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ABSTRACT

DEVELOPMENT AND APPLICATION OF FRACTIONATION PROCEDURE FOR DRINKING WATER ORGANIC MATTERS

by
Yong Pu

USEPA mandates a control of disinfection by-products (DBPs) in finished drinking water and recommends reduction of natural organic matters (NOM), DBP precursors, to achieve this regulatory goal. Studies relating NOM with DBP include fractionation of water samples, characterization of collected organic fractions, fractions' formation potential tests, and jar or similar tests to remove NOM. This study discussed a current resin fractionation procedure on principle, procedure, and its efficiency when applied to water samples of low NOM (< 5mg/L). The primary objective of this research is to develop a fractionation procedure intended for water of low NOM by carefully applying mass balance concept through each fraction's fractionation and a selection of stable ion exchange resins. A new protocol was presented with triple columns of XAD-8 adsorption resin, one column of AG-MP-50 cationic resin, and another column of WA 10 weak anionic resin in sequence. This protocol was experimented and confirmed for its efficiency (±10% loss of mass) with samples from Canal Road (CR) and Raritan Millstone (RM) surface water treatment plants (WTPs) in central New Jersey. The second objective of this study is to develop a statistical model with a potential of online delineation of organic fractions of NOM. The resulting model based on samples of Passaic Valley Water Commission (PVWC) WTP in northern New Jersey was applied to predict organic fractions of samples from CR and RM plants. Paired T-test (paired t ratio 1.15 < t critical 2.02) indicated a good correlation between the predicted and actual

fraction concentration. Finally, samples of Middlesex Water Company (MWC) were fractionated and Trihalomethane formation potential tests (THMFP) on collected fraction showed hydrophilic matters possessed a higher potential to produce TTHM in finished water than hydrophobic matter. Jar tests indicated while coagulation was effective in removing hydrophobic matter, it may not be optimum for removal of hydrophilic matter.

This study developed an accurate fractionation procedure for low NOM waters. It provided a better understanding of organic matter transformation at different treatment stages and jar test performance on removal of organic materials for the studied sample sets.

DEVELOPMENT AND APPLICATION OF FRACTIONATION PROCEDURE FOR DRINKING WATER ORGANIC MATTERS

by
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Dedicated to my lovely wife, Xiangmei Chen, and daughter Amy Pu

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LIST OF ABBREVIATIONS

DOC	Dissolved organic carbon
DOM	Dissolved organic matters
DBP	Disinfection by-products
NOM	Natural organic matters
TOC	Total organic carbon
HPOB	Hydrophobic base
HPOA	Hydrophobic acid
HPON	Hydrophobic neutral
HPIB	Hydrophilic base
HPIA	Hydrophilic acid
HPIN	Hydrophilic neutral
WTP	Water treatment plant
SUVA	Specific UV absorption
CR	Canal Road
MR	Millstone River
MWC	Middlesex Water Company
PVWC	Passiac Valley Water Commission
THM	Trihalomethane
TTHM	Total trihalomethane
HAA	Haloacetic acid

CHAPTER 1

INTRODUCTION AND OBJECTIVES

1.1 Difficulty in Studying NOM in Drinking Water

Natural organic matter (NOM) or its dissolved form, dissolved organic matter (DOM) in drinking water has been receiving extensive focus since 1980. (From now on in the thesis, NOM will be indicated only if necessary) Apart from its historical, well-known problems of aesthetics, taste and odor, DOM in water can increase the solubility of heavy metals and synthetic organic compounds (SOCs) through complexation, chelation, adsorption, and inclusion. If a drinking water source contains a high level of DOM, more efforts are needed for water treatment plants to treat those contaminants or chemicals. DOM in drinking water is not considered hazardous; however, it can introduce potential hazards known as disinfection by-products (DBPs) through reaction with chlorine or other disinfecting chemicals [Marhaba and Washington, 1998]. In view of this, DOMs are conventionally named as DBP precursors. How DOM reacts with disinfecting chemicals to form DBP and how DOM can be efficiently controlled or removed have been and will be subjects of a wide range of drinking water studies in the past 20 years [Richardson, et al., 2002; Richardson, 2003].

Studies of DOM in drinking water usually do not achieve satisfying results compared with initially established objectives of such studies. Difficulties in studying DOM can be of intrinsic sources. DOM is a complicated mixture of organic material present in all drinking water sources, which includes fulvic acids, humic acids, hydrophilic acids, proteins, lipids, aromatic amines, peptides, proteins, alcohols, polysaccharides, amino acids and hydrocarbons [Leenheer and Croué, 2003]. Table 1.1

summarizes possible organic materials normally found in drinking sources [Swietlik et al., 2004].

Table 1.1 Possible organic materials in natural water sources [Swietlik et al., 2004]

Fraction	Abbreviation	Possible Organic Compound
Humic Acid	HA	Humic substances precipitated at pH 1
Hydrophobic Acid	HPOA	Fulvic acids, C5-C9 aliphatic carboxylic acids, 1-and 2-ring aromatic carboxylic acids, 1- and 2-ring phenols
Hydrophobic base	HPOB	1- and 2- ring aromatic amines, except pyridine, proteinaceous substances
Hydrophobic neutral	HPON	> C5 aliphatic alcohols, amides, esters, ketones, baldheads, long chain > C8 carboxylic acids and amines
Hydrophilic acid	HPIA	< C5 aliphatic carboxylic acids, poly-functional carboxylic acids, mixture of various hydroxyl acids
Hydrophilic Base	HPIB	Amportieric proteinaceous materials containing amino acids, amino sugars, peptides and proteins; < C9 aliphatic amines, pyridine
Hydrophilic neutral	HPIN	Short chain aliphatic amines, alcohols, aldehydes, esters, ketones; < C5 aliphatic amides; poly-functional alcohols carbohydrates; cyclic amines; polysaccharides

Complication of studying DOM derives from the fact that DOM is not a single compound but consists of various compounds. The difficulty is further enhanced with

DOM structures' diversities. Even with modern analytical instrumentation such as ^{13}C NMR and MS, information on the DOM structure specifically related to DBP formation is still insufficient or trivial, and in general very few functional groups can be positively identified [Leenheer and Croué, 2003; Richardson, 2003]. DOM studies are often hindered due to inadequacy of available technologies. An example is the discovery of chloroform, the first identified DBP, almost 70 years after the introduction of chlorine disinfection. Even today, there have no established techniques that are able to separate DOM individually; instead, DOM in drinking water is more frequently separated into subgroups, which however are still mixtures of organic materials but are presumed to have similar physical and chemical properties. Such a separation of chemically similar DOM is known as DOM fractionation. Principles of DOM fractionation are based on liquid chromatograph separation; however, instrumentations of DOM fraction are much simpler than those of routine high performance liquid chromatograph. Finally, studies on DOM have to take into consideration spatial and temporal variations (i.e., water quality variation), which could also complicate DOM studies when one attempts to make comparisons among them.

In conclusion, DOM presents a great challenge to be studied because DOM consists of various organic materials with diversified structures and because current research technologies are still inefficient in separating and identifying them.

1.2 Disinfection By-products

During the past two decades, studies of DOM are mainly driven by federal regulations and are all related to DBP formation. For example, Stage 1 Disinfectants and Disinfection By-products Rule (Stage 1 D/DBP Rule; USEPA, 1998) require a certain

removal rate of organic materials in terms of total organic carbon (TOC) for systems using conventional filtration treatment (table 1.2). Therefore, it is worthwhile to discuss DBPs with an intention to clearly address the importance of studying DOM.

Table 1.2 Regulated % removal of TOC in Stage 1 D/DBP rule [USEPA, 1998]

Source Water (TOC mg/L)	Source Water Alkalinity, mg/L as $CaCO_3$		
	0-60	60-120	>120
2.0-4.0	35.0%	25.0%	15.0%
4.0-8.0	45.0%	35.0%	25.0%
>8.0	50.0%	40.0%	30.0%

1.3 History Overview of Disinfection

During water treatment, disinfecting chemicals such as chlorine must be applied, prior to the distribution of finished water, to achieve safe water free from microbiological hazards and to deliver safe water to the end consumer taps. *Code of Federal Register* 40 (141) 72 mandates a minimum of 99.9% and 99.999% inactivation of *Giardia lambila* cysts and viruses, respectively, after disinfection of water. This process to destroy or inactivation of water pathogens has been acclaimed as one of the major public health advances in the 20^{th} century and has been the essential treatment of drinking water. Currently, there are more than 250 million people in the United Sates served with disinfected water by approximately 170,000 public water systems [USEPA, 2001].

Since the first introduction of disinfection in Jersey City, New Jersey in 1908 [Faust & Aly, 1998], water related diseases have been reduced dramatically in the ensuing decades. For example, the incidence of death due to typhoid fever in 1910 was

similar to that of people who die in car accidents of today, 16 of every 100,000 people or 25,000 for the total [USEPA, 2003]; this rate had plummeted to 0.1 per 100,000 by 1950, to almost zero today. Disinfection practices have also helped to wipe out dysentery and cholera.

During the last decade, there were three large water-borne hazardous outbreaks due to inefficient disinfection (Cholera in Peru in 1991, Cryptosporidiosis in Milwaukee, WI, USA 1993, and E. coli-induced gastroenteritis in Walkerton, Ontario, Canada 2000). These water-borne disasters furthermore remind us of an indispensable need of proper disinfection practices and the importance of water disinfection to protect our human from contracting infectious water borne diseases.

In summary, disinfection of drinking water is a critical public health measure that saves thousands of lives in United States each year through:

- Destroying pathogens, such as virus, bacteria, and parasites, in the water
- Preventing adverse biological activities commonly occurring in the distribution system
- Protecting treated water from pathogen re-contamination

Today, approximately 64 percent of community ground water and surface water systems apply chlorine-based disinfectants to treat their water; almost all of the remaining surface water systems, and some of the remaining ground water systems utilize different chemicals, such as ozone or chloramines [USEPA, 2000]. It is highly credited to disinfection that American people can enjoy the safest water in the world.

1.4 Regulatory Overview of DBPs

While the benefits and significance of drinking water disinfection have been well recognized, disinfecting chemicals like chlorine were identified to be reactive with naturally occurring organic materials, which forms harmful DBP in 1974 [Rook 1974; Bellar and Lichtenberg 1974]. In 1974, Rook first reported his discovery of chloroform formed during chlorination. A study of National Research Council [*NCI* 1976] on chloroform, one of the well-studied DBPs now, proved that chloroform produced liver and kidney cancers in experimented mice. Chloroform was realized as a carcinogen to animals and was suspected carcinogenic to human.

The NCI finding stimulated numerous studies on the possible association of DBPs in drinking water with adverse health effects on human. It also made the USEPA to focus more attention on the DBPs and disinfectants in drinking water. Another reason that USEPA started to take actions against disinfectants and DBPs was the increasing use of disinfectants in drinking water treatment plants, while more and more studies emerged to indicate possible health hazards of DBPs on human. The regulation history of USEPA for drinking water (designated by *Safe Drinking Water Act* in 1974 and amendments of 1986, 1996) can be to a large extent considered as a one mainly targeting DBPs. No such regulation was enacted before 1974 because DBPs had not been discovered due to lack of capable analytical methods. In 1979, TTHM (trihalomethanes), proven to be carcinogenic, started being regulated with a Maximum Contaminant Level (MCL) of 100 μg/liter for water systems serving people more than 10,000 [USEPA, 1979]. The effective date for water utilities serving people from 10,000 to 75,000 was set on November 29, 1983 and for water utilities serving more than 75,000 people, the TTHM

MCL became effective on November 29, 1981, two years after the promulgation of 1979 TTHM MCL [USEPA 1979]. In 1988, under the requirements of the *SDWA* 1986 amendments, USEPA published its first *Drinking Water Priority List of Contaminants*, which included, for the first time, disinfectants, in addition to DBPs, for possible regulation [53 FR 1892]. On June 29 1989, USEPA formally set off a lengthy, complicated DBP regulation process by issuing a proposal calling for DBP regulations [USEPA, 1989]]. From then to June 1996, USEPA actively worked on the DBP regulation, such as forming Disinfectant/DBPs (D/DBPs) regulatory negotiation committee in 1992, conducting an extensive re-assessment of its drinking water program in 1995; however, USEPA only came up with a *National Drinking Water Program Redirection Strategy*, in which USEPA acknowledged its incapacity to finalize D/DBPs rules at one time [USEPA, 1996]. Facing the pressure of the Congress again (*SDWA* 1996 amendments), USEPA promulgated and enacted the *Stage 1 D/DBP Rule* on December 16th 1998 and January 16th 2001, respectively [USEPA, 1998]. In the rule, USEPA decreased the MCL of TTHMs from 100 to 80 μg/liter. HAA_5, named for five haloacetic acids, began to be subjected to regulation with a MCL of 60 μg /liter. TTHM and HAA_5 are the only two groups of organic DBPs regulated at this time; bromate and chlorite, formed during ozone and chlorine dioxide disinfection, respectively, are the only two regulated inorganic DBPs.

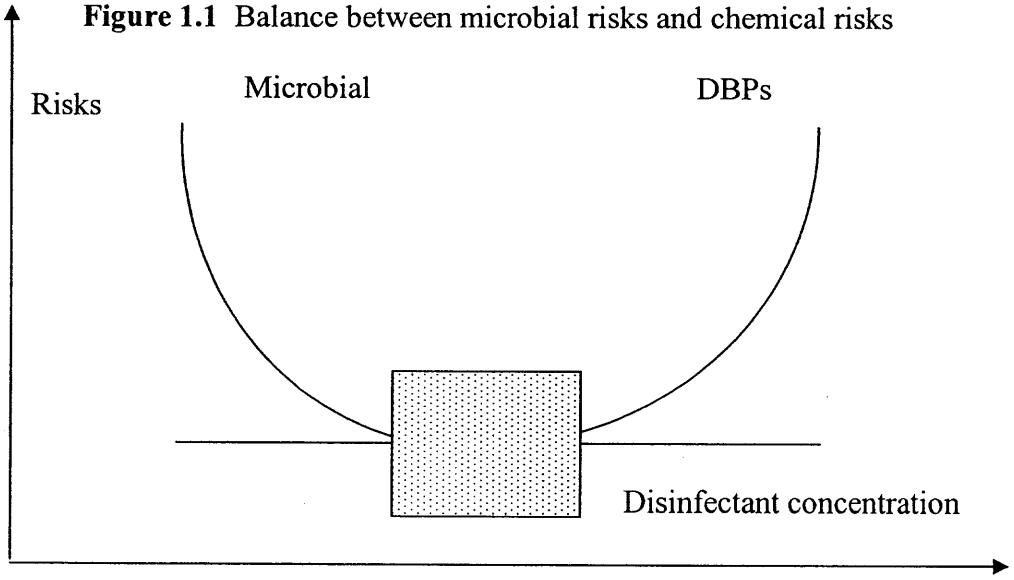
USEPA is developing the Stage 2 D/DBP Rule that is anticipated to be more stringent than the Stage 1 D/DBP Rule in the way to average the DBP level. In the Stage 1 D/DBP Rule, USEPA allows utilities to average DBP over all sampling locations; i.e., the average is calculated over system-wide samples. As a result, the Stage 1 D/DBP Rule

does lend some leeway of allowing higher concentration of DBPs at certain sampling points along the system, provided if the whole utility-range average for the given year is below the regulation. The upcoming stage 2 D/DBP Rule will change to calculate the average based on each sampling location annually. This way of averaging DBP means that if one location fails to meet the MCL requirement on annual sampling, then all the system is concluded to fail to comply with the stage 2 D/DBP Rule [USEPA, 2003]. The more stringent Stage 2 D/DBP Rule will protect consumers spatially as well as temporally from exposure to possible high DBP by allowing no single point of the distribution system to exceed the MCLs of regulated substances.

USEPA had to spend more than two decades developing and finalizing its first comprehensive D/DBP regulation (*Stage 1D/DBPs Rule*) (from 1979 to 2001). USEPA currently is finalizing the *Stage 2 D/DBP* Rule in 2004. The lengthy process for EPA to develop D/DBP Rules indicates the delicacy and difficulty in D/DBPs regulation:

- Drinking water disinfection is the top priority of treatment
- Removal of DBPs are extremely challenging
- Balance between DBP chemical and microbial risks is delicate (Figure 1.1; Marhaba and Washington, 1998)

Figure 1.1 Balance between microbial risks and chemical risks



1.5 Health Risks of DBP

The 1976 NCI conclusion that chloroform was carcinogenic to animals raised concerns of the risks of DBPs to human health and suspicion of the effects of disinfection as an essential water treatment technology [NCI, 1976]. After this study, there have been numerous epidemiological investigations to assess health risks of various DBPs.

While DBPs have been found to contribute to or associate with a number of adverse health risks in human or lab animals, USEPA is more concerned with ***cancer, negative reproductive effects (miscarriage), and injury to the fetus (birth defects)*** in its regulation. USEPA considers cancer as a chronic danger of DBPs due to the fact that people drink disinfected water all their lifetime.

1.5.1 Cancer Risks of DBPs

Epidemiological and controlled animal studies provide evidence of carcinogenicity of various DBPs. A NCI study in 1976 showed production of liver and kidney tumors in laboratory mice. NCI studies [Cantor et al. 1985, 1987, 1990] were able to make an association of an increased bladder cancer in individuals who drank chlorinated water over 40 years. Same association was noticed by McGeehim who compared people served with chlorinated water over 30 years with those of zero exposure [McGeehim, 1993], and by King and Marrett in 1996 who found a significant increase of bladder cancer among people exposed above 35 years than those exposed in less than 10 years. They also found exposure to TTHM levels of $\geq$ 50 μg/liter for more than 35 years (Current MCL of TTHM is 80 μg/liter) increased the risk of colon cancer than people of the same exposure in less than 10 years. Studies in which controlled mice or rats were exposed to individual DBP over a lifetime indicated an increased incidence of liver,

kidney and internal cancers [NCI 1976; Jorgenson 1985; NTP, 1985, 1987, 1989 Deangelo et al. 1991, 1996; WHO 1996].

1.5.2 Birth Defect and Miscarriage Risks of Selected DBPs

The adverse reproductive effects and impairment to the developing fetus (birth defects) are more imminent and acute in consideration of more vulnerability of female and fetuses to DBPs. Differing from the studies of carcinogenic effects of DBPs, data of studies on the potential of DBPs to affect reproductive functions and fetus development are only now being accumulated.

Studies have found low newborn weight, stillbirth for babies whose mothers drank tap water during their pregnancy with at least 10 ppb of TTHMs in Iowa [Kramer et al., 1992], in New Jersey [Bove et al., 1995], and in North Carolina [Savitz et al., 1995]. Researchers also observed increased rates of stillbirth and neonatal deaths attributed to mothers drinking from disinfected public water supplies [Aschengrau et al., 1993]. Exposures to high TTHMs can cause elevated miscarriage [Savita et al., 1995], and statistically increased risk of spontaneous abortion [Waller et al., 1998]. Waller et al. in 2001 further examined the results of their 1998 study with an improved exposure assessment. While the statistical significance was not holding anymore, another statistically significant three-fold increase in spontaneous abortion was observed for pregnant women with a high exposure to ≥ 75 μg/L THMs, consuming ≥ 5 glasses of cold tap water per day. Table 1.3 lists several epidemiology studies and their findings.

Table 1.3 Several studies of adverse epidemiological effects of DBPs

Year	Location	Symptom	DBPs
1992	IA	Low newborn weight	Chloroform >10 μg/l
1993	Massachusetts	Increased rates of stillbirth, neonatal death	
1995	New Jersey	Low newborn weight	THM > 80 μg/l
		Neural tube defects	
		Central nervous system defects	
1995	North Carolina	Elevated incidences of miscarriage	High THMs
1996	Liguria, Italy	Low birth weight	
		Higher rates of neonatal jaundice	
2001		Spontaneous abortion	75 μg/L THMs

USEPA has not reached a conclusion of direct causal effect of DBPs on human cancers at present. Although the risk appears to be not significant, it should be reminded how tremendous the exposed population is (more than 250 million); USEPA has set up a Maximum Contaminant Level Goal as 0 μg/liter for some THMs and HAAs [USEPA, 2001]. It is expected that more and more other DBPs will appear on the regulation list with very low levels permissible to occur in treated water.

In conclusion, "Some disinfectants and disinfection by-products (DBPs) have been shown to cause cancer and reproductive effects in lab animals and suggested

bladder cancer and reproductive effects in humans". Therefore, it is mandatory to control DBP occurrence in treated drinking water to minimize risk exposure to DBPs while still maintaining disinfection benefits.

1.6 Approaches to Control DBPs

A general model can be applied to describe the formation of DBPs

Organic materials + Disinfectants → Disinfection by-products

It can be seen that reduction of DBPs to an allowable level can be achieved through one or combination of the following mechanisms:

- Selection of alternative disinfectants to currently utilized chlorine
- Reduction or elimination of precursor organic materials
- Removal or destruction of DBPs

1.6.1 Alternative Disinfection to Chlorination

Chlorination with free chlorine was virtually the only disinfection practice to kill or inactivate pathogens in the drinking water treatment until 1970s. Even today some water treatment plants apply non-chlorine based disinfection as the primary disinfection; chlorine is necessarily supplemented as a secondary disinfecting chemical to maintain preventive ability in distributed water. Experiences accumulated over one century have proved the following advantages of chlorination with chlorine:

- Effectively disinfects most pathogens
- Provides residual protection of distributed water from contamination
- Oxidize Fe/Mn, H_2S, NH_3, and nitrogenous compounds
- Control taste and odor
- Is applicable to various water quality conditions

- Can be conveniently applied, controlled, and monitored
- The most cost effective

USEPA discussed alternative disinfectants to the popular free chlorine, such as ozone, chloramine, chlorine dioxide, and non-chemical UV; however, none of them can provide a complete solution to DBP problems [USEPA, 1999]. For examples, ozone can form more toxic brominated DBPs; chloramine is a much less effective disinfectant than free chlorine; ClO_2 forms inorganic DBP chlorite and its generation is much more complicated then that of free chlorine. Alternative disinfectants have been shown to achieve better control of THMs and tri-halogenated HAAs than chlorine; however, they could produce DBPs of higher health concern, such as iodinated THMs in a chloramination plant and dichloroacetaldehyde in a plant operating chloramine and ozone [Krasner, 2001]. The fact that ozone by-product bromate is regulated with a MCL of 10 μg/L and chlorine by-product TTHM and HAA_5 are allowed higher as 80 and 60 μg/L respectively in treated water support that by-products of alternative disinfectants may in reality carry more hazards. Table 1.4 lists some DBPs associated with alternative disinfectants.

As long as protective disinfectants must occur in treated potable water, chlorine-based disinfectants have to be added in a residual level. In addition, residual chlorine must be maintained throughout the distribution system to prevent any potential re-growth of pathogens at any point of the system. Therefore, there is always a potential existing that such disinfectants will react with remaining organic materials to form DBPs all the way to the consumer taps.

Table 1.4 Alternative disinfectants and possible associated DBPs [Ashbolt, 2004]

Disinfectant	Generation	DBPs		
		Organohalogenated	Inorganic	Non-halogenated
HClO	Gas or liquid	THM, HAA, HAN, Halofuranones	Chlorate	Aldehydes, benzene, carboxylic acid
ClO_2	$NaOCl+Cl_2$ $NaOCl+HClO$		Chlorite, chlorate	
Chloramine	Cl_2+NH_3	HAN, cyanogens chloride, haloketones	Nitrate, nitrite, chlorate	Aldehydes, ketones, nitrosamines
O_3	Electrical discharge through air	Bromoform, MBS, DBA, dibromoacetone	Chlorate, Iodate, Bromate, HOBr	Aldehydes, Ketoacids, ketones, carboxylic acids

Table 1.5 Advantage and disadvantage of alternative disinfectants

Disinfectant	Advantage	Disadvantage
Cl_2	• Effective for most pathogens • Fe/Mn oxidation • Residual protection possible • Operationally the most reliable • Relatively easy to use • The most cost effective	• DBP formation • Not effective against Cryptosporidium • Taste and odor problem • Safety concern
Chloramine	• More durable residual than Cl_2 • Reduced DBP formation • Lower taste and odor trouble • Technically matured	• Weak than Cl_2, especially against viruses and protozoa • Less effective on Fe/Mn oxidation • Mainly used as secondary disinfectant
ClO_2	• Effective on Cryptosporidium and Giardia • Less taste and odor problem • No THM and HAA formation	• On site Generation • Inorganic DBP formation • Necessary daily monitoring of chlorite and ClO_2 • More expensive • More complicated in operation
O_3	• Most Powerful • Effective against Cryptosporidium • Produces no chlorinated DBPs	• On site production • Technically more complicated • Bromate and other DBP formation • No residual present
UV	• Effective against bacterial, Giardia, and Cryptosporidium • No formation of DBPs at levels of concern	• Affected by water condition • Less effective against some viruses (reoviruses and rotaviruses) • Technically complex • No residual protection

1.6.2 Removal or Destruction of DBPs

Current technologies, so far, are rarely recommended to directly target DBPs to achieve the required control. Stage 1 D/DBP Rule does provide a Best Available Technology (BAT) for the control of DBPs in finished water; nevertheless, the intent of the BAT is to reduce the precursors of DBP prior to disinfection. For some drinking water treatment plants with ozone as primary disinfectant, biologically active filters can be used to remove ozone DBPs. In general, available technologies are either not effective to remove trace DBPs or cost prohibitive to the water treatment plants.

1.6.3 Reduction of DBP Precursors

Removal of DBP precursors seems at present to be a feasible and practical technology available for drinking water treatment plants. The technology suggested by USEAP in Stage 1 D/DBP Rule to control DBP in finished drinking water is Enhanced coagulation and Enhanced softening to remove DBP precursors, quantified as TOC. Advanced technologies for precursor removal include granular activated carbon (GAC) and membranes: nano-filtration or reverse osmosis. Therefore, herein this study will concentrate on organic materials, especially on organic materials fractionation, characterization, and potential of forming DBPs.

1.7 Objectives

Among a series of DBP studies, fractionation of drinking water samples is the key to address the association of DOM in natural water samples with DBP formation. Currently, DBP precursors are represented with the surrogate parameter $SUVA_{254}$. This parameter doesn't in nature provide much information on precursor structures and their relation with DBP formation. Fractionation of natural waters separates DOM into a

maximum of six different organic fractions. DOM of each fraction is presumed to have similar physical and chemical properties with the applied fractionation technology. After fractionation, DOM of each fraction can be further characterized to provide an insight into the nature of structure-specific information and possible correlation to DBP formation. DBP formation potential tests can be conducted on each fraction alone and their combination to investigate problematic DOM. In addition, jar tests of enhanced coagulation or precipitative softening on collected fractions can help to determine an efficient way to achieve the required DBP precursor removal.

Current resin fractionation procedures do not apply mass balance concepts through all fractions. This shortfall inherently results from the fact that only one column XAD-8 resin is used for the three hydrophobic fractions: hydrophobic neutral, acid, and base. Furthermore, strong bleeding of Duolite A7 for hydrophilic acid and neutral fractions brings significant errors into fractions

The main objective of this thesis is to develop a fractionation procedure suitable for waters with low levels of DOM (<5mg/L). To achieve this, the mass balance concept will be applied during each step of fractionation to direct an errorless fractionating protocol. Several anion exchange resins to replace the Duolite A7 will be tested to select a right candidate for hydrophilic neutral and acid fractionation. The developed fractionation procedures will be examined for its effectiveness.

Other objectives of this thesis include a preliminary attempt to develop a model for rapid delineation of fractions based on their feature fluorescence spectrum as well as an application of developed fractionation procedure to study temporal and spatial variation of DOM in terms of their THM formation potential. In addition, another

objective is to examine the effectiveness of jar testing conventional treatment on the removal of fractions and their THM formation potential.

CHAPTER 2

LITERATURE REVIEW

2.1 Organic Material Fractionation Procedure

NOM is a mixture of organic matters of different sources and different characteristics. Although NOM presents in water in particulate and dissolved forms, research has focused on DOM rather than particulate organic materials since in water treatment, conventional processes can settle down and filter almost all particulates. The dissolved organic materials are operationally defined as those organic materials that pass through 0.45 μm membrane when filtered. Due to the heterogeneity of organic materials in water, it is not possible to separate them into individual compound; neither is likely to measure them directly. Surrogate parameters such as dissolved organic carbon (DOC), color, and UV_{254} are used to qualify and quantify organic materials.

Separation of natural water organic materials into individual compounds cannot be achieved; however, natural water organic materials showing similar physical and chemical characteristics can be grouped into chemically similar fractions. It is feasible to apply some separation procedures to divide the water organic mixtures into more specific factions, yet not as specific as individual compound.

The organic materials can be fractionated through size exclusion chromatograph for high-resolution separation and ultra-filtration for low-resolution separation. Size characterization determines molecular weight or size range of studied organic materials. The principles and methods to establish the molecular weight and size ranges have been reviewed by Wershaw and Aiken [1985] and further discussed by Egeberg et al. [2002].

With size characterization, DOM has showed a molecule size ranging from several hundreds to 100,000 Daltons.

The organic materials can also be separated by resin adsorption/exchange in combination with pH adjustment as well as with varied elution for different organic materials [Leenheer, 1981]. Resin fractionation of DOM can concentrate and categorize the water organic complex into structurally more specific and physicochemically more analogous subgroups by retaining DOM onto a series of types of resin followed by elution with different chemicals. By applying this technique, DOM of natural water can be fractionated into hydrophobic fractions, which mainly consist of fulvic and humic acids, and hydrophilic fractions, which comprise of carbohydrates with low molecule weight, proteins, and amino acids. Hydrophobics are structurally more aromatic than hydrophilics and more prone to removal by conventional treatment. Raw water usually has a yellow color at the intake of plants and becomes clear mainly due to the removal of hydrophobic materials. Resin fractionation has been widely applied to investigate various properties of DOM. It has been shown to greatly facilitate subsequent studies associated with DOM, such as the formation of disinfection by-products (DBPs) [Barrett *et al.*, 2000].

There have been some resin fractionation procedures proposed, modified and applied to fractionate DOM [Leenheer and Huffman, 1976; Leenheer and Huffman 1979; Leenheer 1981; Thurman and Malcolm, 1981; Aiken *et al.*, 1992; Malcolm and McCarthy, 1992; Gašparović *et al.*, 1997; Leenheer *et al.*, 2000]. All these procedures can broadly be classified into two categories relying on resin applied. In the first, a system of nonionic XAD-8 and ionic resins [Leenheer and Huffman 1976, 1979;

Leenheer 1981; Leenheer *et al.*, 2000] is implemented. In the second, only nonionic resins (XAD-8 and XAD-4) are utilized [Aiken *et al.*, 1992; Malcolm and McCarthy, 1992]. Procedures of both categories accept the XAD-8 resin for the partition between hydrophobics and hydrophilics since its property and performance have been well studied [Thurman et al., 1977; Aiken *et al.*, 1979; Thurman and Malcolm, 1981; Malcolm and MacCarthy, 1992]. It is also recognized that each fraction is defined more operationally than structurally. Furthermore, no universal fractionation procedure exists for all applications in accordance with the variety of research objective and sample matrix [Aiken and Leenheer, 1993; Leenheer *et al.*, 2000].

Dependent on research objective, DOM in natural water can be fractionated on analytical scale or preparative scale. The two fractionations differ only in instrumentation such as needed volumes of sample water and resin and have no difference in principle and column capacity. The principle discussed by Leenheer and Huffman [1976] laid the ground of the analytical fractionation procedure [Leenheer and Huffman, 1979], as well as that of the preparative fractionation procedure [Leenheer 1981], and was recently improved to cover colloidal organic materials [Leenheer, 2000]. Analytical procedures provide information on the fraction concentration in water while preparative procedure is aimed to collect sufficient organic materials and prepare organic-concentrated fractions for subsequent studies. Analytical and preparative procedures can be comprehensive in the way that all DOM rather than humic substances can be fractionated or sometimes both fractionation are applied just for a simple DOC distribution (humic/non-humic) to facilitate research work. Another advantage of comprehensive fractionation procedures is that the associated operations (resin adsorption, ion exchange, and solvent extraction)

more or less imitate natural conditions, such as some properties of soil and sediment surfaces [Qualls and Haines, 1991]. In water treatment, these operations may provide suggestion to treat the most troublesome candidates to form DBP. Although both the analytical and preparative procedures are useful, the latter is more applied with modifications [Imai, 1998] to complement studies such as disinfection and DBPs formation.

The preparative procedure [Leenheer 1981] has been mostly applied to natural water systems with success; nonetheless, its application to drinking water with DOM less than 5 mg C/L is far less reported. For low DOM samples, collected fraction deviate relatively significantly in DOM measurement because of the impact of matrix used for fraction elution. The Duolite A7 resin suggested in this procedure for hydrophilic acid fraction possesses a severe resin-bleeding problem. The resulted contamination could be remedied to some degree by re-adsorption of bleedings on additional cationic resin. This would introduce extra laborious work and a possible loss of fractions may occur. It is then less desired than preventing such pollution from occurrence.

2.2 Organic Fraction Characterization

2.2.1 Element Ratio Characterization

Application of resin fractionation technique generally separates organic complex into humic and non-humic substances to give a simple DOM profile. Application of resin fractionation can also lead a complicated grouping of organic materials into a total of six fractions: hydrophobic acid, hydrophobic base, hydrophobic neutral, hydrophilic acid, hydrophilic base, and hydrophilic neutral. Fractionation can further be improved to include a fractionation for colloidal organic materials [Leenheer, 2000].

Among the six fractions, hydrophobic acids have been so far the most studied. The hydrophobic acid is defined as precipitated organic materials at pH 2. Hydrophobic acids can be separated into so called humic and fulvic acids. These two terms were invented by soil organic scientists and adopted by water chemists who applied soil extraction procedure to study water humic substances. For this reason, initial water organic fractionation studies mainly attempted on humic substances.

The hydrophobic acid fraction, or equivalently humic substance, has been extensively studied and characterized for its functional groups, composition, structure, and reactive abilities. The atomic ratio of O to C for hydrophobic acids is reported generally between 0.5 and 0.6 [Danenett et al., 1995]. Aiken et al. [1992] studied the Yakima River and found 56.1% and 35.5% for C and O, respectively, which would give a 0.47 for the O: C. The study of Malcolm et al. [1993] separated hydrophobic acids into humic and fulvic acids and the O: C ratio of the humic acid was 0.50, less than that of fulvic acid (0.54). A very similar study for the Apremont Reservoir [Martin 1997] also determined 0.56 for humic acid and 0.60 for fulvic acid. In a recent study [Peuravuori et al., 2002], the O: C ratio can be calculated as 0.51 ± 0.07 for 12 hydrophobic acid fractions of different sources or collected with different resins.

The O: C ratio indicates the relative amount of carbohydrates in the organic materials with a lower ratio for less carbohydrate. Hydrophobic acid fraction, in general, has a lower O: C ratio compared to other fractions [Jean et al., 1999]. The C: H ratio for hydrophobic acid was reported to be around 1.0 [Thurman, 1985]. The lower O: C ratio together with 1 for C: H in hydrophobic acid discloses a possible aromatic character of humic and fulvic acid molecular structure. The base fraction is believed and found to

contain the highest amount of N among all the fractions due to its nature; more N-containing function group, more base the material. A soil water study also demonstrated higher ratio of O: C as well as N: C for hydrophilic fractions than the hydrophobic parts, while the C/H was around 1 and showed no difference between the two fractions [Dilling, 2002]. The element ratio characterization is very instrumental to understand what DOM consists of; however, it has to be used with size or molecule weight characterization to illustrate a clear DOM profile since, for example, some hydrophobic acids and hydrophilic acids show no difference of element ratio but do differ in molecule weight or size.

2.2.2 TOC and DOC Characterization

Element ratio is more specific than aggregate parameters to characterize DOM because it logically induces possible dominant structures or functional groups of studied DOM. Aggregate parameters collectively describe DOM and usually provide less valuable information of DOM. Among few aggregate parameters, total organic carbon (TOC) is the most applied to quantity organic matter in water. The TOC quantification includes all organic materials present in either dissolved form (DOC) or solid form (POC). It should be pointed out that the subdivision of TOC is operationally defined, i.e., DOC is the organic materials able to pass through a arbitrarily decided 0.45 μm membrane and POC is the portion of TOC retained on that membrane. POC generally consists of a less than 10% of TOC [Thurman, 1985].

In drinking water plants, TOC is measured to monitor performance of conventional treatment. Neither TOC nor DOC can be associated with DOM structures.

For this reason, UV_{254} is supplemented to probe possible DOM structure and linked to DBP formation.

2.2.3 UV_{254} and $SUVA_{254}$ Characterization

Elemental ration characterization is achieved through comparison with general formula of known clusters of organic materials. UV absorption at 254 nm, UV_{254}, characterizes DOM for DOM-contained chromophores. Surface water shows a wide range of absorption including UV and visible. The light absorption is attributable to DOM aromatic structure and the absorption shows no instructive distinction at one wavelength from others. This is due to numerous chromophores of different absorption coefficients in DOM. Therefore, most published researches reported absorption at 254nm to indicate the occurrence of aromatic DOM.

Specific UV absorption at 254nm is the relative UV absorption at 254 nm standardized with sample DOC. $SUVA_{254}$ has been adopted in drinking water treatment plants to investigate the potential of DBP precursor removal. It should be noted that overall organic material removal is quantified as TOC reduction. Whether or not DBP precursor can be further removed is judged through DOC.

The $SUVA_{254}$ characterization is more efficient for water of humic type than water of non-humic because humic waters contain aromatic organic materials that are thought sensitive to UV. The $SUVA_{254}$ is more informative than UV_{254} alone because the former expresses relative reactivity of target organic mixtures for given unit mass. McKnight et al. [1994] found a very close relation of the UV absorbance to the hydrophobic fraction of DOM for various sources of water sample. Their nuclear magnetic resonance (NMR) study revealed the aromatic structure of hydrophobic organic

matters in those samples. Leenheer [2003] concluded that NMR is a strong tool to invest the correlation between SUVA and the aromatic carbon contents of a large number of fractions. The study of Chin and co-worker [1994] also showed a strong relation between SUVA and the aromatic carbon contents of a large number of fulvic acids. Since hydrophobic acid fraction consists of most fulvic acid, the strong correlation between SUVA and fulvic acid observed by Chin et al. in 1994 can be postulated as same as that between SUVA and hydrophobic acids. Dilling et al. [2002] concluded through their study that estimation of hydrophobic fraction could be accomplished with UV photometry for hydrophobic fraction dominating water. They also concluded that changes of pH between 2 and 7 had a very small effect on the change of hydrophobic acid structure; therefore, same correlation of SUVA to hydrophobic concentration could be maintained through a fairly wide pH range. However, on the contrary, Egeberg [2002] pointed out that the hydrophobicity of NOM would decrease with an increasing pH as well as increasing content and strength of acidic groups.

SUVA is accepted as a good predictor of the aromatic carbon content of DOM and currently used as a parameter to indicate removal of organic materials in water plants in Stage 1 D/DBP Rule. While the SUVA of the whole water sample is mostly attributed to the amount of hydrophobic acid fraction and this fraction's SUVA, other factors can also impute a certain degree SUVA to the whole sample. Theoretically, any substance of unsaturated structure can absorb UV, but it is much worse for water containing high nitrate and iron, which have strong absorbance as well. Furthermore, conventional treatment in drinking water plants can remove most hydrophobic organic material, as shown by the reduction of SUVA and the reduction of color; hydrophilic contribution to

the SUVA may become more significant than it was in corresponding water source and should be cautiously applied to predict DBP formation potentials. Croue et al. [1999] suggested more works needed on characterization on the hydrophilic fractions of NOM.

2.2.4 Fluorescence Characterization

Fluorescence characterization of NOM has been less applied compared to UV absorbance spectroscopy, DOC, and color. One of the reasons is that the acquired data of fluorescence are extremely complicated and many factors can affect the very sensitive fluorescence measurement (pH, temperature, sample matrix, instrument physical stability, and reaction of sample). Additionally, the fluorescence spectrum of organic mixture will be a composite without distinct features due to absorbance overlapping. Moreover, the structure complexities of DOM make its effects on the intensity and wavelength of the molecular fluorescence very complicated to predict.

Fluorescence spectroscopy is considered more sensitive by at least an order of magnitude to DOM than UV absorbance [Penmanen and Mannio, 1987]. It can collect more information compared to UV spectrophotometry when applied to the same sample. Moreover, synchronous fluorescence spectroscopy of multiple excitations accompanied with multiple emissions can provide MUCH more information than conventional fluorescence spectroscopy, or the single wavelength of UV absorbance [Marhaba et al., 2000].

Fluorescence can occur due to fluorophores present in a variety of substances, such as humic and lignin (hydrophobic acid), phenols, oils, steroids. Excitation of these organic fluorophores can be induced by high energy scanning such as laser. As other

photometry, Beer's law can be applied to describe the absorbed energy of any given fluorophore as

$\mathbf{I_a = I_o \times \{1\text{-}exp\ (-\alpha \times p \times C)\}}$

Where: I_a and I_o are the absorbed and incident intensity, respectively; α is the absorption coefficient, p the effective sample length, and C is the concentration of specific fluorophores. For any samples with C is very small, 1-exp $(-\alpha \times p \times C) = \alpha pC$; and then $I_a = I_o \alpha pC$. With the adsorbed energy, the fluorophore jumps to higher energy states and becomes unstable until it releases the adsorbed energy. However, not all adsorbed energy will be released in an emission of light and I_f, fluorescence intensity can be express as $I_f = \eta I_a$, where $\eta$is quantum yield (< 1). Therefore, for single type of fluorophore,

$\mathbf{I_f = I_o\ \eta \alpha pC}$.

For a sample of mixture at one excitation wavelength, **F** the total fluorescence intensity

$$F = \sum (I_f)_i = \mathrm{pI_o} \sum (\eta \times \alpha_i \times c_i)$$

Synchronous fluorescence spectroscopy scans the excitation at wavelength λ_{ex} and the emission λ_{em} synchronously with an intended wavelength offset $\Delta\lambda = (\lambda_{ex} - \lambda_{em})$. Total fluorescence intensity under synchronously measurement then should be expressed as

$$F = \sum (I_f)_i = \mathrm{pI_o} \sum (\eta(\lambda') \times \alpha_i(\lambda') \times c_i$$

Where the quantum yield and the absorption coefficient now become functions of $\lambda' = \lambda ex$.

The intensity spectrum will show pronounced peaks when the absorption coefficient $\alpha_i(\lambda')$ and quantum yield $\eta(\lambda')$ both reach maximum. Stoke's shift can be used to determine $\Delta\lambda$ of the difference in wavelength of the emission and excitation maximum.

SFS has been applied to wastewater samples with some qualitative success of characterization. With model compounds, Ahmad and Reynolds [1995] were able to show that all settled sewage presented distinct emission at wavelength of 280 nm and 390 nm when excited at 248 nm, which were characters of model amino compounds. They found that the intensities at these two locations decreased drastically in the corresponding final effluent samples, within 50-85% for different plants. They also found that suspended solids increased the emission intensity at 280 nm. Based on the study, they proposed a potential of SFS to quantitatively estimate biodegradable constituents (aromatic amino acids).

Peruravuori et al. [2002] applied SFS to compare resin fractionated hydrophobic acids and neutrals. The SFS spectra of both fractions showed almost identical characteristic excitation wavelength zones: 260-302, 302-340,340-370,370-420,420-438,438-487,487-510, and 510-550 nm. However, emission intensity patterns of the two spectra were much different in that maximum and second maximum excitation/emission occurred at 460/478, 400/418 for hydrophobic acids and 330/348, 460/478 for hydrophobic neutrals, respectively. In addition, the spectrum of hydrophobic acids fractionated by DAX-8 can completely overlap that by DEAE resin as well as the one by XAD-8, speaking of excitation. With comparison of same solutes but different preparative practices, the authors were able to prove no effect of freeze-drying on the possible change of composition of humic isolates. All these observations confirmed the efficiency of SFS to characterize different fractions. SFS was attempted to trace sources of DOM in natural water from different watersheds as well [Cabaniss and Shuman, 1987; Galapate et al., 1998]. By comparing SFS spectra of unpolluted river water, sewage

effluent, and down stream water sample after sewage mixing, Galapate et al. [1998] indicated that SFS can be applied to differentiate DOM in surface water. Therefore, it can be concluded that SFS can at least qualitatively characterize NOM. Table 2.1 lists several fluorescence excitation-emission zones and associated component [Leenheer, 2003]

Table 2.1 Major fluorescence compounds & EX-EM zone [Leenheer, 2003]

Excitation range (nm)	Emission range (nm)	Compounds
330-350	420-480	Humiclike
250-260	380-480	Humiclike
310-320	380-420	Marine humiclike
270-280	300-320	Tyrosine-like, protein-like
270-280	320-350	Trypotophan-like, protein like or phenol-like

Fluorophores in natural organic materials have been liked with phenolic groups of the humic portion [Jean, 2000]. Coble [1996] reported that aromatic amino acids such as tyrosine, tryptophan, and phenyalanine could also be fluorescence excited. However, the study of Ahamd and Reynolds [1995] on model humic acid did not show any emission peak when excited at 248 nm, an observation different from the other two model aromatic amino acids, tyrosine and 4-hydroxy, 3-methoxy, cinnamic acid. Ahamd and Reynolds [1995] did not address the difference of humic acids nor provided its molecular structure. Fluorescence studies sometimes may present surprising even contradictory results if applied and explained inappropriately.

If characterization of DOM with fluorescence proceeded only qualitatively, it would not be much better than a series of UV spectrophotometry. The advantage of fluorescence inherits in its high sensitivity and more in its collected huge yet complicated information. Some information received by SFS is trivial and confusing and information of SFS must be extracted and refined with post data processing with statistics [Marhaba et al., 2000]. With the guidance of statistics, quantification of organic fraction is possible with its characteristic fluorescence spectra and would much benefit to practical use.

2.3 Organic Fractions and Their DBP Formation Potentials

Fractionation of DOM in water is an efficient tool to assist in recognizing the role of each organic fraction on the formation of DBPs. As of today, most studies have been engaged in hydrophobic acids, which are responsible for the color of water. Among the six collected fractions, hydrophobic acids (humic and fulvic acids) have been given more emphases than other fractions, considering surface water usually contains 50-90% of them. The more matured isolation/collection/purification procedure for hydrophobics than that of hydrophilics may explain partly that attention difference.

All the fractions are more or less reactive with chlorine to produce certain amount of DBPs [Kitis et al., 2002; Martin, 1997; Reckhow et al., 1990, Oliver and Thurman 1983]. As a matter of fact, chlorine demand is still in use to characterize fraction reactivity to chlorine. The problem with chlorine demand characterization is various dosage of chlorine in such studies so that comparison is not possible. The fact that all fractions produce DBPs can be explained with two speculations about the reaction mechanisms. Either all the fractions possess certain functional groups reactive to

chlorine or chlorine reacts each fraction without any discrimination or their combination [Marhaba and Van, 2000].

Studies on the chlorination of organic materials in surface water found that the humic fraction contributes significantly to the DBP formation. The hydrophobics can produce DBPs at 40-120 μg $CHCl_3$/ mg Carbon, in which humic acids were found to produce slight more DBPs than fulvic acids [Reckhow et al., 1990]. In the study of Labouyrie [1997], the formation potential of TTHMs was 51 and 55 μg $CHCl_3$/ mg Carbon for hydrophobic neutral and acid, while a maximum of 40 $CHCl_3$/ mg Carbon was found for hydrophilic acid, the dominant hydrophilic fraction. Similar conclusions were also obtained in the work of Rechhow et al. [1990], who studied five surface waters. The humic acid generally formed 10-20 $CHCl_3$/ mg Carbon more than the fulvic acid and the hydrophobics produced more THMs than the hydrophilics. Koshin et al. [1997] also reached the same conclusion in their study, however, in which hydrophobics were isolated by iron oxide rather using XAD-8.

While hydrophobics are currently considered as the main fraction responsible for the formation of DBPs, there are still some cautions about this view. First, most of fraction DBP formation studies focused on source water, or on humic type water. Conventional or enhanced conventional treatment can remove most hydrophobics. This would shift hydrophilic fractions as the dominant organic materials remaining in the water, for which is actually chlorinated. Second, several studies also showed that hydrophilics produced appreciable amounts of DBPs in some waters [Owen et al., 1995; Croue et al., 2000; Lanvik and Holmbom, 1994; Gang et al., 2003; Ketis et al. 2002]. Since the hydrophilics are less amenable to removal compared to hydrophobics and the

relative level of hydrophilics is expected increasing through water treatment chain, their contribution to total DBP formation can have significant implications.

CHAPTER 3

MATERIALS AND METHODS

3.1 Research Protocol and Analyses

A study of high quality at least relies on a thorough understanding and proper operations of involved test methods. It is therefore required for an investigator to have a fundamental knowledge of methods implemented in the study. Familiarity with a proper execution of test methods is then built upon and hands-on experiences can be enhanced. If possible, QA/QC protocols should be coded in each method and be stringently followed with to enhance repeatability and reproducibility.

This study involves a wide range of analyses or tests, from very basic pH measurement to complicated trihalomethane formation potential tests by GC/ECD or GC/MS. Table 3.1 lists most of the analyses conducted in this study and figure 3.1 shows the whole research protocol. This chapter details all test and analysis procedures except sample fractionation procedure that will be discussed in Chapter 4. These procedures are addressed generally in a time sequence of samples being manipulated. To be quickly referred, some analytical procedures are written in a Standard Operation Procedure format and placed as appendices in the final section of the dissertation.

3.2 Sample Pretreatment

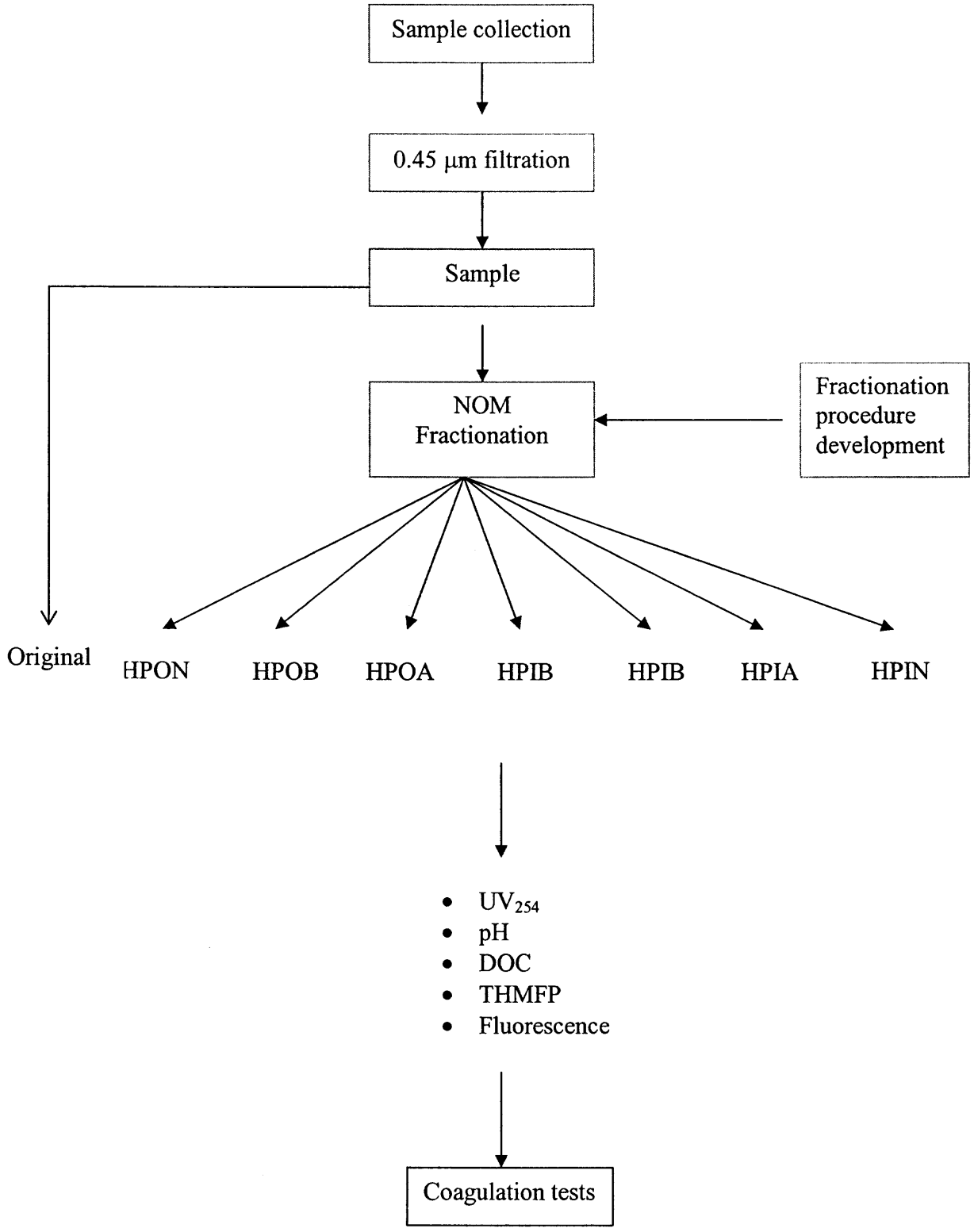
After samples were collected from the water treatment plant of Middlesex Water Company, Edison, New Jersey and sent in, they were filtered through MFS Nylon 0.45 μm membranes (Advantec MFS Inc., Pleasanton, CA) usually within 24 hours to remove particles. Original source samples and fraction samples were saved in amber bottles,

refrigerated at 4°C, and stored in the dark to prevent any interference. Filtration apparatus were pre-heated at 450°C to remove possible organic material carry-in.

Table 3.1 Analysis conducted

Objective	Method	Instrument
PH	Standard Method 4500-H^+ B (3-point calibration)	Accumet® model 50 pH/ion/conductivity meter
Conductivity	Standard Method 2510 B (Single point calibration)	Accumet® model 50 pH/ion/conductivity meter
DOC	Standard Method 5310-D (UV/Persulfate)	Tekmar Dohrmann Phoenix 8000
Alkalinity	Standard method 2320 A	
UV_{254}	Standard method 5910 B	Varian DMS 300 UV/Visible spectrophotometer
Chlorine Residual	Standard method 4500-Cl B	
	Chlorine demand Sample chlorination and incubation	Standard method 5710 B
THMFP	THM extraction THM Analysis	EPA 551.1 Varian 3400 GC/ECD HP 6890 GC/MS
Coagulation	Jar tests	Phipps & Bird™ coagulation apparatus
Resin Purification		Soxhlet extraction apparatus
Fluorescence intensity		Hitachi F-4500 fluorescence spectrophotometer
Fraction collection	Fractionation procedure Distillation and GC determination	Chapter 4
Solvent MTBE purification		Distillation apparatus GC/MS
HPON purification	Rotary vacuum evaporation GC/FID analysis	Buchi RE 111 rotary vacuum evaporator HP 5890GC/FID

Figure 3.1 Research protocol



3.3 pH Calibration and Measurement

Calibration of pH is critical in this study. Hydrophobic fractions are separated by only pH difference: 7±0.1 for hydrophobic neutral, 9.8-10 for hydrophobic base, and 2±0.1 for hydrophobic acid. The pH of sample for hydrophilic acid fractionation determines the amount of resin DOWEX WA 10 since the capacity of this resin is a function of solution pH. The chlorine demand tests are conducted at a required pH around neutral and 5.5 required for THMFP tests. pH is checked in addition to conductivity and DOC to verify resin purification. MQ water passed through purified columns separately containing XAD-8, AG-MP-50, and WA 10 should remain a pH around 5.5.

This study used Accumet® model 50 pH/ion/conductivity meter (Denver Instrument Company, Denver CO). It includes pH and conductivity models, which can be switched between them, providing a convenient, concurrent measurement of pH and conductivity. Furthermore, the meter can be set up with a much wide calibration range and with multiple points of calibration. This facilitates, in this study, the adjustment of sample pH, like from 10 for hydrophobic base fractionation to pH 2 for hydrophobic acid fractionation.

- Select pH model by push down **pH**
- Press **Standardize** and select **2** to clear all previous calibration
- Press **Standardize** and select **1** to initiate a new calibration
- Input 7.00 and **Enter**
- Rinse pH electrodes
- Insert pH probe into pH 7.00 buffer solution,

- Moderately stir with pH probe the solution and wait for 30 seconds
- Press **Enter** to accept pH 7.00 buffer solution)
- Repeat from step 2 to 7 for pH 10.00 buffer solution
- Repeat from step 2 to 7 for pH 4.01 buffer solution
- Start to measure sample pH by inserting pH probe into sample solution
- The S/U at right bottom corner indicates whether pH measurement is Stable/Unstable

It is very important to verify the pH meter by running pH standard buffer solutions as samples. This simple QC/QA practice applies to other measurement alike.

Table 3.2 pH measurement

Process	Sample	pH
Resin purification	MQ water passed through resin	5.5-6.0
	Sample for HPON	7±0.1
	Sample for HPOB	9.8-10
Sample fractionation	Sample for HPOA	2±0.1
	All sample for HPI	2±0.1
Chlorine demand	Sample	7
	Incubated sample	7
THMFP	Extracted sample	5.5

3.4 Alkalinity Measurement

Alkalinity never received so much emphasis of analysis in water treatment as it does today. While water treatment plant monitored alkalinity regularly before, it is predominately for the concern of pH drop during coagulation or softening. Today, alkalinity is the most important parameter next to TOC as required in Stage 1 D/DBP Rule to be examined for performances of enhanced coagulation/Precipitative softening. The more alkalinity in water, the more difficult is TOC treatment, and the less is TOC removal.

Alkalinity measurement is conveniently conducted according to standard method *Alkalinity 2320B Titration* by titration of a certain volume of water samples until pH 4.5.

3.5 Conductivity Calibration and Measurement

Conductivity of samples determines the amount of resins needed to fractionate the original samples. The conductivity has to be measured to calculate how much AG-MP 50 and WA 10 resins are in need for fractionation of hydrophilic base and acid, respectively. Due to procedure modification (see chapter 4), the value of conductivity input to calculate the amount of resins should be the one just after sample being adjusted to pH 10 with NaOH for AG-MP 50 and the one just prior to hydrophilic acid fractionation for WA 10. The conductivity of samples being just sent in will no longer be valid to decide the mass of resins for fractionation. In general, the conductivity of samples being just sent in varied between 130 and 220 μs/cm, dependent on sampling location and time.

- Select conductivity model by press down **Conductivity**
- Press down **Standardize** to calibrate conductivity meter

- Type in standard conductivity buffer value
- Insert conductivity probe into standard solution
- Slightly move probe up and down to drive out air inside the probe
- Press **Enter** and accept calibration
- Immerse probe and start to measure sample conductivity

Selection of standard conductivity solution is the key to an errorless conductivity measurement. The conductivity meter actually applies only one point calibration to set up calibration range; therefore, the conductivity standard solution should be selected to cover possible sample conductivity with an assumed zero conductivity calibration. As a result, a conductivity standard of 10 μs/cm was selected for samples such as MQ water; the conductivity meter when measuring original samples should be calibrated with a standard of 1,034 μs/cm and verified with a standard of 103 μs/cm; a standard solution of 10,400 μs/cm was chosen for samples to be hydrophilic-material fractionated, which had a pH about 2.

3.6 DOC Measurement of Original and Fraction Samples

DOM in samples is represented as mg/L of dissolved organic carbon (DOC) and was measured with a Phoenix 8000 TOC Analyzer (Tekmar Dohrmann, Cincinnati, OH) using the UV/Persulfate oxidation method (Standard Methods 5310-D, 1995). The running mode was selected as simultaneous DOC 0.1–20 mg/L. 0, 1, 2.5, 5 and 10 mg/L standards prepared with a 1000 mg/L DOC stock solution (LabChem, Pittsburgh, PA) were run to calibrate the TOC instrument. The instrument error was controlled within 4% with runs of 5 mg/l standards after every five standard samples and the sample precision of three repeats was controlled within 5%. The calibration must achieve a correlation

above 99.9%. All fraction samples were appropriately pH adjusted and diluted to reduce the contribution of eluant chemicals to DOC if necessary. Milli-Q (Millipore Corp., Bedford, MA) was used for all dilutions, sample preparation, and final glassware washing. All sample glassware was oven dried at a temperature of 500 °C.

The Phoenix 8000 TOC Analyzer has a striking design with an 8 port valves and two reactors so that it can speed up DOC measurement by simultaneous running reactor/tubing rinse, purge of total inorganic carbon (TIC), and DOC. When samples inside the UV reactor (DOC reactor) are being oxidized with UV and persulfate oxidant into DOC that will be monitored with a non-dispersive infrared detector (NDIR), the 8 port valves can introduce new samples into the inorganic carbon reactor (DIC reactor) likewise for phosphoric acid. The sample inside the DIC reactor is acidified and converted into CO_2 that is purged by Nitrogen and can be either detected or just released. At the end of reaction inside the DIC reactor, all inorganic carbon is driven off and samples are diverted into UV reactor ready for only DOC measurement.

3.7 UV_{254} Tests

UV_{254} describes quantitatively the absorption of incident light at 254 nm by samples usually hold in a 1 cm cell. UV_{254} is an aggregate parameter in that any unsaturated organic compound in theory can absorb UV light at a degree determined on compound absorbance coefficient and its concentration. Therefore, UV_{254} doesn't provide much structural information of interested organic materials. UV_{254} is currently monitored in water treatment plant to indicate efficiency of units such as enhanced coagulation to remove organic materials, which is considered as DBP precursors. While UV_{254} is associated with the level of organic materials present in drinking water, it is

believed that it more represents color introducing organic materials and functions quite well with water of hydrophobic type. It does show some degree of successes in examining treatment performance; however, it may be deviating when to predict DBP formation with UV_{254}. However, due to test convenience, UV_{254} is a primary parameter required by USEPA to be monitored. More precisely, it is the specific UV absorption at 254nm ($SUVA_{254}$) defined as UV_{254} divided by DOC that leads to more accurate interpretation on water organic materials to form DBPs.

A double beam UV/Visible spectrophotometer, Varian DMS 300 UV/Visible spectrophotometer, (Varian Inc., Palo Alto, CA) is used in this study to measure UV_{254}. The reference light beam records background UV_{254} absorption and then is zeroed out when reading sample's UV_{254}.

3.8 Fluorescence Spectrophotometry Test

A recent development of NOM characterization is the application of fluorescence spectrophotometry to study NOM. The fluorescence spectrophotometer at first looks like a modified, single beam UV spectrophotometer in that the light being detected exits at a 90-degree away from incident light. However, the theory of fluorescence differs essentially from that of UV absorption. In UV spectrophotometry, light out of tested samples decreases in intensity compared with incident light due to absorption and is detected. The intensity decrement is dependent upon sample specific absorbance coefficient at a given wavelength and sample concentration. In fluorescence spectrophotometry, samples also absorb the coming light; and then samples emit some characteristic light after being elevated to excited states. It is the light that is released during sample molecules' return from the excited states to ground level to be detected.

For this reason, fluorescence spectrophotometer is designed with detectors always sitting 90 degree away from the incident light to eliminate the interference of remaining incident light and fluorescence spectrophotometer must contain two wavelength selectors: one for emission and the other for excitation.

Both UV and fluorescence spectrophotometers are easy in operation. For fluorescence spectrophotometer, a proper operation generally requires wavelength calibration with the sharp spectrum line of Xe lamp, S/N determination by water Raman spectrum at excitation of 350 nm, and spectra correction with Rhodamine B. After the fluorescence spectrophotometer is confirmed in satisfactory running condition, sample can be scanned to collect fluorescence information for both emission and excitation with a much wider, selectable range of wavelength than UV spectrophotometer. It is for this reason as well as an excellent sensitivity of fluorescence spectrophotometer that fluorescence studies are becoming increasingly important to the NOM study.

This study used Hitachi F-4500 Fluorescence spectrophotometer (Hitachi, Ltd. Tokyo, Japan). A typical run for one sample lasts less than 10 seconds. The operation procedure is formalized and placed as an appendix for quick references.

3.9 GC/ECD Determination of THM

Part of this study was to develop a Standard Operation Procedure of EPA 551.1 for THM only used with a Varian 3400 GC/ECD modified from GC/FID (Varian Inc., Palo Alto, CA). For this reason, a chapter (chapter 5) especially addresses the method development based on requirements of EPA 551.1 with modification suitable for instrument involved and research objectives.

3.10 Chlorine Demand Tests

The chlorine demand tests determine or accurately estimate the 7-d sample chlorine demand. The chlorine demand test is the first of a series of time consuming, tedious tests to finally assess the potential of samples to form DBPs. Given as an example of how complicated the whole DBPFP test is, the chlorine demand test is often skipped and the chlorine dosage for incubation of samples to form DBP is arbitrarily set with a constant ratio of DOC/Cl_2, such as Cl_2, mg/L = 3×TOC+NH_3-N [Krasner, 1989]. This ratio correlation may or may not be representing the reality since the dosage of chlorine is undoubtedly a function of the organic materials in water. The essential question is what the function is and how universal it can be.

In this study, chlorine demand test followed steps outlined in the standard procedure of *Formation of Trihalomethanes and Other Disinfection By-products 5710B Trihalomethane Formation Potential*. However, the standard procedure also refers to *Chlorine (Residual) 4500-Cl B Iodometrical Method I* for chlorine titration. It is for such a purpose to quickly access both standard methods that the procedure of chlorine demand tests provided here combines both standard test procedures.

- *Hypochlorite Stock Solution* (4-6% or about 28 mg Cl_2/ml)
  a) Add 3 ml Acetic acid and 1 g KI in 25 ml MQ water
  b) Add 2 ml chlorine stock solution (4-6%) (**Brown color**)
  c) Titrate with 0.1000N $Na_2S_2O_3$ (**Brown color → bright yellow**)
  d) Add 1 ml starch solution when yellow almost discharged (**yellow → blue**)
  e) Continue to titrate until blue color disappears
  f) Calculate chlorine concentration of the stock solution

Stock Hypochlorite, mg Cl_2/ml = (3.545× ml Titrant)/2

- Chlorine dosing solution (5mg Cl_2/mL)

  Calculate the volume of stock solution to prepare 100 ml of 5mg Cl_2/mL

$$\text{mL of required stock solution} = \frac{5\ \text{mg Cl2/ml} \times 100\ \text{ml}}{\text{stoch hypochlorite conc. (mg Cl2/ml)}}$$

- Prepare pH 7.0 phosphate Buffer according following table

Table 3.3 Composition of pH 7.0 buffer solution

Chemicals	Mass in 1 liter (g)
KH_2P0_4	68.1
NaOH	11.7

- Chlorine demand determination

  a) Incubate samples at least 4 hours according to table 3.4

Table 3.4 Incubation sample composition

Solution		Amount (ml)
Phosphate buffer		1
Chlorine dosing		1
Background check	MQ water	Fill to completely full
Tested sample	Sample	Fill to completely full

  b) Add 3 ml acetic acid into 100ml flask

  c) Add about 0.5 g KI

  d) Pour incubated samples into the 100 ml flask added with acetic acid

  e) Titrate with fresh 0.010 N $Na_2S_20_3$ standard solutions till blue color disappears

  f) Calculate sample chorine demand according to the following equation

$$\frac{(Ci\text{-}Cr)\times Vvial}{DOC\times(Vvial\text{-}2)} \times 1000, \text{ mg } Cl_2/\text{ mg C}$$

C_i, initial chlorine (mg Cl_2/ml) $\frac{5 \text{ mg } Cl2/ml \times 1 ml}{Vvial}$

Cr, chlorine residual (mg Cl_2/ml) after at least 4 hrs incubation

$$\frac{0.010 \times 35.45 \times ml \text{ Titrant}}{Vvial}$$

V_{vial}, volume of empty vial (ml)

DOC, organic carbon concentration of samples (mg C/L)

The procedure of chlorine demand test devised in this study differs from the standard procedure in that 43-mL amber vials are used instead of 250-mL bottle due to the limitation of fraction volumes. For the same reason, 1 mL rather than 5 mL of chlorine dosing solution (5mg Cl_2/mL) was added to the 43-mL amber vials, making a dosing strength of 0.116 mg Cl_2 / mL rather than the suggested 0.10 mg Cl_2 / mL. The concentrations of sodium thiosulfate were also changed to 0.10 and 0.010 N to titrate hypochlorite stock solution and the chlorine demanding samples, respectively.

Table 3.5 Chlorine demand test working sheet

	Fraction	Sample	Empty Vial (g)	pH 7 Buffer (mL)	5 mg/ml Dosing (mL)	Filled Vial (g)	DOC (mg/L)	0.01 N Titrant (mL)	Cl_2 Demand mg Cl_2/mg DOC
1	Raw			1	1				
2				1	1				
3				1	1				
4				1	1				
5				1	1				
6				1	1				
7				1	1				
1	HPON			1	1				
2				1	1				
3				1	1				
4				1	1				
5				1	1				
6				1	1				
7				1	1				
1	HPOB			1	1				
2				1	1				
3				1	1				
4				1	1				
5				1	1				
6				1	1				
7				1	1				
1	HPOA			1	1				
2				1	1				
3				1	1				
4				1	1				
5				1	1				
6				1	1				
7				1	1				
1	HPIB			1	1				
2				1	1				
3				1	1				
4				1	1				
5				1	1				
6				1	1				
7				1	1				
1	HPIA			1	1				
2				1	1				
3				1	1				
4				1	1				
5				1	1				
6				1	1				
7				1	1				

3.11 Sample Chlorination and Incubation for THM Formation

Sample chlorination and incubation to form THM is conducted in 68-mL vials. Therefore, the appropriate volume of the 5 mg Cl_2/ mL dosing solution is calculated according to

$$V_D = (\frac{D_{Cl}}{5} \times DOC + 3) \times \frac{Vs}{1000}$$

Where: Vs, volume of vial in mL

V_D, volume of dosing solution in mL

D_{Cl}, sample chlorine demand in mg Cl_2/mg DOC, and sample is chlorinated according to table 3.6.

Table 3.6 Composition of incubated samples

Solution	Amount (ml)
Phosphate buffer	2
Chlorine dosing	V_D
Sample	Fill to completely full

The chlorinated sample is then stored in the dark at 25±2°C for 7 days in an incubator.

As a summary, the THM formation includes determination of Cl_2 in hypochlorite stock solution, preparation of 5mg Cl_2/ml chlorine dosing solution, determination of sample chlorine demand, and sample chlorination and incubation.

Table 3.7 Incubation working sheet

	Fraction	Sample	Empty Vial (g)	pH 7 Buffer (ml)	5 mg/ml Dosing (ml)	Filled vial (g)	DOC (mg/l)	pH after7 days	
1	Raw			1					
2				1					
3				1					
4				1					
5				1					
6				1					
7				1					
1	HPON			1					
2				1					
3				1					
4				1					
5				1					
6				1					
7				1					
1	HPOB			1					
2				1					
3				1					
4				1					
5				1					
6				1					
7				1					
1	HPOA			1					
2				1					
3				1					
4				1					
5				1					
6				1					
7				1					
1	HPIB			1					
2				1					
3				1					
4				1					
5				1					
6				1					
7				1					
1	HPIA			1					
2				1					
3				1					
4				1					
5				1					
6				1					
7				1					

3.12 Preparation of Standard and Sample Solution for THM Tests

Unlike normal standard solution, THM standard solution has to experience an extraction process same as that of samples after initial preparation; therefore, the amount of THM being actually detected is procedurally dependent, allowably different from the original added amount as long as standards and samples are both subjected to identical extraction process. To prepare THM standard solution procedurally is to control that any potential change (loss) of target compounds in samples during extraction is duplicable on standard solutions as well.

The procedural preparation of THM standard solution starts with preparation of aqueous standard solution, in which 25-µl target primary standard solutions and 10-µl surrogate primary solution (10 mg/L) are added into 50 ml of pH 5.2 phosphate/de-chlorinating solution pre-placed in 68-ml vials. The vials are then capped, inverted twice carefully and gently to distribute homogeneously over the whole solution target compounds and surrogate, which are then backwards extracted into MTBE solvent. To facilitate the extraction, 5 g Na_2SO_4 (preferred) or 10 g NaCl are added into the vials right away after 3 ml MTBE addition. Recap, invert and shake the vials vigorously for about 4 minutes and allow phase separation completes until two lays are formed and visually clear. 0.5 ml MTBE phase is pipetted into 0.5 ml GC inserts that are over-packed with 2ml vial. The extracted targets and surrogate now are in organic phase and ready for GC separation and determination with ECD or MS. Prior to GC injection, 1µl internal standard working solution was injected with 1ml sample solution directly into GC inlets.

The sample extraction follows the procedure outlined above for standard solution. Additionally, prior to extraction, incubated samples need de-chlorinating and pH

adjustment. Incubated samples are taken out of the incubator and left for equilibration till room temperature. 18 ml samples are pipetted out for pH measurement and/or residual chlorine determination. The reason to remove 18 ml of incubated sample is to make the final volume of sample being extracted next into 50 ml, equivalent to that of standard solution. Add 2 grams of pH and de-chlorinating mixture and then follow the extraction procedure addressed above for standard solution to extract and test THM.

CHAPTER 4

FRACTIONATION PROCEDURE DEVELOPMENT

4.1 Importance of Fractionation Procedure

Stage 1 D/DBP Rule mandates a control of ≤80 μg/L for TTHM and ≤60 μg/L for HAA_5 in distributed water. TTHM, HAA_5, and other organic DBPs form during chlorine-based disinfection of water that contains DOM. Utilities of surface source or groundwater under direct surface influence are being regulated by USEPA to achieve specific rates of removal of NOM/DOM to minimize exposure to risks of DBP chemicals. The removal of NOM is quantified as the decrement of TOC between paired source and treated water samples. It is attributable to Stage 1 D/DBP Rule that NOM/DOM now receives tremendous study efforts.

USEPA recognizes the potential health hazards of DBPs; however, it identified few techniques for a direct removal of DBPs. DBP, a health hazard, occurs in a level so trace (ppb level) that treatment targeting DBP if any could not be cost attractive to water treatment plants. Control of DBP in treated water is accomplished instead through attacking its precursor NOM or through other cost-effective tactics such as change of chlorination points, application of alternative disinfectants. Hence, understanding NOM/DOM characteristics with a focus on its relation with DBP is crucial for the control of DBPs.

The general approach to study DOM is first to fractionate DOM in water, characterize collected fractions, and conduct DBP formation as well as other tests on individual or reconstructed combined fractions. Fractionation is more than just a means to concentrate trace organic material. Fractionation accumulates organic materials into

different groups with minimal variation of their original properties. Organic materials of same fraction are assumed similar in physical and chemical properties. Fractionation facilitates its followed studies. Therefore, fractionation is the basis of NOM/DOM study and this chapter is devoted to address a fractionation procedure intended for water with low DOM.

4.2 Principle of Resin DOM Fractionation

Leenheer of USGS at Denver, CO has pioneered research on resin DOM fractionation. In 1979, he developed first analytical fractionation procedure [Leenheer and Huffman, 1979]. In 1981, he presented the first preparative fractionation procedure [Leenheer, 1981]. Analytical fractionation aims to inform distribution of DOM among all fractions, i.e., the quantity of each fraction. Analytical fractionation needs far less amount of water sample and resins than those required in preparative fractionation. Preparative fractionation attempts to collect enough fractions to conduct further tests including DBPFP, while to know each fraction concentration is equivalently necessary in preparative fractionation as in analytical fractionation.

Hydrophilic materials are those materials with a strong tendency of associating themselves with water molecules: HYDRO- means water and PHYLIC- means love. Hydrophobic materials dislike water molecules and would remain from water at a distance that is as far as allowed and that is determined by forces between water and hydrophobic materials. Therefore, hydrophobic materials in general have a lower solubility than their counterparts. For example, hexane and acetone used for purification of XAD-8 resin belong to hydrophobic and hydrophilic categories, correspondingly. Hydrophobicity or hydrophilicity of pure compound can be established relative to an

arbitrary reference, usually water. Table 4.1 lists some relative hydrophilic or polar indexes for common organic solvents. An index 9.0 is assigned to water and indexes for other organic solvents are set up against water. It is inferable from the table that hydrophilicity increases from hexane (0) to acetone and methanol (both 5.1), and to water (9.0). It is interesting as well to notice that chloroform is slightly hydrophobic.

Table 4.1 Relative hydrophobic index for common solvents

Relative Hydrophilicity	Compound Formula	Group	Representative Solvent	Example (name, index)
Increase	R-H	Alkanes	Petroleum ethers, hexanes	Hexane, 0.0
	Ar-H	Aromatics	Toluene, benzene	Benzene, 2.7
	R-R	Ethers	Diethyl ether	
	R-X	Alkyl halides	Tetrachloromethane chloroform	Chloroform, 4.1
	R-COOR	Esters	Ethyl acetate	
	R-CO-R	Aldehydes and ketones	Acetone, methyl ethyl ketone	Acetone, 5.1
	R-NH2	Amines	Pyridine	
	R-OH	Alcohols	Methanol, isopropanol	Methanol, 5.1
	R-CONH2	Amides	Dimethylformamide	
	R-COOH	Carboxylic acids	Ethanoic acid	
	H-OH	Water	Water	Water, 9.0

DOM in drinking water contains various hydrophobic and hydrophilic materials and there is no way to single them out. It is preferred to separate DOM in water into groups in a way that organic materials in each group show similar chemical and physical properties. Because of DOM variety, a question arises of how DOM in water can be separated based on hydrophobic or hydrophilic properties.

Leenheer suggested Amberlite XAD-8 resin (Supelco, Supelco Park, Belfonte, PA) resin as the solution to the question [Leenheer and Huffman, 1976]. XAD-8 originally was patented, manufactured, and named as DAX-8 by Rohm and Hass. It is a macro-porous methyl-methacrylate copolymer and is hydrophobic. Later, Supelco bought the patent; however, had to re-name it as XAD-8. A recent study published compared capacities between XAD-8 and DAX-8 [Peruvouir et al., 2002]. For the reason just discussed, it is no surprise to see that the authors claimed no difference between XAD-8 and DAX-8 to adsorb organic materials.

XAD-8 or DAX-8 resin has been widely accepted as the only resin capable to separate DOM between hydrophobic and hydrophilic. It should be pointed out that, unlike pure solvent, hydrophobic and hydrophilic of natural water is arbitrarily designated and operationally defined because XAD-8 can adsorb some solutes with intermediate or even polar (hydrophilic) organic solutes; XAD-8 is not so critically selective against organic materials. To determine if natural water is hydrophobic or hydrophilic in terms of contained organic materials is solely dependent on the quantity of XAD-8 used in fractionation for a given quantity of tested water. Therefore, the hydrophobic-hydrophilic cutting line can be mathematically manipulated. If a research favors more on hydrophobic collection, the amount of XAD-8 can be increased to drive

more organic materials to XAD-8 resin; to the opposite, the amount of XAD-8 should be reduced.

This study adopted a designation identical to that of Leenheer [1981]. Repeated here is "hydrophobic solutes are defined as those solutes that are greater than 50% retained on XAD-8 at a given ratio of resin to water passed through the column, and hydrophilic solutes are defined as those solutes that are greater than 50% eluted at the same ratio of resin to water sample." In a simple explanation, a solute is hydrophobic if more than 50% of its mass in the original water sample is retained on a given amount of XAD-8 at the end of adsorption; otherwise, it is considered as hydrophilic and more than 50% of its original mass will remain in water.

Figure 4.1 illustrates this designation by showing breakthrough curves for three imagined solutes: reference, hydrophobic, and hydrophilic. These solutes have a same initial concentration, but show difference in adsorption. The integrated area above each breakthrough curve represents the solute adsorbed; likewise, the area below is the solute still in the water. For the reference solute, the two areas are identical, yielding 50% for retention and 50% for elution. This solute is neither hydrophobic nor hydrophilic. The solute whose breakthrough curve is to the right side of that of reference is hydrophobic because more than 50% of solute can be retained onto XAD-8 resin under a given amount ratio of water to resin. The hydrophilic materials should behave like the one to the left side of the reference during adsorption.

The volume of XAD-8 resin can be calculated with an equation induced by Leenheer [1981] and generalized here as

$$V_{sample} = V_{resin\_bed} \times \rho \times \left(1 + K'_{0.5r}\right)$$

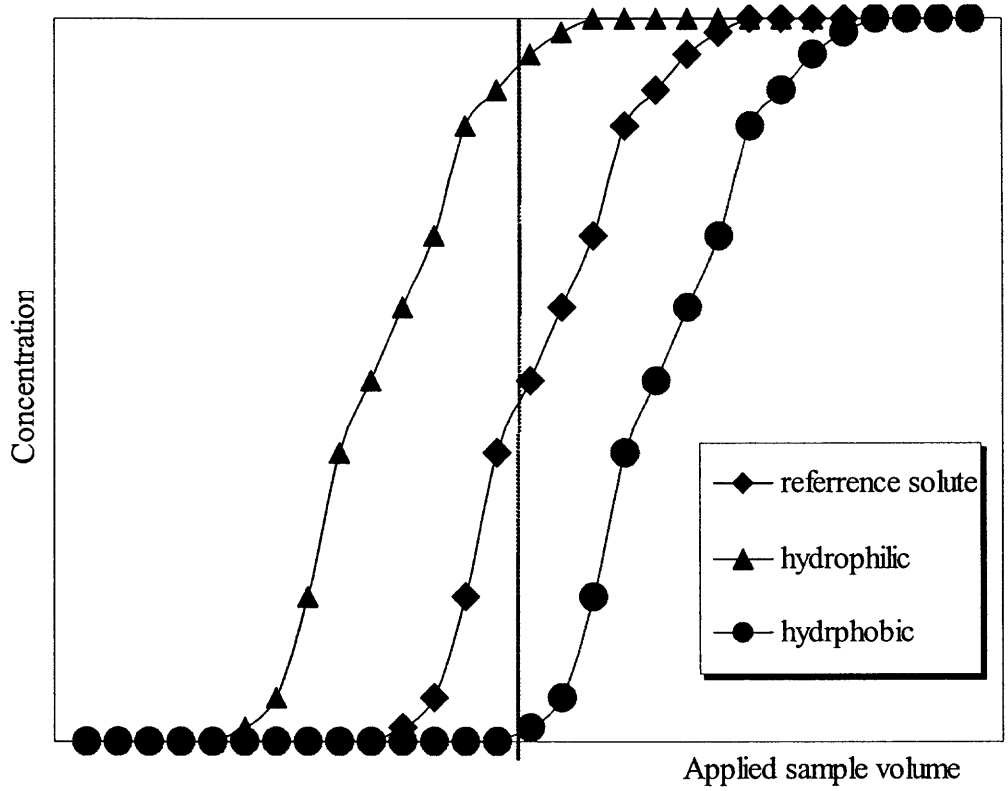
V_{sample}: volume of sample fractionated

V_{resin_bed}: volume of resin bed

ρ: Porosity of resin bed

$K'_{0.5r} = 50$ in this case.

Figure 4.1 Breakthrough curves for three imagined solutes



Leenheer also gave an example for 1-liter sample fractionation. Taking 0.65 for porosity of XAD-8 resin bed, 15 mL of XAD-8 is needed to fractionate 1-liter water sample.

Interestingly, resin XAD-8 amount calculation takes none of sample water quality parameters; so the quantity of XAD-8 for a given amount of water sample is same for all types of water. The amount of XAD-8 is only a function of packed resin (porosity) and the volume of water to be fractionated. This further indicates the operational definition of hydrophobic or hydrophilic [Leenheer, 1981; Leenheer and Croué, 2003].

XAD-8 resin is operated in combination with manipulation on sample pH to fractionate different hydrophobic materials: hydrophobic neutral, base, and acid. The XAD-8 resin is adsorption resin and the adsorption is mainly explained with physical attraction. Simply speaking, it is "hydrophobic to hydrophobic." Adjustment of pH is to decrease any non-hydrophobic forces and facilitate organic materials' affiliation to hydrophobic XAD-8 resin. For this reason, hydrophobic neutral fractionation should be conducted at neutral pH. High and low pH should be selected for hydrophobic base and hydrophobic acid respectively for protonation/de-protonation.

Effluents after samples being processed with hydrophobic fractions contain only hydrophilic organic materials, which can be separated with ionic exchange resins. Hydrophilic base materials are exchanged onto cationic exchange resin. An example is amine group organic materials that are hydrophilic base due to $-NH_2$ and is positively charged at low pH by protonation ($-NH_3^+$). Hydrophilic acids are considered negatively charged so that application of anionic exchange resins can isolate hydrophilic acids. Organic materials left in water sample after all above processes are designated as hydrophilic neutral.

Bio-Rad AG-MP-50 (Bio-Rad, Hercules, CA), a cationic exchange resin, was suggested in the paper of Leenheer [1976] for hydrophilic base fractionation. The amount of such resin is determined by the resin exchange capacity as well as milliequivalents of cations present in sample, which only can be estimated with an empirical equation. To calculate the quantity of AG-MP-50, it is necessary to know conductivity of the water sample. The conductivity should be the one for the original sample rather than that of sample already being pH adjusted. Conductivity of natural

water is usually less than 500 μs /cm. Sample for hydrophilic acid fraction has conductivity more than 3000 μs/cm due to pH adjustment to 2.

Duolite A7 is an anionic exchange resin and was adopted by Leenheer [1981] for hydrophilic acid fractionation. However, this resin has a very sever problem of bleeding that resin itself will break down during purification, adsorption, and fraction elution; therefore, Duolite A7 could release resin breakdown materials and contaminate the last two fractions: hydrophilic neutral and acid. If polluted with resin bleedings, both fractions should have a yellow to orange color and the pollutants (resin breakdown materials) are considered mainly as amines (personal communication with Dr. Leenheer). For this reason, post cleanup with re-adsorption of amine organics onto supplemental AG-MP-50 resins must be performed for purification of hydrophilic acid and neutral fractions.

As discussed above, an accurate fractionation procedure is necessary to determine each fraction concentration in the original samples and collect representative fractions. Application of an accurate fractionation procedure, organic mixture in the original water can be delineated without a significant error. In addition, such an accurate procedure is essential for the investigation of problematic fractions responsible for the most production of DBPs since the collected fraction would be chlorinated. The quality of collected fractions is important as well for further studies to remove those problematic fractions, such as jar tests, enhanced coagulations, and GAC filtration, in order to minimize the production of DBPs.

It is not senseless to explain what the "accurate" means in the fractionation experiments. The "accurate" in this study defines *No cross fractionation of fractions* and

concentration of each fraction is precisely known. For example, no hydrophobics are fractionated into hydrophilics. In the procedure of Leenheer [1981], this inaccuracy occurs mostly during hydrophobic fraction fractionation, in which only one column of XAD-8 was proposed to repeated use for all 3 hydrophobic fractions. It can be felt that cross fractionation is the main reason that quantification by mass balance concept was not done on hydrophobic fractions in Leenheer's procedure [1981]. In fact, some authors intended to co-fractionate two fractions through a procedural modification [Qualls and Haines, 1991]. They fractionated HPOB into HPIB and named the collected fraction simply as Base. The reason of such cross fractionation was very low concentration (mass) of HPOB and HPIB. Combining these two fractions could provide sufficient samples for further studies.

4.3 Modification of Fractionation Procedure

The principles discussed by Leenheer and Huffman [1976] created the basis of the analytical fractionation procedure [Leenheer and Huffman, 1979] and further of the preparative fractionation procedure [Leenheer, 1981]. The analytical procedure is designed to provide information on the fraction distribution of DOM in water and the preparative procedure is aimed to prepare organic-concentrated fractions for subsequent studies without further coping with tremendous volumes of sample. Both procedures are comprehensive since they fractionate all DOMs rather than humic substances, which are of typical interest to researchers. Another advantage of these procedures is that the associated operations (resin adsorption, ion exchange, and solvent extraction) more or less imitate natural conditions, such as some properties of soil and sediment surfaces [Qualls and Haines, 1991]. Although both the analytical and preparative procedures are

useful, the latter is more applied with modifications in studies such as disinfection and DBP formation.

While the preparative procedure [Leenheer 1981] has been mostly applied to natural water systems with success, its application to drinking water with low DOM, less than 5 mg C/L, such as in this study here, is less reported. In a context of low DOM in samples, DOM measurements performed on fractions may deviate relatively significantly due to the strong matrix use to elute fractions. The Duolite A7 resin used in this procedure for hydrophilic (HPIA) fraction presents a severe resin-bleeding problem. Although the resulted contamination could be remedied to some degree by re-adsorption of bleedings on additional cationic resin, it will be laborious; a possible loss of fractions may occur. It is then less preferable to preventing such pollution from occurrence.

The concept of mass balance in the studies of Leenheer and Huffman [1976,1979] to quantify hydrophilic base, acid and hydrophobic neutral, as well as the utilization of the less bleeding AG-MP-1 resin originate the philosophy of this study aimed to maximize the preparative procedure [Leenheer 1981] for low DOM content fractionation. The proposed procedure was experimented with samples from two surface water treatment plants to assess its feasibility in terms of both analytical and preparative fractionation. The goal is to provide data for low DOM water with minimum inaccuracy for finally developing rapid spatial and temporal fluorescent characterization techniques [Marhaba *et al.*, 2000a] and determining the precursory character of DBPs [Marhaba and Van, 2000].

The fractionation procedure suggested in this study was consistent with the preparative one of Leenheer [1981] regarding the separation theory. Although the

currently hydrophobic base is included into hydrophilic base due to its low occurrence in natural water, herein, it was still fractionated independently for future study of its role in disinfection and DBPs. Some changes on this preparative procedure have been made and are also discussed later. The next section will address resin purification to enhance a clear understanding of fractionation procedure.

4.4 Resin Purification Procedure

Resin cleanup procedures had been thoroughly described in paper of Leenheer [1981]. This section emphasizes principles of resin cleanup and examines possible interference of elution on fraction collection.

The XAD-8 resin is saturated with 0.1 N NaOH to remove fine particles. 0.1 N NaOH soaking helps to remove possible hydrophilic impurities carried from resin manufacture as well. The XAD-8 resin is then Soxhlet extracted in sequence with acetone and hexane each for 24 hours. The polarity of solvents used for cleaning up XAD-8 resin decreases in a sequence of that of their being applied. XAD-8 resin is purified in such a sequence so that hydrophilic impurities are removed first and hydrophobic next.

XAD-8 resin is surrounded with non-polar (hydrophobic) solvent, i.e. hexane, after Soxhlet distillation. It will be further washed with MQ water till a point of low DOC close to 0.2 mg/L and conductivity < 2 μs /cm. The two concentration levels are selected only because of instrument consideration: MQ water conductivity is < 2 μs /cm and DOC is measured with a running mode of 0.2 – 20 mg/L.

The MQ water purification of hexane-surrounding XAD-8 resin should be processed after intermediate rinse with methanol considering the drastic change of

polarity from hexane to water; otherwise, a very large volume of MQ water will be required and purification has been found very headache with oily hexane. Prior to MQ water rinse, certain volumes of methanol should be added into a beak or glass wool filled funnel (preferred) that contains XAD-8 resin that is just subjected to hexane extraction. After several rinses with methanol, purification of XAD-8 resin can be continued with MQ water. After several rinses with MQ water, XAD-8 resin can be conveniently packed into and can easily settle down inside columns. XAD-8 resin continues being purified with MQ water until the arrival of purification cut-off point defined above.

For fractionation, not only dose XAD-8 resin need purified till acceptable levels of DOC and conductivity occur in effluents of MQ rinsing water, but also is it necessary to examine possible XAD-8 resin breakdown during real sample runs as well as during elution of fractions. In brief, XAD-8 resin will be subjected to 3 different pHs: 2, neutral, and 9.5-10 during fractionations of sample, and 2 extreme pHs: pH 1 for elution of hydrophobic base and pH 13 for hydrophobic acid.

To examine if XAD-8 deteriorates during adsorption, each of the 3 1-liter synthetic water samples was passed through 15 ml purified XAD-8 resin. The effluent was collected in batches of 50 ml each. The collected effluents were then tested for DOC and conductivity. Results were listed in table 4.2.

In these simulation experiments, water samples were synthesized by first adjusting pH of 3-liter MQ water (pH 5.50, conductivity 1.64 μs/cm, DOC 0.24 mg/L) to 7±0.1 with 0.7 ml of approximate 0.1 N NaOH. Next, the 3 liters of water were added with 0.3 grams of NaCl to raise conductivity to around 220 μs /cm, a number commonly found in drinking water intakes. The synthetic samples were then divided into 3 of 1-liter

samples and two of them were further modified to pH 2 and 10 with concentrated H_2S0_4 and 10 N NaOH, respectively. The synthesized water samples were passed through XAD-8 resin and sample effluents were collected in batches of each 50 mL and tested for the concentration of DOC and conductivity level. Initial 20 mL of effluents contained synthesized water and were discarded.

The results in table 4.2 clearly indicate a very good stability of XAD-8 resin under various pH conditions. Conductivity of effluents remained unchanged for all three types of samples. The relative deviations (RD) were 0.48%, 3%, and 4% for pH 2, 7, and 10 samples accordingly. The excellent stability of XAD-8 was further highlighted when explained with DOC change. While table 4.2 shows a very high relative deviation of DOC among each batch, the average of them showed no difference from the influents. Due to influent DOC concentration so low that close to selected mode lower limits (0.2 – 20 mg/L), the high deviation of each sample effluent DOC from that of influent was expected and not surprising at all.

During fraction collection from XAD-8 resin, XAD-8 resin has to be exposed to extreme pH as well. Hydrophobic base is eluted with 0.25 bed volumes of 0.1 N HCl followed by 1.5 bed volumes of 0.01 N HCl. Hydrophobic acid is extracted into 0.25 bed volumes of 0.1 N NaOH followed with 1.5 bed volumes of 0.01 N NaOH. It can be seen first that desorption is achieved by such philosophy "Base (solution) for acid (fraction) and vice versa". Second, XAD-8 resin must be experimented at pH 1 for hydrophobic base collection and at pH 13 for hydrophobic acid elution.

Prior to fraction collection, synthesized sample water confined in XAD-8 resin bed was displaced with 0.0001 N (pH 10) NaOH for hydrophobic base or 0.01 N (pH 2)

H_2S0_4 for hydrophobic acid. These displacements of sample water provide a consistent pH to keep corresponding fractions remaining on XAD-8 resins.

Table 4.2 Column tests for XAD-8 resin stability during adsorption

Batch number	pH 2		pH 7		pH 10	
	Conductivity (μs/cm)	DOC (mg/L)	Conductivity (μs/cm)	DOC (mg/L)	Conductivity (μs/cm)	DOC (mg/L)
0	4690	0.24	220	0.24	249	0.24
1	4670	0.34	214	0.24	236	0.25
2	4620	0.20	223	0.23	238	0.03
3	4650	0.30	220	0.05	240	0.16
4	4680	0.06	208	0.16	229	0.19
5	4590	0.15	212	0.21	246	0.25
6	4680	0.26	210	0.17	252	0.12
7	4670	0.37	202	0.20	243	0.30
8	4630	0.14	215	0.19	229	0.15
9	4670	0.16	206	0.08	235	0.23
10	4660	0.24	226	0.26	245	0.32
11	4660	0.20	201	0.16	249	0.31
12	4650	0.30	215	0.19	250	0.2
13	4680	0.19	219	0.02	239	0.22
14	4650	0.30	203	0.16	229	0.16
15	4680	0.20	224	0.24	249	0.21
16	4660	0.35	210	0.21	229	0.12
17	4670	0.06	210	0.23	238	0.19
18	4670	0.10	204	0.25	219	0.09
19	4660	0.20	216	0.12	238	0.16
20	4600	0.19	210	0.10	240	0.32
Average	4656	0.22	212	0.17	239	0.20
RD%	0.48	42	3	39	4	40

The exposure of XAD-8 resin to extreme pH (pH 1 with 0.1 N HCl for hydrophobic base and pH 13 with 0.1 N NaOH for hydrophobic acid) would raise a concern of XAD-8 stability in terms of bleeding during fraction collection. For this reason, elution tests were simulated on the two columns of XAD-8 resin that had been filtered with pH 2 and 10 synthetic waters and results are shown in Figure 4.2a and b.

Figure 4.2a shows the breakthrough of pH and conductivity during simulated hydrophobic base elution with 0.25 bed volumes of 0.1 N HCl (conductivity > 10 ms/cm, pH 1.2) followed with 1.5 bed volumes of 0.01 N HCl (conductivity 3.97 μs/cm, pH 1.89). Due to 10^{-4} N NaOH replacement solution constrained in resin bed, initial effluent pH was between 10 and 1 and the conductivity was close to zero. The breakthrough of pH and conductivity began after 0.25 bed volumes of effluents being collected. At the end of elution, effluent maintained a pH 2 and conductivity 6 ms/cm. For the hydrophobic acid, the breakthrough of pH and conductivity began also after 0.25 bed volumes of 0.1 N NaOH had contacted the whole resin bed.

DOC concentration of the effluent was not measured at each sampling; instead, DOC concentration was measured when all eluting effluents for the same fraction were combined to provide sample volumes enough for DOC tests. The concentration of DOC for hydrophobic acid effluents was 0.26 mg/L and 0.21 mg/L for hydrophobic acid; both were comparable with their corresponding influent (0.22 mg/L for both). Theoretically, all the influents and effluents should not have contained any DOC. The above concentrations of DOC were approaching to test mode lower limit (0.2 mg/L). Results of such proved no resin bleeding during hydrophobic fraction elution. Chemicals might

introduce some trace level of DOC. For this reason, it is recommended to boil the prepared eluting solution before their application to extract fractions.

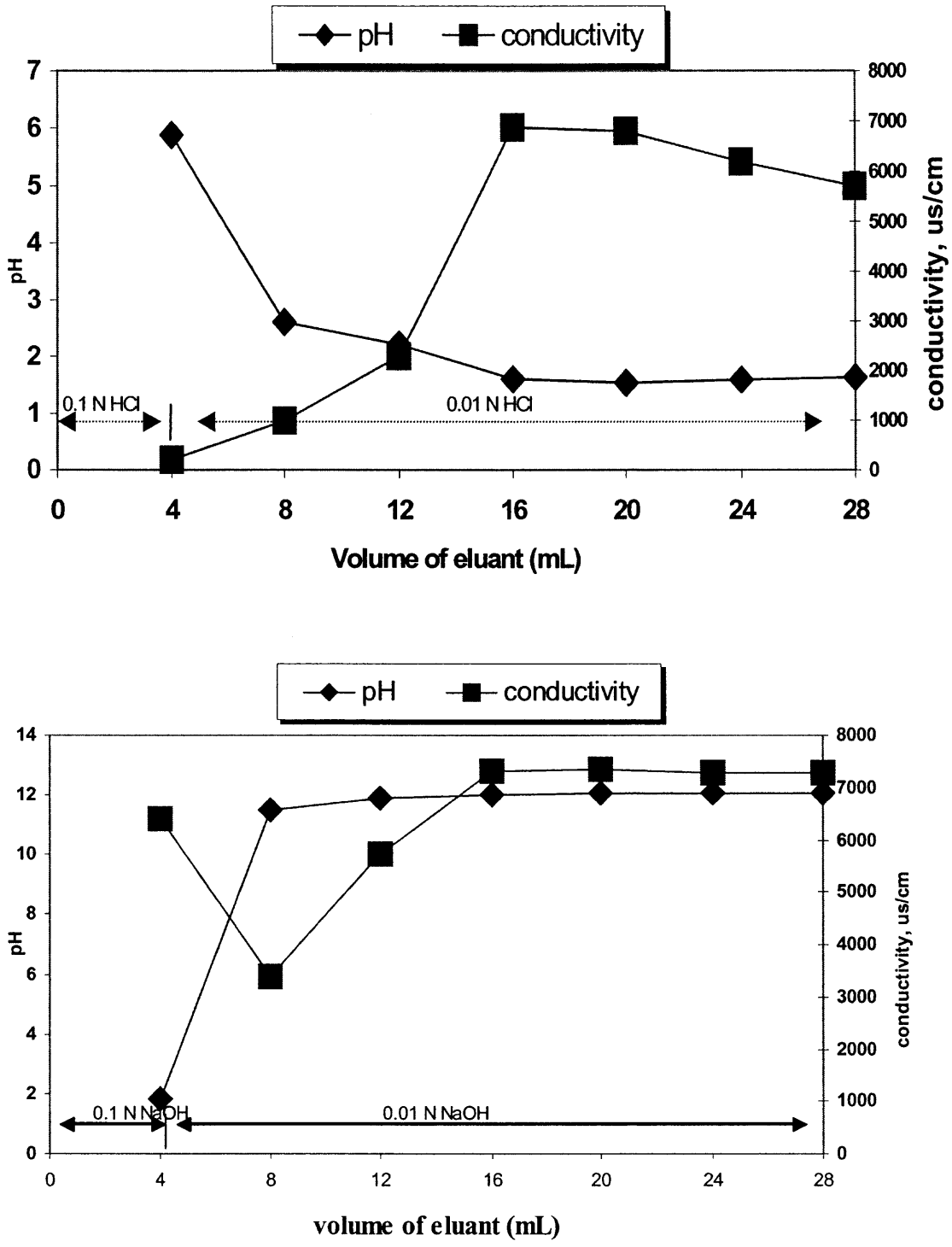
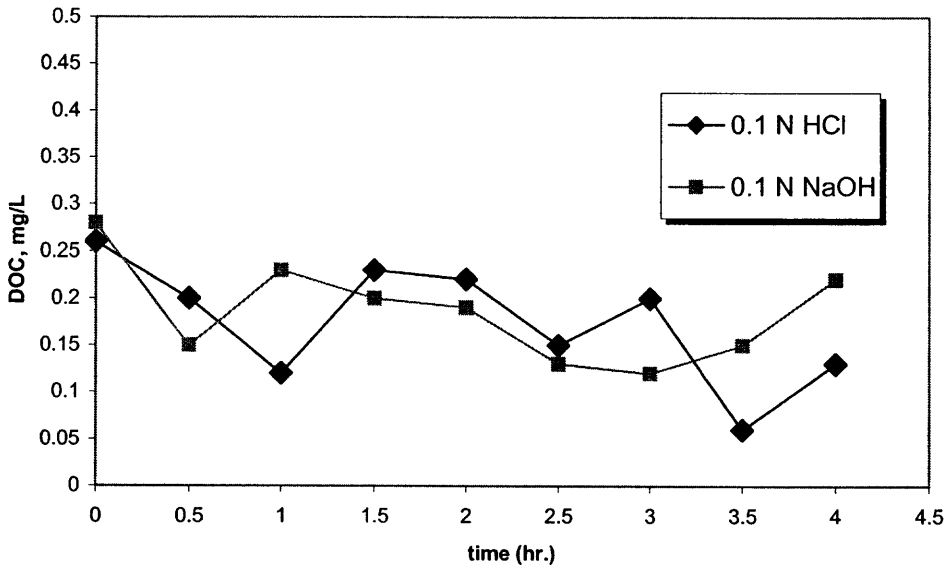


Figure 4.2 a & b Simulated elution of hydrophobic base (a) and acid (b)

Whether or not XAD-8 resin bleeds during fraction extraction was further examined with batch tests in which solutions of 0.1 N HCl or 0.1 N NaOH were mixed with XAD-8 resin by a volume ratio of 2 to 1 into a series of flasks. If resin bleeding were observed in such solutions of higher strength, the bleed would likely occur in column tests as well.

Figure 4.3 Batch tests for XAD-8 resin stability



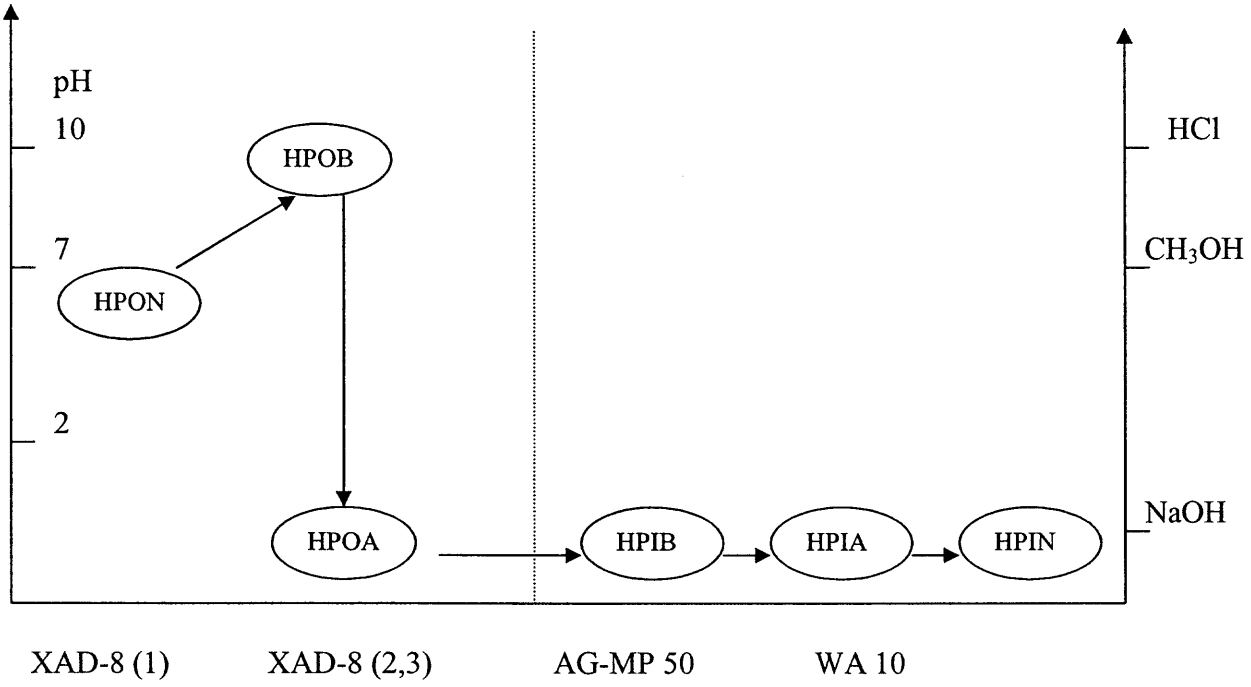
Results of batch tests (figure 4.3) confirmed the excellent stability of XAD-8 resin when exposed to extreme pH environment. Although DOC in both batch solutions fluctuated over experiment period, the variation mainly resulted from instrument limit. It is unlikely for XAD-8 to introduce DOC into fractions.

4.5 Proposed Fractionation Procedure

The proposed fractionation procedure was outlined in Figure 4.4. The amount of XAD-8 (Superlite™ XAD-8, Supelco Inc., Supelco Park, Bellefonte, PA) resin was determined according to Leenheer [1981] with a capacity factor of 50 (K'=50) and a

porosity of 0.60. XAD-8 resin was intensively refined with 0.1N NaOH for 24 h and sequentially extracted with acetone and hexane each for 24 h in a set of Soxhlet extraction apparatus. The refined XAD-8 resin was transferred into beakers or funnels filled with glass wools. The XAD-8 resin was rinsed with certain volumes of methanol to replace non-polar solvent hexane and then packed into columns (2.5 cm×120 cm, Kontes, Vineland, NJ) in slurry of methanol. The packed resin was rinsed with two times 2.5 bed volumes of 0.1N NaOH, 2.5 bed volumes of 0.1 N HCl, and finished with MQ water until the conductivity and DOC of the effluents were below 2 μs/cm and 0.2 mg/L, respectively. This resin cleanup was necessary to eliminate any impurities brought during the resin manufacturing process.

Figure 4.4 Modified fractionation procedure



Hydrophobic neutral (HPON) was the first fraction to be fractionated. The water sample pH was adjusted around 7±0.1 with 0.1 N H_2SO_4 or NaOH and then filtered by

gravity through the XAD-8 resin bed with a flow rate less than 12 bed volumes /h. Sample solution constrained inside resin bed was quickly displaced with 1 bed volume of MQ water and discarded. The column was then turned up side down and the resin was air-retrieved, stored, and dried in desiccators.

XAD-8 resin for HPON fraction was preserved in desiccators until no moisture could be observed. XAD-8 resin was mixed with HPLC grade methanol with a volume ratio of methanol to resin as 2:1 in flasks and shaken with a wrist shaker for 24 hours. Extracted HPON, now dissolved in methanol, was separated from XAD-8 resin particles by filtration using filter apparatus equipped with movable porcelain filter head. The HPON fraction was further purified by two-stage evaporation. First, HPON methanol solution was evaporated at 40°C with a rotary vacuum evaporator to completely dry. Then the flask was added 100 ml of MQ water and shaken for 24 hours. The HPON solution was further purified at 70 °C by vacuum rotary evaporation until insignificant residual level of methanol occurred in HPON fraction. Methanol in HPON fraction was determined with GC equipped with FID detectors.

The operation for hydrophobic base (HPOB) and hydrophobic acid (HPOA) was similar to that of HPON. The sample effluent after HPON was de-protonated to an arbitrary pH 9.5-10 with 10N NaOH and loaded into the second column. The fraction was collected with 0.25 bed volume of 0.1N HCl, followed by 1.5 bed volumes of 0.01N HCl at a flow rate less than 2 bed volumes /h, making a total of 1.75 bed volumes of this fraction, HPOB. The sample effluent after the second XAD-8 resin column was acidified to pH 2 with concentrated H_2SO_4, loaded on the third XAD-8 resin column. Elution of HPOA was conducted with 0.25 bed volumes of 0.1N NaOH followed by 1.5 bed

volumes of 0.01N NaOH with a flow rate no great than 2 bed volumes /h. H_2SO_4 instead of HCl was used for pH adjustment due to the chloride interference with the UV/Persulfate oxidation of carbon.

The removal of hydrophobic substances was concluded after runs of the triple XAD-8 resin columns. The hydrophilic base (HPIB) fractionation followed the procedure of Leenheer [1981] with two modifications. The use of 1.0N $NH_3 \cdot H_2O$ was substituted with 1.0N NaOH as the eluant for releasing the HPIB from the AG-MP-50 cationic resin (BIO-RAD, Hercules, CA). This change resulted from a concern of possible formation of chloramines if the $NH_3 \cdot H_2O$-extracted HPIB was subsequently experimented for its DBPFP with chlorine. The flow rate of sample filtration and resin regeneration were at no greater than 5 and 2 bed volumes /h, respectively. These two procedural changes allowed enough contact for samples to transfer HPIB fraction to resins and for eluants to collect HPIB fraction from the strong cationic exchange resins.

Diaion WA 10 also from Supelco Inc., a weak anion exchange resin, was the final resin applied to isolate HPIA. Effluents after HPIB fractionation were put through the WA 10 resin for the HPIA. The service flow and elution rates were 8 and 4 bed volumes /h, respectively.

4.6 Discussion of Proposed Fractionation Procedure

The proposed procedure herein uses a combination of resins in a sequence of XAD-8, AG-MP-50, and WA 10. The distinct difference of it from the one of Leenheer [1981] is the setup of three columns of XAD-8 independently for HPON, HPOB, and HPOA. It also differs in the use of WA 10 resin to replace Duolite A7 for the HPIA. Furthermore, the HPON is advanced as the first fraction to be fractionated instead of the

last of hydrophobics considering natural water pH approximation to 7. All these modifications allow analytical fractionation of all six fractions through directly sampling influents and effluent of each run while still potentially fulfilling the goal of preparative fractionation. This means that concentration of each fraction can be calculated based on difference of mass before and after each fractionation.

In their analytical procedure, Leenheer and Huffman [1976] reported HPOA and HPOB by directly measuring the collected fractions. However, they reported each hydrophilic fraction as a change of DOM between influents and effluents after every run of respective adsorption. It is noted that XAD-8 resin does not discriminate the adsorption between HPON and HPOB in their procedure [Leenheer & Huffman, 1976, 1979; Day et al., 1991]. Qualls & Haines [1991] raised a concern that the HPON analysis, based on difference of DOM, could include some HPOB. Gasparvoic et al. [1997] also indicated the adsorbates on XAD-8 under natural pH contain both fractions. Consequently, the analytical fractionation of either of them, if measured as DOM difference after each adsorption run, is not appropriate since the mass decrement is the summation of them. Therefore, Leenheer and Huffman [1979] suggested DOM tests directly on both HPOA and HPOB fractions to quantify all hydrophobic fractions. Direct measurement on HPOA or HPOB fractions is favorable only if the test signal of organics in fractions can sufficiently overcome the noise from eluants and instrument and if HOPA or HPOB can be completely recovered from XAD-resin. This often requires DOM in original samples above 5 mg/L or very large volumes of sample have to be fractionated. It is proposed herein, for low DOM samples, that only HPON be first fractionated onto the XAD-8 by protonating HPOB to pH 7. Instead of using those resins

already served for HPON, another column packed with refined raw XAD-8 is exclusively set up for HPOB. HPOB is de-protonated by raising sample pH to 10 and eluted through that column. Analytical fractionation of both fractions is thus possible as shown in the Figure 4.4. It appears that the HPON herein is defined different from that of Leenheer [1981]. The HPON designated in this thesis is the organic mixture that is first adsorbed on XAD-8 at neutral pH and then eluted with methanol. Leenheer [1981] considered the HPON as the XAD-8 adsorbates unable to be eluted with either HCl or NaOH but soluble in methanol. However, due to the proposed pH adjustment in this thesis, both definitions should connote the same type of organic materials.

In the procedure of Leenheer [1981], the XAD-8 resins serve all hydrophobic fractions. Repeated application of the same XAD-8 resin results in that the analytical fractionation by DOM difference may not be possible to carry out for HPOA. Several studies following the protocol of Leenheer's [1981] by the authors found that there was a slight wash out of the previous adsorbed organics during the adsorption for HPOA (unpublished data). The reasons of this re-distribution remain unclear. It has been reported that some organics in water may be of intermediate polarity [Croué et al., 1999]. Their relative degree of hydrophobicity or hydrophilicity may change when exposed in varied pH, and so may their adsorption to XAD-8. In the study of Malcolm and MacCarthy [1992], effluents of XAD-8 were considered to contain not only hydrophilics but also hydrophobics. They suggested that most of the isolates of XAD-4 were hydrophilics but mingled with 5% of fulvic and humic acids lost from XAD-8, and the isolates were therefore named as XAD-4 acids. Aiken & Leenheer [1993] acknowledged that such XAD-4 isolates contained a large amount of humic-like, "hydrophilic fulvic

acid" compounds. Dickenson & Amy [2000] simply named their separated fractions as hydrophobic, transphilic, and hydrophilic fractions, corresponding to the XAD-8/XAD-4 adsorption stages. The "transphilic" is used to describe fractions of an intermediate polarity between hydrophobic and hydrophilic [Leenheer et al., 2000; Croué et al., 2000]. Thorough examination of all above cited studies, it can be demonstrated that these expressions had addressed a similar fraction. The procedure in Qualls and Haines [1991] was the most similar to the Leenheer's [1981] with little change. However, the authors by design reserved their hydrophobic base in water beyond the XAD-8 adsorption. It is thus likely that dissolution of adsorbates with intermediate polarity may occur during the fractionation of HPOA in Leenheer's [1981] procedure. Dissolution of HPOB remnants on XAD-8 when exposed to acidic samples might contribute to the re-distribution.

The solution to it is the setting up of the third column of fresh XAD-8 resins solely for HPOA and thus allows analytical fractionation by DOM difference for all hydrophobics. The procedure of Leenheer [1981] is generally modified regarding the bleeding of Duolite A7. Qualls and Haines [1991] added one column of cationic resin after the Duolite A7 to remedy the bleeding contamination. Day et al. [1991] replaced the Duolite A7 with anionic resin, AG-MP-1. In fact, it was from their concerns about Duolite A7 bleeding, recovery of HPIA, and increase of salinity in collected fractions that Malcolm and MacCarthy [1992] developed what now is one of the two most adopted fractionation protocols (XAD-8/XAD-4 protocol), besides the one of Leenheer [1981]. However, this XAD-8/XAD-4 procedure usually fractionates all DOMs into only hydrophobic, transphilic, and hydrophilic fractions, not as specific as Leenheer [1981]. The XAD-4 is more hydrophobic than the XAD-8. However, the sorption of HPIA to

XAD-4 was attributed to its large surface area, four times greater than of XAD-8 (725 and 160m^2/g for XAD-4 and XAD-8, respectively) [Malcolm and MacCarthy, 1992]. Size exclusion of XAD-4 was first reported by Aiken et al. [1979] and considered to possibly include some humic-like hydrophilics to XAD-4 resin. It can be seen that such XAD-4 isolation differs from the one of Leenheer [1981], in which the HPIA is exchanged/adsorbed by hydrophilic anionic resin, Duolite A7.

To maintain the concept "hydrophilic to hydrophilic" as that of Leenheer [1981], WA 10, another type of weak anionic resin but less hydrophilic than the Duolite A7, was studied. The reason of WA 10 selection was due to its known strong physical and chemical stability. The capacity (meq./g wet) of WA 10 to adsorb H_2SO_4 was determined with a procedure [Kunin, 1990]: pH 1, 3.5; pH 1.5, 1.9; pH 2, 1.5; and pH 3, 1.4 [Figure 4.5]. The amount of WA 10 was calculated with the same formula as in Leenheer [1981] and further multiplied with a safety factor of 1.5.

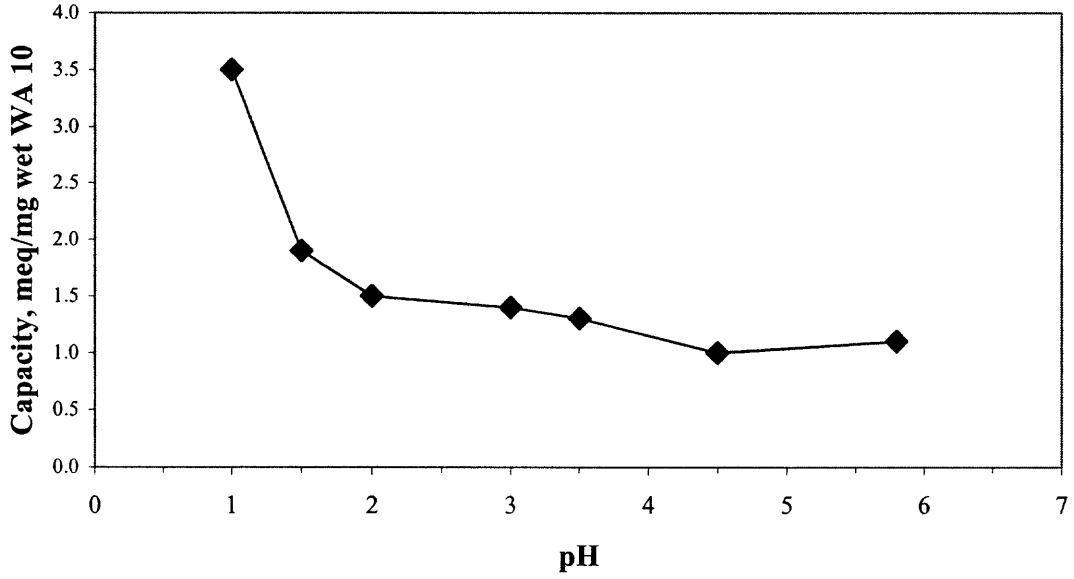


Figure 4.5 Capacity test for WA 10

Figure 4-6: Capacity verfication of WA 10 at pH 2

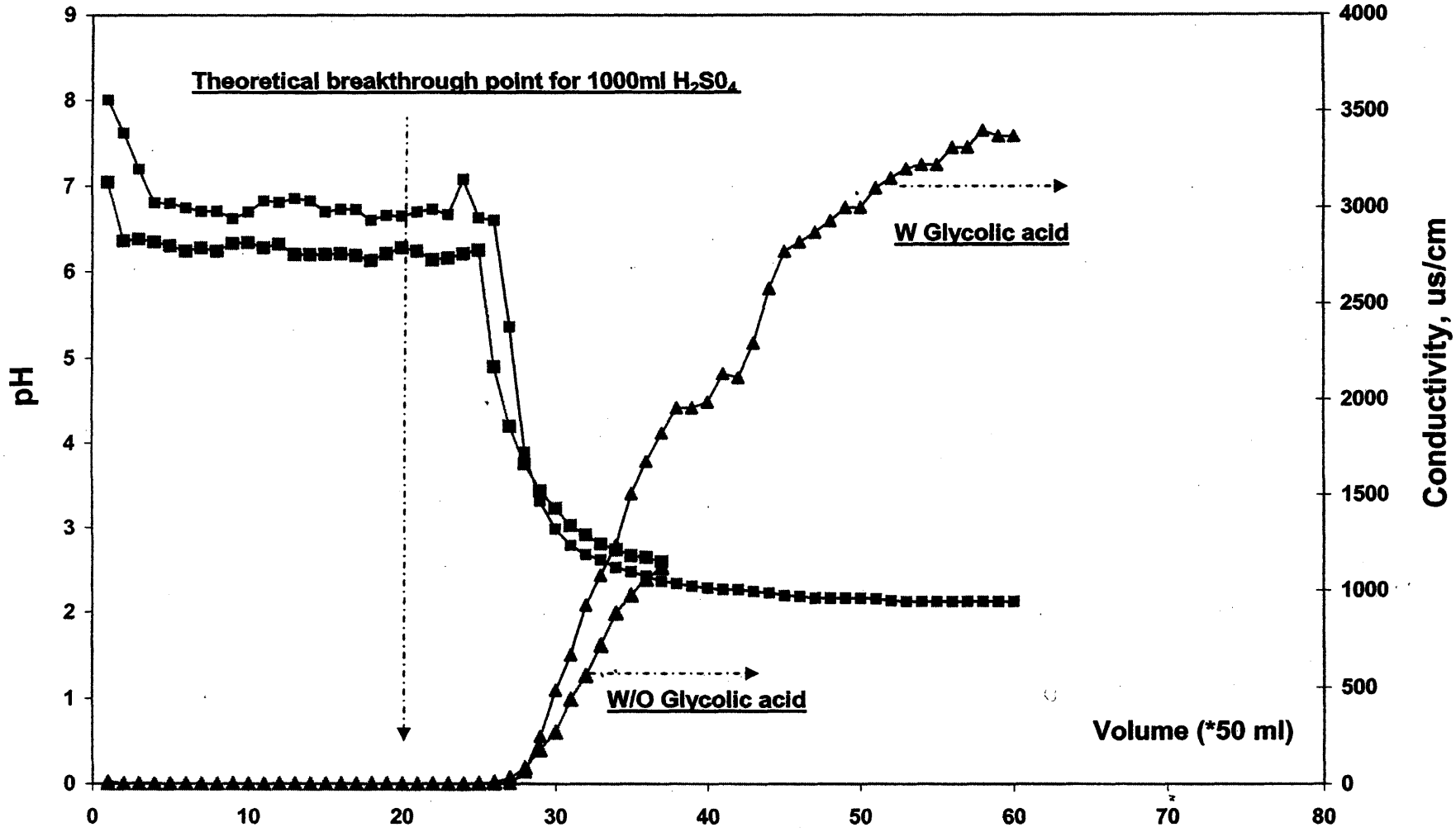


Table 4.3 Verification for WA 10 to adsorb pH 2 H_2SO_4 w/o glycolic acid

Adsorption	Conductivity (µs/cm)	pH	Volume (mL)	Adsorption	Conductivity (µs/cm)	pH	Volume (mL)
1	14.10	8.01	50	31	670	2.78	50
2	1.87	7.62	50	32	925	2.67	50
3	2.72	7.20	50	33	1080	2.61	50
4	2.39	6.81	50	34	1240	2.52	50
5	1.32	6.80	50	35	1510	2.47	50
6	1.64	6.75	50	36	1680	2.42	50
7	1.25	6.71	50	37	1830	2.36	50
8	1.18	6.71	50	38	1960	2.33	50
9	1.19	6.62	50	39	1960	2.30	50
10	0.94	6.70	50	40	1990	2.28	50
11	0.99	6.83	50	41	2140	2.26	50
12	0.96	6.81	50	42	2120	2.26	50
13	0.96	6.86	50	43	2300	2.24	50
14	0.93	6.83	50	44	2580	2.22	50
15	0.96	6.70	50	45	2770	2.19	50
16	0.95	6.73	50	46	2820	2.18	50
17	0.94	6.73	50	47	2870	2.16	50
18	0.81	6.60	50	48	2930	2.16	50
19	0.81	6.66	50	49	3000	2.16	50
20	0.83	6.65	50	50	3000	2.16	50
21	0.76	6.70	50	51	3100	2.15	50
22	0.89	6.73	50	52	3150	2.13	50
23	0.73	6.67	50	53	3200	2.12	50
24	1.24	7.08	50	54	3220	2.12	50
25	0.86	6.63	50	55	3220	2.12	50
26	0.80	6.60	50	56	3310	2.12	50
27	4.23	5.36	50	57	3310	2.12	50
28	62.3	3.89	50	58	3400	2.12	50
29	246	3.31	50	59	3370	2.12	50
30	486	2.98	50	60	3370	2.12	50

Table 4.4 Verification for WA 10 to adsorb pH 2 H_2S0_4 with glycolic acid

Adsorption	Conductivity (µs/cm)	pH	DOC (mg/L)	Volume (ml)	Adsorption	Conductivity (µs/cm)	pH	DOC (mg/L)	Volume (ml)
1	2.36	7.05	0.10	50	20	0.56	6.28	0.01	50
2	1.13	6.36	0.08	50	21	0.63	6.24	0.06	50
3	0.69	6.38	0.07	50	22	0.58	6.14	0.04	50
4	0.65	6.35	0.07	50	23	0.55	6.16	0.07	50
5	0.82	6.30	0.09	50	24	0.62	6.21	0.13	50
6	0.60	6.24	0.09	50	25	0.80	6.25	0.13	50
7	0.53	6.28	0.04	50	26	8	4.90	0.16	50
8	0.62	6.24	0.03	50	27	32	4.20	0.16	50
9	0.65	6.33	0.08	50	28	84	3.75	0.34	50
10	0.61	6.34	0.08	50	29	178	3.43	0.45	50
11	0.64	6.28	0.08	50	30	271	3.23	0.62	50
12	0.60	6.32	0.08	50	31	440	3.02	0.61	50
13	0.62	6.20	0.08	50	32	564	2.91	0.63	50
14	0.60	6.20	0.09	50	33	719	2.80	0.69	50
15	0.56	6.20	0.04	50	34	885	2.73	0.76	50
16	0.54	6.21	0.06	50	35	977	2.66	0.83	50
17	0.56	6.19	0.05	50	36	1060	2.64	0.91	50
18	0.73	6.13	0.06	50	37	1120	2.59	0.91	50
19	0.64	6.21	0.09	50	38	1240	2.50	0.91	50

Figure 4.6, table 4.3 and 4.4 show the adsorption of H_2SO_4 solution (pH 1.9, conductivity 6.6 ms/cm, with or without 1 mg/l DOC added as glycolic acid) by 70 g of wet WA 10 (supposed for 1000 ml of H_2SO_4). It can be seen that the breakthrough of pH and conductivity occurred after 1300 ml of H_2SO_4. The addition of glycolic acid as 1 mg/l DOC did not affect the location of breakthrough point. It was thus concluded that the determined WA 10 capacity, formula [Leenheer, 1981], and a safety factor of 1.5 were appropriate to calculate the amount of WA 10 needed.

Results of a complete test including the adsorption of 1000 ml of H_2SO_4 solution (pH 1.86, conductivity 6.6 ms/cm, and DOC 1.06 mg/l added as glycolic acid), MQ water

replacement, and the desorption with 0.1N NaOH followed with 0.01N NaOH are shown in Figure 4.7 and table 4.5. It was found that the HPIA desorption was completed after elution with 100 ml of 0.1N NaOH and 50 ml of 0.01N NaOH, given 70 g of WA 10 or 85 ml of bed volume.

Figure 4-7, Adsorption, displacement, and desorption tests for WA 10

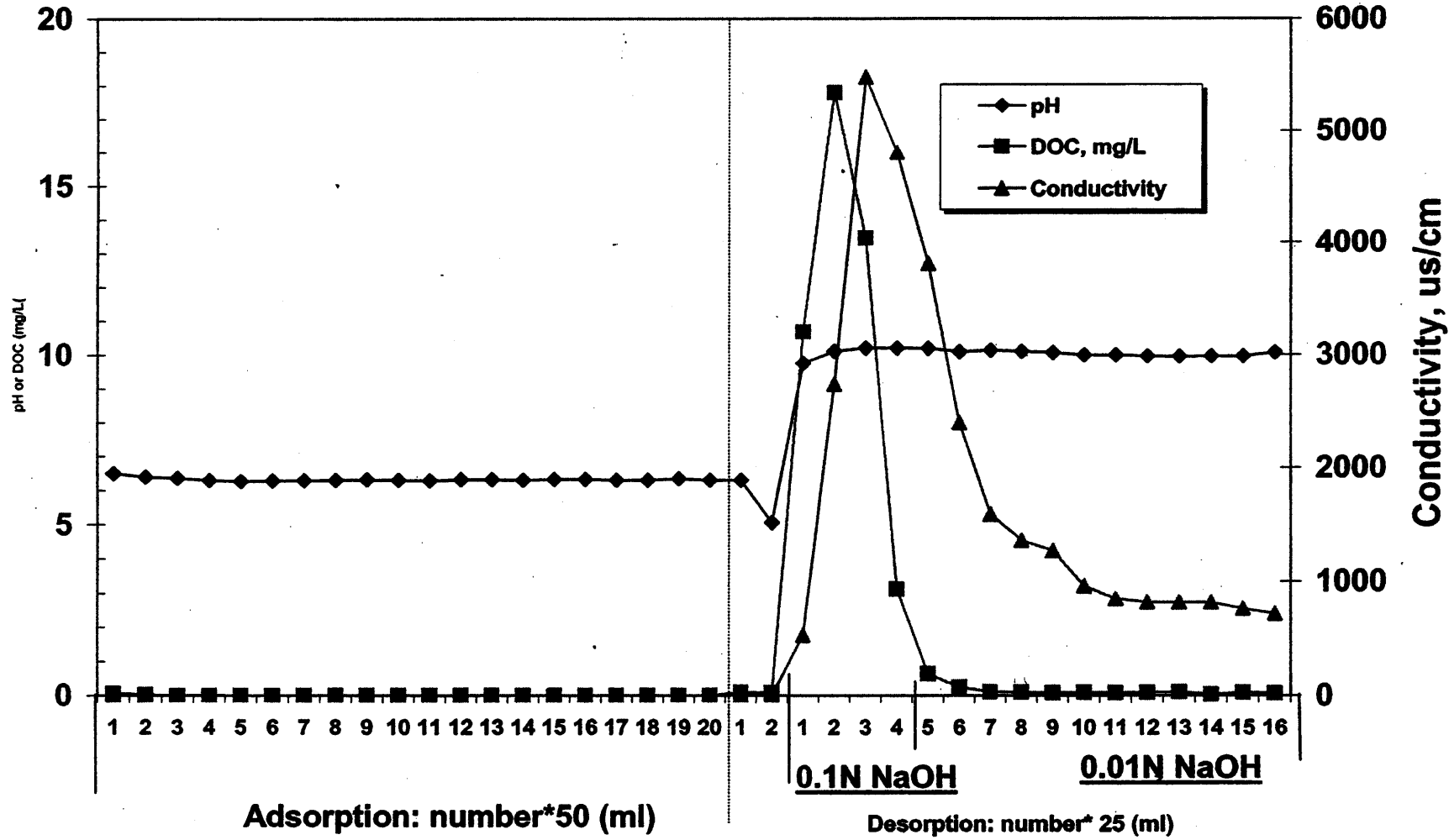


Table 4.5 Results of a simulated, complete tests with WA 10

	Number	pH	DOC (mg/L)	Volume (ml)	Flow rate (mL/min)	Conductivity (us/cm)
Adsorption	1	6.50	0.0658	50	488	1.24
	2	6.40	0.0356	50	328	1.20
	3	6.36	0	50	351	1.44
	4	6.30	0	50	259	1.25
	5	6.27	0	50	260	0.85
	6	6.28	0	50	268	0.89
	7	6.29	0	50	251	0.95
	8	6.30	0	50	251	0.93
	9	6.31	0	50	296	0.88
	10	6.30	0	50	257	0.86
	11	6.28	0	50	261	0.88
	12	6.31	0	50	271	0.89
	13	6.31	0	50	242	0.92
	14	6.30	0	50	270	0.89
	15	6.32	0	50	290	0.90
	16	6.32	0	50	276	0.93
	17	6.30	0	50	278	0.91
	18	6.30	0	50	292	0.96
	19	6.34	0	50	294	0.94
	20	6.30	0	50	362	0.93
MQ displacement	1	6.30	0.0943	25	Fast	0.94
	2	5.05	0.0842	25		0.75
0.1 N NaOH	1	9.75	10.68	25	266	526
	2	10.1	17.82	25	297	2740
	3	10.2	13.46	25	306	5480
	4	10.2	3.114	25	282	4800
0.01 N NaOH	5	10.2	0.6363	25	246	3810
	6	10.1	0.2475	25	259	2400
	7	10.1	0.111	25	267	1590
	8	10.1	0.0989	25	270	1360
	9	9.98	0.0741	25	274	1270
	10	9.98	0.0925	25	280	962
	11	9.95	0.0745	25	298	848
	12	9.94	0.0902	25	258	814
	13	9.95	0.1056	25	218	814
	14	9.94	0.0378	25	230	814
	15	9.95	0.0894	25	250	758
	16	10.1	0.0689	25	299	712

	Concentration (N)	pH	DOC (mg/L)	Conductivity (us/cm)	Note:
H_2SO_4	0.01	1.88	0.019	6700	To draw sorption & desorption curves, DOC N/D was replaced as 0 mg/L. DOC was measure with mode 0.2 –20 mg/L.
NaOH	0.1	12.7	0.048	11200	
NaOH	0.01	11.8	N/D		
MQ water		6.15	0.016	0.82	

4.7 Efficiency of Proposed Procedure

The proposed procedure was experimented with samples from CR and RM WTPs for its efficiency in analytical fractionation of low DOM waters. The two plants having different unit processes exhibited variable changes to DOM fractions. Table 4.6 summarizes the analytical fractionation results based on DOM decrement after obtaining each fraction fractionation and the respective fraction results based on DOC tests on unpurified fractions acquired according to the procedure of Leenheer [1981].

Table 4.6 Fractionation results for two surface water treatment plants

Location	Original	HPON	HPOB	HPOA	HPIB	HPIA	HPIN
CR and RM raw	4.92	1.91/1.89	0.14/0.11	0.63/0.70	0.28/0.35	1.68/1.50	0.37
CR preozonated	4.38	1.57/1.43	0.03/0.55	0.52/0.68	0.40/0.42	1.45/1.52	0.30
CR settled	2.29	0.66/0.60	0.00/0.08	0.25/0.32	0.27/0.20	0.87/0.65	0.42
CR filter influent	1.97	0.60/0.65	0.00/0.06	0.13/0.20	0.20/0.29	0.80/0.76	0.33
CR #6 effluent	1.61	0.20/0.13	0.12/0.05	0.06/0.10	0.24/0.18	0.75/0.70	0.26
CR # 8 effluent	1.65	0.28/0.20	0.09/0.08	0.00/0.09	0.38/0.45	0.59/0.64	0.28
CR finished	1.68	0.28/0.26	0.00/0.07	0.01/0.10	0.35/0.32	0.71/0.75	0.29
CR high pump	1.68	0.35/0.32	0.00/0.09	0.10/0.12	0.35/0.45	0.57/0.50	0.30
RM settled	2.46	0.76/0.70	0.01/0.08	0.29/0.35	0.43/0.42	0.54/0.50	0.33
RM influent	3.02	1.07/0.99	0.17/0.08	0.28/0.29	0.30/0.4	0.46/0.51	0.66
RM effluent	2.59	0.84/0.76	0.00/0.06	0.30/0.40	0.41/0.39	0.70/0.75	0.27
RM finished	2.40	0.50/0.55	0.05/0.08	0.27/0.35	0.36/0.46	0.86/0.90	0.37

Original samples in this study contained less than 5 mg/l of DOC. Therefore, the analytical procedure of Leenheer and Huffman [1979] may not be applicable to determine the content of fractions due to relatively significant test errors from eluants and/or instrument. For example, eluted according to the protocol [1981], 210 ml of HPOB fraction fractionated from 6 liters of original samples in this study contained no greater than 4.9 mg/l and no less than 800 mg/l for DOC and Cl^-, respectively. Chloride ion can interfere in DOC tests by reacting with $K_2S_2O_8$ [Qualls and Haines, 1991] (technique note, Tekmar Dohrmann). Therefore, instead of being performed on collected fractions, DOC of HPOB fraction was based on analyses on water samples, which contained only original background level of Cl^-. The results of HPON based on DOC decrement are similar to those tested on HPON fractions. An average of 90% of recovery was obtained for this fraction. It is not surprising to see this high quantitative recovery from XAD-8 resins. The XAD-8 is concluded as quantitative since the HPOA and HPON can be quantitatively concentrated onto and eluted from this resin [Malcolm and MacCarthy, 1992]. Another reason for this high recovery of HPON is little interference of eluants on the HPON tests since methanol was used for HPON extraction but then removed by a vacuum rotary evaporation. The results of HPOB based on DOC measurements were generally different from their correspondents by DOC decrement calculation. There is always a dilemma to deal with the HPOB fraction test. Dilution can bring down the error due to retarded carbon oxidation of Cl−. Meantime, it also makes the HPOB test more erratic due to very low DOC in diluted HPOB samples. The constant concentration of HPOB for direct measurement shown in table 4.6 may indicate an over dilution of the tested samples; however, the dilution is definitely needed to eliminate the chloride

impact. The results of HPOA, HPIA, and HPIB by measuring fractions were generally close to those based on mass decrement. It is likely that the DOC in these fractions sufficiently overcame the matrix background. However, the matrix background effect on DOC test cannot be eliminated for samples with a concentration of DOC below 0.20 mg/l. The direct measurements for these samples are slightly higher than the respective analytical fractionation. This matrix background is also observed by carefully examining the flat part of desorption curve in Figure 4.7. It was found that the residual DOC in desorption samples after desorption peak remained at an average 0.08 and 0.22 mg/l for 0.01 and 0.1N NaOH, respectively. Therefore, it was very important to conduct preliminary titration, adsorption, and desorption tests with characterized chemicals such as glycolic acid for HPIA in this study to determine the type, concentration, volume of eluants for application to field samples. It is also concluded that for lower DOC water samples, analytical fractionation based on DOC difference is preferable to fraction tests.

Accurate DOC determination on fractions still presents a challenge to this proposed procedure. This is a result of low DOC but high matrix in collected fractions. Preparative fractionation can be achieved further through a very complicated post fraction purification procedure [Leenheer 1991; Leenheer et al., 2000]. It is moderate to be postulated that loss or transformation of certain organics during the purification is unavoidable. However, since the proposed procedure can provide an accurate distribution of DOM in each fraction, the loss of collected organics during purification becomes a less concern in the context of understanding DOM distribution.

As a matter of fact, the current tendency of preparative fractionation is that "recovery of representative portions . . . that is suitable for various spectral

characterization and reactivity studies" rather than "necessarily defined as 100% recovery of the DOM" [Leenheer et al., 2000]. With these points of view, the proposed fractionation procedure herein should be considered more accurate in low DOM water than the analytical procedure of Leenheer and Huffman [1979], however with a sacrifice of two more separate runs, as well as potentially same successful to generate representative fractions as the preparative procedure of Leenheer [1981].

CHAPTER 5

METHOD DEVELOPMENT FOR DETECTION OF TTHM WITH VARIAN GC 3400-ECD

This chapter mainly discusses method development to detect THM with Varian GC-ECD 3400. The EPA Standard Method 551.1 outlines a procedure for determination of all known chlorination disinfection by-products, chlorinated solvents, and halogenated pesticides/herbicides. It is still necessary to explore optimum running conditions related to the GC-ECD being actually used. In special, this study is interested in THM at present; there is no need to set up some parameters to satisfy the identification of other target compounds listed in EPA 551.1.

5.1 Instrument Qualification

The applied GC-ECD instrument has to be examined first for its capability to detect and identify studied compounds. This includes separation efficiency, sensitivity, and chromatograph performance. Results are given in table 5.1 and related figures from 5-1 to 5-4.

The laboratory performance check was conducted with ECD range 1 and 1 μl performance check solution, which contains 0.00020 μg/ml Lindane for sensitivity (Signal /Noise > 3), 0.020 μg/ml Hexachlorocyclopentadiene for chromatograph performance represented by peak Gaussin factor (between 0.8 and 1.15), and paired Bromodichloromethane and Trichlorethylene (each 0.030 μg/ml) for column separation performance (resolution > 0.5). Results of laboratory performance check shows Varian GC-ECD 3400 in this study is qualified for identifying and quantifying target compounds at the given running conditions.

Table 5.1 Results of modified laboratory performance check

LPC	#	Sensitivity		Chromatograph performance			
		Lindane		Hexchlorocyclopentadiene			
		R.T. (min.)	Area	R.T. (min.)	Width (1/2)	Width (1/10)	PGF
ECD Channel A	1	45.985	12000	39.35	0.033	0.061	0.99
	2	45.885	11436	39.35	0.034	0.062	1.00
	3	45.958	12200	39.34	0.034	0.062	1.00
	4	45.900	9920	39.35	0.033	0.061	0.99
	5	45.925	11300	39.35	0.34	0.062	1.00
		S/N	12.7	Symmetry		1.00	

LPC	#	Column performance				
		Bormodichloromethane		Trichloroethylene		Resolution
		R.T. (min.)	Width (min.)	R.T. (min.)	Width (min.)	
ECD Channel A	1	10.190	0.217	10.310	0.212	0.62
	2	10.208	0.218	10.335	0.168	0.66
	3	10.220	0.208	10.347	0.208	0.67
	4	10.223	0.213	10.347	0.212	0.58
	5	10.220	0.209	10.345	0.210	0.60
				Average resolution		0.63

Figure 5.1 General view of LPC chromatogram

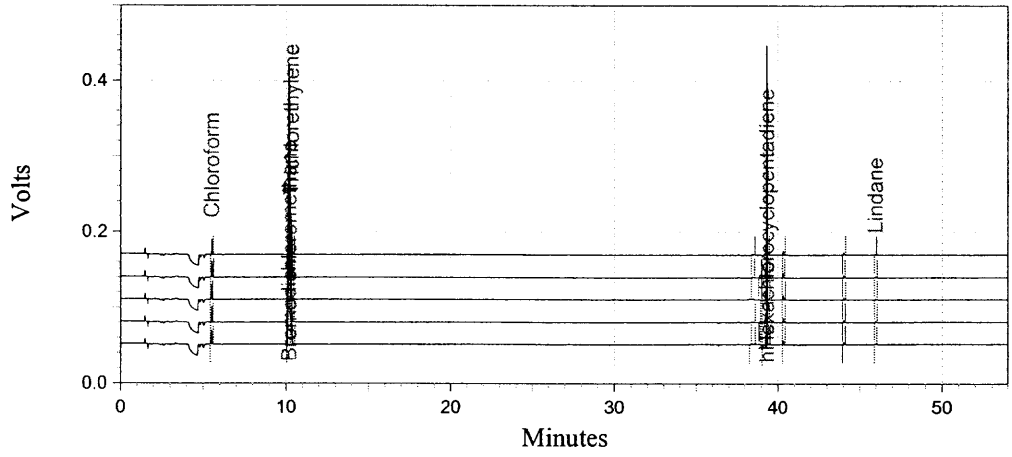


Figure 5.2 Enlarged view of LPC tests for resolution

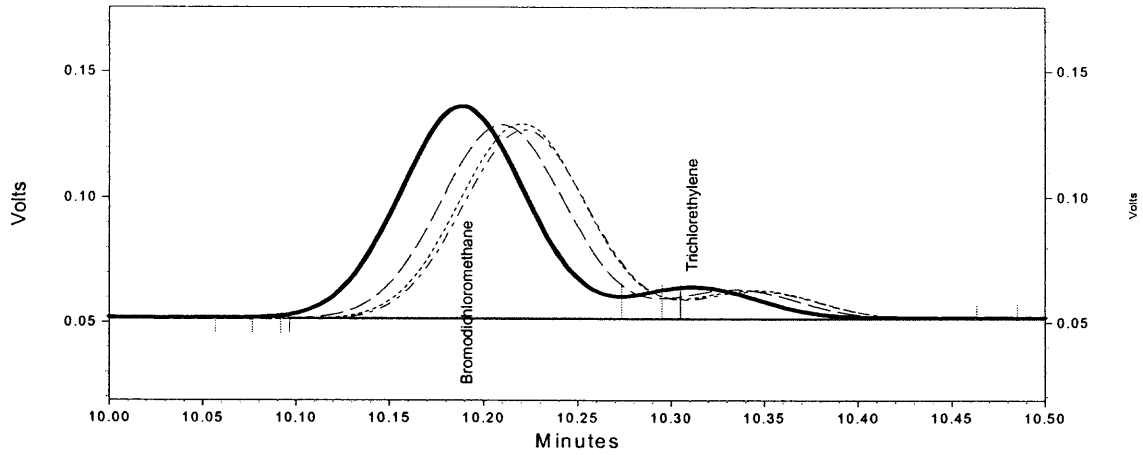


Figure 5.3 Enlarged view of symmetric tests in LPC

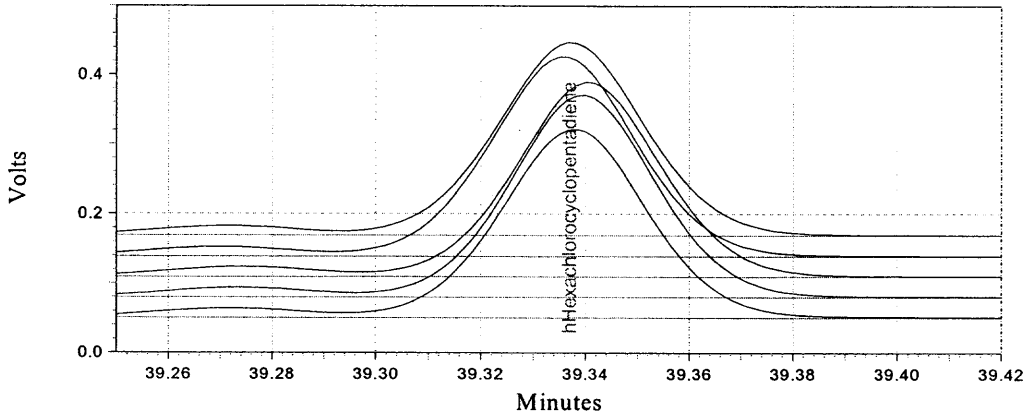
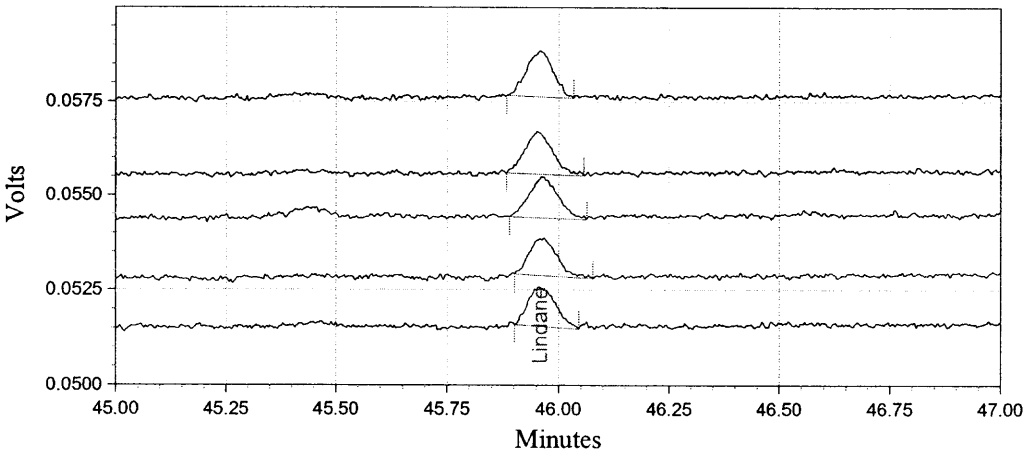


Figure 5.4 Enlarged view of LPC sensitivity tests



5.2 Internal Standard Tests

The EPA 551.1 provides options of external or internal standards. In this study, internal standard (Bromoflurobenzene) was adopted due to the fact that it can eliminate any impact during GC operations by running and comparing standard and sample simultaneously. Table 5.2 and figures shows to determine retention time and response of internal standard prepared into MQ water.

In this study, 1.0 μl internal standard was injected into GC directly with samples. It is different from EPA 551.1, in which 1.0 μl internal standard is added into 1.0 ml samples and then mixture of internal standard and samples is injected into GC. It has been found this modification greatly facilitates sample preparation and provides better repetition. It can be seen that there is a background level of chloroform in MTBE solvent from table 5.2.

Table 5.2 Internal standard determination (ECD A)

Sample	#Run	Chloroform		Internal Standard		Surrogate	
		R.T. (min.)	Area	R.T. (min.)	Area	R.T. (min.)	Area
ECD Channel A	1	5.618	136542	29.947	79340		
	2	5.648	154230	29.948	81949		
	3	5.650	161597	29.937	82470		
	4	5.653	145231	29.953	77429		
	5	5.597	159842	29.947	86454		
Average		5.63	151488	29.95	81528		
% RSD		0.43	7	0.02	4		

Figure 5.5 General view of internal standard tests

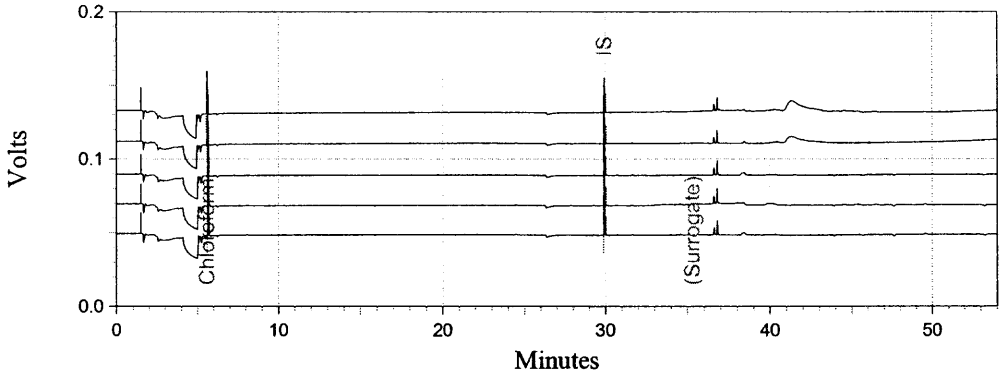
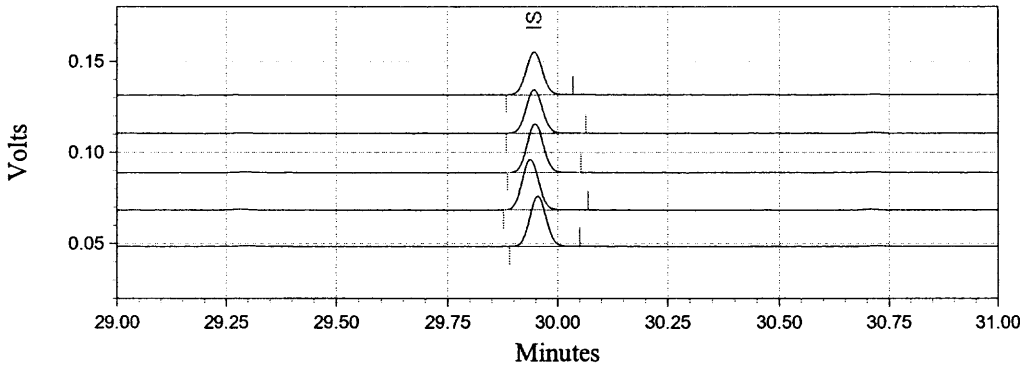


Figure 5.6 Internal standard tests (enlarged view, ECD A)



5.3 Surrogate Tests

The surrogate (Decaflurobiphenyl) was used to examine the MTBE solvent extraction efficiency. The surrogate has to be experienced the same extraction steps as that of samples; therefore, if significant loss has been found on surrogate, it indicates a significant loss on target compounds as well. Table 5.3 and figures 5.7, 5.8 provide results of surrogate tests. To simulate real sample running, internal standard was also included into this surrogate determination tests.

Table 5.3 Surrogate tests

Sample	#Run	Chloroform		IS		Surrogate	
		R.T. (min.)	Area	R.T. (min.)	Area	R.T. (min.)	Area
ECD channel A	1	5.647	162516	29.947	84830	35.303	212200
	2	5.678	154210	29.948	84436	35.297	195241
	3	5.660	160289	29.952	83581	35.303	184563
	4	5.665	174253	29.943	86410	35.295	167845
	5	5.678	160214	29.948	76878	35.298	178924
Average		5.67	162269	29.95	83422	35.30	187754
RD%		0.23	5	0.01	4	0.01	8

Figure 5.7 Chromatogram of surrogate (ECD A)

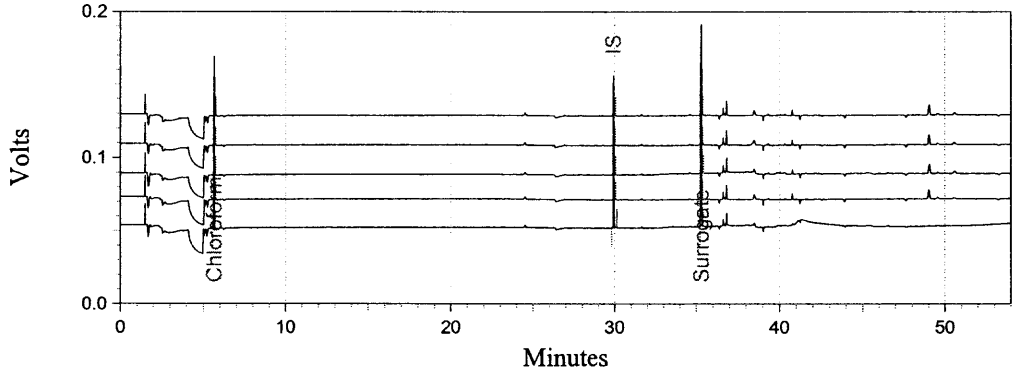
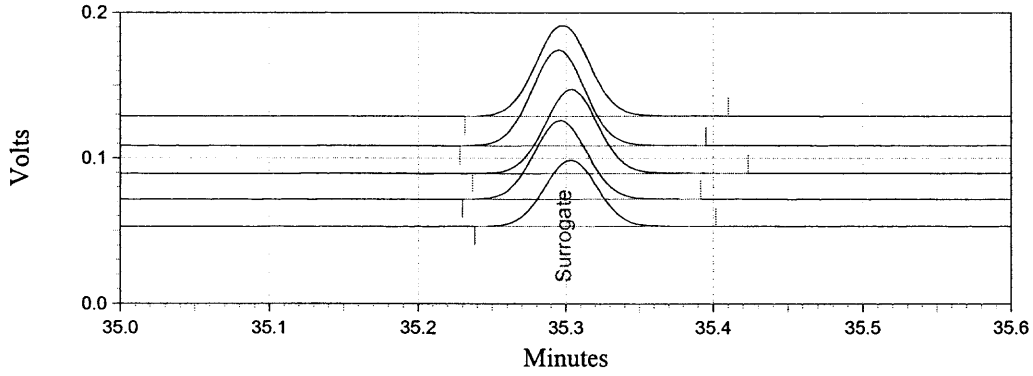


Figure 5.8 Chromatogram of surrogate (ECD A, enlarged)



5.4 Determination of Relative Response Factor for Target Compound

The key to this method development is to investigate the relative response factor for target compounds after GC running parameters set-up. Five standards with concentration 0, 5, 20, 50, and 100 μg/L were run to determine their absolute response

and normalized to corresponding internal standard. Results of one such run is given in table 5.4 and 5.5.

From both tables, it can be found that there is a good linear range for the five tested concentrations for chloroform, dibromochloroform, and Bromoform. The 100 μg/L for dichlorobromomethane was found to exceed the detection upper limit, and this concentration level did not include for the calibration.

Table 5.4 Relative response of target compounds

RRF	Chloroform	Dichlorobromomethane	Dibromochloromethane	Bromoform
1	73	408	367	166
2	98	375	368	148
3	55	434	362	153
4	57	365	336	138
5	59	398	336	153
6	62	402	408	145
7	61	407	378	151
8	63	406	384	136
9	57	373	338	153
10	70	609	433	174
11	64	580	389	155
12	65	634	417	163
Average	65	396	376	153
RSD%	17	5	8	7
R.T. (min.)	5.71	10.29	20.43	28.04

The THM detection method developed was written into a Standard Operating Procedure and included as Appendix B.

CHAPTER 6

APPLICATION OF MODIFIED FRACTIONATION PROCEDURE

Chapter 4 discussed the principle and protocol of the modified fractionation procedure. Results of fractionation for two surface water treatment plants confirm its efficiency in analytical and preparative fractionations (Table 4.6). Fractions collected according to the modified procedure can be further studied to investigate problematic fractions and to develop model with fraction fluorescence characteristics to predict DOM.

6.1 Model Predication of DOM

Fluorescence spectrophotometry has been used to characterize DOM mostly in a qualitative way and several special fluorescence zones of paired excitation and emission have been identified to be characteristic of some fluorophore-containing DOM (Table 2.1). Contrast to the qualitative application, quantification of DOM is seldom tried either theoretically or empirically with received fluorescence data. Quantitative analysis of fluorescence data is a much more complicated process than just pinpointing fluorescence zones. This is because of overlap of fluorescence of excitation or emission, noise of fluorescence spectrum, and most of all, insufficient knowledge on how to find and explain characteristics of samples with collected fluorescence data.

The fluorescence data used herein for model development were collected for 12 locations along the treatment trains of the Canal Road, Raritan Millstone, and Passaic Valley Water Commission water treatment plants (WTPs). All original (non-fractionated) samples and fractions were fluorescence scanned in a band of excitation coupled with banded emission. A trial and error examination of the fluorescence data of the individual fraction revealed major peaks and locations of such peaks that were

considered to represent each fraction. In general, these spectral regions were located in the lower UV range of excitation side. The identified fluorescence zones that are considered unique to each fraction were next explored in original non-fractionated samples to build relations between spectral data of these zones and the known fraction concentrations among original samples. Trial and Error found that the rising slopes and areas under the spectra curve in these regions correlated to fraction concentration and a model could be build statistically to predict each fraction concentration with their characteristic spectrum data of the original sample. Details about how to locate the specific fluorescence zone have been described elsewhere by Van 2000 and Marhaba et al. 2000.

Raw fluorescence data (fluorescence intensity, excitation wavelength, and emission wavelength) have to be polished prior to any application. Such an example is the removal of scatter (i.e., Raman and Raleigh). MQ water Raman band of emission with a fixed excitation at 350 nm is actually used to confirm instrument wavelength by the occurrence of a distinct peak at emission 420 nm; it becomes a noise to sample fluorescence and would lead a false impression as a potential sample peak. Scatter removal was the first step in post-processing analysis of the raw fluorescence data. Upon filtering out the scatters, the required spectral parameters of emissions excited at 225, 237, 249, and 261 nm were determined with a simple code developed with Matlab. These parameters were rising slope (Slope) and spectral area (Area) under the whole fluorescence curves. The Area was an integration of each product of intensity and corresponding emission wavelength slice. The Slope was determined between the initial

emission point (shifted 24 nm after excitation) and the point where emission intensity reached maximum. In a simple equation, the slope was calculated as

$$\text{Slope} = \frac{[Im - Ii]}{[EMm - EMi]}$$

Where: I_m = maximum emission intensity; I_i = initial emission intensity; EM_i = starting emission wavelength; EM_m = emission wavelength at maximum emission intensity.

A general linear regression model (GRL) was developed for predicting the concentration of each fraction over different treatment stages. The dependent variable was the concentration of each fraction (mg/L). The independent variables selected for building the initial GRL model were Slope, Area, Treatment, and Fraction. The interaction between Slope and Area (Slope × Area) was also included into the initial model as an independent variable since it was found to be more representative of a particular DOM fraction than either alone. Among the five independent variables, Slope, Area and their product Slope × Area were quantitative variables, while the Treatment and Fraction variables were qualitative. The Treatment variable had four sub-classes: intake, sedimentation effluent, filtration effluent, and plant effluent. Likewise, there were six sub-classes associated with the Fraction qualitative variable: hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), hydrophilic acid (HPIA), hydrophilic base (HPIB), and hydrophilic neutral (HPIN). There were three sub-classes adopted in the initial model to describe the Treatment variable. These sub-classes were taken as intake INF, sedimentation effluent SED, and filtration effluent FILT. For example, to calculate the concentration of intake sample, the value of INF was set to 1 and the values of SEDI and FILT sub-classes were set to 0. To calculate the concentration

of filtration effluent, the value of FILT was set 1 and the values of the other two sub-classes were set to 0. If the values of all of the selected sub-classes of Treatment variable were set to 0, the model calculated the concentration of plant effluent. The same principle was applicable to the qualitative variable of Fraction for which five of its sub-classes were used to develop the GRL model. The data of quantitative variables and the sub-classes of qualitative variables for PVWC WTP were used to build the GRL model and were provided in the Table 5.1.

Table 6.1 Data of PVWC WTP used for model development

Slope	Area	INF	SED	FILT	HPOA	HPOB	HPON	HPIA	HPIB	C (mg/L)
0.048	962	1	0	0	1	0	0	0	0	0.54
0.048	962	1	0	0	0	1	0	0	0	0.33
0.048	962	1	0	0	0	0	1	0	0	0.45
0.048	962	1	0	0	0	0	0	1	0	1.11
0.048	962	1	0	0	0	0	0	0	0	0.15
0.048	962	1	0	0	0	0	0	0	1	0.20
0.172	518	0	1	0	1	0	0	0	0	0.34
0.172	518	0	1	0	0	1	0	0	0	0.29
0.172	518	0	1	0	0	0	1	0	0	0.51
0.172	518	0	1	0	0	0	0	1	0	0.25
0.172	518	0	1	0	0	0	0	0	0	1.38
0.172	518	0	1	0	0	0	0	0	1	0.25
0.010	578	0	0	1	1	0	0	0	0	0.32
0.010	578	0	0	1	0	1	0	0	0	0.20
0.010	578	0	0	1	0	0	1	0	0	0.37
0.010	578	0	0	1	0	0	0	1	0	0.92
0.010	578	0	0	1	0	0	0	0	0	0.28
0.010	578	0	0	1	0	0	0	0	1	0.21
0.038	227	0	0	0	1	0	0	0	0	0.24
0.038	227	0	0	0	0	1	0	0	0	0.21
0.038	227	0	0	0	0	0	1	0	0	0.34
0.038	227	0	0	0	0	0	0	1	0	0.81
0.038	227	0	0	0	0	0	0	0	0	0.23
0.038	227	0	0	0	0	0	0	0	1	0.20

The initial GRL model was written as:

$$C = \beta_0 + \beta_1 \times \underline{\text{Area}} + \beta_2 \times \underline{\text{Slope}} + \beta_3 \times \underline{\text{Slope}} \times \underline{\text{Area}} + \beta_4 \times \text{HPOA} + \beta_5 \times \text{HPOB} + \beta_6 \times \text{HPON} + \beta_7 \times \text{HPIA} + \beta_8 \times \text{HPIB} + \beta_9 \times \underline{\text{INF}} + \beta_{10} \times \underline{\text{SED}} + \beta_{11} \times \underline{\text{FILT}}$$

Where: C= predicted fraction concentration (mg/L); Area = area of emission spectrum where the fraction major peak exists (intensity × nm); Slope = rising slope of the corresponding fraction spectral major peak (intensity/nm); HPOA = 1 for HPOA fraction concentration, otherwise 0; HPOB = 1 for HPOB fraction concentration, otherwise 0; HPON = 1 for HPON fraction concentration, otherwise 0; HPIA = 1 for HPIA fraction concentration, otherwise 0; HPIB = 1 for HPIB fraction concentration, otherwise 0; INF = 1 for influent concentration, other wise 0; SED = 1 for sedimentation effluent concentration, other wise 0; FILT = 1 for filtration effluent concentration, otherwise 0; β = regression coefficients.

Data of the treatment train of the PVWC WTP were used to refine the initial model using statistical software (*MINITAB 12*, Minitab, State College, PA). The regression results are listed in Table 6.2. The regression analysis indicated that SED, INF, and FILT highly correlated with other independent variables. Their impacts on predicting the concentrations of each fraction could be represented through those highly correlated variables and thus were removed from the model. The revised model was

$$C = -0.0074 + 0.0003548 \times \underline{\text{Area}} + 3.317 \times \underline{\text{Slope}} + 0.00445 \times \underline{\text{Slope}} \times \underline{\text{Area}} + 0.10875 \times \text{HPOA} + 0.0040 \times \text{HPOB} + 0.16475 \times \text{HPON} + 0.80225 \times \text{HPIA} + 0.0225 \times \text{HPIB}$$

The test result of F-ratio was 22.85. With 95% confidence, 8 and 15 degrees of freedom, F (8, 15; 0.05) = 2.64. Since the F-ratio was higher than F-critical, it was

concluded that the refined model was appropriate to predict concentrations of fractions. The small *P*-value for this test 0.001 further confirmed this conclusion. The R^2 was 92.4% and adjusted R^2 was 88.4%, indicating a good correlation between the dependent variable, *C*, and the remaining independent variables.

Table 6.2 Model coefficient and analysis of variance

Coefficient	Value
Constant	-0.0074
Slope	3.317
Area	0.0003548
Slope × Area	-0.00445
HPOA	0.10875
HPOB	0.0040
HPON	0.16475
HPIA	0.80225
HPIB	-0.02550
$F_{critical}$ (8,15; 0.05)	2.64
F_{ratio}	22.85
P_{value}	0.001
R^2	92.4%

The revised model was applied to predict the concentrations of fractions at the PVWC, CR and RM WTPs. Model application results and corresponding actual concentration are provided in Table 6.3 and Table 6.4. Table 6.4 also provides the statistical analysis for predicted and actual concentrations for CR and RM WTPs. The paired *t*-test had a value of 1.15. Given $\alpha = 0.05$ and $N - 1 = 41$, the t_c was 2.02, higher than the paired *t*-test value. Therefore, statistically there was no significant difference for the whole set of data between the predicted concentrations and the actual concentrations for CR and RM WTPs. Generally, there is a good prediction to the actual concentration except for humic substances at Sedimentation and Effluent of CR WTP. One reason may be the different water source of CR from PVWC.

Table 6.3 Model predication of PVWC (mg/L)

Fraction		PVWC INF	SED	FILT	EFF
	P	0.40	0.46	0.31	0.27
HPOA	A	0.54	0.34	0.32	0.24
	P	0.29	0.35	0.21	0.16
HPOB	A	0.33	0.29	0.20	0.21
	P	0.45	0.51	0.37	0.33
HPON	A	0.45	0.51	0.37	0.34
	P	1.14	1.32	0.89	0.76
Humic	A	1.32	1.14	0.89	0.79
HPIA	P	1.09	1.15	1.01	0.96
	A	1.11	1.38	0.92	0.81
HPIB	P	0.26	0.32	0.18	0.14
	A	0.15	0.25	0.28	0.23
HPIN	P	0.29	0.35	0.21	0.16
	A	0.20	0.40	0.21	0.20
	P	1.64	1.82	1.40	1.26
Non-humic	A	1.46	2.03	1.41	1.24

Note: p = predicted with model; a = actual, determined by fractionation

Table 6.4 Verification and prediction for CR and RM

Fraction		CR INF	SED	FILT	EFF	RM SED	FILT	EFF
	P	0.42	0.71	0.32	0.35	0.66	0.26	0.29
HPOA	A	0.46	0.21	0.12	0.11	0.34	0.50	0.19
	P	0.32	0.60	0.22	0.25	0.56	0.16	0.18
HPOB	A	0.23	0.01	0.01	0.01	0.18	0.20	0.12
	P	0.48	0.77	0.38	0.41	0.72	0.33	0.34
HPON	A	0.69	0.33	0.30	0.28	0.65	0.12	0.49
	P	1.22	2.08	0.92	1.01	1.94	0.75	0.81
Humic	A	1.38	0.55	0.43	0.40	1.17	0.82	0.80
	P	1.12	1.40	1.02	1.05	1.36	0.95	0.98
HPIA	A	1.83	1.35	1.12	0.90	1.67	1.40	1.11
	P	0.29	0.58	0.19	0.22	0.53	0.13	0.15
HPIB	A	0.15	0.12	0.11	0.08	0.21	0.14	0.15
	P	0.32	0.60	0.21	0.24	0.55	0.15	0.20
HPIN	A	0.79	0.61	0.53	0.47	0.30	0.15	0.18
	P	1.73	2.58	1.42	1.51	2.44	1.23	1.33
Non-humic	A	2.77	2.08	1.76	1.45	2.18	1.69	1.44
Paired t- ratio					1.15			
t-critical (0.025,41)					2.02			

Note: p = predicted with model; a = actual, determined by fractionation

The developed model in this study was in its elementary stage and is in need of more refinement for several reasons: 1) the model was empirically developed without fundamental theory to support its construction. The fluorescence zones considered as characteristic to collected fractions were identified by trial and error; no association of fraction structures was made with the identification of those unique or representative zones. All characteristic fluorescence exciting at lower band of UV was not accident in nature since fluorophore-containing compounds are more sensitive to UV than to visible light. In theory, fluorescence spectrophotometry differs from UV absorption only in what light is sensed by detectors, not the exciting source. As such a result in instrumentation, detectors of fluorescence have to sit 90 degrees away from the incident, exciting lights in order to eliminate interference of light actually detected right in UV absorption. Therefore, efforts to decide representative fluorescence zones should be put on the search of Stoke shift or similar in the emission side; 2) the developed model took absolute intensity rather relative one. Absolute intensity contains a lot of uncertainties, including sample treatment, temperature, current, and possible impact of instrument. It would be less prone to error if absolute intensity were normalized with the maximum peak intensity and were used for model development; 3) the developed model contains no variables to describe applied treatment. The Treatment variable was included initially, but was removed later. While this removal was solely due to high statistical correlation of Treatment variable with other independent variables, the removal is difficult in explaining with a physical means and the resulted model might be misleading.

6.2 Application of Fractionation Procedure for MWC

The developed fractionation procedure was applied to study DOM for samples from Middlesex Water Company (MWC). For convenience, discussion of fractionation and other test results are given in the sequence of water being sampled.

6.2.1 Samples of August 2003

6.2.1.1 Original water characteristics

8 liters of the four samples, Before $KMNO_4$ (**BFKMNO$_4$**), After $KMNO_4$ (**AFKMNO$_4$**), settled (**SETTLED**), and filtered (**FILTERED**) were filtered with 0.45 μm Nylon membranes; membrane filtered samples were tested for their pH, conductivity, UV_{254} absorbance, and DOC (Table 6.5).

Table 6.5 Characteristics of original samples (August 2003)

Sample	pH	Conductivity (μS/cm at 25 °C)	DOC (mg/L)	UV_{254} (/cm)	$SUVA_{254}$ (L/mg-cm)
BFKMNO$_4$	7.30	130	7.96	0.242	0.030
AFKMNO$_4$	7.19	130	7.22	0.235	0.033
SETTLED	6.09	158	3.43	0.029	0.008
FILTERED	6.19	158	2.66	0.028	0.011

DOC results show insignificant effects of $KMNO_4$ oxidation on the removal of disinfect byproduct precursor (DOC). The significant removals of DOC and $SUVA_{254}$ occurred at the sedimentation stage, in which 47.6% and 74%, respectively, were removed from the sample of **BFKMNO$_4$**. The $KMNO_4$ oxidation and filtration of the settled water each contributed to only 10% removal of the DOC in the sample of **BFKMNO$_4$**; however, none of them introduced any reduction of the $SUVA_{254}$ when compared with their respective previous stages.

6.2.1.2 Organic fractions of original water samples

6 liters of the membrane-filtered water of each original sample were fractionated into a total of 6 fractions: hydrophobic neutral, base, acid, and hydrophilic neutral, base, and acid (HPON, HPOB, HPOA, HPIN, HPIB, and HPIA). Results of the fractionation were given in Table 6.6.

Table 6.6 DOC (mg/L) concentration (August 2003)

	Original	HPO N	HPO B	HPO A	**Humic**	HPIB	HPIA	HPIN	**Non-humic**
BFKMNO$_4$	7.96	2.53	0.50	2.59	**5.62**	0.29	1.66	0.387	**2.34**
AFKMNO$_4$	7.22	1.58	0.78	2.46	**4.82**	0.34	1.71	0.348	**2.40**
SETTLED	3.43	0.93	0.32	0.76	**2.01**	0.17	0.92	0.327	**1.42**
FILTERED	2.66	0.36	0.06	0.74	**1.16**	0.24	0.95	0.308	**1.50**

The fractionation results clearly indicate that most of DOC destruction derived from the removal of hydrophobic materials by the settling process (53%). This is identical with a general recognition that conventional treatment (coagulation, sedimentation, and filtration) is more efficient in removing hydrophobic materials than hydrophilic materials. All processes (oxidation, sedimentation, and filtration,) removed 79.4% hydrophobic materials of the original sample (**BFKMNO$_4$**); but only 14.2% of this hydrophobic material removal was attributable to the oxidation process. As a contrast, the whole treatment only reduced 35.9% hydrophilic materials of the **BFKMNO$_4$** sample. Furthermore, there was no hydrophilic material removed by the $KMNO_4$ oxidation process and thus removal of hydrophilic materials can be linked only to sedimentation and filtration.

The water source sample **BFKMNO$_4$** could be classified as humic type. Hydrophobic organic material is usually synonymous as humic substance. The total of hydrophobic materials (HPON, HPOB, and HPOA) counted 71% of all DOC of this sample. Due to the treatment, the water was not of humic when finished, where DOC in filtered water was composed of 56.4% of hydrophilic materials and 44.6% of hydrophobic materials.

6.2.1.3 SUVA$_{254}$ and THM formation potential of organic fractions

Results of SUVA $_{254}$ and THM formation potential (THMFP) of each fraction and original waters are shown in Table 6.7 and Table 6.8 respectively.

Table 6.7 SUVA $_{254}$ of fractions and original samples (December 2003)

L/mg-cm	Original	HPON	HPOB	HPOA	HPIB	HPIA	HPIN
BFKMNO4	0.030	0.014	0.040	0.039	0.039	0.011	0.074
AFKMNO4	0.033	0.011	0.034	0.032	0.017	0.010	0.036
SETTLED	0.008	0.013	0.024	0.025	0.025	0.008	0.034
FILTERED	0.011	0.015	0.025	0.019	0.049	0.005	0.025

Table 6.8 THMFP (μg/L of original water, August 2003)

	Original (Test)	HPON	HPOB	HPOA	HPIB	HPIA	HPIN	Original (Summation)
BFKMNO4	377	15	136	52	30	46	101	380
AFKMNO4	308	17	89	34	44	46	75	305
SETTLED	205	11	47	59	22	31	102	272
FILTERED	244	20	8	35	40	17	65	184

$SUVA_{254}$ is an aggregate parameter that quantifies the unsaturated, UV reactive organic compounds in water. This parameter is generally associated with hydrophobic organic materials. The highest $SUVA_{254}$ occurred at the hydrophilic neutral fraction (HPIN), a fraction that presented the largest THMFP as well. While it is noticed that high $SUVA_{254}$ of the HPIN fraction was accompanied with high THMFP, there was no

identifiable correlation of $SUVA_{254}$ to THMFP when all six fractions were considered. This may indicate an incapability of $SUVA_{254}$ to evaluate the formation of THMs.

For the sample of **BFKMNO$_4$**, there was slightly higher THMFP from hydrophobic materials than the correspondent hydrophilic materials, 203 and 177 μg/L of original water, respectively. This difference was not enough to conclude a higher yield of THMFP by hydrophobic organic materials than that by hydrophilic in a context of analysis deviation. In this sample, HPOB and HPIN were the two fractions potentially producing most of the THM. Down to the **FILTERED** water, hydrophilic materials were possibly responsible for most of the THM development. The THMFP of hydrophilic materials was 122 μg /L in original water of **FILTERED** while it was 62 μg /L for the hydrophobic fractions. Therefore, in the sample of **BFKMNO$_4$**, the hydrophobic materials dominated over the hydrophilic materials, but had almost equal potential as hydrophilic materials to form THM. Instead, the **FILTERED** sample showed a higher content of hydrophilic materials and a higher potential to produce THMFP than hydrophobic materials.

In the **BFKMNO$_4$**, hydrophilic materials occurred less than hydrophobic materials but produced a similar amount of THM as the hydrophobic materials. This suggests a higher THMFP for the hydrophilic materials when the THMFP was viewed on a basis of mass of carbon. Table 6.9 presents THMFP results for all six fractions when THMFP was interpreted on mass of fraction Carbon.

Table 6.9 THMFP (μg/mg carbon of fraction, August 2003)

	HPON	HPOB	HPOA	HPIB	HPIA	HPIN
BFKMNO$_4$	6	271	20	103	28	262
AFKMNO$_4$	11	114	14	130	26	217
SETTLED	12	147	78	131	33	311
FILTERED	58	140	47	169	19	212

It can be seen that HPIN was the fraction able to produce the highest THM per unit mass of carbon among the 6 fractions. For this reason and the fact that HPIN remained almost constant along the different treatment stages, the HPIN showed the highest potential to form THM in the **FILTERED** water. The HPIB had the second highest potential for this formation as HPOB except in the **BFKMNO$_4$** sample.

6.2.1.4 Results- for samples of August 2003

- The study for samples of August 2003 indicates that $KMNO_4$ oxidation, sedimentation, and filtration were efficient on removal of only hydrophobic materials. A result of such was that water changed to non-humic type after filtration from humic type at **BFKMNO$_4$**.
- Hydrophilic materials (HPIN and HPIB) showed the 1st and 2nd highest potential to form THMFP when THMFP was calculated on a carbon mass basis. This resulted in:
    a. While in the sample of **BFKMNO$_4$**, hydrophilic materials was only 42% of the hydrophobic materials, due to its 1.3 times higher potential of producing THM than hydrophobic organics, hydrophilic materials could have contributed almost equal amount of THMFP in this sample.
    b. In the **FILTERED** water, both the content and THMFP of hydrophilic materials were higher than those of their hydrophobic correspondents;

hydrophilic materials would have produced much more THM than hydrophilic materials.

- While the aggregate parameter $SUVA_{254}$ could be associated with the quantification of aromatic organic compounds, there was no clear link of this parameter to the THMFP in this work. For this reason, although the $SUVA_{254}$ of the un-fractionated **FILTRED** sample was about 1/3 of that of the **$BFKMNO_4$** sample, the filtered sample was able to produce an amount of THM about 65% of that would be produced in the **$BFKNO_4$** sample.
- The significant change of water quality can occur only after sedimentation. After the sedimentation, pH, conductivity, DOC, and $SUVA_{254}$ were much different from those before sedimentation.

6.2.2 Samples of December 2003

6.2.2.1 Original water characteristics

8 liters of the seven samples, Canal Road/ Province (**CR**), Before Outfall (**BFOUTFALL**), Outfall (**OUTALL**), Before KMNO4 (**$BFKMNO_4$**), After KMNO4 (**$AFKMNO_4$**), **SETTLED**, and **FILTERED**, were filtered with 0.45μm Nylon membranes; membrane filtered samples were tested for their pH, conductivity, UV_{254} absorbance, Alkalinity, and DOC.

Table 6.10 Characteristics of original samples (December 2003)

Sample	pH	Conductivity (μS/cm at 25°C)	DOC (mg/L)	UV_{254} (/cm)	$SUVA_{254}$ (L/mg-cm)	Alk. (mg/L)
CR	6.63	146	8.67	0.319	0.0368	
BFOUTFALL	6.86	143	7.80	0.277	0.0355	
OUTFALL	6.82	130	3.95	0.136	0.0344	
BFKMNO4	7.12	223	5.01	0.138	0.0275	
AFKMNO4	6.72	226	4.23	0.128	0.0303	32
Settled	6.72	242	1.53	0.020	0.0130	
Filtered	6.69	262	1.21	0.021	0.0173	

Note: alkalinity (mg/L as $CaCO_3$, pH = 4.0)

There was a significant increase of conductivity from **OUTFALL** to **$BFKMNO_4$**. Since $KMNO_4$ was not added at the stage of **OUTFALL**, this raise of conductivity should be from the addition of other chemicals.

DOC results show a very high concentration at both **CR** and **BFOUTALL**, 8.67 and 7.80 mg/L, respectively. DOC decreased to 3.96 mg/L at **OUTALL** but rose to 5.01 mg/L at **$BFKMNO_4$**. There was an insignificant effect of $KMNO_4$ oxidation on the removal of DOC. The significant removals of DOC and $SUVA_{254}$ occurred at the sedimentation stage, in which 53.8% and 53%, respectively, were removed from the sample of **$BFKMNO_4$**. The KMNO4 oxidation and filtration of the settled water contributed to only 15.8% and 5.8% removal of the DOC in the sample of **$BFKMNO_4$**; however, none of them introduced any reduction of the $SUVA_{254}$ when compared with their respective previous stages.

Table 6.11 Comparisons of DOC, UV_{254}, $SUVA_{254}$ August & December 2003

Sample	DOC (mg /L)		UV_{254} (/cm)		$SUVA_{254}$ (L/mg-cm)	
	Aug. 2003	Dec. 2003	Aug. 2003	Dec.2003	Aug.2003	Dec.2003
BFKMNO$_4$	7.96	5.01	0.242	0.138	0.030	0.0275
AFKMNO$_4$	7.22	4.23	0.235	0.128	0.033	0.0303
SETTLED	3.43	1.53	0.029	0.020	0.008	0.0130
FILTERED	2.66	1.21	0.028	0.021	0.011	0.0173

While DOC and UV_{254} decreased along the treatment stages for both months, this did not happen to $SUVA_{254}$. It can be seen that $SUVA_{254}$ increased in the samples of **AFKMNO$_4$** and **FILTERED** compared with each previous stage. The increase of $SUVA_{254}$ at **AFKMNO$_4$** may be explained with the addition of $KMNO_4$, which shows adsorption of light at 254 nm. The increase of $SUVA_{254}$ after filtration may be due to selective removal of lower adsorption coefficient organic materials.

6.2.2.2 Organic fractions of original water samples

6 liters of the membrane-filtered water of each original sample were fractionated into a total of 6 fractions. Results of the fractionation are given in Table 6.12.

	Original	HPON	HPOB	HPOA	**Humic**	HPIB	HPIA	HPIN	**Non-humic**
CR	8.67	3.07	0.41	2.37	**5.85**	0.32	2.15	0.35	**2.82**
BFOUTFALL	7.80	2.56	0.42	2.09	**5.07**	0.30	2.01	0.42	**2.73**
OUTFALL	3.95	1.60	0.25	0.63	**2.48**	0.23	0.97	0.27	**1.47**
BFKMNO4	5.01	2.15	0.34	0.70	**3.19**	0.15	1.38	0.29	**1.82**
AFKMNO4	4.23	1.41	0.35	0.83	**2.06**	0.12	1.21	0.31	**1.64**
SETTLED	1.53	0.347	0.029	0.12	**0.496**	0.07	0.61	0.36	**1.04**
FILTERED	1.21	0.090	N/D	0.25	**0.34**	0.06	0.54	0.31	**0.91**

Table 6.12 DOC (mg/L) concentration (December 2003)

The fractionation results clearly indicate again that most of DOC removal resulted from the removal of hydrophobic materials by the settling process. Conventional treatment (coagulation, sedimentation, and filtration) preferably removed hydrophobic materials over hydrophilic materials.

All processes (oxidation, sedimentation, and filtration,) removed 89.3% hydrophobic materials of the original sample (**BFKMNO$_4$**); but the oxidation process contributed only 35% of this hydrophobic material removal. As a contrast, the whole treatment only reduced 50% hydrophilic materials of the **BFKMNO$_4$** sample; furthermore, there was only 10% hydrophilic material reduced by the $KMNO_4$ oxidation or 7% from filtration processes and thus most of removal of hydrophilic materials can be associated with sedimentation.

The water source sample **BFKMNO$_4$** could be characterized as humic type. The total of hydrophobic materials (HPON, HPOB, and HPOA) counted 64% of all DOC of this sample. Due to the treatment, the water was no more humic when finished, where DOC in filtered water was composed of 75.3% of hydrophilic materials and 24.7% of hydrophobic materials (Table 6.13).

Table 6.13 Type of water and removal of DOC

		Type of water		Removal of DOC	
	Location	Humic%	Non-humic%	Humic%	Non-humic%
	$BFKMNO_4$	70.6	19.4	56.0	10.5
Aug., 2003	FILTERED	43.6	54.4		
	$BFKMNO_4$	64	36	57.0	18.2
Dec., 2003	FILTERED	24.7	75.3		

Table 6-13 also indicated a closely identical capability of the treatment to remove humic and non-humic materials in these two batches of samples. Therefore, lower DOC in **BFKMNO$_4$** supports a lower DOC in finished water.

6.2.2.3 SUVA254 and THMFP of organic fractions

Results of SUVA 254 and THMFP of each fraction and original waters are shown in Table 6.14 and Table 6.15, respectively.

Table 6.14 SUVA 254 of fractions and original samples (December 2003)

	Original	HPON	HPOB	HPOA	HPIB	HPIA	HPIN
				L/mg-cm			
CR	0.037	0.009	0.048	0.036	0.028	0.009	0.014
BFOUTFALL	0.036	0.008	0.044	0.036	0.026	0.009	0.012
OUTFALL	0.034	0.009	0.042	0.033	0.025	0.008	0.000
BFKMNO4	0.028	0.008	0.031	0.041	0.030	0.008	0.003
AFKMNO4	0.030	0.009	0.038	0.031	0.027	0.009	0.006
SETTLED	0.013	0.007	0.025	0.014	0.037	0.005	0.008
FILTERED	0.017	0.007	0.001	0.012	0.032	0.005	0.006

Table 6.15 THMFP ((μg/L of original water, December 2003)

	Original (Test)	**HPON**	**HPOB**	**HPOA**	**HPIB**	**HPIA**	**HPIN**	**Original** (Summation)
CR	116	1393	33	91	2	23	95	1637
BFOUTFALL	119	861	118	291	1	24	275	1570
OUTFALL	65	157	57	92	1	38	128	473
BFKMNO4	93	58	160	90	1	28	93	430
AFKMNO4	109	57	53	105	1	2	143	360
SETTLED	54	9	20	2	1	1	69	102
FILTERED	95	4	20	3	1	1	145	174

Table 6.16 THMFP (μg/L of original water, August 2003)

	Original (Test)	HPON	HPOB	HPOA	HPIB	HPIA	HPIN	Original (Summation)
BFKMNO4	377	15	136	52	30	46	101	380
AFKMNO4	308	17	89	34	44	46	75	305
SETTLED	205	11	47	59	22	31	102	272
FILTERED	244	20	8	35	40	17	65	184

In samples of December 2003, higher $SUVA_{254}$ occurred to hydrophilic base, (HPIB), hydrophobic acid and base (HPOA and HPOB). However, the fraction that presented the largest THMFP was HPIN. For the sample of **BFKMNO$_4$** of December 2003, there was much higher THMFP by hydrophobic materials than the correspondent hydrophilic materials, 308 and 121 μg/L of original water, respectively. This difference was reversed in the **FILTERED** of December 2003, where 147 and 27 μg/L were observed for hydrophilic and hydrophobic respectively. In this sampling set, HPOB and HPIN were the two fractions potentially producing most of the THM. Similar observations have been noted for samples of August 2003 (comparing table 6.15 and 6. 16). Down to the **FILTERED** water, hydrophilic materials were responsible for most of the THM development. Therefore, in the sample of **BFKMNO$_4$**, the hydrophobic material was more than the hydrophilic material in terms of concentration and THMFP. Instead, the **FILTERED** sample showed a higher content of hydrophilic materials and a higher potential to produce THMFP than hydrophobic materials. Most THMFP reduction came from the reduction of THMFP of hydrophobic materials and came after sedimentation stage.

The summation of six fractions' THMFPs at each location was 2-6 times higher than those THMFPs directly tested on non-fractionated original samples. This would

suggest a necessary caution in applying data of individual fractions to describe whole original samples.

	HPON	HPOB	HPOA	HPIB	HPIA	HPIN
CR	453	81	38	7	11	271
BFOUTFALL	336	281	139	4	12	649
OUTFALL	98	231	145	6	39	476
BFKMNO4	27	472	128	5	20	321
AFKMNO4	40	152	126	6	3	461
SETTLED	25	685	19	17	2	193
FILTERED	46	485	13	20	14	467

Table 6.17 THMFP (μg/mg Carbon of fraction, December 2003)

Table 6.17 and 6.18 presents THMFP results for all six fractions of August and December 2003 when THMFP was interpreted on mass of fraction C.

	HPON	HPOB	HPOA	HPIB	HPIA	HPIN
BFKMNO4	6	271	20	103	28	262
AFKMNO4	11	114	14	130	26	217
SETTLED	12	147	78	131	33	311
FILTERED	58	140	47	169	19	212

Table 6.18 THMFP (μg/mg Carbon of fraction, August 2003)

It can be seen that HPIN was the fraction to be able to produce the highest THM per unit mass of carbon among the 6 fractions for these two times of samples. For this reason and the fact that HPIN remained almost constant along the different treatment stages, the HPIN showed the highest potential to form THM in the **FILTERED** water. The HPOB had the second highest potential for this formation.

6.2.2.4 Jar tests for December 2003

Jar tests were conducted on 2 liters of each original and MQ water diluted fractions with parameters provided by Middlesex Water Company. The MQ water diluted fractions were first pH adjusted to ±0.2 around that of AFKMNO4 original and further adjusted, if necessary, to alkalinity at least 32 mg/L. Due to low concentration of both hydrophobic base and hydrophilic base, these two fractions were combined and named as BASE. Tests Results are provided in table 6-19 (2 liters of samples; KMN04, 1.4 mg/L, FeCl3, 18 mg/L, Catfloc 2.3 mg/L, PAC 3.0 mg/L, and Blanked polymer 0.3 mg/L in sequence; rapid mixing at 200 RPM for 2 minutes, followed by slow mixing at 40 RPM for 5 minutes and another 5 minutes of settling)

Table 6.19 Jar tests results

Fraction	PH		DOC (mg/L)		THMFP (μg/L)	
	Before	After	Before	After	Before	After
Original	6.86	6.25	4.45	1.63	127	102
HPON	7.05	6.28	1.96	0.72	66	72
HPOA	6.95	6.42	3.29	1.11	96	62
HPIN	6.89	6.03	0.22	0.79	110	-----
HPIA	6.72	6.07	1.31	0.56	5	7
BASE	7.10	6.43	1.28	1.46	19	-----

The jar tests results clearly show that coagulation was effective to remove hydrophobic materials. For the original, a 63% reduction of organic materials can be achieved. The removal of HPOA and HPON were 63% and 36%, respectively. However, the formation potential did not show such high removal except for the HPOA fraction. This was not in consistence with results on table 6.19. Furthermore, more DOC were observed in coagulated samples of HPIN and BASE. This could be due to the

addition of organic polymers and applied coagulation parameters were not at optimum to remove these two fractions as well as precipitating polymers.

6.2.2.5 Results of December 2003

- This study further indicated that KMNO4 oxidation, sedimentation, and filtration were efficient on removal of only hydrophobic materials. A result of such was that water changed to non-humic type after filtration from humic type at **BFKMNO$_4$**.
- Results of December 2003 further proved that most THMFP reduction occurred after sedimentation.
- Hydrophilic materials showed the highest potential to form THMFP when calculated on a Carbon mass basis. In the **FILTERED** sample, both the content and THMFP of hydrophilic materials were higher than those of their hydrophobic correspondents, hydrophilic materials would have produced much more THM than hydrophobic materials.
- The significant change of water quality can occur only after sedimentation. After the sedimentation, pH, conductivity, DOC, and SUVA were much different from those before sedimentation.
- Jar tests proved the effectiveness of conventional treatment to remove hydrophobic materials.
- Jar tests did not show significant reduction of THMFP of each fraction.
- Jar tests indicated that coagulation, which is optimum to some fractions, might not be optimum to remove other fractions.

- Applying results of THMFP and Jar tests on fractions might not truly represent originals.

CHAPTER 7

GENERAL CONCLUSION AND RECOMMENDATIONS

7.1 Conclusion

Among a series study related to DBPs, fractionation of drinking water samples is the firsts step necessary to address the association of DOM in natural water with DBP formation and the control of DBP through its precursor DOM reduction by enhanced coagulation and precipitate softening. Through this study

1) A fractionation procedure intended for water of low DOM (< 5 mg/L) was developed by using triple columns of XAD-8 adsorption resin, one column of AG-MP-50 cationic resin, and another column of WA 10 weak anionic exchange resin in sequence
2) Mass balance concept can be successfully applied during each fraction's fractionation, which enables a rigid quality control on fractionation procedure and a quantification of each fraction through mass difference at each fractionation step
3) The selected WA 10 weak anionic exchange resin was proved to be bleeding free under high acidic conditions (pH < 2). No breakdown of WA 10 was observed during hydrophilic acid and neutral fraction fractionation
4) The capacity (meq. /g wet) of WA 10 to adsorb H_2SO_4 was determined as 3.5 at pH 1, 1.9 at pH 1.5, 1.5 at pH 2, and 1.4 at pH 3, [Figure 4.5]. The amount of WA 10 to fractionate hydrophilic acid can be calculated per the formula of Leenheer [1981] and with a safety factor of 1.5
5) The proposed fractionation procedure was experimented with samples obtained at various treatment stages through two surface water treatment plants (CR and RM)

to examine its effectiveness. Results and discussion proved its accuracy in fractionation of low DOM water (±10% of loss of mass)

6) Based on fluorescence features of each fraction of PVWC samples collected according to the proposed fractionation procedure, a multi-variable linear regression model was built and applied to predict fraction concentration of samples of CR and RM water treatment plants. Statistical analysis showed no significant difference between model-predicted and the actual fractionation results (paired t ratio 1.15 < t critical 2.02).
7) Fractionation and DBPFP tests on MWC water treatment plant samples of August and December 2003 indicated that $KMNO_4$ oxidation, sedimentation, and filtration were efficient on removal of hydrophobic materials. A result of such was that water changed to non-humic type after filtration from humic type at **Before $KMNO_4$**.
8) Conducted jar tests on MWC samples indicated that coagulation, which is optimum to some hydrophobic fractions, might not be optimum to remove other fractions.
9) Applying results of THMFP and Jar tests on fractions might not truly represent original water conditions

This study developed an accurate fractionation procedure for low NOM waters. It provided a better understanding of organic matter transformation at different treatment stages and jar test performance on removal of organic materials for studied sample sets

7.2 Recommendations

This research attempted first to develop an appropriate fractionation protocol for water with low DOM. In order to delineate organic fraction in an affordable timeline, a statistic model was built and examined. Further experiments of fractionation, DBPFP, and jar tests were made to investigate the change of organic material along treatment chains. Through an overview of studies already performed, the following topics are recommended:

1) Refine the developed statistical model through a more scientific way: associating structures with fluorescence features by studying some model compounds and/or applying other analyses such as NMR in conjunction with fluorescence
2) Searching discrete fluorescence paired zone based on the theory of Stoke's shift
3) Perform jar tests on re-constructed fraction mixtures in addition to each fraction present alone to investigate organic fractions' impact on DBP formation
4) Explore optimum coagulant dosage according to USEPA Enhanced Coagulation and Precipitative Softening to remove the problematic precursors that have been identified and confirmed, taking water quality spatial and temporal variations into consideration
5) The selected WA 10, while proven to be bleeding free, is less capable (1.5 meq/ml wet at pH 2) than Duolite A7 (7 meq/ml at pH 2). More selection researches are suggested to be conducted to look for a anionic resin with no problem of bleeding and with a high capacity

APPENDIX A

STANDARD OPERATING PROCEDURE OF HITACHI F-4500 FLUORESCENCE SPECTROPHOTOMETER

This appendix describes the Standard Operation Procedure for Hitachi F-4500 fluorescence spectrophotometer. To collect accurate fluorescence spectrum of samples, the Hitachi F-4500 should be wavelength confirmed and meet Signal to Noise requirement. Response from only instrument needs recorded prior to sample analyses to enable measuring a true spectrum of samples.

1. Wavelength Confirmation

To confirm the wavelength accuracy, the sharp line spectrum of the Xe lamp at 450.1± 2.0 nm is used as a reference for both excitation and emission side. When examining the excitation side, the slit of excitation mono-chromator is narrowed to 1 nm. The scan model is selected as Excitation from 440 to 480 nm. To prevent the interference of Emission side, the scan wavelength of Emission is set at 0 nm (no emission scan). The same principle is applied for wavelength confirmation at emission side.

1.1. Excitation wavelength confirmation

- Place the furnished diffuser to cell holder in the sample compartment
- Select the Wavelength Scan mode in the Menu Select screen
- Open the Instrument Parameters screen and set each parameter as in table A-1
- Open Scan Parameters setting screen and set each parameter as in table A-1
- Perform pre-scan by clicking "Pre-scan"
- Click "Ok" to set the measuring parameters

- Click "Start Scan" to start a measurement
- Read out the wavelength of the first peak by clicking "Cursor" function and moving the arrow

If the wavelength of the first peak is not within 450.1± 2.0 nm, confirmation of wavelength on the excitation side fails and call instrument manufacture for repairing suggestion. Otherwise, continue to examine wavelength accuracy on the emission side.

Table A.1 instrument and scan parameters for Excitation side

Instrument parameter		Scan parameter	
Slit (EX/EM)	1.0/5.0 nm	Scan mode	Excitation
PMT voltage	400 v	Data mode	Luminescence
Response	0.5 s	EX starting WL	440 nm
Shutter control	Off	EX ending WL	480 nm
Corrected spectra	Off	EM WL	0 nm
		Scan speed	60 nm/min

1.2. Emission wavelength confirmation

Repeat above steps as for excitation side for emission side except setting instrument and scan parameters as in table A-2.

Table A.2 Instrument and scan parameters for Emission side

Instrument parameter		Scan parameter	
Slit (EX/EM)	**5.0/1.0** nm	Scan mode	Emission
PMT voltage	400 v	Data mode	Luminescence
Response	0.5 s	**EM starting WL**	**440 nm**
Shutter control	Off	**EM ending WL**	**480 nm**
Corrected spectra	Off	**EX WL**	**0 nm**
		Scan speed	60 nm/min

If the wavelength is not within 450.1± 2.0 nm, confirmation of wavelength on the emission side fails and call instrument manufacture for repair. Otherwise, confirmation of wavelength is done.

2. Signal to Noise Verification

The instrument S/N is measured through continuous monitoring the emission peak of water Raman spectrum excited at 350 nm. The water Raman emission band is first scanned from 350 to 420 nm to determine the peak wavelength of Raman spectrum. The fluorescence intensity of the decided Raman peak excited at 350 nm is continuous monitored and accumulated data are used to calculate S/N with a computer program provided by the manufacture.

2.1. Finding of Raman peak wavelength

- Fill the furnished quartz cell with MQ water, and place it on the cell holder
- Select the Wavelength Scan mode in the Menu Select screen
- Open the Instrument Parameters screen and set each parameter as in table A-3
- Open the Scan Parameters setting screen and set each parameter as in table A-3
- Perform Pre-scan
- Wait for disappearance of "Parameter setting"
- Click "Start scan" to start the water Raman emission band measurement
- Read out the peak wavelength of the Raman spectrum

Table A.3 Parameters to find Raman peak

Instrument parameter		Scan parameter	
Slit (EX/EM)	5.0/5.0 nm	Scan mode	Emission
PMT voltage	700 v	Data mode	Fluorescence
Response	Auto	EM starting WL	350 nm
Shutter control	Off	EM ending WL	420 nm
Corrected spectra	Off	EX WL	0 nm
		Scan speed	60 nm/min

2.2. Continuous monitoring of Raman peak

- Quit all above operation windows back to Menu Select screen
- Select the Time Scan mode
- Open the Instrument Parameters screen and set each parameter as in table A-4
- Open the Scan Parameters setting screen and set each parameter as table A-4
- Click "OK" and wait for disappearance of "Parameter setting".
- Click "Start scan" to monitor Raman peak
- Wait for approximate 10 minutes then click "Stop" to interrupt the monitoring.

Table A.4 Prameters to acquire S/N data

Instrument parameter		Scan parameter	
Slit (EX/EM)	5.0/5.0 nm	Data mode	Fluorescence
PMT voltage	700 v	Unit	Sec
Response	2 s	EM WL	Peak wavelength of Raman spectrum
Shutter control	Off	EX WL	350 nm
		Total time	2400
		Delay time	0
		Ordinate	0-10

2.3. Calculation of S/N

- Go to Utility menu to select File Convert
- Select "Convert ASCII File (Format 1)"
- Confirm the path as "C:\FL00\SPECTRUM"
- Input "NOISE" as the file name
- Click "OK" to convert to ASCII file
- Quit all fluorescence application window
- Run MS-DOS window
- Change path to "C:\FLOO\SPECTRUM>"
- Type "NOISE" and Enter

The computer will run "NOISE.exe" to calculate S/N and Drift. The S/N should be above 100 and Drift should be within 2%. Otherwise, check Troubleshooting Table for possible reason.

3. Corrected spectra

Spectrum correction is performed to acquire a true spectrum of tested sample by eliminating instrument response such as wavelength characteristics of the mono-chromator or detectors.

Generating EX Side Instrumental Response

Set PMT voltage to 400 V in Instrument Parameters; Choose OK

Set Data Mode to Fluorescence in Scan Parameter; Choose OK

Perform Zero Adjust to calibrate zero point

Fill Rhodamine B into a triangular cell furnished by manufacture

Place the triangular into sample holder with metal filling block the incident light

Select instrument Response on the Control drop down menu

Select Ex (200-600 nm) and choose Run

At this point, the instrument is automatically set according table A-5 and the EX mono-chromator scans, generates the EX response, and stores

Table A.5 Parameters to correct Excitation side spectrum

Instrument parameter		Scan parameter	
Slit (EX/EM)	5.0/20.0 nm	Scan mode	Excitation
PMT voltage	400 v	Data mode	Fluorescence
Response	Auto	EX starting WL	198.6
		EM ending WL	601.4
		EX WL	640
		Scan speed	60 nm/min

Generating EM Side Instrumental Response

Set PMT voltage to 400 V in Instrument Parameters; Choose OK

Set Data Mode to Fluorescence in Scan Parameter; Choose OK

Perform Zero Adjust to calibrate zero point

Place manufacture furnished diffuser into sample placeholder

Select instrument Response on the Control drop down menu

Select Em (200-600 nm) and choose Run

At this point, the instrument is automatically set according table A-6 and the EM mono-chromator scans, generates the EX response, and stores

Table A.6 Parameters to correct Emission side spectrum

Instrument parameter		Scan parameter	
Slit (EX/EM)	5.0/20.0 nm	Scan mode	Emission
PMT voltage	400 v	Data mode	Fluorescence
Response	Auto	EX starting WL	198.6
		EM ending WL	601.4
		EX WL	198.6
		Scan speed	60 nm/min

APPENDIX B

STANDARD OPERATING PROCEDURE FOR DETECTION OF THM WITH VARIAN GC-ECD 3400

This SOP is for testing of TTHM with Varian GC-ECD 3400 based on EPA 551.1 with a focus on THM only.

1. Scope and Application

- This method is used to determine the concentrations of four trihalomethanes in extracts from aqueous samples.
- The four trihalomethanes listed below have been tested by this method:

  Chloroform, Bromodichloromethane, Bromoform, Dibromochloromethane
- The THMs are separated with two parallel columns sharing a single injection port and detected with two Electron Capture Detectors (ECDs).

2. Summary of Method

- A 50 ml of sample is extracted with 3 ml MTBE.
- After extraction, 0.25 ml of extract phase is transferred into a 0.25 ml insert out-packed with 2 ml GC vials.
- Extracts are analyzed by injecting 1 μl aliquot together with 1μl internal standard into the gas chromatograph equipped with two parallel columns each followed with its own ECD.
- The total run is 45 minutes.

3. Interferences

- Sources of interference in this method can be grouped into two categories:

  Contaminated solvents, reagents, and sample processing hardware

  Contaminated GC carrier gas, parts, column, and detectors
- The extracting solvent MTBE has been found containing residual chloroform. Distillation of MTBE between 50 and 60 °C can decrease but not eliminate

background level of chloroform. Solvent background is examined for subtraction from sample response.

- Samples, standards, and reagents are stored in sealed amber vials with Teflon caps to prevent any contamination in the laboratory.

4. Sample Handling and Preservation

- Incubated samples for THMFP are in 68 ml vials capped with Teflon lined septa.
- Extracted samples are in 0.25 ml clear GC inserts placed into 2 ml amber GC vials to protect from light.
- Extracted samples and standards are stored under 4 °C in a refrigerator.

5. Laboratory Apparatus

- Varian 3300 with CAC A200S Auto sampler and injector
- Primary column 30 m × 0.25 mm ID × 1.0 μm (RTX-1301, catalog # 10153)
- Confirmative column 30 m × 0.25 mm ID × 1.0 μm (RTX-1, catalog # 16053)
- EZ CHROM Elite software (Version 2.61)
- Carrier gas: ultra high purity grade He
- Make up gas: Nitrogen

6. Regents and Standards

- MTBE: HPLC grade (Fisher catalog # E127-4)
- Acetone: HPLC grade (Fisher catalog # A949-4)

- Stock standards

Name	Compound	Conc. (mg/L)	Catalog #	Company
THM	Chloroform Bromodichloromethane Chlorodibromomethane Bromoform	2,000	3021	Restek
LPC	Bromodichloromethane	30	M-551.1-MLPC-	AccuStandard
	Hexachlorocyclopentadiene	20	PAK	
	G-BHC	0.2		
	Trichloroethene	30		
IS	Bromofluorbenzene	10,000	M-551.1-IS-100X	AccuStandard
Surrogate	Decafluorbiphenyl	1,000	M-551.1-SS-100X	AccuStandard

- Primary and working standard

LPC	Stock	Primary	Working
Solvent	MTBE	MTBE	MTBE
Concentration	Varied	Varied	Varied
Preparation	Commercial	1 ml of stock into 10 ml MTBE	100 µl of primary into 10 ml MTBE

Surrogate	Stock	Primary	Working
Solvent	Acetone	Acetone	Buffer/dechlorating solution
Concentration	1000 mg/L	10 mg/L	10 µg/L
Preparation	Commercial	500 µl of stock into 50 ml Acetone	50 µl of primary into 50 ml buffer/dechlorating solution

IS	Stock	Primary	Working
Solvent	Acetone	Acetone	MTBE
Concentration	10,000 mg/L	100 mg/L	1 mg/L
Preparation	Commercial	500 µl of stock into 50 ml Acetone	1 µl of primary directly into GC injector

7. Procedure

7.1. Laboratory Performance check

- Directly inject 1 µl LPC working solution into GC for 5 repetitions under the following conditions:

Initial column temperature-	35 °C
Initial column hold time -	22 min
Program 1 final column temperature -	145 °C
Program #1 column temperature rate -	10 °C/min
Program #1 final temperature holding time-	2 min
Program #2 final column temperature -	225 °C
Program #2 column temperature rate -	20 °C/min
Program #2 final temperature holding time-	1 min
Program #3 final column temperature -	250 °C
Program #3 column temperature rate -	25 °C/min
Program #3 final temperature holding time-	3 min
Injector temperature -	150 °C
Detector temperature -	290 °C
Detector A initial range -	1
Detector B initial range -	1

- Check if LPC performance meets criteria listed in table

Parameter	Analyte	Conc. (µg/ml)	Criteria
Sensitivity	G-BHC	0.00020	S/N > 3
Chromatographic performance	Hexachlorocyclopentadiene	0.020	0.8 < PGF < 1.15
Column performance	Bromodichloromethane	0.030	Resolution > 0.50
	Trichlorethylene	0.030	

$$\underline{\textbf{PGF}} \text{ (Peak Gaussian Factor)} = \frac{1.83 \times W\,(1/2)}{W\,(1/10)}$$

Where W (1/2) is the peak width at half height, W (1/10) is the peak width at tenth peak height

Resolution = $\frac{Rt2 - Rt1}{(W1 + W2)/2}$, Where $Rt2 - Rt1$ is the retention time difference between the two designated compounds and $(W1 + W2)/2$ is the average peak width between them

S/N is defined as the average response of the five runs of LPC working standards divided by the standard deviation.

7.2. Initial calibration

- Initial calibration is to determine target average relative response factor (RRF) and retention time (R.T.) as followings:

$$RRF = \frac{[Response/conc.]_{target}}{[Response/conc.]_{IS}}$$

RT window = average retention time ± 3 standard deviation

- Five calibration standards, containing each individual component of THM, are prepared at 0, 5, 20, 50, and 100 μg/L.
- Inject each standard with three repetitions.
- Determine average RRF and RT windows for each compound.
- The initial calibration must confirm a less than 15% relative standard deviation (%RSD) for each RRF and surrogate response. For internal standard, the % RSD of response must be less than 10%. Otherwise, investigate possible causes of exceeding these criteria.

7.3. Method Blank

In this SOP, the method blank is the same as the standard 0 μg/L

7.4. Calibration verification

- The calibration verification or so-called continuous calibration is to check the RRF and RT window determined during initial calibration is still applicable
- Inject a mixture standard of 50 μg/L 3 times (standard solution from providers other than the one of initial calibration is preferred)
- Calculate RRF and R.T. for each compound.
- Calibration verification should verify RRF of each target is within ± 20% of that determined in initial calibration R.T. falls into RT window determined in initial calibration Response of internal and surrogate standards should be less than ± 20% of those determined in initial calibration

7.5. Blank and blank spike

- The blank sample is different from method blank in that blank sample is subjected to 7 days incubation
- Blank is to examine possible contamination during incubation
- Blank spike is prepared at the same time as Blank by adding 34 μl of primary standard into Blank to make a final concentration of 50 μg/L for Blank spike.
- There should have no or insignificant amount of target compound able to be detected in Blank. The relative recovery of each target compound in Blank Spike should be within ± 10%.

7.6. Matrix and Matrix Spike

- Except for original samples, all fraction samples are prepared with MQ water with some NaOH and HCl (at most 0.1 N NaOH or HCl). It is presumed that no matrix interference presents during incubation and GC identification. It is expected that matrix of original sample is not harsh enough to result significant interference. This SOP suggests an optional run for matrix or matrix spike.

7.7. Sample

- When all above runs are confirmed to meet corresponding criteria, runs of samples can be initiated.
- For every run of 5 samples, a calibration check follows to examine if instrument is in acceptable running condition.
- An end check must be arranged at the end of each batch.
- Criteria for calibration check and end check is the same as Continuous Calibration.

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