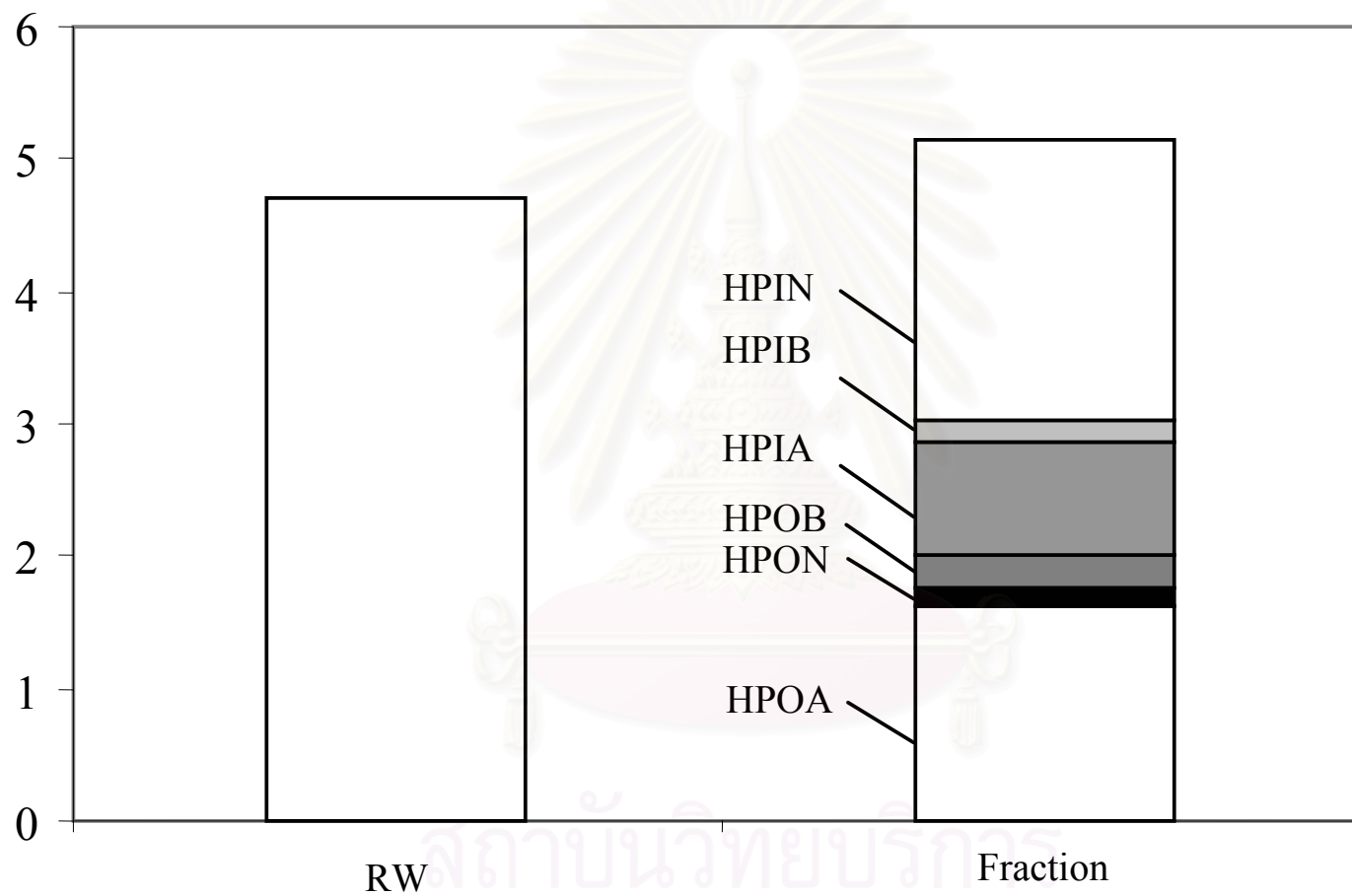


Figure 4.2 DOC of raw water (RW) sample and its associated organic fraction

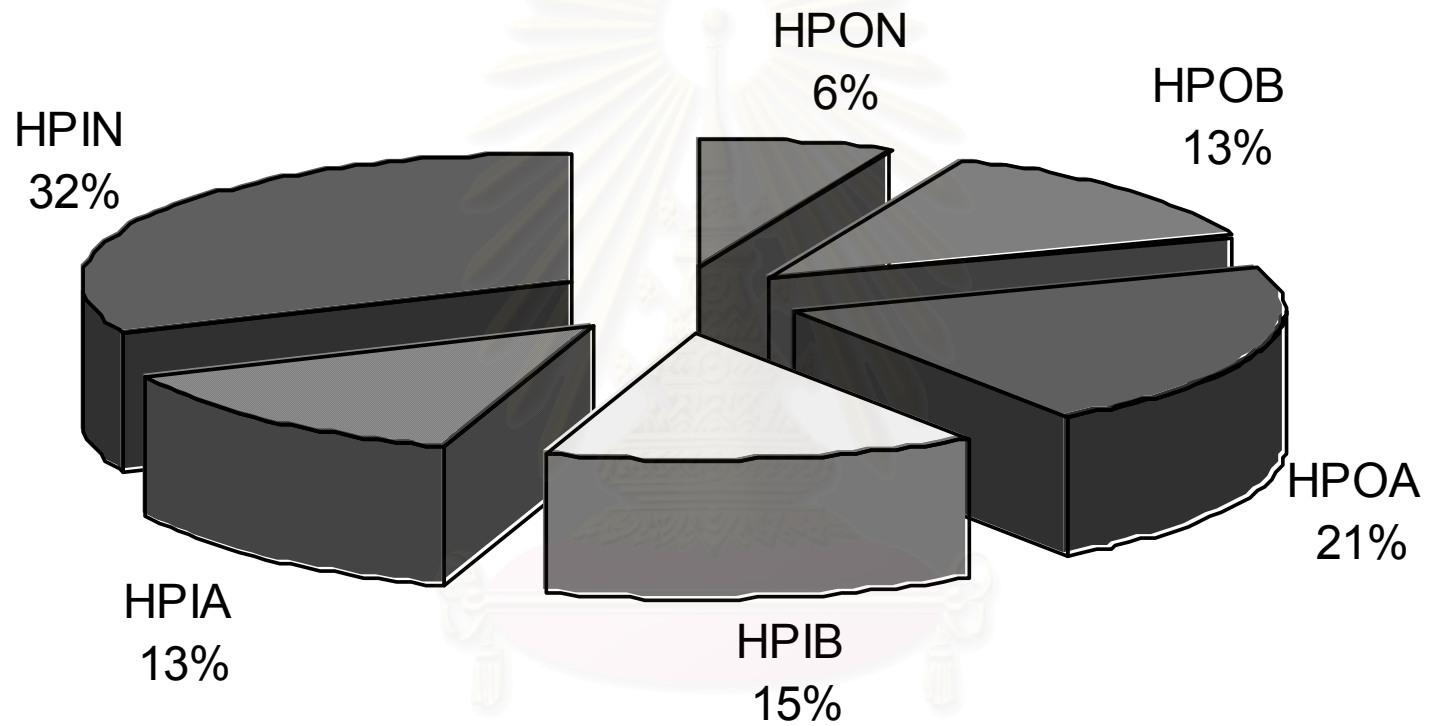


Figure 4.3 Percent distribution of THMFPP obtained from each organic fraction

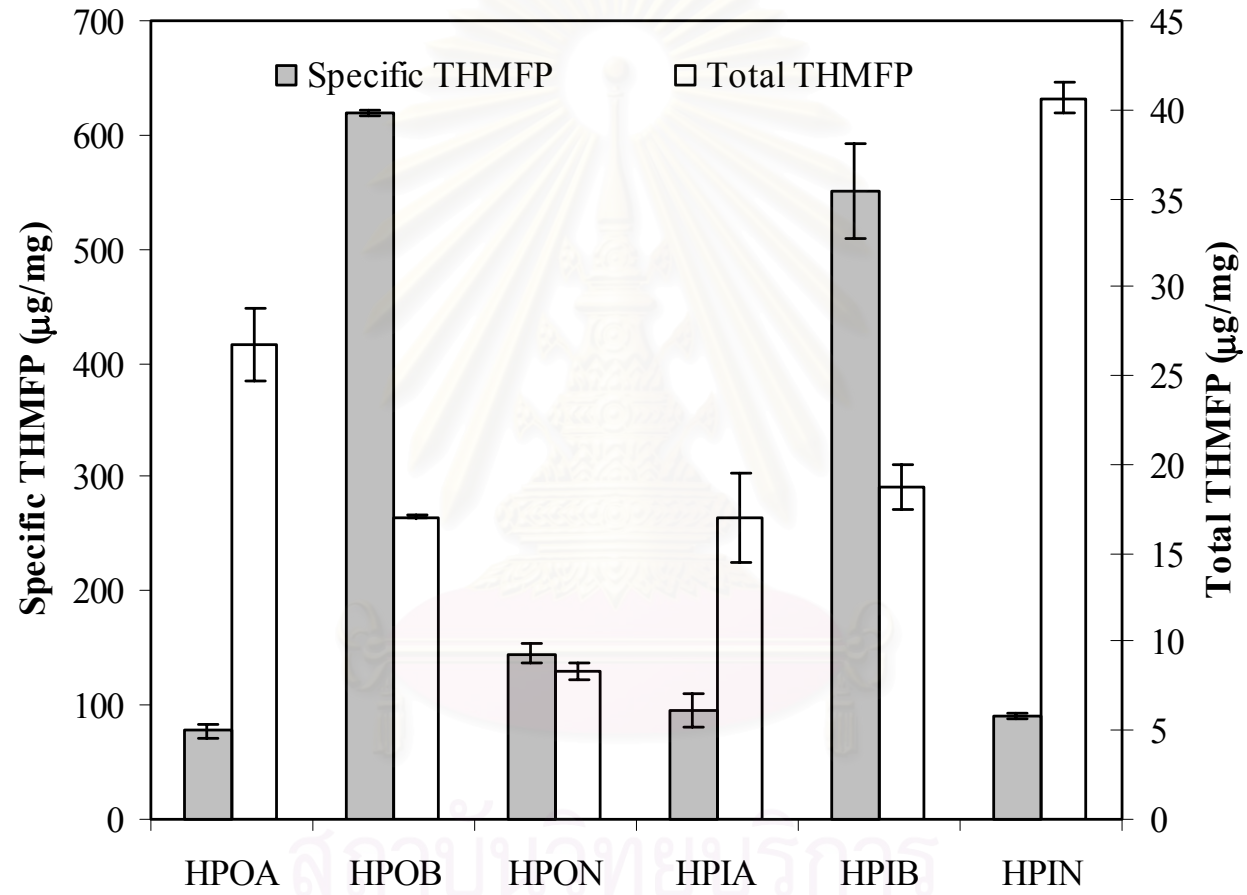


Figure 4.4 Specific and total THMFP

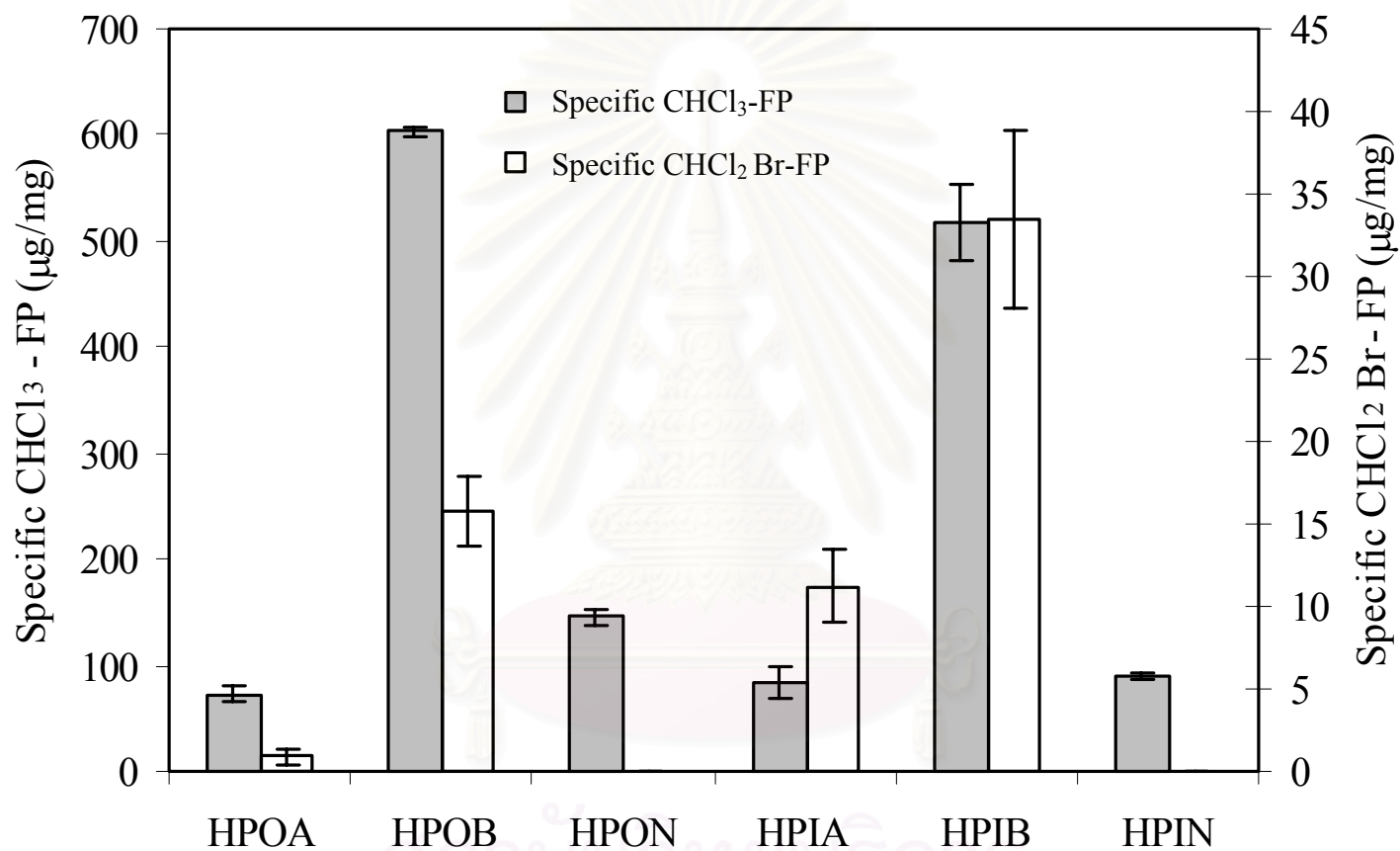


Figure 4.5 (a) Specific THM species formation potential from each organic fraction

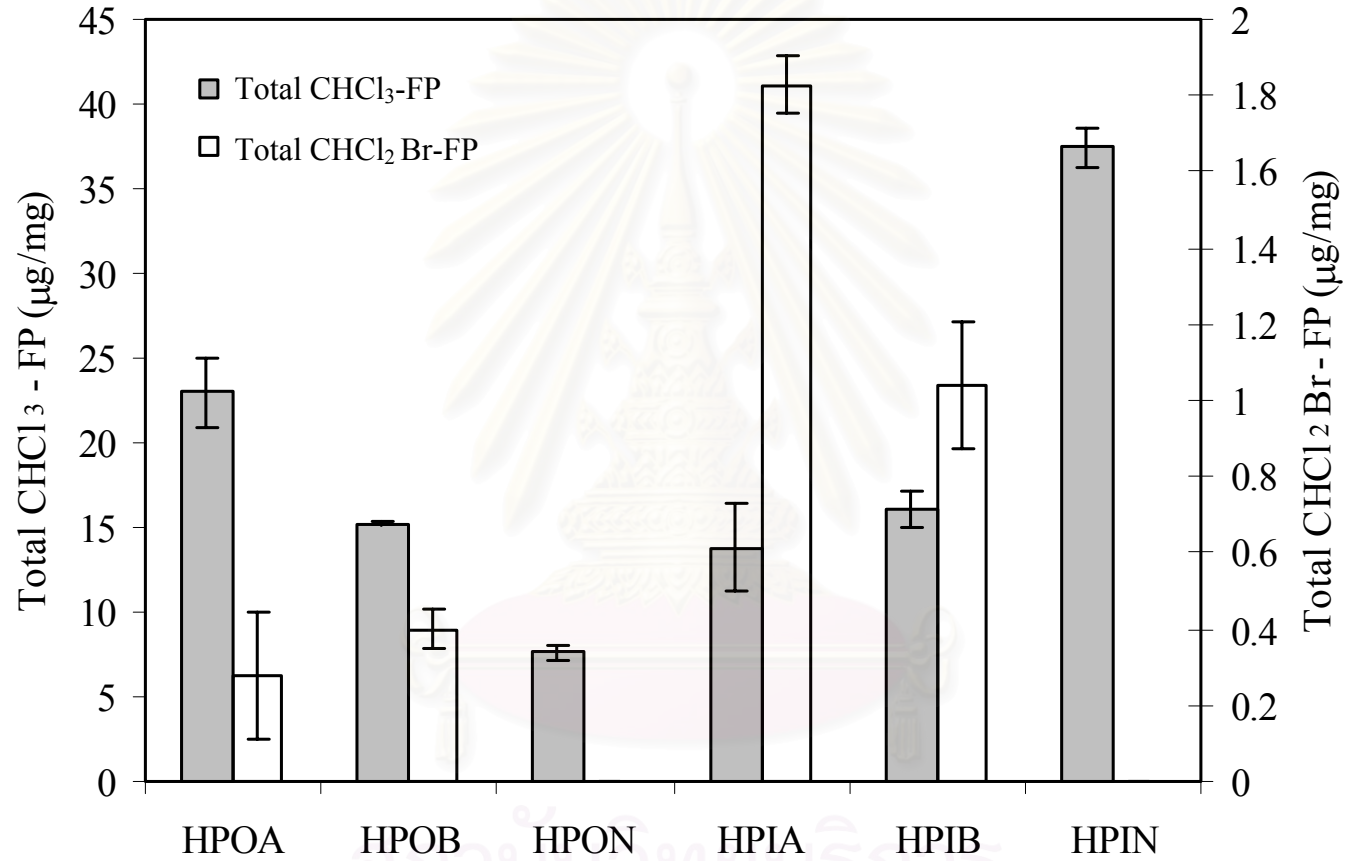


Figure 4.5 (b) Total THM species formation potential from each organic fraction

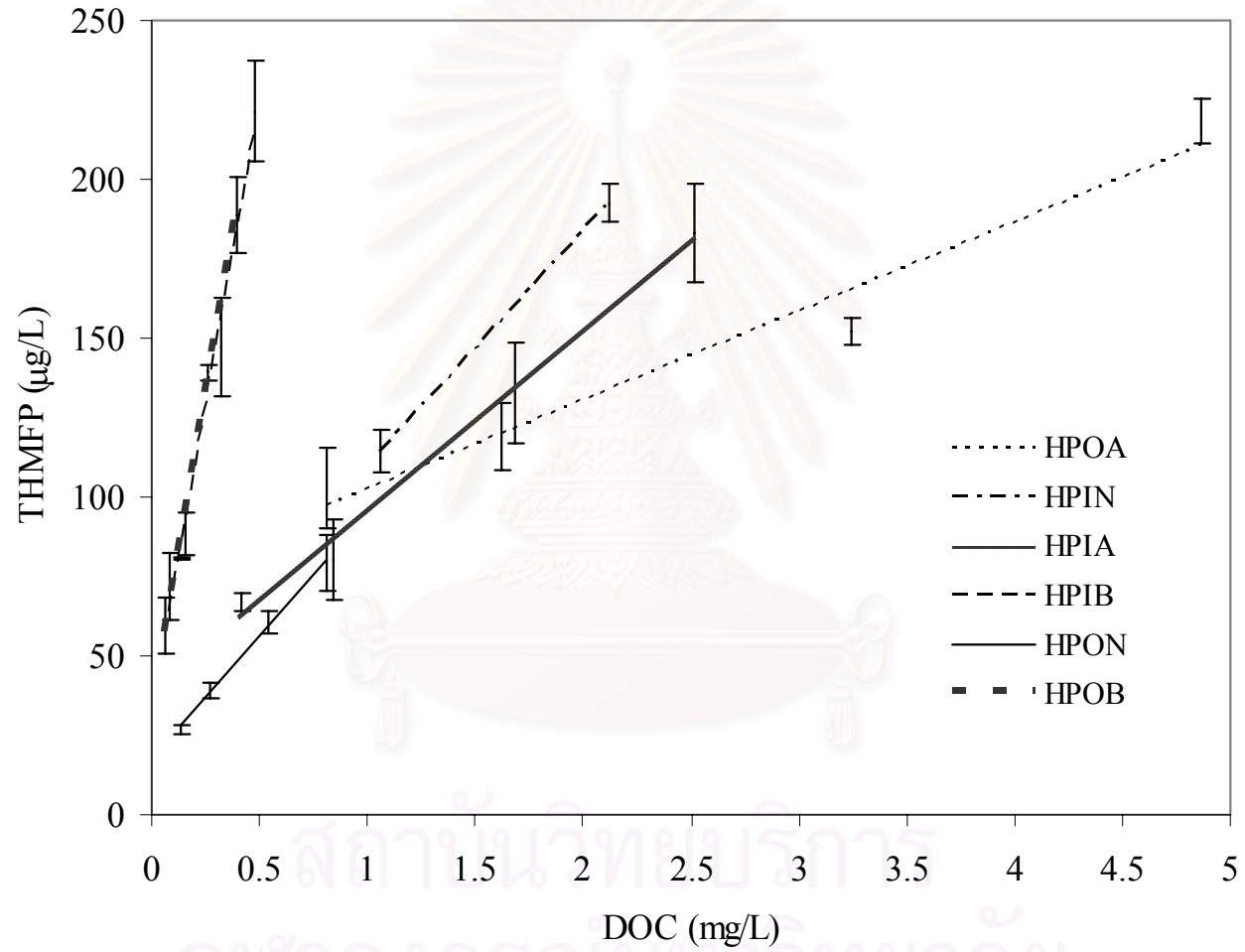


Figure 4.6 THMF of each organic fraction

CHAPTER V

KINETICS OF TRIHALOMETHANE FORMATION

5.1 Introduction and Purposes of this Chapter

Trihalomethanes consist of several methane derivative compounds. Chloroform (CHCl_3) is normally the predominant THM species in most water sources. However, in the water containing bromide, brominated trihalomethanes, i.e. bromodichloromethane (CHCl_2Br), dibromochloromethane (CHBr_2Cl) and bromoform (CHBr_3) can also be formed. Details of these THMs species are provided in Section 2.3.3 in Chapter 2. Brominated THM species were suspected to be much stronger carcinogens and mutagens than their chloride-containing analogues (Nobokawa and Sanukida, 2001). Therefore brominated THM species are considered more toxic than nonbrominated species. Fortunately, brominated THM species was commonly found to account for only about 20-25% of the total THMs value (Marhaba and Van, 1999).

To date, the investigation on the formation of THMs was limited to the total THMs, and not for each specific THM species. It is common to realize that, in the absence of bromide, all THM will be confined to chloroform. However, in several watercourses including all the fresh water sources, there always exists at least a tiny amount of bromide. Hence, the brominated THM species could always be found. In this chapter, the generation of each specific THM species was investigated. The influence of the fractionation method on the bromide level in each organic fraction could potentially affect the formation of different THM species. This was also examined in this chapter.

5.2 Materials and Methods

Similar experiment as that carried out in Chapter 4 was repeated here. Briefly, the resin adsorption technique as proposed by Marhaba *et al.* (2003) was employed to separate the dissolved organic matters in the water sample into six different fractions. Detailed procedure for the fractionation method and the experimental method on THM formation potential test (THMFP) are provided in Chapter 3 (Section 3.3).

5.3 Results and Discussion

5.3.1 Organic Content in Raw Water from Bangkhen Water Treatment Plant

The results from the analysis (DOC and UV) and the fractionation of raw water from the Bangkhen water treatment plant are illustrated in Table 5.1. A 9% weight surplus of the organic constituents in the six organic fractions from the original organic content in the water sample was observed. This weight surplus may have come from resin bleeding during the elution process Leenheer, 1981. This fractionation technique was often reported to give as much as 8-15% tolerance of DOM recovery (Day *et al.*, 1991; and Marhaba and Pipada, 2000) and therefore this level of inaccuracy was considered acceptable. HPIN was found to be the major organic component in this water source, whereas the rest of organic components were ordered according to their quantities from large to small as HPOA, HPIA, HPON, HPIB, and HPOB, respectively.

5.3.2 THM Species Formation Potential

Four THM species, including chloroform (CHCl_3), bromodichloromethane (CHCl_2Br), dibromochloromethane (CHClBr_2), and bromoform (CHBr_3), were considered in this work. The results in Table 5.2 revealed that only chloroform and bromodichloromethane were generated from the chlorination of each organic fraction, and the different organic fractions were observed to have different influence on the formation of these two THM species. Most chloroform (approx. 33% of the total chloroform) was found to occur as a result of the chlorination of HPIN species whereas chloroform from HPOA was responsible for another 20%. HPIB, HPOB, and HPIA resulted in a similar range of chloroform formation (12-14%), whilst HPON was least significant in forming chloroform (7%). For bromodichloromethane, HPIA was observed to be the most important reactant for this water source where as much as 52% of bromodichloromethane was obtained from the chlorination of this fraction alone. The rest could be ordered from the most significant to the least as follows: HPIB, HPOB, and HPOA. Interestingly, bromodichloromethane was not detected from the chlorinated HPIN and HPON samples.

To examine the reaction kinetics of THM species, each organic fraction was adjusted to various concentration levels and tested for its THMFP. The results displayed in Figure 5.1 suggested that linear relationships could be established in all cases. Note that, dibromochloromethane was detected from the HPIA sample when the concentration of HPIA was increased above twice as much as the raw water concentration. It was possible that dibromochloromethane was also formed at low HPIA concentration, but with the quantity below the detection limit of the measuring method employed in this work. Similarly, bromodichloromethane was not found from the HPON fraction at original organic concentration. However, at elevated level of HPON, bromodichloromethane was observed which could be a result of the detection limit or it might be that the original HPON concentration was far too low for the generation of bromodichloromethane. Results in Figure 5.1 could be employed to formulate the equations that described the formation of each THM species as follows:

For HPOA fraction:

$$\text{Chloroform} = 27.538 \text{ DOC} + 74.141 \quad \text{--(5.1)}$$

$$\text{Bromodichloromethane} = 0.393 \text{ DOC} + 0.815 \quad \text{--(5.2)}$$

For HPOB fraction:

$$\text{Chloroform} = 390.47 \text{ DOC} + 3.063 \quad \text{--(5.3)}$$

$$\text{Bromodichloromethane} = 15.216 \text{ DOC} + 0.215 \quad \text{--(5.4)}$$

For HPON fraction:

$$\text{Chloroform} = 73.4 \text{ DOC} + 18.443 \quad \text{--(5.5)}$$

$$\text{Bromodichloromethane} = 3.101 \text{ DOC} - 0.598 \quad \text{--(5.6)}$$

For HPIA fraction:

$$\text{Chloroform} = 49.225 \text{ DOC} + 34.717 \quad \text{--(5.7)}$$

$$\text{Bromodichloromethane} = 7.251 \text{ DOC} + 3.846 \quad \text{--(5.8)}$$

$$\text{Dibromochloromethane} = 0.823 \text{ DOC} - 0.66 \quad \text{--(5.9)}$$

For HPIB fraction:

$$\text{Chloroform} = 347.99 \text{ DOC} + 32.611 \quad \text{--(5.10)}$$

$$\text{Bromodichloromethane} = 31.053 \text{ DOC} + 1.052 \quad \text{--(5.11)}$$

For HPIN fraction:

$$\text{Chloroform} = 73.694 \text{ DOC} + 36.298 \quad \text{--(5.12)}$$

5.3.3 Effect of Fractionation Method on THMFP

Table 5.3 demonstrates interesting results on the THMFP of the various water samples from the same source. The first row reports the THM species obtained from the chlorination test of the raw water without passing through the fractionation resins. This sample is called “raw water sample (RW)” hereafter. The second row was the result from the mixed sample where the six organic fractions were mixed together before the THMFP test (this is called “mixed sample” or “MS”). The last row was the summation of the test results from each organic fraction and is called “fractionated samples” or “FS”.

Let us first focus on the brominated species, Table 5.3 clearly stated that more brominated species were formed in the RW than in the MS and FS. Specifically, the total brominated species in the RW was 50.74 $\mu\text{g/L}$ (43.76 $\mu\text{g/L}$ of bromodichloromethane and 6.98 $\mu\text{g/L}$ of dibromochloromethane), whilst 14.01 and 18.23 $\mu\text{g/L}$ were found in the MS and FS, respectively. To understand this variation in the formation of brominated species in these various samples, it was useful to look at the bromide concentration in the samples which was demonstrated in Table 4.2. The raw water from Bangkok water treatment plant was found to contain a rather high level of bromide (1.002 mg/L). This bromide, however, was neither adsorbed by the DAX-8 (non-ionic) nor AG-MP-50 (cationic) resins, and this resulted in a quite low bromide level in each organic fraction eluted from these resins. There was an exception for HPIA where bromide concentration was found to be extremely high in this fraction. The reason for a high bromide concentration in this fraction still could not be concluded at the time of this work, but it could be that some bromide ion was released from the molecular structure of the various organic compounds during the harsh fractionation conditions. In addition, the resulting high bromide level in this fraction might be because the anionic WA-10 resin had very high adsorption capacity for bromide. This adsorbed bromide was then eluted together with HPIA fraction and this led to a high bromide level only in this organic fraction. Therefore, during the THMFP test, most organic fractions were subject to an extremely “low” bromide concentration (much lower than the raw water concentration). This led to an absence of brominated species in these fractions as observed from the results in Table 5.2. It is

worth noting here that HPIA must not be active for the formation of dibromochloromethane. This was obvious from the results where a high bromide level in HPIA was observed without generating dibromochloromethane at its original organic concentration. This dibrominated species could only be seen in the case where the concentration of HPIA was increased by three times (see the previous section).

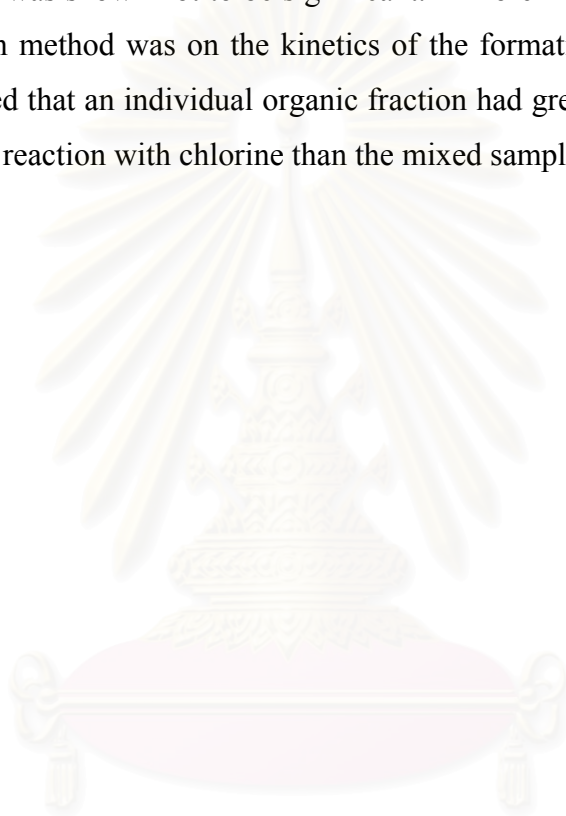
Although there seemed to be a limitation on the use of resin adsorption technique on the samples that contained high level of bromide, the error obtained from the absence brominated species only accounted for approximately 10-12% when compared to the total THMFP obtained from the raw water sample. This level of inaccuracy should be tolerable compared with the errors associated with the fractionation procedure or THMFP test.

A more significant deviation of THMFP results was observed in the test for the THMFP for each organic fraction. Table 5.3 indicates that THMFP of the RW was far lower (almost 100% lower) than that of the FS. The results demonstrated clearly that this deficiency was due to the chloroform species as the chloroform generated from the FS was as great as 582 $\mu\text{g/L}$, whereas that of RW was only 262 $\mu\text{g/L}$. By adding the six fractions together, the chloroform formation was reduced greatly from 582 to 291 $\mu\text{g/L}$ (as obtained from the MS sample). The level obtained from the MS sample was in the same level as that of RW. This demonstrated that there must exist some inhibition effect on the formation of THMs when the six organic fractions were present together in the same sample during the chlorination process.

5.4 Concluding Remarks

Water samples from Bangkok water treatment plant was analyzed to examine the potential that THMs were formed during the chlorination process. This work revealed that the two main organic components this water source, i.e. HPIN and HPOA, although might not be the most active, were the main precursors for THMs. The key THM component obtained from these organic fractions was chloroform which accounted for as much as 52 wt% of the total THMs. On the other hand, most brominated species were found to occur from the chlorination of other organic components. Interestingly, experiment results indicated that bromide levels in the

fractionated samples were not the same as that of the original water source as the different resins possessed different affinity for bromide. It was the last resin in the procedure (WA-10) which was observed to have great affinity for bromide, and there for a high bromide level was detected in the HPIA fraction eluted from this resin. It was demonstrated that, although the different bromide adsorption capacities from each resin could lead to some confusion in the interpretation of the results, its associated error was shown not to be significant. A more important finding regarding the fractionation method was on the kinetics of the formation of THMs. The results clearly illustrated that an individual organic fraction had greater capability in forming THMs from the reaction with chlorine than the mixed samples.



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5.5 Tables and Figures

Table 5.1 Characteristics of organic fraction and raw water.

	TOC (mg/L)	UV (cm ⁻¹)
RW	4.72	0.122
HPOA	1.62	0.027
HPOB	0.13	0.003
HPON	0.27	0.007
HPIA	0.84	0.006
HPIB	0.16	0.004
HPIN	2.12	0.020
Total	5.14	

Note: RW = Raw water, HPOA = Hydrophobic acid, HPOB = Hydrophobic base, HPON = Hydrophobic neutral, HPIA = Hydrophilic acid, HPIB = Hydrophilic base, HPIN = Hydrophilic neutral

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Table 5.2 Trihalomethane formation potential from each organic fraction.

	CHCl ₃ (µg/L)	CHBrCl ₂ (µg/L)	CHBr ₂ Cl (µg/L)	CHBr ₃ (µg/L)	Total THMs (µg/L)	Chlorine demand (mg/L)
HPOA	118	1.42	ND	ND	120	1.3
HPOB	78	2.06	ND	ND	80	0.2
HPON	39	ND	ND	ND	39	0.6
HPIA	71	9.4	ND	ND	80	0.4
HPIB	83	5.35	ND	ND	88	1.3
HPIN	193	ND	ND	ND	193	3.5
Total of each THM species (ΣFP)	582	18.23	ND	ND	600	7.3

Remark: ND = not detected

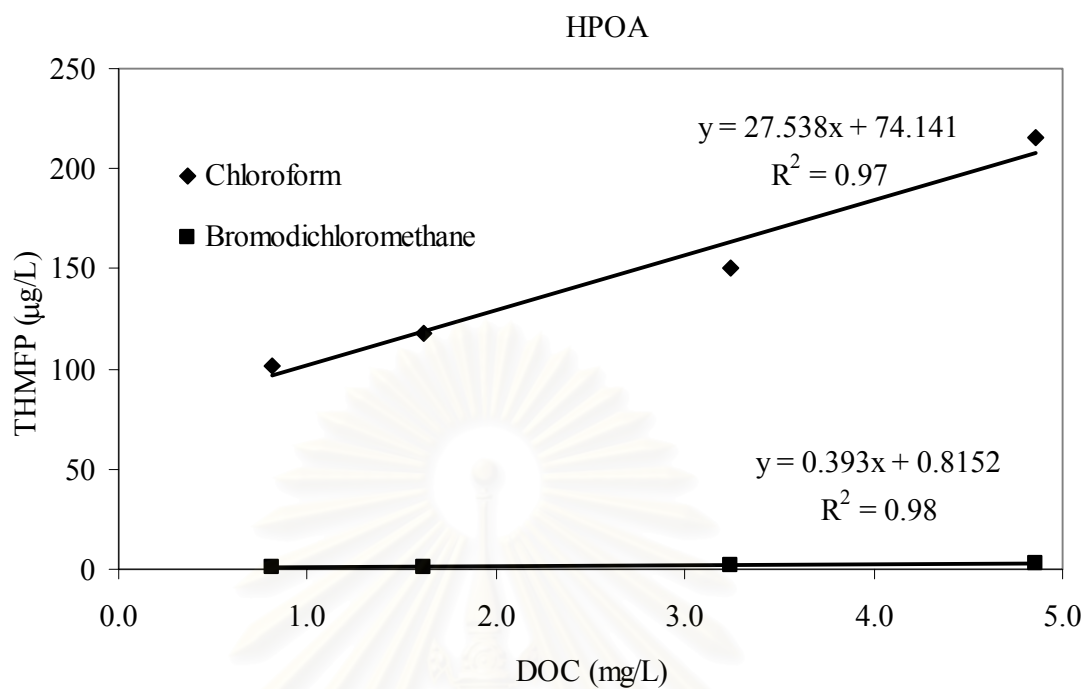
Table 5.3 Trihalomethane formation potential from raw water and mixed fraction.

	CHCl ₃ (µg/L)	CHBrCl ₂ (µg/L)	CHBr ₂ Cl (µg/L)	CHBr ₃ (µg/L)	Total (µg/L)	Chlorine demand (mg/L)
Raw water	262	43.8	6.98	ND	313	9
Mixed Fractions**	291	14.0	ND	ND	305	6
ΣFP*	582	18.2	ND	ND	600	7.3

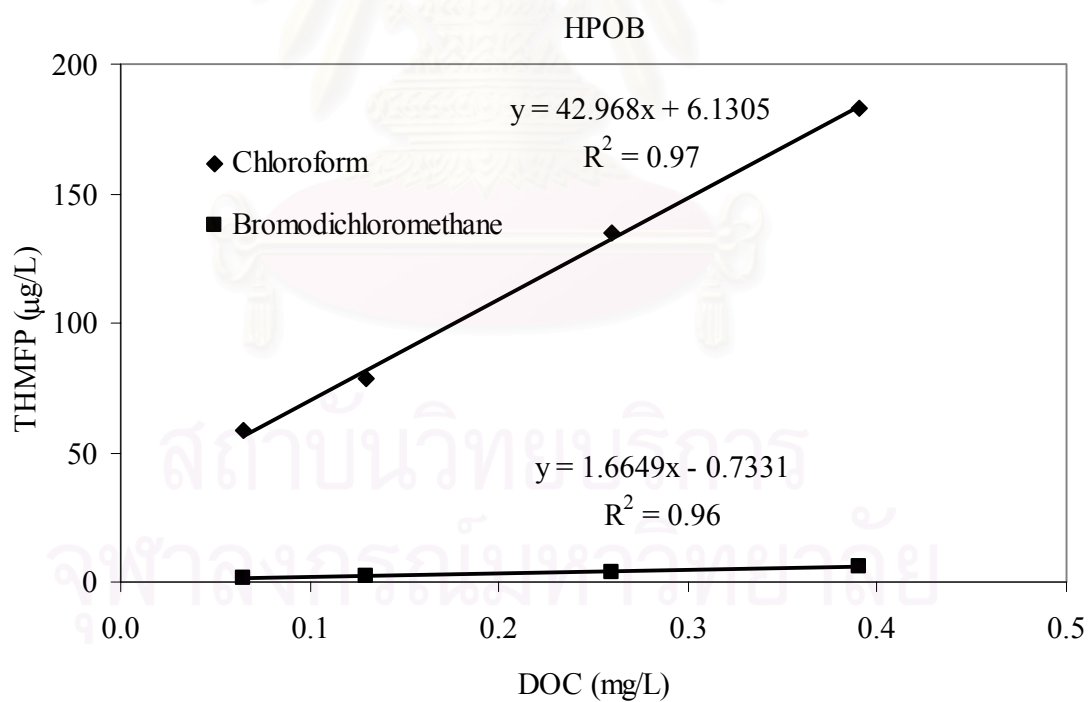
Remark: ND = not detected

* ΣFP = Sum of the THMFPP from the chlorination of each organic fraction (Mixed sample)

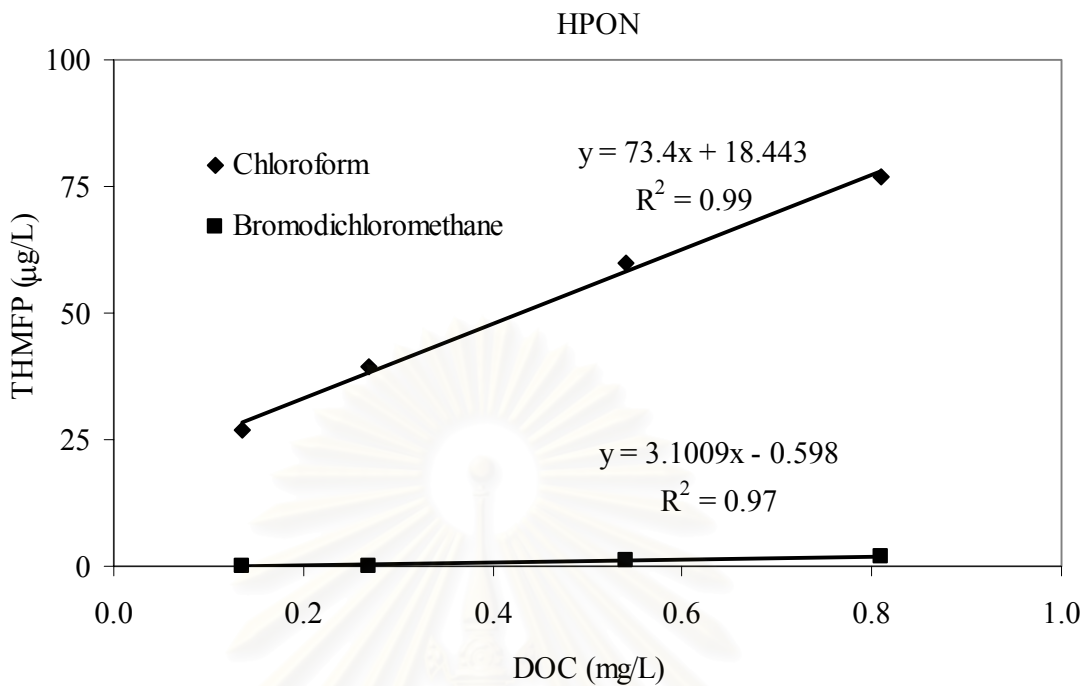
** Mixed Fractions = THMFPP from the mixed organic fractions (Fractionated sample)



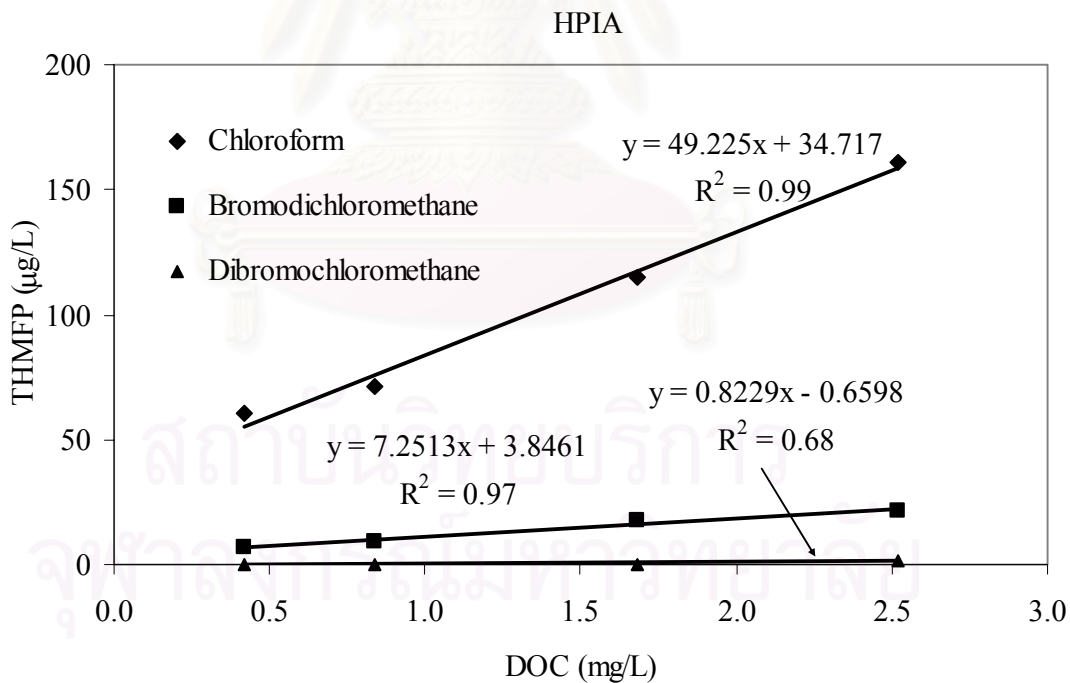
(a)



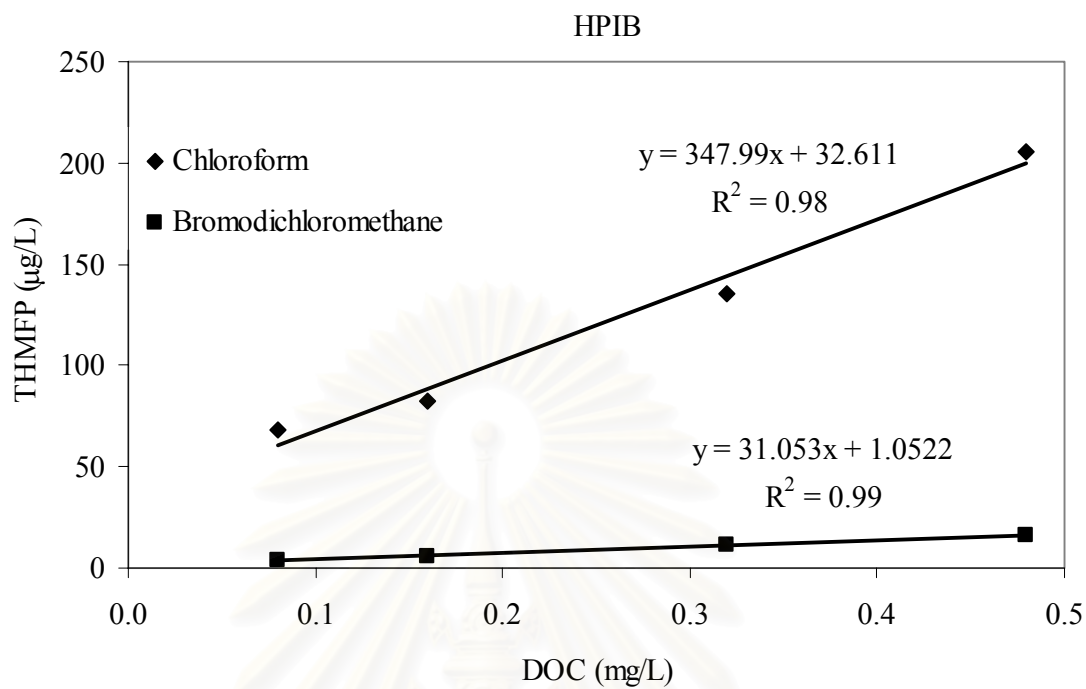
(b)



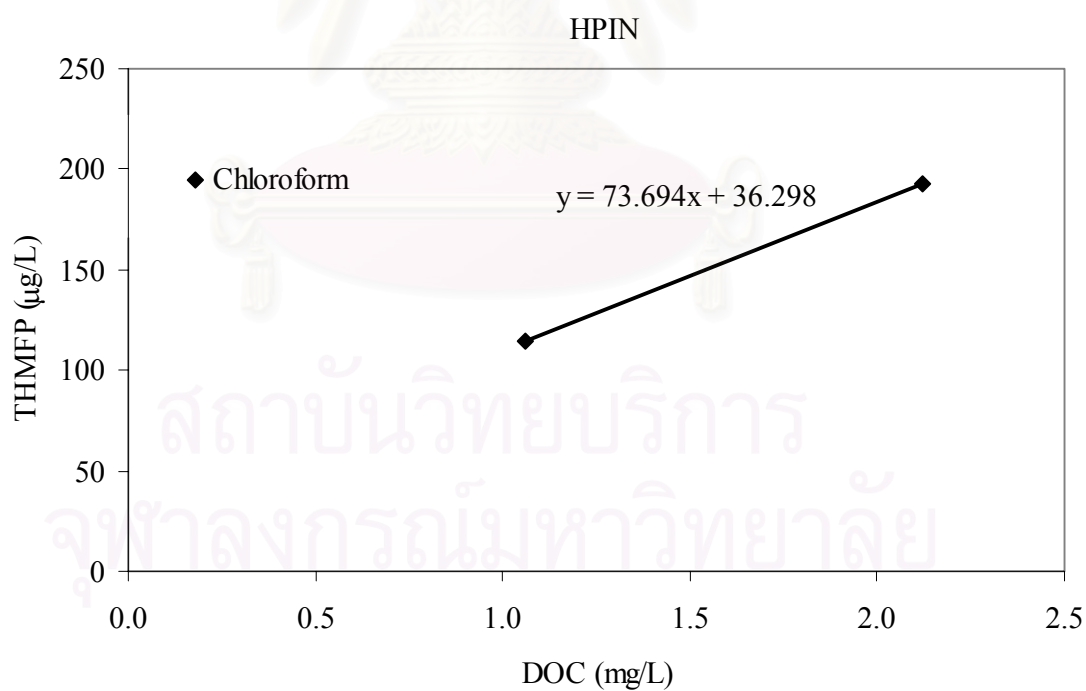
(c)



(d)



(e)



(f)

Figure 5.1 THM species formation potential from each organic fraction: (a) HPOA, (b) HPOB, (c) HPON, (d) HPIA, (e) HPIB, (f) HPIN.

CHAPTER VI

REMOVAL OF THM PRECURSORS BY COAGULATION WITH ALUM AND POLYMERS

6.1 Introduction

In the water treatment plant, coagulation is one of the most applied processes due to its simplicity and cost-effective nature. The main purpose of coagulation is to remove colloidal materials. Proper coagulation will facilitate the subsequent treatments such as filtration and disinfection. Literature showed that coagulation could also be applied to controlling the disinfection by-products (DBPs) as some of the organic compounds were also being removed with particle settling process (Amy and Chadik, 1983; Krasner and Amy, 1995; Huang and Shiu, 1996; and Exall and Vanloon, 2000). Normally, polymers are used as coagulant aids in the coagulation and with a proper combination with other coagulants such as alum or ferric chloride, the coagulation could significantly improve the removal of THM precursors resulting in the reduction of THMs formation. Table 2.4 provides a brief summary regarding the work on using polymers and other common coagulants in treating organic substances that could lead to the formation of THMs. It can be observed from this summary that the dosages of coagulants and coagulant aids were dependent significantly on the source water characteristics (DOC, turbidity, alkalinity, etc.). This implies the needs to regulate suitable coagulation conditions for each individual water source to ensure the best removal efficiency for organic contaminants and for an effective control of DBPs.

6.2 Purpose of this Chapter

This work was set out to investigate the mechanism of the coagulation of organic contents with alum and polymers in controlling the generation of THMs during the chlorination process of the water from Bangkhen Water Treatment Plant, Bangkok, Thailand. This would provide an insight into the use of coagulation technique for the removal of THM organic precursors. The fractionation was carried out for the raw water and the treated water with enhanced coagulation to examine the mechanism of coagulation in the removal of each organic fraction.

6.3 Materials and Methods

6.3.1 Coagulation

Coagulation experiments were carried out according to the procedure provided in Figure 6.1 where details of THM formation potential test (THMFP) and coagulation conditions are provided in Sections 3.3.3 and 3.4, Chapter 3, respectively. The resin adsorption technique proposed by Marhaba *et al.* (2003) was employed to separate coagulated samples. However, due to a large number of coagulated water samples, the fractionation of all samples was considered not practical. The criterion for the selection of water samples was the THM removal rate, i.e. only the samples that were proven to provide the highest removal in THMFP for specific sets of the combinations between alum and each individual polymer would be selected for the fractionation. Detailed procedure for the fractionation method are provided in Chapter 3 (Section 3.3).

6.3.2 Type of Polymers used in this Work

The first group of organic polymers employed in this work was polyacrylamide which consisted of cationic and anionic polyacrylamides. Polyacrylamides are among the most widely used coagulants in the water treatment plants in Thailand. Two more groups of polymers i.e. polydiallyl dimethyl ammonium chloride (or commonly known as DADMAC) and epichlorohydrin dimethyl amine (EpiDMA) which were reported to be the most frequently used polymers in the USA (Fielding *et al.*, 1999) were also examined here. The characteristics and structures of polymers are provided in Table 6.1 and Figure 6.2.

6.3.3 Calculation

The THMFP removal efficiency in this experiment was calculated by comparing the THMFP of the treated sample and that of the raw water (RW).

$$\% \text{THMFP Removal} = \frac{(\text{THMFP of RW} - \text{THMFP of treated sample}) \times 100}{\text{THMFP of RW}} \quad \text{--(6.1)}$$

6.4 Results and Discussion

6.4.1 Coagulation by Alum

Characteristics of raw water sample used in this experiment are showed in Table 6.2. The effects of coagulation at various pH conditions on the changes in SUVA and DOC, along with the THMFP removal efficiency are shown in Figure 6.3. The optimal pH for the coagulation was observed to be at 5.5 as all parameters were illustrated to be removed at the greatest extent at this pH. For instance, the level of SUVA could be reduced from 2.6 to 2 L/mg-m, and DOC from 4.7 to 3 mg/L by the coagulation at this pH, which were equivalent to approximately 23% and 36% reductions in the two parameters, respectively. The %THMFP reduction was found to follow the trends of both DOC and SUVA, and therefore a higher %THMFP reduction was also obtained at pH of 5.5. The examination at a lower pH level than 5.5 is not recommended as alum would change its state to ionic form which is soluble in water (Amirtharajah and Mills, 1982) and will not provide effective sweep-floc mechanism. At high pH, alum would turn into an anionic complex not suitable for the removal of anionic compounds which was often the main character of the DOC contaminants (Amirtharajah and Mills, 1982). This result suggested that DOC in this water source was mainly with anionic nature, and hence, no changes in the levels of SUVA and DOC were observed for the coagulation with alum at a high pH range. Note that at pH of 5.5, alum formed cationic flocculant species (Duan and Gregory, 2003) which was suitable to form flocs with the anionic DOC contaminants.

It is interesting to have a quick glance at the %THMFP reduction in Figure 6.3. It can be seen that, at low alum dose (15mg/L), the same level of %THMFP reduction was obtained from the coagulation at pH 5.5 and 7.0. This was because, with this low alum dose, approximately the same level of DOC removal was obtained from the two pH levels. As the alum dose increased, a higher DOC removal from the coagulation at low pH (5.5) became more obvious, and this reflected in a higher removal of THMFP. At pH 8.5, however, the performance of the coagulation was always low regardless of the alum dose.

In several occasions, the SUVA removal curve in Figure 6.3 could not explain the difference in the %THMFP reduction. For instance, at the alum dose of 15 mg/L, the results showed that SUVA from the sample with the pH of 5.5 was significantly lower than that with pH of 7.0. This should have indicated that the sample at pH 5.5 had lower aromatic compounds than that at 7.0 and therefore it was anticipated that THMFP of the sample at pH 5.5 should be lower than that of 7.0. However, the results did not support this explanation. Or in another case at pH 5.5, an increase in the alum dose from 15 to 30 mg/L demonstrated a clear increase in the %THMFP reduction. It was therefore expected that there should also appear a reduction in SUVA as there should have been a direct relationship between SUVA and the THMFP. However, again, the results did not support this explanation.

This experiment also illustrates the effect of alum dose which was found to have significant influence on the coagulation efficiency. The results in Figure 6.3 suggested that, with an appropriate pH level (pH = 5.5 in this case), a higher alum dose would lead to better removal efficiency. An optimal alum dose was found to be around 30 mg/L for this water sample. A lower alum dose than 30 mg/L would lead to low DOC removal which, in turn, resulted in a low THMFP removal efficiency. On the other hand, a higher dose than 30 mg/L did not seem to have an appreciably improved performance of the coagulation, where both DOC and SUVA were only marginally affected, and only a small increase in the THMFP removal efficiency was observed.

Note that there should be precaution in the use of alum as a coagulant, as although alum could improve THMFP removal at high dosage, it also could leave a high level of aluminium ion residual in the product water which is not recommended for the application where high quality water is needed such as drinking water. The addition of some kind of polymers could help reduce the requirement for alum. This is discussed in the following section.

6.4.2 Coagulation by Alum and Polymers

Subsequent coagulation experiments were carried out at pH of 5.5, but with varying combinations of alum and polymer doses. Four types of polymers were

examined here, i.e. anionic polyacrylamide (AnPAM), cationic polyacrylamide (CatPAM), polydiallyl dimethyl ammonium chloride (DADMAC), and epichlorohydrin dimethyl amine (EpiDMA). AnPAM and CatPAM were selected for the investigation as they are among the most commonly used coagulant/flocculant-aids in several municipal water treatment facilities in Thailand. DADMAC and EpiDMA were, on the other hand, mostly applied in literature, and reported to have superior performance to CatPAM as they contained a higher charged density (Chang, *et al.*, 2005; and Bolto, 1995).

Figure 6.4 demonstrates the comparative performance between the removal of THMFP and the coagulation with alum and the combination of alum and the four types of polymers. Note that the results in Figure 6.4 were obtained from the coagulation at pH of 5.5, alum dose of 15 mg/L, and polymers dose of 0.5 mg/L. It was clear that the use of AnPAM with alum was not beneficial for the removal of THMFP as the %removal in this case (9.8%) was even lower than the coagulation with alum alone (17.4%). This was because AnPAM was an anionic charged polymer which was believed to be the same with the organic matter (negative charged) presented in water. Therefore AnPAM could not help in charge neutralization of the organic components leading to poor DOC removal and, hence, subsequent poor THMFP removal was observed.

The efficiencies of THMFP removal from other three cationic polymers were all found to be superior to the coagulation with alum alone, and these could be ordered from high to low as follows: alum with DADMAC (39%), alum with EpiDMA (32%), and alum with CatPAM (21%). Detail analysis of the coagulation with these cationic polymers are given in the following subsections.

6.4.2.1 Alum and Cationic Polyacrylamide (CatPAM)

The relation between alum and polymer doses on SUVA, DOC and THMFP removal were shown in Figure 6.5. Similar to the discussion on the use of alum, SUVA could not explain the variation in the THMFP removal. For example, at the alum dose of 15 mg/L, the best THMFP removal was obtained at CatPAM dose of 0.1 mg/L, followed by the dose of 1.0 and 0.5 mg/L, respectively. As SUVA should have

been directly proportional to the aromatic precursors, it was expected that SUVA of the coagulated sample with CatPAM dose of 0.1 mg/L was the lowest among the three, followed by that at the dose of 1.0 and 0.5 mg/L, respectively. However, SUVA of the coagulated sample with CatPAM of 0.5 mg/L was the lowest and with CatPAM of 0.1 mg/L was the highest. This is not to mention SUVA for the case with pure alum which was even lower than any of the three samples with polymer. It was therefore concluded at this point that, for the water source examined in this work, SUVA could not be used as a parameter that indicates the level of THMFP. Similarly, the level of DOC in each coagulated sample varied without realizable trends such that no relationship between the remaining DOC and the THMFP removal could be formulated. It was possible that polymer preferentially removed some humic-fulvic fractions which were highly active to form THMs even in small quantity (Amy and Chadik, 1983) which rendered the analysis of DOC not significantly reliable. Therefore from this point onwards, the discussion is only limited to the relationship between THMFP removal and the alum and polymer doses.

To explain the effect of coagulation on the removal of organic compounds, it is recommended to examine how the floc was formed in each individual case. This was illustrated by the experiment in the Jar Test set. Figure 6.6 (a) illustrates that, at the condition of alum dose 30 mg/L and polymer dose 0.1 and 0.5 mg/L, the floc formation was normal but with an increase in polymer dose to 1.0 mg/L, the formation of big pellets were observed at the bottom of the beaker, but not as a suspension in the slow mixing step. This was not suitable for the coagulation as all conditions which led to the formation of big pellets always ended up with a poor THMFP removal efficiency. In fact, the excess of polymer was reported to adversely affect the coagulation as it caused the restabilization of colloidal particles whereas the residual polymer could also form another, new and difficult to remove, organic phase (Lee *et al.*, 1998). Although these statements were not proven in the present study, they could also be used to explain the results rather well. In summary, the optimal polymer dose at the different alum doses were:

Alum dose (mg/L)	Polymer dose (mg/L)
15	0.1
30	0.5
45	0.1

6.4.2.2 Alum and Polydiallyl Dimethyl Ammonium Chloride (DADMAC)

DADMAC was described as a chlorine-resistant polymer (Chang *et al.*, 1999) which meant that its residual in the water would not easily form THMs. Therefore it was widely used in literature. In addition, this polymer has been proven to improve THMFP removal by strengthening the linkage between particles and flocs, which enlarged the size of floc and accelerated the settling velocity (Chang *et al.*, 2005). Figure 6.6 (b) demonstrates that this polymer produced good floc formation at all dosage ranges. As a result, there was no significant difference in the %THMFP removal using this polymer as a coagulant aid (see Figure 6.7) provided that there was adequate quantity of alum. Figure 6.7 illustrates that, to obtain high removal performance, the alum dose must be at least 30 mg/L. As there was no difference in the performance of coagulation, the optimal dose of this polymer was considered from the economical point of view which implied the smallest quantity, i.e. 0.1 mg/L.

6.4.2.3 Alum and Epichlorohydrin Dimethyl Amine (EpiDMA)

Similar to the DADMAC, EpiDMA produced good floc formation at all dosage range as shown in Figure 6.6 (c). Therefore it provided relatively good THMFP removal efficiency, provided that there was sufficient level of alum, which in this case, was 30 mg/L (see Figure 6.8). In this figure, the best THMFP removal occurred at two different dosage combinations, i.e. at alum dose of 30 mg/L and polymer 1.0 mg/L, and at alum dose of 45 mg/L and polymer 0.1 mg/L. The selection between these two combinations would then be confined to economical consideration. However, it should be noted that high polymer dose could result in a residual of the polymer which could then be converted to THMs during the chlorination.

6.4.3 Effectiveness Evaluation of Alum and Polymer on the Removal of Organic Precursors

As stated earlier in this Chapter, the evaluation of the coagulation could be achieved by examining the fractionation results of the sample before and after the coagulation. However, the fractionation was a time-consuming step and it could not be applied to all of the samples with all combinations of alum and polymers. Therefore only the combinations that provided the best removal efficiency for each individual type of polymers were selected for the subsequent fractionation experiment. The summary of the coagulated samples undergone the fractionation is given in Table 6.3. In fact, the specific THMFP and total THMFP of each organic fraction were already examined in Section 4.4.2, Chapter 4, and the results are discussed here again (see Figure 4.4) along with the fractionation results from other samples. The discussion on this aspect follows.

6.4.3.1 HPOA

In Figure 6.9, the first bar in the group (the black shade bar) is the fractionation results of the raw water sample without treatment. This could therefore be used as a reference for the comparison with the others which were the results from the samples that passed through the coagulation step. Alum and the combination of alum with three cationic coagulants provided similar removal rate (about 30% removal efficiency) for HPOA. AnPAM was, as expected, the poorest in terms of removal efficiency (20%) for this specific fraction. This finding agreed well with that of Bolto *et al.* (1999) who also stated that alum was most effective for the removal of HPOA fraction. Marhaba and Van (2000) reported similar finding that about 35% removal could be achieved with the coagulation and sedimentation.

Note that HPOA was the second most abundant organic species in the water source examined in this work. Therefore the information on the removal of this organic fraction was important for the future control of the disinfection by-products.

6.4.3.2 HPOB

Literature showed that HPOB could be effectively removed by conventional coagulation/sedimentation (Marhaba and Van, 2000; and Marhaba and Pipada, 2000). In contrast, the results obtained in this experiment revealed that conventional alum coagulation could not significantly remove such organic fraction. DADMAC seemed

to be the most effective polymer that helped remove this fraction (with the removal efficiency of 46%) followed by EpiDMA (40%) and CatPAM (23%). It is worth noted here that this fraction was most active among the six fraction in reacting with chlorine and had a high potential to forming THMs. Therefore the removal of this fraction, even by small amount, could lead to a significant change in the quantity of THMs formed during disinfection.

6.4.3.3 HPON

HPON was the least active in forming THMs as illustrated by its low specific and total THMFP. Figure 6.9 demonstrates, however, that this fraction could well be removed very effectively with the combination of alum and CatPAM (89%). EpiDMA and DADMAC could also provide a rather impressive level of HPON removal efficiency (74% and 63%, respectively). This result suggested that CatPAM should be focused in the water treatment plant strategy for the control of THMs, in the case of high HPON level in raw water.

6.4.3.4 HPIA

Alum alone was most effective in removing HPIA fraction (54% DOC removal – see Figure 6.9). In fact, this fraction could also be appreciably removed by alum and AnPAM (51% removal) which was, in this case, more effective than using any of the cationic polymers, i.e. EpiDMA (39%), CatPAM (38%), and DADMAC (35%). Such 51% reduction was also reported by Marhaba and Pipada (2000), however, this hydrophilic fraction was often reported not to be effectively removed by conventional alum coagulation (Amy *et al.*, 1992; Croue *et al.*, 1995; and Marhaba and Van, 2000). This emphasized that there were differences in the properties of organic fractions from various different locations. Interestingly, all cationic polymers could not deliver effective removal of this organic fraction. This might be because of the hydrophilic property of this fraction that obstructed the coagulation reaction.

6.4.3.5 HPIB

This fraction possessed the second highest specific THMFP. Therefore, although it was only presented in small quantity, only a slight accomplishment in reducing its content would be helpful in controlling the quantity of THMs in the

product water. Alum with DADMAC and alum with EpiDMA were found to be able to achieve 66% and 63% removal of this fraction, respectively. Interestingly, the coagulated sample by alum with CatPAM and AnPAM seemed to contain the same level of HPIB as the original water. This could be due to the property of PAM polymer as it was composed of amide which possibly expressed the hydrophilic base property when dissolved in water. In other words, the removal of the hydrophilic base by coagulation might have been compensated by the augment in the organics with similar properties from the polymer.

6.4.3.6 HPIN

Alum with DADMAC performs as well as alum with EpiDMA and alum with CatPAM in removing such fraction as more than half of HPIN could simply be removed. As HPIN was the fraction that gave the highest total THMFP fraction in this water source, these three polymers were considered suitable for this water sample

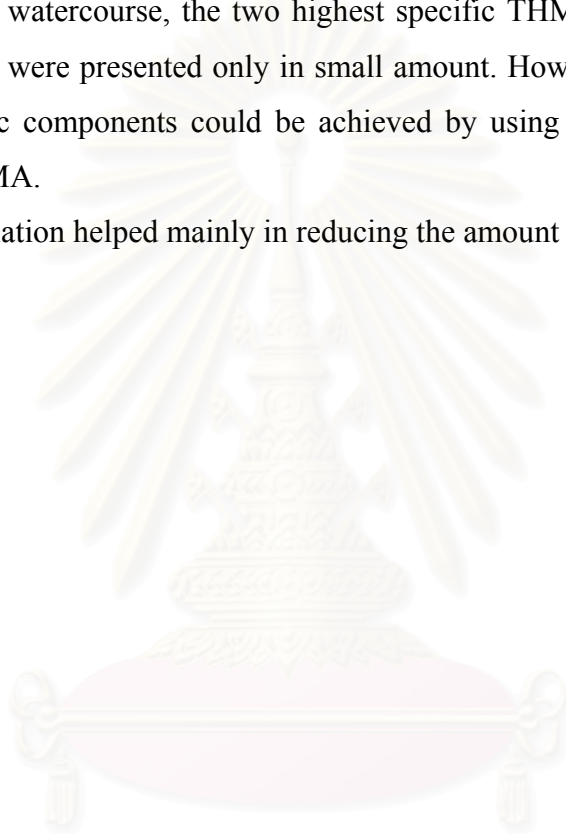
6.4.4 Effect of Coagulation on THM Species Removal

Similar to the THMFP of the raw water sample, THMFP of water samples after coagulation/sedimentation also contained three THM species, i.e. chloroform (CHCl_3), bromodichloromethane (CHBrCl_2), and dibromochloromethane (CHBr_2Cl) (see Table 6.4). The coagulation by alum alone was observed to only be able to lower the chance of chloroform being produced in the THMFP test. However, the use of other polymer coagulation aids could also help decrease the bromodichloromethane but only in a small quantity. In all cases, no reduction in dibromochloromethane could be obtained from the coagulation.

6.5 Conclusions

This chapter revealed that there was possibility in using coagulation in controlling the formation of THMs. To achieve this, the coagulation needed to be conducted under a well controlled environment, particularly where the pH was regulated at around 5.5. Main findings from this chapter could be summarized as follows:

- The highest efficiency in the removal of THMFP from the coagulation with the combination of alum and polymer could be ordered from high to low as: alum with DADMAC, alum with EpiDMA, alum with CatPAM, alum with AnPAM, and alum alone.
- The removal of the most abundant organic fractions (HPIN and HPOA) could be achieved by using alum or alum with cationic polymers.
- In this watercourse, the two highest specific THMFP fractions (HPOB and HPIB) were presented only in small amount. However, the removal of such organic components could be achieved by using alum with DADMAC or EpiDMA.
- Coagulation helped mainly in reducing the amount of chloroform precursors.



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6.6 Tables and Figures

Table 6.1 Characteristic of polymers

Polymer name	Policat C-84EF (CatPAM)	Magnafloc 308 (AnPAM)	C 591 (DADMAC)	C 319 (EpiDMA)
Ionic character	Cationic	Anionic	Cationic	Cationic
Charge density	High	Low	-	High
Molecular weight	High	High	High	High
Physical form	White powder	White granular powder	Amber liquid	Clear amber-red liquid
Chemical nature	Polyacrylamide	Polyacrylamide	Epichlorohydrin dimethyl amine	Polydiallyl dimethyl ammonium chloride

Table 6.2 Characteristics of raw water

Parameter	Value
DOC	4.72 mg/L
UV-254	0.122 cm ⁻¹
Turbidity	105.2 NTU
pH	8.12
Alkalinity	96 mg/L as CaCO ₃

Table 6.3 Optimum coagulation condition by alum and polymers

Coagulant	Alum dose (mg/L)	Polymer dose (mg/L)
Alum	45	0
Alum + DADMAC	45	1.0
Alum + EpiDMA	30	1.0
Alum + CatPAM	45	0.1
Alum + AnPAM	30	0.5

Table 6.4 THM species formation potential of treated samples

	CHCl ₃ (µg/L)	CHBrCl ₂ (µg/L)	CHBr ₂ Cl (µg/L)	CHBr ₃ (µg/L)
Raw water	262	44	7	ND
Alum	181	42	9	ND
Alum+AnPAM	136	32	8	ND
Alum+CatPAM	147	37	9	ND
Alum+DADMAC	130	32	9	ND
Alum+EpiDMA	138	33	8	ND

Remark: ND = not detected

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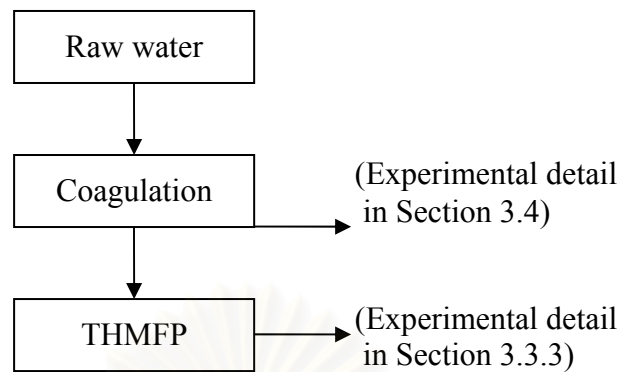
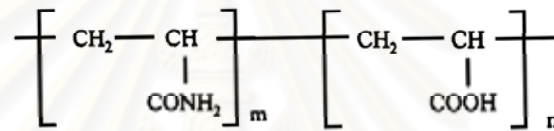
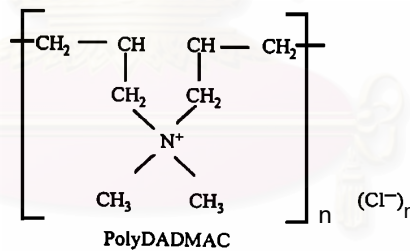


Figure 6.1 Experimental procedure

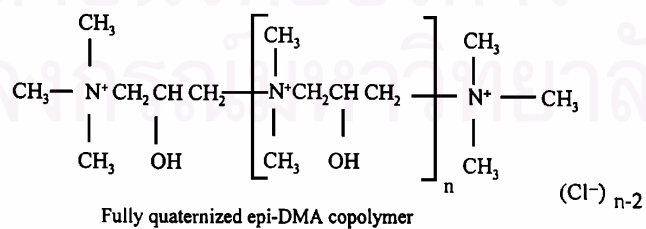


Acrylamide - acrylic acid copolymer

(a)



b)



(c)

Figure 6.2 Polymer Structure (AWWARF, 1999) (a) PAM
(b) DADMAC (c) EpiDMA

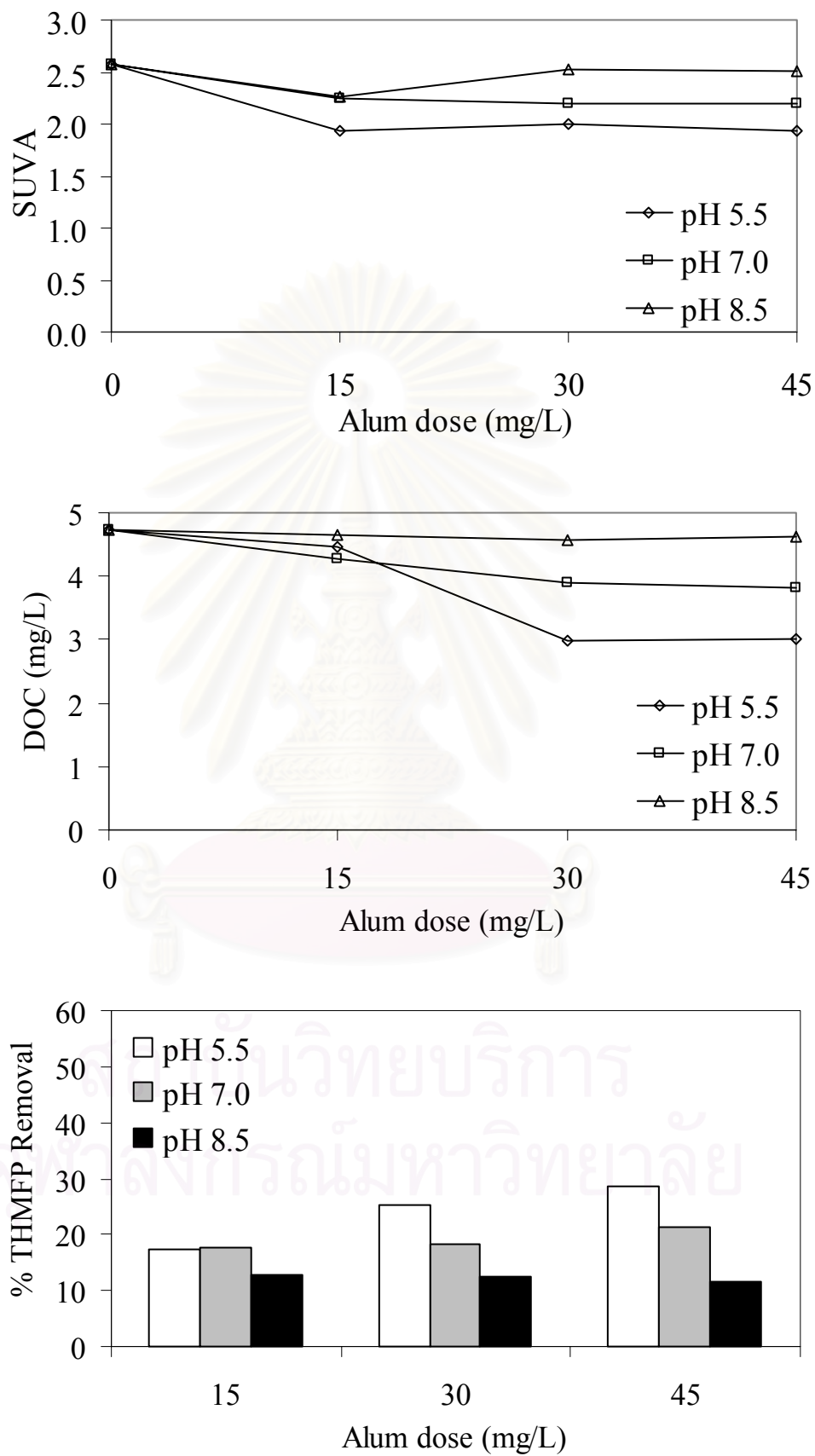


Figure 6.3 SUVA, DOC, and THMFP removal by using alum

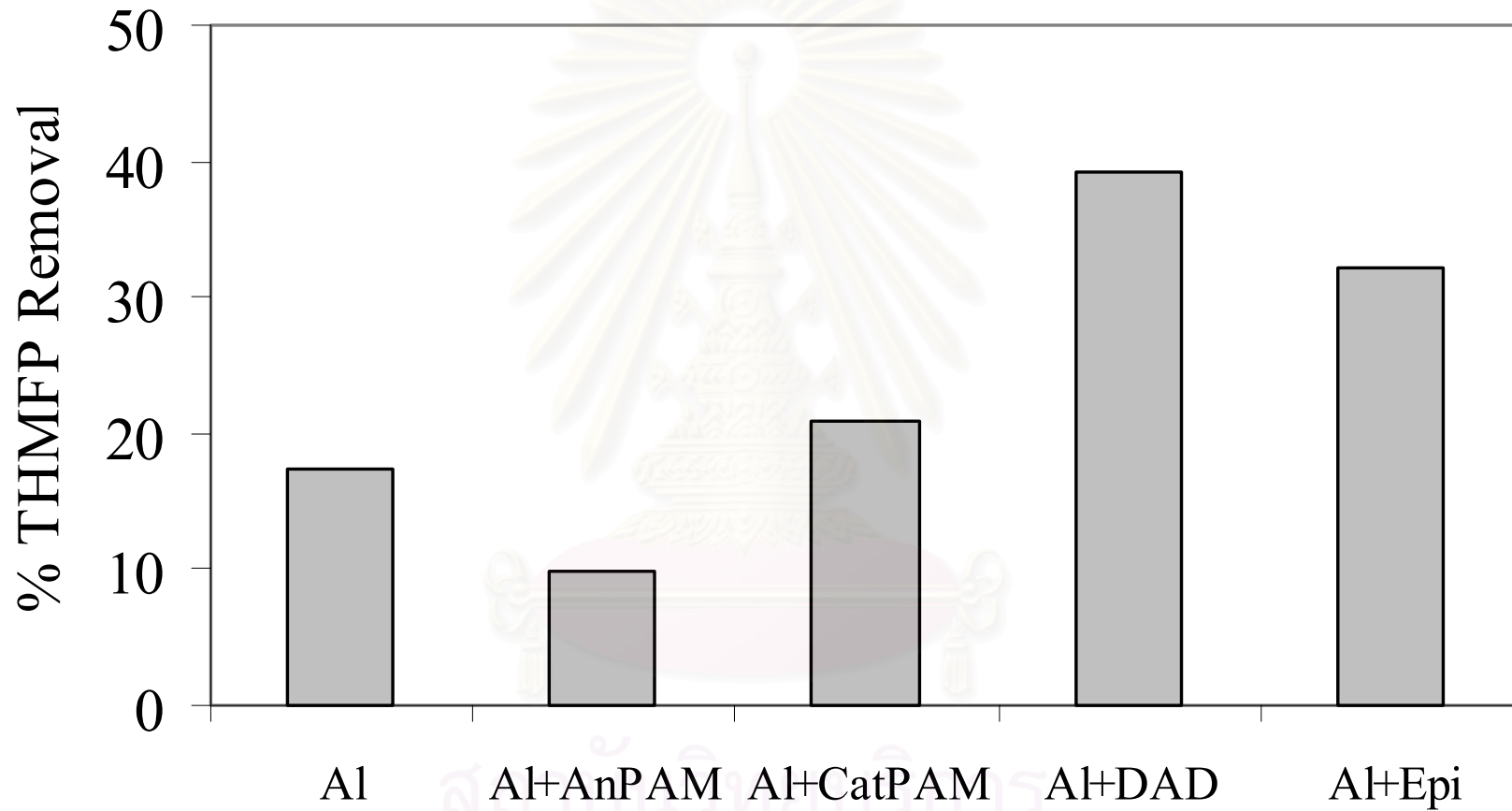


Figure 6.4 Comparison of THMFP removal at the coagulation condition of pH 5.5, alum dose 15 mg/L, and polymer 0.5 mg/L

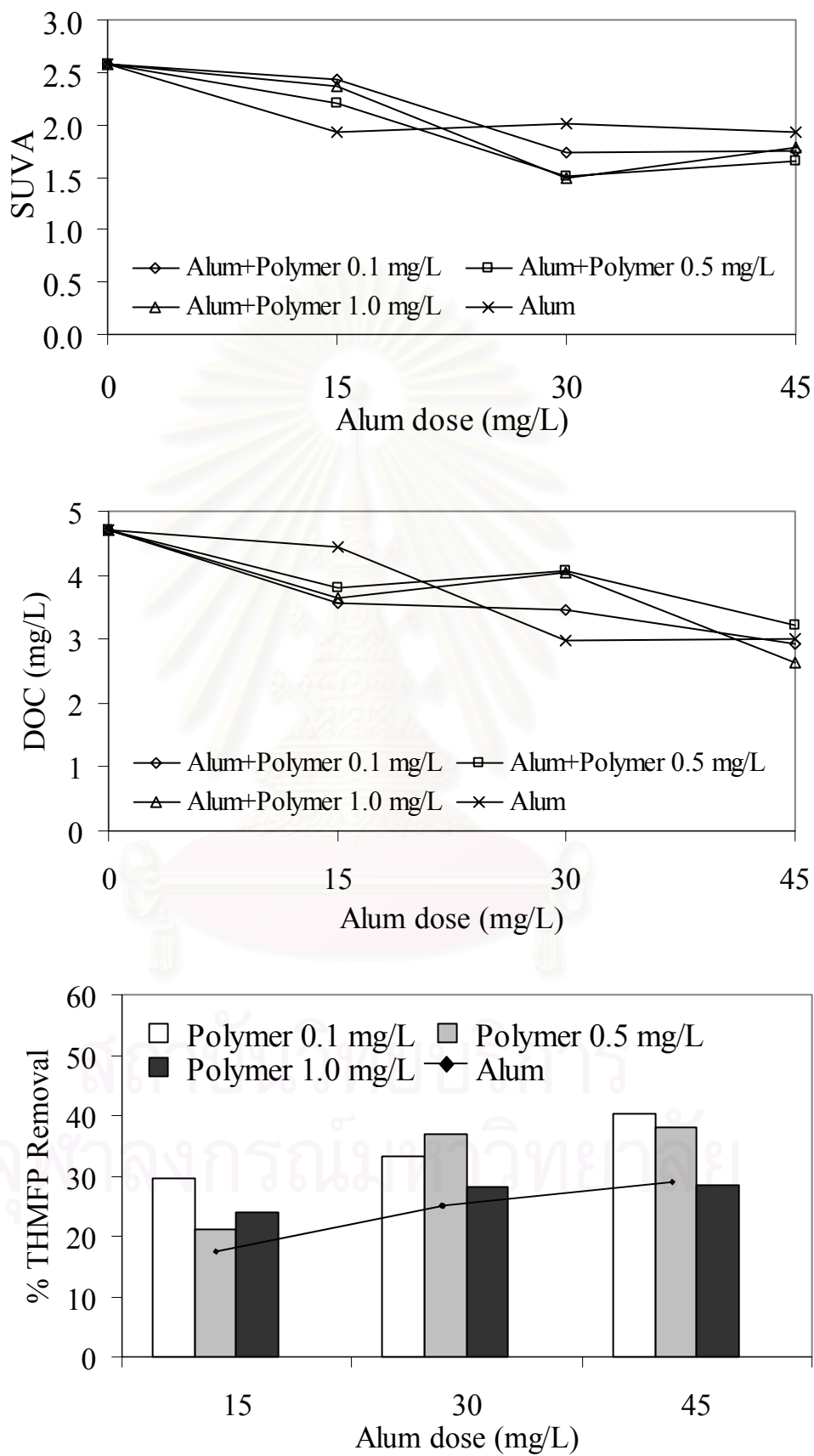


Figure 6.5 SUVA, DOC, and THMFP removal by using alum and CatPAM

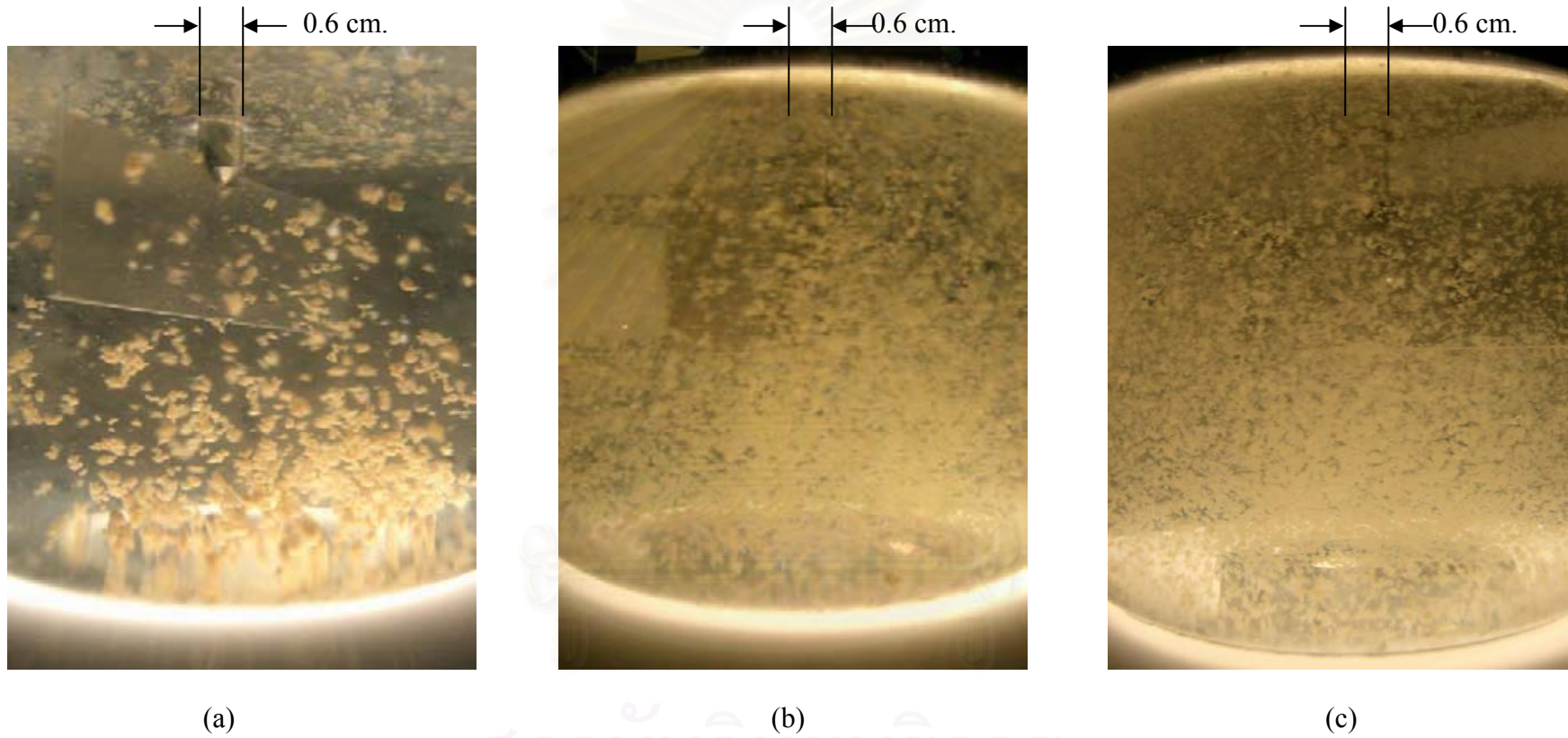


Figure 6.6 Floc forming from coagulation by alum 30 mg/L and polymer 1 mg/L (a) alum and CatPAM (b) alum and DADMAC (c) alum and EpiDMA

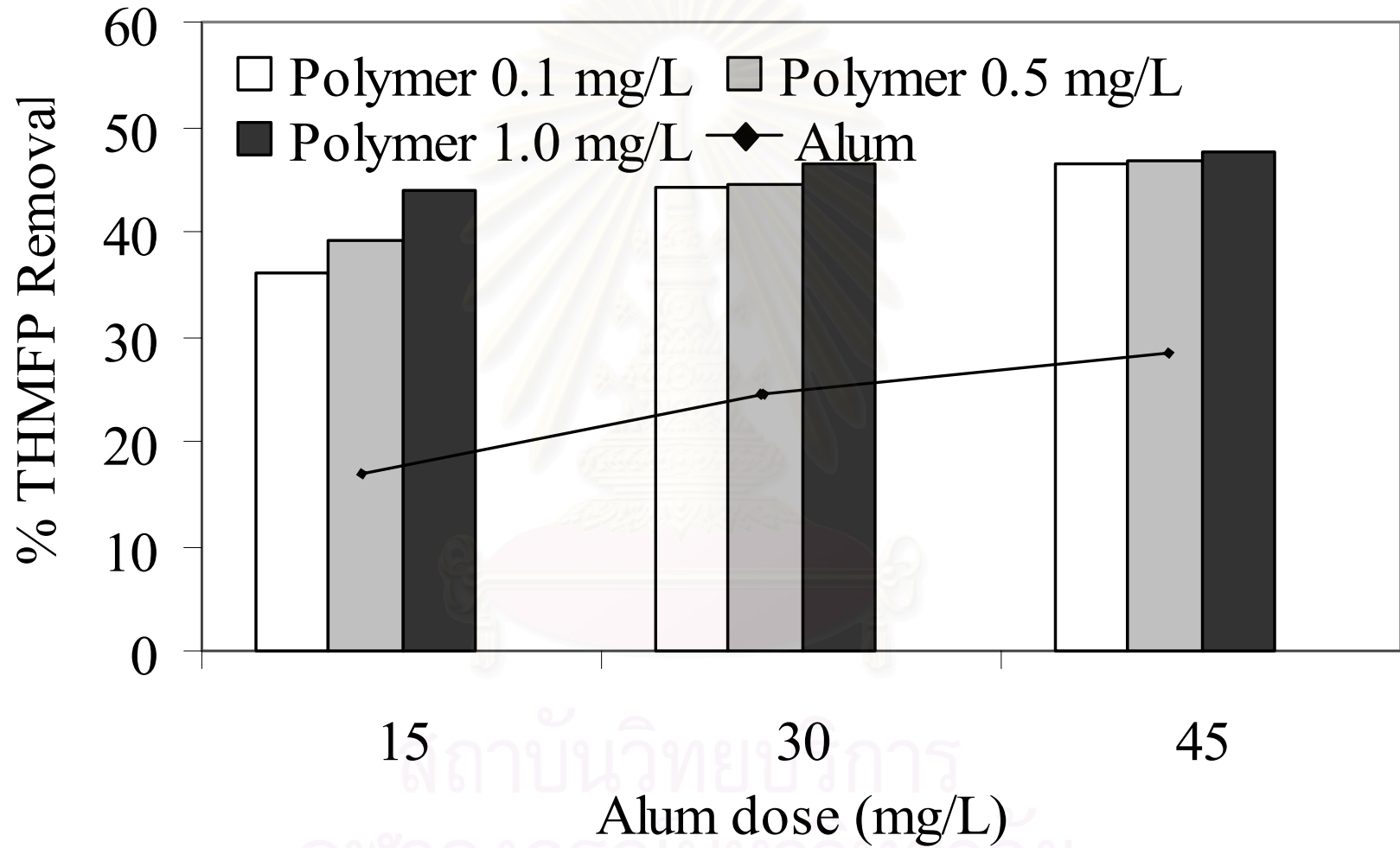


Figure 6.7 THMFP removal by using alum and DADMAC

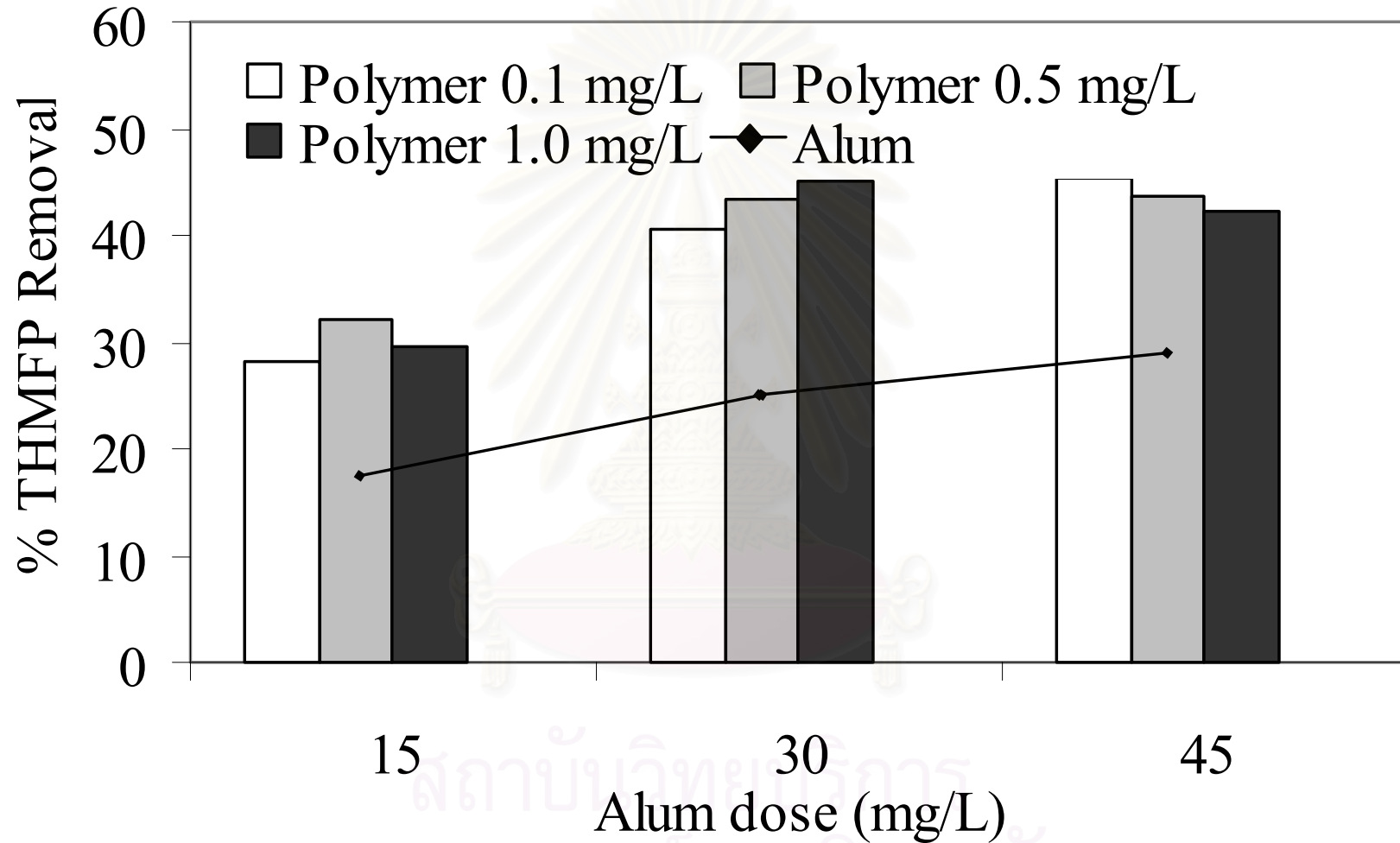


Figure 6.8 THMFP removal by using alum and EpiDMA

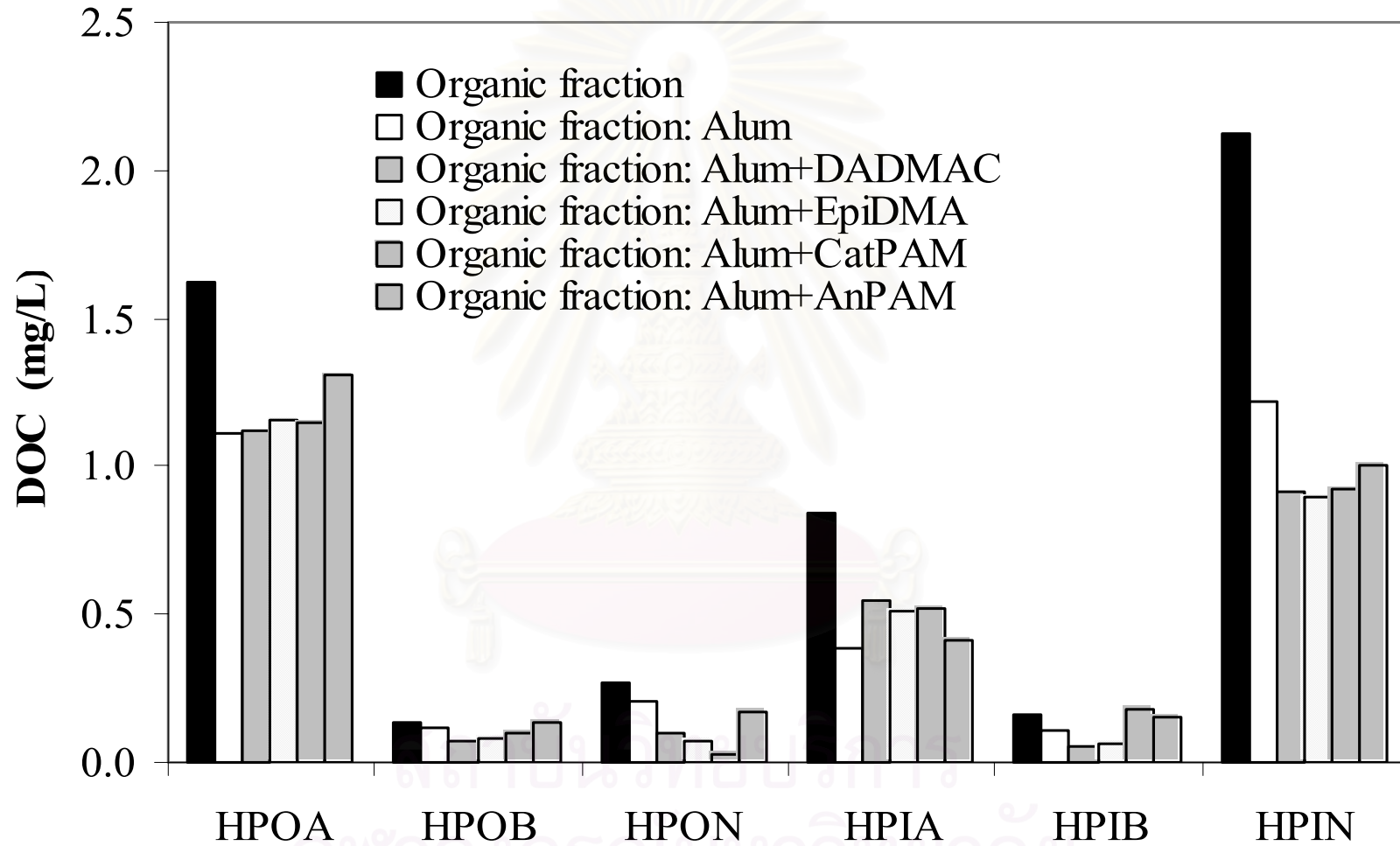


Figure 6.9 Organic fraction removal by each coagulant

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The main conclusions from this work can be summarized below.

- HPIN and HPOA were found to be the major organic components in the source water of the Bangkok Water treatment plant at the time of this investigation. The other organic components could be ordered from high to low as: HPIA, HPON, HPIB, and HPOB.
- HPIN and HPOA were the most problematic organic fractions in this water source as they were the main sources of THMFP.
- HPOB and HPIB were the two most active organic fractions (high specific THMFP). These two fractions should therefore be used as warning signals of THMs formation in the water treatment plant.
- The correlation between DOC of each organic fraction and its associated THMFP was found to be linear.
- The key THMs component from this water source was chloroform and followed by bromodichloromethane and dibromochloromethane, respectively.
- At the original concentrations, brominated THM species were only found to form from the chlorination of HPIA, HPIB, HPOB, and HPOA.
- Coagulation by alum alone can remove THMFP but not as effectively as that by coagulation of alum combined with polymer.
- The type of polymers used as coagulant aids in the removal of THMFP could be ordered according to their THMFP removal efficiency (from the highest to the lowest) as: DADMAC, EpiDMA, CatPAM, and AnPAM, respectively.
- Each polymer exhibited unique preference for the removal of organic fractions, i.e. CatPAM was most suitable for HPON, DADMAC for HPOB, EpiDMA for HPIN, and alum alone for HPOA and HPIA.

7.2 Contributions of this work

This work attempted to identify the type of organic contaminants in the raw water of one of the biggest water treatment plants in Thailand. The information obtained from this work can be further employed in the design of the control technique and management strategies for the water treatment plant. In fact, it was proven that a simple coagulation method could well be employed to control the level of THMs provided that a proper condition and the ratio between the various coagulants were selected. This finding should be beneficial for most existing water treatment plants as it implies that the efficiency of the treatment process could well be enhanced just by adjusting operational parameters without the need to invest in new construction or equipments. It should be mentioned, however, that the conclusion obtained from this work was only based on the quality of the water source during the collection period.

In particular, for a specific case of Bangkhen water treatment plant, the results from this work suggests that, to minimize the potential of the formation of THMs, the coagulation should be performed with the combination of alum and DADMAC or EpiDMA at pH 5.5 as this could best remove THM precursors (now at Bangkhen water treatment plant use alum combined with AnPAM which provided low THMF removal). However, it is generally accepted that the use of polymer as a coagulant aid with a specific target on the removal of dissolved organic matter could decrease the efficiency in the removal of turbidity. This could subsequently affect downstream processes such as the filter which could have a significantly shorten life time as it has to be operated with water at higher turbidity or suspended solid loadings.

7.3 Recommendations for further work

This work was successful in pointing out the problematic precursors for the possible formation of harmful disinfection by-products, i.e. THMs. However, it is far from being completed. Further work should be conducted to

- Investigate the effect of seasonal variation on the quality of organic matters and their THM formation potential.
- Examine the coagulation by other polymer groups or other common coagulants, such as ferric chloride and polyaluminium chloride.

- Investigate the water quality along the length of the river to identify the problematic areas in terms of disinfection precursor sources. This will be useful for the most effective system of managing and controlling the raw water quality.
- Study the potential of replacing the time-consuming resin fractionation by other more rapid analyzing methods for the determination of precursor organic species such as fluorescent spectroscopy.



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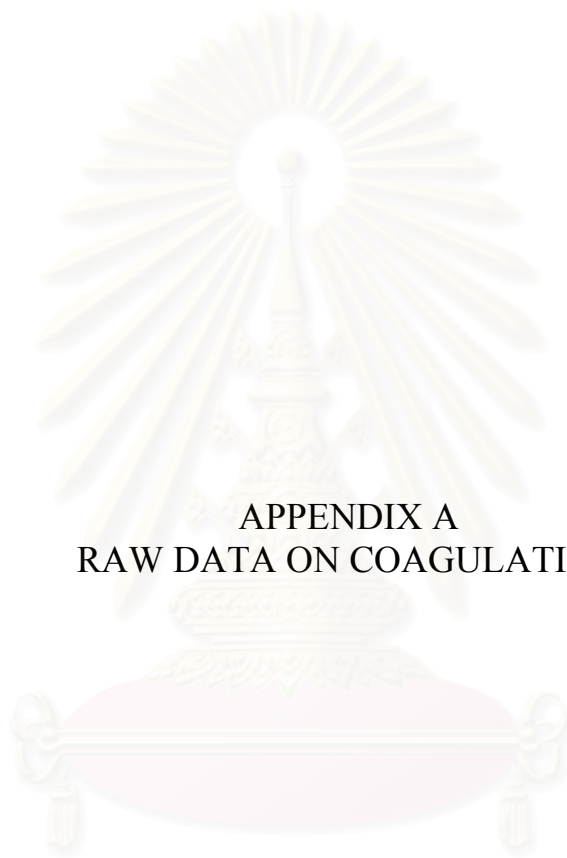


สถาบันวิทยบริการ
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APPENDICES

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APPENDIX A
RAW DATA ON COAGULATION

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Table-A 1: Coagulation by alum

pH 5.5

Alum dose	UV-254	TOC	SUVA	THMFP
15	0.086	4.45	1.93	269
30	0.06	2.99	2.01	244
45	0.058	3.00	1.93	232
60	0.053	3.24	1.64	224

pH 7.0

Alum dose	UV-254	TOC	SUVA	THMFP
15	0.096	4.28	2.24	268
30	0.086	3.91	2.20	266
45	0.084	3.83	2.19	256
60	0.081	3.90	2.08	240

pH 8.5

Alum dose	UV-254	TOC	SUVA	THMFP
15	0.105	4.65	2.26	284
30	0.115	4.56	2.52	285
45	0.116	4.61	2.51	287
60	0.114	4.38	2.61	287

Table A-2: Coagulation by alum and CatPAM

Alum 15 mg/L

Polymer dose	pH	UV	TOC	SUVA	THMFP
0.1	5.5	0.087	3.57	2.44	230
	7	0.099	4.28	2.32	251
	8.5	0.107	4.19	2.55	260
0.5	5.5	0.084	3.81	2.21	257
	7	0.095	3.90	2.44	252
	8.5	0.106	4.35	2.44	280
1	5.5	0.086	3.63	2.37	248
	7	0.093	3.94	2.36	240
	8.5	0.103	4.25	2.42	280

Alum 30 mg/L

Polymer dose	pH	UV	TOC	SUVA	THMFP
0.1	5.5	0.060	3.47	1.73	217
	7	0.089	3.77	2.36	245
	8.5	0.107	4.47	2.39	284
0.5	5.5	0.061	4.06	1.50	205
	7	0.088	4.64	1.89	244
	8.5	0.104	4.69	2.22	276
1	5.5	0.060	4.04	1.49	234
	7	0.085	4.69	1.81	261
	8.5	0.104	4.71	2.21	265

Alum 45 mg/L

Polymer dose	pH	UV	TOC	SUVA	THMFP
0.1	5.5	0.051	2.92	1.75	194
	7	0.082	3.66	2.24	227
	8.5	0.101	4.41	2.29	257
0.5	5.5	0.053	3.21	1.65	202
	7	0.080	3.75	2.13	187
	8.5	0.103	4.25	2.42	231
1	5.5	0.047	2.64	1.78	233
	7	0.061	3.03	2.01	292
	8.5	0.111	4.23	2.62	295

Table A-3: Coagulation by alum and AnPAM

Alum 15 mg/L

Polymer dose	pH	UV	TOC	SUVA	THMFP
0.1	5.5	0.085	3.56	2.39	288
	7	0.097	3.94	2.46	293
	8.5	0.103	3.96	2.60	287
0.5	5.5	0.078	3.56	2.19	294
	7	0.096	3.83	2.51	298
	8.5	0.100	4.02	2.49	289
1	5.5	0.081	3.80	2.13	293
	7	0.093	4.26	2.18	300
	8.5	0.098	4.27	2.29	285

Alum 30 mg/L

Polymer dose	pH	UV	TOC	SUVA	THMFP
0.1	5.5	0.057	2.92	1.95	244
	7	0.086	3.78	2.28	287
	8.5	0.089	3.75	2.37	274
0.5	5.5	0.060	3.18	1.89	218
	7	0.079	3.33	2.37	250
	8.5	0.107	3.61	2.97	266
1	5.5	0.070	2.89	2.42	228
	7	0.078	3.60	2.16	256
	8.5	0.105	3.88	2.70	272

Alum 45 mg/L

Polymer dose	pH	UV	TOC	SUVA	THMFP
0.1	5.5	0.050	2.63	1.90	215
	7	0.066	2.96	2.23	256
	8.5	0.111	4.12	2.70	301
0.5	5.5	0.049	2.80	1.75	219
	7	0.067	3.34	2.01	247
	8.5	0.112	4.36	2.57	299
1	5.5	0.047	2.55	1.84	231
	7	0.068	3.28	2.07	273
	8.5	0.117	4.39	2.67	296

Table A-4: Coagulation by alum and DADMAC

Alum 15 mg/L

Polymer dose	pH	UV	TOC	SUVA	THMFP
0.1	5.5	0.077	3.24	2.38	208
	7	0.086	3.49	2.46	218
	8.5	0.102	3.64	2.80	220
0.5	5.5	0.068	3.04	2.24	198
	7	0.076	3.21	2.37	208
	8.5	0.091	3.55	2.56	219
1	5.5	0.045	2.43	1.85	182
	7	0.058	2.89	2.01	193
	8.5	0.068	3.23	2.11	205

Alum 30 mg/L

Poly dose	pH	UV	TOC	SUVA	THMFP
0.1	5.5	0.068	2.84	2.40	181
	7	0.077	3.40	2.26	190
	8.5	0.102	3.63	2.81	218
0.5	5.5	0.060	2.71	2.21	180
	7	0.068	3.21	2.12	205
	8.5	0.089	3.67	2.43	289
1	5.5	0.045	2.77	1.62	174
	7	0.066	3.15	2.10	185
	8.5	0.080	3.37	2.38	241

Alum 45 mg/L

Poly dose	pH	UV	TOC	SUVA	THMFP
0.1	5.5	0.048	2.63	1.83	175
	7	0.068	3.08	2.21	200
	8.5	0.096	3.61	2.66	219
0.5	5.5	0.042	2.37	1.77	173
	7	0.058	3.12	1.86	188
	8.5	0.083	3.59	2.31	219
1	5.5	0.040	2.55	1.57	171
	7	0.052	2.81	1.85	187
	8.5	0.074	3.24	2.28	198

Table A-5: Coagulation by alum and EpiDMA

Alum 15 mg/L

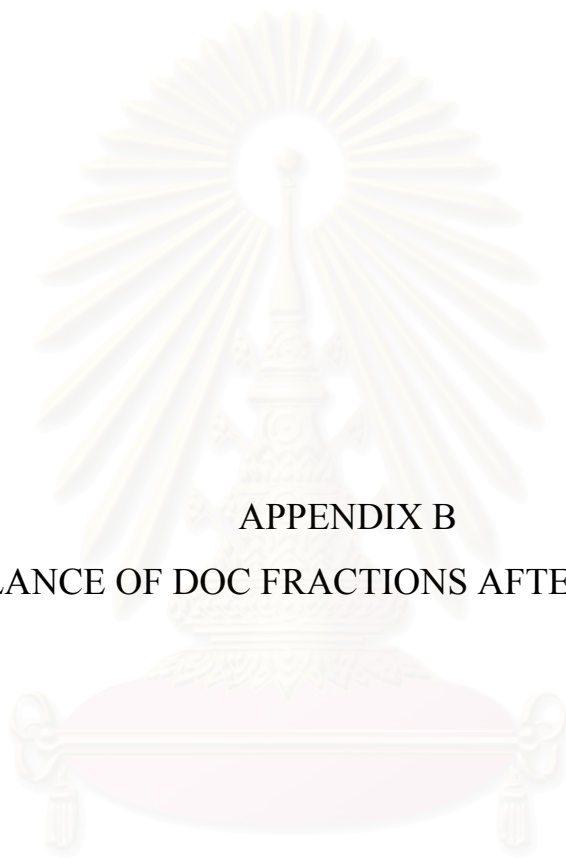
Polymer dose	pH	UV	TOC	SUVA	THMFP
0.1	5.5	0.080	3.23	2.48	234
	7	0.096	3.76	2.56	241
	8.5	0.11	4.01	2.74	247
0.5	5.5	0.079	3.28	2.41	221
	7	0.091	3.68	2.47	235
	8.5	0.105	3.77	2.78	249
1	5.5	0.075	3.20	2.34	229
	7	0.087	3.68	2.36	235
	8.5	0.100	3.85	2.59	242

Alum 30 mg/L

Polymer dose	pH	UV	TOC	SUVA	THMFP
0.1	5.5	0.065	3.16	2.06	194
	7	0.079	3.40	2.33	223
	8.5	0.104	4.02	2.59	248
0.5	5.5	0.056	2.75	2.03	184
	7	0.076	3.39	2.25	216
	8.5	0.095	3.80	2.50	230
1	5.5	0.053	2.65	2.00	179
	7	0.074	3.33	2.22	212
	8.5	0.099	3.72	2.66	236

Alum 45 mg/L

Polymer dose	pH	UV	TOC	SUVA	THMFP
0.1	5.5	0.047	2.32	2.02	178
	7	0.071	3.18	2.23	205
	8.5	0.101	3.66	2.76	230
0.5	5.5	0.046	2.37	1.95	183
	7	0.070	3.18	2.20	207
	8.5	0.100	3.68	2.72	248
1	5.5	0.045	2.33	1.93	188
	7	0.066	3.07	2.15	204
	8.5	0.088	3.57	2.46	216



APPENDIX B

MASS BALANCE OF DOC FRACTIONS AFTER COAGULATION

สถาบันวิทยบริการ
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Table B: Mass balance of DOC fractions after coagulation

	DOC (mg/L)	HPOA (mg/L)	HPOB (mg/L)	HPON (mg/L)	HPIA (mg/L)	HPIB (mg/L)	HPIN (mg/L)	Sum 6 Fractions (mg/L)
RW	4.72	1.62	0.13	0.27	0.84	0.16	2.12	5.14
Alum	3.00	1.11	0.12	0.21	0.39	0.11	1.22	3.16
Alum + AnPAM	2.75	1.30	0.13	0.17	0.41	0.15	1.00	3.17
Alum + CatPAM	2.55	1.15	0.10	0.03	0.52	0.18	0.92	2.90
Alum + DADMAC	2.63	1.12	0.07	0.10	0.55	0.05	0.91	2.80
Alum + EpiDMA	2.50	1.16	0.08	0.07	0.51	0.06	0.90	2.78



APPENDIX C
PUBLICATION-1

สถาบันวิทยบริการ
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Characterization of precursors to trihalomethanes formation in Bangkok source water

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Abstract

Resin adsorption techniques using three types of resin (DAX-8, AG-MP-50, and WA-10) were employed to characterize the raw water (RW) from the major 3 million m³/day (793 million gal/day) drinking water treatment plant in Bangkok, Thailand. The dissolved organic carbon (DOC) mass distribution sequences of the six organic fractions in raw water, from high to low, were hydrophilic neutral (HPIN), hydrophobic acid (HPOA), hydrophilic acid (HPIA), hydrophobic neutral (HPON), hydrophilic base (HPIB), and hydrophobic base (HPOB). HPIN and HPOA were the two main precursors for trihalomethanes formation (THMFP) in this water source following chlorination. The chlorination of HPON and HPIN fractions only led to the formation of mostly chloroform, while other organic fractions formed both chloroform and bromodichloromethane. The linear dependency between each organic fraction concentration and THMFP indicated that the reactions of each organic fraction with chlorine were first-order.

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Keywords: THMFP; Disinfection by-products; Organic matter; Surface water; Fractionation

1. Introduction

Often, surface water is reported to contain organic matter derived both from natural degradation of some organic substances within the ecological systems and from human activities. Organic contaminants in surface water are different from location to location due to the differences in the

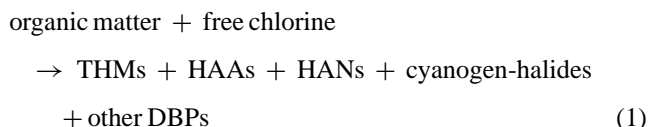
ecosystem and the activities of human beings in each specific location. This organic matter cannot easily be captured using normal water treatment techniques such as coagulation, and therefore it can enter the municipal water treatment system and then distributed through the water supply network. Moreover, during the disinfection process with chlorine, which is a common treatment technique in municipal water supply facilities, the organic matter could potentially be converted to potentially harmful disinfection by-products (DBPs) such as trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs). THMs are identified as potential adverse health agents for which U.S. Environmental Protection Agency (USEPA) proposed the drinking water standard under the disinfectants/disinfection by-products (D/DBP) rule (with a maximum contaminant level of 0.04 mg/L). THMs are usually measured in terms of the sum of four methane

Abbreviations: RW, raw water; NOM, natural organic matter; DBPs, disinfection by-products; THMs, trihalomethanes; HAAs, haloacetic acids; HAN, haloacetonitrile; THMFP, trihalomethane formation potential; DOC, dissolved organic carbon; TOC, total organic carbon; TOXFP, total organohalide formation potential; HPIA, hydrophilic acid; HPIB, hydrophilic base; HPIN, hydrophilic neutral; HPOA, hydrophobic acid; HPOB, hydrophobic base; HPON, hydrophobic neutral

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derivatives, i.e. chloroform, bromodichloromethane, dibromochloromethane, and bromoform concentrations. The general reaction of organic matter with chlorine can be expressed as follows [1]:



To better understand the formation kinetics of THMs, one can characterize the organic matter. The differentiation between each organic species might not be practical and therefore several past researches focused on grouping the organic matters into several common groups according to the physical/chemical properties of organic species, e.g. size, polarity, molecular weight, etc. Resin adsorption has lately been successfully employed as a successful fractionation technique for organic matter. Generally, DAX-8 resin was used to fractionate dissolved organic matter (DOM) into hydrophobic and hydrophilic fractions [2–5]. With a proper arrangement of a few adsorption resins, Leenheer [6] could separate DOMs into six organic fractions, i.e. hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), and hydrophilic acid (HPIA), hydrophilic base (HPIB), and hydrophilic neutral (HPIN). This technique was then employed for the characterization of other water sources [7–9]. The fractionation allowed a thorough investigation of the formation of THMs from the organic matters in water sources. For instance, hydrophobic fraction was often found to have higher THMs reactivity than the hydrophilic [3]. Korshin et al. [7] tested total organo-halide formation potential (TOXFP) of water samples. The hydrophobic acid fraction exhibited the highest level of TOXFP, and TOXFP decreased in the order from HPOA > HPIA > HPIN. Marhaba and Van [8] reported that hydrophobic base fraction was the most reactive in the formation of THMs followed by the hydrophilic acid fraction. Chang et al. [5] demonstrated that 76% of dissolved organic carbon (DOC) was the hydrophilic and hydrophobic acid fractions and it was the hydrophobic acid fraction that exhibited the greatest ability in the formation of THMs.

Lately, Marhaba et al. [10] modified the technique proposed by Leenheer [6] by replacing one of the resins to reduce the contamination from the back elution of the organics. This allowed a more reliable result of the fractionation particularly for the water source that contained low levels of total organic carbon (TOC), less than 5 mg/L.

The main purpose of this paper was to investigate the mass distribution of dissolved organic fraction and their relationship with THMFP using the adsorption technique proposed by Marhaba et al. [10]. The water samples were taken from the Bangkhen Water Treatment Plant (Bangkok, Thailand), which takes raw water (RW) from the Chao Phraya River, the main river in Thailand. This plant is the largest water supply facility (from the total of three water supply facilities) in Bangkok, and produces about 3 million m³/day (793

million gal/day). The characterization of this water source will be useful in the future management of this water treatment facility which services the millions of people living in Bangkok.

2. Methodology

Experimental work herein follows the steps specified in Fig. 1 and is detailed as follows. Note that: Milli-Q water (ELGA, Ultra Analytical) was used for all dilutions, samples and chemicals preparation, and final glassware cleansing in this work.

2.1. Sample collection and preservation

The collection of raw water sample was only performed once, with 400 L of sample being collected on 5 August 2003. This water sample was used for all experiments in this work.

Samples were prepared by filtering through a 0.45 µm membrane and stored in a cold room with a temperature controlled at 4 °C before and after fractionation.

2.2. Fractionation

The resin adsorption procedure as proposed by Marhaba et al. [10] was used to classify DOC into six fractions; HPOA, HPOB, HPON, and HPIA, HPIB, and HPIN by using three types of resin (DAX-8, nonionic resin (Supelco), AG-MP-50, cationic resin (Bio-Rad), and WA-10, weak anionic resin (Supelco)). Only one sample was obtained for each organic fraction, and each sample was then diluted to four concentration levels for the THMFP tests. The fractionation follows the steps below (see also Fig. 2):

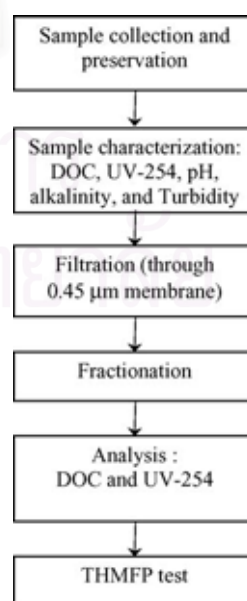


Fig. 1. Experimental procedure.

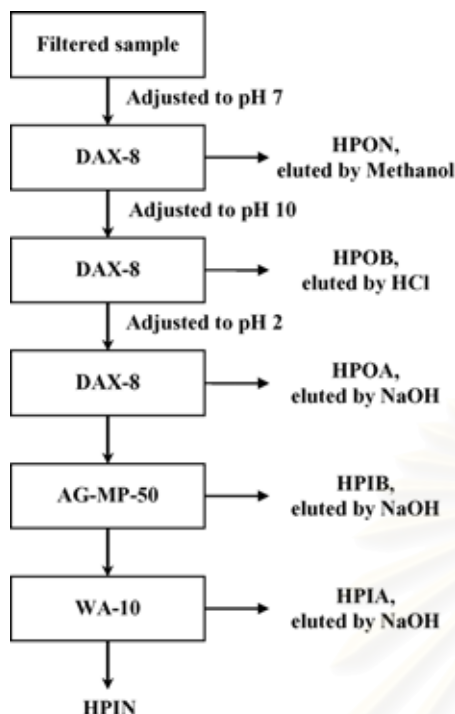


Fig. 2. Fractionation procedure.

1. The filtered sample was adjusted to pH 7 and passed through the packed column with DAX-8 resin. The hydrophobic neutral fraction was retained in the resin and was extracted out by CH₃OH (analytical grade).
2. The sample effluent was then adjusted to pH 10 by using 2 N NaOH and passed to the second DAX-8 resin packed column. This time, the hydrophobic base fraction was retained and eluted from the resin with 0.1 N HCl at 0.25 bed volume and 0.01 N HCl at 1.5 bed volumes.
3. The effluent was then acidified to pH 2 with 6 N H₂SO₄ and passed through the last DAX-8 resin packed column. The hydrophobic acid fraction was eluted from resin with 0.1 N NaOH at 0.25 bed volume and 0.01 N NaOH at 1.25 bed volumes.
4. The effluent, free of hydrophobic fractions, was passed through AG-MP-50 resin. The hydrophilic base fraction was eluted from the resin with 1 N NaOH at 1 bed volume.
5. The effluent was then passed through the WA-10 resin packed column. The effluent contained hydrophilic neutral and the adsorbate, hydrophilic acid was eluted with 0.1 N NaOH at 1.5 bed volumes and 0.01 N NaOH at 1 bed volume.

2.3. Trihalomethane formation potential (THMFP)

As stated in the previous section, each fractionated sample was diluted to four concentration levels prior to the THMFP test. The four concentration levels included the original concentration, and the rests were half, twice, and three times the original. For a quality control of the experimental results,

the THMFP test was triplicate to minimize the error from the experimental procedure. THMFP test were carried out according to the 7-day chlorine test procedure available in the Standard Methods 5710B [11]. The neutralized solutions were buffered by a phosphate solution prior to the incubation at $25 \pm 2^\circ\text{C}$ in amber bottles with PTFE liners. At the end of 7 days reaction period, samples must have a remaining free chlorine residual of between 3 and 5 mg/L. THMs were extracted with pentane according to the procedures mentioned in the Standard Methods 6232B [11]. THMs were then analyzed by the gas chromatography (GC) with electron capture detector (ECD) (series 6890 Agilent with DB 624 column, J&W Science) with the operating conditions as provided in Appendix A.

2.4. Analytical methods

The DOC was measured from the filtered sample using the TOC analyzer (OI Analytical model 1010, 1051) followed the Standard Methods 5310-C [11]. At least three replications of each measurement were carried out and more replications were executed in the cases where the variation between each measurement exceeded 5%. Milli-Q water was run every three samples to clean the system.

UV-254 (absorbance of ultraviolet at a wavelength of 254 nm) was reported to represent the aromatic character of organic matters as they imparted an ability to absorb light in the UV range [12]. UV-254 was measured with a Genesys 10 UV thermo-spectronic with a 1 cm quartz cell. All fractionated samples were adjusted to pH 7 by NaOH or H₂SO₄ prior to the measure of DOC and UV-254. Specific ultraviolet absorbent (SUVA) could subsequently be estimated as the ratio between UV-254 and DOC of the same water sample.

In this work, bromide content was measured by using an ion chromatography instrument (DIONEX, ICS-2500).

3. Results and discussion

3.1. Characterization

The results from the analysis of the water samples and from the fractionation are illustrated in Fig. 3. The DOC mass distribution sequences of the six organic fractions in raw water from high to low were HPIN, HPOA, HPIA, HPON, HPIB, and HPOB. It can be seen that the total weight of all organic fractions was about 9% more than the original weight in the water sample. This weight surplus may have come from resin bleeding during the elution process [6]. This level of inaccuracy was considered acceptable as this fractionation technique was often reported to give as much as 10–15% tolerance of DOM recovery [13,14]. Variation from 8 to 12% was also reported by Croue et al. [15].

The results from Fig. 3 revealed that hydrophilic neutral (HPIN) fraction was the major component in the water sample (45%) whilst the hydrophobic acid (HPOA) was the second

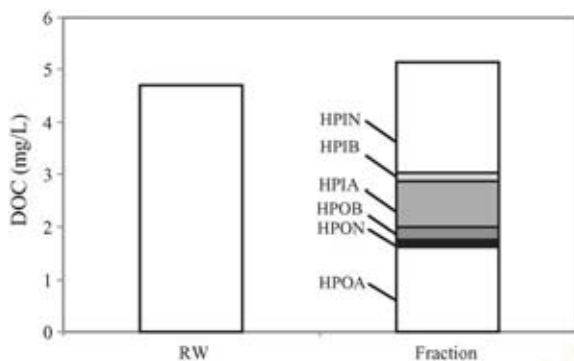


Fig. 3. DOC of raw water (RW) sample and its associated organic fractions.

(34%). These two fractions alone constituted as much as 79% of the total organic content. The remaining of the organic fractions were HPIA (18%) and HPON (6%) whereas the last two fractions (HPIB and HPOB) existed in slight quantity (each at 3%). Comparative evaluation of these results along with the reported data from literature was provided hereafter.

3.2. THMFP

Percentage distribution of THMFP of each organic fraction is shown in Fig. 4. The first two main precursors of THMFP were found to be HPIN and HPOA with 32 and 21% by weight of THMFP obtained from these two fractions, respectively. HPIA, HPOB and HPIB produced the same level of THMFP at around 13–15% by weight, whereas HPON was found to give the smallest quantity of THMFP. The THMFP results of each fraction were evaluated against the other reported data in the following subsections.

Fig. 5 illustrates the comparison between the total THMFP and the specific THMFP from each organic fraction. The total THMFP was defined as the ratio between THMFP from each organic fraction and DOC of the water sample. This was to give an overall picture of how THMs were formed in the water sample. The specific THMFP, on the other hand, was the ratio between THMFP and DOC of each organic fraction. This facilitated the analysis of the reactivity of each organic fraction on the formation of THMs. The total THMFP was derived from each organic fraction with HPIN being the main source whereas HPOA the second. This finding was not

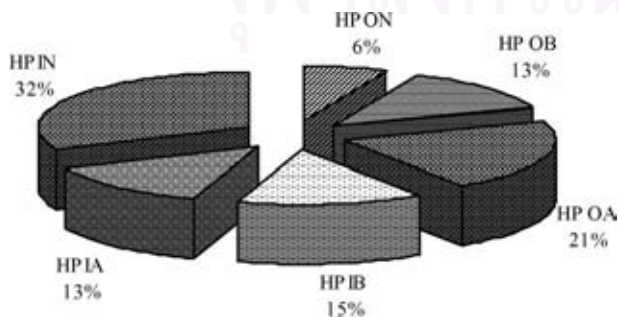


Fig. 4. Percent distribution of THMFP obtained from each organic fraction.

surprising as these two fractions were the two main organic components (79%) in this water source. Other fractions could be ordered according to their capability in forming THMs from high to low as: HPIB, HPOB, HPIA, and HPON, respectively. It should be mentioned, however, that, although organic fractions with larger quantity could potentially lead to more THMs formed during the chlorination, the reactivity of such organic fractions might not follow the same trend. The results from the analysis revealed that the main precursors of THMs in this water source were not observed to be the most active THM precursor, and rather, they were among the most inactive as discussed further below.

3.2.1. HPOA and THMFP

The concentration of HPOA was found to be about 34% (DOC 1.62 mg/L) in raw water and this was capable of producing 21% by weight of THMs (see Figs. 3 and 4). This level was found to be in the reported range of 8–68% in raw waters elsewhere [1,7,13]. In terms of the total THMFP, this fraction was the second most important source and it was the main source of THMFP among the hydrophobic species. However, according to its specific THMFP, this fraction was one of the least active sources (see Fig. 5). This implied that HPOA was the major precursor of THMFP simply because it was presented in large quantity in raw water. This finding was found to be different from other reports. For instance, Chang et al. [5] demonstrated that HPOA fraction was the greatest precursor for disinfection by-products, particularly THMs. This might be due to the differences in the character of the organic species in the water samples.

3.2.2. HPOB and THMFP

This fraction was observed to give the highest specific THMFP at 619 $\mu\text{g}/\text{mg}$. This indicated that HPOB was highly reactive with chlorine in forming THMs. This corresponded well with the report of Marhaba and Van [8]. More importantly, Marhaba and Van [16] reported that this fraction could not be effectively removed by coagulation from the raw water. For this reason, this fraction could be used as one of the

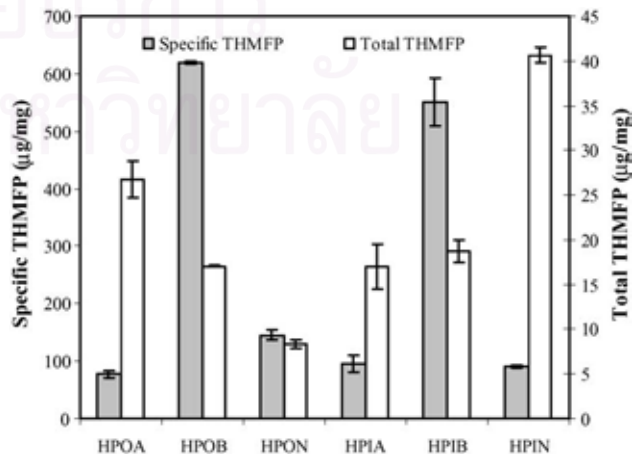


Fig. 5. Specific and total THMFP.

warning signals of THMs in the treatment process. However, in this case, its relatively low total THMFP suggested that this fraction did not exist in large quantity with only 3% by weight of the DOC content in the raw water. This finding was similar to other reports which indicated that the range of HPOB in other water sources was in the range of 0–22% by weight [1,13,7].

3.2.3. HPON and THMFP

HPON was the least problematic precursor to THMs in the water sample as its contribution to the total THMFP was the lowest among the six organic fractions, and it also was relatively inactive to the reaction with chlorine (low specific THMFP). Hence, this fraction was not considered as a problematic precursor for THMs in this water source. In addition, HPON in the water sample existed in a relatively lower quantity (only 6%). The reported data on the quantity of HPON in other water sources were quite variable with the smallest of 0% [7] to the largest of 36% [6]. Other reported data [5,8,16] indicated that this organic fraction did not exhibit high specific THMFP when compared to other organic fractions, which agreed well with the finding in this work.

3.2.4. HPIA and THMFP

Fig. 5 illustrates that HPIA had a rather low specific THMFP compared to other organic constituents in this water sample (in the same level as HPOA and HPIN). This meant that HPIA was quite inactive in forming THMs in the chlorination process. However, the total THMFP from this fraction was quite high. This was because it existed in a large quantity in the water source (18% by weight). This result was quite different from other reports, i.e. Marhaba and Van [8,16] illustrated that HPIA was among the most active organic fraction in the formation of THMs. This was possibly due to the differences in the nature of HPIA from the different water sources. Note, however, that the quantity of HPIA obtained from this work lied within the reported range of 8–53% from other water sources [7,8,13,16]. Nevertheless, the presence of such organic species was rather significant in terms of future management of the treatment plant, as previous investigation [8] revealed that HPIA fraction was one of the most difficult components to be removed by coagulation. Therefore, with its high quantity presented in the water source, this organic species could then be considered a problematic THM precursor.

3.2.5. HPIB and THMFP

Although HPIB was only presented in small quantity in this water source, the results in Fig. 5 demonstrate that the total THMFP from this fraction was relatively high. The same figure shows that HPIB was actually the most active precursor of THMs as its specific THMFP was the second highest among the six organic fractions, and the greatest among the three hydrophilic fractions. It is therefore a major concern for the operation of water treatment plant as an only tiny amount of HPIB could lead to a formation of THMs in large quan-

ty. In addition, the coagulation/sedimentation or filtration was not an effective means in removing this organic fraction [16].

HPIB was also found to be presented in small quantity in the water source reported in [7,8,16]. However, the reactivity of this fraction was only found to be moderate by Marhaba and Van [8]. This meant that HPIB from the two water sources might consist of different organic species.

3.2.6. HPIN and THMFP

Specific THMFP as illustrated in Fig. 5 indicates that HPIN was one of the most inactive organic precursors of THMs. A similar result was reported by Marhaba and Van [8]. This was possible as Bruchet et al. [17] reported that this organic fraction was primarily composed of polysaccharides, which were not quite reactive with chlorine. However, an extremely high total THMFP was obtained from this organic fraction. This was because HPIN was the most dominant constituent among the six organic fractions in this water sample (45% DOC). This was the highest among the reported data which stated that HPIN was in the range from 5 to 19% of the total organic content [6–8,10,16]. Hence, for this particular water source, this fraction should be considered as the major concern in this water treatment facility as the main cause of THMs.

3.2.7. SUVA and THMFP

Table 1 illustrates the level of SUVA obtained from each organic fraction compared with the specific THMFP. The numbers in the table represented the average values of the parameters. The standard deviation was also added to the column to indicate the level of scattering on the experimental results. As can be observed from the previous section, the base fractions, either hydrophobic or hydrophilic properties, seemed to be the most reactive organic species with chlorine. Interestingly, these two base fractions also provided relatively high SUVA values (greater than 2 L/mg m). High SUVA was reported to imply high aromatic character [18,19] and therefore this result implied that the aromatic organic compounds were the active precursors of THMs. The HPON fraction, however, also exhibited high level of SUVA but its specific THMFP was rather low. This meant that only the aromatic content with base property that was active in the chlorination reaction and despite a high content of aromatics, the neutral

Table 1
SUVA and Specific THMFP of organic fractions

Source	SUVA (L/mg m)	Specific THMFP ($\mu\text{g}/\text{mg}$)
Hydrophobic		
Acid	1.67	77.9 \pm 6.5
Base	2.31	619 \pm 2.3
Neutral	2.59	145 \pm 8.6
Hydrophilic		
Acid	0.71	95.6 \pm 15
Base	2.50	551 \pm 41
Neutral	0.94	90.6 \pm 2.8

property of the HPON fraction did not lead to a production of THMs.

3.3. THM species formation potential

THMs evaluated for each sample were the sum of four species, i.e. chloroform (CHCl_3), bromodichloromethane (CHCl_2Br), dibromochloromethane (CHClBr_2), and bromoform (CHBr_3). The results from the evaluation of THMFP of each water sample revealed that only chloroform and bromodichloromethane were formed during the chlorination of each organic fraction. The two brominated species, i.e. dibromochloromethane and bromoform, were not detected from the method employed in this work.

Fig. 6a displays the specific chloroform formation potential (CHCl_3 -FP) and specific bromodichloromethane formation potential (CHCl_2Br -FP) obtained from each organic fraction. The trend of specific CHCl_3 -FP followed that of specific THMFP quite closely. In other words, specific CHCl_3 -FP was generated mostly from the HPOB fraction followed in order from high to low by HPIB, HPON, HPIN, HPIA, and HPOA. This was because most of the THMFP formed in the water sample was chloroform, and the bromo-species (only bromodichloromethane in this case) was only responsible for as small as 3% of the total THMFP. Fig. 6b illustrates that most

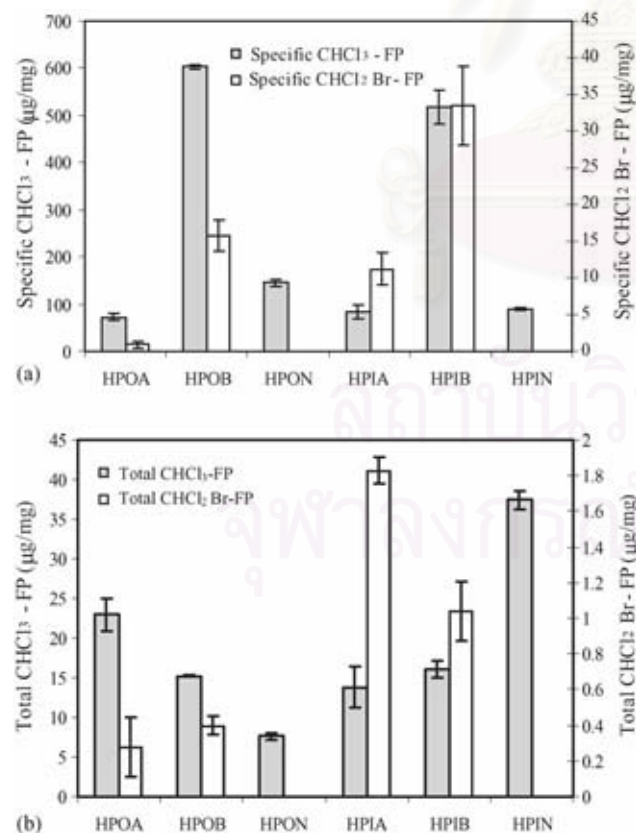


Fig. 6. (a) Specific THM species formation potential from each organic fraction. (b) Total THM species formation potential from each organic fraction.

Table 2
Bromide ion concentration in water samples

Sample	Bromide ion (mg/L)
RW	1.002
HPOA	0.002
HPOB	0.016
HPON	0.007
HPIA	0.069
HPIB	0.004
HPIN	0.000

of the THMs species in the samples was chloroform species where the total CHCl_3 -FP had the same trend as that for total THMFP. In other words, HPIN was the main source of CHCl_3 -FP, and HPOA was the second most important.

The specific CHCl_2Br -FP, however, did not quite follow the trend of the specific THMFP. The most active precursor for this THM species became the HPIB, followed by HPOB, HPIA and HPOA from high to low, respectively. HPON was found not to react with bromide at all. HPIN, however, was not found to give bromodichloromethane but the analysis for the bromide content in this organic fraction revealed an absence of bromide ion (see Table 2). Hence, it could not be concluded that bromide did not involve in the chlorination reaction of HPIN. Fig. 6b shows that the bromo-THM species was only presented in small quantity when compared to that of chloroform. Hence, unlike the case of CHCl_3 -FP, the contribution of CHCl_2Br -FP on the total THMFP was not obvious.

It is interesting to note that each organic fraction contained different amount of bromide ion as indicated in Table 2. This means that the resins used in the fractionation had different capacity in retaining bromide ions and therefore the organic eluants from the back-elution of the organic fractions consisted of bromide ion at different levels. The different bromide ions in each organic fraction might affect the species of the THMs in each fraction of water sample. For instance, HPOA was found not to be active when compared with that of HPIA, but the level of bromide ions presented in HPOA fraction (0.002 mg/L) was also significantly lower than that in HPIA fraction (0.069 mg/L). Hence, it was difficult to conclude that HPIA was more active in forming bromodichloromethane than HPOA. On the other hand, it was clear that HPOB was significantly more active in reacting with bromide ions than other species as there was only a relatively small level of bromide ions in this organic fraction (0.016 mg/L). However, the amount of brominated THM species only accounted for as much as 12% of the total THMs, and our preliminary results (not shown here) also revealed that the influence of bromide concentration (in the range found in the work) on the formation of the various THM species was at most 12%. Hence, the effect of bromide ion concentration was not included in this discussion.

3.4. Relationship between DOC and THMFP

Further investigation was conducted to examine the relationship between the level of organic content and the THMFP

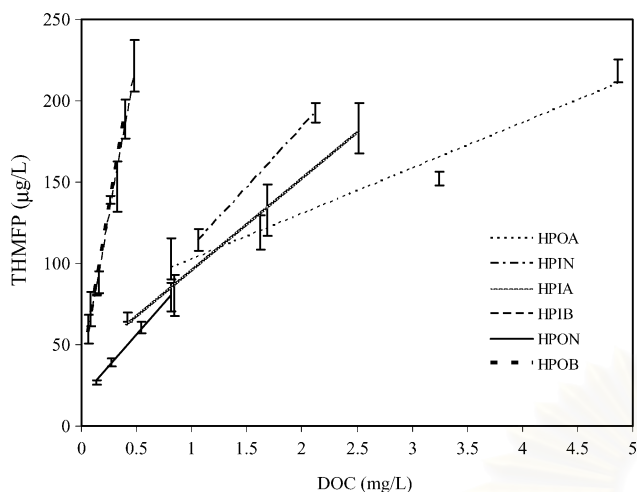


Fig. 7. THMFPP of each organic fraction.

from each organic fraction. Hence, each organic fraction was diluted to four concentration levels, each of which was tested for its THMFPP. The results are displayed in Fig. 7. Linear relationships were found in all cases with the correlations between THMFPP and the DOC of each organic fraction as follows:

$$Y_1 = 27.955X_1 + 74.644(R^2 = 0.966, N = 11) \quad (2)$$

$$Y_2 = 405.85X_2 + 31.363(R^2 = 0.998, N = 12) \quad (3)$$

$$Y_3 = 76.502X_3 + 17.845(R^2 = 0.996, N = 11) \quad (4)$$

$$Y_4 = 56.865X_4 + 38.193(R^2 = 0.993, N = 11) \quad (5)$$

$$Y_5 = 379.04X_5 + 33.665(R^2 = 0.986, N = 12) \quad (6)$$

$$Y_6 = 75.675X_6 + 31.535(N = 7) \quad (7)$$

where Y_{1-6} are the THMFPP of HPOA, HPOB, HPON, HPIA, HPIB, and HPIN, respectively ($\mu\text{g/L}$), and X_{1-6} are DOC of HPOA, HPOB, HPON, HPIA, HPIB, and HPIN, respectively (mg/L).

The number of data points used to construct Eqs. (2)–(6) was equal to twelve as there were four concentration levels and the test at each level was triplicate. However, those out-of-range data points were removed in some circumstances and therefore the number of samples was some time reduced to eleven. In addition, the HPIN fraction could not be prepared in a highly concentrated form and therefore there were only two concentration levels available for the construction of such relationship with THMFPP. This made the total sample number of six and with an extra set of experimental data conducted in the formulation of Eq. (7), the total number of samples for this equation became 7. Overall, the linear dependency between the various organic species and THMFPP indicated that the reactions between these organic fractions with chlorine were

first-order, at least for the range of concentrations and source water reported in this work.

4. Conclusion

The investigation illustrated the organic characteristics of the water from the Bangkhen Water Treatment Plant, which is the main water supply facility in Bangkok, Thailand. The dominant organic fractions in this water source were HPIN and HPOA. THMFPP obtained from these two fractions were also found to be in largest quantities when compared to other species. However, the results indicated that the most active precursors for THMFPP were not the species that were present in large quantity, but were HPOB and HPIB. These two species were also found to be quite active in forming chloroform species but the brominated THM species was found to be derived mostly from HPIB and HPOB. The information obtained from this work can be further employed in the design of the control technique and management strategies for the water treatment plant. For example, the choice of coagulant aids might be chosen to ensure the selective removal of the target organic precursors. Finally, it should be mentioned, however, that the conclusion obtained from this work was only based on the quality of the water source during the collection period (August 2003). Future work should therefore be conducted to investigate the effect of seasonal variation on the quality of organic matters and their THM formation potential.

Acknowledgements

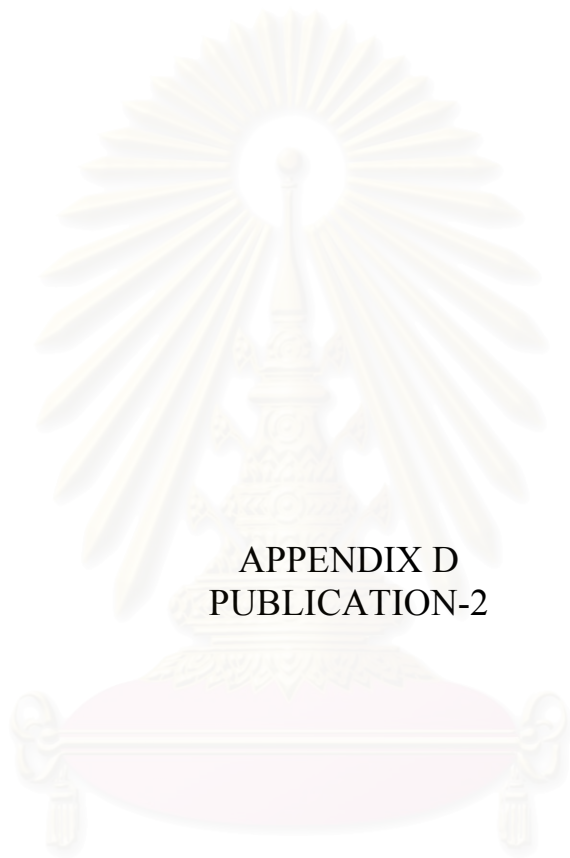
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Appendix A. GC condition for the determination of THMs

Manufacture name/model	Agilent 6890 series
Column	DB 624, J&W Science
Detector	ECD
Injection temperature	225 °C
Initial temperature	75 °C
Temperature program	–15 °C/min to 100 °C holding time 1 min –15 °C/min to 130 °C holding time 1 min –15 °C/min to 180 °C holding time 1 min
Final time duration	11 min

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APPENDIX D
PUBLICATION-2

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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P-12

KINETICS OF TRIHALOMETHANE FORMATION FROM ORGANIC CONTAMINANTS IN RAW WATER OF BANGKHEN WATER TREATMENT PLANT

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Abstract

Our preliminary work revealed that raw water from Bangkhen Water Treatment Plant (in Bangkok, Thailand) was contaminated with dissolved organic substance. Although they were present in tiny quantity, the chlorination of such organic contaminants could lead to the generation of potential carcinogenic trihalomethanes (THMs). There is a clear need for the thorough investigation of the formation of these harmful substances from the water source which is the main water supply for at least 4 million people in Bangkok. To accomplish this goal, it is important that these organic constituents be identified and the kinetics of the chlorination reactions be determined so that a proper treatment and management of the water treatment facility could be proposed. In this work, the identification of organic THM precursors will be achieved using the resin adsorption technique. Three types of resins; DAX-8, AG-MP-50, and WA-10, will be used to fractionate the raw water into six organic fractions, i.e. hydrophilic neutral (HPIN), hydrophilic acid (HPIA), hydrophilic base (HPIB), hydrophobic neutral (HPON), hydrophobic acid (HPOA), and hydrophobic base (HPOB). The chlorination of each organic fraction will be carried out to determine the nature of the kinetics of the reaction. The results will also be compared to that of the raw water to investigate the effect of fractionation on the formation of THMs. The study will include the influence of the presence of bromide ion on the formation of the different species of THMs.

Keywords: disinfection by-products, hydrophilic, hydrophobic

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