



## CHAPTER V

### FORMATION MECHANISM OF HALOACETIC ACIDS

#### 5.1 Motivations and theoretical background

The previous chapter illustrated that the complexity of the organic matter could be simplified by applying a suitable fractionation method. As DOC was broken down into different organic fractions with different properties, the formation of HAAs was better understood. To extend the evaluation of HAAs formation, the various organic fractions should undergo further analysis that provides more details, preferably to the molecular structure level. Indeed, the best examination is to separate the organic compounds into individual species which might not be achievable in practice. One of the well established evaluation methods is to examine the functional groups presented in the sample which, in many circumstances, offers significant information for the evaluation of possible reaction pathways. This could be accomplished through the application of Fourier Transform InfraRed (FTIR) instrument.

FTIR spectrophotometer is an instrument that determines the absorption spectrum for a compound by detection of various molecular vibrations (rotations and stretches). When the frequency of the infrared radiation entering a solution or crystal of an organic compound corresponds to the frequency of a molecular motion in the organic compound, radiation is absorbed. The spectrophotometer determines the relative strengths and positions of all the absorptions in the infrared region and plots this on a piece of calibrated chart paper. A plot of percent transmission versus frequency indicates the relative amounts of molecular stretching and bending vibrations of various atoms in the molecule. This plot of absorption intensity versus wavenumber or wavelength is referred to infrared spectrum of the compound. Comprehensive interpretation of FTIR spectra of pure compounds is complex because so many absorption bands are generated.

Paradoxically, the complexity of the fractionated DOC simplifies interpretation of the spectra because only the strongest bands can be identified and associated with the predominant structures. FTIR spectrometry can also serve as an assay of the purity of DOC fractions because it allows bicarbonate, carbonate, nitrate, phosphate, silicate, and sulfate salts in the sample to be readily detected. Inorganic salts (with the exception of chloride salts) can be a major interference, so purification requirements are significant for FTIR spectrometry.

Few researchers have been working on the determination of functional groups related with DBPs formation as performed in Table 5-1. However, most of the previous works focused on the chemical compounds which were targeted for THMs formation. This experiment, on the other hand, was the first attempt to examine the functional groups that played an important role in the formation of HAAs.

## **5.2 Objective of this chapter**

The objective of this chapter was to determine functional groups of organic matters and to evaluate how the functional groups were associated with the formation of HAAs.

## **5.3 Methodology**

The experiment was carried out according to the procedure as described in Section 3.9, Chapter 3.

## **5.4 Results and discussion**

### **5.4.1 DOC**

As mentioned in Chapter 4, 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 >

hydrophobic base. 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 approx. 0.16 and 0.13 mg/l, respectively.

The carbon-normalized 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 were known to indicate high molecular weight, hydrophobic and aromatic character components (Thompon *et al.*, 1997, Li *et al.*, 1998, Jame *et al.*, 2003, and Liang and Singer, 2003). This simply meant that SUVA was used to suggest the possibility of organic matters to form hazardous disinfection by-products, and therefore it could be treated as a possible indicator for the formation of disinfection by-products (Krasner and Amy, 1995). SUVA in this study was 2.373 L/mg-m in raw water. SUVAs of the six organic fractions were shown in Table 5-2. 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 *et al.* (2000) who found that HPIA possessed the lowest level of SUVA in the center 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.

#### **5.4.2 HAAFP**

HAAFP of raw water in this investigation was 288.25  $\mu\text{g/L}$ , which was not dramatically deviated from the sum of 304.19  $\mu\text{g/L}$  obtained from the HAAFP test of each single organic fraction. As stated in Chapter 4, 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, and this has the unit of " $\mu\text{g HAAs/mg DOC}$ " (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 5-2 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 5-2 could be converted to Figure 5-1 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 (1999) and Chang *et al.* (2001) who reported that HPIA and HPOA possessed the highest potency in forming specific HAAs, respectively. Table 5-2 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

### 5.4.3 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. Comprehensive interpretation of FTIR spectra is complicated as a large number of absorption bands are generated and the overlaps of these spectra could prevent accurate examination of some compounds that present in small quantity. The structure of the fractionated DOC was interpreted, therefore, only for those strongest bands that could be identified. FTIR results in Figure 5-2 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 transformed mechanisms of each organic fraction were discussed further below.

#### ***5.4.3.1 Hydrophobic neutral (HPON)***

FTIR results in Figure 5-2a demonstrate that a significant alcohol content was indicated by the O-H stretching peak at 3500-3200 and C-O stretching peak at 1250-1100  $\text{cm}^{-1}$ . However, some researcher (Benner *et al.*, 1987, and Leenheer and Hoffman, 1979) stated that HPON consisted of alcohol in aliphatic structure. Aldehydes were reported to be one of functional groups found in this fraction (Leenheer and Hoffman, 1979), however, no clear evidences of peak bands at 2850 and 2750  $\text{cm}^{-1}$  were noticed. This might be due to the overlap of the absorbance with the O-H peak.

The C=O stretch at approximately 1700  $\text{cm}^{-1}$  (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  $\text{cm}^{-1}$ ), 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, and therefore, was suspected to be one of the HAAs precursors.

HPON was reported to contain considerable quantity of ash with small carbon content which led to a low HAAFP level (Krasner and Amy, 1995). 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 61.48  $\mu\text{g}/\text{mg}$ ). FTIR results also indicated that the differences in pre- and post-HAAFP spectra were only marginal which emphasized that this fraction was, as a result of its high ash content, rather inactive in forming HAAs from the chlorination reaction.

#### 5.4.3.2 Hydrophobic base (HPOB)

FTIR results in Figure 5-2b illustrate an obvious C-H stretching peak at 3500-3300  $\text{cm}^{-1}$ , and C=C stretching peak at 1600 and 1475  $\text{cm}^{-1}$ . The spectrum was somewhat unusual because a strong amide-1 peak near 1660  $\text{cm}^{-1}$  was established without an amide-2 peak near 1550  $\text{cm}^{-1}$ . 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 (Croue *et al.*, 2000). Aliphatic carbon peak at around 2900  $\text{cm}^{-1}$  was also observed which suggested that there might exist some aromatic components in this sample (Howe *et al.*, 2002).

Table 5-2 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 (Liang *et al.*, 1999; Butterfield *et al.*, 2002).

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 sample. As the HAAFP of HPOB was highest (207.69  $\mu\text{g}/\text{mg}$ ), 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 ( $\text{COO}^-$  stretching near 1600 and 1400  $\text{cm}^{-1}$ ) and primary amine salts (N-H stretching in the middle range of 3300-2600  $\text{cm}^{-1}$  and N-H bending at 1610-1500 $\text{cm}^{-1}$ ) in pre-HAAFP samples and these groups were dramatically decreased in the post-HAAFP. This agreed with the findings of Marhaba and Van (1999) and Butterfield *et al.* (2002) who suggested that amino acids in HPOB fraction were prone to and could rapidly react with chlorine to produce HAAs and other DBPs.

#### 5.4.3.3 *Hydrophobic acid (HPOA)*

Strong broad H-bond peak at 3400-2500, C=O band at 1720-1700  $\text{cm}^{-1}$ , and C-O band nears 1320-1210  $\text{cm}^{-1}$  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 aromatic in humic materials (Benner *et al.*, 1987). 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 (Leenheer and Huffman, 1979, and Marhaba and Pipada, 2000). 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 Bangkok 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.

#### 5.4.3.4 *Hydrophilic base (HPIB)*

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  $\text{cm}^{-1}$ . As stated by Leenheer and Huffman (1979), HPIB comprised pyridines, pures, and pyrimidines. However, only pyridine peak was found for this fraction at 1550 and 1450  $\text{cm}^{-1}$ . 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  $\text{cm}^{-1}$  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.

It is evident that the base species (both hydrophobic base and hydrophilic base fractions) contained nitrogen atom. Nitrogen presented in this species might be a mainly key factor in forming HAAs. However, the mechanism of nitrogen to form HAAs was not clear in this set of this experiment.

#### ***5.4.3.5 Hydrophilic acid (HPIA)***

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 3400-2500  $\text{cm}^{-1}$ . 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  $\text{cm}^{-1}$  (Howe *et al.*, 2002). The reason why the aromatic peaks became clearer in the post- 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.

#### ***5.4.3.6 Hydrophilic neutral (HPIN)***

A significant alcohol content was indicated by the C-O stretching peak near 1250–1000  $\text{cm}^{-1}$ . The major difference between the pre- and post-HAAFP spectra was that the peak of -NH stretching at 3400 and 3100  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  was illustrated in pre-HAAFP. This ketone might have different characters than that found in the HPON fraction as Leenheer and Huffman (1979) 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 5-3 summarizes the target function groups associated with each organic fraction that could have undergone the reaction with chlorine. Note that FTIR results did not 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  $\text{cm}^{-1}$  and sodium sulfite at 1150-900  $\text{cm}^{-1}$ . 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.

As mentioned in the methodology (Section 3.9), all samples were prepared by using freeze dryer prior to test with FTIR. This led to a loss in volatile fraction. In other words, only non-volatile organic compounds remained in the sample with FTIR test. Hence, the results in this section demonstrated only the non-volatile problematic precursors of HAAs. This is unavoidable as it is the main drawback inherited from the application of FTIR.

## 5.5 Concluding remarks

This work was the first attempt in trying to configure the formation mechanism of HAAs in the water source from one of the largest water treatment facilities in Thailand. HPIN was found to be the most abundant (approx. 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 were observed to be carboxylic acids, aromatic

characteristics, amide, amino acids, and ketone. This finding is important for the operation and a future management of the treatment facility in Bangkhen WTP.

**Table 5-1** Functional groups reactive to DBPs formation in various sources of water

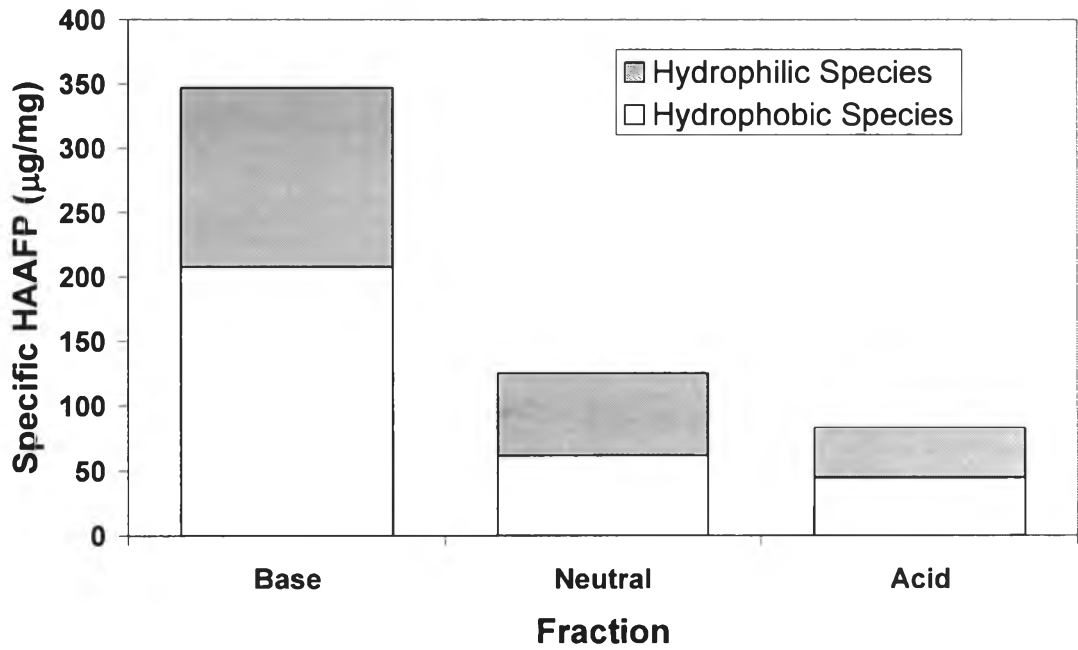
Water source	Target functional group for DBPs	References
Dilute aqueous solution	Dihydroxyaromatic	Boyce and Hornig, 1983
Various treated industrial wastewaters	Organic nitrogen, Phenolic-OH	Galapate <i>et al.</i> , 1999
Minaga reservoir water	Phenolic-OH	Galapate <i>et al.</i> , 2001
Diluted humic acid solution	Phenolic group and arboxyl group	Lin <i>et al.</i> , 2001
Reclaimed water in ground water, Los Angeles County, California	Phenol structures	Leenheer <i>et al.</i> , 2001
Surface water and Humic material solutions	Dihydroxyaromatic compounds(Resorcinol-type structures), $\beta$ -diketone, $\beta$ -ketoacids, and phenolic-OH	Gallard and Gunten, 2002
Santa Fe River, St. Marys River, Newnans Lake	Aromatic content and phenolic character	Wu <i>et al.</i> , 2000
South Platte River	$\beta$ -hydroxyacids and $\beta$ -ketones	Croue <i>et al.</i> , 2000

**Table 5-2** Characteristics of water source and its organic fractions

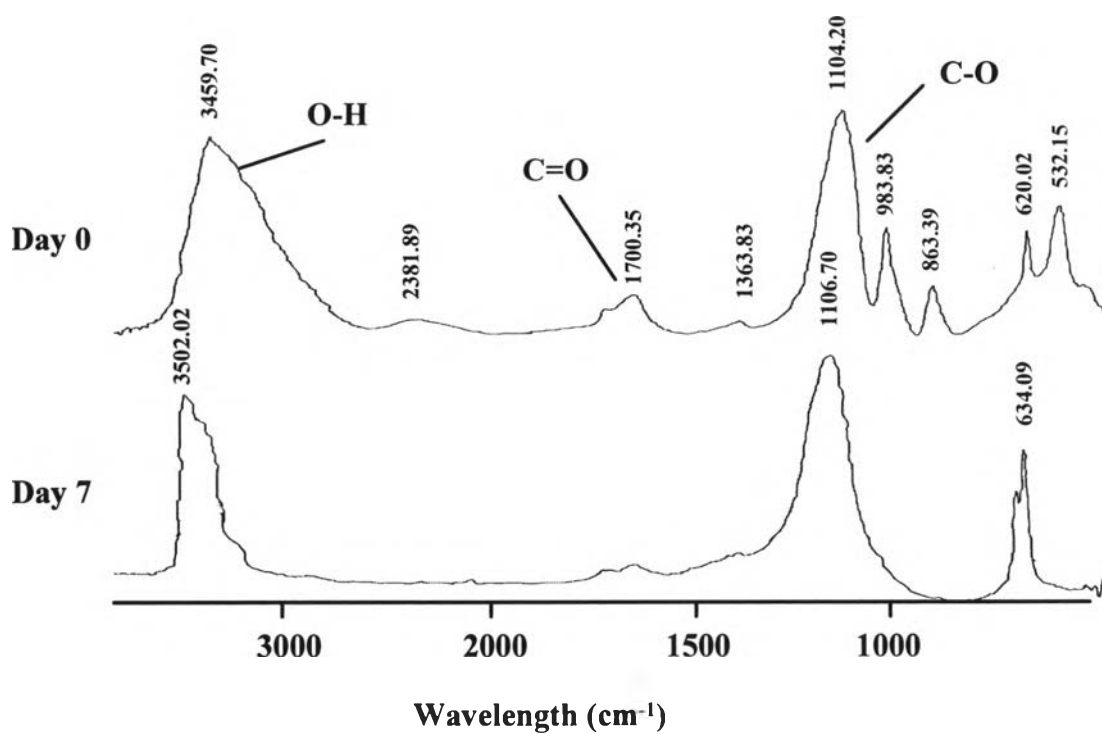
	DOC (mg/l)	SUVA (l/mg-m)	Total HAAFP ( $\mu$ g/mg)	Specific HAAFP ( $\mu$ g/mg)
Raw water	4.72	2.373	61.07	61.07
HPOA	1.63	1.667	15.21	44.31
HPOB	0.13	2.308	5.72	207.69
HPON	0.27	2.593	3.52	61.48
HPIA	0.84	0.714	6.78	38.11
HPIB	0.16	2.500	4.72	139.31
HPIN	2.12	1.038	28.50	63.45

**Table 5-3** Possible target functional groups for the formation of HAAs

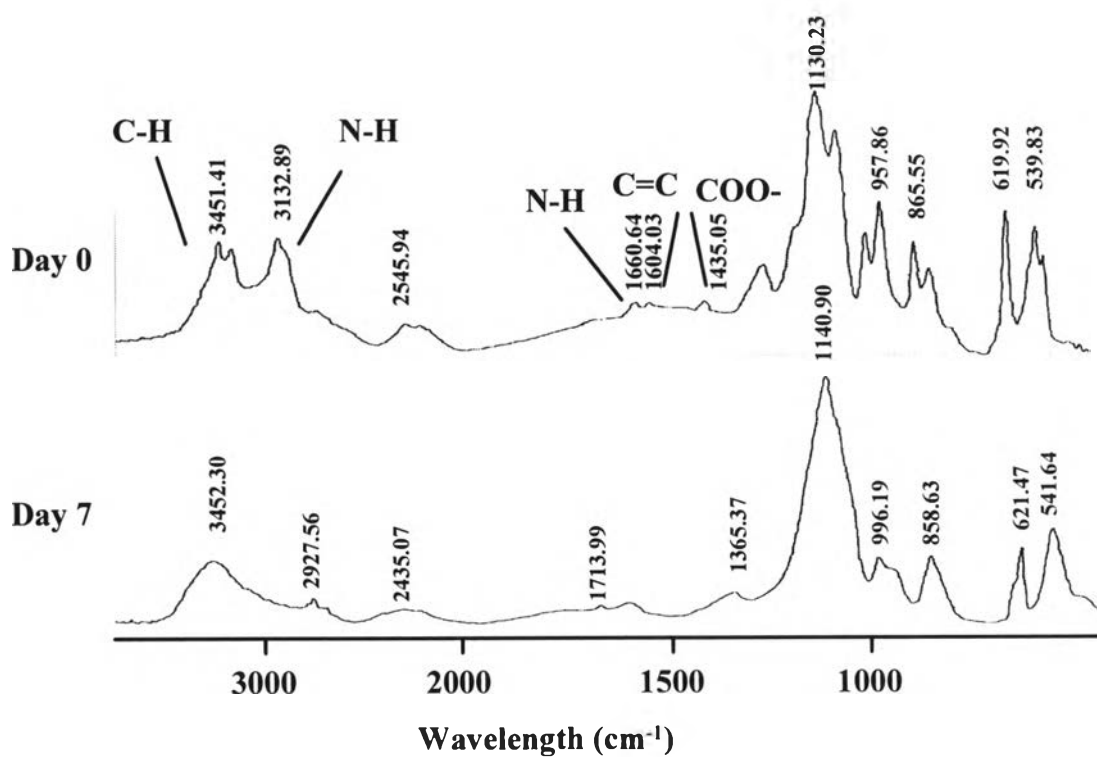
Fraction	Possible functional groups presented in the sample	Target functional groups for HAAs
HPOA	Carboxylic acids of five to nine carbon, Phenol	Carboxylic acids
HPOB	Aromatic characteristic, Primary amide, Amino acids	Amide, Amino acids
HPON	Alcohol, Ketone	Ketone
HPIA	Low molecular weight carboxylic acids	Carboxylic acids
HPIB	Primary aliphatic amines, Pyridines	-
HPIN	Alcohol, Amide, Kctone less than five carbons	Amide, Ketone



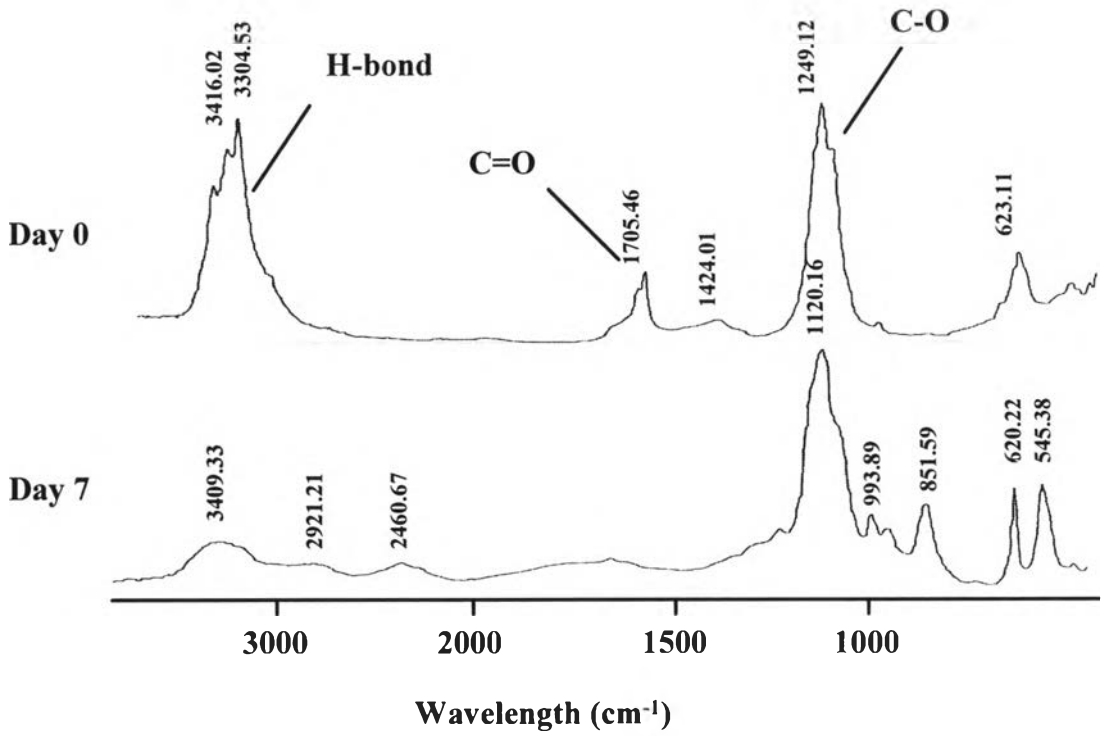
**Figure 5-1** Specific HAAFP of hydrophobic and hydrophilic species



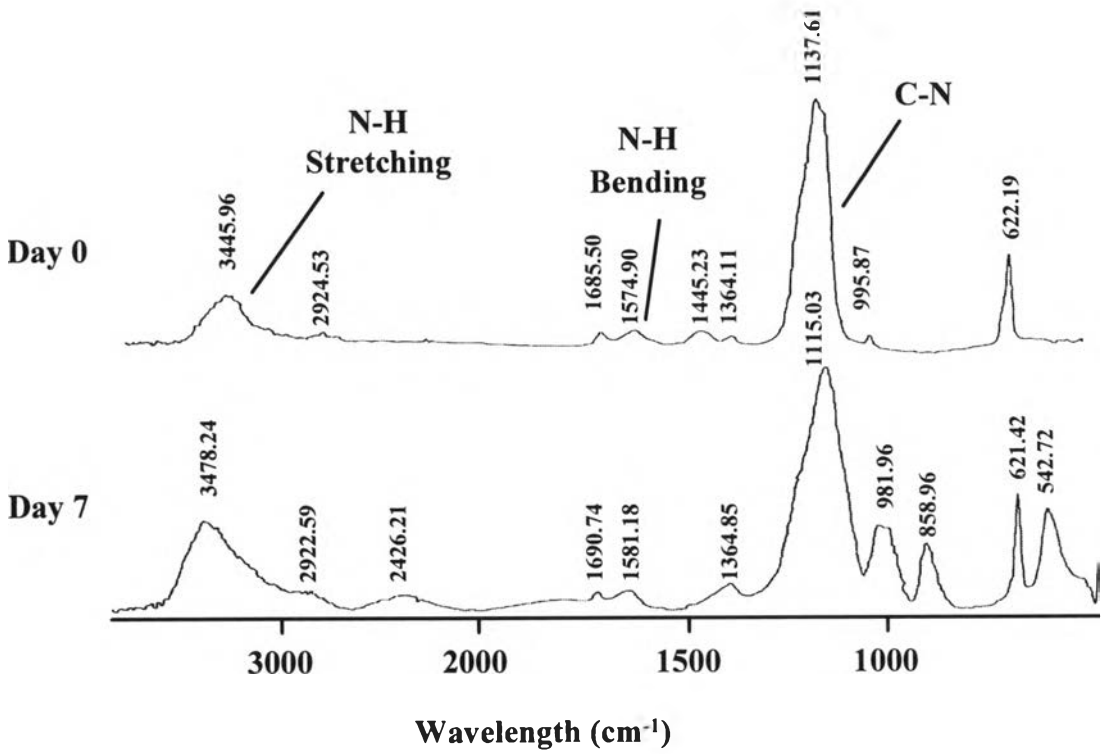
a. Hydrophobic neutral



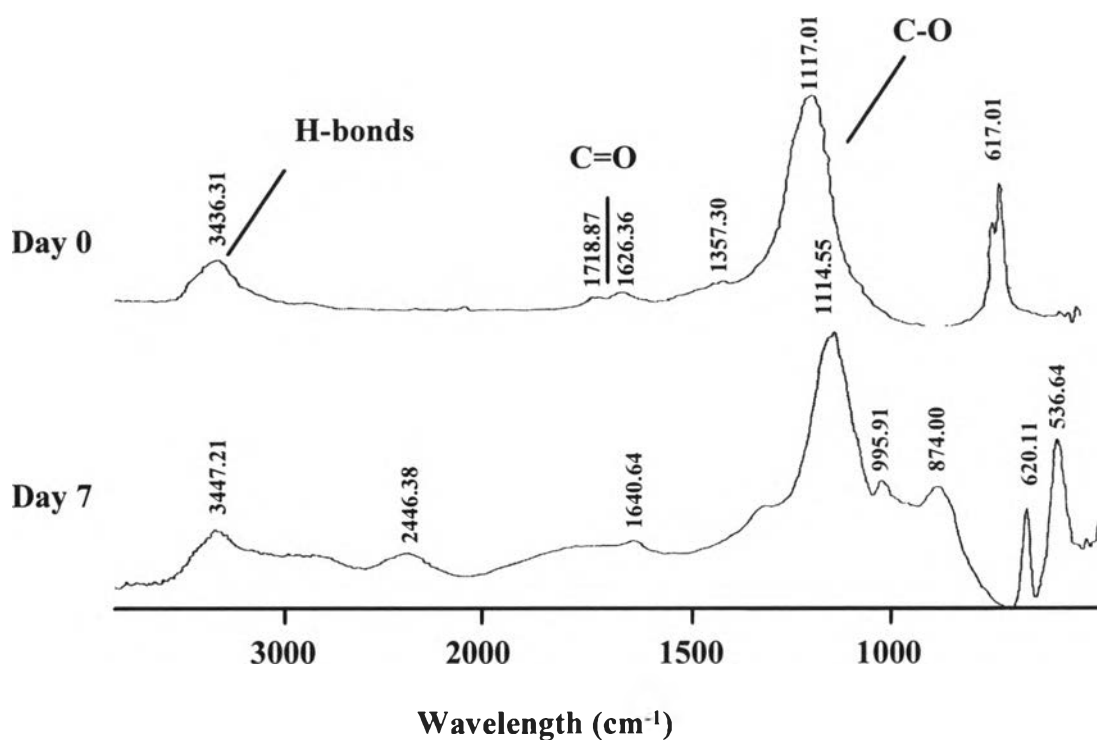
b. Hydrophobic base



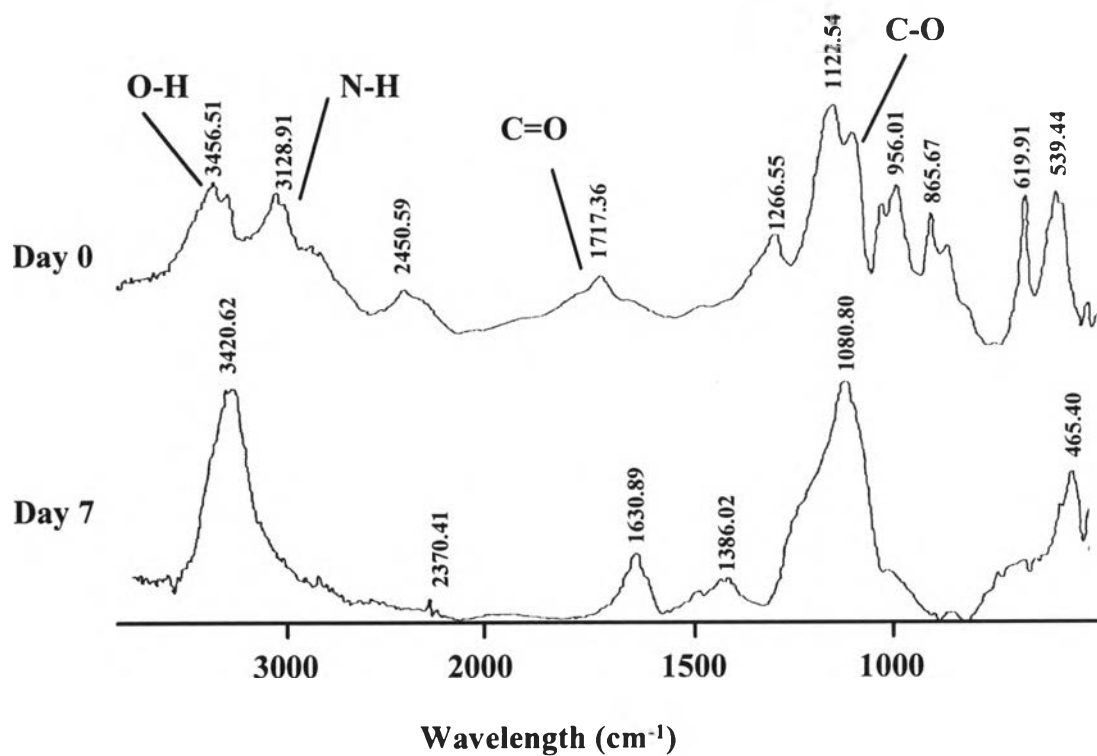
c. Hydrophobic acid



d. Hydrophilic base



e. Hydrophilic acid



f. Hydrophilic neutral

Figure 5-2 FTIR spectra between Day 0 and Day 7 of DOC fractions