

REDUCTION OF TRIHALOMETHANE CREATED FROM SIX FRACTIONS  
OF DISSOLVED ORGANIC MATTERS IN RAW WATER SUPPLY  
BY ALUM COAGULATION



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สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

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การลดสารไตรฮาโลมีเทนที่เกิดจากสารอินทรีย์ละลายน้ำ 6 กลุ่มในน้ำดิบประปา

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การศึกษาการลดสารไตรฮาโลมีเทนที่เกิดจากสารอินทรีย์ละลายน้ำ 6 กลุ่มโดยการโคแอกกูเลชันด้วย  
สารส้มในน้ำดิบประปาจากอ่างเก็บน้ำของการนิคมอุตสาหกรรมภาคเหนือ จ.ลำพูน ในครั้งนี้พบว่า ในน้ำดิบที่  
กรองผ่านการกรอง และผ่านการแยกองค์ประกอบสารอินทรีย์ละลายน้ำโดยอนุกรมของเรซิน DAX-8, AG-MP-  
50 และ WA-10 ประกอบด้วยสารอินทรีย์ละลายน้ำกลุ่ม hydrophobic acid (HPOA) 41.6 เปอร์เซ็นต์,  
hydrophilic neutral (HPON) 12.1 เปอร์เซ็นต์, hydrophobic base (HPOB) 3.4 เปอร์เซ็นต์, hydrophilic  
acid (HPIA) 20.5 เปอร์เซ็นต์, hydrophilic neutral (HPIN) 17.7 เปอร์เซ็นต์ และ hydrophilic base (HPIB)  
4.8 เปอร์เซ็นต์ พบว่าสารอินทรีย์ละลายน้ำส่วนใหญ่เป็นสารกลุ่ม HPOA และ HPIA โดยมีปริมาณรวมกัน  
เท่ากับ 62 เปอร์เซ็นต์จากสัดส่วนของสารอินทรีย์ละลายน้ำทั้งหมด จากผลการศึกษาโอกาสการก่อตัวของสาร  
ไตรฮาโลมีเทน (THMFP) ที่เกิดจากสารอินทรีย์ละลายน้ำแต่ละกลุ่มในน้ำดิบประปานั้น พบว่าค่า THMFP ของ  
สารกลุ่ม HPOA ที่ตรวจพบมีค่าเท่ากับ 247.1 ไมโครกรัม/ลิตร, HPIA มีค่าเท่ากับ 112.6 ไมโครกรัม/ลิตร, HPIB  
มีค่าเท่ากับ 67.9 ไมโครกรัม/ลิตร, HPIN มีค่าเท่ากับ 64.9 ไมโครกรัม/ลิตร, HPOB มีค่าเท่ากับ 41.4 ไมโครกรัม/  
ลิตร และ HPON มีค่าเท่ากับ 68 ไมโครกรัม/ลิตร จากผลการศึกษากำจัดสารอินทรีย์โดยการโคแอกกูเลชัน  
ด้วยสารส้มในสภาวะควบคุม pH ที่ค่าต่างๆในช่วง pH 5 ถึง 8 และปริมาณสารส้มตั้งแต่ 10 ถึง 80 มิลลิกรัมต่อ  
ลิตร ซึ่งพบว่าปริมาณสารส้ม 40 มิลลิกรัมต่อลิตร และ ที่สภาวะควบคุม pH เท่ากับ 5 เป็นสภาวะที่เหมาะสมใน  
การลดปริมาณสารอินทรีย์ละลายน้ำ โดยสภาวะดังกล่าวสามารถลดสารไตรฮาโลมีเทนที่เกิดจากสารอินทรีย์  
ละลายน้ำกลุ่ม HPOA, HPON, HPOB, HPIA, HPIN และ HPIB ได้เท่ากับ 57.1, 53.7, 41.4, 40.6, 29.8 และ  
15.2 เปอร์เซ็นต์ ตามลำดับ และในการแสดงลักษณะของสารอินทรีย์ธรรมชาติในน้ำดิบประปาและกลุ่ม  
สารอินทรีย์ธรรมชาติทั้ง 6 กลุ่มโดยใช้เทคนิค Three-Dimensional Fluorescence Spectroscopy นั้นพบว่า  
ลักษณะสัญญาณ EEM สามารถนำมาประยุกต์ใช้เพื่อจำแนกกลุ่มของสารอินทรีย์ละลายน้ำแต่ละกลุ่มเบื้องต้น  
ได้ โดยการวิเคราะห์ตำแหน่งของ peak และ fluorescent intensity ในลักษณะสัญญาณ EEM ของสารอินทรีย์  
ละลายน้ำแต่ละกลุ่มดังกล่าว

สาขาวิชาการจัดการสิ่งแวดล้อม  
ปีการศึกษา 2547

ลายมือชื่อนิติ.....  
ลายมือชื่ออาจารย์ที่ปรึกษา.....

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KEY WORD: TRIHALOMETHANE FORMATION POTENTIAL (THMFP) / DISSOLVED ORGANIC MATTER (DOM) / FRACTIONATION / THREE-DIMENSIONAL FLUORESCENCE SPECTROSCOPY (EXCITATION-EMISSION MATRIX; EEM) / ALUM COAGULATION

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Reduction of THM created from six fractions of DOM by alum coagulation was studied in raw water supply from the reservoir of the Northern Industrial Estate, Lamphun province, Thailand. DOM was fractionated into six fractions including HPON, HPOB, HPOA, HPIB, HPIA, and HPIN by resin adsorption technique using the series of DAX-8, AG-MP-50, and WA-10 resins. Based on the results obtained, it was investigated that HPOA of 41.6%, HPIA of 20.5%, HPIN of 17.7%, HPON of 12.1%, HPIB of 4.8%, and HPOB of 3.4% were the fractions of DOMs in terms of DOC containing in filtered raw water. Accordingly, HPOA and HPIA fractions were found as the major DOM fractions which were 62% of total DOM. Regarding THMFP created from each DOM fraction, THMFP (HPOA) of 247.1  $\mu\text{g/L}$ , THMFP (HPIA) of 112.60  $\mu\text{g/L}$ , THMFP (HPON) of 68.0  $\mu\text{g/L}$ , THMFP (HPIB) of 67.9  $\mu\text{g/L}$ , THMFP (HPIN) of 64.90  $\mu\text{g/L}$ , and THMFP (HPOB) of 41.4  $\mu\text{g/L}$  were determined. However, the THMFP/DOC ratio of HPOA, HPIA, HPON, HPIB, HPIN, and HPOB were 101.0  $\mu\text{g/mg}$ , 93.3  $\mu\text{g/mg}$ , 95.6  $\mu\text{g/mg}$ , 242.5  $\mu\text{g/mg}$ , 62.1  $\mu\text{g/mg}$ , and 206.4  $\mu\text{g/mg}$ , respectively. According to the results from alum coagulation experiments under the conditions of pH values ranging from 5 to 8 and alum dosages of between 10 and 80  $\text{mg/L}$ , it was found that the optimal condition for DOM removal was at the pH of 5.5 with an alum dosage of 40  $\text{mg/L}$ . The percent reductions of THMFP created from each DOM fraction at the optimal alum coagulation were 57.1% for THMFP (HPOA), 53.7% for THMFP (HPON), 41.4% for THMFP (HPIN), 40.6% for THMFP (HPIB), 29.8% for THMFP (HPIA), and 15.2% for THMFP (HPOB). It can be concluded that alum coagulation could reduce THMFP (HPOA) more effectively than those of THMFP created from other DOM fractions. In addition, the EEM technique could be applied for preliminary classification of the major DOM fractions in water according to their peak positions and fluorescent intensities.

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## ABBREVIATIONS AND SYMBOLS

abs.	Absorbance
Al	Aluminium
Al(OH) <sub>3</sub>	Aluminium Hydroxide
Al <sub>2</sub> O <sub>3</sub>	Aluminium Oxide
Al <sub>2</sub> SO <sub>4</sub>	Aluminium Sulfate
AlCl <sub>3</sub>	Aluminium Chloride
amu	apparent molecular unit
AMW	Apparent Molecular Weight
AWWA	American Water Works Association
CaCO <sub>3</sub>	Calcium Carbonate
CHBr <sub>3</sub>	Bromoform
CHCl <sub>2</sub> Br	Bromodichloromethane
CHCl <sub>3</sub>	Chloroform
CHClBr <sub>2</sub>	Dibromochloromethane
Cl	Chlorine
cm	Centimeter
°C	Degree Celsius
D/DBP	Disinfection /Disinfection by product ratio
DBPs	Disinfection by Products
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DPD	<i>N, N</i> -diethyl- <i>p</i> -phenylenediamine
ECD	Electron Capture Detector
EDTA	Disodiummethylenediamine Tetraacetate Dehydrate
EPA	Environmental Protection Agency
FAS	Ferrous Ammonium Sulfate
g/cm <sup>3</sup>	Gram per Cubic Centimeter
g/L	Gram per Liter
g/mol	Gram per Molar
GC	Gas Chromatograph

hr	Hour
HA	Humic Acid
HAAs	Haloacetic acid
HANs	Haloacetonitrile
HPIA	Hydrophilic acid
HPIB	Hydrophilic base
HPIN	Hydrophilic neutral
HPOA	Hydrophobic acid
HPOB	Hydrophobic base
HPON	Hydrophobic neutral
KHP	Potassium Hydrogen Phthalate
KI	Potassium Iodide
L/mg-m	Liter per milligram-meter
m	Meter
M	Molar
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
µg/L	Microgram per Liter
mg/L	Milligram per Liter
MW	Molecular Weight
Nm	Nanometer
NOM	Natural Organic Matter
NTU	Nepheo Turbidity Unit
ppm	Part per Million
SUVA	Specific Ultraviolet Absorption
THMFP	Trihalomethanes Formation Potential
THMs	Trihalomethanes
TOC	Total Organic Carbon
TTHM	Total Trihalomethanes
USEPA	United States Environmental Protection Agency
UV-254	Ultraviolet absorbtion at wave length 254 nanometer
UV	Ultraviolet Absorbtion

# CHAPTER I

## INTRODUCTION

### 1.1 Motivation

Dissolved organic matter (DOM), defined as the complex matrix of organic material present in natural waters, affects significantly many aspects of water treatment. As a result, DOM acts upon potable water quality by contributing to disinfection by-products (DBP), biological re-growth in the distribution system, color, taste, and odor (Owen et al., 1995).

DOM has become critically important as it significantly influences many aspects of water treatment, including the efficiency of unit processes, quantity and frequency of disinfectant application, and inactivation of microorganisms (Marhaba et al., 2000). Water treatment plant processes generally consist of coagulation, flocculation, sedimentation, filtration and chlorination. Various water treatment processes can either directly or indirectly remove aquatic organic matter from raw water depending on their operational conditions and the specific characteristics of the DOM such as molecular weight distribution (MWD), carboxylic acidity, and humic substances content (Collins et al., 1985).

It has been known for more than 20 years that DOMs form THM and other DBPs on chlorination of drinking waters. DOM even though present in a tiny quantity, can react with chlorine to form halogenated disinfection by-products (DBPs) such as trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitrile (HANs) and cynogen halides, which are all classified as potentially carcinogenic substances (Rook, 1974).

Trihalomethanes (THMs) are compounds that are primarily formed in raw or treated water through the reaction of chlorine or bromine with humic acids associated



with decaying vegetation. Chlorine can react with humic substances in dissolved organic matter (DOM) to form THMs. Surveys have illustrated that THMs are ubiquitous in chlorinated drinking water supplies (Hubel and Edzwald, 1987). They are all considered to be possible carcinogens and therefore, human exposure to such compounds should be minimized (Norin and Renberg, 1980). The most well known health hazard is that THMs cause not only a depression of the central nervous system but also hepatotoxicity, nephrotoxicity, teratogenicity, and carcinogenicity. The U.S. Environmental Protection Agency (USEPA) has set a maximum contaminant level (MCL) of 100  $\mu\text{g/L}$  for total trihalomethanes and has set a new MCL of 80  $\mu\text{g/L}$  for stage 1 of the disinfection by product rule (D/DBP Rule; USEPA 1998). In stage 2, the D/DBP Rule may lower the MCL for THMs to 40  $\mu\text{g/L}$ .

A high regard is given to the reaction of DOM with chlorine to form DBPs especially, THMs and thus the characterization of DOM according to their potential to form DBPs is a familiar topic in water treatment research. It is also important that DOM in water be characterized by its organic content in order to determine proper treatment for the removal of DOM in such water prior to it being used as raw water.

Normally, DOM can be distinguished in terms of hydrophobic and hydrophilic groups. DOM portions can be fractionated into six fractions including hydrophobic acid, hydrophobic neutral, hydrophobic base, hydrophilic acid, hydrophilic neutral, and hydrophilic base by utilizing the resin adsorption method. Differing quantities and nature of DOM fractions have differing potential to form trihalomethane.

As no single analytical technique is capable of measuring the widely varied characteristics of DOM, surrogate parameters must be used to describe DOM. Commonly used DOM surrogates include TOC and DOC, UV-254, SUVA, and THMFP. However, there are some techniques that have been developed to identify DOM more closely in terms of their physical and chemical nature. Excitation-emission fluorescence spectroscopy technique (excitation and emission matrix, EEM) in one such technique and was developed in order to establish the signatures of DOM in water.

DBP precursor removal results in a reduction in the formation of DBPs. DOM react with disinfectants to form DBPs; therefore, lowering the concentration of DOMs can reduce DBP formation. The effective coagulation and subsequent removal of raw water organic matter prior to chlorination can help control THM levels in water supplies. Accordingly, this research was proposed to reduce DOMs in water by using alum coagulation in order to also reduce trihalomethane created from six DOM fractions in raw water supply. Moreover, EEM was utilized to establish signatures of six DOM fractions in order to describe DOMs more closely in terms of their physical and chemical nature.

## 1.2 Objectives

- To characterize dissolved organic matters (DOMs) in raw water, alum coagulated water, and their fractionated waters.
- To determine suitable conditions for alum coagulation of DOM reduction in water.
- To investigate THMFP created from each DOM fraction and THMFP reduction after alum coagulation.
- To introduce a three-dimensional fluorescence spectroscopy (excitation-emission matrix; EEM) technique for DOM characterization in water.

## 1.2 Hypotheses

- Different DOM fractions may produce different THMFP.
- Alum coagulation could be used to remove DOMs and their THMFP in water.
- EEM technique may be utilized to characterize DOM in water.

### 1.3 Scopes of work

- Water samples were taken in October 2004 from the raw water supply reservoir of Northern Region Industrial Estate, Lamphun, Thailand.
- The alum coagulation under the variation of controlled pH between 5 and 8 and alum dosage ranging from 10 to 80 mg/L were experimented so as to obtain an optimal condition for DOM removal.
- DOMs in raw water and coagulated water from the Northern Region Industrial Estate reservoir were fractionated into six components that consist of hydrophobic acid (HPOA), base (HPOB), neutral (HPON), and hydrophilic acid (HPIA), base (HPIB), and neutral (HPIN) by utilizing the resin fractionation procedure developed by Marhaba (2003).
- Resin fractionation was performed by using a series of DAX-8, AG-MP-50, and WA-10 resins, respectively.
- THMFP in raw water and coagulated water including THMFP in fractionated water for both filtered raw water and coagulated water were determined.
- The excitation-emission matrix (EEM) for filtered raw water, alum coagulated water, and their fractionated waters were also introduced.

### 1.4 Benefits of this work

The result obtained from this research can be conclusively used:

- To illustrate trihalomethane reduction created from six DOM fractions.
- To demonstrate the suitable condition of alum coagulation for DOM reduction.
- To describe DOM fractions in raw water supply and its reduction by alum coagulation of the Northern Region Industrial Estate reservoir Lamphun, Thailand.

## CHAPTER II

### BACKGROUND AND LITERATURE REVIEWS

#### 2.1 Trihalomethanes (THMs)

In 1974 researchers reported that trihalomethanes (THMs) were formed when chlorine reacted with naturally occurring humic substances in water treatment plants and water distribution systems. The first identification of chloro- and bromo-trihalomethanes (THMs) was done by Johannes Rook in 1974. The first class of halogenated disinfection by-products (DBPs) discovered in chlorinated drinking water. Since that time, the reduction of THMs has been the subject of intensive investigation in the water treatment field. Symon et al. (1975) described a survey of halogenated organic compounds from 80 water supply plants. THMs have been found to be the most widespread organic contaminants in drinking water, and occur at higher concentrations than other disinfection by-products. The four THMs (chloroform, bromodichloromethane, dibromochloromethane and bromoform) are formed when chlorine-based disinfectants are added to source water with fairly high organic content, such as surface water. THMs are included among the 25 volatile organic compounds regulated under the Safe Drinking Water Act (SDWA) of 1987. These compounds are persistent and mobile, and pose a cancer risk to humans (Pereira, M.A. 1983; Munro, N.B. and Travis, C.C. 1986). Chloroform ( $\text{CHCl}_3$ ), the most common THM, is a proven animal carcinogen and a suspected human carcinogen.

THMs can be taken in by drinking the water and breathing its vapours (for example when showering). They are then metabolised and eliminated rapidly. Most THMs are metabolised into a less-toxic form, but some are transformed into more reactive substances, especially at high concentrations. The THMs are absorbed, metabolized and eliminated rapidly by mammals after oral or inhalation exposure. Following absorption, the highest tissue concentrations are attained in the fat, liver and kidneys. THMs induce cytotoxicity in the liver and kidneys of rodents exposed to

doses of about 0.5 mmol/kg of body weight. A maximum contaminant level (MCL) of 100 µg/L for total trihalomethanes (TTHMs) in finished drinking water was established by the US Environmental Protection Agency (USEPA) in the National Interim Primary Drinking Water Regulations in 1979. The USEPA has set a new MCL of 80 µg/L for stage 1 of the disinfection by product rule (D/DBP Rule; USEPA 1998). In stage 2, the D/DBP Rule may lower the MCL for THMs to 40 µg/L.

### **2.1.1 Chemistry of Trihalomethanes (THMs)**

Trihalomethane (THM) is one of a family of organic compounds named as derivative of methane. Trihalomethanes are an important and predominant group of chlorinated drinking water byproducts that can occur as a result of the reaction between natural organic matter in the water and chlorine added as a disinfectant. A class of organic compounds, based on the methane molecule ( $\text{CH}_4$ ) where the hydrogen atoms normally present are replaced by three halogen atoms that may be chlorine, bromine, fluorine or iodine. The term 'Total Trihalomethanes' (TTHM) describes four disinfection by products, chloroform, bromodichloromethane, dibromochloromethane, and bromoform that may be sampled in a water sample. The THM usually present in highest concentration is chloroform, followed by dibromochloromethane. The primary biochemical ancestors of THM identified by many researchers are humic substances including humic acid and fulvic acid (Rook, 1976; Trussell and Umphes, 1978; Oliver and Lawrence, 1979). These materials also contribute to the natural color of the water (Amy et al., 1983).

Four THM species actually occur in water supplies including Chloroform, Bromodichloromethane, Dibromochloroform and Bromoform are shown in table 2.1.

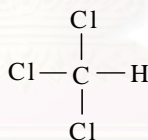
**Table 2.1** Classes of currently known DBPs

DBP Class	Individual DBPs	Chemical Formular
Trihalomethanes ; THMs	Chloroform	$\text{CHCl}_3$
	Bromodichloromethane	$\text{CHCl}_2\text{Br}$
	Dibromochloroform	$\text{CHClBr}_2$
	Bromoform	$\text{CHBr}_3$

(addaped from Krasner, 1999)

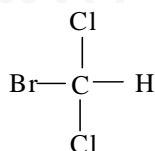
### 2.1.1.1 Chloroform

Chloroform is largely present in drinking water. It is colorless and has a pleasant, nonirritating odor with a slightly sweet taste. It evaporates easily into the air and dissolves easily in water. The chemical structure of Chloroform or trichloromethane ( $\text{CHCl}_3$ ) is depicted as follow:



### 2.1.1.2 Bromodichloromethane

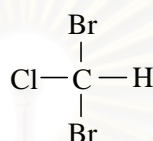
The chemical structure of dichlorbromomethane or Bromodichloromethane ( $\text{CHCl}_2\text{Br}$ ) is depicted as follow:





### 2.1.1.3 Dibromochloromethane

Dibromochloromethane is an organic compound, of the trihalomethane group. It is a colorless to yellow heavy, nonflammable, liquid with a sweet odor. It is slightly soluble in water and readily evaporates to air. The chemical structure of Dibromochloromethane or chlorodibromomethane ( $\text{CHClBr}_2$ ) chemical structure is as follows:



### 2.1.1.4 Bromoform

Bromoform is a colorless heavy liquid that smell and taste like chloroform. It is slightly soluble in water. The chemical structure of Bromoform or tribromomethane or methyl tribromide ( $\text{CHBr}_3$ ) is as follows:

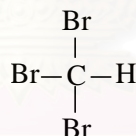


Table 2.2 demonstrate the chemical and physical properties of THMs that include Chloroform, Bromodichloro methane, Dibromochloromethane and Bromoform.

**Table 2.2** Basic chemical and physical characteristics of Chloroform, Bromodichloro methane, Dibromochloromethane and Bromoform

Empirical Formula	Molecular weight (g/mol)	Specific gravity ( $\text{g/cm}^3$ )	Boiling point ( $^{\circ}\text{C}$ )	Melting point ( $^{\circ}\text{C}$ )	Solubility in water (g/L)
$\text{CHCl}_3$	119.37	1.472	61	-63	8.1
$\text{CHCl}_2\text{Br}$	163.82	1.472	90.1	-57.1	Insoluble
$\text{CHClBr}_2$	208.29	2.38	120	-63	4.75
$\text{CHBr}_3$	257.73	2.894	150	8.3	Insoluble

(Source: Ghazali, 1989)



### 2.1.2 Possible reaction pathway of THMs in water treatment

Reckhow and Singer (1990) demonstrated a possible reaction that illustrates steps by which chloroform can be produced during water treatment as shown in Figure 2.1.

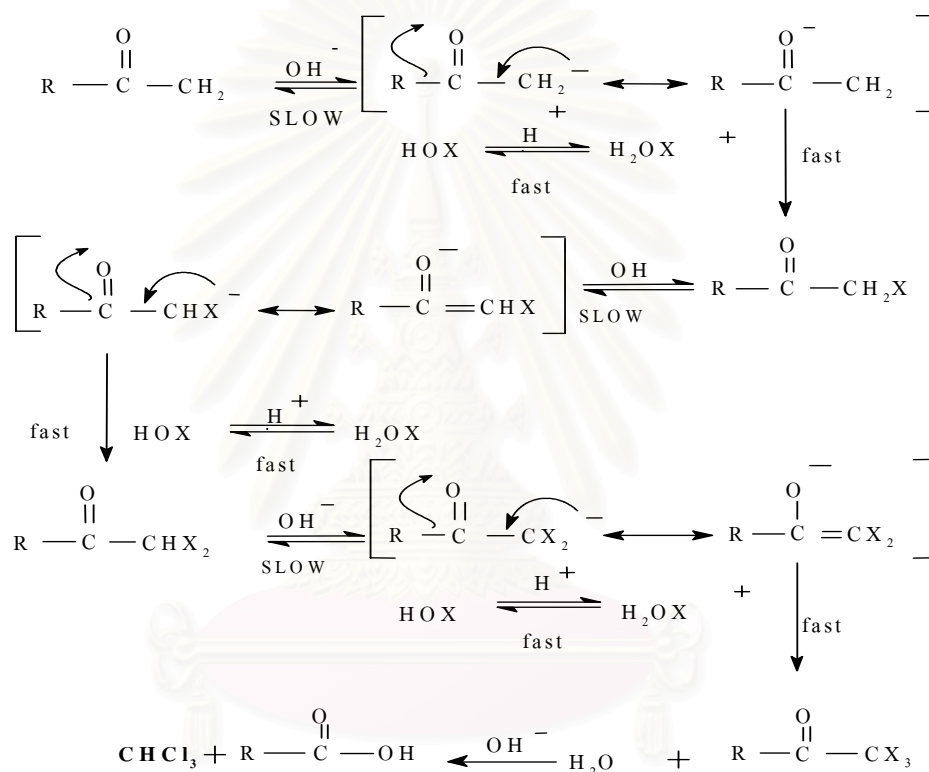
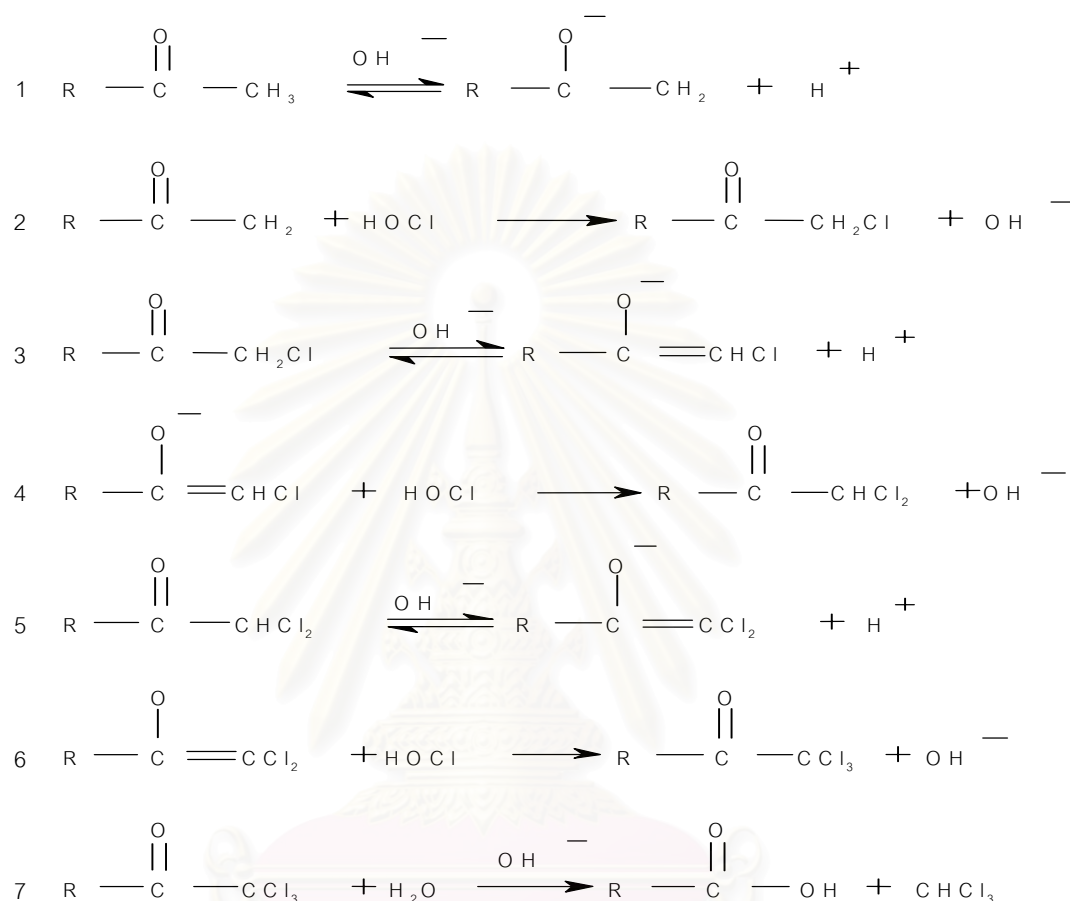


Figure 2.1 Haloform reaction pathways

The National Environmental Board (1984) demonstrated a series of reactions of chloroform that may be created during water treatment as shown in Figure 2.2.



**Figure 2.2** Reaction steps of chloroform produced during water treatment

### 2.1.3 Trihalomethane Formation Potential (THMFP)

THMFP determines the potential of DOM to form THMs under relatively extreme chlorination conditions. THMFP is defined as the difference between the concentration of THMs after the collected sample has been subjected to chlorination (Term-THM) and the concentration of THMs at the time of sampling (Inst-THM). The recommended (Standard Methods, 1995) chlorination conditions for THMFP tests include an incubation time of seven days with a free chlorine residual of 3 to 5 mg/L at the end of the incubation period. The recommended incubation temperature is

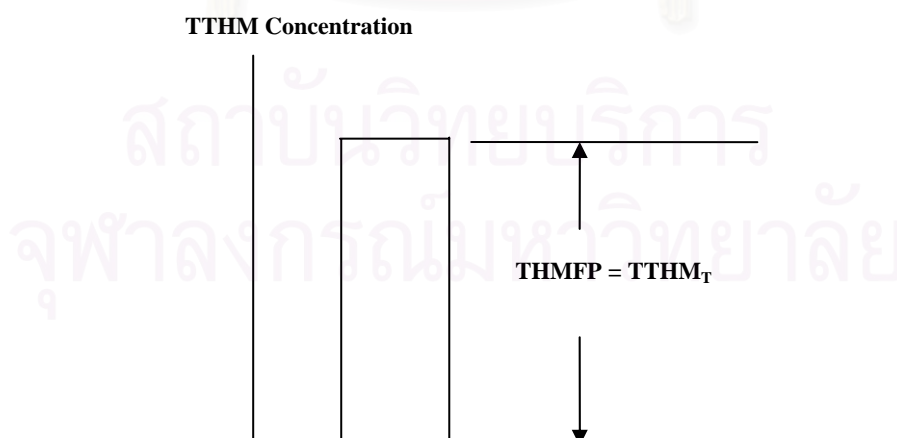
$25 \pm 2^\circ\text{C}$  and the recommended pH is  $7.0 \pm 0.2$  with phosphate buffer. The definition terms of THMFP are described as follows:

Total trihalomethanes (TTHMs) are the sum of all four compounds concentration, which include chloroform, bromoform, dichlorobromomethane and dibromochloromethane.

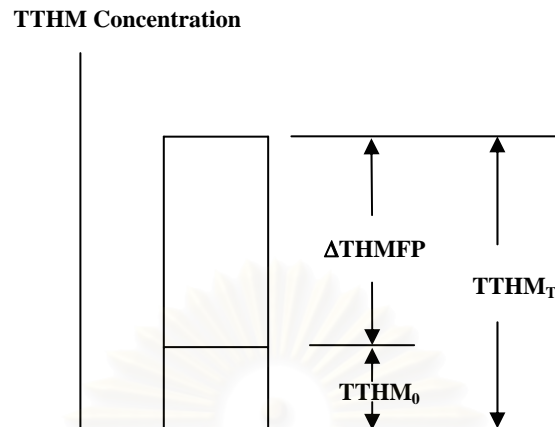
$\text{TTHM}_0$  is the total THMs concentration at the time of the sampling. It can range from non-detectable to several hundred micrograms per liter if the sample has been chlorinated.

$\text{TTHM}_7$  is the total concentration of all four THMs compounds that are formed when the sample is incubated at  $25 \pm 2^\circ\text{C}$  in the presence of excess free chlorine over a 7-day reaction time under the recommended chlorination conditions for THMFP (Standard Methods, 1995).

THMFP or  $\Delta\text{THMFP}$  is the difference between the final  $\text{TTHM}_T$  concentration and the initial  $\text{TTHM}_0$  concentration as shown in Figure 2.3 and 2.4, respectively. THMFP determinations provide a worst-case scenario of the concentration of THMs that may be formed.



**Figure 2.3** Definition used in the formation potential test of a sample without free chlorine at the time of sampling.



**Figure 2.4** Definition used in the formation potential test, of a sample with free chlorine at the time of sampling

El-Shahat, Abdel-Halim and Hassan (1998) evaluated trihalomethnes in water treatment plants output in Cairo, at three sampling locations, Mostord, Tebbin and Rod El-Frag. Mean values of THMs in the water treatment plants outputs (Sept. 1991- Dec. 1991) ranged from 31.70 to 61.41  $\mu\text{g/L}$ . Moreover, mean vaules of THMs in water treatment plant outputs (Jan. 1992 - August 1992) ranged from 19.19 to 42.30  $\mu\text{g/L}$ .

El-Shahat, Abdel-Halim and Hassan (2001) investigated THMs in various stages of the water treatment process at the Tebbin, Rod El-Farag and Mostorod water treatment plants during summer and water seasons. Stages of the water treatment process that were investigated consist of raw water, clarifier and filter effluent and finished water. The results showed that the highest THMs concentration occurred in finish water and its range was between 41.70 and 54.50  $\mu\text{g/L}$  in the summer, and 29.00 and 34.90  $\mu\text{g/L}$  in the winter. Moreover, THMs concentration in filter effluent is higher than that of clarifier and THMs concentrations in clarifier is higher than that of raw water.

## 2.1.4 Factors influencing THM formation

The extensive literature regarding to THM levels in disinfected source waters and control of THMs by various treatment processes testifies to the wide variety of factors influencing THM formation the complex interrelationships between these factors. Variables including pH, the concentration and characteristics of precursor, chlorine concentration, temperature and contact time all play a role in THM formation reactions.

### 2.1.4.1 pH

The impact of pH on THM concentrations has been reported by a number of researchers (Stevens et al., 1976; Lange & Kawczynski, 1978; Trussell & Umphres, 1978). In general, increasing pH has been associated with increasing concentrations of THMs. The rate of THM formation increases with the pH (Stevens et al., 1976). Kavanaugh et.al. (1980) reported a 3-fold increase in the reaction rate per unit pH.

Rook (1976) suggested that THM formation increased significantly at pH values of 8 to 10, whereas in the range pH 1 to 7, pH has less of an influence on THM formation. Trussell (1978) demonstrated that THM can form in none existing of chlorine residual once the pH is raised. The chlorinated intermediates form at low pH and hydrolyze to form THMs once the pH is raised. Carlson & Hardy (1998) reported that at pH levels greater than 9.0, THM formation decreased with increasing pH. It is possible that the shift in chlorine species from hypochlorous acid to hypochlorite affects THM formation during short reaction times. AWWARF (1991) observed no relationship between pH and the concentrations of THMs at eight utilities over time, suggesting that although THM concentrations for a particular water are known to be pH dependent, factors other than pH influence THM concentrations over a variety of source waters.

#### **2.1.4.2 Precursor concentration and characteristics**

THM formation is a result of a reaction between chlorine and THM precursors. It is obvious that the precursor concentrations would influence THM concentrations. Rook (1976) studies varied concentrations of organic precursors, which are called total organic carbon (TOC) should be reduced before chlorinating. In this regard, it was found that Chloroform production from organic matter is linear in concentration up to 250 mg/l TOC.

Young and Singer (1979) showed that quantity of chloroform produced is depended upon TOC concentration in raw water. Chloroform formation increased as non-volatile TOC increased. The removal of TOC is a conservative indicator of the removal of the precursors of THMs (Milter, Nolan and Summers, 1994).

THM formation was found to be directly related with the dissolved organic carbon (DOC) content. However when different source waters were compared, poor relationships between DOC and THM formation have been observed (EPA, 1981). This suggests that factors such as chemical functional groups in the DOC play an important role in the formation of THMs.

#### **2.1.4.3 Chlorine concentration**

Chlorine concentration is a factor affecting the type and concentration of DBPs formed. The THM level rises with increasing chlorine dose (Kavanaugh et al., 1980). However, there is some disagreement regarding the quantitative relations between chlorine concentration and THM levels (or the rate of THM production). Most investigators found a linear relationship between chlorine consumption and THM production, with an order of reaction greater than or equal to unity (Trussell & Umphres, 1978; Kavanaugh et al., 1980). However, it is also possible that the order of reaction changes during the course of the reaction.

Trussell and Umphres (1978) conducted a laboratory test with synthetic water prepared by adding 10 mg/L of humic acid, 1 mg/L of  $\text{NH}_3\text{Cl}$  (as  $\text{NH}_3$ ) and 10 mg/L of standard pH 7 buffers to demineralized water (TOC 0.2 mg/L). Different amounts of chlorine were added to various portions. After 2 hours of contact time, the results show that higher THM concentration occurred within a certain range of chlorine precursor to form THM as chlorine has been used up to react with ammonia, bacterial disinfecting, etc. Muttamara et al. (1995) showed the relationship between THM concentrations and chlorine dosages. THM concentrations increased as the chlorine dosages increased. At dosages of 7 and 10 mg/L chlorine, the total THM concentrations at the end of the test run were found to be 124.5  $\mu\text{g/L}$  and 158.3  $\mu\text{g/L}$ , respectively. The level of THM concentration increased with respect to the level of THM precursors.

#### **2.1.4.4 Temperature**

On a conceptual basis, it may be that rapidly forming compounds are more reactive and form DBPs regardless of temperature. On the other hand, slowly forming compounds require higher activation energy, and an increase in the temperature supplies the energy. In addition to reaction kinetics, the temperature of source water can also affect disinfection efficiency. The formation rates of THMs have been shown to increase with temperature (AWWARF, 1991; Siddiqui & Amy, 1993). In studies on the effect of temperature on THMs, Peters et al. (1980) found an Arrhenius dependency between the rate constant and temperature with activation energy of 10-20 kJ/mol. The impact of temperature on THMs was strongest at longer contact times (Carlson and Hardy, 1998).

The effect of temperature on the rate of THM formation was investigated by Stevens et al. (1976) using the Ohio River water collected from the winter to the summer. The results showed that the temperature differentials could easily account for most of the winter to summer in THMs concentration variations.



The concentrations of THMs were higher during the summer and autumn than in the winter and spring.

#### **2.1.4.5 Contact time**

After chlorine addition, there is a period of rapid THM formation for the initial few hours (e.g., 4 h), followed by a decline in the rate of THM formation, suggesting fast and slow DOM reactive sites. Recknow and Singer (1984) ran a few sets of experiments. One of these experiments studied the formation of these chlorinated products as a function of the reaction time. They found that by varying the chlorine contact time, chloroform and total THM increases rapidly in the first few hours and then slows to a generally steady rate of increase. Many authors have indicated that the concentration of chloroform appears to increase slowly even after 96 h, suggesting that as long as low concentrations of free chlorine are present, chloroform continues to form. Bromochlorinated THM species have been found to form more rapidly than chloroform. Further data from many sources indicate that bromoform formation slows at approximately 7-8 h and levels off almost completely after 20 h (AWWARF, 1991; Koch et al., 1991).

## **2.2 Dissolved Organic Matter (DOM)**

Dissolved organic matter (DOM), defined as the complex matrix of organic material present in natural waters, affects significantly many aspects of water treatment. DOM even though present in a tiny quantity, can react with chlorine during chlorination to form halogenated disinfection by-products (DBPs) which are all classified as carcinogenic substances. DOM consists of humic substances, amino acids, sugars aliphatic acids, and a large number of organic molecules (Malcolm Pirnie Inc., 1993). Humic substances include humic and fulvic acids; while non-humic substances include hydrophilic acids, proteins, carbohydrates, carboxylic acids, amino acids, and hydrocarbons (Thurman, 1985; Amy, 1993). DOM can be separate into

humic and non-humic fraction. The humic fraction has a more hydrophobic character than the non-humic fraction. The humic fraction consists of humic and fuvic acids. The non-humic consists of hydrophilic acids, proteins, amino acids and carbohydrate. However, in terms of their chemical properties and implication for water treatment, the humic substance is the most important (Owen, 1995). DOM which consists of humic and fuvic acid (aquatic humic), cause natural color, is the most important (Edzwald, 1993).

DOM plays a role in many aspects of water treatment. DOM is capable of forming complexes with metals such as iron. It can serve as a substrate for microbial growth and can exert significant oxidant demand, thereby interfering with both oxidation and disinfection during drinking water treatment. Depending on the concentration and type of DOM, the acidity of water can also be affected. DOM serves as the organic precursor. DBP formation is influenced by water quality (e.g., TOC, pH, temperature) and treatment conditions (e.g., disinfectant dose, contact time, removal of DOM before the point of disinfectant application, prior addition of disinfectant).

Non-humic substances, such as algae and their extracellular products, have been shown to be precursors to THMs (Morris and Baum, 1978; Oliver and Shindler, 1980). Oliver and Shindler (1980) observed faster reaction kinetics between chlorine and algae than between chlorine and aquatic humic materials. Their results suggest that algae in surface waters may be a major contributor to THM production. Humic acids have generally been found to be more reactive with chlorine than fulvic acids. There is also evidence that the humic fraction produces greater concentrations of HAAs and THMs than the non-humic fraction.

Marhaba and Washington (1998) reported that DOM contains precursors for disinfection by-product formation during water treatment disinfection operation. Furthermore, humic substances were characterized by non specific parameters, which are based on their organic carbon content (i.e., TOC), their ability to absorb UV light

at 254 nm (i.e., UV 254), and their potential to form trihalomethanes (i.e., THMFP) have become a useful technique to characterize DOM.

Normally, DOM is characterized by nonspecific or Surrogate parameters. The surrogate parameters must be used to describe DOM because no single analytical technique is capable of measuring the widely varied characteristics of DOM. Commonly used DOM surrogates include total organic carbon (TOC), dissolved organic carbon (DOC), ultraviolet absorbance at wavelength of 254 nm (UV- 254) and THMFP. Moreover, THMFP removal is also presented to highlight any difference between TOC and THMFP removal (USEPA, 1999). DOM surrogate parameters are described below.

### **2.2.1 Total Organic Carbon (TOC)**

TOC is defined as all carbon atom covalence bonded in organic molecules. TOC represents the total amount of organic carbon in water samples. The organic carbon in water and wastewater consists of a variety of organic compounds in various oxidation states. TOC is independent of the oxidation state of organic matter and does not measure other organically bound elements such as hydrogen and nitrogen (APHA, AWWA, and WEF, 1995).

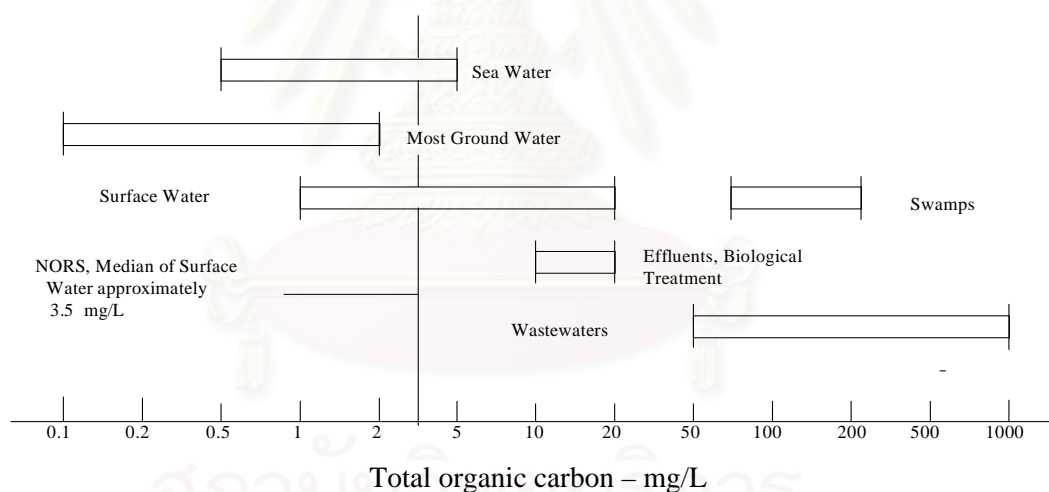
Young and Singer (1979) showed that quantity of chloroform produced is depended upon TOC concentration in raw water. Chloroform formation increased as non-volatile TOC increased. The removal of TOC is a conservative indicator of the removal of the precursors of THMs (Milter, Nolan and Summers, 1994). Therefore, the percent removal of TOC is correlation to the percent removal of DBPs. The USEPA proposed the percentage TOC required for enhanced coagulation and softening. It will depend upon the TOC and alkaline concentration in raw water. The details are shown in Table 2.3 (USEPA, 1999).

**Table 2.3** Percent removal of TOC requirements for enhanced coagulation and softening

Source Water TOC (mg/L)	Source Water Alkalinity (mg/L as CaCO <sub>3</sub> )		
	0 - 60	>60 - 120	>120*
2.0 - 4.0	35%	25%	15%
4.0 - 8.0	45%	35%	25%
>8.0	50%	40%	30%

(Source: USEPA, 1999)

Kavanaugh (1978) demonstrated range of TOC for a variety of natural water, shown in Figure 2.5



**Figure 2.5** Range of TOC reported for a variety of natural water

### 2.2.2 Dissolve Organic Carbon (DOC)

Dissolved organic carbons are defined as the fraction of TOC that passes through a 0.7  $\mu\text{m}$  GF/F filter paper. DOC is independent of the oxidation state of the organic matter. Organic carbon in natural water can be composed in two fractions,

particulate organic carbon (POC) and dissolve organic carbon (DOC). In surface water, between 50 and 60 % of humic substances are DOC (Thurman, 1985).

### **2.2.3 UV Absorbance at wavelength 254 nm (UV- 254)**

This relationship has led to the use of  $UVA_{254}$  measurements as surrogate parameters for estimating the extent of DBP formation. Ultra-violet (UV) absorption at a wavelength of 253.7 nm is used to provide an indication of the aggregate concentration of UV-absorbing organic constituents, such as humic substances and various aromatic compounds (APHA, AWWA, WEF, 1995). As noted by Edzwald et al. (1985), humic aromatic compounds and molecules with conjugated double bonds absorb UV light, whereas simple aliphatic acids, alcohol, and sugars do not absorb UV light.

Organic compounds that are aromatic or that have conjugated double bonds absorb light in the ultraviolet wavelength region. Therefore, UV absorbance is a well-known technique for measuring the presence of naturally occurring organic matter such as humic substances. UV analysis is also affected by pH and turbidity (Edzwald, Becker, and Wattier, 1985). UV absorption is a useful surrogate measure for DOM or precursor of THMs because humic substrates strongly absorb ultraviolet radiation (Eaton, 1995)

### **2.2.4 Specific Ultraviolet Absorbance**

The ratio between UV absorbance to DOC, referred to as specific absorbance (SUVA) ( $\text{cm}^{-1}\text{mg}^{-1}\text{L}$ ) demonstrates a relative index of humic content (Edzwald, 1993 and Owen et al., 1993). Specific absorbance could suggest the nature of DOM and its consequent THM formation (Krasner et al., 1996). Higher specific absorbance values tend to indicate higher humic content. Specific absorbance of a humic sample depends upon the molecular weight of the substances. (Pettersen et al., 1995)

SUVA can be used as an indicator of its coagulation (or softening) ability to remove THM precursors. Water having a high SUVA ( $SUVA > 3 \text{ L/mg-m}$ ) have been found to contain organic matter that is more humic-like in character, higher in apparent molecular weight (AMW), and more readily removed by coagulation (Edzwald, 1993) whereas lower SUVA values ( $< 3 \text{ L/mg-m}$ ) indicate the presence of organic matter of lower AMW that is more fulvic-like in character and more difficult to remove.

### **2.3 Resin Fractionation**

Goslan (2004) fractionated raw water from a reservoir in the United Kingdom (UK) by the resin adsorptions technique into its hydrophobic fraction and hydrophilic fraction. The hydrophobic fraction was further separate into a humic acid fraction and a fulvic acid fraction by precipitation of the humic fraction at pH 1. The non-adsorbed material was designated the name hydrophilic non acid fraction.

Leenheer (1981) proposed the comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural water. He showed that DOM in a water sample can be fractionated by resin adsorption into six fractions including hydrophobic acid, hydrophobic neutral, hydrophobic base, hydrophilic acid, hydrophilic neutral and hydrophilic base with a recovery of greater than 90 %.

Marhaba and Pu (2000) and Marhaba et al (2003) utilized resin adsorption to isolate and fractionate dissolve organic matter (DOM) into six different fractions which are operationally categorized as hydrophobic acid, hydrophobic neutral, hydrophobic base, hydrophilic acid, hydrophilic neutral and hydrophilic base

Leenheer and Croué (2003) demonstrated the relationships between organic compounds and the DOM fractions that are as follows; a hydrophobic neutral fraction (HPON) comprises hydrocarbons/tannins, a hydrophobic base fraction (HPOB) comprises aromatic amines, a hydrophobic acid fraction (HPOA) comprises fulvic acid, a hydrophilic neutral fraction (HPIN) comprises sugars, a hydrophilic base



fraction (HPIB) comprises peptides/ amino and a hydrophilic acid fraction (HPIA) comprises polyuronic acids.

## **2.4 Three-Dimensional Fluorescence Spectroscopy**

Marhaba and Pu (2000) reported that the Fluorescence spectrometry (EEM) is the total sum of emission spectra of a sample at different excitation wavelengths, recorded as a matrix of fluorescent intensity in coordinates of excitation (EX) and emission (EM) wavelengths, in a definite spectral window.

Coble (1996) said that fluorescence spectrometry has been widely used due to its simplicity and its requirement of minimal sample amounts and pretreatment. A three-dimensional excitation-emission matrix (EEM) obtained by fluorescent spectrometry scanning the wavelengths of both excitation and emission can be used to distinguish DOMs in natural water.

Coble et al. (1990) said that once the EEM has been fully corrected for instrumental configuration. Data can be analyzed as excitation spectra, emission spectra or synchronous scan spectra, even though originally collected as emission scans.

Croue et al., (2000) has recently summarized the methods used to characterize DOMs e.g., the use of chemical components such as amino acids and carbohydrates, molecular weight/size distribution, pyro-chromatogram and fluorescence spectrum.

Musikavong et al., (2004) showed that major organic fractions could be characterized by the EEM spectrum; the peak positions on the EEM of these major organic fractions were similar to the peak positions on the EEM of raw water from the wastewater treatment facility at the Industrial Estate in Lumphun.

Musikavong et al., (2005) demonstrated correlations of THMFP and fluorescent intensity of the influent wastewater and water samples from each pond at the wastewater treatment plant of the Northern Region Industrial Estate, Lamphun,



Thailand. Their reported results showed that EEM could be used to quantify the THMFP in the water source.

Chen et al., (2003) defined excitation and emission boundaries into five regions based largely upon supporting literature. EEM peaks have been associated with humic-like, tyrosine-like, tryptophan-like, or phenol-like organic compounds. In general, peaks at shorter excitation wavelengths (<250 nm) and shorter emission wavelengths (<350 nm) are related to simple aromatic proteins such as tyrosine (Regions I and II). Peaks at intermediate excitation wavelengths (250-  $\phi$  280 nm) and shorter emission wavelengths (<380 nm) are related to soluble microbial byproduct-like material (Region IV). Peaks at longer excitation wavelengths (>280 nm) and longer emission wavelengths (>380 nm) are related to humic acid-like organics (Region V). For fulvic acids, EEMs with minimum excitation wavelengths of 250 nm indicated shoulders of EEM peaks located at shorter excitation wavelengths. Therefore, peaks at shorter excitation wavelengths (<250 nm) and longer emission wavelengths (>350 nm) are related to fulvic acid-like materials (Region III).

## **2.5 Removal of THMs by alum coagulation**

Various methods of precursor removal have been proposed, although chemical coagulation is already operational at many treatment plants for turbidity has the potential to remove both turbidity and THM precursors when the process is optimized. The numbers of researchers are working to find new methods that could control the by-products caused by current methods. Some alternatives to the complex situation of reactions are good and others produce unwanted compounds.

The coagulants that are the most widely used in water treatment are aluminium and iron salts. Aluminum salts are employed more frequently than iron salts because they are usually cheaper. Therefore, the most coagulation process in water treatment generally uses aluminum salts as coagulant in order to remove turbidity and DOM in water.

Olive and Lawrence (1979) reported that alum treatment followed by sand filtration can remove about two-thirds of precursor. Chlorination of this treated water yields quite low haloform concentration.

Babcock and Singer (1979); Chadik and Amy (1983); Dempsey et.al. (1984) focus on coagulation with alum in relation to THM precursor removal. Reckhow and Singer (1984) also investigated the importance of alum coagulation in the removal of total organic halide precursors as well as THM precursors.

Hubel and Edzwald (1987) described that the removal of THM precursors by coagulation using alum, high-molecular-weight polymers, cationic polymers and various combination of these coagulants. High-charge-density cationic polymers with alum as a coagulant aid provided good precursor removal at low alum dosages.

Amirtharajah and O'Melia (1990) said that the coagulation/filtration process has traditionally been used to remove turbidity from drinking water supplies. However, the process is not restricted to the removal of particles. Coagulants render some dissolved species (e.g., DOM, inorganics, and hydrophobic SOCs) insoluble, and the metal hydroxide particles produced by the addition of metal salt coagulants can adsorb other dissolved species. Humic substances react with most coagulants.

Edzwald et al. (1990) reported that waters with low SUVA values contain primarily non-humic matter and are not amenable to coagulation. SUVA is an alternative compliance criterion for demonstrating compliance with TOC removal requirements. If the SUVA of raw water is  $\leq 2.0$  L/mg-m, enhanced coagulation or enhanced softening are not able to remove organic matter from the water.

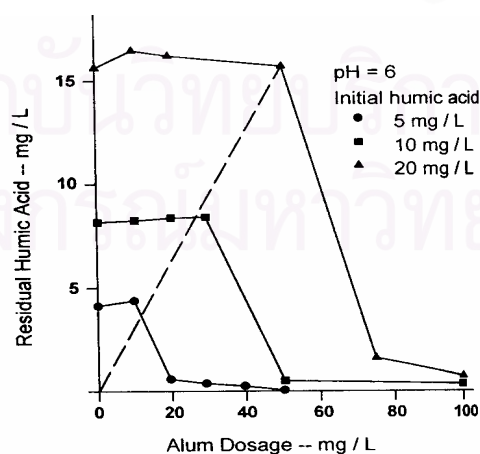
USEPA (1999) proposed that the coagulation process was able to remove organic matter from water which contained more than 2 mg/L-m of SUVA. As the values of SUVA of the raw water complied with these criteria, it might be possible for coagulation to be applied as part of the water supply process for the removal of certain THM surrogate parameters in the water.

Bolto et al. (1999) investigated the treatability of the various fractions for very hydrophobic compounds (DOMinally humic acid) and less hydrophobic compounds (DOMinally fulvic acid) where alum was used as the most effective reagent. And for neutral hydrophobic compounds (DOMinally carbohydrates), very minor component, alum was by far the most effective.

### 2.5.1 Alum coagulation

Aluminum sulfate or “Alum” is a widely used coagulant in the coagulation process in water treatment. The principle factors affecting the coagulation and flocculation of water or wastewater are turbidity, suspended solids, temperature, pH, cationic and anionic, compositions and concentrations, duration and degree of agitation during coagulation and flocculation.

The stoichiometric relationship between DOM removals is depicted in Figure 2.6 for the removal of humic acid by alum. In these situations, stoichiometry is defined as the required initial dosage proportional to the DOM concentration. It could be established for a given treatment situation. It should be noted that over dosing (exceeding the stoichiometry) might lead to restabilization of the DOM. This is possible where cationic polymers are employed as coagulation acids.



(Source: Faust and Aly, 1998)

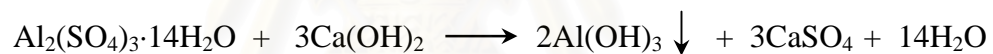
**Figure 2.6** Stoichiometric relationships between alum dosage and humic acid Concentration

### 2.5.2 Chemical reaction of alum

Generally, the water must contain sufficient alkalinity in order to react with aluminum sulfate to produce the hydroxide floc. For the pH ranges involved, the alkalinity is in the form of a bicarbonate ion. When alum is added to water that containing alkalinity, the simplified chemical reaction to produce the floc is as follows:



In the case of water that has insufficient alkalinity to react with alum, alkalinity must be added. Alkalinity in the form of a hydroxide ion is usually added by the addition of calcium hydroxide (slaked or hydrated lime). The coagulation reaction with calcium hydroxide is as follows:



Alkalinity may also be added in the form of a carbonate ion by the addition of sodium carbonate (soda ash). Most water has sufficient alkalinity, so no chemical needs to be added other than aluminum sulfate. The optimum pH range for alum is from about 4.5 to 8.0. Alum sulfate is available in dry or liquid form; however, the dry form is more common. The dry chemical may be in granular, powdered, or lump form; the granular form being the one most widely used. The granular form, which is 15 to 22 %  $\text{Al}_2\text{O}_3$  contain approximately 14 water of crystallization, a weight from 60 to 63 lb/ft<sup>3</sup> (Reynolds and Richards, 1996)

### 2.5.3 Ability of alum coagulation to remove THMs precursors

The removal of THM precursors from natural waters by chemical coagulation has been reported in a limited basis. Alum is a widely used coagulant for treatment of surface water supplies. Early studied on the coagulation of turbidity and color with alum were conducted by Black and Hannah, 1963. The research of Hall

and Packham, 1965 revealed the importance of pH on the optimum alum dosages. The optimum pH for alum coagulation of humic matter was found to be 5-6 and the primary mechanism was the formation of insoluble aluminum-humates.

TOC removal by  $\text{Al}_2(\text{SO}_4)_3$  coagulation is superior when the solution pH values is around 5.5 to 6. The TOC removal achieved within this pH range can be substantial; TOC removals of greater than 50 percent have been widely reported in the literature. Alum coagulation is also effective for DBPP removal.

Cheng et al. (1995) observed approximately a 30 percent removal of THM precursors and a 30 percent removal of HAA precursors removal with 20 mg/L  $\text{Al}_2(\text{SO}_4)_3$  at a pH of 5.5 to 6.3 in their work for the State Project on the Colorado River water in Southern California.

Oliver and Lawrence (1978) found that THM production of a Canadian river water supply was reduced by 61 percent with alum coagulation and rapid sand filtration.

Young and Singer (1979) reported that coagulation with an alum dosage of 25 mg/L reduced the THMFP of North Carolina water by 60 percent.

Chadik and Amy (1983) demonstrated that TOC and THMFP decrease as a function of the coagulation dosage. For Mississippi River water, the untreated THMFP of 313  $\mu\text{g}/\text{L}$  was reduced to 131  $\mu\text{g}/\text{L}$  by alum coagulation. The indicated coagulant dosage was 15 mg Al/L.

Hubel and Edzwald (1987) determined the optimum alum dosages for coagulation of the Grasse River water. The result showed the optimum condition that were the pH value of 5.5, the optimum dose was 30 mg/L and it removed turbidity from 50 to 67 percent, soluble UV from 82 to 83 percent, TOC at 73 percent, and TTHMFP at 69 percent.



Sakornarun (1987) demonstrated that THMs contents in treated water from Chao Phraya River as the post-chlorination were significantly less than those treated with pre-chlorination. Coagulation by alum reduced TOC by 34.30 percent and THMs by 47.86 percent in raw water.

Edzwald (1993) demonstrated that the coagulant dosages guidelines for alum; a pH of about 5.5 was used for 0.5 mg of Al per mg of DOC, and a pH value of 7 was used for 1 mg of Al per mg of DOC. From bench, pilot and full-scale studies at an alum dosage about 175 mg/L of water sample from the Grasse River (Canton, NY), 80 percent of UV, 72 percent of TTHMFP and 72 percent of DOC were removed.

Cheng et al. (1995) optimized pH and alum dosages to remove TOC and to reduce THMFP. The results showed two conditions for the purpose. The first condition was at a pH value of 5.5 and an alum dosage of 20 mg/L. The second condition was at a pH value of 6.3 and an alum dosage 40 mg/L. Those two conditions were effective to remove 20-30 percent of TOC and 30 percent of THMFP.

Vrijenhoek et al. (1998) determined the optimum removal of THM precursors from two water sources (the Colorado River water and the California State Project water). The optimum removal of THM precursors was achieved at a pH of 5.5. Particles were effectively removed at alum doses of 20-60 mg/L; further increases in the alum dosage had little effect.

Marhaba and Pipada (2000) determined the maximum removal of six DOM fractions in drinking water by coagulation with alum over a range of pH. The results indicated that the maximum TOC reduction occurred at two different dosages for HPIA, HPIB, HPIN and HPON fractions at a pH of 6 and an alum dosage of 60 mg/L. For HPOA and HPOB, their fraction maximum reduction occurred at a pH of 6 and an alum dosage of 40 mg/L.

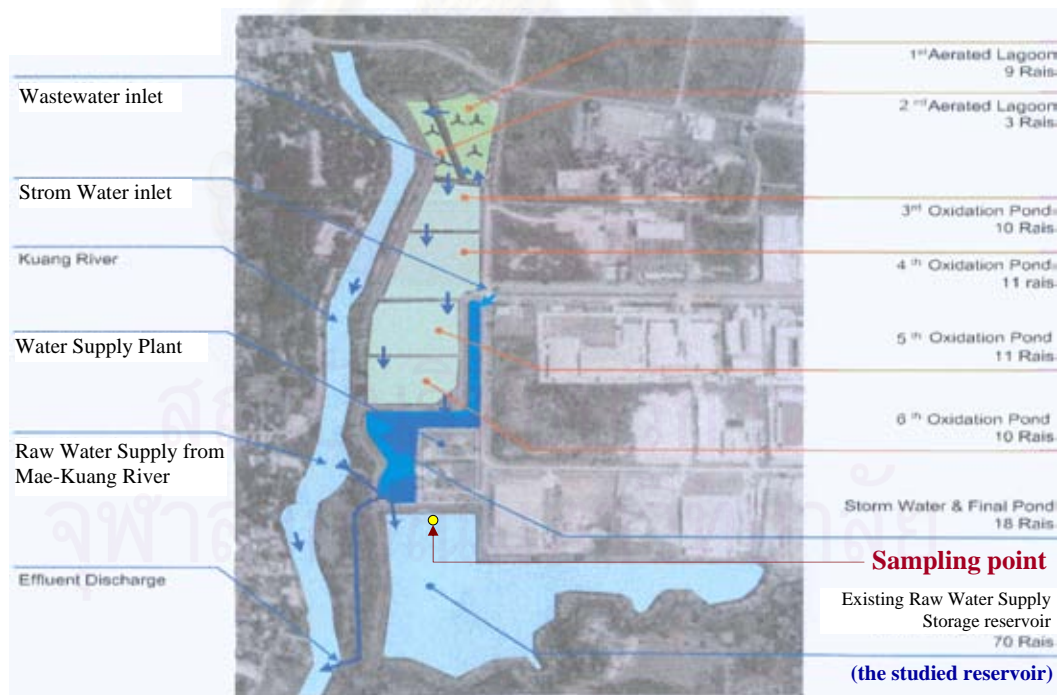


# CHAPTER III

## METHODOLOGY

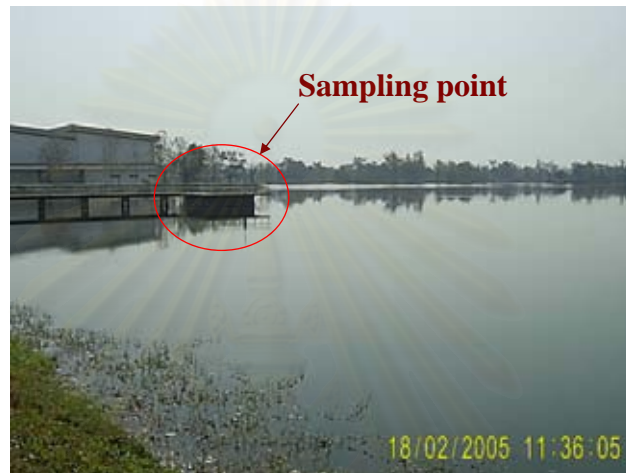
### 3.1 Studied Reservoir

Raw water supply reservoir of the Northern Region Industrial Estate, Lamphun province, Thailand was selected to be the studied reservoir for water sampling. As shown in Figure 3.1, the studied reservoir is situated in the utility areas of water and wastewater treatment. The surface area of the reservoir is more or less 70 Rais. Receiving water from the nearby Mae-Kuang River, about 600,000 cu.m is stored in the reservoir. The water from this reservoir is utilized as raw water to supply approximately 14,400 cu.m per day to the industrial estate.



**Figure 3.1** Plan of the studied reservoir located in the utility areas of water and wastewater treatment of the Northern Region Industrial Estate

Water from the studied reservoir was sampled from the sampling point at the intake of raw water supply to water supply plant as shown in Figure 3.2, in October 2004. All experiments and analytical works of this research were conducted in the laboratory of the Department of Environmental Engineering, Faculty of Engineering, Chiang Mai University.



**Figure 3.2** Water sampling point in the Northern Region Industrial Estate reservoir

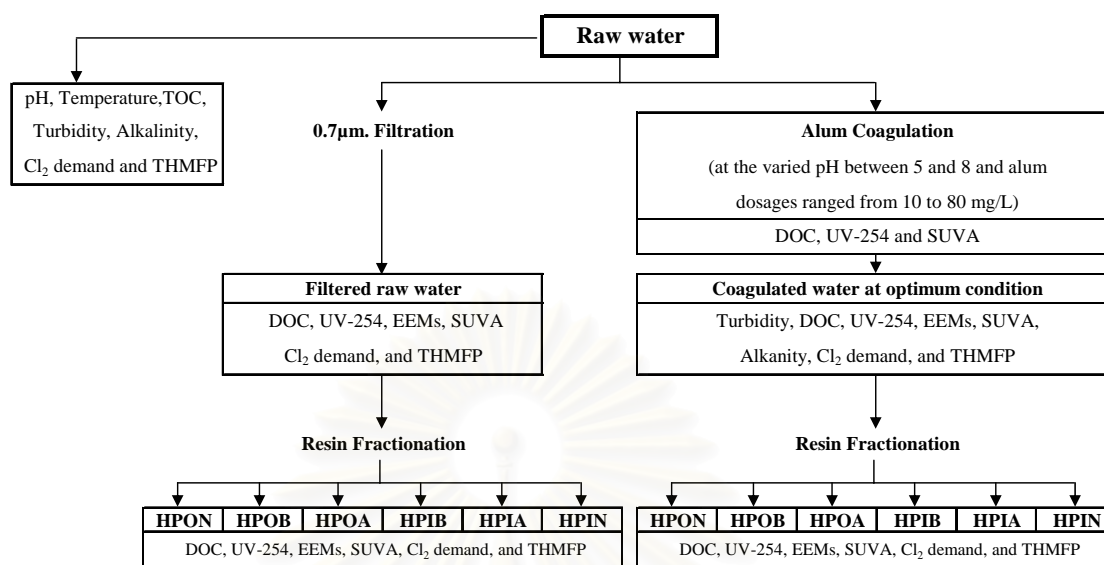
## 3.2 Procedure

### 3.2.1 Experimental Procedure

One hundred liters of grab sample from the studied reservoir of the Northern Region Industrial Estate, Lamphun province were collected and preserved with sodium thiosulfate prior to storage at 4 °C. The experimental procedure is briefly shown in the following steps and is conclusively described in the diagram in Figure 3.3.

1. pH, temperature, turbidity, alkalinity, total organic carbon (TOC), chlorine demand, and trihalomethane formation potential (THMFP) were the analyzed parameters for DOM characterization in raw water.

2. Water samples were split into 2 portions:
  - Portion 1: For raw water and its fractionated water analysis and experiment.
  - Portion 2: For coagulated water and its fractionated water analysis and experiment.
3. Water sample portion 1 was filtered through 0.7 $\mu$ m GF/F filter paper and kept in amber glass bottles with TFE-lined screw caps.
4. Characteristic parameters of unfractionated and filtered raw water were UV-254, DOC, SUVA, EEMs, chlorine demand, and THMFP.
5. The optimal condition of alum coagulation was determined for water sample portion 2, by varying the range of controlled pH from 5 to 8 and alum dosages from 10 to 80 mg/L. The experiment was conducted by using Jar-Test apparatus as briefly described below.
  - Coagulation was performed at 100 rpm for 1 minute.
  - Flocculation was carried out at 30 rpm for 30 minutes.
  - Sedimentation was allowed at a settling time of 1 hour.
  - Filtration was done by using 0.7  $\mu$ m – GF/F filter paper.
6. Analytical parameters of coagulated water at the optimal condition were turbidity, alkalinity, UV-254, DOC, SUVA, EEMs, chlorine demand, and THMFP.
7. The filtered raw water and coagulated water at optimal condition were then fractionated into 6 fractions as described in section 3.2.1.1 and were analyzed for UV-254, DOC, SUVA, EEMs, chlorine demand, and THMFP.



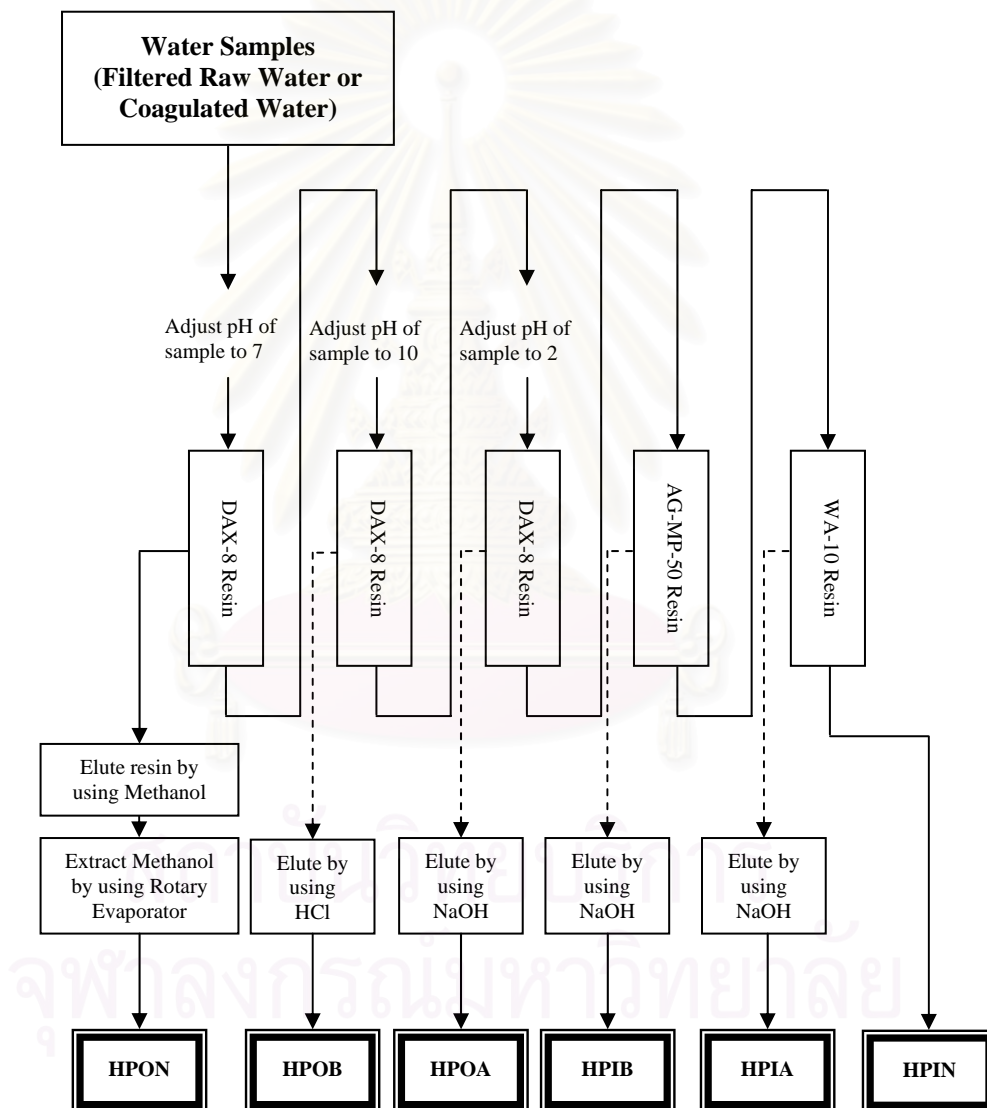
**Figure 3.3** Diagram of the experimental procedures of water samples

### 3.2.1.1 Resin Fractionation Procedure

Resin adsorption procedures were used to isolate DOM fractions into 6 fractions consisting of hydrophobic acid (HPOA), base (HPOB), neutral (HPON), and hydrophilic acid (HPIA), base (HPIB), and neutral (HPIN) by using a series of DAX-8, AG-MP-50 (Leenheer, 1981), and WA-10 (Marhaba, Pu and Bengraine, 2003) resin, respectively. The diagram of the resin fractionation procedure (Marhaba, Pu, and Bengraine, 2003) is presented in Figure 3.4 and is described as follows:

1. For each water sample the pH of which is adjusted to 7, was pumped through a DAX-8 column (2.5cm × 120cm) and then HPON is extracted from DAX -8 by CH<sub>3</sub>OH.
2. The effluent sample then has its pH altered to 10 by NaOH and was then pumped to DAX-8 resin. HPOB was eluted from DAX-8 resin with NaOH.
3. The effluent was then acidified to pH 2 with HCl and recycled to DAX-8 resin. HPOA was eluted from resin with NaOH.

4. The effluent was pumped through an AG-MP-50 resin column (2.5cm × 120cm). HPIB is eluted from resin with NaOH.
5. The effluent was then pumped through a WA 10 resin column (2.5cm × 120cm). The effluent comprises HPIN and the adsorbate was eluted with NaOH as HPIA.



**Figure 3.4** Diagram of resin fractionation procedure

### 3.2.1.2 Resin Preparations

#### 1. DAX-8

The amount of DAX-8 resin were determined according to Leenheer (1981) with a capacity factor of 50 ( $K'=50$ ) and a porosity of 0.6.

- The DAX-8 resin was intensively refined with 0.1N NaOH for 24 hours and sequentially extracted with Acetone and Hexane for another 24 hours in a set of Soxhlet extraction apparatus as shown in Figure 3.5.
- The refined DAX-8 resin was transferred into columns in a slurry of Methanol.
- The packed resin was rinsed twice with 2.5 bed volumes of 0.1 N of each NaOH (first) and then HCl, and finished with Mill-Q water until the conductivity and DOC of the effluents were lower than 10 us/cm and 0.2 mg/L, respectively.

#### 2. AG-MP-50

The amounts of AG-MP-50 resin were determined with a capacity factor of 50 ( $K'=50$ ) and a porosity of 0.3.

- The AG-MP-50 resin was extracted with Methanol for 24 hours in a set of Soxhlet extraction apparatus.

#### 3. WA-10

The amounts of AG-MP-50 resin were determined with a capacity factor of 50 ( $K'=50$ ) and a porosity of 0.5.

- The AG-MP-50 resin was soaked with Methanol for 24 hours.





**Figure 3.5** Soxhlet extraction apparatus

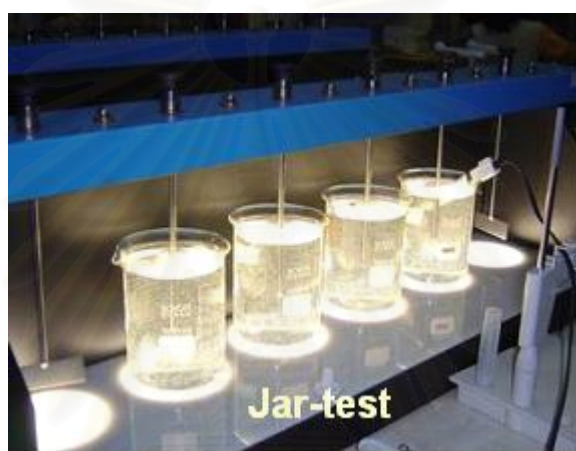
### **3.2.2 Coagulation Experiment**

Most coagulation processes in water treatment generally use alum as coagulant in order to mainly remove turbidity in water. Therefore, alum may be suitable for DOM removal and its THMFP reduction in water. The factors affecting the coagulation of water are pH and the coagulant dosages and these are normally determined from the Jar-Test experiment. In this research, the Jar-Test technique was also used to determine the proper pH value and optimal dosage of coagulant for DOM removal.

#### **3.2.2.1 Jar-Test Apparatus and Process**

The experiment utilized a multistage stirrer apparatus and simultaneous tests were conducted on a series of samples covering a range of alum concentration for each controlled pH. The water samples entered in each jar were pH adjusted to each desired pH level. They were then placed on PB-900<sup>TM</sup> Jar-Tester model 7790-902 as shown in Figure 3.6, coagulating with a rapid mix at 100 rpm for one minute, flocculating at 30 rpm for 30 minutes and settling for 1 hour. The desired alum doses were added during rapid mixing at high speeds. Concurrently, lime or caustic soda was added if necessary, to maintain pH in low alkalinity water when pH control was

desired. After a given time of Jar-Test cessation and floc formation, the supernatant samples were filtered through 0.7  $\mu\text{m}$  GF/F filter paper prior to determine their turbidity, alkalinity, DOC, UV-254, SUVA, EEMs, chlorine demand, and THMFP. The same range of alum concentration in the next desired pH levels was used in the same set of jar-tests to determine the optimal condition of coagulation. The optimal condition was then chosen as the alum dose and pH value that resulted in the greatest removal of DOC.



**Figure 3.6** Jar-Test apparatus (PB-900<sup>TM</sup> Jar-Tester model 7790-902)

### 3.2.2.2 The Jar-Test Conditions

In order to determine the optimal condition for DOM reduction, alum coagulation with a controlled variation of pH and alum dosage were performed utilizing the jar-test technique. The jar-test experiments were carried out under the conditions of different alum dosages and various controlled pH as listed in Table 3.1.

**Table 3.1** The experimental jar-test conditions

Coagulant	Coagulant dosage (mg/L)	Controlled pH
Alum (Aluminum sulfate)	10, 20, 30, 40, 60, and 80	5, 5.5, 6, 6.5, 7 and 8

### 3.2.2.3 Coagulant

Regular-grade aluminum sulfate or alum ( $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ ) typically in powder form containing approximately 97 percent of  $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$  was used for preparing the 10 g/L (10mg/mL) stock solution in the experiments.

## 3.3 Analytical Methods

Grab samples of water from Northern Region Industrial Estate reservoir were placed into amber glass bottles with TFE-lined screw caps and preserved with sodium thiosulfate prior to storage at 4 °C. The water samples were analyzed for pH, turbidity, alkalinity, TOC, UV-254, DOC, SUVA, EEMs, chlorine demand, UFC and THMFP. Table 3.3 demonstrates the summary of analytical methods and standards used for analyzing the mentioned parameters. These parameters are described below.

### 3.3.1 Alkalinity

The alkalinity of water samples were determined in accordance with standard method 2320 Alkalinity; section 2320 B, Titration Method.

### 3.3.2 pH

The pH of water samples were measured by a Horiba pH meter, Model D-13E with an accuracy of  $\pm 0.01$  pH unit.

### 3.3.3 Turbidity

Turbidity was directly measured by a HACH 2100, Turbidity Meter.

### 3.3.4 Temperature

Temperature of water samples were measured by a Thermometer.

### 3.3.5 UV 254 nm

UV 254 of water samples were measured in accordance with standard method 5910 B Ultraviolet Absorption Method. The samples were filtered through a 0.7  $\mu\text{m}$  GF/F filter paper prior to measurement by Perkin-Elmer Model Lambda 25, UV/VIS spectrophotometer.

### 3.3.6 TOC and DOC

TOC of water samples were measured in accordance with standard method 5310 Total Organic Carbon (TOC); section 5310 C Persulfate-Ultraviolet Oxidation Method by O.I. analytical 1010 TOC Analyzer.

### 3.3.7 THMs Species

The four THMs species detected during the experiment were Chloroform, Bromodichloroform, Chlorodibromoform and Bromoform. In addition to analyzing THMs, three analytical methods were used to analyze the water samples. The details are briefly described below:

#### 3.3.7.1 THMs

THMs were measured in accordance with standard method 5710, Formation of Trihalomethanes and Other Disinfection By-Products. Gas Chromatography was used (Agilent 6890 Series Gas Chromatographic with ECD detector) under the following conditions:

##### *Inlet Condition*

Mode: Split, Initial temp: 225°C., Pressure: 31.33 psi, Split ratio: 10:1 Split flow 15.9 mL/min, Gas Type: Helium and Total flow: 20.5 mL/min

### *Oven Condition*

The temperature programs of oven adjusted for analyzing THMs are shown in Table 3.2.

**Table 3.2** Temperature programs for analyzing THMs

<b>Ramp</b>	<b>Rate (°C/min)</b>	<b>Final temperature (°C)</b>	<b>Holding time of final temperature (min)</b>
1	15	180	1.00*
2	15	130	1.00
3	15	180	1.00

\* Initial temperature: 75°C, Initial temperature holding time: 1.00 min

### *Detector Condition*

Temperature: 300 °C, Mode: Constant make up flow, Makeup flow: 60 mL/min, Makeup Gas Type: Nitrogen

#### **3.3.7.2 Free Chlorine Residual**

Free chlorine residual was measured in accordance with Standard method 4500-Cl G. DPD Colorimetric Method. Due to THMFP analysis, the chlorinated water samples must have 3 mg/L to 5 mg/L free chlorine residual.

#### **3.3.7.3 Liquid-Liquid Extraction**

Water samples were extracted in accordance with standard method 6232 B Liquid-Liquid Extraction Gas Chromatography Method.

#### **3.3.8 The three-dimensional fluorescence spectroscopy (excitation-emission matrix, EEM)**

EEM is the total sum of emission spectra of a sample at different excitation wavelengths, recorded as a matrix of fluorescent intensity in coordinates of

excitation (EX) and emission (EM) wavelengths, in a definite spectral window. EEMs represent in physical signatures by JASCO FP-6200 Spectrofluorometer.

**Table 3.3** Analytical parameters, analytical methods, standards and instruments used in this study

Parameters	Analytical Method	Standard	Instruments
<b>pH</b>	Direct Measurement	-	Horibra pH-meter Model F-21
<b>Turbidity</b>	Direct Measurement	-	HACH Turbidity meter Model 2100
<b>Alkalinity</b>	Titration Method	Standard method 2320 B	-
<b>UV-254</b>	Ultraviolet Absorption Method	Standard method 5910 B	Jasco V-350 UV/VIS spectrophotometer
<b>TOC</b>	Wet - Oxidation Method	Standard method 5310 D	O.I. Analytical 1010 TOC Analyzer
<b>DOC</b>	Wet - Oxidation Method	Standard method 5310 D	O.I. Analytical 1010 TOC Analyzer
<b>EEMs</b>	-	-	JASCO FP-6200 Spectrofluorometer
<b>Free chlorine residual</b>	DPD Colorimetric Method	Standard method 4500 Cl G	-
<b>UFC&amp; THMFP</b>	Formation of Trihalomethanes and Other Disinfection By-Products and Liquid-Liquid Extraction Gas Chromatography Method	Standard method 5710 and 6232 B	Gas Chromatography with electron capture detector (GC/ECD)

Analyzing in accordance with Standard method or USEPA method;\* Filtered by 1.2 µm GFC

\*\*Filtered by 0.7 µm GF/F

The analyzed parameters were done by duplicate samples. The results of these analyses should be within  $\pm 5\%$ , or corrective action is necessary (Kebbekus and Mitra, 1998).



## CHAPTER IV

### RESULTS AND DISCUSSIONS

Each particular topic of the obtained results from the study is separately presented as follows:

#### 4.1 DOM characteristics in raw water and filtered raw water

The physical characteristics and DOM surrogate parameters of raw water were determined to gain an understanding of the physical and chemical properties as well as the quantity of DOM in such water. pH, temperature, turbidity, alkalinity, TOC, chlorine demand and THMFP of raw water were 7.84, 26.1, 8.25 NTU, 82 mg/L (as CaCO<sub>3</sub>), 5.72 mg/L, 27.04 mg/L, and 487.8 µg/L respectively. The UV-254, DOC, SUVA, chlorine demand, and THMFP of 0.7 µm filtered raw water were 0.1395 1/cm, 5.37 mg/L, 2.59 L/mg-m, 8.98 mg/L(as CaCO<sub>3</sub>), and 382.4 µg/L, respectively.

Waters with low SUVA values contain primarily non-humic matters and are not amenable to coagulation. SUVA is an alternative compliance criterion for demonstrating compliance with TOC removal requirements. If the SUVA of raw water is  $\leq 2.0$  L/mg-m, enhanced coagulation is not able to remove organic matter from the water (Edzwald and Benschoten, 1990). In this study, turbidity, TOC, DOC, alkalinity, and SUVA of the raw water were all high enough to be treated by alum coagulation.

#### 4.2 DOM characteristics in coagulated water

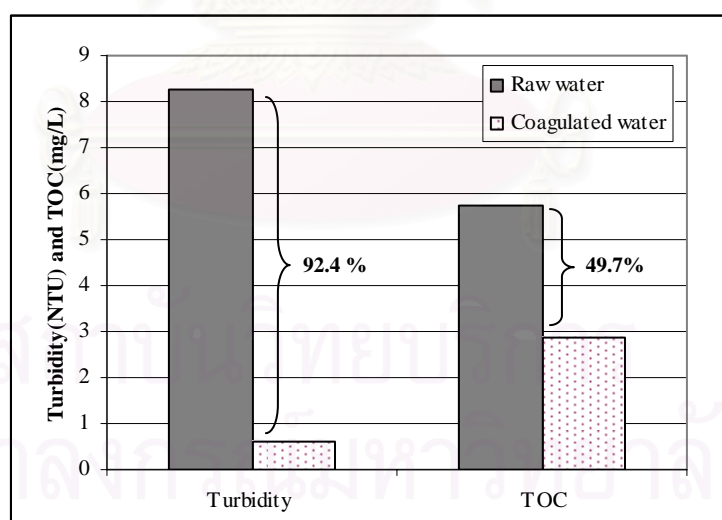
The obtained optimal condition of alum coagulation for raw water supply from the Northern Region Industrial Estate reservoir was at pH 5.5 and alum dosage at 40 mg/L using turbidity, DOC, and UV-254 as criteria that are depicted in appendix A. The physical characteristics and DOM surrogate parameters including

turbidity, alkalinity, DOC, UV-254, SUVA, chlorine demand, and THMFP were 0.63 NTU, 9 mg/L (as CaCO<sub>3</sub>), 2.88 mg/L, 0.0512 1/cm, 1.78 L/mg-m, 6.46 mg/L, and 268.6 µg/L, respectively.

The treatment efficiency of raw water by alum coagulation for the Northern Region Industrial Estate reservoir is hastily demonstrated through parameters listed in Table 4.1 and depicted in Figure 4.1

**Table 4.1** DOM characteristics in raw water and coagulated water

Parameter	Raw water	Coagulated water	% Reduction
Turbidity (NTU)	8.25	0.63	92.4
TOC (mg/L)	5.72	2.88	49.7
UV-254 (1/cm)	-	0.0512	-
SUVA (L/mg-m)	-	1.78	-
Cl <sub>2</sub> demand (mg/L)	27.04	6.46	76.1
THMFP (µg/L)	487.8	268.6	44.9



**Figure 4.1** Reduction of turbidity and TOC in raw water

According to the obtained results, the optimal condition for alum coagulation for the Northern Region Industrial Estate reservoir was achieved at a pH value of 5.5 and an alum dosage of 40 mg/L. This condition was in the pH range of 5-

6 and an alum dosage range of 20-60 mg/L. TOC and THMFP removal were more than 30 percent. This corresponds well to supporting literatures. Cheng et al. (1995) and Vrijenhoek et al. (1998) reported that the optimal removal of THM precursors was achieved at a pH of 5.5. Particles were effectively removed at alum doses of 20-60 mg/L.

### **4.3 Fractionated filtered raw water and coagulated water**

#### **4.3.1 Characteristics of DOM fractions in filtered raw water**

The DOC, UV-254, SUVA, chlorine demand, and THMFP values of DOM fractions in filtered raw water are reported in Table 4.2. The DOC mass distribution of DOM fractions in filtered raw water is depicted in Figure 4.2. It was observed that hydrophobic and hydrophilic organics accounted for 57.1% and 43.9% of total DOC, respectively. In terms of the distribution of organic fractions, the HPOA fraction was found to be the major DOM fraction in this water as it accounted for 41.6% of total DOC. The other organic fractions, ordered according to their quantity present in the water, were as follows: HPIA (20.5%), HPIN (17.7%), HPON (12.1 %), HPIB (4.8%), and HPOB (3.4%) as shown in Figure 4.4.

#### **4.3.2 Characteristics of DOM fractions in coagulated water**

The surrogate parameters including DOC, UV-254, SUVA, chlorine demand, and THMFP of DOM fractions in coagulated water are conclusively reported in Table 4.3. The DOC mass distribution of DOM fractions in coagulated water is illustrated in Figure 4.3. It was found that hydrophobic and hydrophilic organics accounted for 62% and 38% of total DOC. In terms of the distribution of organic fractions as shown in Figure 4.5, the HPOA fraction was found to be the major DOM fraction in this water as it accounted for 45.3% of total DOC. The other organic fractions, ordered according to their quantity present in the water, were HPIA: 20.3 %, HPON: 10.7 %, HPIN: 9.4%, HPIB: 8.4%, and HPOB: 6%, respectively.

**Table 4.2** Characteristics of DOM fractions in filtered raw water

Parameter	Fractionated water						HPO + HPI	Unfractionated water (Filtered raw water)	%Diff*
	Hydrophobic fraction (HPO)			Hydrophilic fraction (HPI)					
	HPON	HPOB	HPOA	HPIB	HPIA	HPIN			
DOC(mg)	3.64	1.02	12.54	1.43	6.20	5.32	30.16	27.5	9.7
%DOC mass	12.1	3.4	41.6	4.8	20.5	17.7	100.00	-	-
DOC(mg/L)	0.71	0.20	2.45	0.28	1.21	1.04	5.89	5.37	9.7
UV-254(1/cm)	0.0066	0.0030	0.0478	0.0062	0.0084	0.0029	-	0.1395	-
SUVA(L/mg-m)	0.93	1.50	1.95	2.21	0.69	0.28	-	-	-
Cl <sub>2</sub> demand (mg/L)	0.33	0.11	2.57	0.59	4.98	0.28	8.86	8.98	1.3
THMFP (µg/L)	68.00	41.40	247.10	67.90	112.60	64.90	601.90	382.4	57.4
% THMFP	11.3	6.9	41.1	11.3	18.7	10.8	100.0	-	-

Note: HPO = HPON+HPOB+HPOA

HPI = HPIB+HPIA+HPIN

%Diff\* = (Unfractionated water - fractionated water) / Unfractionated water × 100

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**Table 4.3** Characteristics of DOM fractions in coagulated water

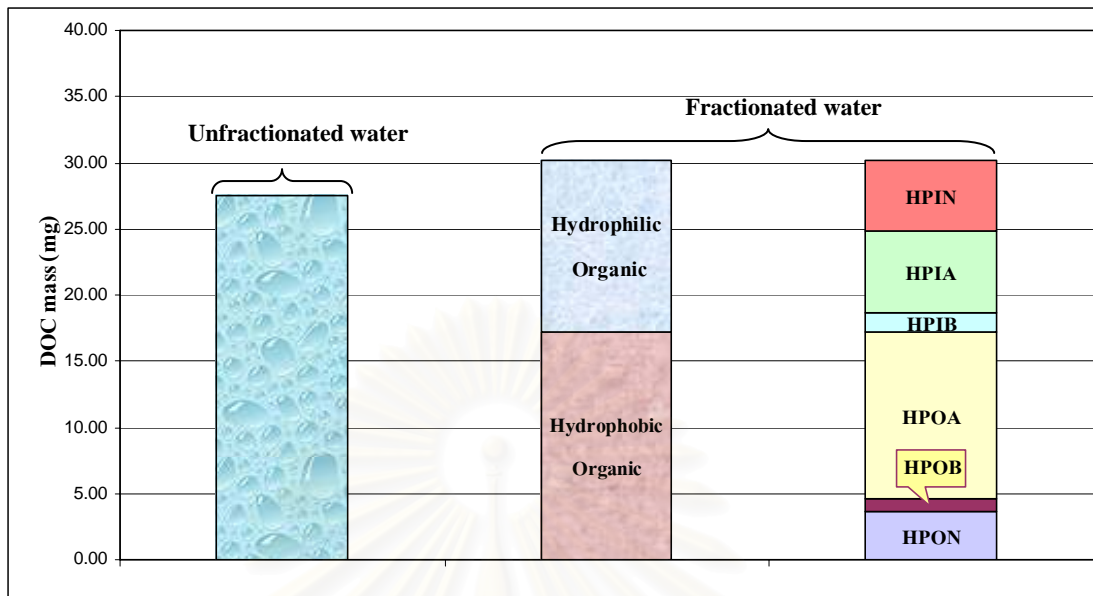
Parameter	Fractionated water						HPO + HPI	Unfractionated water	% Diff*
	Hydrophobic fraction (HPO)			Hydrophilic fraction (HPI)				(Coagulated water)	
	HPON	HPOB	HPOA	HPIB	HPIA	HPIN			
DOC (mg)	1.62	0.91	6.87	1.27	3.08	1.42	15.17	14.6	3.78
%DOC mass	10.7	6.0	45.3	8.4	20.3	9.4	100.00	-	-
DOC (mg/L)	0.32	0.18	1.36	0.25	0.61	0.28	2.99	2.884	3.78
UV-254 (1/cm)	0.0047	0.0019	0.0187	0.0052	0.0072	0.0016	-	0.0512	-
SUVA (L/mg-m)	1.47	1.06	1.38	2.08	1.18	0.57	-	1.78	-
Cl <sub>2</sub> demand (mg/L)	0.28	0.09	1.18	0.39	2.21	0.25	4.40	6.46	28.6
THMFP (µg/L)	31.5	35.1	106.0	40.3	79.1	38.0	330.0	268.6	22.9
% THMFP	9.5	10.6	32.1	12.2	24.0	11.5	100.0	-	-

Note: HPO = HPON+HPOB+HPOA

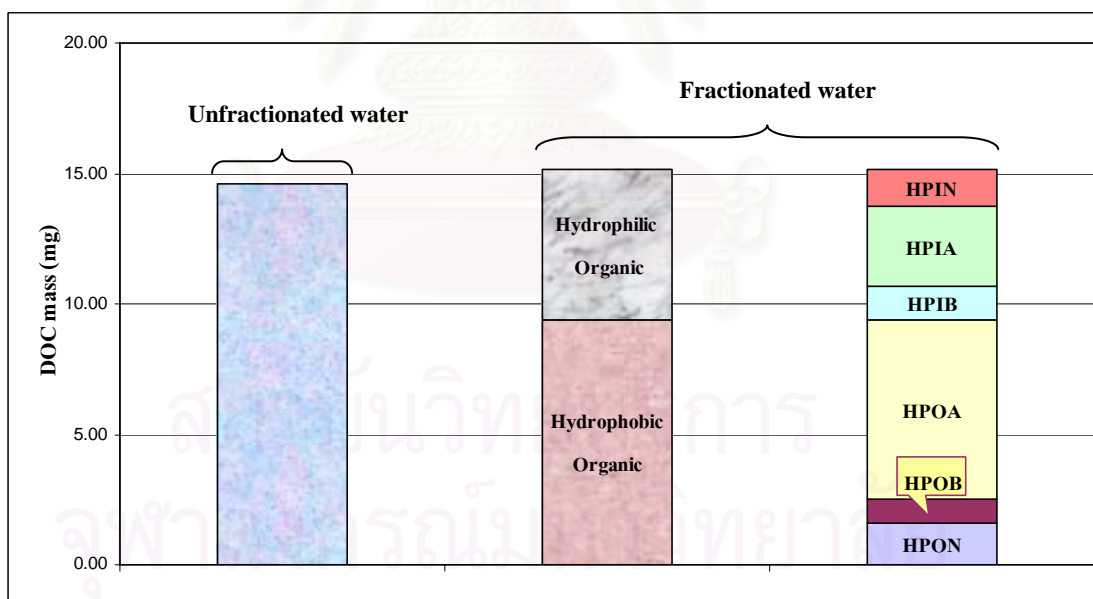
HPI = HPIB+HPIA+HPIN

%Diff\* = (Unfractionated water - fractionated water) / Unfractionated water × 100

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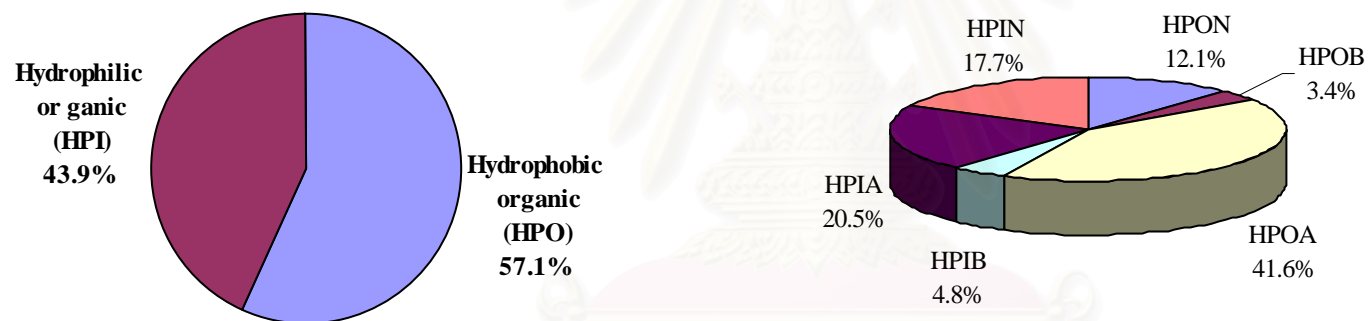


**Figure 4.2** DOC mass distribution of DOM fractions in filtered raw water



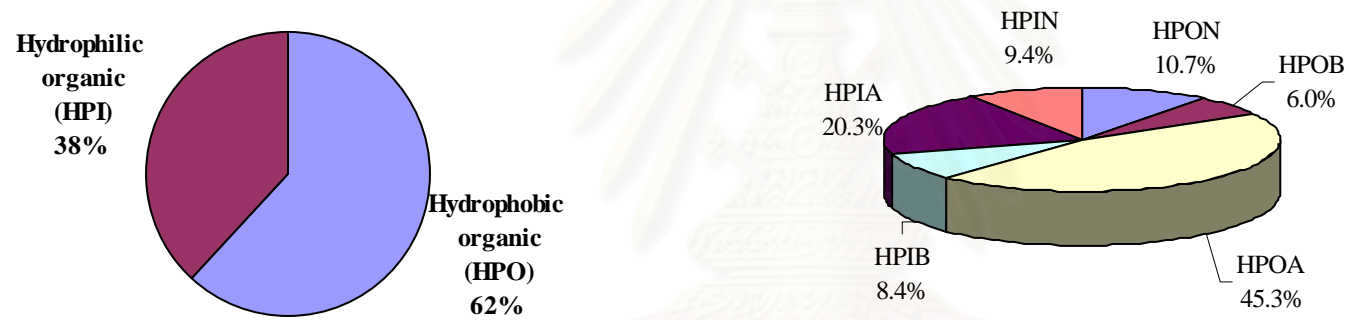
**Figure 4.3** DOC mass distribution of DOM fractions in coagulated water





**Figure 4.4** Percent distribution of each DOM fraction in filtered raw water

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**Figure 4.5** Percent distribution of each organic fraction in coagulated water

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According to the obtained results, the total weight of DOC mass distribution among six fractions in both filtered raw water and coagulated water as shown in Table 4.2 and 4.3 was more than the initial weight of DOC mass before fractionation and was about 9.7% for filtered raw water and 3.8% for coagulated water. These relevantly corresponded to the reported results by Leenheer (1981) that the total weight surplus may have come from resin bleeding during the elution process. Day et al., 1991 and Marhaba and Pipada, 2000 demonstrated that 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. Moreover, Croue et al., 1993 also reported the variation from 8-12%.

As reported by Musikavong (2004), the major DOM fractions in treated Northern Region Industrial Estate wastewater, were HPOA, and HPIA and were similar to the major DOM fractions in filtered raw water from this reservoir. Whilst the results of DOM reduction after treating with alum coagulation showed that the major organic fractions remaining in coagulated water were also the HPOA (45.3% of total DOC) and HPIA (20.3% of total DOC) fractions.

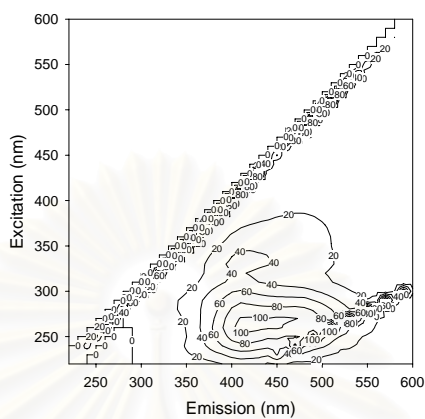
Leenheer and Croué (2003) explained that DOM is a complex mixture of aromatic and aliphatic hydrocarbon structures that have attached amide, carboxyl, hydroxyl, ketone, and various minor functional groups. Heterogeneous molecular aggregates in natural waters increase DOM complexity. The relationships between organic compounds and the DOM fractions are as follows: a hydrophobic neutral fraction (HPON) is hydrocarbons/tannins; a hydrophobic base fraction (HPOB) is aromatic amines; a hydrophobic acid fraction (HPOA) is fulvic acid; a hydrophilic base fraction (HPIB) is peptides/ amino; a hydrophilic acid fraction (HPIA) is polyuronic acids; and a hydrophilic neutral fraction (HPIN) is sugars. According to the results obtained in this study, HPOA and HPIA fractions were the major DOM fractions in filtered raw water and coagulated water. Consequently, it can be implied that most organic compounds contained in filter water and coagulated water from the Northern Region Industrial Estate reservoir might consist of fulvic acid and polyuronic acids.

### 4.3.3 EEM signatures of DOMs

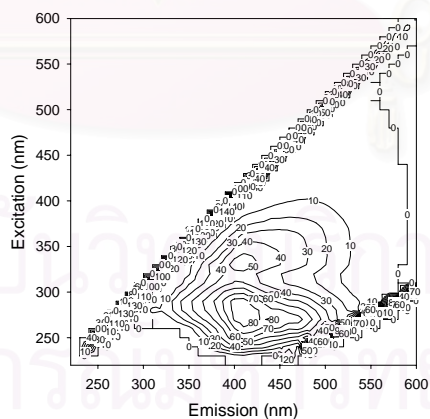
Three-dimensional fluorescence spectroscopy (Excitation - emission matrixes: EEMs) provides the total summary of the emission spectra of a sample at different excitation wavelengths, recorded as a matrix of fluorescent intensities in coordinates of excitation (EX) and emission (EM) wavelengths. Recently, EEM was successfully employed to establish the fingerprint of organic compounds in water (Marhaba, Pu, and Bengraine, 2003; Nakajima, Hanabusa, and Furumai, 2002). The filtered raw water, coagulated water and their fractionated waters were adjusted to neutral pH (~7) before analyzing with a spectrofluorometer.

In order to characterize DOM in all waters, the EEMs of all waters and their fractions were established. The peak position on the EEM was the highest fluorescent intensity of each DOM signature that was exhibited in each position and also reported in coordinates of “nm in excitation (ex) and nm emission (em)”. The EEMs of filtered raw water, coagulated water and their DOM fractions are presented in Figures 4.6, 4.7, 4.8 and 4.9, respectively.

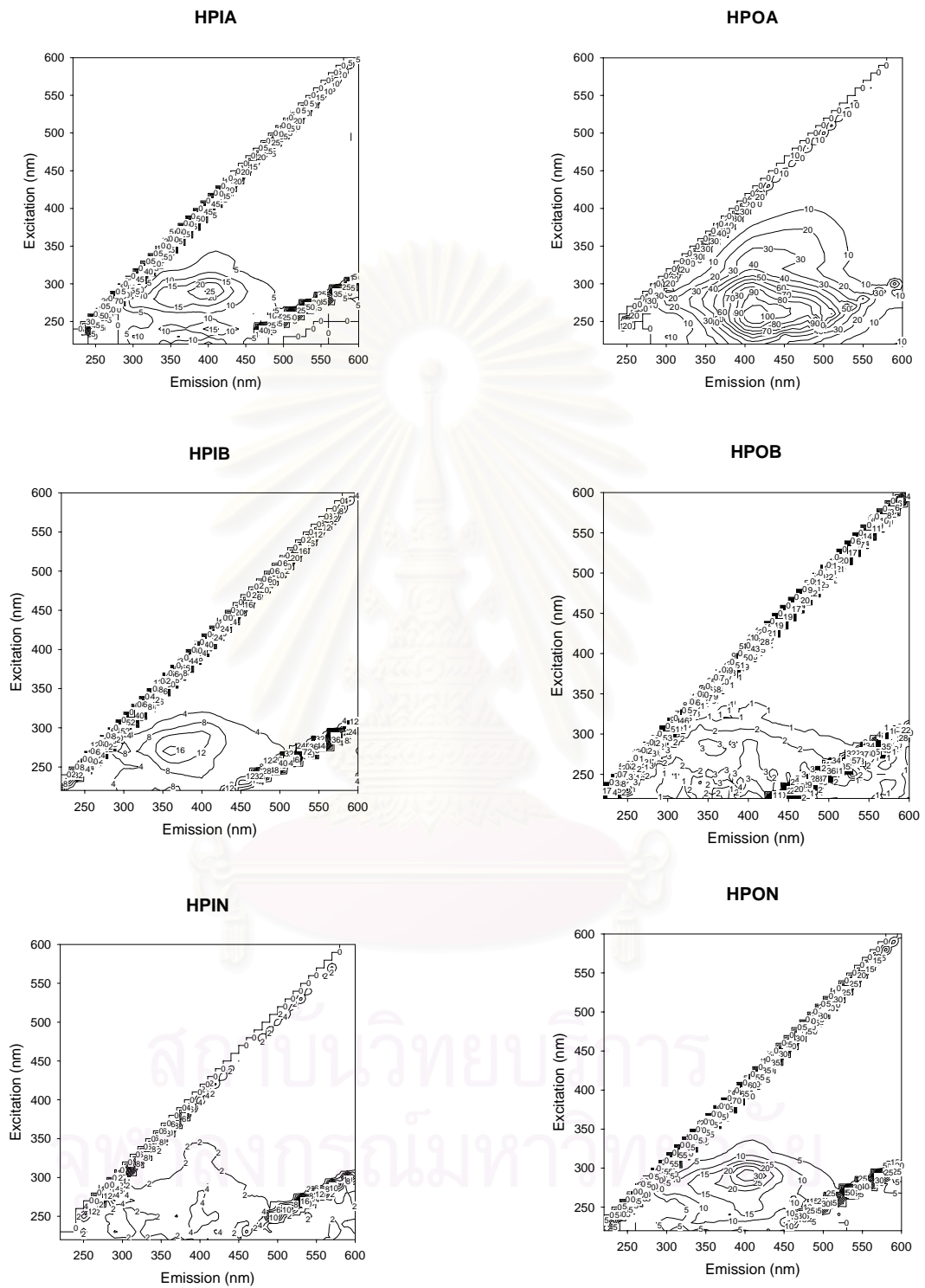
Figure 4.6 illustrates the EEM of the filtered raw water that established two peaks within a broad range EEM at 220-450/290-730 nm (excitation/emission). A strong peak appeared at 260/420 nm and a weak one at 330 nm/410 nm. According to the data from Figure 4.8, the HPOA fraction (41.6% of total DOC) established a broad peak at 220-390 nm/230-620 nm with a strong peak at 250-260nm/410 nm; whereas the HPIA fraction (20.5% of total DOC) exhibited two weak peaks at around 295 nm/410 nm and 330nm/410 nm. The HPIN fraction (17.7% of total DOC) had a rather weak broad peak at 230-300nm/340-520nm. The HPON fraction (12.1% of total DOC) had a very weak small peak at around 280-300nm/400-430nm. There were rather weak broad peak observed from the HPIB (4.8% of total DOC) and HPOB (3.4% of total DOC) fractions at 250-300nm/330-420nm and 220-320 nm/280-490nm, respectively.



**Figure 4.6** EEM signature of filtered raw water from Northern Region Industrial Estate reservoir presented with a contour interval of 2 QSU

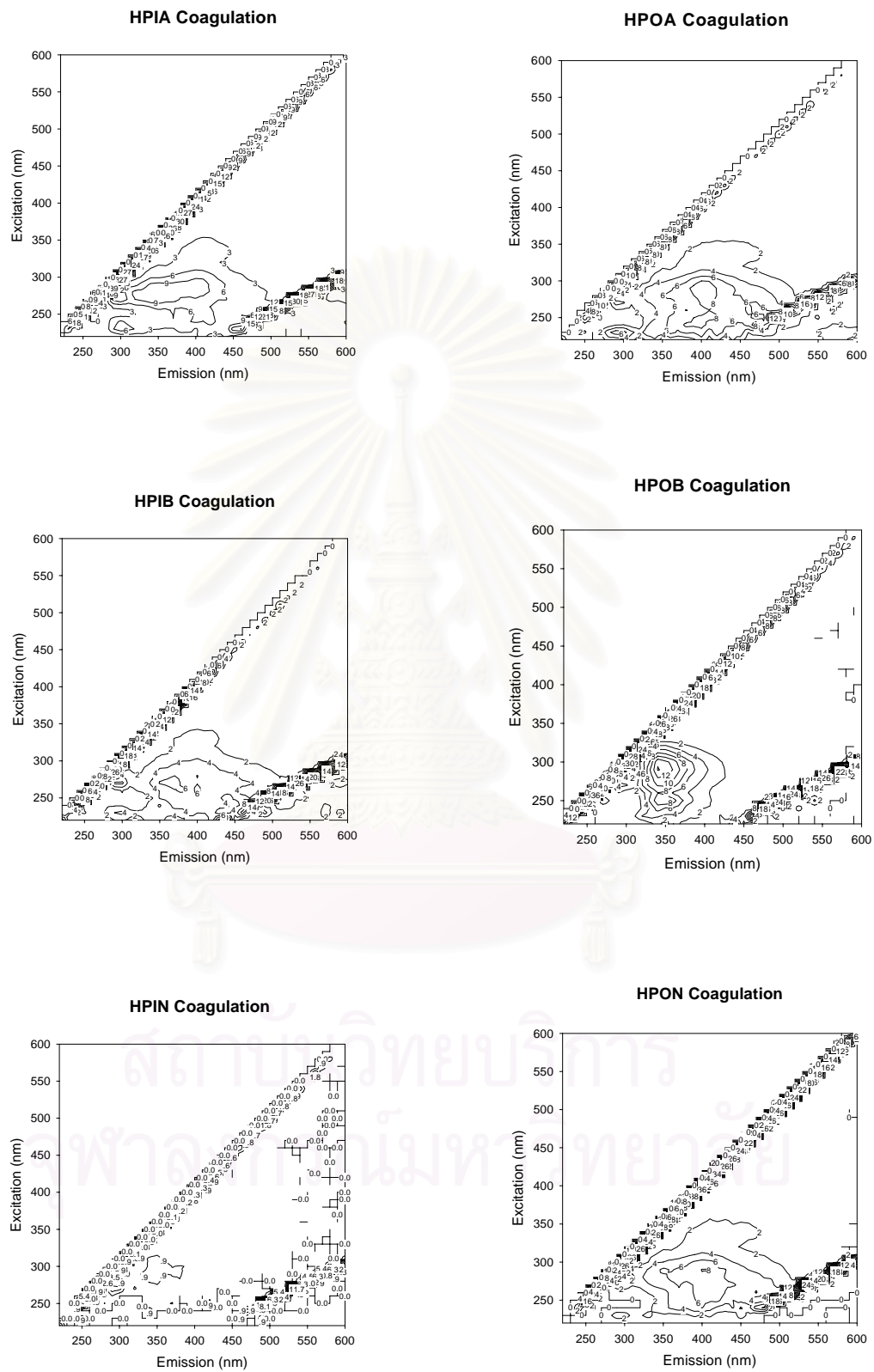


**Figure 4.7** EEM signature of coagulated water from Northern Region Industrial Estate reservoir presented with a contour interval of 2 QSU



**Figure 4.8** EEM signatures of each DOM fraction in filtered raw water presented with contour intervals of 2 QSU



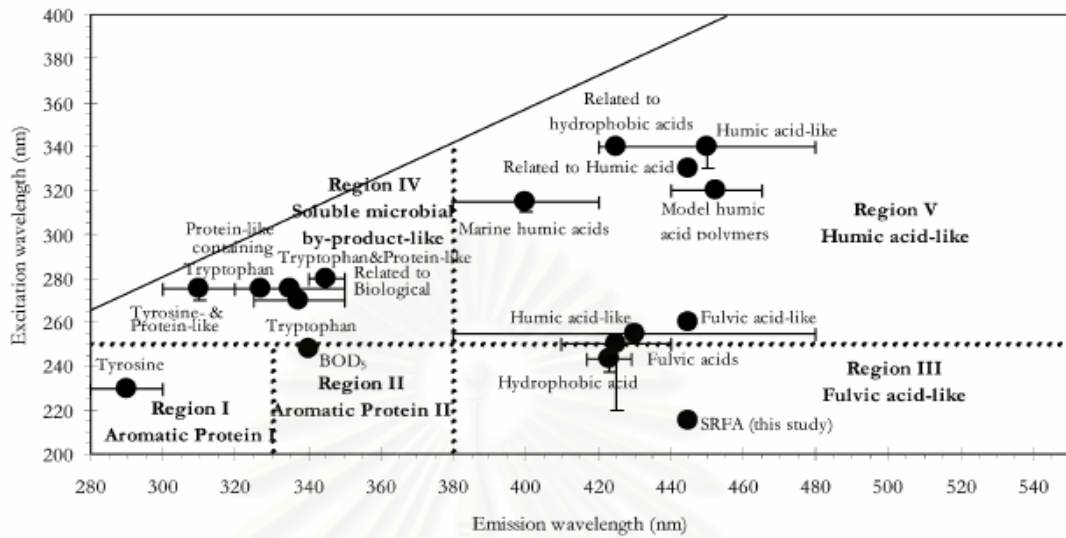


**Figure 4.9** EEM signatures of each DOM fraction in coagulated water presented with contour intervals of 2 QSU

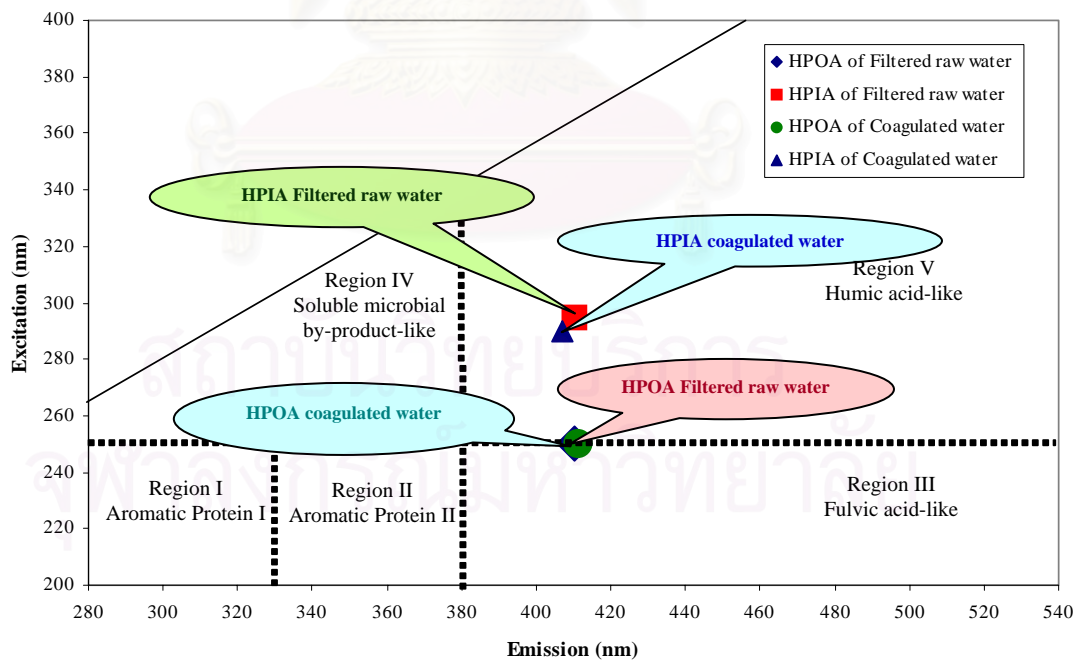
After alum coagulation, coagulated water exhibited weak broad peak at 200-400nm/290-523 nm with a peak at 270nm/415nm as shown in Figure 4.7. HPOA fraction (45.3% of total DOC) established broad peaks at 220-320 nm/330-500 nm with a peak at 250nm/411 nm; whereas the HPIA fraction (20.3% of total DOC) exhibited a weak peak at around 290 nm/407 nm. The HPON fraction (10.7% of total DOC) had a weak broad peak at 230-300nm/400-430nm. The HPIN fraction (9.4% of total DOC) had a rather weak broad peak at 230-300nm/350-430nm. There were two very weak small peaks observed from the HPIB fraction (8.4% of total DOC) at 250-270nm/350-380 and 390-400nm. The HPOB (6% of total DOC) fraction established a very weak peak at 280-300nm/350nm.

Using consistent excitation and emission wavelength boundaries for each EEM, Chen et al. (2003) operationally defined excitation and emission boundaries into five regions based largely upon supporting literature. EEM peaks have been associated with humic-like, tyrosine-like, tryptophan-like, or phenol-like organic compounds. In general, peaks at shorter excitation wavelengths (<250 nm) and shorter emission wavelengths (<350 nm) are related to simple aromatic proteins such as tyrosine (Regions I and II). Peaks at intermediate excitation wavelengths (250-  $\phi$  280 nm) and shorter emission wavelengths (<380 nm) are related to soluble microbial by-product-like material (Region IV). Peaks at longer excitation wavelengths (>280 nm) and longer emission wavelengths (>380 nm) are related to humic acid-like organics (Region V). For fulvic acids, EEMs with minimum excitation wavelengths of 250 nm indicate shoulders of EEM peaks located at shorter excitation wavelengths. Therefore, peaks at shorter excitation wavelengths (<250 nm) and longer emission wavelengths (>350 nm) are related to fulvic acid-like materials (Region III). All these five regions are separately demonstrated in Figure 4.10.

These demonstrate the relationships between EEM peak position and organic compounds and might be utilized to explain the characteristics of organic compounds in the studied waters. An aim of this study was to characterize DOM fractions in waters by utilizing the EEM technique. EEM peaks of the major DOM fractions were compared with the location of EEM peaks based on literature reports by Chen et al, 2003.



**Figure 4.10** Location of EEM peaks and excitation and emission wavelength boundaries for five EEM regions based on literature reports by Chen et al., 2003



**Figure 4.11** EEM peak locations of HPOA and HPIA fractions of filtered raw water and coagulated water obtained in this study

This might explain the organic compounds of DOM contained in waters. According to observed EEM signature results of all fractionated water, HPOA and HPIA in both filtered raw water and coagulated water that were the major DOM fractions are located in regions II and III following separate regions from Chen et al. (2003) as depicted in Figure 4.11. Consequently, it can be implied that most organic compounds contained in water from the Northern Region Industrial Estate reservoir may consist of fulvic acids-like and humic acids-like substances. Interestingly, only the DOM fractions with high DOC responded well to fluorescent excitation which implies that they could be easily characterized using EEM. Moreover, peak positions on the EEM of the major DOM fractions were similar to the peak positions on the EEM of the filtered raw water and coagulated water.

#### **4.3.4 DOM surrogate reduction**

Normally, DOM is characterized by nonspecific parameters or surrogate parameters. The surrogate parameters must be used to describe DOM because no single analytical technique is capable of measuring the widely varied characteristics of DOM. Commonly used DOM surrogates include TOC, DOC, UV-254, SUVA, and THMFP (USEPA, 1999). DOM surrogates in the Northern Region Industrial Estate reservoir water that were reduced by alum coagulation are demonstrated in Table 4.4. Figure 4.12 and Figure 4.13 demonstrate DOC and THMFP reduction of filtered raw water in comparison with coagulated water.

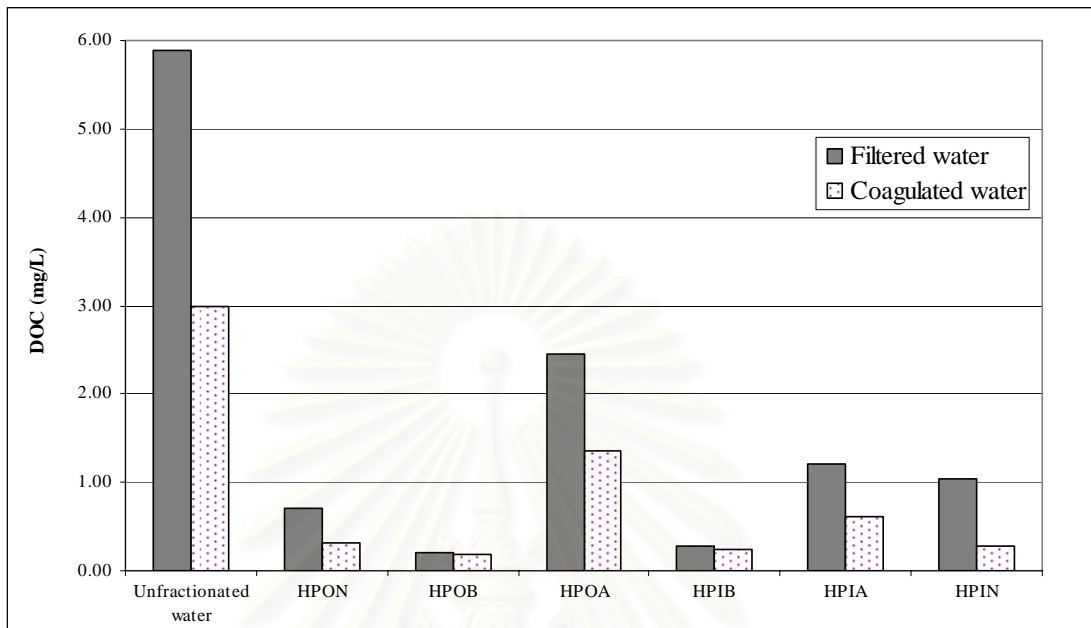
According to the obtained results, the most effective treatment that was more than a 50% reduction for DOC was the HPIN (73.2%) and HPON (55%) fractions for the Northern Region Industrial Estate reservoir water. However, 44.6% and 49.6% of the major DOM fractions like HPOA and HPIA were removed. The HPOA fraction (60.9%) most effectively removed UV-254. HPOA and HPIA fractions reduced chlorine demand by 54.1% and 55.6%, respectively. After treating, chlorine demand for each fraction of coagulated water varied on the residual DOC concentration. The HPOA and HPIA fractions made up the bulk of the organics in coagulated water (~ 65%) as reported in Table 4.3. SUVA values of each DOM

**Table 4.4** Characteristics of each DOM fraction in filtered raw water and coagulated water

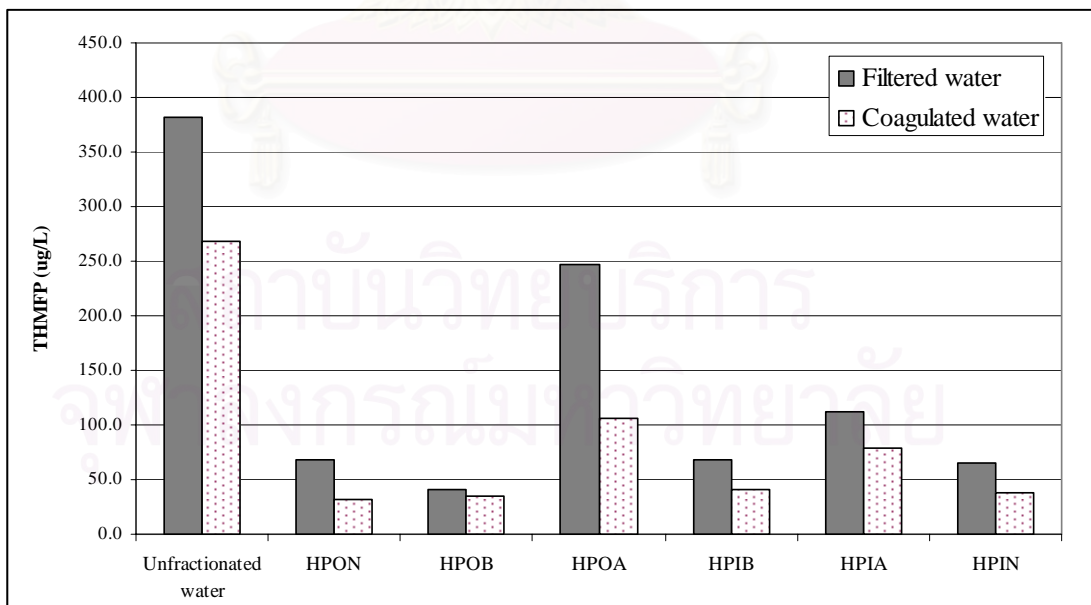
Fraction	DOC (mg/L)		% Reduction	THMFP ( $\mu\text{g/L}$ )		% Reduction	SUVA (L/mg-m)		% Reduction
	Filtered raw water	Coagulated water		Filtered raw water	Coagulated water		Filtered raw water	Coagulated water	
HPON	0.71	0.32	55.0	68.0	31.5	53.7	0.93	1.47	-
HPOB	0.20	0.18	10.2	41.4	35.1	15.2	1.50	1.06	29.6
HPOA	2.45	1.36	44.6	247.1	106.0	57.1	1.95	1.38	29.4
HPIB	0.28	0.25	10.7	67.9	40.3	40.6	2.21	2.08	6.1
HPIA	1.21	0.61	49.6	112.6	79.1	29.8	0.70	1.18	-
HPIN	1.04	0.28	73.2	64.9	38.0	41.4	0.28	0.68	-

Fraction	UV-254 (1/cm)		% Reduction	Cl <sub>2</sub> demand (mg/L)		% Reduction
	Filtered raw water	Coagulated water		Filtered raw water	Coagulated water	
HPON	0.0066	0.0047	28.8	0.33	0.28	15.2
HPOB	0.0030	0.0019	36.7	0.11	0.09	18.2
HPOA	0.0478	0.0187	60.9	2.57	1.18	54.1
HPIB	0.0062	0.0052	16.1	0.59	0.39	33.9
HPIA	0.0084	0.0072	14.3	4.98	2.21	55.6
HPIN	0.0029	0.0019	34.5	0.28	0.25	10.7



**Figure 4.12** DOC reduction by alum coagulation

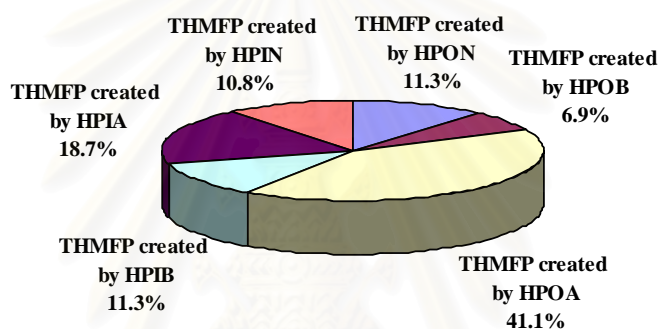


**Figure 4.13** THMFP reduction by alum coagulation

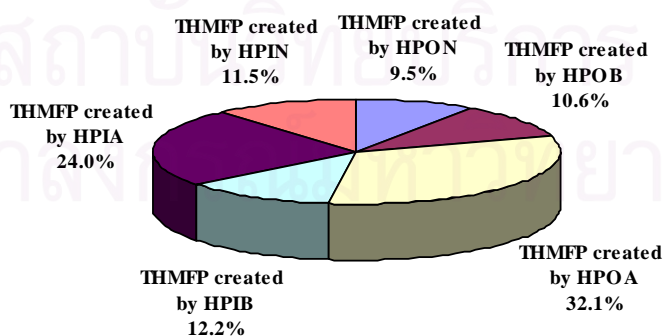


fraction apart from the HPOA and HPOB fractions were unable to be reduced by coagulation. However, these were reduced ineffectively according to their low level of SUVA values. This was related to the report by Edzwald and Benschoten (1990) that found that if the SUVA of water is  $\leq 2.0$  L/mg-m, enhanced coagulation is not able to remove organic matter from the water.

THMFP distribution of each DOM fraction in filtered raw water and coagulated raw water are illustrated in Figure 4.14 and Figure 4.15.



**Figure 4.14** THMFP distribution created by each DOM fraction in filtered raw water



**Figure 4.15** THMFP distribution created by each DOM fraction in coagulated water

THMFP created from DOMs in filtered raw water was 382.4  $\mu\text{g/L}$ . The first two main THMFP precursors found in filtered raw water were the two major DOM fractions and were HPOA (41.1%) and HPIA (18.7%) according to their large quantity present in water. These results are similar to reported results from Marhaba and Van (1999) that illustrate that HPOA could create THMs at around 8-68% in raw water and HPIA at around 8-53%. HPIB, HPON, and HPIN created THMs in the same level at around 10-12%. Whereas it was found that the HPOB fraction could create the least amount of THMs.

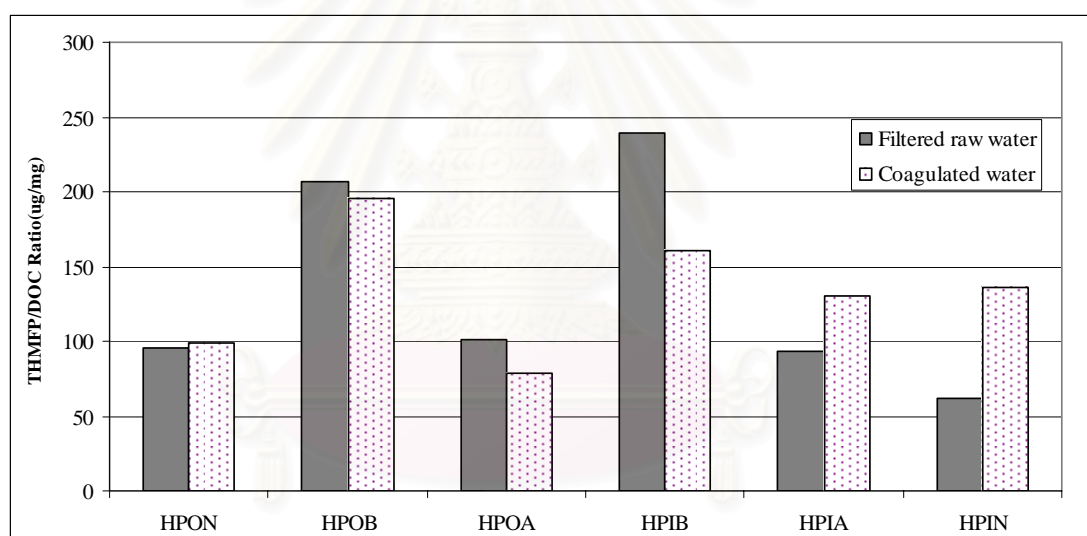
THMFP created from DOMs in coagulated water was 268.6  $\mu\text{g/L}$ . THMFP of each fraction after coagulating was reduced by about 30% overall when compared with filtered raw water. The two main THMFP precursors found in coagulated water were still the two major DOM fractions of HPOA (32.1%) and HPIA (24%). While the HPIB, HPON, HPIN, and HPOB fractions created the same level of THMs at around 9-12%.

THMFP reduction of Northern Region Industrial Estate reservoir water by alum coagulation was effectively done for the main fraction, HPOA, by 57.1%. Otherwise, the HPON fraction was also effectively reduced by 53.7%. Whereas, HPIA was removed by just 29.8% despite that it was also a major DOM fraction. HPIN and HPIB were reduced by 41.4% and 40.6%, respectively. HPOB was the least efficient in reducing THMFP.

Determination of the THMFP active precursor can be derived by comparing the ratio between THMFP and DOC. This can be utilized to explain THMFP created per mg DOC for each DOM fraction. Moreover, it also facilitates the reactivity analysis of each DOM fraction in THMFP. Table 4.5 demonstrates the ratio of THMFP and DOC for each DOM fraction in both filtered raw water and coagulated water. These ratios are conclusively depicted in Figure 4.16.

**Table 4.5** Ratio of THMFP and DOC for each DOM fraction in filtered raw water and coagulated water

DOM fraction	Filtered raw water		Coagulated water		THMFP/DOC ( $\mu\text{g}/\text{mg}$ )	
	DOC (mg/L)	THMFP ( $\mu\text{g}/\text{L}$ )	DOC (mg/L)	THMFP ( $\mu\text{g}/\text{L}$ )	Filtered raw water	Coagulated water
HPON	0.71	68	0.32	31.5	95.6	98.4
HPOB	0.20	41.4	0.18	35.1	206.4	195.0
HPOA	2.45	247.1	1.36	106.0	101.0	78.2
HPIB	0.28	67.9	0.25	40.3	239.7	161.2
HPIA	1.21	112.6	0.61	79.1	93.3	130.1
HPIN	1.04	64.9	0.28	38.0	62.1	135.7



**Figure 4.16** THMFP / DOC Ratio of each DOM fraction in filtered raw water and coagulated water

According to the reported results, in filtered raw water the HPIB and HPOB fractions were the two most reactive precursors that could create THMs. The results show that HPIB created the highest THMFP/DOC ratio at 239.7  $\mu\text{g}$  THMFP/mg DOC followed by HPOB at 206.4  $\mu\text{g}$  THMFP/mg DOC. In coagulated water, HPOB had the highest THMFP/DOC ratio at 195  $\mu\text{g}$  THMFP/mg DOC and was followed by HPIB at 161.2  $\mu\text{g}$  THMFP/mg DOC. This is related to the reported

result from Marhaba and Van (1999) which indicate that the HPOB fraction was the most highly active in creating THMs. Interestingly, HPIB and HPOB although present in a tiny quantity of DOC, were highly active in reacting with chlorine to form THMs. However, the HPOB fraction could not effectively reduce THMFP by alum coagulation as reported in Table 4.4. The results show that the efficiency of THMFP reduction for the HPOB fraction was 15.2%. This also relates to reported result from Marhaba and Van (1999) that demonstrate that the HPOB fraction could not be effectively removed by coagulation. In addition, the HPIB fraction was similar to the HPOB fraction in that it too was not an effective means of removing THMFP by coagulation. It is therefore important that these two fractions were the major concern for water treatment because even when present in a tiny quantity, they could create large quantities of THMs. Nevertheless, their low THMFP in this study suggested that these fractions did not exist in the large quantity around 3-8 % (of total DOC) in both filtered raw water and coagulated water.

The HPIA and HPIN fractions were the two fractions that were least active in creating THMs in filtered raw water, but their THMFP were at moderately high levels. It can be said that these two fractions were the major THMFP precursors because of their large existing quantity in filtered raw water (20% for HPIA and 17.7 for HPIN% from total DOC). After treating in coagulated water HPIA and HPIN were moderately active to form THMs due to their DOC reduction. However, they could be problematic THMs precursors because of their existing quantity that was difficult to treat by coagulation as reported by Marhaba and Van (1999).

The HPON fraction was the least active in creating THMs, both before and after treating by coagulation. In particular, THMFP created from this fraction was at the lowest level after coagulation as shown in Figure 4.16. Hence, this was not considered to be a problematic fraction to the formation of THMs.

Interestingly, the HPOA fraction was in the least of three inactive fractions to form THMs in filtered raw water and the lowest in coagulated water to create THMs in spite of the fact that it was the main major THMFP precursor in both

filtered raw water and coagulated water. However, it could be considered to be a THMs precursor because its quantity largely exists in water that had the most organics (more than 40% of total DOC among the six fractions).

#### 4.3.5 THM species

The term, “Total Trihalomethanes” (TTHM) describes four disinfection by-product species, chloroform, bromodichloromethane, dibromochloromethane, and bromoform that may be found in a water sample. Reduction of THM species in each DOM fraction for filtered raw water and coagulated water obtained from this study were also investigated and are conclusively illustrated in Table 4.6.

The THM usually present in the highest concentration is chloroform, followed by dibromochloromethane ([www.greenfacts.org/glossary/def/chloroform](http://www.greenfacts.org/glossary/def/chloroform)). This is exactly related to the obtained results showing that chloroform was the highest species for total THMFP of each DOM fraction for both filtered raw water and coagulated water. Moreover, dibromochloroform was the second highest species. As illustrated in Table 4.6, chloroform species for all DOM fractions in both filtered raw water and coagulated water were present in a greatest level and were more than 80% of total THMFP. Most chloroform was found to have come from the chlorination of the HPOA fraction for filtered raw water (approximately 44%) and for coagulated water (approximately 34%). Chloroform created by the HPIA fraction was responsible for further 18% for filtered raw water and 23% for coagulated water. Most dibromochloroform was created by the HPIA fraction for both filtered raw water and coagulated water, at around 28% for filtered raw water and 27% for coagulated water. The HPOA fraction was the most effective for THMFP reduction among the six fractions (approximately 57%) followed by the HPON fraction (53.7%). Interestingly, THMFP of the HPIA fraction was reduced by just 29.7% in spite of high levels of chloroform also created. According to the reported results, it can be implied that THMFP reduction was a relative result of chloroform reduction.

**Table 4.6** THM species of each DOM fraction in filtered raw water and coagulated water

Fraction	Filtered raw water					Coagulated water				
	THMFP (µg/L)					THMFP (µg/L)				
	Chloroform	Bromodichloroform	Dibromochloroform	Bromoform	Total THMFP	Chloroform	Bromodichloroform	Dibromochloroform	Bromoform	Total THMFP
HPON	62.4	0.0	5.6	0.0	68.0	28.7	0.0	2.8	0.0	31.5
HPOB	31.5	4.6	2.8	2.5	41.4	28.6	4.5	2.0	0.0	35.1
HPOA	224.7	10.2	12.1	0.0	247.1	98.7	1.2	6.2	0.0	106.0
HPIB	45.6	5.4	6.2	10.8	67.9	32.6	2.4	5.4	0.0	40.3
HPIA	89.5	9.3	13.8	0.0	112.6	64.5	6.4	8.2	0.0	79.1
HPIN	53.7	3.1	8.1	0.0	64.9	32.8	0.0	5.2	0.0	38.0
<b>Total</b>	507.5	32.6	48.6	13.3	602.0	285.9	14.4	29.8	0.0	330.2

Fraction	% Reduction by Alum Coagulation				
	THMFP (µg/L)				
	Chloroform	Bromodichloroform	Dibromochloroform	Bromoform	Total THMFP
HPON	54.0	0.0	49.9	0.0	53.7
HPOB	9.3	1.6	28.1	100.0	15.2
HPOA	56.1	88.6	49.0	0.0	57.1
HPIB	28.6	56.4	12.0	100.0	40.6
HPIA	27.9	31.2	40.6	0.0	29.7
HPIN	38.9	100.0	35.8	0.0	41.4



The results in Table 4.6 show that there were some brominated THM species in both filtered raw water and coagulated water. However, these bromo-THM species were present in low levels when compared with chloroform. So it may be noted that each organic fraction contained some bromide ion. In addition the resin used in fractionation had different capacities for retaining bromide ions of each organic fraction and thus the extracted organics contained bromide ions in different levels. Bromide ions could affect the speciation of DBPs within a class of compounds such as THMs or HAAs (Cooper et al., 1983 and 1985; Amy et al., 1998). Rook et al. (1978) reported that bromine is more effective than chlorine in participating in substitution reactions with organic molecules. Furthermore, precursor materials may differ in their susceptibility to bromination versus chlorination reactions.

#### **4.4 Management and Application**

According to the gained results, DOM characteristics in water and treated water of the studied reservoir from the Northern Region Industrial Estate, Lamphun Province, Thailand showed that the main organic fractions were in the acid organic group- hydrophobic acid (HPOA) and hydrophilic acid (HPIA). It was found that both the HPOA and HPIA fractions were the problematical organic fraction. They were not only the major DOM fractions but also the main THMFP precursors. However, there was some evidence in this study relating to supporting literatures that they could be treated by alum coagulation. DOC and THMFP reduction by alum coagulation was implicitly used for studied reservoir water from the Northern Region Industrial Estate and may apply to other water resources. Nevertheless, the best coagulant or coagulant aid for the best reduction of the major DOM fractions and their THMFP should be determined in order to be utilized to remove the problematic organics effectively and reduce their THMFP to acceptable levels in accordance with the USEPA standard. This will be effective to general water treatment in order to produce a good quality water supply or drinking water for our country resulting in improving our health and life quality.

## CHAPTER 5

### CONCLUSIONS

Based on the obtained results from the study of reduction of trihalomethane created from six fractions of DOMs in raw water supply by alum coagulation in October, 2004, the following conclusions could be drawn.

1. DOM fractions in filtered raw water ordered according to their DOC quantities present in water are as follows: HPOA, the main fraction, 41.6%, HPIA (20.5%), HPIN (17.7%), HPON (12.1%), HPIB (4.8%), and HPOB (3.4%), respectively. DOM fractions of coagulated water ordered according to their DOC quantities present in water are as follows: HPOA, the main fraction, 45.3% of total DOC. HPIA (20.3%), HPON (10.7%), HPIN (9.4%), HPIB (8.4%), and HPOB (6.0%), respectively.
2. Major DOM fractions in both filtered raw water and coagulated water were the HPOA and HPIA fractions.
3. The optimal condition of alum coagulation for DOM removal was achieved at a pH value of 5.5 and with an alum dosage of 40 mg/L.
4. Alum coagulation could reduce THMFP of the HPOA fraction by 57.1% and the HPON fraction by 53.7%. Whilst HPIN, HPIB, HPIA, and HPOB fractions were reduced by 41.4%, 40.6%, 29.8%, and 15.2%, respectively.
5. The main THMFP precursors in both filtered raw water and coagulated water were the HPOA and HPIA fractions. In addition, the most reactive DOM fractions for reacting with chlorine to form THMs were the HPIB and HPOB fractions.

6. EEM technique could be applied for preliminary classification of the major DOM fractions in water according to their peak positions and fluorescent intensities.



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## CHAPTER 6

### RECOMMENDATIONS FOR FUTURE WORK

The recommendations for future studies are notified in the following statements.

1. Coagulation using polymer and other coagulants such as polyaluminium chloride (PACl) and ferric chloride is recommended.
2. The effect of seasonal variation on the reduction of trihalomethane created from six fractions of DOMs in raw water supply by alum coagulation should be studied.
3. The other chlorinated DBPs in terms of HAAs, HANs, and cyanogen halides should be also considered.



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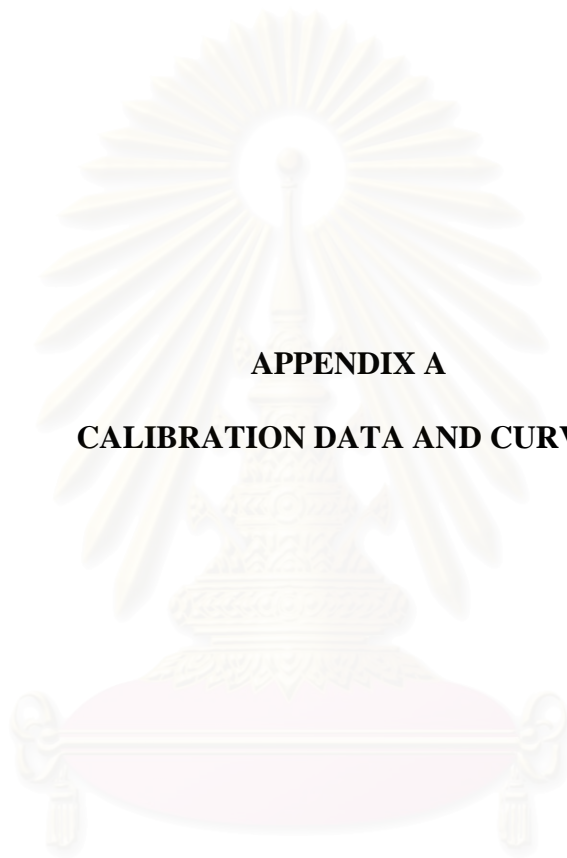
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**APPENDIX**

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**APPENDIX A**

**CALIBRATION DATA AND CURVES**

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**Table A-1:** Calibration data of UV-254

Date : 15/12/2002    Time : 19:51:41

CALIBRATION

---

Date: 15/12/02    Time: 19:51:37 AM  
Instrument: PerkinElmer Lambda 25    Serial No: 101N2020507  
Method: JIM03  
Ordinate mode: Single Wavelength  
Baseline: No correction ( 0.00    0.00 )  
Analyst:

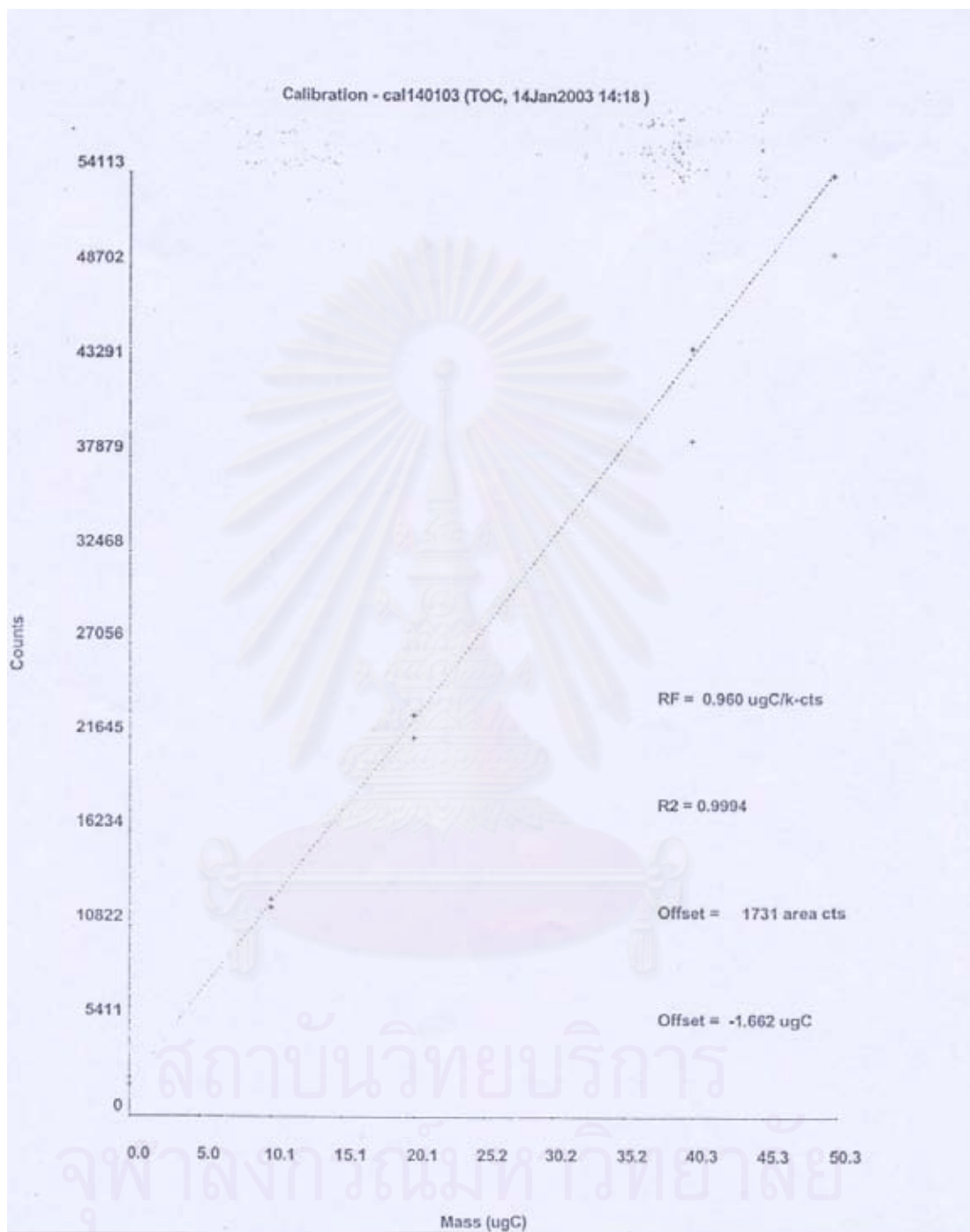
---

Wavelength(s)	Sample ID	Concentration	Ord. value	Comment
253.7	0.0 KHP.A01	2.0000 mg/L	0.0357	
253.7	0.0 KHP.A02	4.0000 mg/L	0.0649	
253.7	0.0 KHP.A03	8.0000 mg/L	0.1249	
253.7	0.0 KHP.A04	16.0000 mg/L	0.2171	
253.7	0.0 KHP.A05	20.0000 mg/L	0.2457	

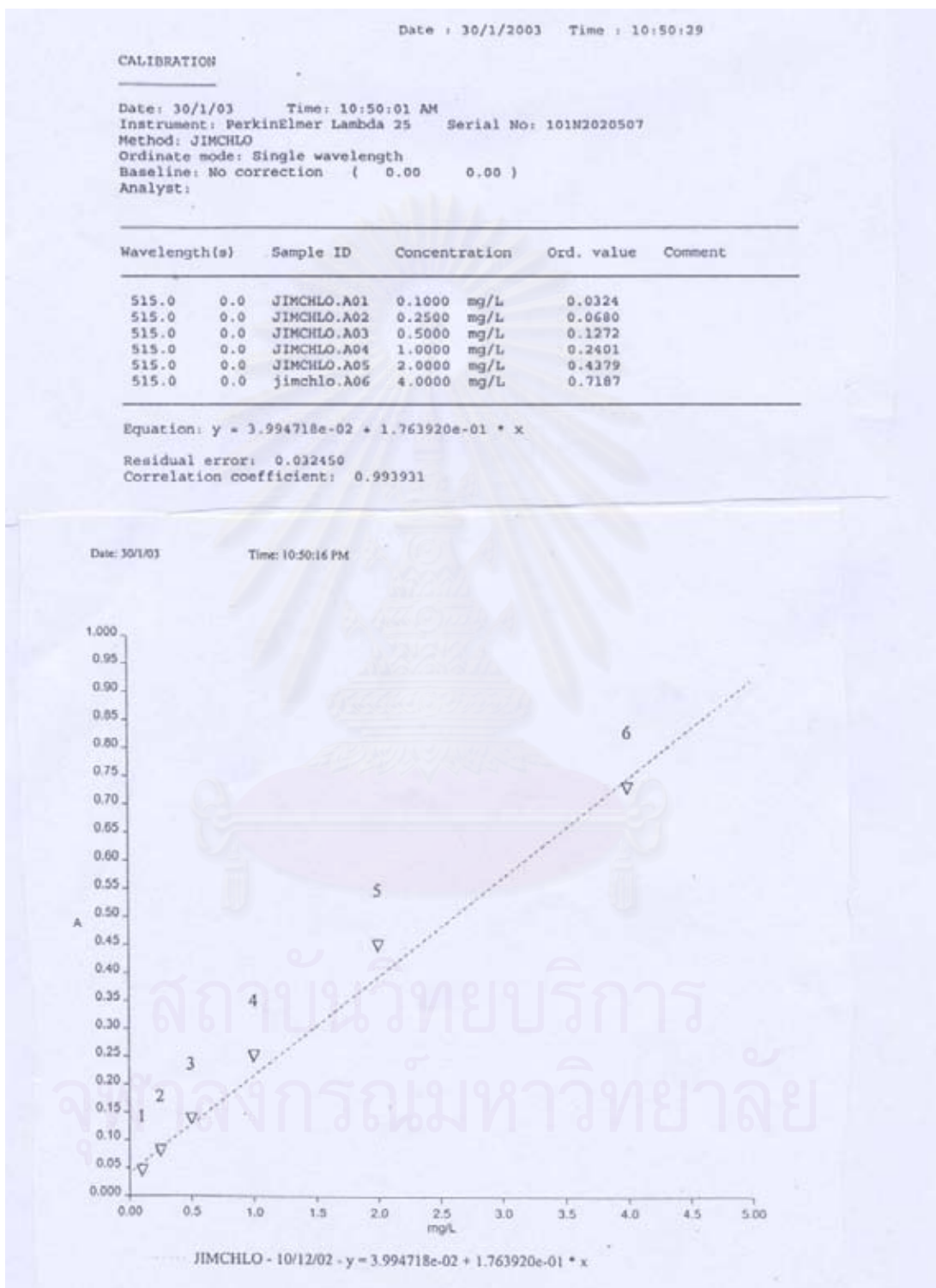
---

Equation:  $y = 1.956467e-02 + 1.180933e-02 * x$   
R dual error: 0.010841  
Correlation coefficient: 0.994775

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**Figure A-1:** Calibration curve of TOC

**Table A-2:** Calibration data of free chlorine residual**Figure A-2:** Calibration curve of free chlorine residual

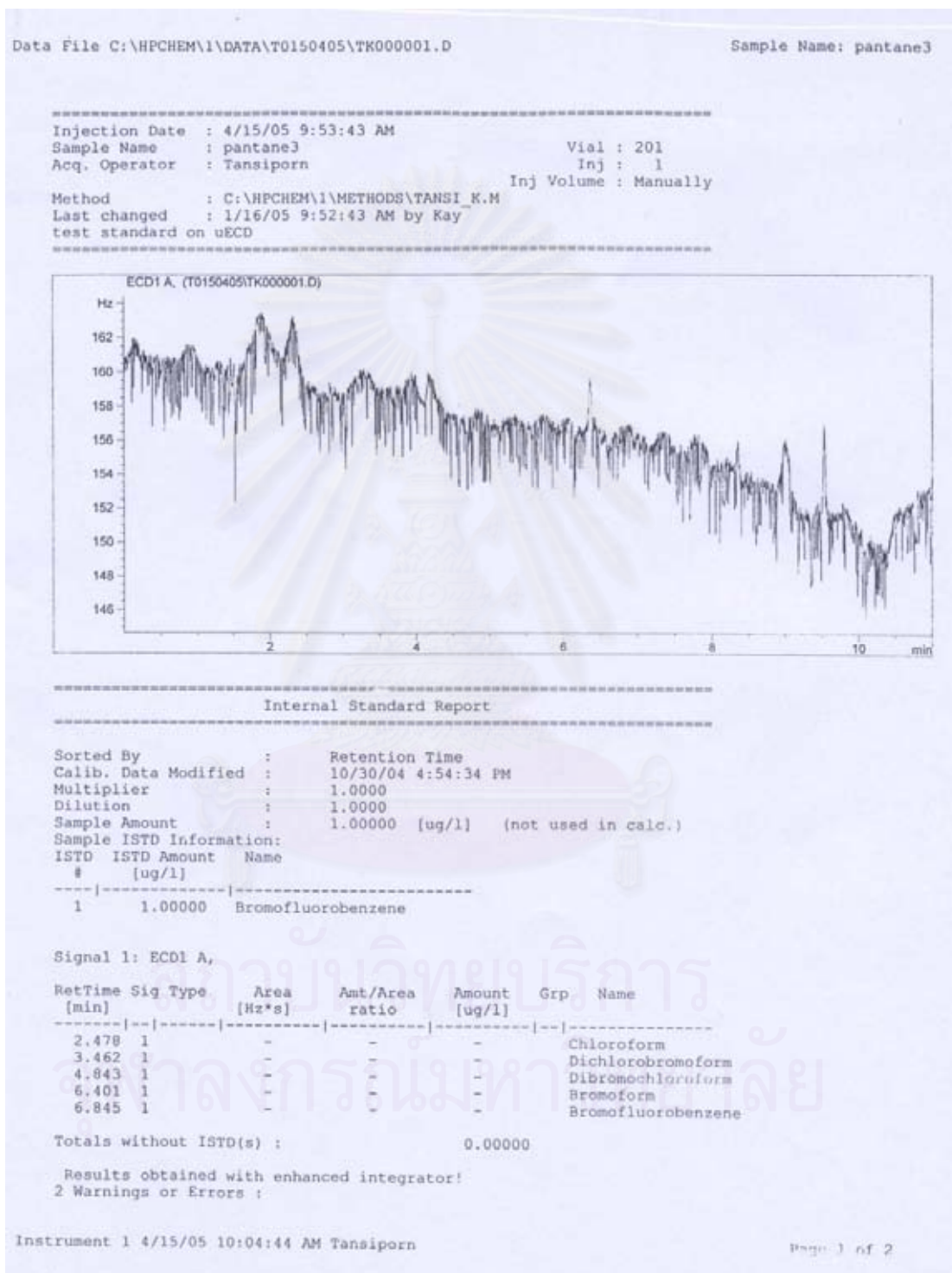
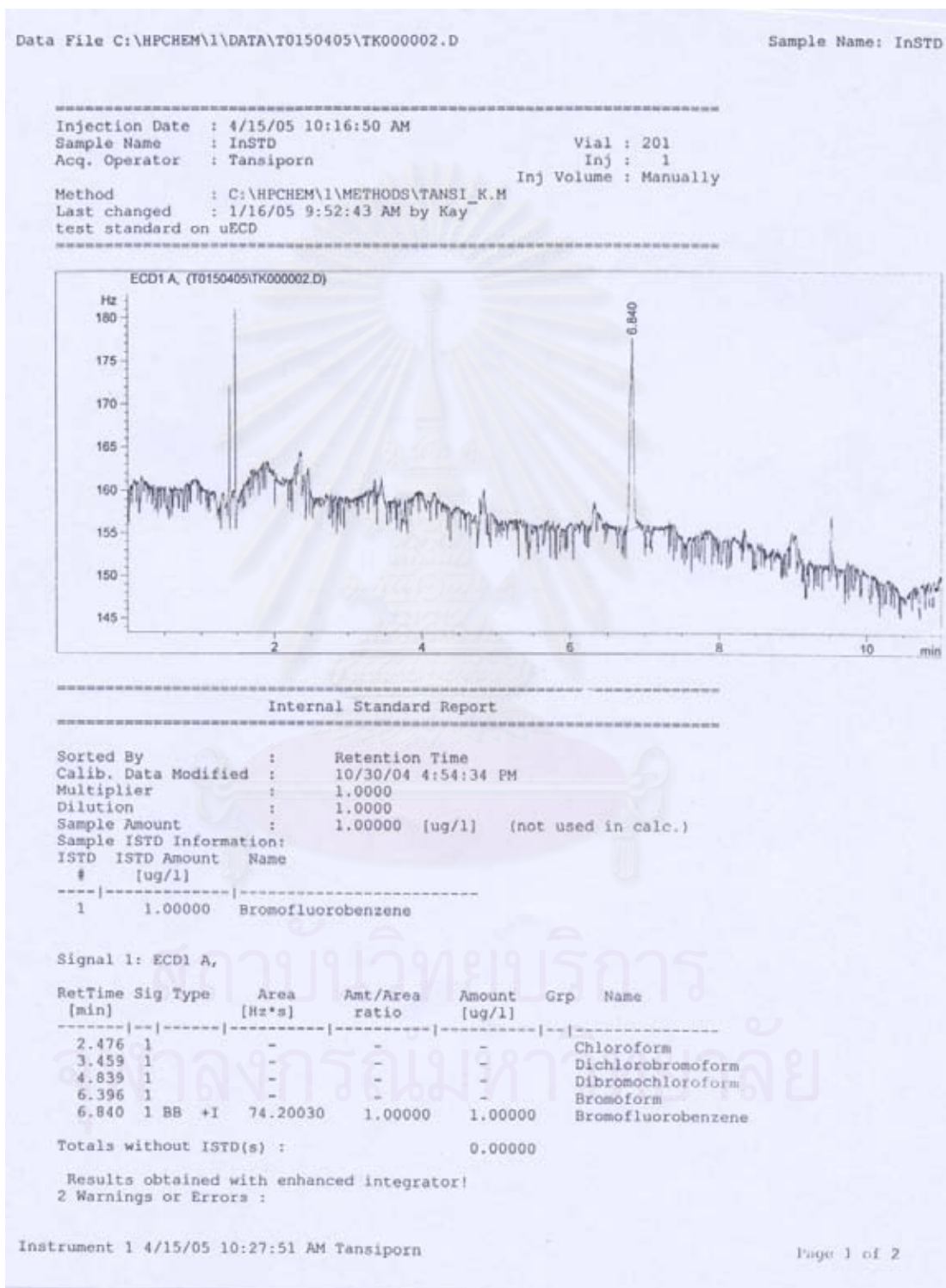


Figure A-3: Chromatogram of blank and oven temperature





**Figure A-4:** Chromatogram of internal standard and oven temperature



Table A-3: Calibration data of TTHM

Method C:\HPCHEM\1\METHODS\TANSI\_K.M

```

=====
                        Calibration Table
=====

```

Calib. Data Modified : 4/15/05 2:46:06 PM

Calculate : Internal Standard  
Based on : Peak Area

Rel. Reference Window : 10.000 %  
Abs. Reference Window : 0.000 min  
Rel. Non-ref. Window : 10.000 %  
Abs. Non-ref. Window : 0.000 min  
Uncalibrated Peaks : not reported  
Partial Calibration : Yes, identified peaks are recalibrated  
Correct All Ret. Times: No, only for identified peaks

Curve Type : Linear  
Origin : Forced  
Weight : Equal

Recalibration Settings:  
Average Response : Average all calibrations  
Average Retention Time: Floating Average New 75%

Calibration Report Options :  
Printout of recalibrations within a sequence:  
Calibration Table after Recalibration  
Normal Report after Recalibration  
If the sequence is done with bracketing:  
Results of first cycle (ending previous bracket)

Default Sample ISTD Information (if not set in sample table):  
ISTD ISTD Amount Name  
# [ug/l]

```

-----|-----|-----|-----|-----|-----|
1 25.00000 bromofluorobenzene

```

Signal 1: ECD1 A,

RetTime [min]	Lvl Sig	Amount [ug/l]	Area	Amt/Area	Ref Grp	Name
2.493	1	25.00000	162.05576	1.54268e-1	1	chloroform
	2	50.00000	314.92676	1.58767e-1		
	3	100.00000	481.66641	2.07613e-1		
	4	150.00000	794.07727	1.88898e-1		
	5	300.00000	1528.63684	1.96253e-1		
	6	500.00000	2594.84839	1.92689e-1		
	7	700.00000	3624.11890	1.93150e-1		
3.476	1	25.00000	504.91705	4.95131e-2	1	dichlorobromoform
	2	50.00000	950.41412	5.26086e-2		
	3	100.00000	1510.15942	6.62182e-2		
	4	150.00000	2505.93359	5.98579e-2		
	5	300.00000	4948.20215	6.06281e-2		
	6	500.00000	8604.84082	5.81068e-2		
	7	700.00000	1.23752e4	5.65646e-2		
4.854	1	25.00000	400.24161	6.24623e-2	1	dibromochloroform
	2	50.00000	763.29706	6.55053e-2		
	3	100.00000	1189.56372	8.40644e-2		
	4	150.00000	1968.21204	7.62113e-2		
	5	300.00000	4002.79761	7.49476e-2		
	6	500.00000	6868.57080	7.27953e-2		
	7	700.00000	9789.02539	7.15087e-2		
6.410	1	25.00000	192.59471	1.29806e-1	1	bromoform
	2	50.00000	396.80045	1.26008e-1		

Instrument 1 4/15/05 2:50:41 PM Tansiporn

Page 1 of 3

Method C:\HPCHEM\1\METHODS\TANSI\_K.M

RetTime [min]	Sig	Lvl	Amount [ug/l]	Area	Amt/Area	Ref Grp Name
		3	100.00000	589.74384	1.69565e-1	
		4	150.00000	936.05920	1.60246e-1	
		5	300.00000	1770.17896	1.69474e-1	
		6	500.00000	2847.02759	1.75622e-1	
		7	700.00000	4038.54663	1.73330e-1	
6.850	1	1	1.00000	65.50924	1.52650e-2	+11 bromofluorobenzene
		2	1.00000	82.14703	1.21733e-2	
		3	1.00000	50.71712	1.97172e-2	
		4	1.00000	64.94865	1.53968e-2	
		5	1.00000	98.54705	1.01474e-2	
		6	1.00000	85.64991	1.16754e-2	
		7	1.00000	90.92514	1.09981e-2	

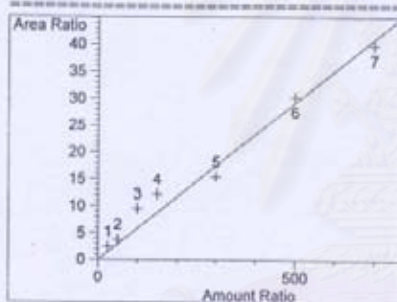
1 Warnings or Errors :

Warning : Overlapping peak time windows at 6.41 min, signal 1

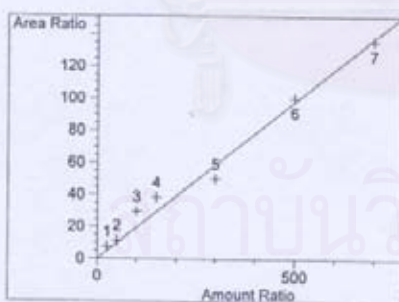
## Peak Sum Table

\*\*\*No Entries in table\*\*\*

## Calibration Curves

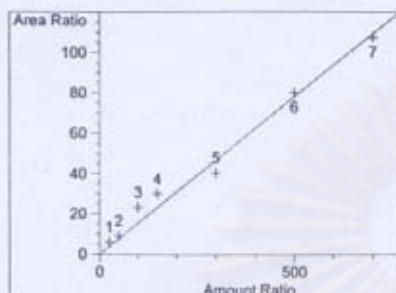


chloroform at exp. RT: 2.493  
 ECD1 A,  
 Correlation: 0.99442  
 Residual Std. Dev.: 2.36254  
 Formula:  $y = mx$   
 m: 5.86160e-2  
 x: Amount Ratio  
 y: Area Ratio

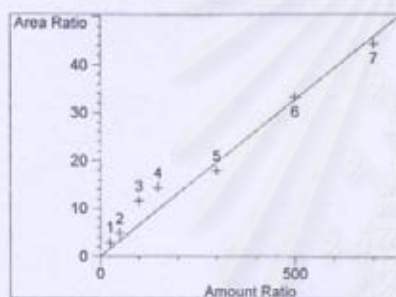


dichlorobromoform at exp. RT: 3.476  
 ECD1 A,  
 Correlation: 0.99584  
 Residual Std. Dev.: 6.82783  
 Formula:  $y = mx$   
 m: 1.96511e-1  
 x: Amount Ratio  
 y: Area Ratio

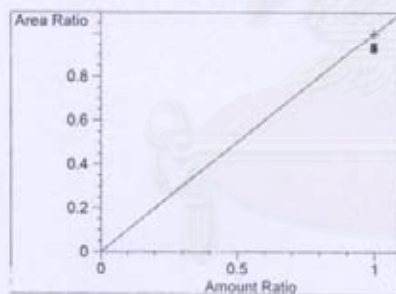
Method C:\HPCHEM\1\METHODS\TANSI\_K.M



dibromochloroform at exp. RT: 4.854  
ECD1 A,  
Correlation: 0.99619  
Residual Std. Dev.: 5.19386  
Formula:  $y = mx$   
m: 1.56133e-1  
x: Amount Ratio  
y: Area Ratio

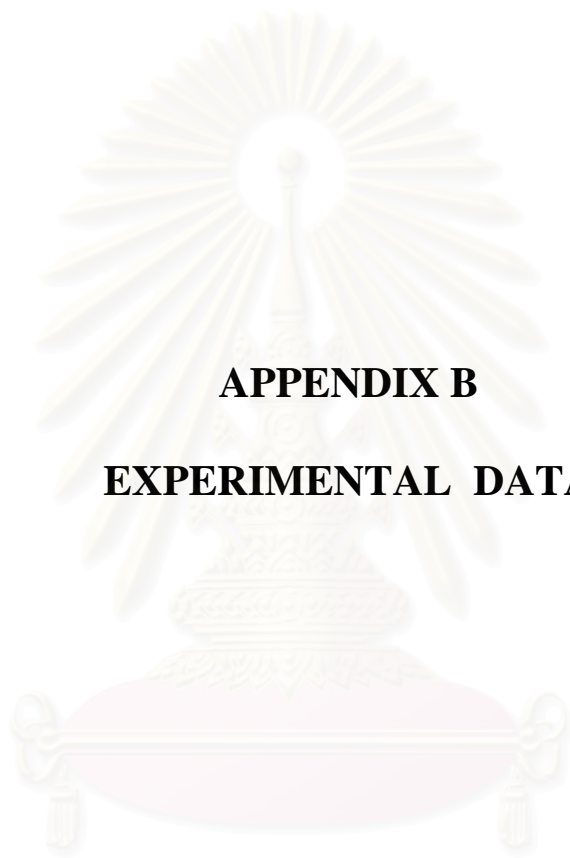


bromoform at exp. RT: 6.410  
ECD1 A,  
Correlation: 0.99254  
Residual Std. Dev.: 3.05742  
Formula:  $y = mx$   
m: 6.55480e-2  
x: Amount Ratio  
y: Area Ratio



bromofluorobenzene at exp. RT: 6.850  
ECD1 A,  
Correlation: 1.00000  
Residual Std. Dev.: 0.00000  
Formula:  $y = mx$   
m: 1.00000  
x: Amount Ratio  
y: Area Ratio

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**APPENDIX B**

**EXPERIMENTAL DATA**

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## **Determination of optimal condition for alum coagulation**

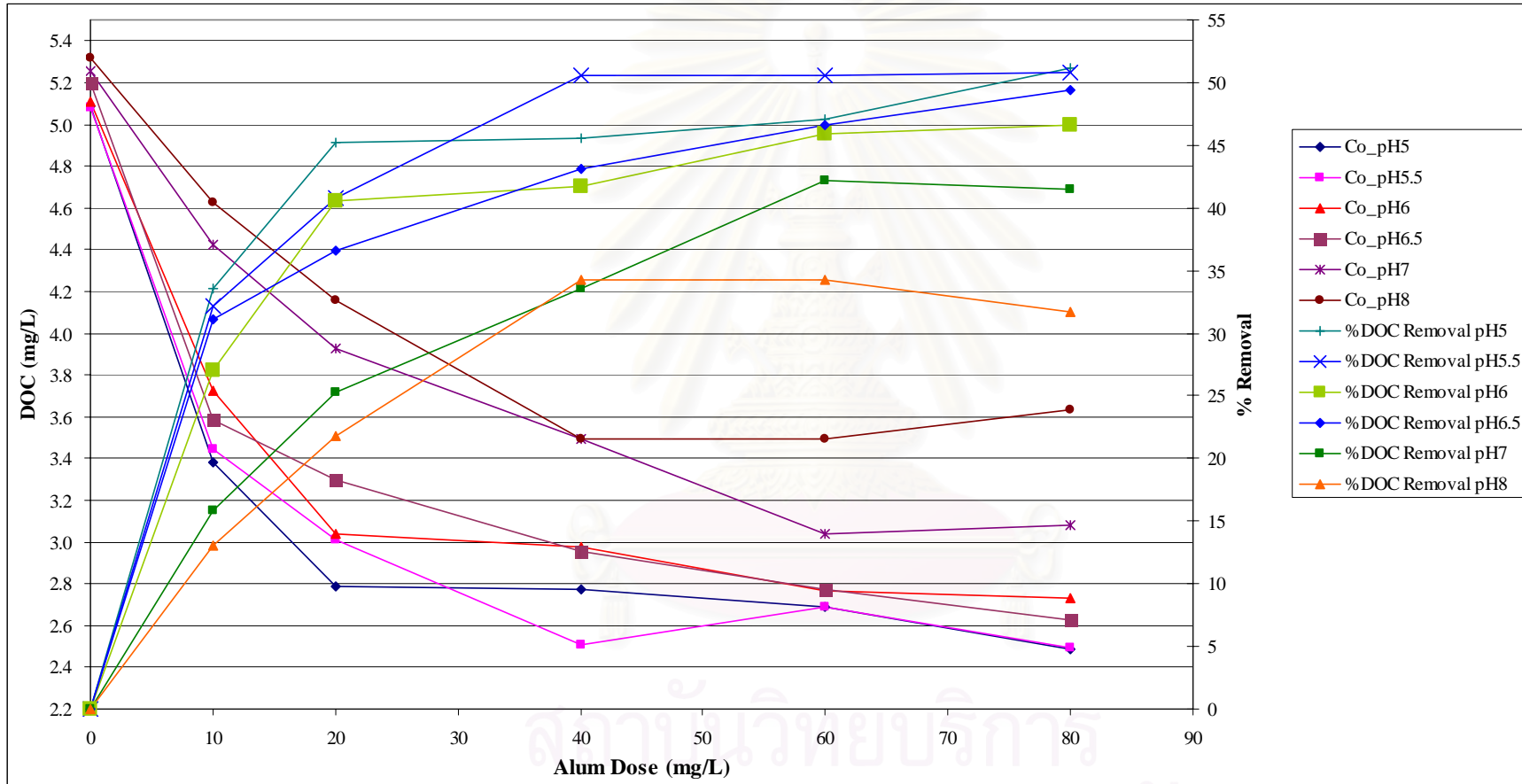
According to determining optimum condition of alum coagulation for the Northern Region Industrial Estate reservoir water, the variation of pH and alum dosages was conducted in jar-test experiments. The results of parameters in coagulated water including DOC, UV-254 and SUVA that were used as criteria are as separately demonstrated in following Figure.

As shown in Figure B-1, alum coagulation at pH of 5.5 and at alum dosage of 40 mg/L could remove DOC approximately 48.5% comparing with the maximum DOC removal about 50.9% that occurred at pH of 5.5 and at alum dosage of 80 mg/L. This corresponds well to such supporting literatures. The optimum coagulation of DOM by alum has been illustrated to occur at pH 5-6 (White, 1999).

Regard to USEPA enhanced coagulation (table 2.3), the values of DOC and alkalinity in raw water about 4-8 mg/L and 60-120 mg/L as CaCO<sub>3</sub>, respectively, were required for 35 percent DOC reduction. As obtained results, this condition could achieve to remove contained organic compound in raw water from the studied water.

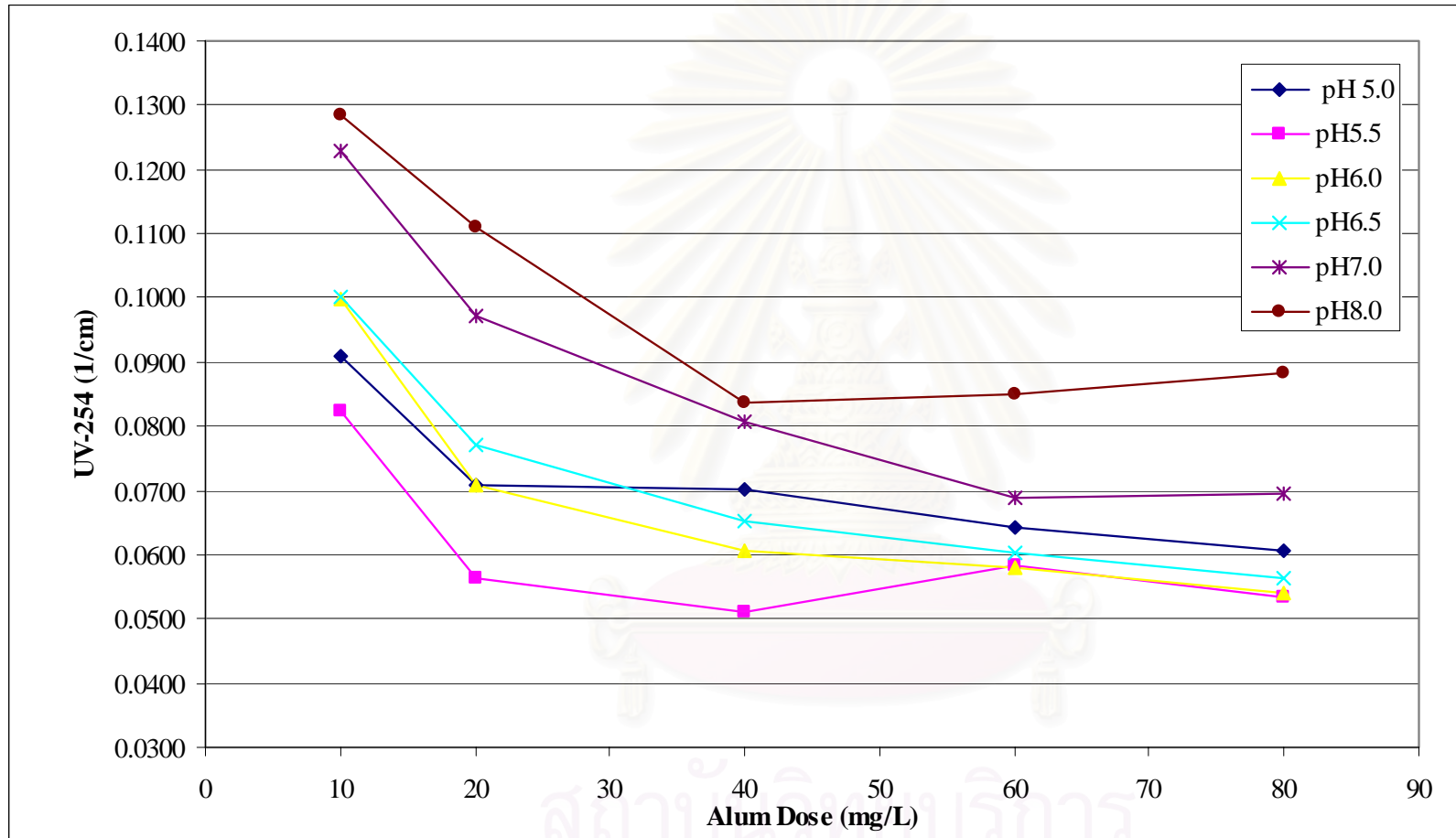
UV-254 that represents the ability of light absorbance for organic contained in water and SUVA that represent the level of aromatic compound in water were considered to be the other criteria. The condition at pH of 5.5 and alum dosage of 40 mg/L demonstrated UV-254 and SUVA at the lowest level. It could be drawn that DOC removal could be also used to removed UV-254 and SUVA. Consequently, this condition that was selected from DOC removal and the low level of UV-254 and SUVA was the optimum condition of alum coagulation for the Northern Region Industrial Estate reservoir water.



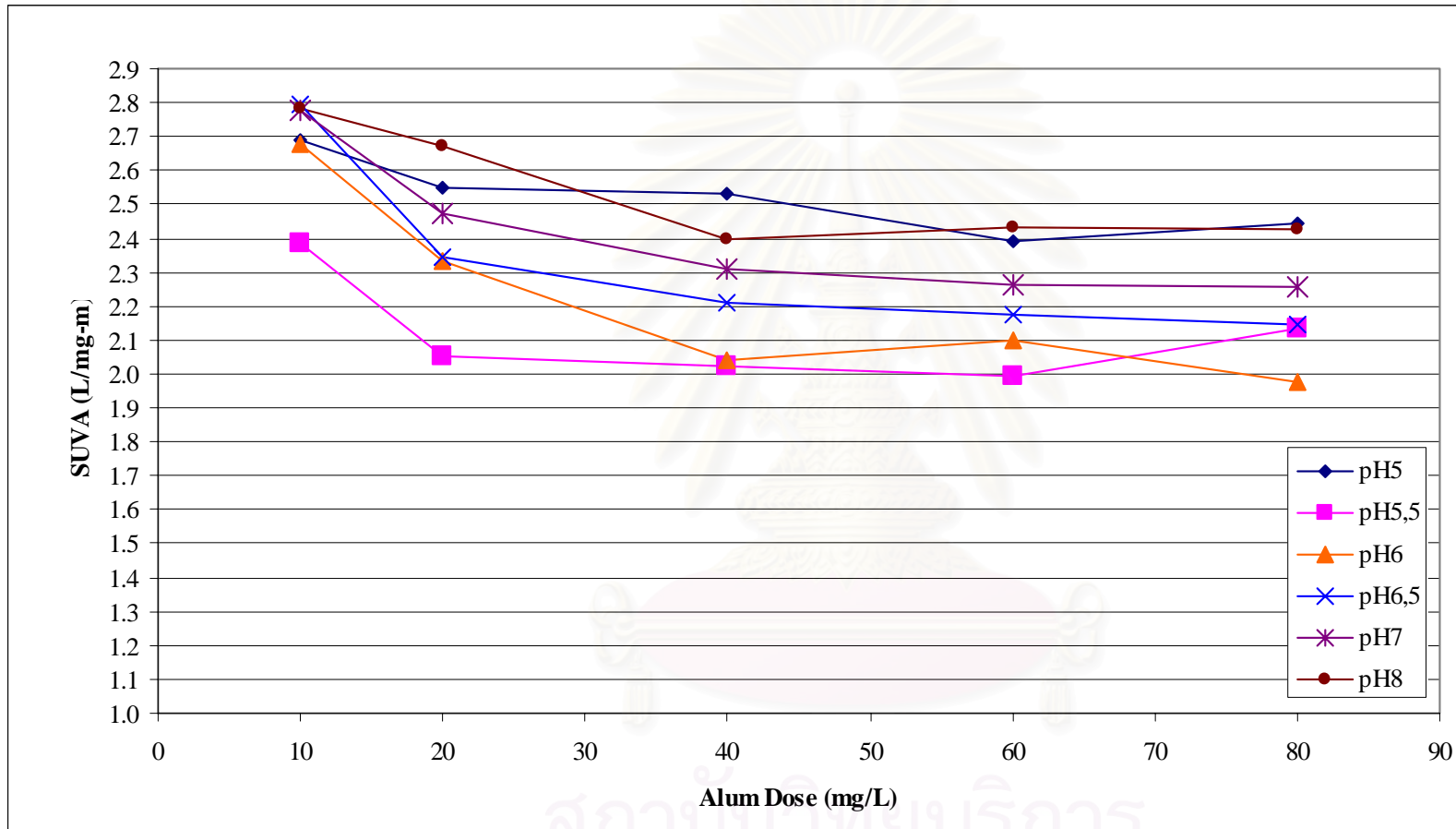


**Figure B-1:** DOC and % DOC removal for the determination of alum coagulation condition





**Figure B-2:** UV-254 for the determination of alum coagulation condition



**Figure B-3** SUVA for the determination of alum coagulation condition

**Table B-1 Results of analyzed parameters of filtered raw water and coagulated water**

Parameter	NTU	mg/L	mg/L	l/cm	L/mg-m	mg/L	µg/L	mg/L	°c	
	pH	Turbidity	TOC	DOC	UV-254	SUVA	Cl <sub>2</sub> demand	THMFP	Alkalinity	temp
Raw water	7.84	8.25	5.72				27.04	487.8	82	26.1
0.7 filtered raw water	7.84			5.37	0.14	2.60	8.98	382.4	<b>82</b>	<b>26.1</b>
HPON	7			0.71	0.0066	0.93	0.33	68		
HPOB	10			0.20	0.003	1.50	0.11	41.4		
HPOA	2			2.45	0.0478	1.95	2.57	247.1		
HPIB				0.28	0.0062	2.19	0.59	67.9		
HPIA				1.21	0.0084	0.70	4.98	112.6		
HPIN				1.04	0.0029	0.28	0.28	64.9		
			total	5.89						
	pH	alum dose	turbidity	DOC	UV-254	SUVA	Cl <sub>2</sub> demand	THMFP	Alk	
Coagulated water	5.5	40	0.36	2.88	0.0512	1.78	6.46	268.6	9	
HPON	7			0.32	0.0047	1.47	0.28	31.5		
HPOB	10			0.18	0.0019	1.06	0.09	35.1		
HPOA	2			1.36	0.0187	1.38	1.18	106.0		
HPIB				0.25	0.0052	2.08	0.39	40.3		
HPIA				0.61	0.0072	1.18	2.21	79.1		
HPIN				0.28	0.0019	0.68	0.25	38.0		
			total	2.99						

**Table B-2 Determination of DOM reduction of each DOM fraction for filtered raw water and coagulated water**

DOC (mg/L) of	DOC in water	Hydrophobic fraction (HPO)			Hydrophilic fraction (HPI)			HPO + HPI	%
		HPON	HPOB	HPOA	HPIB	HPIA	HPIN	Total	Diff*
<b>Filtered water</b>	5.37	0.71	0.20	2.45	0.28	1.21	1.04	5.89	9.68
<b>Coagulated water</b>	2.88	0.32	0.18	1.36	0.25	0.61	0.28	2.99	3.78
<b>% Reduction</b>	46.3	54.9	10.0	44.7	10.7	49.8	73.1	49.2	

**Table B-3 Determination of THMFP reduction of each DOM fraction for filtered raw water and coagulated water**

THMFP (µg/L) of	THMFP in water	Hydrophobic fraction (HPO)			ΣHPO	Hydrophilic fraction (HPI)			ΣHPI	HPO + HPI	%
		HPON	HPOB	HPOA		HPIB	HPIA	HPIN		Total	Diff*
<b>Filtered water</b>	382.4	68.0	41.4	247.1	356.5	67.9	112.6	64.9	245.4	601.9	57.4
<b>Coagulated water</b>	268.6	31.5	35.1	106.0	172.6	40.3	79.1	38.0	157.4	330.0	22.9
<b>% Reduction</b>	29.8	53.7	15.2	57.1		40.6	29.8	41.4		45.2	

**Table B-4 Chlorine demand determination of raw water and coagulated water**

Raw water	Cl <sub>2</sub> dose mg/L	Cl <sub>2</sub> residual mg/L				Cl <sub>2</sub> demand mg/L
		1	2	3	av	
Raw water	31.7	4.66	4.67	4.66	4.66	27.04
filter water	15.35	6.4	6.3	6.42	6.37	8.98
HPON	4.80	4.47	4.43	4.50	4.47	0.33
HPOB	4.52	4.41	4.41	4.40	4.41	0.11
HPOA	7.46	4.88	4.92	4.87	4.89	2.57
HPIB	4.01	3.42	3.42	3.42	3.42	0.59
HPIA	10.94	5.99	5.98	5.92	5.96	4.98
HPIN	6.18	5.89	5.95	5.98	5.94	0.24

Coagulated water	Cl <sub>2</sub> dose mg/L	Cl <sub>2</sub> residual mg/L				Cl <sub>2</sub> demand mg/L
		1	2	3	av	
Coagulated water	10	3.5	3.56	3.56	3.54	6.46
HPON	5.20	4.71	4.71	4.70	4.71	0.49
HPOB	4.45	4.37	4.37	4.35	4.36	0.09
HPOA	6.00	4.81	4.81	4.83	4.82	1.18
HPIB	3.80	3.41	3.41	3.41	3.41	0.39
HPIA	6.00	5.46	5.46	0.45	3.79	2.21
HPIN	6.00	5.74	5.73	5.78	5.75	0.25

**Table B-5 Determination of optimal condition of alum coagulation**

		Alum Dose(mg/l)					
		0	10	20	40	60	80
pH5.0	UV-254(1/cm)		0.0910	0.0710	0.0701	0.0643	0.0607
	DOC(mg/l)	5.0870	3.381	2.786	2.770	2.692	2.485
	SUVA(L/mg-m)		2.6915	2.5485	2.5307	2.3886	2.4427
pH5.5	UV-254(1/cm)		0.0823	0.0564	0.0508	0.0524	0.0533
	DOC(mg/l)	5.079	3.4470	2.7510	2.6150	2.6290	2.4960
	SUVA(L/mg-m)		2.38758341	2.05016358	1.94263862	1.99315329	2.13541667
pH6.0	UV-254(1/cm)		0.0999	0.0709	0.0607	0.0580	0.0540
	DOC(mg/l)	5.111	3.727	3.040	2.978	2.766	2.729
	SUVA(L/mg-m)		2.68044003	2.33223684	2.03828073	2.09689082	1.97874679
pH6.5	UV-254(1/cm)		0.1001	0.0773	0.0653	0.0603	0.0563
	DOC(mg/l)	5.196	3.581	3.295	2.953	2.773	2.627
	SUVA(L/mg-m)		2.7960067	2.3447648	2.21018174	2.17345835	2.14293871
pH7.0	UV-254(1/cm)		0.1228	0.0971	0.0807	0.0687	0.0695
	DOC(mg/l)	5.257	4.426	3.926	3.495	3.039	3.078
	SUVA(L/mg-m)		2.77530502	2.473892	2.30844063	2.26214764	2.25882608
pH8.0	UV-254(1/cm)		0.1285	0.1111	0.0837	0.0850	0.0882
	DOC(mg/l)	5.315	4.623	4.158	3.492	3.496	3.632
	SUVA(L/mg-m)		2.78015719	2.67121767	2.39673876	2.43091005	2.42772577

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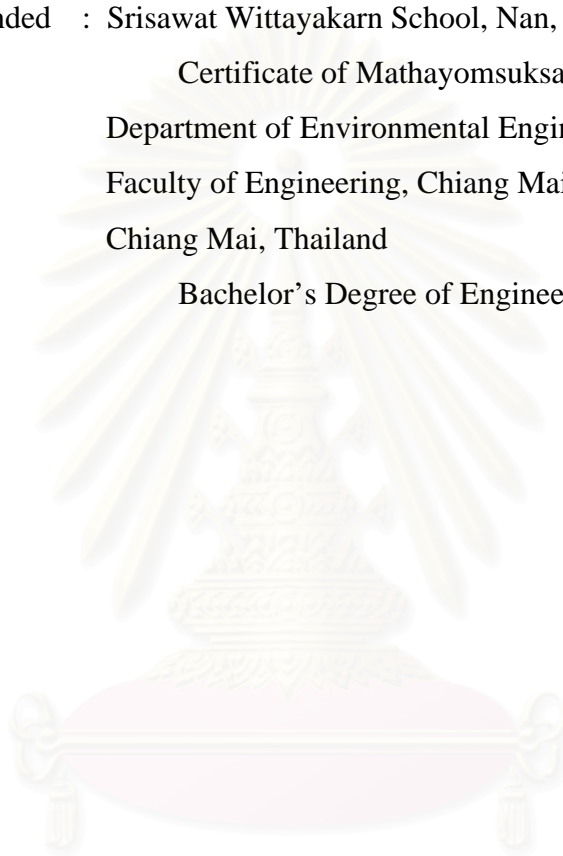
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