

FTIR evaluation of functional groups involved in the formation of haloacetic acids during the chlorination of raw water

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Abstract

This work investigated the formation potential of haloacetic acid (HAA) compounds in the raw water for the Bangkok water treatment plant (Bangkok, Thailand). The resin adsorption technique (with three different types of resins, i.e. DAX-8, AG-MP-50 and WA-10) was employed to characterize the organic content in the raw water into six fractions, i.e. hydrophobic neutral (HPON), hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophilic neutral (HPIN), hydrophilic acid (HPIA) and hydrophilic base (HPIB). Hydrophilic species appeared to be the predominant organic species in this water source (approximately 60%) with the neutral fraction being the most abundant (approximately 40%). Hydrophobic species, on the other hand, played the most important role in the formation of haloacetic acids as they contributed to as much as approximately 56% of total HAA formation potential. Among the three hydrophobic species, the hydrophobic base exhibited the highest specific HAA formation with 208 µg HAAs/mg of dissolved organic carbon (DOC). Each organic fraction was examined for its associated functional groups by Fourier transform infrared (FTIR). The investigation of the formation of HAAs was achieved by tracking the changes in the FTIR results of the same water sample before and after the chlorination reaction. Based on the results obtained from this study, carboxylic acids, ketone, amide, amino acids and aromatic characteristic organics seemed to be the main precursors to HAA formation.

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1. Introduction

Dissolved organic carbon (DOC) present in water can form a variety of disinfection by-products during the final chlorination process in water treatment. Some of these by-products are known to be potentially carcinogenic and are being regulated. One of the main classes of these by-products is haloacetic acids (HAAs), which comprise the sum of nine species: mono-, di-, trichloroacetic acid; mono-, di-, tribromoacetic acid; monochloro-; bromodichloro-; dibromochloroacetic acid. However, only the first five of the nine

HAAs species mentioned above are regulated by the United States Environmental Protection Agency (USEPA) and the control of these species should be considered in the management of water-treatment facilities. Conventionally, the terms haloacetic acids formation potential (HAAFP) is used to reflect the potential of the water sample to form haloacetic acid disinfection by-products.

Often, the predominant pathway for HAAs formation was reported to be the reaction of chlorine with humic organic materials particularly those with aromatic structure [1,2]. However, the information on the reaction for the formation of HAAs is still limited. To better understand the reaction pathway, it is recommended that major organic species be specified along with the identification of potential functional

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groups that could lead to the formation of HAAs. Recently, fractionation procedures by various types of resin adsorption have been proposed for the categorization of DOC. This technique has recently gained crucial attention as a method that provides deeper detail of organic matter in the water samples. The procedure developed by Leenheer [3] was among the most widely adopted and it was subsequently modified by Marhaba and Pu [4], and Marhaba et al. [5] to minimize the organic loss during the extraction by changing the type of resin resulting in a method capable of fractionating the dissolved organic carbon into six fractions, i.e. hydrophobic acids (HPOA), hydrophobic bases (HPOB), hydrophobic neutrals (HPON), hydrophilic acids (HPIA), hydrophilic bases (HPIB) and hydrophilic neutrals (HPIN). Such detailed information on organic species facilitated the analysis of the main problematic organic precursors. Often, the main precursors for HAAs were found to be location specific depending significantly on the nature of that specific water source, e.g. HPOA was found to be the main HAA precursor in New Jersey surface water [6] whereas HPIA fraction was for Chang-Hsin waterworks [7].

A large number of research works have been allocated to the identification of functional groups that could potentially lead to the formation of disinfection by-products as this helped in the future development of the abatement technology to prevent the formation of such compounds, e.g. amino acid, aromatic characteristic organics, etc. In the interpretation of the functional groups, Fourier transform infrared (FTIR) is a crucial instrument. FTIR has been widely used for the structural investigation of humic substances. Samples exposed to infrared light absorb energy corresponding to the vibrational energy of atomic bonds. The resulting absorption spectrum is a unique fingerprint of compound(s). FTIR analysis allowed the identification of inorganic and organic functional groups as well as elemental composition.

Bangkhen Water Treatment Plant (WTP) is one of the three major sources for supplying potable water to more than four million people in Bangkok, Thailand. The formation of HAAs as a result of the disinfectant reaction with the organic matter in the water, therefore, could have an impact on consumers who drink the water. The purpose of this study was to investigate the relationship between the changes in functional groups due to the chlorination and the associated formation of HAAs from the organic components in the raw water obtained from Bangkhen WTP. This paper presented a discussion on the results based on the DOC isolation and the potential chemical reactivities examined by the fractionation approach and FTIR tests.

2. Methodology

2.1. Sample collection

Samples of about 30 l were collected from the intake location of the Bangkhen water treatment plant on August 5, 2003.

Analytical methods for the various parameters are described here briefly. The sample was filtrated through a pre-rinsed 0.45 μm cellulose filter to remove particles and also suspended organic matters and stored in the dark at 4 °C to minimize interference from environment.

2.2. Fractionation procedure

Dissolved organic compounds were isolated and concentrated from water samples by a sequentially extraction method using three types of adsorbents, i.e. a nonionic DAX-8 (SUPELCO) resin, a cationic exchange AG-MP-50 (Bio-Rad) resin and a weak anionic WA-10 (SUPELCO) resin. Organic materials eluted from these three resins are: hydrophobic neutral, hydrophobic base, hydrophobic acid, hydrophilic base, hydrophilic acid and hydrophilic neutral as mentioned in Marhaba and Van [6]. The fractionation procedure was briefly described as follows. Firstly, all of the resin columns were rinsed through with plenty of Milli-Q water until the DOC in the rinsed water was lower than 0.05 mg/l and the conductivity lower than 2 $\mu\text{s/cm}$. The water sample was adjusted to pH 7 ± 2 with H_2SO_4 and/or NaOH and was pumped through a series of DAX-8 columns. HPON fraction was adsorbed and eluted from the first DAX-8 column with methanol. HPON was subsequently separated from methanol using rotary vacuum evaporator. The pH of the sample was then adjusted to 10 before passing through the second DAX-8 column where HPOB fraction was adsorbed and eluted with HCl. After that, the sample was acidified to pH 2 and pumped through the third DAX-8 column. HPOA fraction was eluted by NaOH. The fourth column containing AG-MP-50 resin was then used to isolate HPIB fraction which was eluted from the column by using NaOH. HPIA fraction was contained in the last WA-10 column whereas the remaining sample that passed through the five columns was HPIN. HPIA was also eluted with NaOH.

2.3. Dissolved organic carbon measurement

DOC measurement was conducted with a TOC analyzer model 1010 (O.I. Corp.) with an autosampler (model 1051), persulfate-ultraviolet oxidation followed the Standard Methods 5310-C [8]. The analyzer was programmed according to the manufacture's recommendation, i.e. with 200 μl of 5% (v/v) orthophosphoric acid (CARLO ERBA) as an acid, 1000 μl of 100 g/l sodium peroxodisulphate (Fluka) as an oxidant and for a 10-min reaction time. At least three measurements were performed for each sample and analytical precision was typically less than $\pm 5\%$. Potassium hydrogen phthalate (KHP) (CARLO ERBA) solutions at 0, 1, 2.5, 5 and 10 mg/l were used. Ultraviolet (UV) absorbance was measured with spectrophotometer (Helios Alpha, Beta) at a wavelength of 254 nm using a quartz cell. All samples were adjusted to pH 7 with H_2SO_4 and NaOH before measurement. Milli-Q water (ELGA, Ultra Analytical) was used in the preparation of standard calibration

and blank samples. Note that the detection limit for TOC is 0.01 mg/l.

2.4. Formation potential test

A 7-day chlorination HAAFP test was carried out in accordance with the Standard Method 5710B. Chlorine solution was prepared in a form of concentrated sodium hypochlorite (100 mg Cl/l). The chlorine dosage for each water sample was determined such that a final residual chlorine concentration of 3–5 mg/l was remained in the sample after the 7 days test. All samples were adjusted to a pH 7 ± 0.2 using H_2SO_4 and NaOH. The neutralized solution was then buffered with a phosphate solution prior to the incubation at $25 \pm 2^\circ C$ in amber bottles for 7 days. At the end of the incubation, samples were dechlorinated using sodium sulfite (Na_2SO_3) as the sole dechlorinating agent as recommended by the EPA 552.2 method. The samples were then evaluated for their HAAs. The difference between concentrations of HAAs before and after the chlorination was taken as HAAFP.

2.5. Analysis for haloacetic acids

For the analysis of HAAs, the sample was extracted with methyl-*tert*-butyl-ether (MTBE) and the extract was then analyzed using a gas chromatography (Agilent Technologies) with two fused silica columns (DB-XLB, 0.32 mm \times 30 m ID and 1.0 μm film thickness), a micro-electron capture detector (μECD), and an autosampler (Agilent Technologies 7683 Series). SUPLECO standard solutions were prepared for the calibration of the five HAA species. All analyses followed quality assurance/quality control (QA/QC) as stated in the Standard Methods 5710B with liquid–liquid extraction procedure including preservation techniques, detection limits, internal standards, surrogate standards [8].

2.6. FTIR analysis

DOCs of the organic isolates both before and after the 7-day reaction period were freeze–dried and kept in a desiccators over silica gel prior to the FTIR analysis by Perkin-Elmer 1760X. Infrared spectra were obtained using 2–4 mg of filtrated sampling isolates in 150 mg of potassium bromide pellets. FTIR was set to scan from 4000 to 400 cm^{-1} , averaging eight scans at 1.0 cm^{-1} interval. All spectra were normalized after acquisition to a maximum absorbance of 1.0 for comparative purposes. FTIR libraries were referenced from Pavia et al. [9] and Fiveash Data Management Inc. (2003).

2.7. Quality assurance/quality control

Quality assurance/quality control (QA/QC) plans were set for all steps of the experiments to obtain accurate and reliable results: (i) all chemicals in this work were analytical grade, (ii) every container was neatly cleaned with a particular washing liquid for laboratory purposes, and was

Table 1
Characteristics of water source and its organic fractions

	DOC (mg/l)	SUVA (l/(mg m))	Total HAAFP ($\mu g/mg$)
Raw water	4.72	2.373	61.06
HPOA	1.63	1.667	15.21
HPOB	0.13	2.308	5.72
HPON	0.27	2.593	3.52
HPIA	0.84	0.714	6.78
HPIB	0.16	2.500	4.72
HPIN	2.12	1.038	28.50

rinsed with Milli-Q water, and heated at 105 $^\circ C$ for more than 2 h before use, (iii) TFE-screw cap with amber glass bottles were used to store samples for HAAFP test, (iv) the instruments were regularly calibrated step by step as noted in the instrument guidelines, (v) during the fractionation process, resins and glass wool were cleaned and purified by soxhlet extraction as described in Leenheer (1979) and Leenheer [3] and (vi) 1,2,3-trichloropropane (internal standard) and 2,3-dibromopropionic acid (surrogate standard) were used in the GC measurement of HAAs, which followed the QA/QC procedure mentioned in the EPA method (AWWA).

3. Results and discussion

3.1. DOC

Table 1 summarizes the analytical fractionation results based on DOC test. The total dissolved organic content of this raw water was approximately 4.7 mg/l and the sequence of the six organic fractions could be summarized in order from large to small as: hydrophilic neutral > hydrophobic acid > hydrophilic acid > hydrophobic neutral > hydrophilic base \geq hydrophobic base, as illustrated in Table 1 and Fig. 1. The summation of DOC concentrations from six fractions was approximately 5.1 mg/l, on the other hand, it was about 8% surplus for this set of fractionation procedure. Note that the quantities of hydrophilic base and hydrophobic base were not significantly different from each other and in this case, the amounts of hydrophilic and hydrophobic base components were equal to approximately 0.16 and 0.13 mg/l, respectively.

The specific UV absorbance or SUVA (the ratio between UV and DOC) was often employed to indicate the level of aromatic materials in the water sample. High SUVA values

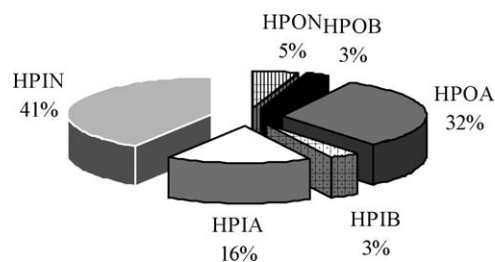


Fig. 1. Organic fraction distribution of Bangkhen water treatment plant.

were known to indicate high molecular weight, hydrophobic and aromatic character components [10–13]. This simply meant that SUVA was used to suggest the possibility of organic matters to form potentially harmful disinfection by-products if presented in adequate quantity, and therefore it could be treated as a possible indicator for the formation of disinfection by-products [14]. SUVA in this study was 2.373 l/(mg m) in raw water and SUVAs of the six organic fractions were shown in Table 1. HPON presented the highest SUVA value (2.593 l/(mg m)) whereas that of HPIA was least (0.714 l/(mg m)). This result was similar to the previous report by Marhaba and Pu [4] who found that HPIA possessed the lowest level of SUVA in central New Jersey surface water.

All of hydrophobic fractions exhibited higher SUVA than the hydrophilics (except for the base fraction). This meant that hydrophobic species consisted of more aromatic structured components than hydrophilics and therefore should have higher potential to form disinfection by-products.

3.2. Haloacetic acid formation potential

HAAFP is a measure of the potential of the organic materials (for each DOC isolate) to form HAAs after reacted with

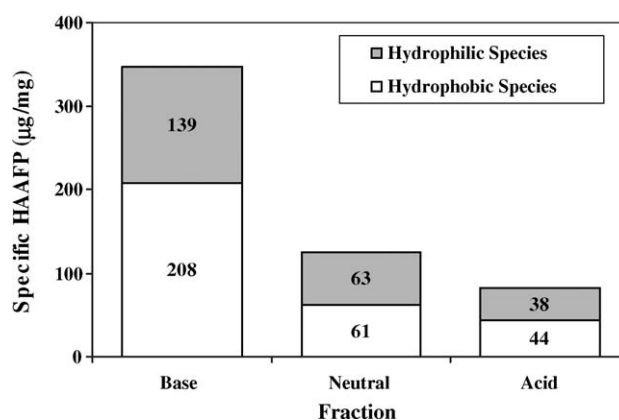


Fig. 2. Specific HAAFP of hydrophobic and hydrophilic species.

excess chlorine. HAAFP of raw water in this investigation was 288 µg/mg, which was not dramatically deviated from the sum of 304 µg/mg obtained from the HAAFP test of each single organic fraction. In this work, HAAFP was reported as (i) total HAAFP and (ii) specific HAAFP. The total HAAFP was the ratio between the actual HAAs from the FP test and the total dissolved organic content in the water sample,

Table 2
SUVA and HAAFP in some water sources

Water source	DOC (mg/l)	SUVA (l/(mg m))	Specific HAAFP	Reference
WTP in Canada	Raw water = 1.1		Approximately 23 µg/mg	William et al. [15]
Canal Road WTP	HPOA = 0.42 HPOB = 0.21 HPON = 0.63 HPIA = 1.67 HPIB = 0.13 HPIN = 0.72		22 µg/mg 22.5 µg/mg 21.5 µg/mg 8 µg/mg 11 µg/mg 5 µg/mg	Marhaba and Van [6]
Zegrzynskie Lake	Raw water = 7–17		Approximately 0.6–7.5 µg/mg	Dojlido et al. [16]
Wakarusa River	Raw water = 5.4		Approximately 2.8 µg/mg } Approximately 2.4 µg/mg } Approximately 30 µg/mg }	Pomes et al. [17]; Dalvi et al. [18]
Clinton Lake	Raw water = 4.1			
Al-Jubail Plant	Raw water = 3.2			
Pan-Hsin River	HPOA = 0.2 HPOB = 0.07 HPON = 0.18 Hydrophilic = 0.02		HPOA = 150 HPOB = 20 HPON = 40 Hydrophilic = 120	Chang et al. [7]
Han River		Raw water = 3.11	6.5 µg/mg } 7.7 µg/mg } 16.3 µg/mg } 4.7 µg/mg }	Kim et al. [19]
Daechung Lake		Raw water = 3.33		
Youngsan River		Raw water = 3.06		
Nackdong River		Raw water = 2.27		
Sainte Foy WTP	Raw water = 2.4		Approximately 4 µg/mg } Approximately 68 µg/mg } Approximately 35 µg/mg }	Serodes et al. [20]
Charlesbourg WTP	Raw water = 1.6			
Quebec WTP	Raw water = 1.7			
South Fork Tolt River, Seattle		Raw water = 4.7	0.36 µmol/mg C } 0.22 µmol/mg C } 0.29 µmol/mg C } 0.17 µmol/mg C } 0.21 µmol/mg C }	Liang and Singer [13]
Lake Manatee Reservoir, Bradenton		Raw water = 4.4		
Poquonnock reservoir, Groton		Raw water = 3.6		
Mississippi, E. St. Louis		Raw water = 3.3		
White River, Indianapolis		Raw water = 3.1		
St. Lawrence River		Raw water = 4.86	Approximately 20 µg/mg	Rodriguez et al. [21]
Bangkhen WTP	Raw water = 4.72	Raw water = 2.37	57.9 µg/mg	This work

Table 3
Possible target functional groups for the formation of DBPs

Water source	Target functional groups	Reference
Dilute aqueous solution	Dihydroxyaromatic	Boyce and Hornig [22]
Various treated industrial wastewaters	Organic nitrogen, phenolic-OH	Galapate et al. [23]
South Platte River	β -Hydroxyacids and β -ketones	Croue et al. [1]
Minaga reservoir water	Phenolic-OH	Galapate et al. [24]
Diluted humic acid solution	Phenolic group and carboxyl group	Lin et al. [25]
Reclaimed water in ground water, Los Angeles County, California	Phenol structures	Leenheer et al. [26]
Surface water and humic material solutions	Dihydroxyaromatic compounds (resorcinol-type structures), β -diketone, β -ketoacids and phenolic-OH	Gallard and Gunten [27]

and this has the unit of “ $\mu\text{g HAA/mg DOC}$ ” (or “ $\mu\text{g/mg}$ ” in short). Specific HAAFP, on the other hand, was the ratio between HAAs from each organic fraction and the DOC of that particular fraction (which, therefore, takes the same unit as total HAAFP). This was to indicate the actual reactivity of the organic fraction in the formation of HAAs. In the discussion hereafter, HAAFP will be referred to as specific HAAFP unless specified otherwise. Table 1 demonstrates that the quantity of HAA generated from each organic fraction follows an order from high to low as: base fractions > neutral fractions > acid fractions. This result suggested that the main precursors for HAAFP for this water source were the base organic fractions. Data in Table 1 could be converted to Fig. 2 which illustrates further that the hydrophobic fractions were, in all cases, more active in forming HAAs during the chlorination. From the previous section, it was shown that most hydrophobic fractions exhibited higher level of SUVA. Therefore, the results from this work emphasized the statement that water sources with higher SUVA had higher potential of forming HAAs.

The observation from this work, however, was different from that of Marhaba and Van [6] and Chang et al. [7] who reported that HPIA and HPOA possessed the highest potency in forming specific HAAs, respectively. Table 2 summarizes the findings on the HAA formation from various water which shows that the main organic precursors depended significantly on source location. Hence, it is difficult to conclude on the main organic precursor for HAAs as organic precursors presented in different water sources were variable and even the same organic fraction if presented in different sources could lead to different levels of HAAs.

3.3. FTIR

The FTIR analysis of the isolate samples informs about the distribution of functional groups within the organic fractions and provides a basis for comparison of compositional differences between isolates and among samples that can be suspected to be as DBPs, precursors. The precursors were different from various watercourses as shown in Table 3. Comprehensive interpretation of FTIR spectra is compli-

cated as a large number of absorption bands are generated and the overlaps of these spectra could prevent accurate examination of some compounds that are present in small quantities. The structure of the fractionated DOC was interpreted, therefore, only for those strongest bands that could be identified. FTIR results in Fig. 3 illustrate that the six fractions isolated contained both different functional groups, and similar groups with different concentrations. The differences in the functional groups of the six fractions observed pre- and post-HAAFP test suggested that the chlorination reaction were highly selective for some specific compounds that were attacked and broken down to form HAAs. Some transformations of each organic fraction were discussed further below.

3.3.1. Hydrophobic acid

Strong broad H-bond peak at $3400\text{--}2500\text{ cm}^{-1}$, C=O band at $1720\text{--}1700\text{ cm}^{-1}$, and C–O band nears $1320\text{--}1210\text{ cm}^{-1}$ effectively indicated that carboxylic acids existed as a major functional group in the HPOA fraction. Small shifts in the wavelength were often observed, which was not uncommon for the interpretation of compound complex as there might have existed the merging of the peaks of components that exhibited absorbance characters at similar range of wavelength. The spectrum for HPOA isolates may be a result of the higher aromatic lignin carbon content, a primary precursor for aromatics in humic materials [28]. A decrease in carboxylic acids spectrum after the formation potential test meant that carboxylic acids group could be one of the target groups that played an important role in generating HAAs.

Note that phenol was often reported to be one of the functional groups in the HPOA fraction [29,30]. However, there was no clear phenol band appearing in the water sample examined in this work. It was possible that the amount of phenol was too small that the peak was overlapped with other absorbance bands. In addition, as phenol was often obtained from anthropogenic sources but the sampling point at Bangkhen water treatment facility was rather further downstream from the industrial area, and this might have given adequate time for phenol to escape from the water.

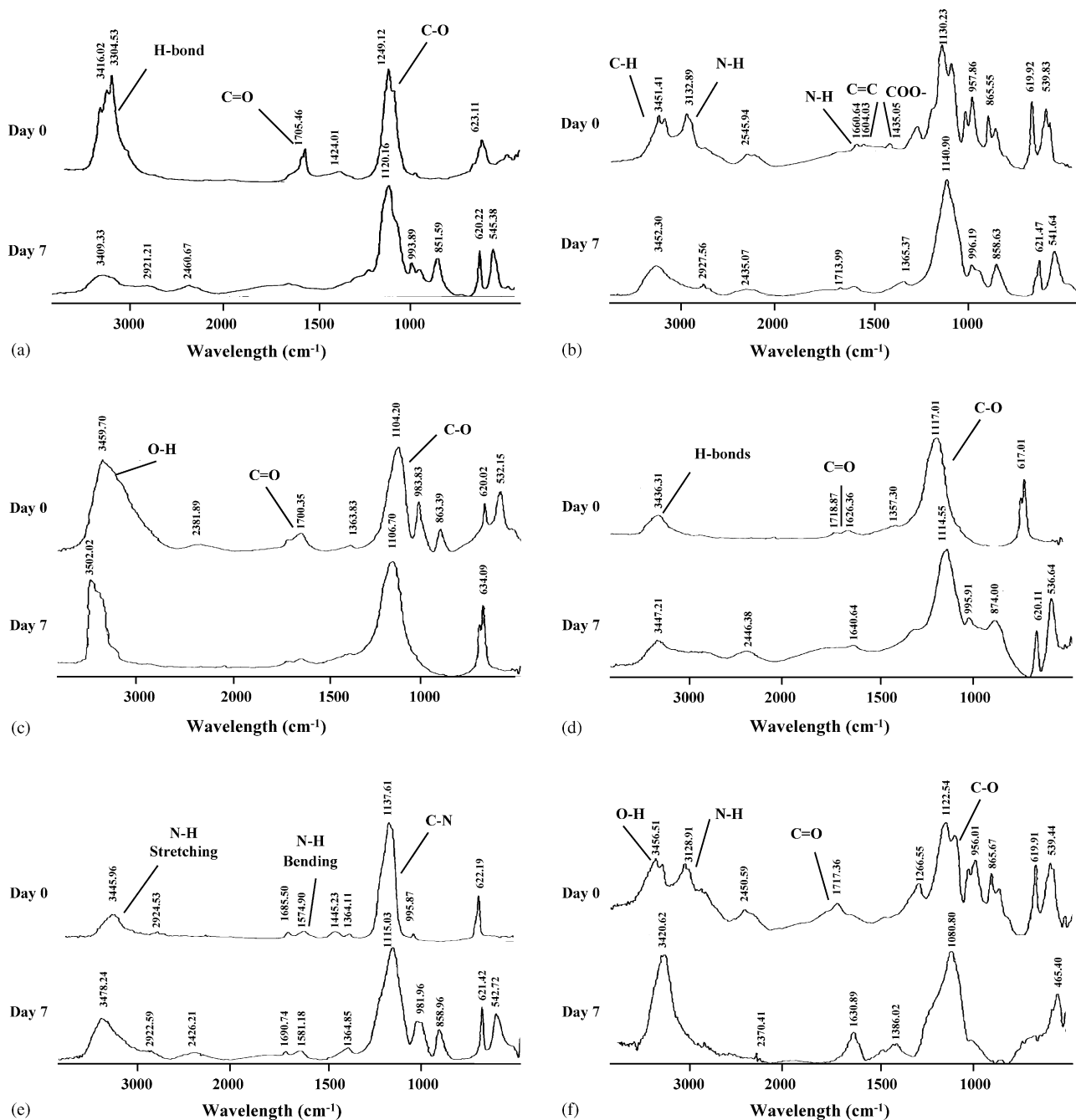


Fig. 3. FTIR spectra between day 0 and 7 of NOM fractions.

3.3.2. Hydrophobic base

FTIR results of the sample before the FP test in Fig. 3b illustrate an obvious C–H stretching peak at 3500–3300 cm^{-1} , and C=C stretching peak at 1600 and 1475 cm^{-1} . The spectrum was somewhat unusual because a strong amide-1 peak near 1660 cm^{-1} was established without an amide-2 peak near 1550 cm^{-1} . This indicated that this fraction was not protein, but it might have contained primary amide functional groups, possibly formed by the incorporation of ammonia into the molecular structure of the organic species [1]. After the FP test, aliphatic carbon peak at around

2900 cm^{-1} was observed which suggested that there might exist some aromatic aliphatic components in this sample [31].

Table 1 demonstrates that most of the hydrophobic fractions exhibited higher SUVA values and gave higher HAAFP than the hydrophilic fractions. In this section, it was shown that the aromatic character peak intensity was always diminished after the FP test. This result emphasized the belief that organics rich in aromatic content should be the major HAA precursor in natural waters [13,32].

In addition, it was revealed that amide was also attacked by chlorine during the disinfection process as the amide peak

disappeared in the post-FP test samples. As the HAAFP of HPOB was highest (208 $\mu\text{g}/\text{mg}$), it was possible that amide was rather active with chlorine and might have led to the formation of HAAs.

Spectrum of amino acids showed that there existed a combination of carboxylate (COO^- stretching near 1600 and 1400 cm^{-1}) and primary amine salts (N–H stretching in the middle range of 3300–2600 cm^{-1} and N–H bending at 1610–1500 cm^{-1}) in pre-HAAFP samples and these groups were dramatically decreased in the post-HAAFP. This agreed with the findings of Marhaba and Van [6] and Butterfield et al. [32] who suggested that amino acids in HPOB fraction were prone to and could rapidly react with chlorine to produce HAAs and other DBPs.

Regarding the function of amino acid, or amide groups in the formation of HAA, it has been known that these compounds consist of rich average N content molecules which were expected to be organic-base species. Croue et al. [1] indicated that C/N ratio in organic fraction decreased with increasing hydrophilic character. This could imply that the high C/N ratio compounds such as amino acid, or amide groups could present hydrophobic character with high SUVA values as is the character of HPOB fraction. Therefore, it could be suggested that this group could be an important precursor for the generation of HAAs.

3.3.3. Hydrophobic neutral

A significant alcohol content was indicated by the O–H stretching peak at 3500–3200 and C–O stretching peak at 1250–1100 cm^{-1} . However, some researchers [28,29] stated that HPON consisted of alcohol in aliphatic structure. Aldehydes were reported to be one of functional groups found in this fraction [29], however, no clear evidences of peak bands at 2850 and 2750 cm^{-1} were noticed. This might be due to the overlap of the absorbance with the O–H peak.

The C=O stretch at approximately 1700 cm^{-1} (the spectrum of ketone) also appeared in this fraction. In fact, this peak was not exactly found at the ketone wavelength (peak stretching at 1715), as there might be the effect of the combination of ketone with other functional groups. In the post-HAAFP spectrum, this combined ketone peak disappeared. Hence, it could be possible that ketone or, more specifically, the carbon–carbon bond in the ketone structure was a suspected HAAs precursor.

HPON was reported to contain considerable quantity of ash with small carbon content which led to a low HAAFP level (Krasner and Amy [14]). This was observed to be true for this investigation. In this work, this fraction exhibited a rather high value of SUVA (at 2.593 l/(mg m)), but only small quantity of HAAFP was detected (at 61 $\mu\text{g}/\text{mg}$). FTIR results also indicated that the differences in pre- and post-HAAFP spectra were only marginal which suggested that this fraction could be, as a result of its high ash content, rather inactive in forming HAAs from the chlorination reaction.

3.3.4. Hydrophilic acid

A carboxylic acid peak was more clearly observed after the FP test as indicated by an extremely broad O–H absorbance peak in the region from 3400 to 2500 cm^{-1} . HPIA isolate was distinctive that it contained more aliphatic and less aromatic carbon than all other isolates (suspected results from its low SUVA value at 0.714 l/(mg m)). Interestingly, SUVA after the HAAFP test was found to have higher value than the initial SUVA (post-FP test SUVA = 1.3 l/(mg m)). This result was emphasized by the FTIR spectra where an aromatic peak was found as indicated in the post-FP peak at around 875 cm^{-1} [31]. The reason why the aromatic peaks became clearer in the post-FTIR than in the pre-FTIR spectra was not clear with this set of experimental data. Two possible scenarios were anticipated. Firstly, aromatic group remained unaltered whilst other functional groups were undergone chlorination reaction. This resulted in a clearer aromatic peak. Secondly, the aromatic functional group was a by-product of the disinfection of HPIA fraction.

3.3.5. Hydrophilic base

The FTIR spectra indicated that the majority of this fraction was primary aliphatic amines as illustrated by peaks at 3500–3400, 1650–1580 and 1250–1020 cm^{-1} . As stated by Leenheer and Huffman [29], HPIB comprised pyridines, pures, and pyrimidines. However, only pyridine peak was found for this fraction at 1550 and 1450 cm^{-1} . The FTIR spectra characteristics of this functional group were similar to those of HPIA where a higher aromatic content was found after the FP test as the peaks at around 875 cm^{-1} became more apparent. Surprisingly, HPIB showed extremely high HAAFP and also high SUVA which suggested that there should have existed high content of aromatic components. However, the results from FTIR could not clearly indicate potential functional groups that could lead to the formation of HAAs.

3.3.6. Hydrophilic neutral

A significant alcohol content was indicated by the C–O stretching peak near 1250–1000 cm^{-1} . The major difference between the pre- and post-HAAFP spectra was that the peak of $-\text{NH}_2$ stretching at 3400 and 3100 cm^{-1} were much less apparent in the day 7 than in the day 0. This effect might have been a result of the involvement of amides in the HAAs formation reaction. Ketone stretching frequency at 1715 cm^{-1} was illustrated in pre-HAAFP. This ketone might have different characters than that found in the HPON fraction as Leenheer and Huffman [29] suggested that ketone found in HPIN fraction was the one with less than five carbon atoms. The ketone was shown to be removed in the post-HAAFP sample which was similar to the observation of the HPON fraction as stated above. Hence, it could be stated that ketone was one of the precursors to the formation of HAAs.

Table 4 summarizes the target function groups associated with each organic fraction that could have undergone the reaction with chlorine. Note that FTIR results did not

Table 4
Possible target functional groups for the formation of HAAs

Fraction	Possible functional groups presented in the sample	Target functional groups for HAAs
HPOA	Carboxylic acids of five to nine carbon, phenol	Carboxylic acids
HPOB	Aromatic characteristic, primary amide, amino acids	Amide, amino acids
HPON	Alcohol, ketone	Ketone
HPIA	Low molecular weight carboxylic acids	Carboxylic acids
HPIB	Primary aliphatic amines, pyridines	–
HPIN	Alcohol, amide, Ketone less than five carbons	Amide, ketone

just demonstrate the peaks of organic functional groups, rather, it was evident that majority of the fractions were inorganic constituents, such as silica compounds as indicated by peaks at 1050, 800 and 460 cm^{-1} and sodium sulfite at 1150–900 cm^{-1} . These inorganic peaks were often found to cover a wide range of IR frequency and this could obstruct the observation of some active organic peaks particularly those with low concentration.

4. Conclusions

This work was the first attempt in trying to configure the formation of HAAs in the water source of one of the largest water treatment facilities in Thailand. HPIN was found to be the most abundant (approximately 40%) of all fractions in the water source and also the main organic precursor for HAAs (highest total HAAFP). However, due to the aliphatic nature of HPIN, this fraction was not found to be the most active HAA precursor. Instead, the most active precursor for HAAs in this water source was HPOB and HPIB which were more abundant in aromatic functional groups. HPON fraction, in particular, was found to possess the richest aromatic nature, but it did not provide high HAAFP which could be a result from its high ash content. FTIR analyses of the pre- and post-chlorinated water samples provided a better understanding of the possible functional groups associated with the formation of HAAs which could potentially be carboxylic acids, aromatic, amide, amino acids, and ketone. These findings are important for the operation of water treatment facilities and sourcewater management. For instance, one could manage to eliminate the potential target functional groups prior to the chlorination, or one could look back further upstream from the point of sampling to identify the sources of potentially problematic precursors with suspected functional groups, and to superimpose a proper management strategy in controlling the quality of the effluent before being discharged into the watersource.

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References

- [1] P.J. Croue, G.V. Korshin, M. Benjamin, Characterization of natural organic matter in drinking water, *J. AWWA U.S.A.* (2000).
- [2] D.A. Reckhow, P.C. Singer, R.L. Malcolm, Chlorination of humic materials byproduct formation and chemical interpretations, *Environ. Sci. Technol.* 24 (1990) 1655–1664.
- [3] J.A. Leenheer, Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters, *Environ. Sci. Technol.* 15 (5) (1981) 578–587.
- [4] T.F. Marhaba, Y. Pu, Rapid delineation of humic and non-humic organic matter fractions in water, *J. Hazard. Mater. A* 73 (2000) 221–234.
- [5] T.F. Marhaba, Y. Pu, K. Bengraïne, Modified dissolved organic matter fraction technique for natural water, *J. Hazard. Mater. B* 101 (2003) 43–53.
- [6] T.F. Marhaba, D. Van, Chlorinated disinfection by-product formation potential of dissolved organic matter fractions at an ozonation water treatment plant, *Adv. Environ. Res.* 3 (3) (1999) 255–268.
- [7] E.E. Chang, P.C. Chiang, Y.M. Ko, W.H. Lan, Characteristics of organic precursors and their relationship with disinfection by-products, *Chemosphere* 44 (2001) 1231–1236.
- [8] Standard Methods for the Examination of Water and Waste Water, 20th ed., American Public Health Association, American Water Works Association and Water Pollution Control Federation, 1998.
- [9] L.D. Pavia, M.G. Lampman, S.G. Kriz Jr., Introduction to Spectroscopy: A Guide for Students of Organic Chemistry, W.B. Saunders Company, Department of Chemistry, Western Washington University, Belling Ham, Washington, 1979.
- [10] J.D. Thompson, M.C. White, G.W. Harrington, P.C. Singer, Enhanced softening: factors influencing DBP precursor removal, *J. AWWA* 89 (6) (1997) 94–105.
- [11] C.W. Li, G.V. Korshin, M.M. Benjamin, Monitoring DBP formation with differential UV spectroscopy, *J. AWWA* 90 (8) (1998) 88–100.
- [12] W.L. James, G.R. Aiken, B.A. Bergamashi, M.S. Fram, R. Fujii, K. Mopper, Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon, *Environ. Sci. Technol.* 37 (2003) 4702–4708.
- [13] L. Liang, P.C. Singer, Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water, *Environ. Sci. Technol.* 37 (2003) 2920–2928.
- [14] S.W. Krasner, G. Amy, Jar test evaluations of enhanced coagulation, *J. AWWA* 87 (12) (1995) 93–107.
- [15] D.T. William, G.L. LeBel, F.M. Benoit, Disinfection by-products in Canada drinking water, *Chemosphere* 34 (2) (1997) 299–316.
- [16] J. Dojlido, E. Zbiec, R. Swietlik, Formation of the haloacetic acids during ozonation and chlorination of water in Warsaw waterworks (Poland), *Water Res.* 33 (14) (1999) 3111–3118.

- [17] M.I. Pomes, C.K. Larive, M.R. Thurman, R.W. Green, W.H. Orem, C.E. Rostad, T.B. Coplan, B.J. Cutak, A.M. Dixon, Sources and haloacetic acid/trihalomethane formation potentials of aquatic humic substances in the Wakarusa River and Clinton Lake near Lawrence, Kansas, *Environ. Sci. Technol.* 34 (2000) 4278–4286.
- [18] A.G. Dalvi, R. Al-Rasheed, M.A. Javeed, Haloacetic acids (HAAs) formation in desalination processes from disinfectants, *Desalination* 129 (2000) 261–271.
- [19] J. Kim, Y. Chung, D. Shin, M. Kim, Y. Lee, Y. Lim, D. Lee, Chlorination by-products in surface water treatment process, *Desalination* 151 (2002) 1–9.
- [20] J.B. Serodes, M.J. Rodriguez, H. Li, C. Bouchard, Occurrence of THMs and HAAs in experimental chlorinated waters of the Quebec City Area (Canada), *Chemosphere* 51 (2003) 253–263.
- [21] M.J. Rodriguez, J.B. Serodes, P. Levallois, Behavior of trihalomethanes and haloacetic acids in a drinking water distribution system, *Water Res.* 38 (2004) 4367–4382.
- [22] S.D. Boyce, J.F. Hornig, Reaction pathways of trihalomethane formation from the halogenation of dihydroxyaromatic model compounds for humic acid, *Environ. Sci. Technol.* 17 (1983) 202–211.
- [23] R.P. Galapate, A.U. Baes, K. ITO, K. Iwase, M. Okada, Trihalomethane formation potential prediction using some chemical functional groups and bulk parameters, *Water Res.* 33 (1999) 2555–2560.
- [24] R.P. Galapate, A.U. Baes, M. Okada, Transformation of dissolved organic matter during ozonation: Effects on trihalomethane formation potential, *Water Res.* 35 (2001) 2201–2206.
- [25] C.F. Lin, S.H. Liu, O.J. Hao, Effect of functional groups of humic substances on ultrafiltration performance, *Water Res.* 35 (2001) 2395–2402.
- [26] J.A. Leenheer, C.E. Rostad, L.B. Barber, R.A. Schroeder, R. Anders, M.L. Davisson, Nature and chlorine reactivity of organic constituents from reclaimed water in groundwater, Los Angeles country, California, *Environ. Sci. Technol.* 35 (2001) 3869–3876.
- [27] H. Gallard, U.V. Gunten, Chlorination of natural organic matter: Kinetics of chlorination and of THM formation, *Water Res.* 36 (2002) 65–74.
- [28] R. Benner, M.L. Fogel, E.K. Sprague, R.E. Hodson, Depletion of ^{13}C in lignin and its implications for stable carbon isotopic studies, *Nature* 329 (1987) 708–710.
- [29] J.A. Leenheer, E.W. Huffman Jr., Analytical method for dissolved-organic carbon, *Water Resour. Invest.* 79 (4) (1979) 1–16.
- [30] T.F. Marhaba, N.S. Pipada, Coagulation: effectiveness in removing dissolved organic matter fractions, *Environ. Eng. Sci.* 17 (2) (2000) 107–116.
- [31] K.J. Howe, K.P. Ishida, M.M. Clark, Use of ATR/FTIR spectrometry to study fouling of microfiltration membranes by natural waters, *Desalination* 147 (2002) 251–255.
- [32] P.W. Butterfield, A.K. Camper, B.D. Ellis, W.L. Jones, Chlorination of model drinking water biofilm: implications for growth and organic carbon removal, *Water Res.* 36 (2002) 4391–4405.