CHAPTER II

BACKGROUNDS AND LITERATURE REVIEWS

Disinfection of drinking water using chlorine has been practiced since the early 1900s. In the late 1800s and early 1900s, acute waterborne diseases such as cholera and typhoid fever threatened human health and these were the motivation behind the development of chlorination process. Chlorine has been the most widely used means in many water treatment plants to inactivate microorganisms and maintain a residual concentration through the water distribution system. Despite obvious advantages in terms of controlling microbes in drinking water, chlorination also has disadvantages because of the formation of disinfection by-products (DBPs). In 1974, Rook found that the use of chlorine for disinfection purposes of drinking water leads to the formation of many by-products potentially harmful for human health. Among all the chlorinated by-products, trihalomethanes, which exhibit a potentially carcinogenic activity, are certainly the class of compounds that has been investigated most thoroughly during the last 20 years.

Dissolved organic material can react with chlorine during water disinfection for potable supply to form trihalomethanes (THMs, haloforms). For effective disinfection an excess of chlorine over the sample consumption is needed and this free chlorine can react with organic compounds present in the water during storage or distribution of the treated water.

2.1 Disinfection by-product (DBPs)

The first DBPs to be identified are trihalomethanes (THMs) and are usually the most abundant DBPs found in drinking water. DBPs do not only include trihalomethane but also haloacetic acids (HAAs), haloacetonitrites (HANs) and haloketones (HKs).

Table 2.1: List of DBPs

Disinfection by-product (DBPs)	Formula
Trihalomethanes (THMs)	
Chloroform	$CHCl_3$
Bromodichloromethane	$CHCl_2Br$
Dibromochloromethane	$CHClBr_2$
Bromoform	$CHBr_3$
Haloacetic acids (HAAs)	
Monochloroacetic acid	$CH_2ClCOOH$
Dichloroacetic acid	$CHCl_2COOH$
Trichloroacetic acid	CCl_3COOH
Monobromoacetic acid	$CH_2BrCOOH$
Dibromoacetic acid	$CCl_3CH(OH)_2$
Haloacetonitrites (HANs)	
Dichloroacetonitrite	$C_2HNClBr$
Bromochloroacetonitrite	C_2HNBr_2
Dibromoacetonitrite	C_2HNCl_2
Trichloroacetonitrite	C_2NCl_3
Haloketones (HKs)	
1,1-Dichloropropanone	$C_3H_4Cl_2O$
1,1,1-Trichloropropanone	$C_3H_3Cl_3O$

2.1.1 Chemistry of THMs

Trihalomethanes (THMs) are halogen-substituted single-carbon compounds with a general formula of CHX_3, where X may be fluorine, chlorine, bromine, iodine, or combinations thereof. THMs are a group of organic chemicals formed in water when chlorine reacts with natural organic matters (such as humic acids from decaying vegetation). Classical trihalomethanes consist of chloroform

(CHCl₃), dichlorobromoform (CHCL₂Br), dibromochloroform (CHBr₂Cl), and bromoform (CHBr₃).

2.1.1.1 Chloroform

Chloroform not only causes the depression of the central nervous system, but also hepatotoxicity, nephrotoxicity, teratogenicity, and carcinogenicity (USEPA, 1998). The basic chemical and physical characteristics of chloroform or trichloromethane ($CHCL_3$) are shown in Table 2.2 and its chemical structure is as follows:
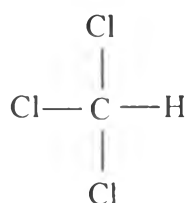
$$Cl—\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}—H$$

Table 2.2: Basic chemical and physical characteristics of chloroform

Characteristics	Value
Empirical Formula	$CHCl_3$
Molecular weight (g/mol)	119.37
Specific gravity (g/cm³)	1.472
Boiling point (°C)	61
Melting point (°C)	-63
Solubility in water	8.1

(Source: Ghazali, 1989)

2.1.1.2 Bromodichloromethane

The basic chemical and physical characteristics of bromodichloromethane or dichlorobromomethane ($CHCl_2Br$) are shown in Table 2.3 and its chemical structure is as follows:
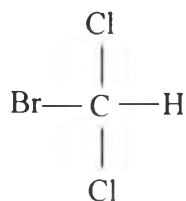
$$Cl$$
$$|$$
$$Br\text{—}C\text{—}H$$
$$|$$
$$Cl$$

Table 2.3: Basic chemical and physical characteristics of bromodichloromethane

Characteristics	Value
Empirical Formula	$CHCl_2Br$
Molecular weight (g/mol)	163.82
Specific gravity (g/cm^3)	1.472
Boiling point (°C)	90.1
Melting point (°C)	-57.1
Solubility in water	Insoluble

(Source: Ghazali, 1989)

2.1.1.3 Dibromochloromethane

The basic chemical and physical characteristics of dibromochloromethane or chlorodibromomethane ($CHClBr_2$) are shown in Table 2.4 and its chemical structure is as follows:
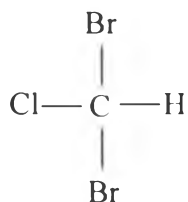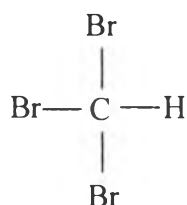
$$Br$$
$$|$$
$$Cl\text{—}C\text{—}H$$
$$|$$
$$Br$$

Table 2.4: Basic chemical and physical characteristics of dibromochloromethane

Characteristics	Value
Empirical Formula	$CHClBr_2$
Molecular weight (g/mol)	208.29
Specific gravity (g/cm^3)	2.38
Boiling point (°C)	120
Melting point (°C)	-63
Solubility in water	4.75

(Source: Ghazali, 1989)

2.1.1.4 Bromoform

The basic chemical and physical characteristics of bromoform, tribromomethane, or methyl tribromide ($CHBr_3$) are shown in Table 2.5 and its chemical structure is as follows:

$$\begin{array}{c} Br \\ | \\ Br - C - H \\ | \\ Br \end{array}$$

Table 2.5: Basic chemical and physical characteristics of bromoform

Characteristics	Value
Empirical Formula	$CHBr_3$
Molecular weight (g/mol)	257.73
Specific gravity (g/cm^3)	2.894
Boiling point (°C)	150
Melting point (°C)	8.3
Solubility in water	Insoluble

(Source: Ghazali, 1989)

2.1.2 Toxicity of Disinfection By-Products

The chemical risks associated with disinfected drinking water are potentially based on several routes of exposure: (i) ingestion of DBPs in drinking water; (ii) ingestion of chemical disinfectants in drinking water and the concomitants formation of DBPs in the stomach; and (iii) inhalation of volatile DBPs during showering.

Human exposure is a function of both DBP concentration and exposure time. More specifically, human health effects are a function of exposure to complex of DBPs (e.g., THMs versus HAAs, chlorinated versus brominated species) that can change seasonally/temporally (e.g., as a function of temperature, nature, and concentration individual chemical disinfectant can form a mixture of DBPs; combinations of chemical disinfectants can form even more complex mixtures.

The THMs have been shown to have both genotoxic and carcinogenic effects particularly in the liver and kidney. Because the four compounds usually occur together, it has been the practice to consider these as a group and a number of countries have set potable quality guidelines on this basis. However, the WHO guideline values for water disinfection products are now set separately at 200 µg/L for chloroform, 100 µg/L for bromoform and dibromochloroform and 60 µg/L for dichlorobromoform (WHO, 1993)

A recently reported cohort study found an increased risk of early miscarriage associated with heavy consumption of water (five or more glasses of cold tap water per day) containing high levels ($\geq$ 75 µg/L) of THMs. When specific THMs were considered, only heavy consumption of water containing bromodichloromethane ($\geq$ 18 µg/L) was associated with a risk of miscarriage. This is the first study to suggest an adverse reproductive effect associated with a brominated by-product, a scientific panel recommended that another study be conducted in a different geographic area to attempt to replicate these results and that additional efforts be made to evaluate exposures of the cohort to other water contaminants

Breathing about 900 ppm of chloroform for a short time can cause dizziness, fatigue and headache. Breathing air, eating food, or drinking water containing high levels of chloroform for long periods of time many damage the liver and kidneys. Moreover, animal studies have shown that miscarriages occurred in rats and mice that breathed air containing 30 to 300 ppm chloroform during pregnancy and also in rats that ate chloroform during pregnancy. Offspring of rats and mice that breathed chloroform during pregnancy has birth defects. Abnormal sperm were found in mice that breathed air containing 400 ppm chloroform for a few days.

Animal studies indicate that the liver, kidney, and central nervous system are affected by exposure to bromodichloromethane. There is evidence that eating or drinking bromodichloromethane causes liver, kidney and intestinal cancer in rats and mice. The Department of Health and Human Services (DHHS) has determined that bromodichloromethane is reasonably anticipated to be a human carcinogen. The effects of high doses on the central nervous system include sleepiness and incoordination. Longer exposure to lower doses causes damage to the liver and kidneys. There is some evidence from animal studies that bromodichloromethane may cause birth defects at doses high enough to make the mother sick. It is not known if lower doses would cause birth defects.

Several recorded cases of overdose of bromoform indicate that high doses affect the central nervous system causing unconsciousness, loss of reflexes, shallow breathing, constricted pupils, and tremors. Animal studies indicate that the liver, kidney, and central nervous system are affected by exposure to bromoform and chlorodibromomethane. The effects on the central nervous system appear quickly after exposure to high doses and include labored breathing, incoordination, sedation, and death. Longer-term exposure to lower doses causes drowsiness, increased liver weight, and liver and kidney damage.

The health effects of THMs have been investigated. Table 2.6 summarises the health effects in accordance with the classification scheme described by Table 2.7. Note that EPA is in the process of revising the Cancer Guidelines (USEPA, 1996)

Table 2.6: Cancer classification of THMs

Substance	cancer classification*
Chloroform	B_2
Bromodichloromethane	B_2
Dibromochloromethane	C
Bromoform	B_2

*Based on inhalation exposure

Table 2.7: Scheme for categorizing chemicals according to carcinogen potential

Group	Classification	Definition
A	Human carcinogen	Sufficient evidence in epidemiologic studies to support causal association between exposure and cancer.
B	Probable human carcinogen	Limited evidence in epidemiologic studies (Group B1) and/or sufficient evidence from animal studies (Group B2).
C	Possible human carcinogen	Limited evidence from animal studies and inadequate or no data in human.
D	Not classifiable	Inadequate or no human animal evidence of carcinogenicity.
F	No evidence of human	No evidence of carcinogenicity in at least two adequate animal tests in different species or in adequate epidemiology and animal studies carcinogenicity.

2.1.3 Regulations

As part of the 1986 amendments to the Safe Drinking Water Act, the United State Environmental Protection Agency (USEPA) has proposed the Disinfectants/Disinfection By-Products (D/DBP) Rule in two stages. Stage 1 of the D/DBP rule was promulgated in December 1998 (USEPA, 1998). It lowered the total

trihalomethane (THM) maximum contaminant level (MCL) from 0.100 to 0.080 mg/L and provided MCLs for three other classes of DBPs : the sum of the five haloacetic acids (HAA5, mono-, di-, trichloroacetice acids, monobromo-, and dibromoacetic acid) at 0.060 mg/L, bromate ion at 0.010mg/L and chlorite ion at 1.0 mg/L. stage 1

of the rule also sets maximum residual disinfectant levels (MRDL) for three disinfectants: chlorine at 4 mg/L, chloramines at 4 mg/L, and chlorine dioxide at 0.8 mg/L. Stage 2 regulations are anticipated to be even more stringent (e.g. anticipated total THM MCL to be 0.040 mg/L and HAA5 MCL to be 0.030 mg/L (Marhaba and Van, 2000). Table 2.8 shows the MCLs and MCLG that relate to THMs.

Table 2.8 National Primary Drinking Water Regulation Establishing Maximum Contaminant Levels (MCLs) and Maximum Contaminant Level Goals (MCLGs) Related to THMs

Compound	MCLG (mg/L)	MCL (mg/L)	Potential health effects	Sources of drinking water contamination
Chloroform	Zero	See TTHMs	Cancer, liver, kidney, reproductive effects	Drinking water chlorination and chlorination by-product
Bromodichloromethane	Zero[b]	See TTHMs	Cancer, liver, kidney, reproductive effects	Drinking water chlorination and chloramination by-product
Dibromochloromethane	0.6[a]	See TTHMs	Nervous system, liver, kidney, reproductive effects	Drinking water chlorination and chloramination by-product
Bromoform	Zero[a]	See TTHMs	Cancer, nervous system, liver, kidney effect	Drinking water ozonation, chloramination, and chlorination by-product
Total trihalomethanes (TTHMs)[c]	N/A	0.08[b]	Cancer and other effects	Drinking water chlorination and chloramination by-product

Source: 63 Federal Register 69390
  a Finalized on December 16, 1998 (63 Federal Register 69390) as established in 40 CFR 141.53.
  b Finalized on December 16, 1998 (63 Federal Register 69390) as established in 40 CFR 141.64
  c Total Trihalomethanes are the sum of the concentrations of bromodichloromethane, dibromochloromethane, bromoform and chloroform expressed in mg/L

2.1.4 Trihalomethane Formation Potential

Definition of Terms

Total trihalomethane ($TTHM_T$) is the sum of all four THM compound concentrations produced during period T (usually day).

$TTHM_0$ is the total THM concentration at the time of sampling. $TTHM_0$ concentration can range from non-detectable, which usually means the sample has not been chlorinated, to several hundred micrograms per liter if the sample has been chlorinated.

$TTHM_7$ is the sum of all four THM compound concentrations produced during reactions of sample precursors with excess free chlorine over a 7-d reaction time.

Trihalomethane formation potential (THMFP or ΔTHMFP) is the difference between the final $TTHM_T$ concentration and the initial $TTHM_0$ concentration. Figure 2.1 illustrate the relationships between definitions used in the formation potential test, for a sample that did not contain free chlorine at the time of sampling. Total THM concentration at the time of sampling ($TTHM_0$) was very close to or equal to zero; therefore, the THM formation potential for the 7-d reaction time (THMFP, with a free chlorine residual of at least 3 mg/L.) was essentially equal in the total THM concentration in the sample at the end of the reaction storage time (TTHM) (USEPA, 1998).
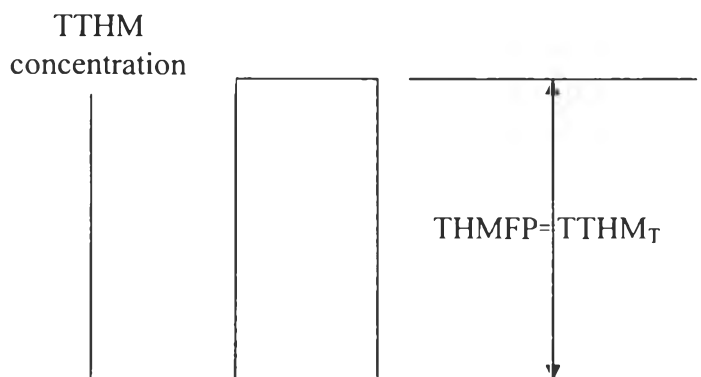
TTHM
concentration

$THMFP = TTHM_T$

Figure 2.1: Relationships between definitions used in the formation potential test, for a sample that did not contain free chlorine at the time of sampling.

Figure 2.2 Relationships between definitions used in the formation potential test, for a sample that already contained free chlorine at the time of sampling. Total THM concentration at the time of sampling ($TTHM_0$) was a significant fraction of the final value obtained after 7-d storage ($TTHM_7$) with an excess of at least 3 mg/L free chlorine. $\Delta THMFP$ is the difference between these two values(USEPA, 1998).
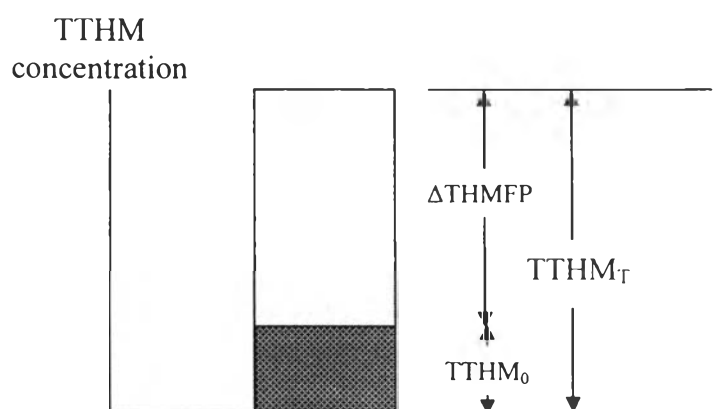
TTHM
concentration

$\Delta THMFP$

$TTHM_T$

$TTHM_0$

Figure 2.2: Relationships between definitions used in the formation potential test, for a sample that already contained free chlorine at the time of sampling.

2.1.5 Factors effecting THM formation.

Previous studies have shown the importance of m any parameters for the formation of THMs, such as dose of chlorine, reaction time, concentration of bromide and ammonia, pH, temperature, concentration and type of the organic precursor compound (Gallard and Gunten, 2002; Trussell and Umphres, 1978; Peter et al., 1980; Alawi, Khalill, and Sahili, 1994) The general reaction of DOM with chlorine, which produces THMs and other DBPs, is as follow:

DOM + free chlorine $\rightarrow$ THMs + HAAs + cyanogen halide + other DBPs.

It i s k nown t hat d ifferent n atural w aters m ay v ary s ignificantly w ith respect to concentration and type of precursors to form THMs. Therefore, different natural waters and humic materials were studied with respect to THM formation at pH 7(Gallard and Gunten, 2002).

2.1.5.1 Natural organic matter and UV absorbance at 254 nm

NOM consists of a mixture of humic substances (humic and fluvic acids) and non-humic (hydrophilic) material. Both the amount (as indicated by TOC or UVA_{254}) and the character (as described by UV-254) of NOM can affect DBP formation. NOM provides the precursor material from which organic DBPs are formed; consequently, increasing concentrations of NOM lead to increasing concentrations of by-products. This relationship has led to the use of TOC and UV-254 measurements as surrogate parameters for estimating the extent of DBP formation.

In an investigation of the nature of humic and fulvic acids isolated from a variety of natural waters, (Reckhow, Singer, and Malcolm (1990) found that the fulvic fractions had a lower aromatic content and smaller molecular size than the humic fractions. UV absorbance was correspondingly higher for the humic fractions, owing to the higher aromatic content and larger size. Support from other researchers shows that the UV absorbance measurement is an indicator of the

nature of the precursor material present in a sample. This measurement, in conjunction with the TOC or DOC measurement, can be employed in the evaluation of data to provide an indication of the reactivity of NOM towards forming DBPs.

2.1.5.2 pH

The impact of pH on THM concentration has been reported by a number of water of industry researchers (Stevens, Slocum, Seeger, et al., 1976; Lange and Kawczynski, 1978; Trussell and Umphres, 1978). More recently, the impact of pH on a number of other chlorination by-products has been reported (Miller and Uden, 1983; Reckhow and Singer, 1985). The rate of THM formation increases with pH (Stevens, Slocum, Seeger, et al., 1976).

In general, increasing pH has been associated with increasing concentrations of THMs and decreasing concentrations of HAAs. Carlson and 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.

Nieminski, Chaudhuri, and Lamoreaux (1993) reported that treatment plants with a pH of about 5.5 in finished water produced equal amounts of THMs and HAAs, whereas plants with pHs greater than 7.0 in finished water produced higher amounts of THMs as compared with HAAs.

2.1.5.3 Bromide

The presence of bromide ions during water disinfection can lead to the formation of DBPs such as brominated organics and bromate ions. Low

but significant levels of bromide, the ultimate precursor to bromate and other brominated compounds, may occur in drinking-water sources as a result of pollution and saltwater intrusion in addition to bromide from natural sources. An understanding of the sources and levels of bromide ions in different source waters is crucial for and understanding of the bromate ion formation potential in drinking-waters.

The impact of bromide on the speciation of DBPs within a class of compounds such as THMs or HAAs has been discussed by Cooper, Meyer, Bofill et al.(1983) and Cooper, Zika, and Steinhauer (1985) and Amy, Siddiqui, Ozekin et al. (1998). Rook, Gras, Vander Heijden 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 reaction.

Bromide, often present in raw water, from either natural or anthropogenic sources has an important effect on the speciation of any THMs produced. During chlorination, bromide is oxidized by chlorine to bromine and chlorination and bromination become competitive reactions. Bromine appears to be more effective as a halogen substituting agent and, if bromine acts as an oxidant, it will be reduced to the bromide ion, which may then be re-oxidized by chlorine. This results in high bromine incorporation into the THMs and may account for the mutagenic activity of chlorinated waters which cannot be solely ascribed to chloroform (Peter, Wilson, Amy et al.,1993; Stuart, Gooddy, Kinniburgh et al., 2001).

2.1.5.4 Temperature

The formation rates of THMs have been shown to increase with temperature (AWWARF, 1991; Siddiqui and Amy, 1993). The impact of temperature on THMs was strongest at longer contact times (Carlson and Hardy, 1998). On a conceptual basis, it may be that rapidly forming compounds are more reactive and forming compound requires 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.

2.1.5.5. Reaction rate

After chlorine addition, there is a period of rapid THM formation for the initial few hours (e.g., 4 hr), followed by a decline in the rate of THM formation, suggesting fast and slow NOM reactive sites. Many authors have indicated that the concentration of chloroform appears to increase slowly even after 96 hr, 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 off almost completely after 20 hr (AWWARF, 1991; Koch, Kransner, Sclimenti et al., 1991).

2.1.5.6 Disinfectant dose

Chlorine dose is a factor affecting the type and concentration of DBPs formed. The THM levels rise with increasing chlorine dose (Kavanaugh, Trussell, Cromer 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 and Umphres, 1978; Kavanaugh, Trussell, Cromer et al., 1980). However, it is also possible that the order of reaction changes during the course of the reaction.

Reckhow and Singer (1985) found that the concentration of chloroform was about 150 µg/L in a sample dosed with 10 mg of chlorine /L but was approximately 200 µg/L in a sample dosed with 20 mg of chlorine /L. Thus, it is imperative to have uniform chlorine doses for performing DBP formation kinetic measurement.

2.1.6 THMs precursor parameters

In the absence of DBP data, surrogates such as chlorine dose (or chlorine demand), TOC (or ultraviolet absorbance at 254 nm [UV-254]) or bromide can be used to indirectly estimate exposure. While TOC serves as a good surrogate for organic DBP precursors, UV-254 provides additional insight into NOM characteristics, which can vary geographically. Two key water quality variables, pH and bromide, have been identified as significantly affecting the type and concentration of DBPs that are produced.

2.2 Dissolved organic matter

Natural waters used as sources for drinking water supplies contain a variety of types of organic matter. Some of this organic matter comes from natural sources. When organisms die, a mixture of biological and chemical processes takes place. These processes produce a mixture of compounds that are collectively referred to as dissolved organic matter (DOM). DOM can be highly variable, depending on its source and extent of degradation. Many factors besides native flora and fauna influence DOM composition. These include temperature, rainfall/humidity, light, microbial populations and geography. There is a complex interplay among the native flora and fauna as well as the climate and season. There is much interest in understanding the makeup of this material. 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. (Leenheer, Noyes, and Steer et al., 1982). The dissolved organic matter fraction and chemical groups are shown in Table 2.9.

Table 2.9: Dissolved organic matter fraction and chemical group

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

(Sources: Leenheer, Noyes, and Steer, 1982; Leenheer and Noyes, 1984; and Reckhow, Bose, Bexbarua et al., 1992

2.2.1 DOM precursor parameters

In addition, Stage I specifies treatment criteria for background NOM measured as total organic carbon (TOC). Based on the concentrations of source water TOC and alkalinity, a water treatment facility will be required to reduce the TOC concentration before applying chlorine for primary disinfection.

2.2.1.1 DOC and TOC

TOC is a direct measure of water organic carbon content, but it does not provide an indication of the aromaticity, aliphatic nature, functional group chemistry, or chemical bonding associated with natural organic molecules. The

reactivity of chemical bonds and functional groups is likely to be a significant factor in explaining why different waters with the same TOC concentration will form different DBP concentrations under identical disinfection conditions and bromide level (USEPA, 1999).

DOC is also a commonly used surrogate measure of DBP precursor concentrations. DOC is operationally defined as a portion of TOC. Dissolved phase organics may be more reactive than particulate phase organics. Thus, the ration of DOC to TOC may also be considered an important factor in explaining why different waters having the same TOC concentration will form different DBP concentrations under identical disinfection conditions and bromide levels.

If the DOC/TOC ratio is relatively low (i.e. a large amount of organic material is in particulate form), physical processes such as sedimentation and filtration can be expected to remove a significant amount of the organic matter. On the other hand, relatively high DOC/TOC ratio indicates that much of the organic matter is in soluble form. Therefore, other processes such as coagulation, GAC adsorption, and membrane filtration are required to achieve significant removal.

2.2.1.2. Ultraviolet light Absorbance at 254 nm

One of the most commonly used surrogates in drinking water research has been the measurement of water's ability to absorb ultraviolet light at a wavelength of 254 nm (UV-254). UV-254 absorbance indicates the concentration of organic molecules with aromatic groupings or extended conjugation (USEPA, 1999).

Other limitations may also affect the use of UV-254 as an indicator of unit process performance for DBP precursor removal. These limitations primarily result from interference by inorganic species that also absorb ultraviolet light at wavelengths near 254 nm. For instance, monochloramine and dissolved ozone absorb ultraviolet light at wavelengths of 243 nm and 260 nm, respectively. Evaluations of unit process performance for reduction of UV-254 should recognize this potential interference. (USEPA, 1999)

2.2.1.3. Specific Ultraviolet Absorption (SUVA)

SUVA has proven to be a good indicator of the humic content of water (Edzwald and Van Benschoten, 1990). SUVA is defined as UV-254 (measured in m^{-1}) divided by DOC concentration (in mg/L), resulting in SUVA units of L/mg-m. SUVA values of less than about 3 L/mg-m signify water containing mostly non-humic material. SUVA values of 4 to 5 L/mg-m are typical of waters containing primarily humic material (Edzwald and Van Benschoten, 1990).

SUVA can also be predictive of the removal capability of water treatment practices (Edzwald, Becker, and Wattier, 1985). Several studies (Krasner, Amy, and Zhu, 1994; Cheng, Krasner, Green et al., 1995; White, Thompson, Harrington et al., 1997; Chowdhury, Roberson, and Owen, 1990) reported that waters with a high SUVA value exhibited large reductions in SUVA and TOC as a result of enhanced coagulation, indicating an overall substantial removal of NOM. Waters with low SUVA values, however, exhibited relatively low reductions in SUVA and TOC, indicating an overall insignificant removal of NOM

2.2.1.4 Fluorescence spectroscopy

Fluorescence spectroscopy is a promising technique for environmental analyses, among the benefits of fluorescence spectroscopy is the adaptability to field measurements, the high sensitivity to a wide array of potential analyses, and, in general the avoidance of consumable reagents and extensive sample pretreatment.(JiJi, Cooper, and Booksh,1999).

2.3 Resin Fractionation

One of the most widely used methods to characterize DOM is the fractionation according to sorption to XAD-8 resin (Leenheer, 1981). Those compounds sorbing to XAD-8 fall into the so-called hydrophobic fraction whereas those compounds that do not absorb on to XAD-8 are the so-called hydrophilic fraction. The hydrophobic fraction is more refractory and interacts strongly with Al and Fe oxides and

hydroxides and with hydrophobic organic pollutants (Kaiser, Guggenberger, and Zech, 2001 ; Kukkonen, McCarthy, and Oikari, 1990 and Dilling and Kaiser, 2002) whereas the hydrophilic fraction is more susceptible to microbial decay and transports nutrients (Jandi and Sollins, 1997; Qualls and Haines, 1991 and Dilling and Kaiser, 2002).

Resin Fractionation of dissolved organic materials (DOM) in water is a technique to concentrate and categorize the water organic complex into structurally more specific, physiochemically more analogous subgroups by retaining DOMs onto a series of types of resin followed by eluting with elutants. By applying this technique, DOMs of natural water can be characterized into hydrophobics, which mainly consist of fulvic and humic acids, and hydrophilics, which comprise of carbohydrates with low molecular weight, protein and amino acids. Hydrophobic are more structurally aromatic than hydrophilic and more prone to conventional treatment. This technique has been widely applied to investigate various properties of DOM. It has been shown that it greatly facilitates subsequent association with DOM, such as the formation of disinfection by-products (DBPs) (Barrett, Krasner, and Amy, 2000; Marhaba, Pu, and Bengraine, 2003).

2.4 Removal of THM precursor by coagulation

The coagulation of water treatment is traditionally focused on the removal of either color or turbidity. Recently, some water treatment facilities have started to optimize their work purely on the removal of natural organic matter (Chow, Van Leeuwen, Fabris et al., 2000). As most NOM is anionic at the pH of natural water (pH 4-8) it has a strong affinity to cationic additives such as metal coagulants and cationic polyelectrolyte. Consequently, coagulation is regarded as an essential unit process when treating a water source for the removal of organic matter (Lind, 1 995; Volk, Bell, Ibrahim et al., 2000 and Fearing, Goslan, Banks et al., 2004).

Low molecular weight of the organic matter fraction seems to be more difficult to remove Low molecular weight of the organic matter fraction consists mostly from fulvic acids. Fulvic acids are more soluble, smaller in average molecular

weight, and more highly charged than humic acids. Fulvic acids also typically have higher oxygen content, with higher carboxylic acid (COOH) and lower aromatic hydroxyl content than humic acid (Hayes, MacCarthy, Malcolm et al., 1989). They are therefore more difficult to destabilize by aluminium coagulation dosages commonly employed in water treatment (Matilainen, Lindqvist, Korhonen et al.,2002)

Alum coagulation alone was found not to be sufficient to produce microbiologically stable drinking waters. THM formation can be significantly reduced by alum treatment as the likely potential precursors such as aromatic components of DOM are preferentially removed by alum treatment (Page, Van Leeuwen, Spark et.al., 2002).

Bell-Ajy, Abbaszadegan, Ibrahim et al (2000) evaluated the optimized coagulation by jar test using raw waters from 16 water utilities throughout the United States. Parameters such as TOC, DOC, UV-254, turbidity and particle removals were used to identify the optimized treatments from which disinfection by product formation potential (DBPFP) and organic species were evaluated. The result showed that TOC removal was a conservative indicator of DBPFP removals, whereas 254 was an over predictor of the removal of DBPFP. Moreover, the reduction in THM and THMFPs were also observed with enhanced coagulation (Bell-Ajy, Abbaszadegan, Ibrahim et al., 2000).

Coagulation has been shown to remove certain NOM fractions preferentially: humic (hydrophobic) NOM and higher molecular weight NOM are more effectively removed than their counterpart NOM fractions (AWWARF, 1993 and Krasner and Amy, 1995).

The USEPA, in the Interim Enhanced Surface Water Treatment (IESWTR) Rule (USEPA, 1998b) and the Disinfectant/ Disinfection By-Product (D/DBP) Rule (USEPA, 1998a), has proposed enhanced coagulation as the best available technology (BAT) for the control of precursors to organic DBPs such as total trihalomethanes (TTHMs) and haloacetic acids 5 (HAA$_5$) (Marhaba and Pipada, 2000).

Furthermore, the regulation negotiation advisory committee requested that the USEPA designate enhanced coagulation as a BAT in stage 1 to control DBP precursors via TOC removals. In addition, enhanced coagulation was determined by the regulatory negotiation advisory committee and its technology workgroup to be a BAT for complying with the TTHM and HAA_5 stage 1 standards. The performance criteria for TOC removal percentage will be based on influent TOC and alkalinity (Table 2.10). The enhanced coagulation requirement will apply to conventional treatment plants (with sedimentation basins) that treat surface water or groundwater under the influence of surface water unless the TOC level prior to continuous in-plant disinfection is < 2 mg/L (Cheng, Krasner, Green et al., 1995).

Table 2.10 Enhanced coagulation requirement for TOC removal, stage 1 of D/DBP rule (USEPA, 1999)

TOC (mg/L)	TOC removal (%)		
	Source water alkalinity		
	0-60 mg/L	>60-120 mg/L	>120 mg/L
≤ 2.0	No action	No action	No action
>2.0-4.0	40	30	20
>4.0-8.0	45	35	25
>8.0	50	40	30

Marhaba and Pipada (2000) determined the maximum removal of six dissolved organic matter fractions (hydrophobic acid, base, neutral and hydrophilic acid, base, neutral) by alum coagulation that was performed over a range of pH and alum dosages. The result showed that greater TOC, UVA and SUVA reduction of all six fractions occurred at pH 6 than at pH 8. Except for hydrophobic base and perhaps the hydrophobic acid fractions, there was still incremental removal with further additions of alum.

A study by White, Thompson, Harrington et al., (1997) showed that waters with high initial SUVA values exhibited significant reductions in SUVA as a result of

coagulation, demonstrating a substantial removal of the humic (and other UV-absorbing) components of the organic matter, whereas waters with low initial SUVA values exhibited relatively low reductions in SUVA. The ability of SUVA to indicate the amount of humic matter present and enhanced coagulation's ability to preferentially remove humic matter, establishes SUVA as an indicator of enhanced coagulation's ability to remove humic substances from water. Therefore, in addition to TOC, the USEPA in the D/DBP rule (USEPA, 1998a) included a SUVA of 2 L/mg-m as a criteria that triggers enhanced coagulation (Marhaba and Pipada, 2000).
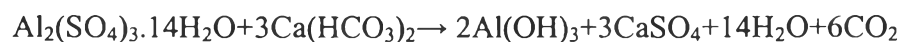
2.5 Coagulation

2.5.1 Coagulants

The most widely used coagulants in water treatment are aluminum sulfate and iron salts. Aluminum sulfate (filter alum) is employed more frequently than iron salts because it is usually cheaper. The principal factors affecting the coagulation and flocculation of water or wastewater are turbidity, suspended solids, temperature, pH, cationic and anionic composition, and concentration, duration and degree of agitation during coagulation and flocculation, dosage and nature of the coagulant, and if required, the coagulant aid. The selection of a coagulant requires the use of laboratory or pilot plant coagulation studies, since a given water or wastewater may show optimum coagulation results for a particular coagulant. Usually laboratory studies using the jar test are adequate for selecting a coagulant for a water treatment plant, whereas laboratory and frequently pilot studies are required for wastewaters. As shown in the previous section, coagulation chemistry is complex, and theoretical chemical equations to determine the amount of the metallic hydroxides produced give only approximate result. In this section, the common coagulants, their chemical reactions with alkalinity, and their characteristics are discussed.
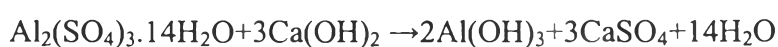
2.5.1.1 Aluminum sulfate

Sufficient alkalinity must be present in the water to react with the aluminum 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

$$Al_2(SO_4)_3.14H_2O+3Ca(HCO_3)_2 \rightarrow 2Al(OH)_3+3CaSO_4+14H_2O+6CO_2$$

Certain waters may not have sufficient alkalinity to react with the alum, so 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

$$Al_2(SO_4)_3.14H_2O+3Ca(OH)_2 \rightarrow 2Al(OH)_3+3CaSO_4+14H_2O$$

Alkalinity may also be added in the form of the carbonate ion by the addition of sodium carbonate (soda ash). Most waters have 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, since aluminum hydroxide is relatively insoluble within this range. These usually produce an oversaturated solution of aluminum hydroxide. Aluminum 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 being the most widely used, the granules, which are 15 to 22 % Al_2O_3, contain approximately 14 waters of crystallization, weigh from 60 to 63 lb/ft^3 (960 to 1010 kg/m^3) (Reynolds and Richards, 1996).

2.5.1.2 Coagulant aids

Alkalinity additions

An alkalinity addition is required to aid coagulation if the natural alkalinity is insufficient to produce a good floc. Lime is usually used, and it may be fed as slaked lime (milk of lime) or hydrate lime. Soda ash (sodium carbonate) is used to a lesser extent than lime since it is more expensive than quicklime. Na_2CO_3 and is available as a powder and may be dry fed.

Adjustment of pH

Adjustment of pH is required if the pH of the coagulated water dose not fall within the pH range for minimum solubility of the metallic hydroxide. Increasing the pH is usually done by the addition of NaOH; pH reduction is usually accomplished by the addition of a mineral acid, such as sulfuric acid.

2.5.2 Jar test

The laboratory technique of the jar test is usually used to determine the proper coagulant and coagulant aid, if needed, and the chemical dosages required for the coagulation of particular water. In this test, samples of water are poured into a series of glass beakers, and various dosage of the coagulant and coagulant aid are added to the beakers. The contents are rapidly stirred to simulate rapid mixing and then gently stirred to simulate flocculation. After a given time, the stirring is ceased and the floc formed is allowed to settle. The most important aspects to note are the time for floc formation, the floc size, its settling characteristics, the percent turbidity and color removal and the final pH of the coagulated and settled water. The chemical dosage determined from the procedure gives an estimate of the dosage required for the treatment plant.