Measurement of Organic Halogens in Boiler Feedwater





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Measurement of organic halogens in boiler feedwater

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Abstract

Materials of steam water cycles can suffer from corrosion induced by halide anions in feedwater. Organic halogen compounds in feedwater can be degraded and release halide anions under high temperature and pressure. Therefore it is necessary to be able to measure the organic halogen concentration.

Existing measurements including Adsorbable Organic Halogens and Gas Chromatography are either not convenient, affordable, accurate or reproducible enough at these very low concentrations, meaning a new method should be developed. In this research the option of destroying the organic compounds to release the halide anions and measure them with ion chromatography was studied. The question is, which is the best way to destroy the organic compounds and release the halides anions.

Six organic halogen model compounds were tested: aliphatic and aromatic fluorine, chlorine and bromine containing compounds. Two main methods were studied: UV/vacuumUV (VUV) photolysis and wet chemical oxidation with $K_2S_2O_8$. There are three phases in the research:

1. Study different UV lamps and oxidants on the target compounds and find the optimal combinations.

2. Try different dosages of $K_2S_2O_8$ and find an optimum.

3. Test halide release of target compounds in power plant conditions.

In the experiments, three kinds of lamps were applied: VUV, low pressure (LP) lamp and medium pressure (MP) lamp. H_2O_2 and TiO_2 were used as a catalyst. Last but not least, wet chemical oxidation was tested, with varying dosages of $K_2S_2O_8$. The experiments were executed with both single compounds and mixed compounds.

The results show that the organic fluorine is the hardest to degrade while organic bromine is the easiest. Aromatic compounds are easier to degrade than aliphatic compounds. This happens not only in AOP process, but also in power plant conditions. The recovery of bromide and chloride in most methods could reach 95% while aliphatic fluorine could only reach at most 70%.

It can be concluded that MP/H_2O_2 is the most effective method for degradation of organic halogen compounds since it requires less time for the reaction to be completed, but wet chemical oxidation also showed high recoveries for all halide anions. The advantage of wet chemical oxidation is simple equipment and universality. The method with the lowest degradation rate and recovery is UV/TiO_2.

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Glossary

AOP	Advanced oxidation process
IC	Ion chromatography
TOX	Total organic halogens
AOX	Adsorbable organic halogens
LP	Low pressure
MP	medium pressure
UV	Ultraviolet
VUV	Vacuum ultraviolet
BFW	Boiler feed water
THM	Trihalomethane
SCC	Stress corrosion cracking
TCA	Trichloroethane
TCE	Trichloroethylene
DON	Dissolved organic carbon
DOC	Dissolved organic nitrogen
TCP	Trichlorophenol

1. Introduction

1.1 Halogen related damage in steam-water cycles

Boilers, used for producing steam, are applied for power generation in fossil fuel and nuclear power plants. The corrosion of boiler and turbines is a serious problem that can threaten power supply and human lives. Pit corrosion and stress corrosion cracking (SCC), especially caused by chloride, are important causes of boiler and turbine deterioration, so demineralized boiler feedwater has to meet stringent water quality demand. Oxygen, low pH and anions in BFW can lead to the corrosion. Corrosion from halide ions including fluoride (F^-), chloride (Cl^-) and bromide (Br^-) is a threat to the boilers in working conditions. The initiation corrosion is an electrochemical reaction:

Anodic reaction: $Fe \rightarrow Fe^{2+} + 2e^-$

Cathodic reaction: $0.5O_2 + H_2O + 2e^- \rightarrow 2OH^-$

As a result the anodic area gains positive charges and attract chloride to the corroding area. When the iron precipitates, the corroding area will become more acidic as follows:

$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$

The formula shows that the existences of chloride cause the corrosion of boilers and turbines. The electrochemical attraction of chloride into the corroding area, lowers local pH. This will lead to acceleration of further corrosion. Figure 1-1 shows how the ions react with iron visually.

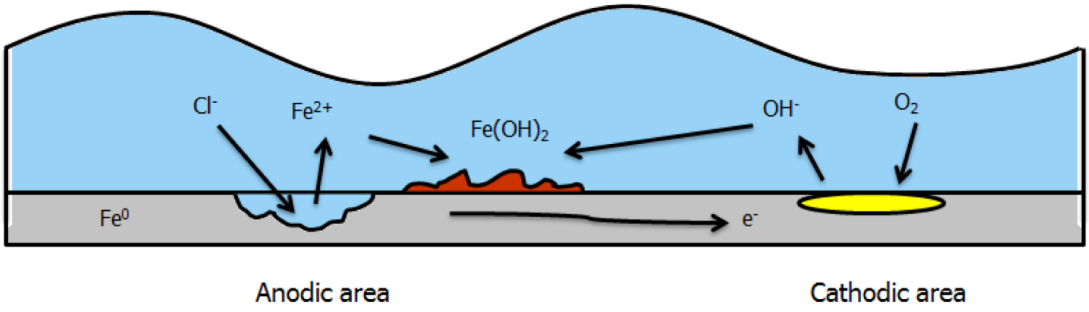

Figure 1-1 Schematic representation of corrosion mechanisms

The concentration of halide ions affects pit corrosion. From such a pit SSC can propagate. Rates of chloride induced SCC propagation can vary from 0.6 mm/year at temperature of 40 °C to >30 mm/year at 100 °C (Speidel, 1981; Turnbull et al., 2008). The higher temperature could also lower the limit concentration of chloride for SCC up to 1/4 of original from 20 °C to 100 °C (McIntyre et al., 1985).

Kari (2006) looked into a corrosion incident at a power plant and found traces of chloride in all the corroded parts. In a well-operated steam-water cycle, a magnetite layer can be developed on a clean metal surface. But the presence of chloride could hinder this process and break this layer. Some power plants state that the halogen concentration should be no more than 10 µg/l (Kari, 2006). The Electrical Power Research Institute (EPRI) sets a limit to 3 µg/l of chloride for feed water of Steam Generator Power Operation (K. Fruzzetti 2004). Halogens, however, could also enter the system through halide containing organic compounds. These compounds pass through ion exchange based demineralization and hydrothermally decompose in the boiler, introducing halogens unnoticed (Van Eeden et al.,

2012) and are expressed as Total Organic Halogen (TOX). Sources can be bacteria, industrial effluent and disinfection steps in water treatment. Two main processes can effectively remove halide ions: ion exchange and reverse osmosis. Ion exchange has the advantages of low cost and high efficiency. The problem is that it cannot remove the neutral organic charge compounds.

Lépine et al. (1994) tested the thermal degradation of 16 ppm of Natural Organic Matter (NOM) under the temperature of 260 °C and 300 °C for 7 days. The results showed that the concentrations of fluoride and chloride increase from below detection to 0.208 and 1.64 ppm respectively after thermal degradation. The concentration of TOC and various kinds of organic halogens decrease a lot. Lépine et al. (1992) tested the degradation of chloroform in make-up water. The result shows the thermal-stability of chloroform is weak. The reaction is as follows:

$$CHCl_3 + H_2O \rightarrow CO + 3HCl$$

The Chloroform decreases rapidly, with half-life of 6 s at 260 °C. It can be expected that other kinds of THMs can also be degraded in this condition and release halide ions.

Kari (2006) found that over-dosing of sodium hypochlorite during pre-treatment could lead to unpredictable rise of the chloride concentration in BFW. When the dosing pump was stopped, the chloride dropped to a normal concentration after several days.

Considering the importance of maintaining low halogen concentrations in boiler feedwater, a TOX measurement is recommended.

1.2 Existing organic halogen determinations

1.2.1 AOX

There is no direct method to measure the TOX in water, only by destroying the bond between the organic compounds and the halide anions. The most important one is AOX that measures the organic halogens that could be adsorbed by activated carbon.

According to Hua et al. (2006), a pyrolytic analyzer using pure O_2 and off-line IC combined with a standard TOX carbon (coconut-based) could measure the TOX. The recovery could achieve at least 95%, The AOX method could measure the organic halogen relatively accurately. But it also shows some disadvantages:

1. The process is too complex. A lot of instruments are applied in these processes. The instruments are expensive and the process is time consuming.

2. In low concentrations, the reproducibility and repeatability are not very high.

3. Some organic halogens are not strongly adsorbed by activated carbon. AOX can't present these kinds of compound.

Kristiana et al. (2009) has validated the AOX method from Hua et al. by using some other compounds that Hua didn't apply. The result shows that the recovery is acceptable but in a large range of 85% to 109%, which indicates that the method is not so accurate in actual application.

1.2.2 GC-ECD and GC-MS

GC-ECD and GC-MS are good methods to detect low boiling point organic halide compounds. In the Method 508 (Graves 1989), EPA confirmed that 38 kinds of chlorine pesticide could be analyzed by GC-ECD. Lefkovitz et al (2002) found that both GC-ECD and GC-MS are viable and high quality method to detect PCBs and chlorine pesticides.

For both of the methods, it requires certain determination of the compounds, and it's difficult to show the range of TOX.

1.2.3 Ion Chromatography (IC)

Another way to measure the TOX concentration in water is detecting the concentration of halogens before and after degradation of organic material. IC provides a low sample amount demanding, fast and accurate methodology in simultaneous determine of many kinds of anions including fluoride, chloride and bromide at the same time. Miskaki et al. (2007) tested these ions in a Metrohm IC for linearity, repeatability and reproducibility. The results could meet the requirement of measurement fully. The disadvantage of measuring TOX this way, is that it only works with low background concentrations of anions, which is the case when measuring TOX in boiler feedwater.

1.3 Goal of the search

1.3.1 Problem definition

In a steam-water cycle, it is necessary to use demineralized water as feed water in order to protect the boiler and tubes when generating steam at high temperature and pressure. The removal of halogens is paramount to preventing corrosion. As previously discussed, halogens can be present in organic compounds. Some cannot be removed by ion exchange, due to their neutral charge. Under power plant conditions, this TOX will be degraded by hydrothermolysis into halide ions, thereby possibly damaging the steam-water cycle. Whether organic halogens will be a problem can only be determined with an easy and accurate measurement to determine TOX in demineralized water.

1.3.2 Objectives

The main goal for this study is to find the optimal method to degrade organic halogens, prior to ion chromatography measurement. The parameters taken into consideration include recovery, kinetics and economic factors.

The objectives of the study are:

1. Try different UV lamps and different oxidants on the halogen compounds. Compare the recovery of each method.

2. Comparing different category both different elements and different molecule structure of organic halogen react in the same methods.

3. Test sample compounds degradation under power plant conditions to see the halogen release. The sample compounds thermal stability under boiler conditions are unknown. It should be known what is the behavior of the sample compounds under power plant conditions to make sure these compounds are significant for the research.

2. Possible methods to destroy TOX

Many methods to destroy organic compounds exist. This can be done chemically or physically. Advanced oxidation processes (AOPs) are used as technologies in both drinking water and wastewater treatment to remove all kinds of organic compounds. The performance of AOP could be affected by many parameters, such as compound categories, alkalinity, suspended solids, color and pH.

In principle mineralization happens after AOP. Organic compounds can react with hydroxyl radicals and can be degraded into carbon dioxide and inorganic ion. But in actual applications most compounds are transferred into different kinds of small molecules and further oxidation could be more difficult and expensive.

The following AOPs are mentioned in literature: UV with H_2O_2, UV with ozone, Vacuum-UV (VUV) photolysis, Fenton process and heterogeneous photo oxidation. These are briefly explained in the following sections.

2.1 Photolysis and photo catalysis

UV radiation is the electromagnetic radiation with wavelengths between 10 and 400 nm. Both the pollutants and the water irradiated by UVC (200-280 nm) with a catalyst can be oxidized. Now UVC is widely applied in disinfection process in drinking water treatment. The vacuum UV (VUV) region within the 100-200 nm ranges is also a field of interest of AOP. There are not so many surveys on the TOC removal with complex organic compounds, but a lot of researches focus on single compound destruction.

2.1.1 UV/H_2O_2 oxidation

It is well known that UV/H_2O_2 is widely applied in drinking water disinfection as it could break DNA and RNA of the bacteria. It is also used as an effective method to destroy organic compounds. In the case of 254 nm UV, hydroxyl radicals are produced from peroxide bond:

$$\mathrm{H_2O_2 + hv \rightarrow 2OH\cdot}$$

Hydroxyl radical is the most important and strongest oxidant in the oxidation process. It could react with TOX in water:

$$TOX + OH\cdot \rightarrow Cl^- + \mathrm{Organic\ by-product}$$

The product of these by-products could be potentially completely mineralized by hydroxyl:

$$\text{Organic compounds} + OH\cdot \rightarrow CO_2 + H_2O$$

Nienow et al. (2009) find that UV/H_2O_2 is a much faster method to remove 3-MCPD comparing to other hydrolysis and photolysis.

Chu et al. (2009) studied the conversion of 2,4-D. They found that the UV/ H_2O_2 process is more effective for removing 2,4-D than UV irradiation alone, at the same reaction conditions. By means of micro-aeration the efficiency can be further improved by increases the production rate of •OH radicals.

2.1.2 VUV photolysis

Photolysis in vacuum-ultraviolet (VUV) spectral range (10nm—200nm, especially 140-200nm) is not very often applied, due to the limited penetration depth of the VUV radiation. The hydroxyl radical can be produced by the 185 nm vacuum-UV according to:

$H_2O + hv(< 190\ nm) \rightarrow H\cdot + HO\cdot$

$H_2O + hv(< 190\ nm) \rightarrow H^+ + e^- + HO\cdot$

Then the hydroxyl radicals in turn react with organic compounds. The biggest advantage of VUV oxidation is that it does not need dosing of an oxidant or catalyst.

Immoberdorf et al. (2011) studied the 2,4-D degradation under 185 nm vacuum-UV in the flow-through reactor in batch and continuous mode. The result shows that the initial concentration of 2,4-D in ultrapure water doesn't affect the start degradation rate in the batch reactor, but the rate decreases over the period of reaction. The rate also reduced with the presence of alkalinity and natural surface water application. In continuous mode, 2,4-D conversion could reach 97% and 65% when inlet concentration was 1 and 10 mg/l respectively.

Han et al. (2004) studied the degradation of p-chlorobenzoic acid (p-CBA) under photolysis of VUV of 185 nm and UV of 254 nm, and photo catalysis by titanium dioxide under VUV and UV. The initial concentration affected the rate constant of VUV and VUV/TiO_2, but no effect for rate constant of UV and UV/TiO_2 was observed. The results also show that the reaction of VUV/TiO_2 is the combination of two independent reactions: VUV photolysis and UV/TiO_2 photo catalysis.

2.1.3 Heterogeneous photo catalysis

Heterogeneous catalysis can be used to improve the efficiency of photolysis, but in water treatment it is not often used. From the point of view of water treatment application, immobilized particles have the advantages of easy operation and energy saving, but a reduced rate of reaction due to mass transfer effects is shown in applications. It is proven that TiO_2 could largely increase the reaction rate of oxidation.

When the electrode in the valence band (V.B.) absorbs the irradiation of wavelength shorter than 415 nm (3.0 eV), it will transit to conduct band (C.B.). There will be a photo-generated hole in the valence band, which can produce hydroxyl radicals or oxidize organic compounds. The schematic figure is shown in Figure 2-1.

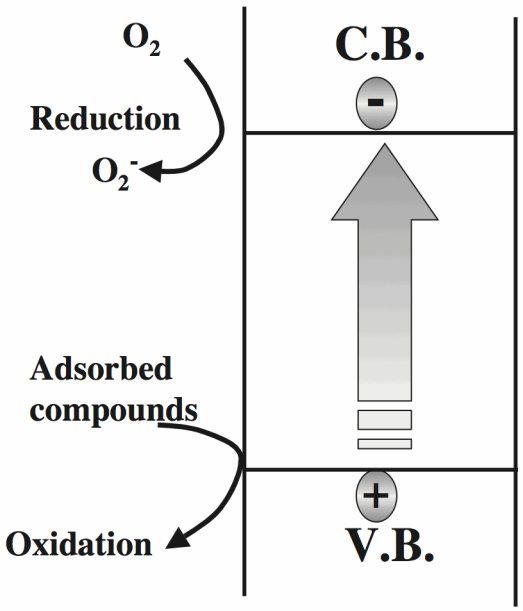

Figure 2-1 Schematic diagram of energy band for TiO_2 (Hashimoto et al. 2005)

The whole reaction can be summarized as:

$$e^- + O_2 \rightarrow {O_2}^-$$

$${O_2}^-(ad) + H^+ \rightarrow HO_2 \cdot (ad)$$

$$h^+ + H_2O \rightarrow OH \cdot (ad) + H^+$$

$$h^+ + {O_2}^-(ad) \rightarrow 2O \cdot (ad)$$

Coleman et al. (2007) studied the effect of TiO_2 on the 1,4-dioxane removal. They found that TiO_2 photo catalysis with both UV and solar light is effective in decomposition of 1,4-dioxane, and is much more efficient than the H_2O_2/UV process and UV alone. A TiO_2 slurry reactor system is used in the experiment.

2.2 Wet oxidation process

Persulfate salts (such as $K_2S_2O_8$) are also a potential oxidant as an alternative of H_2O_2 since it's very stable under the normal temperature and very soluble in water. The byproduct of persulfate reduction is sulfate, which is harmless.

In reactions, sulfate radicals are generated by photolysis or heating of persulfate ions:

$${S_2O_8}^{2-} \xrightarrow{\Delta \, or \, UV} 2{SO_4}^{2-} \cdot$$

The sulfate radicals can also react with water to generate hydroxyl radicals (Hayon et al. 1972)

$${SO_4}^- \cdot + H_2O \rightarrow H^+ + {SO_4}^{2-} + OH \cdot$$

This reaction is relatively slow ($k<60\ M^{-1}s^{-1}$), but in the basic solution, another reaction takes place to accelerate the formation of hydroxyl:

$${SO_4}^- + OH^- \rightarrow {SO_4}^{2-} + OH \cdot$$

Kolthoff and Miller (1951), Goulden and Anthony (1978), and Peyton et al. (1988) studied the kinetic of persulfate thermolysis. An Arrhenius plot of the experimentally determined rate constants is shown in Figure 2-2. From the figure, k value at temperature of 100 °C is 0.001 s^{-1}. The half-life of persulfate ion can be calculated as 11.6 min.

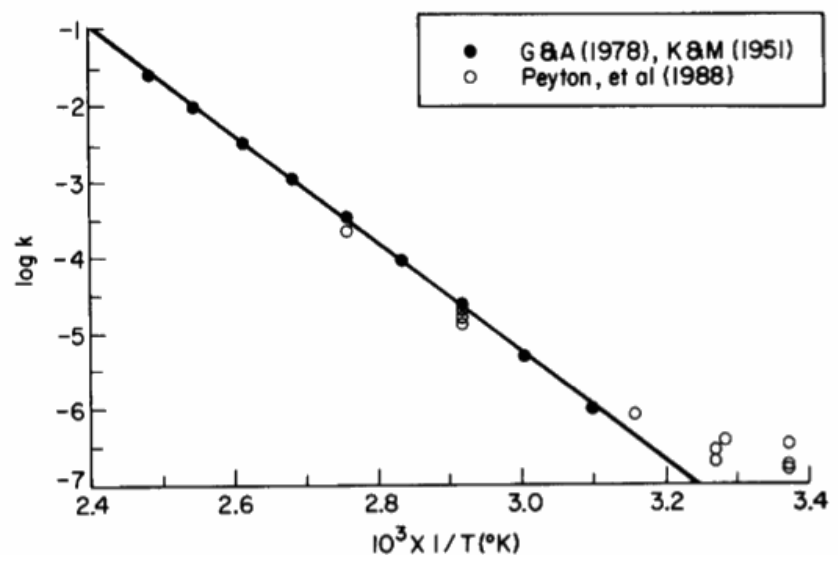

Figure 2-2 Arrhetius plot of rate constant for persulfate thermolysis (Peyton, 1993)

Chen et al. (2003) found that under thermally activated persulfate oxidations, higher temperatures, oxidant/contaminant molar ratios, and longer reaction times are required to make TCE and TCA completely degrade.

Doyle et al. (2004) is studied the persulfate digestion with FIA. He found it accurate, fast and inexpensive in the lab with high DOC and DON recovery.

2.3 Ozone reactions

2.3.1 Ozone oxidation

In recent decades, replacing chlorine, ozone has played an increasingly important role in water treatment. The short lifespan in water (about 20 min) and safe by-product (oxygen) make it the better choice for disinfection. The ozone application in AOPs is being investigated for a long time.

The resonance structure of ozone shows that a negative charge exists on one of the terminal oxygen atoms. The charge offers the nucleophilic character of ozone molecules. Because of that ozone can react with compounds with nucleophilic positions. Literature shows that ozone reacts with C-C double bonds, aromatic rings and functional groups containing sulfur, phosphorous, nitrogen and oxygen atoms. It means that ozone reactions are extremely selective.

Figure 2-3 shows the reaction of decomposition and mechanism of decomposition for ozone in aqueous solutions.

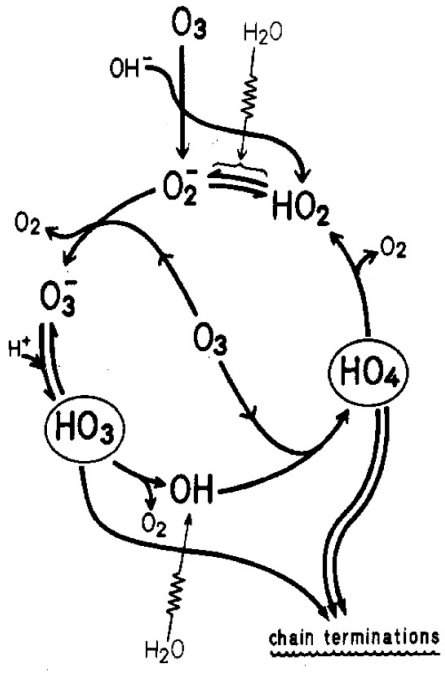

Figure 2-3 Reaction for ozone decomposition process (Staehelin et al., 1984)

From the figures, higher OH^- ion concentrations and a higher concentration or partial pressure of ozone could lead to higher initial rates of reaction and higher mass transfer efficiency. So pH, temperature and ozone concentration determine the decomposition of rate of ozone.

Graham et al. (2003) studied the reaction of 2,4,6-trichlorophenol (TCP) with ozone using a gas bubble/liquid contacting system. The degradation rate of TCP at pH 2 was 7.6 M^{-1}/s^{-1}, and increase to 77.2 M^{-1}/s^{-1} when pH reaches 7.5. At pH 7.5, the degradation of TCP is 90% after 10 minutes when 2 mol of chloride ion release per mol TCP. When hydrogen peroxide

appears in the solution, the degradation and rate aren't significantly affected but the release of chloride ions increase to 2.7 mol per mol TCP. The Low concentration of humid acid formed initially in the reaction could raise the degradation rate, but the high concentration has the opposite effect.

2.3.2 UV/O_3 photolysis

When ozone irradiated by UV light of which the wavelength is lower than 310 nm, then the ozone produces hydroxyl radicals. Additional steps also exist so that irradiation of the ozone reagent produces hydrogen peroxide. Then the photolysis of hydrogen peroxide forms hydroxyl radicals:

$$O_3 \xrightarrow{hv<310\,nm} O_2 + O(^1D)$$

$$O(^1D) + H_2O \rightarrow 2OH\cdot$$

$$O_3 + H_2O \xrightarrow{hv} H_2O_2 + O_2$$

$$H_2O_2 \xrightarrow{hv} 2OH\cdot$$

A cycle of organic compounds reacting with hydroxyl radicals is showed in schematically in figure 2-4:

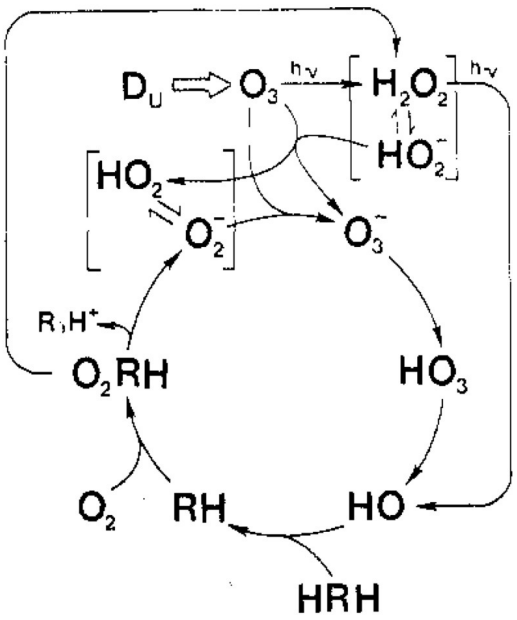

Figure 2-4 Ozone decomposition process by photolysis at 253.7 nm (Peyton and Glaze, 1988)

A lot of research was performed to discover the optimal conditions of organic matter UV/O_3 degradation. Chin and Berube (2005) studied the removal efficacy of DBPs by ozone, UV and UV/O_3. The result shows that the mineralization of organic carbon is very rapid in the batch reactor, as 50% of TOC removal in 60 minutes. It is much faster than ozone and UV treatment alone. The formation of THM and HAA, which is two important kinds of DBPs, can be reduced to approximately 30% and 20% under treatment of UV/O_3. It can be concluded that UV/O_3 process has the potential to treat the low TOC water in some situations only.

Mineralization of 4-chloro-3,5-dimethylphenol (PCMX) was studied by Song et al (2009). The optimal pH for the ozone oxidation is 4. The temperature of reaction is complex due to the effect on the chemical reaction activation energy and ozone solubility.

Ozone is an effective oxidant to destroy organic halides, but it is not stable under atmospheric conditions. The gas is also harmful to human health. Large-scale special set-ups are required to produce ozone and keep it unreleased to the environment. It is not so convenient and cheap as a laboratory method. So ozone-related method is not studied in this research.

2.4 Fenton process

The Fenton reagent, first invented by Henry J. Fenton in 1894 (Fenton 1894), is a combination of hydrogen peroxide (oxidant) and ionic iron (catalyst) solution. In the reagent, Fe (II) and Fe (III) react with hydrogen peroxide to produce hydroxyl radicals. The reaction is summarized as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\cdot$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\cdot + H^+$$

$$Fe^{2+} + HO_2\cdot + H^+ \rightarrow Fe^{3+} + H_2O_2$$

$$Fe^{3+} + HO_2\cdot \rightarrow Fe^{2+} + O_2H^+$$

$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2\uparrow$$

The formulas show that both ferric and ferrous iron could react with hydrogen peroxide in the chain simultaneously, so the initial dosing could be either ferric or ferrous. Ferrous iron could hydrolyze according to following reaction:

$$Fe^{2+} + 2H_2O \leftrightarrow FeOH^- + H_3O^+$$

$$Fe^{2+} + 4H_2O \leftrightarrow Fe(OH)_2 + 2H_3O^+$$

The ferrous iron appears in water in three forms: Fe^{2+}, $FeOH^-$ and $Fe(OH)_2$. Only Fe^{2+} can react with hydrogen peroxide. So the pH of the reaction system should be kept below 3. A higher pH value will accelerate the reaction above and reduce the reactions that produce hydroxyl radicals. When the pH rises above 5, the Fenton reaction produces other intermediates.

Some inorganic ions and organic compounds react with iron ions and hydrogen peroxide. Phosphate complexes with Fe (III) are insoluble in neutral aqueous solutions that stop Fe (III) from joining the Fenton reaction. Some other ions like chloride and bromide ion react with hydroxyl radical by the following route:

$$HO\cdot + X^- \leftrightarrow HOX\cdot^- \overset{H^+}{\leftrightarrow} X\cdot \overset{X^-}{\leftrightarrow} X_2^-\cdot$$

The reaction is fast if enough X^- and H^+ appear in the reagent. A high concentration of halide salts limits the Fenton reactions. $X_2^-\cdot$ can also react with organic compounds, but the rate is much slower than hydroxyl radicals.

The Fenton reaction requires dosing and always produces ferric and ferrous ion in the sample. Change of pH will significantly change their appearance in water. At higher pH, $Fe(OH)_2$ and $Fe(OH)_3$ and other iron contained complex are formed as precipitations. These make it hard to make the Fenton reaction happen and filters are needed to remove it from the solutions. Therefore the Fenton reaction is not studied in this research.

2.5 Conclusions from literature

To sum up the findings from literature, UV/H_2O_2, UV/TiO_2 and wet chemical oxidation have the advantage of a high reaction rate, simple experimental equipment and flexible reaction conditions. So these processes are selected for further studies in my search for a suitable means for degradation of organic halogens.

3. Materials and methods

As described in the objectives, the research consists of three parts: UV degradation, wet oxidation and heat degradation. The applied chemicals are introduced in 3.1. The experimental setup of these parts will be introduced in 3.2, 3.3 and 3.4 respectively. The analytical method is introduced in 3.5.

3.1 Dosing of chemicals

In the experiments, organic halogen compounds were studied. In order to cover as many kinds of organic halogens, 6 organic halogen compounds including aliphatic and aromatic compounds were selected. Each of these compounds contains only carbon, hydrogen, oxygen and only one kind of halogen atom. All selected compounds are listed below:

Addition	Category	Dosed chemical	Brand	Purity	Molar mass
Organic fluorine	Aliphatic compound	Sodium chloroacetate (SCA)	Sigma-Aldrich	97%	116.5
	Aromatic compound	2,4-Dichlorophenoxyacetic acid (2,4-D)	Sigma-Aldrich	98%	221.04
Organic chlorine	Aliphatic compound	4,4,4-trifluorobutyric acid (TFBA)	Sigma-Aldrich	97%	142.08
	Aromatic compound	4-fluorobenzoic acid (4-FBA)	Sigma-Aldrich	97%	140.11
Organic bromine	Aliphatic compound	3-bromopropionic acid (3-BPA)	Sigma-Aldrich	97%	152.97
	Aromatic compound	2-bromobenzoic acid (2-BBA)	Sigma-Aldrich	97%	201.02

Each organic halogen compound is dissolved in ultrapure water made by an Elga Purelab Ultra, to make sure no other halogen ions get into the solution. The solubility is increased by adding 0.1 mol/l NaOH solution. Before the experiment, the original solution was diluted into the required concentration (1 mg/l or 10 mg/l).

Two kinds of mixed compound solution are made for the experiments. One for the aliphatic and one for the aromatic compounds:

Aliphatic compounds	Aromatic compounds
Sodium chloroacetate	2,4-Dichlorophenoxyacetic acid
4,4,4-trifluorobutyric acid	4-fluorobenzoic acid
3-bromopropionic acid	2-bromobenzoic acid

3.2 UV degradation experiments

3.2.1 Experimental set-up

In the UV degradation experiments, a UV laboratory reactor system built by UV-Consulting Peschl has been used. A schematic of this reactor is shown in Figure 3-1.

The whole system includes a UV reactor, a magnetic stirrer, a power transformer and a cooling water pump. The reactor has a volume of 0.8 liter. Three kinds of UV lamps will be used in the reactor: dual wavelength (183 nm and 254 nm) lamp (ozone generating lamp), 254 nm low-pressure lamp (ozone free lamp) and medium pressure lamp (TQ 150). The UV lamp is protected by the cooling system that is powered by a cooling pump. This is very

important for a medium UV lamp especially, since it produces much more heat than low-pressure lamp and VUV lamp.

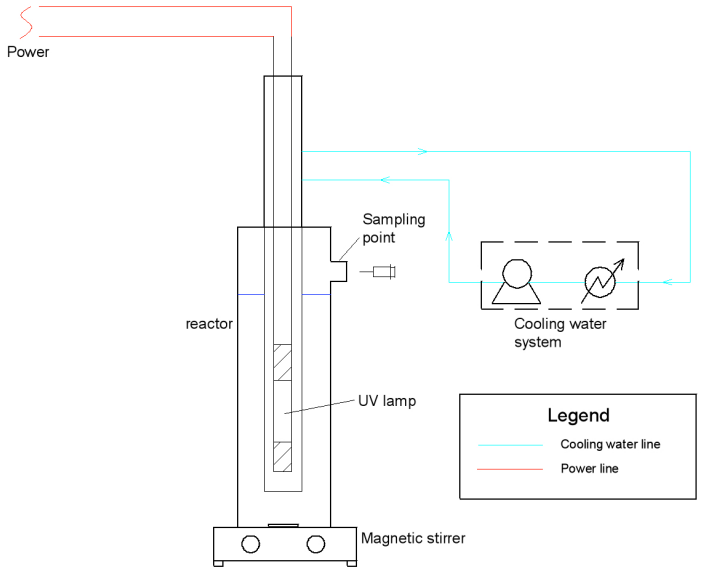

Figure 3-1 Schematic of reactor for UV degradation of organic halogen

3.2.1 Experimental procedure

The experiments were performed under room temperature and pressure. First, 0.8L of organic halogen solution was poured into the reactor. When using dual wavelength lamp, no catalysis was added. Application of the low-pressure lamp and medium pressure lam led to the necessary addition of catalysis (H_2O_2 or powdered TiO_2 as anastase (Sigma Aldrich), with concentrations 5 mg/l and 500 mg/l respectively). Before the start of each experiment, the magnetic stirrer and cooling pump were turned on. The samples were taken via a syringe connected to a tube. The TiO_2/UV samples was filtered through 0.45-µm filters. Each experiment was performed twice identically. The samples were detected by IC.

3.3 Wet oxidation experiments

3.3.1 Experimental set-up

A stirred temperature controlled set-up was applied in the wet oxidation experiment. The set-up is shown in figure 3-2.



Figure 3-2 Wet chemical oxidation experiment set-up

The system consists of a 2L glass vessel containing the reaction solution, an IKA C-MAG HS 7 hotplate stirrer supplying the necessary heat, and an IKA ETS-D5 electronic contact thermometer connected to the hotplate stirrer used for controlling the temperature of the solution.

3.3.2 Experimental procedure

The experiments were performed under atmospheric pressure. First, 1 L of organic halogen solution with certain amount of $K_2S_2O_8$ is introduced into the vessel. Then heating and stirring was started. The samples were taken with a 10 mL pipette when the temperature reached 40 °C, 60 °C, 80 °C, 90°C and 95 °C. When the temperature stayed around 95 °C, samples were taken every 5 minutes for half an hour. The samples were cooled immediately and detected by IC. Each experiment was performed twice identically.

3.4 Heat degradation experiments

3.4.1 Experimental set-up

To find the characteristic of the compounds under boiler condition, a flow reactor was applied to simulate the conditions of a boiler in a steam-water cycle in experimental fashion. A schematic drawing of the reactor is shown in figure 3-3.

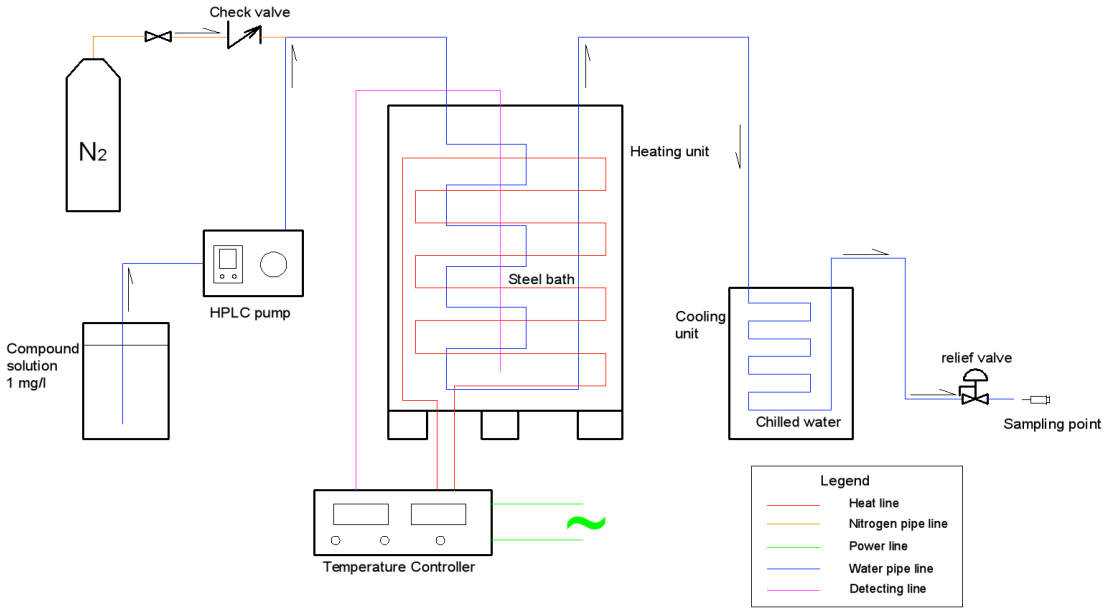

Figure 3-3 Schematic of the flow reactor applied for hydrothermal organic halogen degradation

The whole system consists of a 2 liter glass vessel containing the solution of interest, with an HPLC pump inlet with a filter, a nitrogen source that could offer pressure of 200 bar, an HPLC pump that provided pressure to send water into the system at an accurate flow rate from 0.01-10 ml/min, an SS316-L cylinder containing small (<1 mm) steel balls for heat transfer, a 4838 Parr temperature controller to ensure constant temperature, a cooling spiral with chilled water inside to cool the water immediately and an adjustable relief valve to maintain 175 bars of pressure. All the parts are connected with 1/8" stainless steel tubes. Volume of the tube inside the steel bath is 8 ml.

3.4.2 Experimental procedure

The chosen boiler temperature to be simulated was 352 °C, therefore the relief valve was set to 175 bar to prevent steam flashing in the system. The vessel was filled with 1 L organic halogen solution. To create a pH of 10, 1 ml of 1 mol/l NH_3 (Sigma Aldrich 99,9% trace metals basis) is added to the solution to protect the stainless steel tube under high temperature and pressure and to simulate boiler conditions. In the meanwhile, the steel bath was heated. Just before the experiment started, the solution was pumped through the

system, after which the tubing was purged with nitrogen. When temperature was stable again, the experiment started and a 4 mL sample was created at the desired contact time, after which the tubing was purged with nitrogen again. This was repeated for all dosed chemicals and contact times that were selected. The samples were detected by IC.

3.5 Analytical method

Analysis of halogen anions was performed on a Metrohm 881 ion chromatography with chemical suppression, eluent degassing and CO_2 stripping. It ran with a Metrohm A Supp 16 100/4.0 anion column operated at 67°C and the eluent used contained 2.5 mM Na_2CO_3 + 0.6 mM NaOH. The suppressor was regenerated with 50 mM H_2SO_4 and all ultrapure water used was purified by an Elga Purelab Ultra. The resulting analytical technique could measure halogens ions simultaneously within ±1 ppb accuracy. The calibration curve is made by multi-element ion chromatography standard solution containing 1g/l of bromide, chloride ion and fluoride ion offered by (Fulka, Sigma Aldrich).

The concentrations of halogen ions are compared with the theoretical value to calculate the recovery:

$$Recovery = \frac{Measure\ halogen\ concentration\ (mg/L)}{theoretical\ concentration\ from\ compound\ (mg/L)} * 100\%$$

A higher recovery means more halogen in the organic compound released as F^-, Cl^- and Br^-

4. Results and discussion

4.1 Results of UV degradation

The results for three different types of UV degradation experiments are shown and discussed in the next sections. The results of single compound experiment are listed in 4.1.1, results of mixed compounds experiments are shown in 4.1.2

4.1.1 Single compound experiments

Organic chlorine aromatic compounds experiments

Figure 4-1 shows the chlorine recovery when using the different lamps. When using the LP and MP lamp combined with H_2O_2 the reaction rate is faster than that of using just the VUV lamp. Applying an initial concentration of 1 mg/l, the MP lamp and LP lamp have almost the same reaction rate. VUV needs a much longer retention time to reach the same recovery.

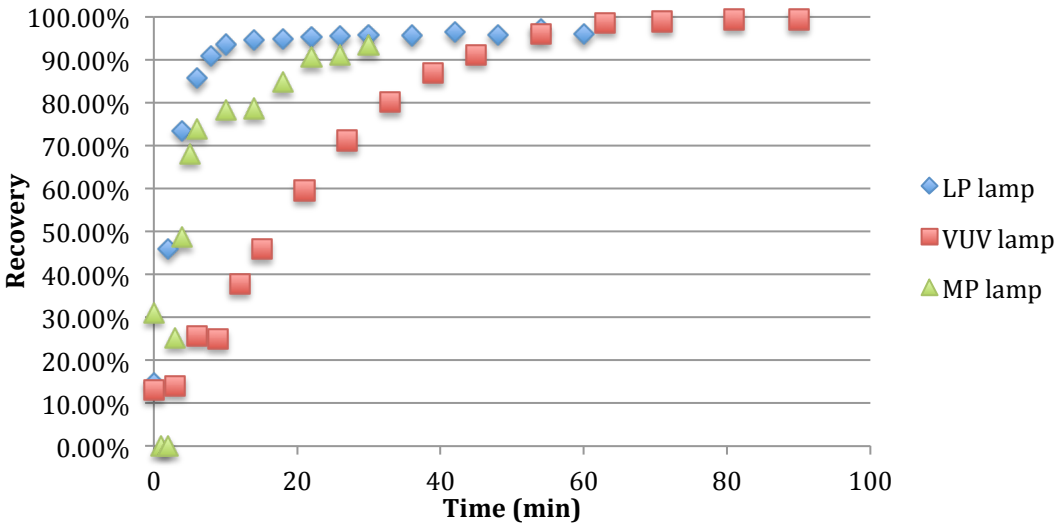

Figure 4-1 Chloride recovery of UV degradation of 2,4-D in H_2O_2/LP, H_2O_2/MP and VUV lamp.

Imoberdorf et al. (2011) tested 2,4-D degradation using a dual wavelength lamp. While the same initial concentration of 1 mg/l was applied, no 2,4-D could be detected after 2 minutes. This result indicates that VUV could be very effective for organic bound chlorine degradation. The results of this research however, showed a low efficiency of degradation. A possible reason is the structure of reactor. VUV has a low permeability in water (10mm), which means that it is better when no water exists between the VUV lamp and the reaction solution. It was necessary to ensure cooling though. This limitation affects the adsorption of VUV by the reaction solution. This problem also appears in other VUV experiments conducted in this research. The VUV lamp showed a relatively low ion recovery and reaction rate comparing to LP and MP lamps. UVB and UVC (the wavelengths LP and MP lamps emit) could penetrate through the water and the energy was adsorbed by the H_2O_2 in the reagent to produce enough hydroxyl radicals to support the degradation reactions. Therefore the lamps performed much better than the dual wavelength lamp.

On the other hand Imoberdorf et al. (2011) measured the remaining concentration of 2,4-D, not the chloride concentration. This could mean that although the 2,4-D was degraded, other chlorine containing halogens might have been created. Since the degradation of organic material is a process that needs several steps to come to complete mineralization, this is a possible explanation for the much higher efficiency found in that specific research.

Organic chlorine aliphatic compound experiments

Chloride recovery from SCA at an initial concentration of 1 mg/l was tested with all three lamps. Figure 4-2 presents the chlorine recovery in the experiment.

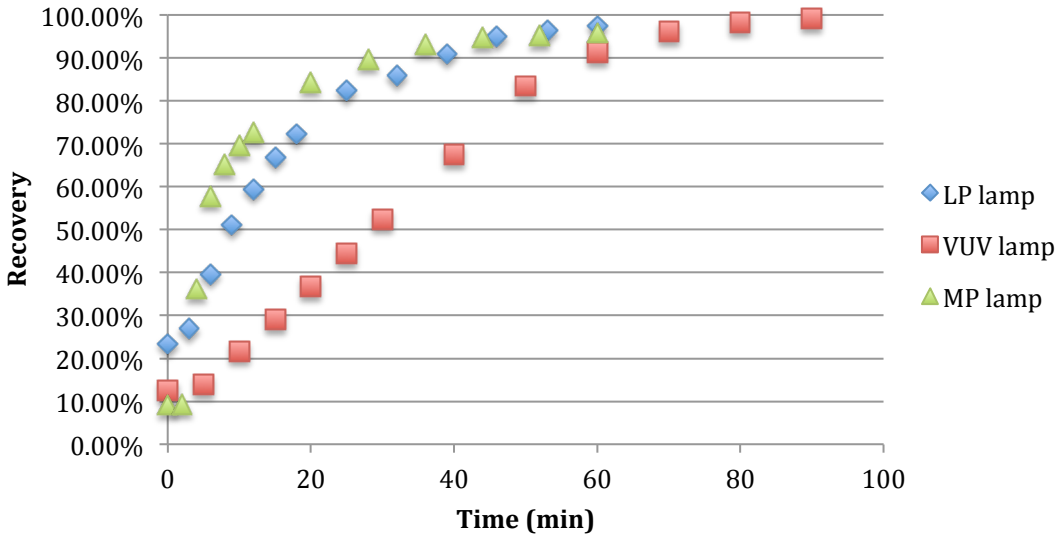

Figure 4-2 Chloride recovery of UV degradation of SCA in H_2O_2/LP, H_2O_2/MP and VUV lamp.

The graph shows that the reaction rate of the VUV lamp is again lower than with the MP and LP lamps. Compared to the reaction rate of aromatic compounds of 1 mg/l, it can be seen that all reaction rates are lower for the aliphatic compounds. In this case, the aromatic compound releases chlorine faster than the aliphatic compound when treated with UV.

Organic fluorine aromatic compound experiments

According to the results shown in Figure 4-3, the three kinds of lamps behave differently for the degradation of the applied aromatic fluorine compound. The MP lamp could degrade 4-FBA well and reached a recovery of 90% after 20 minutes. The LP lamp shows a much lower degradation rate, 60 minutes of reaction time leads to 80% of recovery. VUV lamp showed its poor degradation ability (in this specific set-up) as 30% recovery is reached in 1.5 hours. The reaction rate for the MP lamp is almost the same as with 2,4-D and CAA degradation, but the rates of the LP and VUV lamps are much lower. Since the same set-up was applied for every UV experiments, the results perfectly demonstrate the effects of different wavelength on the compounds.

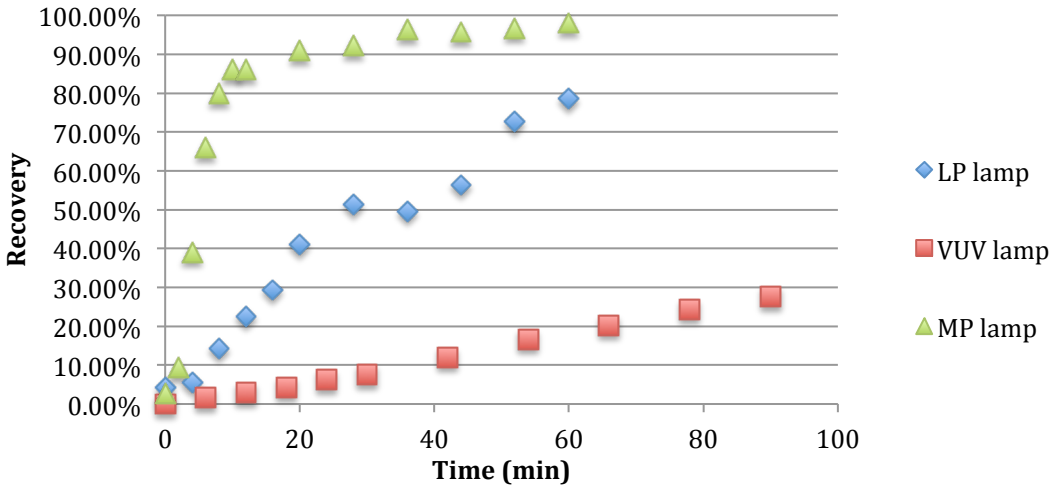

Figure 4-3 Fluoride recovery of UV degradation of FBA in H_2O_2/LP, H_2O_2/MP and VUV lamp.

Organic fluorine aliphatic compound experiments

The results of TFBA degradation shown in Figure 4-4 illustrate that the MP and VUV lamp could degrade TFBA, but at a very low rate and that the rate is almost the same. The recovery could reach at most 20% after 1 hour. The LP result is fluctuating up and down. A possible reason to explain this is that the produced fluoride could react with another by-product of the experiment. A trend for all the TFBA experiments is that the activity between hydroxyl radicals and fluorine in TFBA is very low. The bond energy of C-F is higher than the C-C bond, which shows that it is difficult to break C-F. The produced hydroxyl radicals may attack the C-C bond in the molecule first. That could explain the low reaction rate for all three lamps. Like with the organic chlorine compounds, the aromatic fluorine compound shows higher reaction rates for C-X bond breaking.

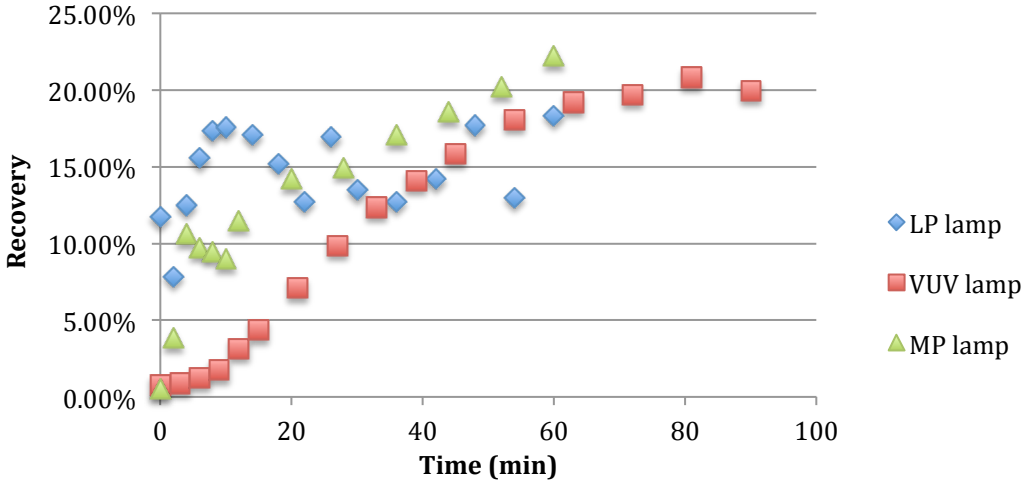

Figure 4-4 Fluoride recovery of UV degradation of TFBA with H_2O_2/LP, H_2O_2/MP and VUV lamp.

Organic bromine aromatic compound experiments

The 2-BBA results introduced in Figure 4-5 show a rapid reaction under MP UV conditions, for which all C-Br bonds broke within 10 minutes. The other two lamps showed an almost identical rate of degradation. The rates are all faster than that of 3-BPA (see next graph). It means that again aromatic compounds react faster than aliphatic compounds. Comparing to organic fluorine and chlorine, reaction rates of all lamps are higher, which shows that the C-Br bond is destroyed first during molecule destruction. This is coherent with the fact that the bond energy value for C-Br is lower than that of C-F, C-Cl and C-C.

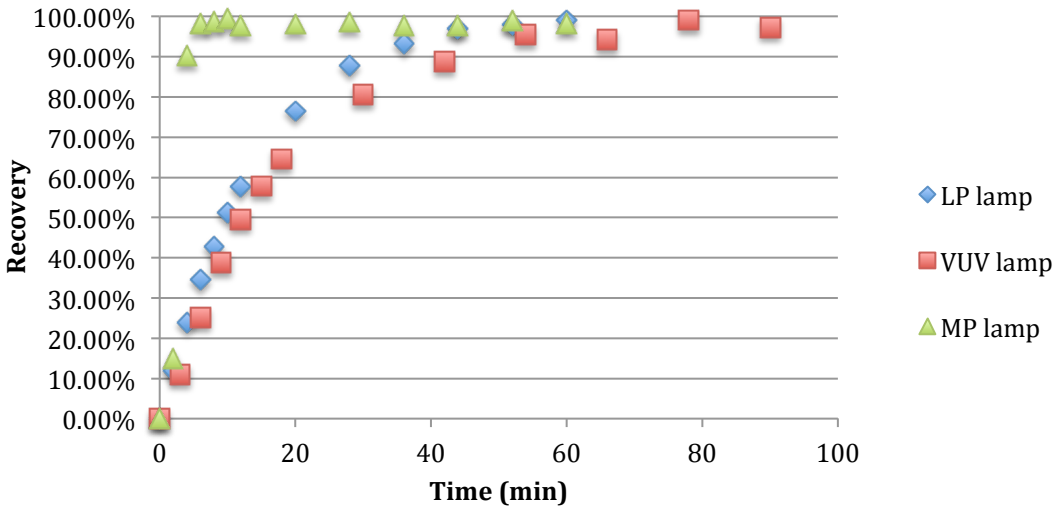

Figure 4-5 Bromide recovery of UV degradation of 2-BBA with H_2O_2/LP, H_2O_2/MP and VUV lamp.

Organic bromine aliphatic compound experiments

From Figure 4-6, an almost identically high reaction rate for both LP and MP lamps appears during 3-BPA degradation and 90% of recovery is reached after 20 minutes. Again the VUV lamp shows a much lower rate of degradation than the other two lamps. It spent 90 minutes to reach 70% of recovery. All lamps showed an approximately equal reaction rate to that of CAA, but much faster than that of TFBA.

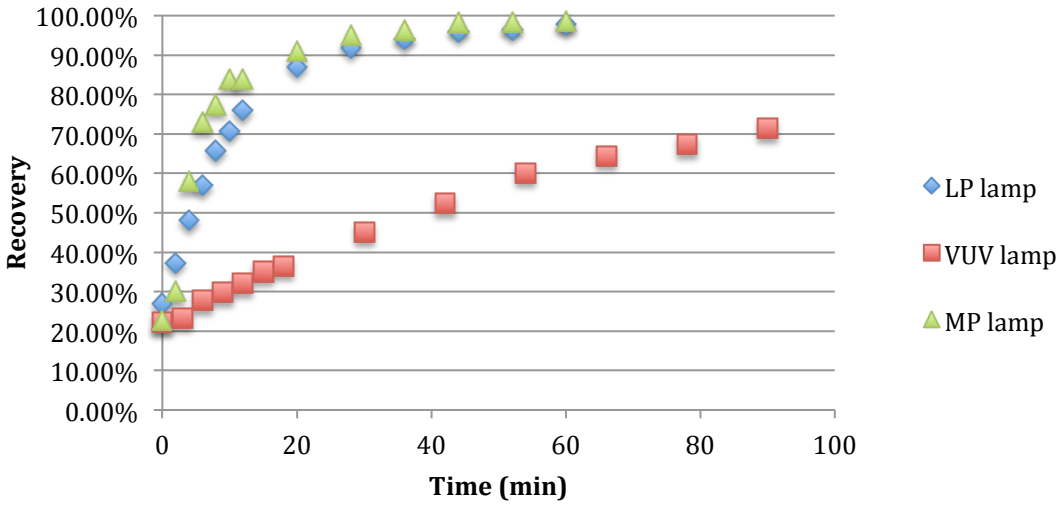

Figure 4-6 Bromide recovery of UV degradation of 3-BPA with H_2O_2/LP, H_2O_2/MP and VUV lamp.

From the single compound experiments, except for TFBA, all the compounds could degrade and release halide anions and reach high recoveries. For most compounds, MP/H_2O_2 is the fastest process. Limited by the structure of reactor, VUV is the slowest process. Organic bromine compounds are the easiest to degrade while organic fluorine is the hardest, which can be explained by the energy required to break the bond. Aliphatic compounds show less halide anion release than aromatic compounds during the same exposure time. The results meet the bond energy well that the standard bond energy of C-F (116 kCal/mol) is higher than C-Cl (81 kCal/mol) and C-Br (68 kCal/mol).

4.1.2 Mixed compound experiments

UV/H_2O_2 and VUV experiments

Figure 4-7, 4-8 and 4-9 show mixed aromatic compound degradation under LP, VUV and MP lamp irradiation respectively. In the LP lamp experiment, the recovery of fluoride, chloride and bromide could reach at least 80%. The degradation rate of organic fluorine is higher than in the single compound experiment. The rate of organic bromine is the same, while the degradation rate of organic chlorine is lower than in the single compound experiment. The VUV lamp showed a higher rate in all three ions than with the single experiment and all recoveries could reach 85% after 1 hour. The reason for this phenomenon remains unclear. The rates for the MP lamp experiment are almost the same as the rates of the three single compound experiments.

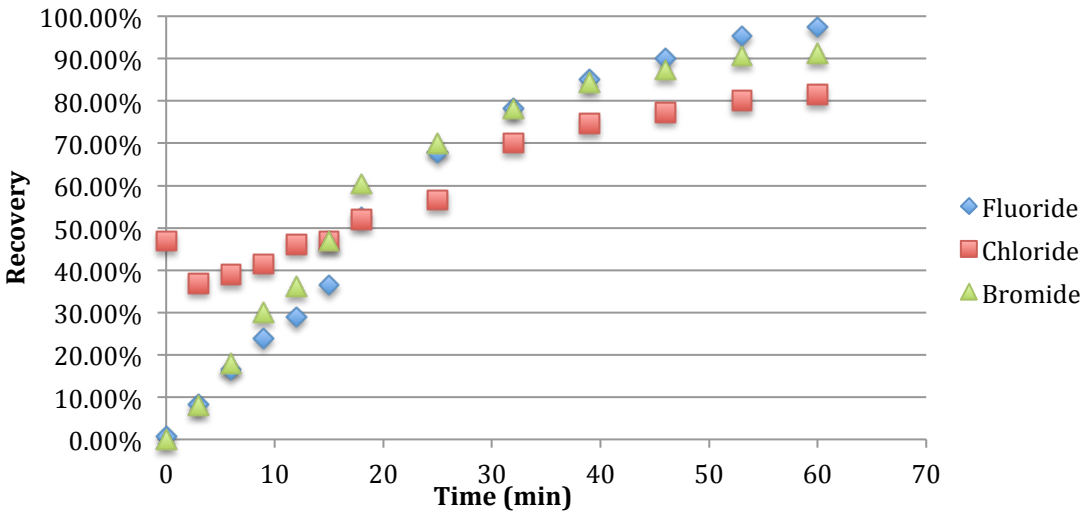

Figure 4-7 Ion recovery of UV degradation of mixed aromatic compounds with H_2O_2/LP.

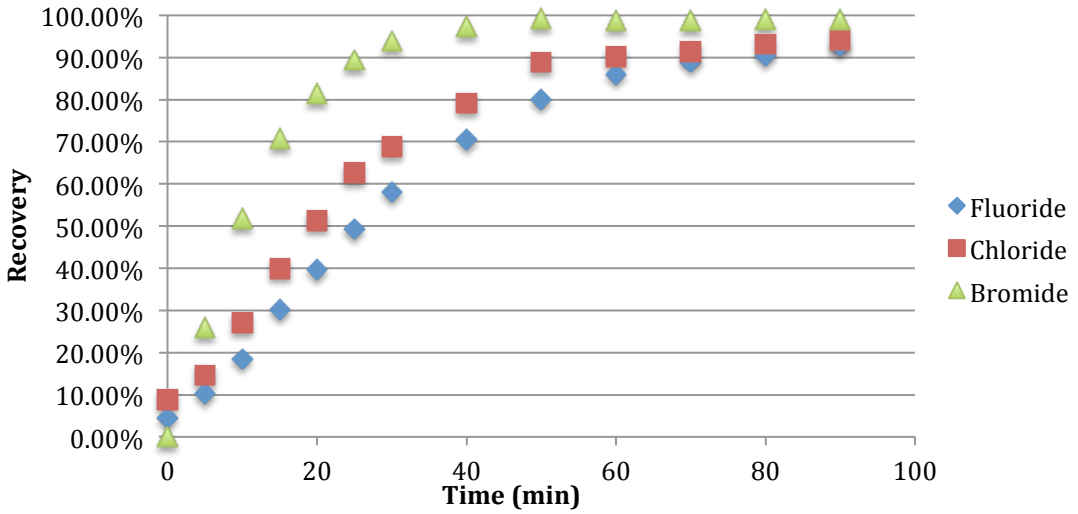

Figure 4-8 Ion recovery of UV degradation of mixed aromatic compounds with VUV lamp.

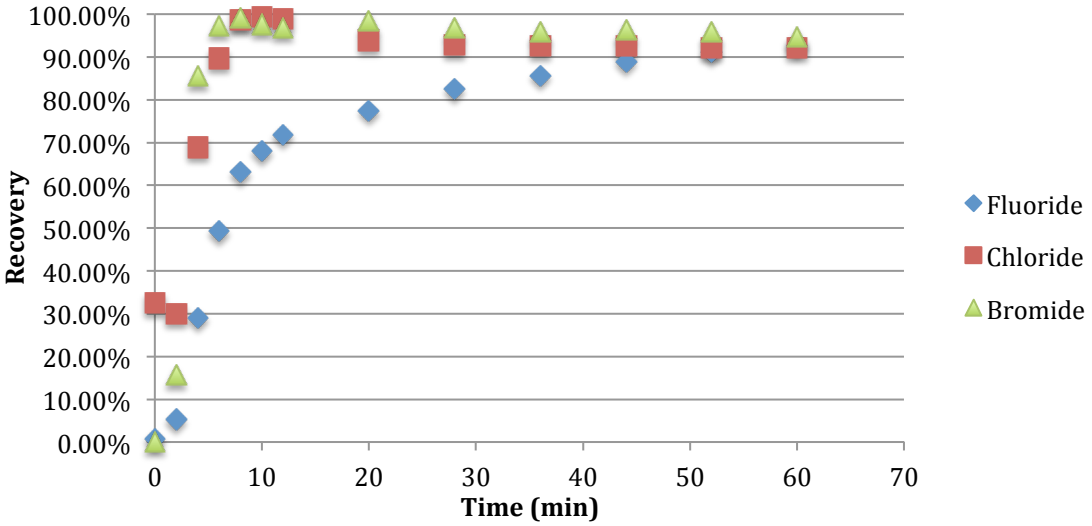

Figure 4-9 Ion recovery of UV degradation of mixed aromatic compounds with H_2O_2/MP.

Figure 4-10, 4-11 and 4-12 present the results of mixed aliphatic compounds degradation under VUV, LP and MP irradiation respectively. The VUV lamp results show a low degradation

efficiency compared to the single compound experiments for all three compounds. The bromide recovery reached 70% only, fluoride and chloride cannot reach 50% recovery after 90 minutes. During the reaction time, a similar reaction rate is observed for all the compounds. The energy into the water is limited so that it cannot make enough hydroxyl radicals to support the reactions.

Figure 4-11 shows the recovery for each ion under the LP lamp. Chloride and bromide could reach almost 100% after 1 hour. Fluoride is as low as 15%, as was seen in the single compound experiment.

From Figure 4-12 can be seen that the reaction rate of 3-PBA and SCA with MP treatment is higher than in the single compound experiment, 90% of recovery is reached in less than 20 minutes. But there is a significant difference in the fact that TFBA does not react in this experiment. The recovery is lower than 10% after 60 minutes. The results indicate that the competition of hydroxyl radical between these halogen groups based on the bond energy. C-Br, which has the lowest bond energy, reacts fastest than other function groups. C-F, which has higher bond energy than C-C, is more difficulty to react than C-Cl and C-C. It could also mean that the degradation products of the organic bromine and chlorine compounds, form new non-degradable molecule with the fluoride.

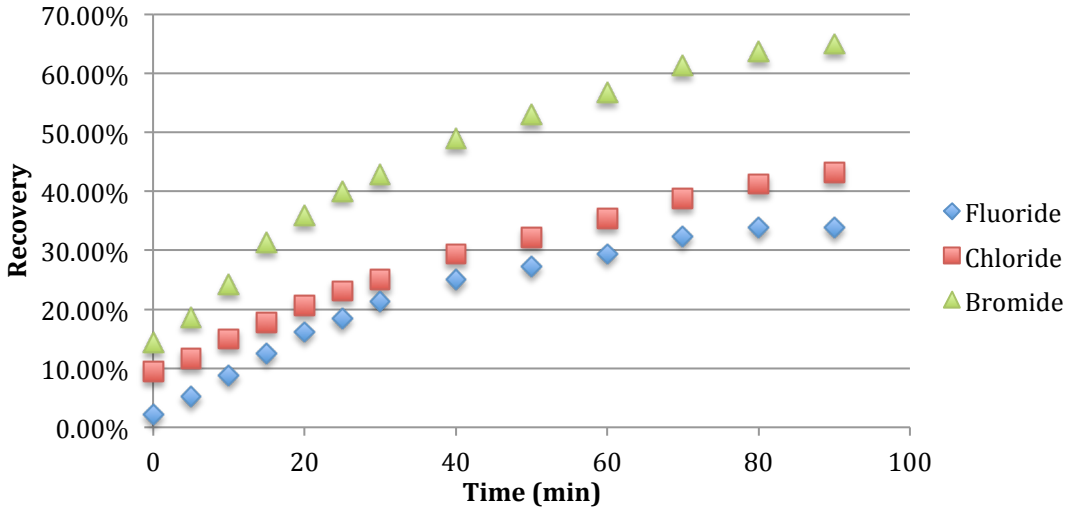

Figure 4-10 Ion recovery of UV degradation of mixed aliphatic compounds with VUV lamp.

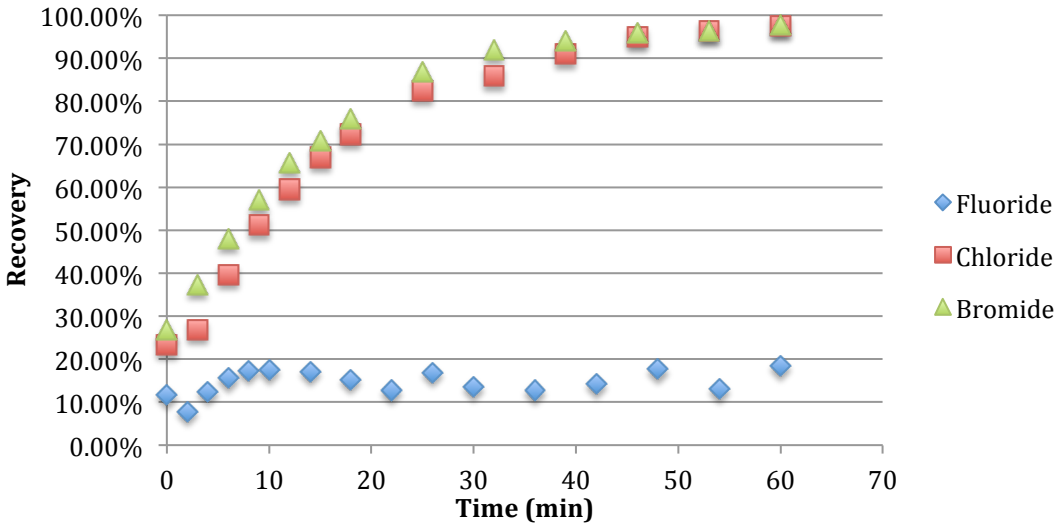

Figure 4-11 Ion recovery of UV degradation of mixed aliphatic compounds with H_2O_2/LP

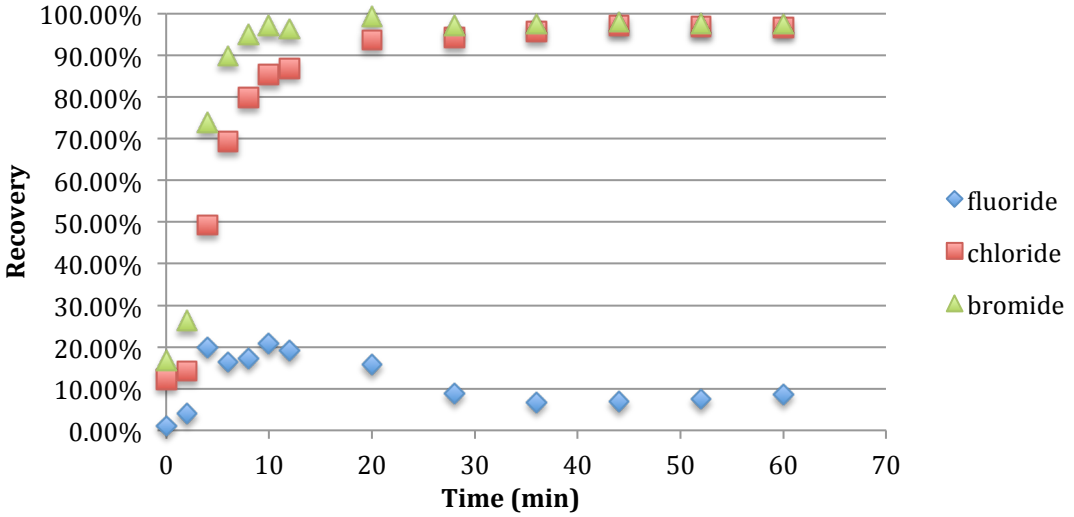

Figure 4-12 Ion recovery of UV degradation of mixed aliphatic compounds with H_2O_2/MP.

UV/TiO_2 experiments

UV with TiO_2 has also been applied in the mixed aromatic compound experiment, to see the effect of a different catalyst. Figure 4-13 and 4-14 illustrate the result of the MP and LP lamp respectively. From the two figures, a different trend can be observed compared to the result of VUV and UV/H_2O_2. Under influence of the MP lamp, the bromide recovery is very low and does not increase in time. Recovery of chloride and fluoride increases steadily, but both have an initial 25 and 8% recovery respectively, which is hard to explain. Under influence of the LP lamp, only fluoride increased a little while concentrations of chloride and bromide ion were fluctuating and no increase over the duration of the whole experiment was observed.

The result does not comply with previous observations that organic bromine can degrade more easily and reach a higher recovery. A possible reason for this is that when the electron in the valence band absorbs the light to transition in the conduction band to a photoelectron, the valence band will produce a positive hole. The hole can adsorb the organic pollutant and oxidize the pollutant molecules. Therefore the efficiency of removal is highly affected by the ability of the molecules to be adsorbed by TiO_2. As a positive hole should be more attractive to negative polar groups, degradation of organic fluorine is stronger than that of organic bromine. Another explanation is that the light penetration in water with the suspended TiO_2 is low, so the reaction area is only occurring round the lamp, which limits the degradation rate.

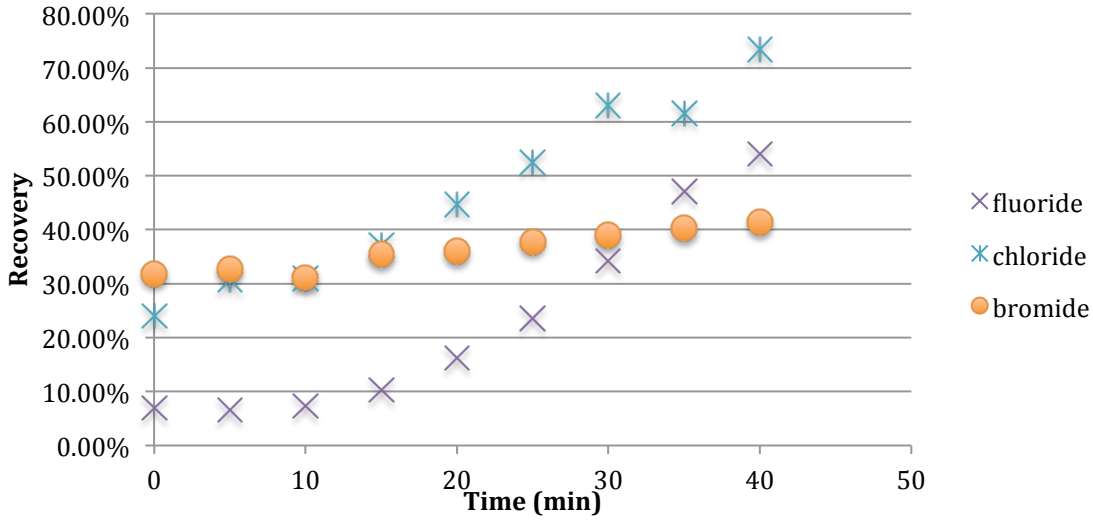

Figure 4-13 Ion recovery of UV degradation of mixed aromatic compounds with TiO_2/MP lamp

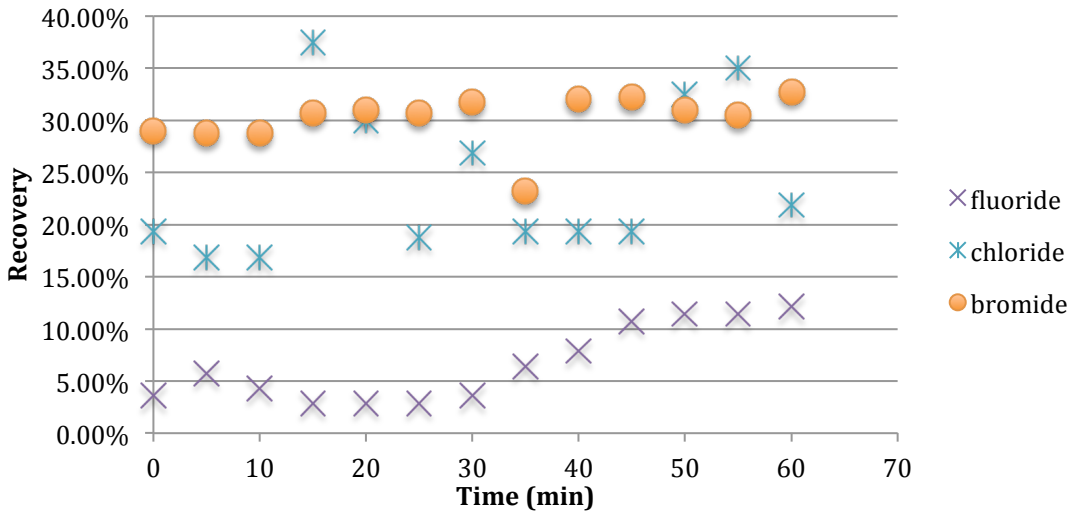

Figure 4-14 Ion recovery of UV degradation of mixed aromatic compounds with TiO_2/LP lamp

4.2 Results of wet chemical oxidation experiments

4.2.1 Mixed aromatic compounds experiments

The results for the mixed aromatic compound wet chemical oxidation experiments are illustrated in figure 4-15 and 4-16. Both the temperature and recoveries of all halogens are plotted in the figures. From the result of $K_2S_2O_8$ dosage of 20 mg/l in the figure 4-20, it can be seen that degradation starts at 20 minutes when the temperature reaches 80 °C. In the following 20 minutes, the rate of degradation for all organic halogens is the highest. At the end of the reaction time of about 60 minutes, the recovery of bromide reaches almost 100%, while the chloride and fluoride could reach a recovery of 87 and 80% respectively.

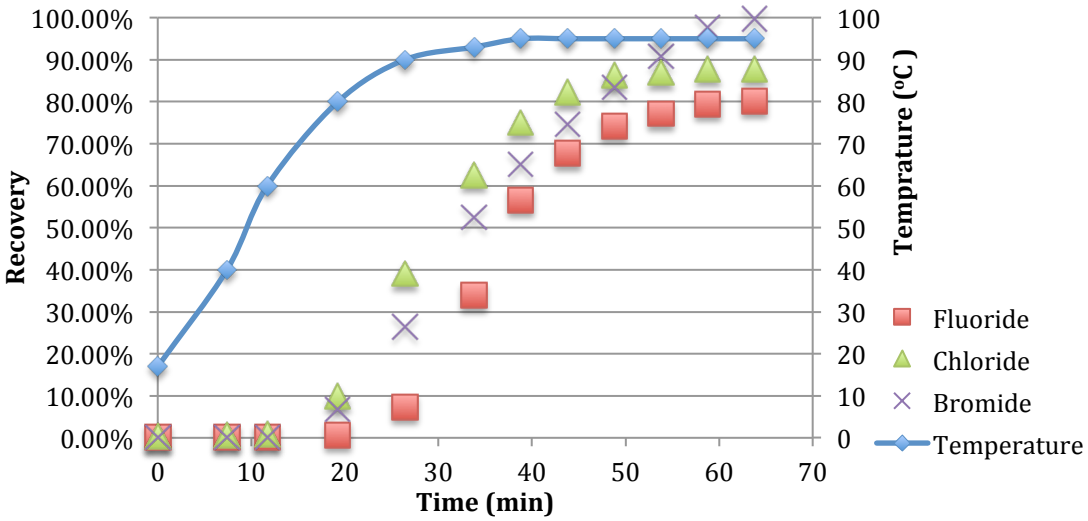

Figure 4-15 Ion recovery of mixed aromatic compounds under wet chemical oxidation. Initial concentration: 1 mg/l for all organic compounds, 20 mg/l of $K_2S_2O_8$.

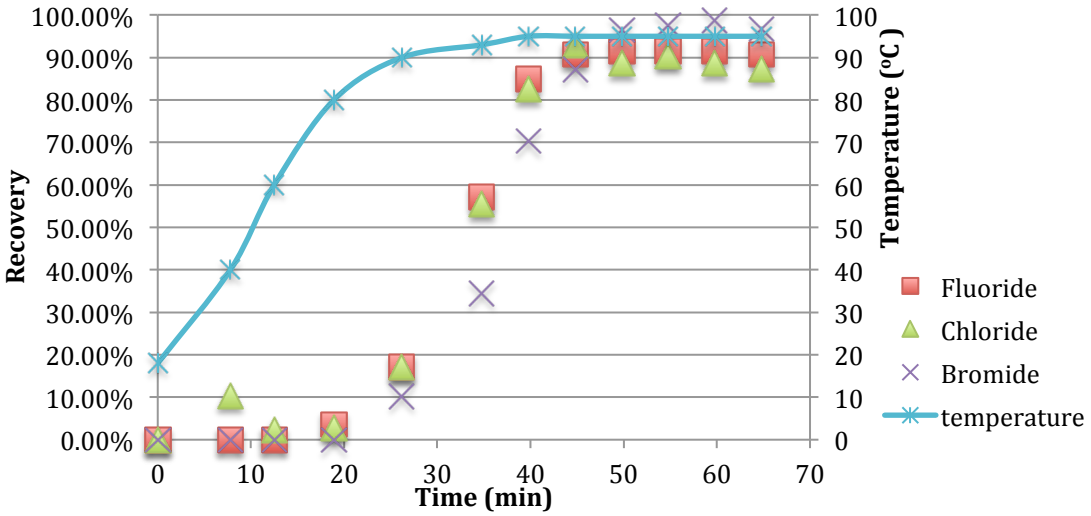

Figure 4-16 Ion recovery of mixed aromatic compounds under wet chemical oxidation. Initial concentration: 1 mg/l for all organic compounds, 40 mg/l of $K_2S_2O_8$.

Comparing figure 4-16 with figure 4-15, it can be seen that the dosage of $K_2S_2O_8$ affects the degradation. The degradation again starts at 20 minutes at a temperature of 80 °C, and already at 40 minutes, the reaction is pretty much over. The concentration of each ion does not change in the remaining 20 minutes. All the halogen recoveries are over 90%, so the 40 mg/l dosages showed a better effect than the dosage of 20 mg/l.

4.2.2 Mixed aliphatic compounds experiments

The results of the mixed aromatic compound wet chemical oxidation experiments are demonstrated in Figure 4-17 and 4-18. Aliphatic compounds showed again different ion recoveries compared to the aromatic compounds. In Figure 3-21, where the dosage of $K_2S_2O_8$ is 20 mg/l, the degradation still starts at a temperature of 80°C, after 22 minutes. Then the organic chlorine reacts fast and reaches 100% recovery at the end of the reaction at about 60 minutes. The bromide concentration peaks when temperature just reaches 95°C and stays stable for several minutes, before it drops to 30% recovery at the end of the reaction. The fluoride concentration rises at a constant rate after 20 minutes until the end of the reaction, the recovery reaches 60%.

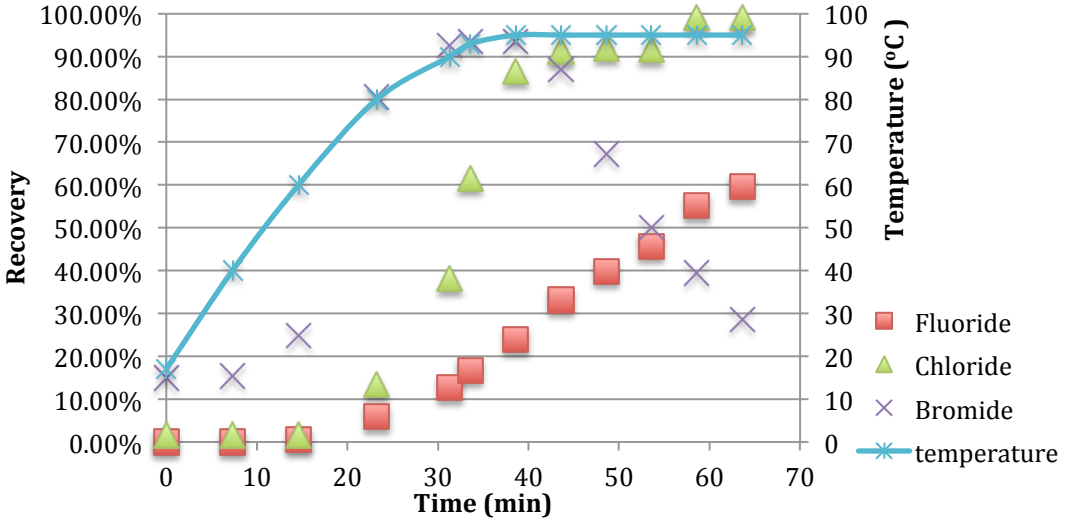

Figure 4-17 Ion recovery of mixed aliphatic compounds under wet chemical oxidation. Initial concentration: 1 mg/l for all organic compounds, 40 mg/l of $K_2S_2O_8$.

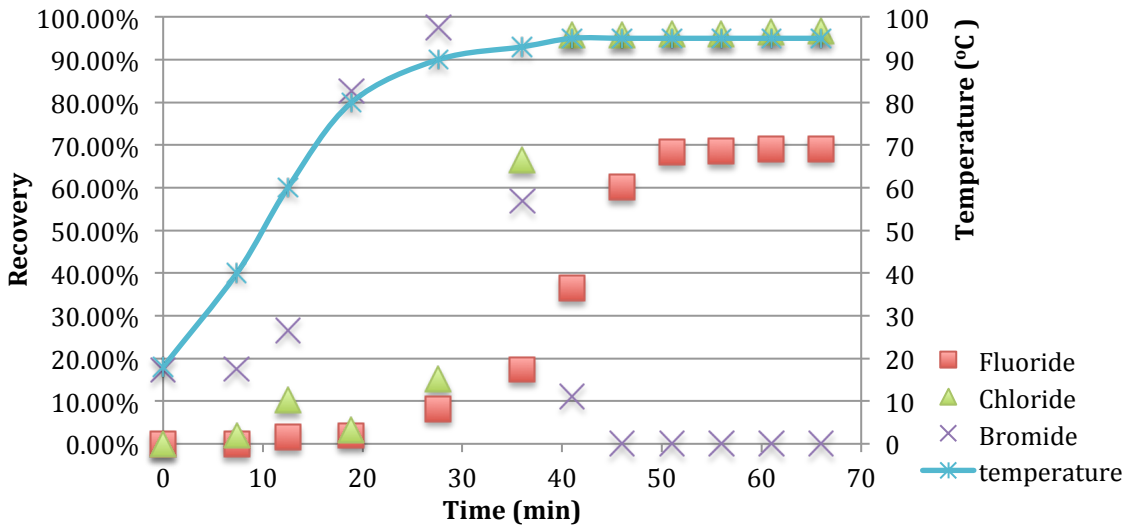

Figure 4-18 Ion recovery of mixed aliphatic compounds under wet chemical oxidation. Initial concentration: 1 mg/l for all organic compounds, 40 mg/l of $K_2S_2O_8$.

In Figure 3-22, the results for the 40 mg/l $K_2S_2O_8$ dosage show a higher degradation rate compared to the 20 mg/l dosage. Fluoride and chloride reach equilibrium after 50 minutes, the recoveries are 70% and 95% respectively. The organic bromine degrades when temperature reaches 60 °C and gets close to 100% recovery before the temperature reaches 95 °C. Then the measured concentration of bromide drops to 0 in 15 minutes and stays absent during the remaining duration of the experiment. This can be explained as follows:

The following reaction occurs during the experiment:

$S_2O_8{}^{2-} + 2e \rightarrow 2SO_4{}^{2-}$ E_0=2.01 V

Bromine also can accept electrons and be reduced to bromide:

$Br_2 + 2e \rightarrow 2Br^-$ E_0=1.06 V

Based on the oxidation potential value, persulfate has stronger oxidative capability than bromine. From these equations, it appears the solution in the experiment has the right conditions for bromide to be oxidized into bromine by persulfate. From the analytical method applied in this experiment, it is very difficult to trace the bromine. Also, with the temperature of the experiments bromine is boiled into air (Boiling point: 59 °C). The bromine is formed during the latter part of the reaction when bromide is disappearing.

4.2.3 Effects of pH

The bromide disappearance is happening in the aliphatic compound experiments, but not the in aromatic compound experiments. pH could be an important factor in the experiment. The IC measurements did not just show concentrations of halide anions, but also organic acid anions. During the experiment pH will decrease since more anions are formed cations and more hydrogen is ionized.

Figure 4-19 shows the results for aliphatic compound degradation at a different initial pH value. The initial pH value is this time higher than in the original experiment. The pH values are listed in table 4-1. It is clear that the aromatic compounds experiment has a smaller pH range than aliphatic compounds experiment have. It seems that aliphatic compounds degradation forms more organic acid anions to make pH lower.

Table 4-1 pH values before and after reactions under different conditions

	Aromatic compounds	Aliphatic compounds normal	Aliphatic compounds adjusted pH
Initial pH value	11	5.6	10.8
End pH value	8.8	3.2	4.2

Comparing figure 4-19 with figure 4-18, it can be seen that the degradation of organic fluorine is faster and gets a high recovery, so it can be concluded that high pH value could make more organic bound fluorine mineralize.. The bromide concentration reaches its peak and remains in ionic form for a longer time compared to the lower pH situation. At a high pH, the activity of the sulfate radical is high. When pH is below 7, $S_2O_8^{2-}$ uses its oxidative capabilities to oxidize bromide to (probably) bromine. In 44 minutes, all the halide anions reach their maximum level, but unfortunately the bromide concentration drops soon after.

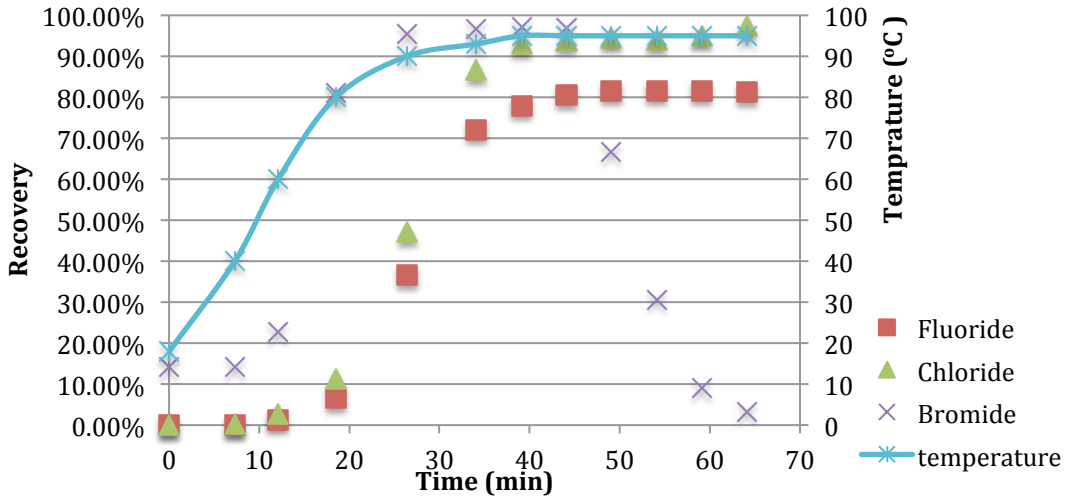

Figure 4-19 Ion recovery of mixed aliphatic compounds under wet chemical oxidation with initial solution pH=10.8. Initial concentration: 1 mg/l for all organic compounds, 40 mg/l of $K_2S_2O_8$.

The phenomenon that bromide forms then disappear happens not only in wet oxidation, but also in some UV experiment. It means that bromine ion can be oxidized to other forms easier than other halogen ions.

4.3 Heat degradation results

The aliphatic and aromatic compound mixed solutions were tested under the same conditions separately. The results are shown in Figure 4-20 and 4-21

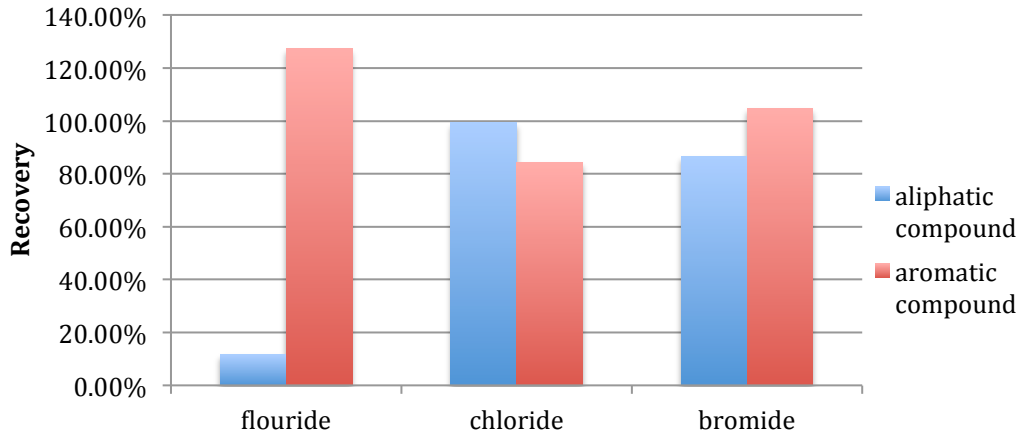

Figure 4-20 Ion recovery of mixed compounds after thermal degradation at 352°C, 175 bar at a retention time of 16 minutes

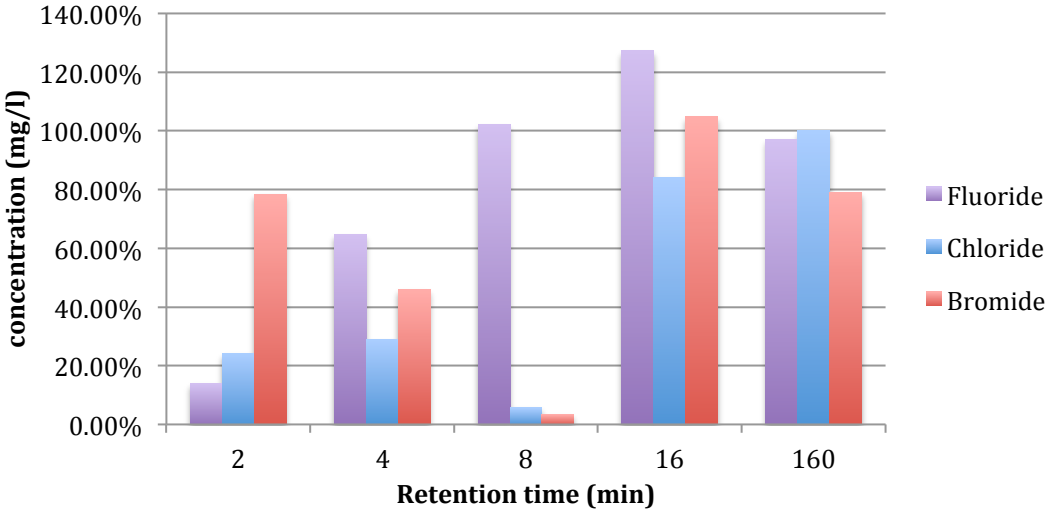

Figure 4-21 Ion recovery of mixed aromatic compounds after thermal degradation at 352°C, 175 bar at several retention times.

Figure 4-20 shows the halide anion recovery after degradation at a 16 minute retention time, which is a plausible water retention time in a boiler. There is no significant difference of organic chlorine and bromine degradation. Both aliphatic and aromatic have a very high degradation percentage. But the fluorine has much difference. The aromatic compound degrades much more than the aliphatic compound.

Figure 4-21 shows results of the thermal degradation of the aromatic compound solution. As expected, there is an increase of release percentage with increasing retention time.

The bond dissociation energies of halogen atoms combined with methyl and ethyl functional groups are higher than the bond dissociation energy of halogens atoms combined with phenyl. So the results of the experiment meet the theoretical background well.

From the figure above, it can be concluded that the tested compounds undergo sufficient thermal degradation to be a threat to a steam-water cycle. It means that measures should be taken to prevent these compounds from flowing into the boiler.

4.4 Comparison of applied methods

4.4.1 Reaction time and recovery

To compare the efficiency of the applied methods in degrading organic halogens prior to ion chromatography, two factors are taken into consideration: reaction time and recovery. Reaction time represents the required time for the reaction to reach equilibrium. Recoveries represent the extent of degradation. The results for all methods are summarized in Table 4-2 and 4-3.

Table 4-2 Effect of different methods on the degradation of organic aromatic halogens

Aromatic compounds	**Fluorine**		**Chlorine**		**Bromine**	
Methods	Reaction time (min)	Recovery	Reaction time (min)	Recovery	Reaction time (min)	Recovery
VUV	>90	93%	80	94%	50	99%
LP/H_2O_2	>60	97%	60	90%	60	92%
MP/H_2O_2	25	98%	10	99%	8	99%
TiO_2/UV	>60	55%	>60	75%	>60	45%
Wet oxidation	40	90%	40	92%	50	99%

Table 4-3 Effect of different methods on the degradation of organic aliphatic halogens

Aliphatic compounds	**Fluorine**		**Chlorine**		**Bromine**	
Methods	Reaction time (min)	Recovery	Reaction time (min)	Recovery	Reaction time (min)	Recovery
VUV	>90	34%	>90	44%	>90	65%
LP/H2O2	>60	18%	60	98%	60	98%
MP/H2O2	30	10%	20	99%	20	99%
TiO2/UV	-	-	-	-	-	-
Wet oxidation	45	70%	40	95%	30	99%

The tables show that the MP lamp has the highest recovery and lowest reaction time of all methods. But for the organic aliphatic fluorine, the recovery is not ideal. Wet chemical oxidation also showed a relatively short reaction time, but a fairly high recovery for all organic compounds. The VUV lamp is also effective for all compounds but it needs much more time than other methods. TiO_2/UV and the LP lamp show no advantages over the other possibilities, but it should be admitted that 100% anastase is probably not the most efficient type of TiO_2 catalyst.

4.4.2 Practical considerations

For the application of each method, reaction time and recovery are not the only parameters. There are also more practical factors that should be taken into consideration. These include: special equipment needed, oxidant dosage and safety measures.

For the VUV lamp no oxidant is needed. A special VUV lamp is necessary to supply VUV light. A special shield reactor is necessary for the reaction to prevent UV light leakage. The lamp is water cooled for which a thermostat is needed. Another possible setup would consist of a quartz glass tube around a VUV lamp, through which the sample is pumped. This could make VUV application much more effective and would eliminate the need for cooling. Magnetic stirring ensures a homogenized solution.

For the LP lamp setup the dosing of 5 mg/l of H_2O_2 is necessary. A special reactor and LP lamp are of course required. The system is water cooled and safety goggles to protect the eyes from the UV radiation is recommended. Magnetic stirring ensures a homogenized solution.

The MP lamp also requires 5 mg/l of H_2O_2 to be dosed. A special reactor and lamp are again required. As a lot of heat produced during the reaction by the lamp, a heat exchanger is required to protect the lamp. Magnetic stirring ensures a homogenized solution.

For TiO_2/UV each liter of water needs 0.5 g of TiO_2 powder. A special reactor and lamp are again required. A heat exchanger is required to protect the lamp. A 0.45 µm of filter is required to remove TiO_2 particals before IC detects the samples. Magnetic stirring ensures a homogenized solution.

Wet chemical oxidation needs 40 mg/l of $K_2S_2O_8$. Only heating equipment is required. Magnetic stirring ensures a homogenized solution.

This is summarized in Table 3-4

Table 3-4 Comparison of several methods on practical considerations

	Equipment	**Oxidant dosage**	**Safety measures**
VUV	Stirrer, VUV lamp, Shield reactor with cooling mechanism, or flow reactor	No	Protective eyewear
LP/H2O2	Stirrer, LP lamp, Shield reactor with cooling mechanism	5 mg/l H_2O_2	Protective eyewear
MP/H2O2	Stirrer, MP lamp, shield reactor with cooling mechanism	5 mg/l H_2O_2	Protective eyewear
TiO2/UV	Stirrer, UV lamp, shield reactor with cooling mechanism	0.5 g/l TiO_2	Protective eyewear
Wet chemical oxidation	Stirrer, heat supplier and control	40 mg/l $K_2S_2O_8$ (NaOH for pH adjustment)	No

The medium pressure lamp with H_2O_2 and wet chemical oxidation seem to be the best methods considering the high recoveries, but the simplicity of the latter setup could be a major advantage. Relatively inexpensive laboratory equipment is required. The heating consumes much more energy than the UV lamps, but considering that this is a laboratory method, it will probably not be an issue. With a few adjustments to ensure the low wavelengths will reach the sample (for example by letting the solution flow directly past the UV lamp), the VUV system might turn out to be a very good option.

5. Conclusions & Recommendations

5.1 Conclusions

The effect of VUV, LP/H_2O_2, MP/H_2O_2, UV/TiO_2 and wet chemical oxidation on the mineralization of 6 sample organic halide compounds has been tested. Although the compounds concentrations used in experiments are much higher than in the real situation, the possibility of degrading organic halogens with these methods has (to in varying degree) been confirmed. Summarizing the results, the best methods for removing organic halogens depends on the situation.

1. Under boiler condition (352 °C and 175 Bar), all the tested organic halogens can be degraded and release halide anions. Five out of six compounds showed 80-100% degradation at a contact time of 16 minutes. The reaction rate comparison is F<Cl<Br. There is a proportional relation between contact time and halide anion release.

2. In the relatively high-energy consuming methods like MP/H_2O_2 the reaction time of a single compound experiment is similar to that of mixed compound experiment. For low-energy consuming methods including LP/H_2O_2 and VUV, the result is different between single and mixed compounds. For single compounds, the recovery is lower and reaction time is longer. The rate comparison is F<Cl<Br.

3. The MP lamp with 5 mg/l of H_2O_2 was capable of degrading all the organic halogens except aliphatic organic fluorine. The recovery for most halogens could reach 90% in 30 minutes. In fact, aliphatic fluorine that has recovery of 10% in MP/H_2O_2 is also has about 10% of recovery in boiler conditions. It indicates that degradation-resistant compounds in UV show the same behavior in high temperature and pressure water. Combined with relatively low chemical consumption, it can be said that it is a good method for TOX destruction in demineralized water.

4. Wet chemical oxidation with 40 mg/l of $K_2S_2O_8$ at a temperature of 95 °C is capable of degrading to all kinds of organic halogens, although the observed disappearance of bromide can be considered an issue. This could easily be countered by raising the pH though. The recovery could reach at least 70% in one test compound and more than 90% in all the other for all the tested compounds. The produced sulfate ion has no effect on the IC measurement. It's universality and simplicity could mean it is in practice a more convenient and affordable technique. Still there is some degree of underestimation of TOX occurring.

5. VUV is also effective for all kinds of organic halogens, but the degradation is slower than most of the methods studied. Longer exposure times for the sample and more effective reactors could prove to be a solution to this issue. VUV has the major advantage of not needing any chemical additives, thereby minimizing the threat of sample pollution.

6. MP with 0.5 g/l of TiO_2 (100% anastase) was not effective at organic halogen degradation. It is worth mentioning though, that it was the only method that could degrade more organic fluorine than organic bromine. Perhaps with a better TiO_2 catalyst (80:20 anastase:rutile nano-powder) better results can be obtained.

7. LP/H_2O_2 shows similar behavior to MP/H_2O_2, but the reaction rate and recovery is lower than with MP/H_2O_2. It could also be seen that some substances were not very sensitive to the 254 nm wavelength.

5.2 Recommendations

In the experiments, several methods that can destroy organic halogen compounds on a laboratory scale have been taken into consideration. As many process parameters as possible have been taken into consideration. Based on the results, MP/H2O2 and wet chemical oxidation are the optimal methods for organic halogen degradation. The recommended irradiation time for the MP lamp is 45 minutes, though this is based on a specific reactor design and lamp. From the wet chemical oxidation experiments, we have primarily found some important tips for applying the wet chemical oxidation method:

1. The solution should add sodium hydroxide to reach pH of higher than 11. That could prevent the sudden decrease of bromide. In the lower TOX concentrations found in actual boiler feedwater, this effect could be negligible.

2. The optimal oxidant dosing we found is 40 mg/l. A lower dosage will lead to more reaction time and energy consumption. A high dosage will lead to sudden decrease of bromide and burden for the IC. Again, the lower concentrations in boiler feedwater could mean less persulfate is required.

3. Under atmospheric pressure, 95 °C is an ideal final temperature for the reaction. A lower temperature will lead to a lower reaction rate. A higher temperature will lead to boiling of the water and possibly evaporate some organic compounds out of the solution, which affects the accuracy of measurement.

4. 10 minutes after the final temperature is reached the reaction (degradation) rate is at its peak.

Although many methods and factors are investigated, there are still much more questions that could be looked into thoroughly, such as:

1. From literature, the dual wavelength lamp has proven to be an effective ways to destroy organic molecules. But the experiments did not confirm this finding. The structure of the reactor is regarded as the decisive factor, since cooling water can strongly absorb most of the VUV light. If some modification were to be applied to the reactor in further experiments, the results could be more reliable.

2. In the experiments, pH is not considered as an important factor for the different compounds. As mentioned in the reviewed literature, different pH values could affect the activity of hydroxyl radicals and sulfate radicals. So different other pH level tests can also be a useful addition, since boiler feed water has a pH between 9 and 10.

3. Ion transfer after mineralization (especially for the bromine ion) is an interesting secondary finding of the experiments. In the results, bromine ion could reach a high recovery and then disappear. From the analytical methods applied right now, we are unable to trace the bromine transfer. Perhaps with another analytical method, this bromine could be traced.

4. This research has investigated 6 compounds to represent all kinds of organic halogens. In fact more organic halogens should be test in further research. Testing neutral and long chain compounds found in industrial effluent could be an interesting addition.

5. The experiments in the research only use model compounds to simulate actual boiler feedwater. The chosen method for application can be used to determine TOX in boiler feedwater from several sources in the further studies.

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Measurement of Organic Halogens in Boiler Feedwater

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