

## CHAPTER 2



### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Background and Regulatory History of Trihalomethanes

The first class halogenated disinfection by product (DBPs) was discovered by J.J.Rook. The naturally occurring humates in surface water were precursors that can react with chlorine during chlorination process in water treatment plant to form haloform.(Rook, 1974). Beller, et.al. (1974) proposed that THMs, including chloroform, bromodichloromethane and dibromochloromethane, had been detected in several water supplies. Symon, et al. (1975) conducted a survey of halogenated organic compounds from 80 water supplies plant. The four THMs; chloroform, dichlorobromomethane, dibromochloromethane, and bromoform were found in chlorinated drinking water in United State. However, they were not detected in the raw water tested. Steven, et al. (1975) proposed that chloroform dichlorobromomethane, dibromochloromethane, bromoform in the chlorinated water supplies from Missouri River were in the range of 0 and 311 $\mu$ g/L, of 0 and 116  $\mu$ g/L, of 0 and 100  $\mu$ g/L and of 0 and 92  $\mu$ g/L, respectively, Oliver and Lawrence (1979) proposed that humic materials, which presented at high concentration in most surface water, seemed to be the main haloform precursors in the natural water. Young and Singer (1979) showed that quantity of chloroform produced is depend upon TOC concentration in raw water. Chloroform formation increased as non-volatile total organic carbon (TOC) increased. United State Environmental Protection Agency (USEPA) set a maximum contaminant level (MCL) for total THMs (TTHMs) at 0.10 mg/L in 1979. The standard applied to system that serving over 10,000 people. Due to wide occurrence and potential health risks of DBPs, the USEPA issued the Disinfection/Disinfection By-products (D/DBPs) Rule in two stages. Stage 1 of D/DBPs Rule was proposed in December 1998. It proposed TTHMS MCLs of 0.080 mg/L. Stage 2 of D/DBPs Rule were anticipated to be more stringent which required lower MCLs for DBPS than Stage 1, (0.040 mg/L). (USEPA, 1998) In 1999, USEPA proposed enhanced coagulation and enhanced precipitative softening to produce THMs and HAAs below the MCLs of 0.080 and 0.060 mg/L. (USEPA, 1999)

## 2.2 Chemistry of Trihalomethanes

Over the last several years, public awareness about drinking water quality issues has arisen. The issue of greatest concern was disinfection by-products. DBPs was the results of chemical reaction between disinfectants used and natural organic matter (NOM) presented in raw drinking water. (Department of Environmental and labor, 2000)

Marhaba and Washington (1998) demonstrated chlorinated disinfection by-product (DBPs), which are shown in Table 2.1.

**Table 2.1** Chlorinated DBPs

Chemical class	Chemical compound
Trihalomethanes (THMs)	Chloroform
	Bromodichloromethane
	Dibromochloromethane
	Bromoform
Haloacetic acids (HAAs)	Monochloroacetic acid (MCAA)
	Dichloroacetic acid (DCAA)
	Trichloroacetic acid (TCAA)
	Monobromoacetic acid (MBAA)
	Dibromoacetic acid (DBAA)
	Tribromoacetic acid (TBAA)
	Bromochloroacetic acid (BCAA)
	Bromodichloroacetic acid (BDAA)
	Chlorodibromoacetic acid (CDBAA)
Haloacetonitrile (HANs)	Dichloroacetonitrile
	Trichloroacetonitrile
	Dibromoacetonitrile
	Bromochloroacetonitrile
Cyanogen halides	Cyanogen chloride
	Cyanogen bromide

(Source; Marhaba and Washington., 1998)

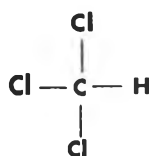
THMs are the by-products of water chlorination. During the chlorination process, which is commonly used for disinfection, chlorine can react with humic substances in the natural organic matter form (NOM) to form THMs. THMs represent structural variation of the methane molecule (CH<sub>4</sub>) in which hydrogen atoms is substituted by four halogen atoms (F, Cl, Br, or I). The common species of THMs generally formed in water supply are chloroform (CHCl<sub>3</sub>), bromodichloromethane (CHBrCl<sub>2</sub>), dibromochloroform (CHBr<sub>2</sub>Cl) and bromoform (CHBr<sub>3</sub>). The USEPA has issued a limit on the concentration of THMs in American drinking water supplies not to exceed 80 µg/l and may be lowered to 40 µg/l in several years (USEPA, 1998)

Morris et al. (1992) found a positive association between consumption of chlorination by-products in drinking water and bladder and rectal cancer in human.

It has been estimated that the absorbed dose of chloroform from 10 minutes shower is equivalent to that from drinking 2 liters of chlorinated water (Jo et al., 1990)

### 2.2.1 Chloroform

Chloroform or trichloromethane (CHCl<sub>3</sub>) has a chemical structure as follow:



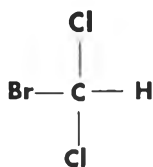
Basic chemical, physical data and other properties of chloroform are listed below

- Colorless, highly refraction, heavy, volatile liquid, characteristic odor, sweet taste
- Miscible with alcohol, ether, benzene, carbon disulfide, carbon tetrachloride and slightly soluble in water
- Molecular weight 119.37 g/mol, specific gravity of 1.472, boiling point of 61°C, melting point of -63 °C and solubility in water of 8.1 g/L

Chloroform causes not only a central nervous system depression, but also causes hepatotoxicity, nephrotoxicity, teratogenicity and carcinogenicity. (USEPA, 1998)

### 2.2.2 Bromodichloromethane

Bromodichloromethane or dichlorobromo-methane ( $\text{CHCl}_2\text{Br}$ ) has a chemical structure as follow:

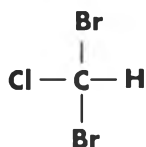


Basic chemical, physical data and other properties of bromodichloromethane are listed below

- Molecular weight 163.82 g/mol, boiling point of 90°C, melting point of 57.1 °C.

### 2.2.3 Dibromochloromethane

Dibromochloromethane or chlorodibromo-methane ( $\text{CHClBr}_2$ ) has a chemical structure as follow:

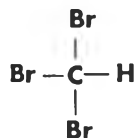


Basic chemical, physical data and other properties of dibromochloromethane are listed below:

- Colorless and heavy liquid
- Molecular weight 208.29 g/mol, specific gravity of 2.38, boiling point of 120°C, melting point of -63 °C and solubility in water of 4.75 g/L

### 2.2.4 Bromoform

Bromoform or tribromomethane ( $\text{CHBr}_3$ ) has a chemical structure as follow:



Basic chemical, physical data and other properties of bromoform are listed below:

- Colorless heavy liquid, that smells and taste like chloroform
- Soluble in alcohol, ether, chloroform benzene, naphtha and slightly soluble in water
- Molecular weight 252.73 g/mol, specific gravity of 2.87, boiling point of 150°C, melting point of 8.3 °C
- Non-flammable

### 2.2.5 Possible Reaction Pathway in Water Treatment

Trussell and Umphres (1978) proposed the haloform reaction. The traditional haloform reaction is outlined in Figure 2.1.

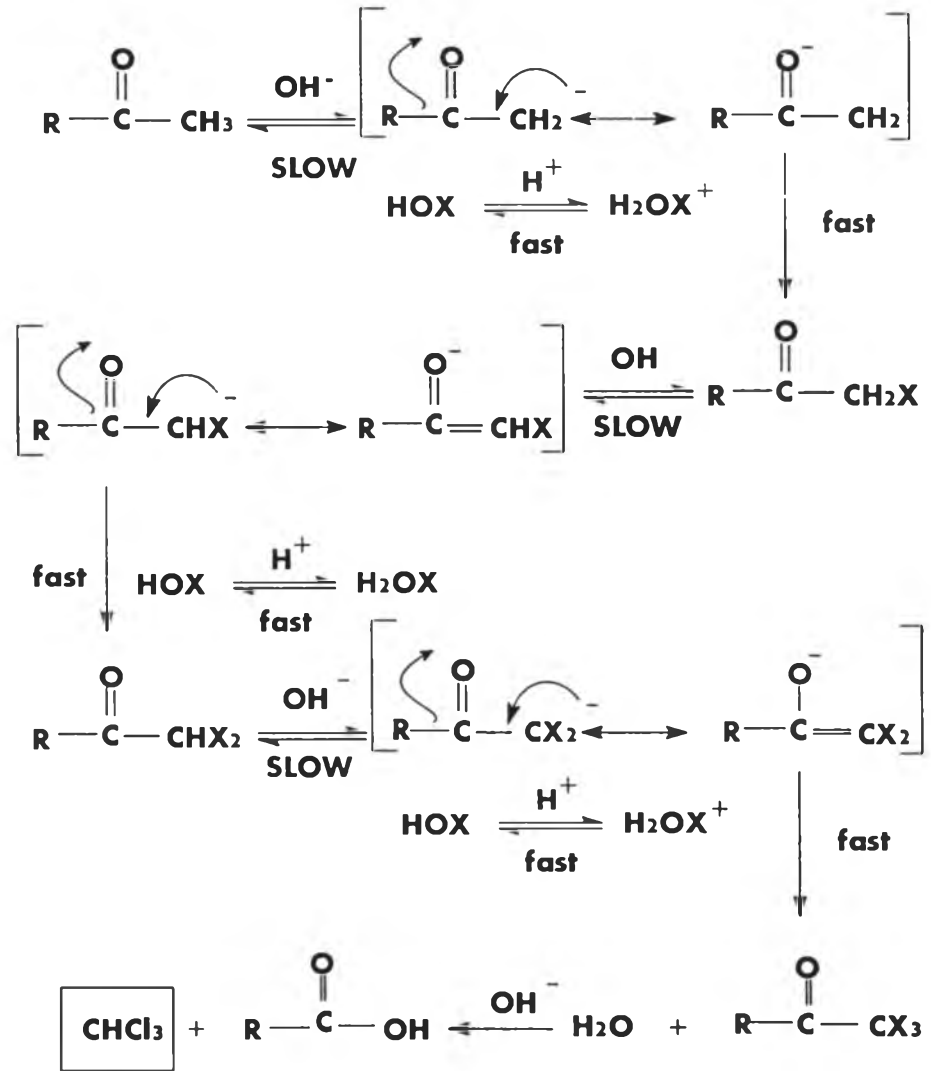
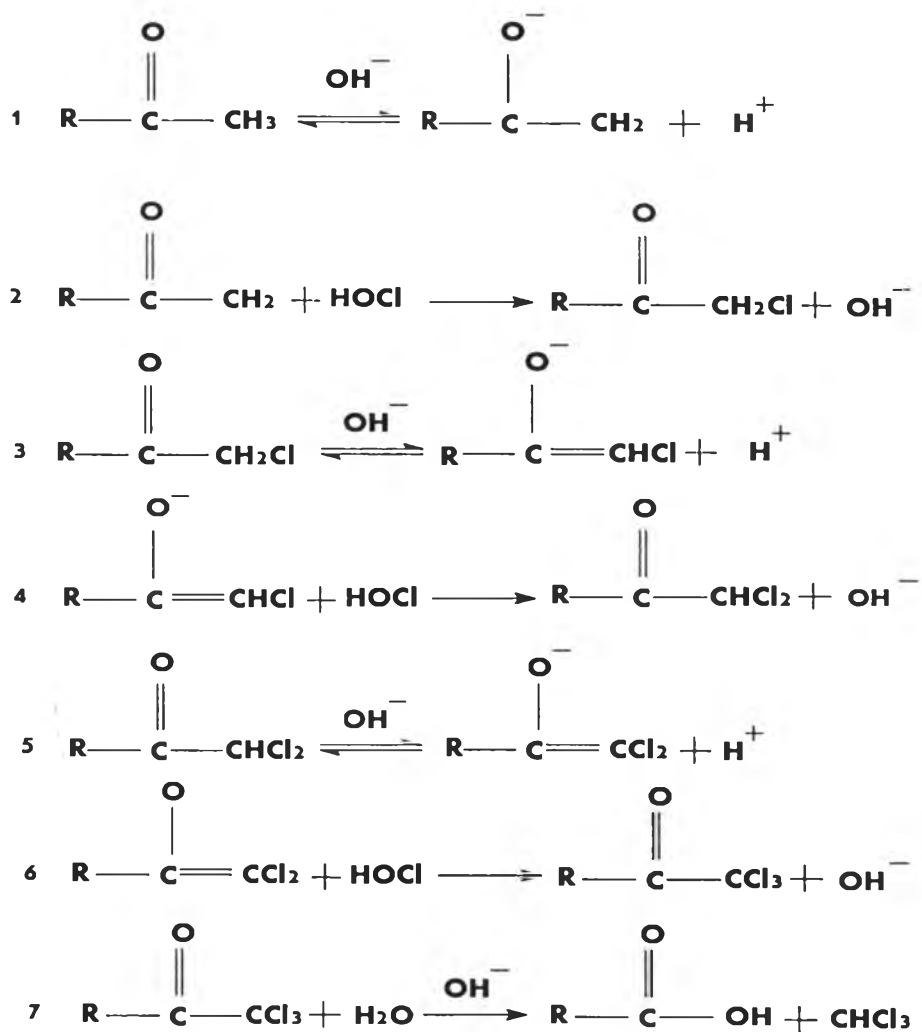


Figure 2.1 Haloform reaction pathways

Natural Environmental board, (1984) demonstrated a series of reaction of chloroform that may be produced during water treatment. The diagrams are shown in Figure 2.2.



**Figure 2.2** Basic steps of reaction of chloroform that may be produced during water treatment

## 2.3 Trihalomethane Formation Potentials (THMFP)

### 2.3.1 Definition of Terms

Total trihalomethanes ( $TTHM_T$ ) is the sum of all four compound concentrations, which include chloroform, dichlorobromomethane, dibromochloromethane and bromoform, produced at any time T (usually day).

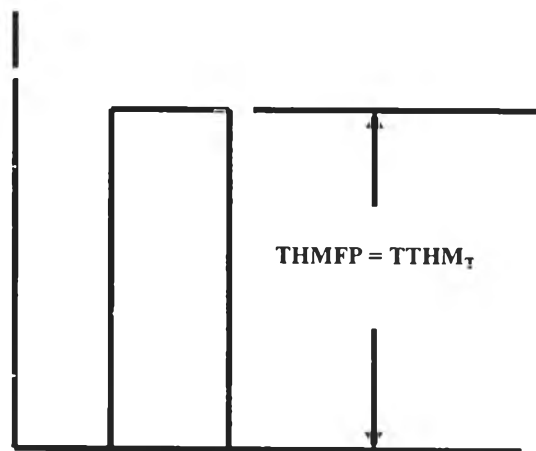
$TTHM_0$  is the total THMs concentration at the time of sampling. It can have range between non-detectable to several hundred micrograms per liter if sample has been chlorinated.

$TTHM_7$  is the total concentration of all four THMs compound produced during reaction of sample precursors with excess free chlorine over a 7-day reaction time at standard reaction conditions which are as follows: free chlorine residual at least 3 mg/L and not more than 5 mg/L at the end of a 7-day reaction (incubation) period with sample incubation temperature of  $25 \pm 2^\circ\text{C}$ , and pH controlled at  $7 \pm 0.2^\circ\text{C}$  with phosphate buffer.

THMFP or  $\Delta THMFP$  is the difference between the final  $TTHM_T$  concentration and the initial  $TTHM_0$  concentration. For the sample, which does not contain chlorine at the time of sampling,  $TTHM_0$  will be close to zero. Therefore the term THMFP may be used. For the sample, which contain chlorine at the time of sampling,  $TTHM_0$  will be detected. Therefore the term  $\Delta THMFP$  may be used when reporting the difference between TTHM concentrations. (Standard method, 1995)

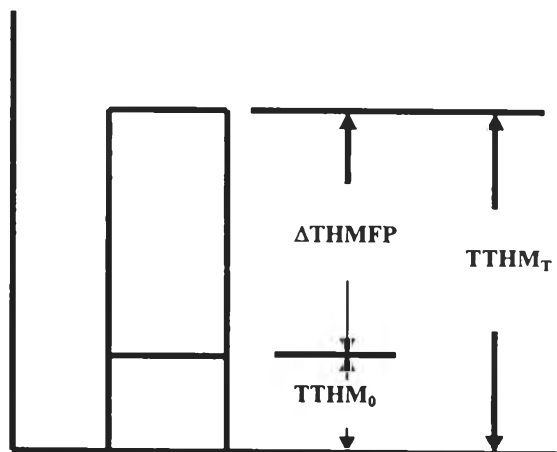


TTHM Concentration



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

TTHM Concentration



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

Suporn Sakomarun (1987) did a comparative study of THMs content in water as a result of pre-chlorination and post chlorination and a study the relationship between TOC and THMs produced. Water samples from 4 sources, Chao Phraya River in Bangkok and in Ayudtaya Province, Klong Prapa at Samsen and Bangken were collected and added chlorine dosage of 3, 5, 7, 10, 15, and 20 ppm. under contact time of 1, 3, 6,12, and 24 h. THMs concentration were analyzed before and after chlorination. Headspace method and Gas Chromatography with Electron Capture Detector (GC/ECD) were used to analyze THMs. The results showed that THMs concentration in treated water with post chlorination were significantly less than those of with pre-chlorination. Coagulation by alum could reduce TOC and THM by 34.30 and 47.86 percent in raw water, respectively.

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

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

## 2.4 Factors Influencing THMs Formation

Factors influencing THMs formation are listed as follow:

### 2.4.1 Contact Time

Department of Environmental and labor (2000), proposed that chlorine efficiency increased as contact time increased. Samorn Muttamara (1995) illustrated the reaction rate for the formation of total THM from the chlorination of filtered water. In the case of chlorine dose 7 mg/l and 10 mg/L, the 100 µg/L permissible limit was reached after 11- hour and 6- hour A.A Stevens et al. (1976), demonstrated the effect of reaction time to chloroform and TTHM. The result showed that chloroform and TTHM increased as reaction time increased.

### 2.4.2. Chlorine or Disinfectant Dosage

Department of Environmental and labor (2000), showed that chlorine efficiency increased as chlorine dose increased. Natural Environmental board, (1984), illustrated the relationship between chloroform level in water distribution system and chlorination rate. The chloroform level increased from 20 µg/L to 220 µg/L after chlorine dose was varied from 4mg/L to 30 mg/L. At chlorine dosage 22 mg/L, chloroform level was the highest. R. Rhodes Trussell (1978), reported effected of chlorine dose on THM formation. Different chlorine concentration between 1 and 80 mg/L were added into synthetic water, with TOC of approximately 0.2 mg/L. In the region of low concentration of chlorine, THMs were inefficiently formed. After the region of low concentration, THMs rapidly developed. After chlorine concentration about 20 mg/L, a substantial Cl<sub>2</sub> residual developed, however THMs development were curtailed.

### 2.4.3 Turbidity

Department of Environmental and labor (2000), illustrated that chlorine efficiency increased as turbidity was decreased. This is attributed to the fact that turbidity interfered with the interaction between chlorine and substances in water.

#### **2.4.4 Water Temperature**

Department of Environmental and labor (2000), presented that chlorine efficiency increased as water temperature increased. A.A Stevens et al (1976), demonstrated chloroform production at 3, 25 and 40 °C. in case of high temperature such as 40 °C and long contact time, the concentration of chloroform was approximately 150 – 225 µg/L occurred.

#### **2.4.5 pH**

R. Rhodes Trussell (1978) demonstrated that a THM reduction of well over 50 percent can be obtained by reducing the pH to 7. Natural Environmental Board, (1984), proposed the effect of reaction pH on the chloroform production. Under the condition of temperature, TOC and chlorine dose were constant. Chloroform concentration decreased as pH value decreased. A.A Stevens et al (1976), illustrated effect of pH on trihalomethane production. In case of 1 mg/L Humic acid, chlorine dosage 10 mg/L, and temperature 25 °C, THMs concentration under the condition of pH values from 3.4 to 9.2 were in order concentration from at pH 9.2, 6.2, 5.2, and 3.4 respectively.

#### **2.4.6 Precursor Concentration**

Natural Environmental Board, (1984), demonstrated the relationship between TOC in raw water and total THM concentration after chlorination. Under the condition of chlorine dosage 10 mg/L and temperature 20 °C with contact time 24 hour , the results showed that Total THM concentration increased as TOC increased. In the result, Total THM concentration ranged from 1 to 250 µg/L while TOC ranged from 1 to 11 mg/L.

## 2.5 Trihalomethane Precursors

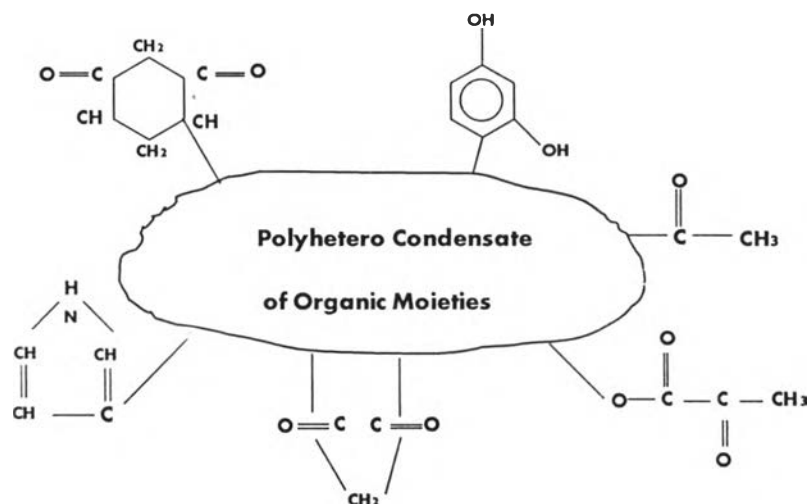
### 2.5.1 Natural Organic Matter(NOM)

NOM is the term used to describe the complex mixture of organic material in natural water. NOM can react with chlorine in chlorination process to form disinfection by-product (DBPs). NOM can be separated 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 the term of chemical properties and implication for water treatment, the humic substance is the most important. (Owen, 1995)

NOM is both hydrophobic and hydrophilic in nature, however, hydrophobic acid, which consist of humic and fuvic acid (aquatic humic) that cause natural color, is the most important. (J.K.Edzwald., 1993)

The molecular weight of fuvic acids typically range from 500 and 2,000 a.m.u. (Thurman, 1985; Amy et. al., 1992). Fuvic acids have a higher charge density and are less amenable to coagulation by charge neutralization. (Amy et al., 1992). Fuvic acid are also more prevalent and more soluble than humic acids. The SUVA of fuvic acid at 254 nm ranges from 2.9 to 4.3 L/mg-m. Humic acids have a molecular weight greater than 2,000 a.m.u. and usually less than 100,000 a.m.u. The SUVA of humic acids ranges from 4.8 to 7.4 L/mg-m (Reckhow et al., 1990)

Trussell and Umphres (1978) demonstrated model of humic compound which are shown in Figure 2.5.



**Figure 2.5.** Model humic compound

(Source; Kavanaugh., 1978)

Marhaba and Washington (1998) presented that NOM contained precursors for disinfection by-products formation during water treatment disinfection operation. Furthermore, humic substances were characterized by non specific parameters, which were based on their organic carbon content (i.e., total organic carbon, TOC), their ability to absorb UV light at 254 nm (i.e., UV 254), and their potential to form trihalomethanes (i.e., trihalomethanes formation potential, THMFP). Fluorescence spectroscopy in UV-visible wavelength range also had become a useful technique to characterize NOM.

Leenheer et al., (1982), Leenheer and Noyes, (1984) and Reckhow et. at., (1992), proposed natural organic matter fraction and chemical group, which are shown in Table 2.6.

**Table 2.2** Natural organic matter fractions and chemical groups.

Fraction	Chemical group
<u>Hydrophobic</u>	
<u>Acids</u>	
Strong	Humic and fuvic acid, high MW alkyl monocarboxylic and dicarboxylic acids, aromatic acids Phenols, tannins, intermediate MW alkyl
Weak	monocarboxylic and dicarboxylic acids, aromatic acids
<u>Bases</u>	Proteins, aromatic amines, high MW alkyl Amines
<u>Neutrals</u>	Hydrocarbon, aldehydes, high MW methyl ketones and alkyl alcohols, ethers, furan, pyrrole
<u>Hydrophilic</u>	
<u>Acids</u>	Hydroxy acids, sugars, sulfonics, low MW alkyl monocarboxylic and dicarboxylic acids
<u>Bases</u>	Amino acids, purines, pyrimidines, low MW alkyl amines
<u>Neutrals</u>	Polysaccharides; low MW alkyl alcohols, aldehydes and ketones

(Sources: Leenheer et al., 1982; Leenheer and Noyes, 1984; and Reckhow et al., 1992)

Samorn Muttamara (1995) illustrated the effect of humic acid on THM formation. Humic acid concentration 3, 5, and 10 mg/L at chlorine dose 3, 5, and 10 mg/L were utilized in the study. It can be concluded that due to the same initial chlorine dosage, higher THM formation was formed at higher concentration of humic acid.

### 2.5.2 Surrogate Parameter for NOM

To describe the characteristic of NOM, surrogate parameters must be used because no single analytical technique is capable of measuring the widely varied characteristics of NOM. Commonly used NOM surrogates include TOC, Dissolve Organic Carbon (DOC), ultraviolet absorbance at wavelength of 254 nm (UV- 254) and THMFP. Moreover, THMFP removals are also present to highlight any difference between TOC and THMFP removals (USEPA, 1999)

Edzwald, Becker and Wattier, (1985) demonstrated surrogate measurements of water quality for potable water treatment, which is shown in Table 2.7

**Table 2.3** Surrogate measurements of water quality for potable water treatment

Surrogate Parameter	Measurement
Turbidity	Surrogate measure of suspended particles; standard of 1 ntu; traditional parameter to measure water plant performance
Color	Surrogate measure of humic matter; secondary standard of 15 Pt-co units; no standard instrument method of measurement; traditional aesthetic parameter
Coliform	Indicator or surrogate measure of pathogenic microorganisms
TOC	Collective or group measure of organic matter; no standard or criterion
TTHMFP	Indirect measure of THM precursors; no standard on precursors; standard on THMs formed
UV(254nm) absorbance	Surrogate measure of TOC and THM precursors

(Source; Edzwald, Becker and Wattier., 1985)

It was not practical to analyze each individual chemical compound in NOM, consequently, NOM was evaluated in term of surrogate parameters as follow;



### 2.5.2.1 Total Organic Carbon(TOC)

The organic carbon in water and waste water is composed of a variety of organic compounds in various oxidation states. Nevertheless, TOC is independent of oxidation state of organic matter and does not measure other organically bound element such as hydrogen, nitrogen, and inorganic. TOC is defined as all carbon atom covalently bonded in organic molecules. (Standard method 1995)

Issam N Najm (1994) found that from many research projects the percentage of THMFP reduction upon coagulation has normally been slightly higher than the percentage of TOC reduction.

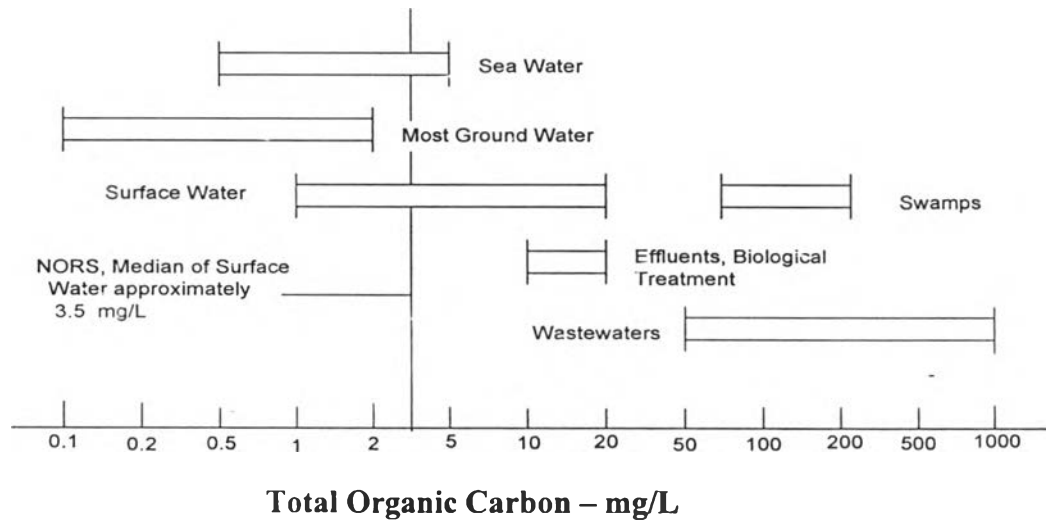
For removal of DBPPs, TOC is commonly used as a surrogate parameter for DBPPs. Consequently, the percentage of TOC removal is correlated to the percentage of DBPPs removal. Moreover, USEPA proposed the percentage of TOC required for enhanced coagulation and softening. It will depend upon the TOC and alkalinity concentration in raw water. The details are shown in Table 2.4 (USEPA, 1999)

**Table 2.4** Percentage of TOC removal 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

\* System which softening must achieve the percentage removals in this column  
(Source; USEPA 1999)

Kavanaugh (1978) demonstrated range of TOC for a variety of natural water, which is shown in Figure 2.6



**Figure 2.6** Range of TOC reported for a variety of natural water.

### 2.5.2.2 Dissolve Organic Carbon (DOC)

Dissolve organic carbons are defined as the fraction of TOC that passes through a 0.45- $\mu$ m-pore-diam filter. (Standard method, 1995)

Organic carbon in natural water can be composed in two fraction, particulate organic carbon (POC) and dissolve organic carbon (DOC), Normally DOC is operationally defined as passing a 0.45  $\mu$ m. (J.K. Edzwald, 1993). In surface water, between 50 and 60 % of humic substances are DOC (Thurman, 1985)

### 2.5.2.3 UV Absorbance at Wavelength 254 nm (UV- 254)

Organic compounds that are aromatic or that have conjugated double bonds absorb light in the ultraviolet (UV) wave length region. Therefore, UV absorbance is a well known technique for measuring the presence of naturally occurring organic matter such as humic substances. Nevertheless, some types of organic compound such as simple aliphatic acids, alcohol and sugar do not absorb UV light. Moreover, pH also affects UV absorbance. UV absorbance increased as pH value increased. (Edzwald, Becker and Wattier., 1985)

Humic substrates strongly absorb ultraviolet (UV) radiation. Therefore, UV adsorbtion was a useful surrogate measurement for NOM or precursor of THMs. The wavelength of 254 nm was the standard wavelength that minimizes interferences from others compounds with maximum adsorption by the interest compound. (Andrew Eaton 1995)

The ratio between UV absorbance in TOC, referred to as specific absorbance (SUVA) ( $\text{cm}^{-1}\text{mg}^{-1}\text{L}$ ), demonstrated a relative index of humic content (Owen et al. 1993). Specific adsorbance suggested the nature of NOM and its consequent THM formation (Krasner et al 1996). Higher specific adsorbance values tended to indicate higher humic content. Specific adsorbance of humic samples depended upon the molecular weight of the substances. (Pettersson et al. 1994)

Issam N Najm (1994) demonstrated that from many research projects the percentage of TTHMFP reduction upon coagulation has normally been slightly lower than percentage of UV-254 reduction.

## **2.6 Removal of THMs Precursors by Coagulation**

### **2.6.1 Coagulation, Flocculation, Sedimentation and Filtration**

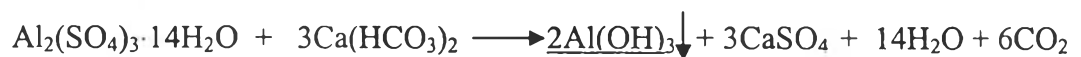
The term “Coagulation” is the addition and rapid mixing of coagulants to destabilize the colloidal and fine suspended solids. Initial aggregation of the destabilized particles occurs in this process. Flocculation is the slow stirring or gentle agitation to aggregate the destabilized particles and form a rapid settling floc. Sedimentation is solid-liquid separation ulilizing gravitational settling to remove suspended solids. It is commonly used in water tratment plants for settling of coagulated and flocculated waters to rapid sand filtration. Filtration is a solid liquid separation in which the liquid passes through a porous medium or other porous material to remove as much fine suspended solid as possible. In water treatment, it is used to filtrate settled waters to produce high-quality water. (Reynolds and Richards., 1996)

Coagulation is typically used for treating drinking water including metal-salts coagulants such as alum, ferric chloride and ferrous sulfate, polymerized metal-salt coagulants such as polyaluminium chloride (PACl), and organic polymers that may be cationic, anionic and noionic. This coagulation not only destabilizes particles, but also removes a fraction of natural organic matter present in natural water.

## 2.6.2 Coagulants

### 2.6.2.1 Aluminum Sulfate

Normally, sufficient alkalinity must be present in water to react with aluminium sulfate to produce the hydroxide floc. Usually, for the pH ranges involved, the alkalinity is in the form of the bicarbonate ion. The simplified chemical reaction to produce the floc is



In the case of water that may not have sufficient alkalinity to react with alum, alkalinity must be added. Usually alkalinity in the form of the hydroxide ion is added by the addition of calcium hydroxide (slaked or hydrated lime). The coagulation reaction with calcium hydroxide is



Alkalinity may also be added in the form of carbonate ion by the addition of sodium carbonate (soda ash). Most water has sufficient alkalinity, so no chemical needs to be added other than aluminium 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 common. The dry chemical may be in granular, powdered, or lump form, the granular being the most widely used. The granulars, which are 15 to 22 %  $\text{Al}_2\text{O}_3$  contain approximately 14 water of crystallization, weight from 60 to 63 lb/ft<sup>3</sup> (Reynolds and Richards, 1996)

### 2.6.2.2 Ferric Chloride

The simplified reaction of ferric chloride with natural bicarbonate alkalinity to form ferric hydroxide is



If the natural alkalinity is insufficient for the reaction, slaked lime may be added to form the hydroxide, as given by the equation.



The optimum pH range for ferric chloride is from about 4 to 12. The floc formed is generally a dense, rapid settling floc. Ferric chloride is available in dry or liquid form. The dry chemical may be in powder or lump form, lump form being more common. The lump, which is 59 to 61% ferric chloride, contains six waters of crystallization and weight from 60 to 61 lb/ft<sup>3</sup> (960 to 1026 kg/m<sup>3</sup>). The powdered or anhydrous form is 98% ferric chloride, contains no water of crystallization, and weight from 85 to 90 lb/ft<sup>3</sup> (1360 to 1440 kg/m<sup>3</sup>). The liquid form is 37 to 47% ferric chloride. (Reynolds and Richards., 1996)

### 2.6.2.3 Ferric Sulfate

The simplified reaction of ferric sulfate with natural bicarbonate alkalinity to form ferric hydroxide is



The reaction usually produces a dense, rapid-settling floc. If the natural alkalinity is sufficient for the reaction, slaked lime may be used instead. The optimum pH range of ferric sulfate is from about 4 to 12. Ferric sulfate is available in dry form as granules or as a powder, the granule being the more common. The granules are 90 to 94 % ferric sulfate, contain nine waters of crystallization, and weigh from 70 to 72 lb/ft<sup>3</sup> (1120 to 1155 kg/m<sup>3</sup>) (Reynolds and Richards., 1996)

#### 2.6.2.4 Ferrous Sulfate

Ferrous sulfate requires alkalinity in the form of hydroxide ion in order to produce a rapid reaction. Consequently, slaked or hydrated lime,  $\text{Ca}(\text{OH})_2$ , is usually added to raise the pH to a level where the ferrous ions are precipitated as ferric hydroxide. This reaction is an oxidation-reduction reaction requiring some dissolved oxygen in water. In the coagulation reaction, the oxygen is reduced and the ferrous ion is oxidized to the ferric state, where it precipitates as ferric hydroxide. The simplified reaction is



For this reaction to occur, the pH must be raised to about 9.5, and sometimes stabilization is required for excess lime employed. Ferrous sulfate and lime coagulation is usually more expensive than alum. In general, when the precipitate is formed, ferric hydroxide, is a dense, quick settling floc. Ferrous sulfate is available in dry and liquid form; however, the dry is more common. The dry chemical may be granules or lumps, the granules being more common widely used. The granules, which are 55 % ferric sulfate, common seven water of crystallization, weight from 63 to 66 lb/ft<sup>3</sup> (1010 to 1060 kg/m<sup>3</sup>). (Reynolds and Richards., 1996)

#### 2.6.2.5 Characteristics of Metal hydrolysis Product

When metal-salt coagulants are added to water, it undergoes a series of hydrolysis reaction, resulting in the formation of variety of monometric and polymeric metal hydroxide species, the release of proton (which lower pH) and, if the dosage is sufficient, the precipitation of metal hydroxide solids. The relative amount of each species is depend on the coagulant dosage, solution pH, the initial alkalinity, temperature, the ionic composition of the water, and the type and concentration of organic matter present (AWWA, 1999)

The distribution of metal-salt hydrolysis products may be summarized graphically, as a function of pH, in which known as a pC-pH diagram, as shown in Figure 2.7 and 2.8 for alum and iron respectively. Figure 2.7 and 2.8 were constructed using the values list by Amirtharajah and O, Melia (1990) and ignoring organic complexes.

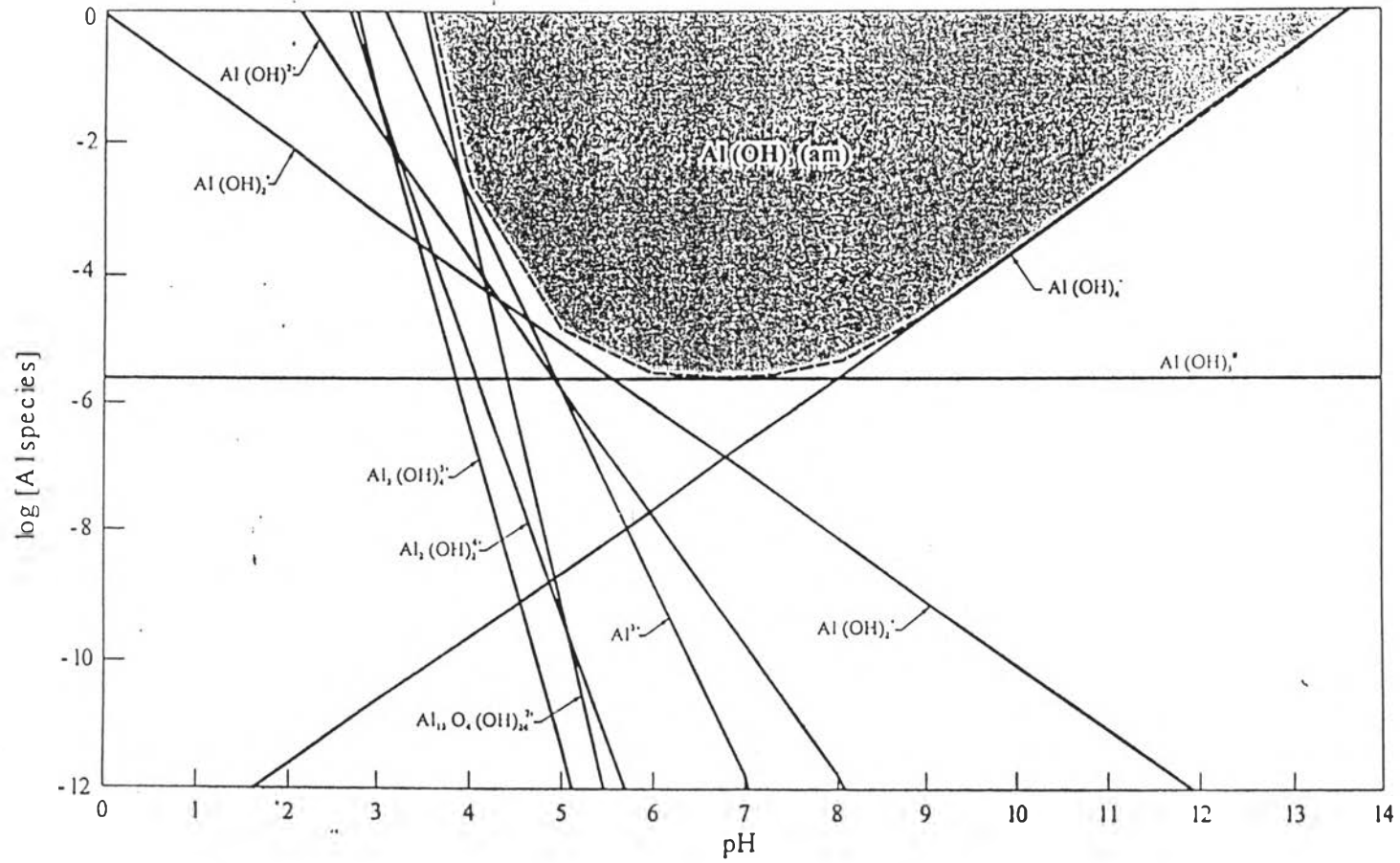


Figure 2.7 The pC-pH diagram for aluminum hydroxide

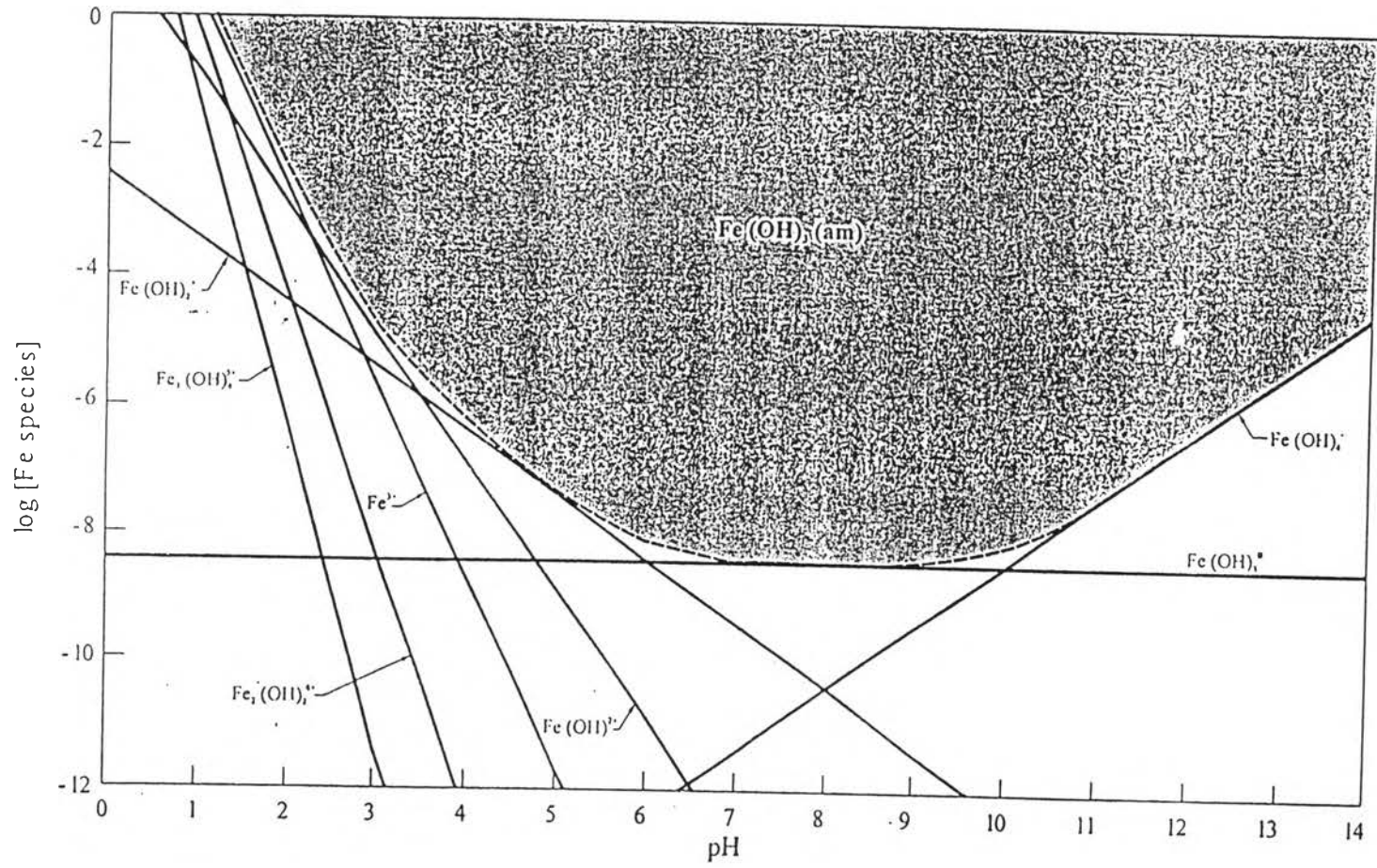


Figure 2.8 The pC-pH diagram for ferric hydroxide



## 2.6.3 The Ability of Coagulants Used to Remove THMs Precursor

### 2.6.3.1 THMs Precursor Removal by Aluminum Sulfate Coagulation

Oliver and Lawrence (1978) showed 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) demonstrated that coagulation with an alum dosage of 25 mg/L reduced the THMFP of North Carolina water by 60 percent.

Chadik and Amy (1983) removed trihalomethanes precursors from various natural waters by alum and ferric chloride. The experiment was conducted in two pH condition. First condition was conducted at ambient pH value (8.5). The others were conducted at modified pH value (6.0). The results indicated that TOC and THMFP decrease as a function of coagulation dosage. For Mississippi River Water, the untreated THMFP of 313  $\mu\text{g/L}$  was reduced to 131  $\mu\text{g/L}$  by alum coagulation. The indicated coagulant dosage was 15 mg Al/L.

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

Marhaba and Pipada (2000) determined the maximum removal of NOM in drinking water by coagulation with alum sulfate over a range of pH. Resin adsorption procedures were used to isolate and fractionate NOM into six dissolve organic matter (DOM) fractions; hydrophobic acid (FA), base (FB), neutral (FN), and hydrophilic acid (PA), base (PB), neutral (PN). The results indicated that the maximum TOC reduction occurred at two different dosages for PA, PB, PN and FN fractions at pH 6 and alum dosage 60 mg/L. For FA and FB fraction maximum reduction occurred at pH 6 and alum dosage 40 mg/L.

Hubel and Edzwald (1987) determined the optimum alum dosages for coagulation of Grasse River Water. In case of pH value of 7.2, optimum dose was 65 mg/L and it removed turbidity from 24 to 57 percent, soluble UV-254 from 71 to 74 percent, TOC 53 percent, and TTHMFP 53 percent. In case of pH value of 5.5, optimum dose was 30 mg/L and it removed turbidity from 50 to 67 percent, soluble UV from 82 to 83 percent, TOC 73 percent, and TTHMFP 69 percent.

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

#### **2.6.3.2 THMs Precursor Removal by Ferric Chloride Coagulation**

Chadik and Amy (1983) at Mississippi River Water, the untreated THMFP of 313 ug/L were reduced to 141 ug/L by ferric chloride coagulation. The indicated coagulant dosage was 20 mg Fe/L.

Crozes, White and Marshall (1995) studied TOC removal by alum, ferric chloride and a cationic synthetic polymer. Ferric chloride dosage between 40 and 60 mg/l and pH value between 5.5 and 6 were the optimum condition for TOC removal.

#### **2.6.3.3 THMs Precursor Removal by Polyaluminum Chloride Coagulation**

Fryters, R.E.T. (2001) studied alum and poly-aluminium chlorine (PACl) as the coagulant. 250 ppm. Alum resulted in color and turbidity values reaching standard value, however, the pH adjustment and operating cost forced the operation to change to PACl. The amount of PACl used was only 70 ppm and the result showed that organic carbon was reduced from 0.11 mg/l Ave. to 0.045-mg/l Ave.