Development of a Rapid and Easy Measurement Protocol for Perfluorinated Carboxylic Acids (PFCAs) by a Continuous Flow Analysis

2015

DINH QUANG HUNG

ACKNOWLEDGMENT

I wish to express deepest gratitude to my advisors, ***Prof. Shigeo Fujii*** for his advice, guidance and continuous support throughout the research that has been a rewarding experience to me.

I am also grateful to ***Assoc. Prof. Shuhei Tanaka*** my co-adviser, for his contribution to this study.

I express my gratitude to ***Asst. Prof. Hidenori Harada*** for his suggestions. I am thankful to Dr. Chinagarn Kunacheva for his kindness and sharing his knowledge on PFCs research.

I would like to extend my gratitude to ***Assoc. Prof. Huynh Trung Hai*** (Institute for Environmental Science and Technology, Hanoi University of Science Technology, Vietnam). I also wish to express my gratitude to ***EML program*** for the financial assistance and support to my study and research in the Kyoto University.

I am truly thankful to the staffs of the GSGES, Kyoto University for their support, help and encouragements.

My gratitude also goes to my colleagues in the PFCs group, and other lab members. Also, I would like to give my appreciation to Fukunaga-san, Shiozaki-san, and Yasuba-san for their kind supports and guidance during my stay in Japan

I am thankful to professors and colleagues at the Institute for Environmental Science and Technology (INEST) at Hanoi University of Science and Technology for helping me and creating good conditions for me to study in the Kyoto University.

I would like to give my special thank to all Vietnamese friends here in the Kyoto for everything that they did and shared with me during more than 4 years living in Kyoto.

Finally, and most of all, I would like to extend my deepest gratitude for the continuous support, care, understanding and love that I received from my wife Van Hong, and my family; I have enormous debt of my gratitude to them for their love, eternal support and unlimited patience which can hardly be repaid.

ABSTRACT

Water contamination by perfluorinated compounds (PFCs) is a major environmental issue. These compounds are considered as persistent, toxic, and bio-accumulated chemicals and are widespread in the environment. The stability of these chemicals makes them difficult to be treated by conventional wastewater and water treatment processes. Reports on PFCs in water environments and industries related to PFCs are limited since the current analytical methods are extremely expensive and complicated. Therefore, it is essential to develop a fast and easy measurement protocol for these compounds. One possible method is a continuous flow analysis, which would measure fluoride ions by a colorimetric method after PFCs decomposition, using AutoAnalyzer 3. Six kinds of PFCAs (PFBA, PFPA, PFHxA, PFHpA, PFOA, and PFNA) were selected for this research. The analytical system consisted of five parts: an auto sampler, a decomposition unit, a distillation unit, a detection unit, and a peristaltic pump.

This study selected Da Nang, Vietnam, for investigating PFC concentrations in drinking water, surface water, and wastewater. The level of PFC concentration found in Da Nang was used for the development of an experimental system for the continuous flow analysis of PFCs. A field survey was conducted from July 30 to August 3, 2011, to collect water samples. Among five tap water samples, TW1 (52 ng/L) had the highest PFC content. PFOA was predominant and it`s concentration was from 2 to 40 ng/L. For 18 surface water samples, SW8 had the highest concentration (132 ng/L) followed by SW7 (128 ng/L). For samples from two DWWTPs (Phu Loc and Hoa Cuong), two IWWTPs (Hoa Khanh and Tho Quang), and a landfill site (New Khanh Son Landfill), the highest PFCs concentration was founded at the landfill site. Total PFC concentrations in the leachate, mixture of leachate and septic wastewater and treated effluent from the landfill site were 200 ng/L, 516 ng/L, and 75 ng/L, respectively. PFC concentrations from IWWTPs were from 42 to 63 ng/L. However, a high PFC concentration (292 ng/L) was found in the discharging channel of an industrial zone (IZ), which indicated that some industrial factories discharged their wastewater with high PFC concentration into the drainage system without proper treatment. Thus,

industrial activities are the major source of PFC contamination in the water environment in Da Nang.

Then, an experimental system for the continuous decomposition of PFCAs was developed. The system consisted of a UV/heating unit and a peristaltic pump. PFCAs in effluents coming out of the UV/heating unit were analysed by HPLC-MS/MS for the calculation of decomposition rates. Effects of irradiation-heating times and wavelengths on decomposition of PFOA and PFNA dissolved in *Milli-Q* water at a concentration of 10 μg/L were investigated. Results showed the possibility of decomposition of PFOA and PFNA by a UV photolysis process. It was observed that the target PFCAs were decomposed faster under irradiation of $UV_{254+185}$ light in comparison to UV_{254}. It was also found that 100% of PFOA was decomposed under irradiation of $UV_{254+185}$ light in 60 min. At the same condition of 60 min irradiation, a lower decomposition rate was observed in case of PFNA (99%).

In the next step, an experimental system which allowed continuous decomposition of PFCAs and quantification of the released fluoride was developed. The system consisted of five units: an auto sampler, a decomposition unit, a distillation unit, a detection unit and a peristaltic pump. However, the developed system was improved since the recorded fluoride signals were not in a steady state. A modification of the system with the installation of a debubbler/rebubbler unit for the UV/heating unit and a debubbler together with a stabilizer for the flow cell (30 mm length) was made to achieve better signals for better quantification of the fluoride concentration. The following steps were focused on application of the modified experimental system in a study on the effects of experimental conditions on the decomposition of PFCAs. In the first step, we focused on a study on the effects of acid and oxidant concentrations on CFA of PFCAs using a colorimetric method. We used 42 different decomposition reagents of an acid (H_2SO_4, six levels: 0–2 mol/L) and oxidant ($K_2S_2O_8$, seven levels: 0–0.16 mol/L) to investigate the effects on the decomposition rates of six PFCAs at a concentration of 3 mg/L. Under irradiation of $UV_{254+185}$ light and temperature of 65 °C, the highest decomposition rates of PFCAs were observed in conditions of 0.4 mol/L of H_2SO_4 and 0.16 mol/L of $K_2S_2O_8$. Increasing the concentration of H_2SO_4 from 0.4 to 2.0 mol/L did not increase

the decomposition rate of PFCAs. We recorded the irradiation-heating time was 12 min. Since the operating temperature would have an effect on the reaction rates, we focussed on studying the effects of temperature as well as the initial PFCA concentrations on the decomposition rates. We used 20 (= 4 × 5) different experimental conditions to find the effects of initial PFCAs concentrations (five levels) and concentrations of $K_2S_2O_8$ (four levels) on the decomposition rates of PFCAs. The results showed that the decomposition rates at higher concentrations of PFCAs were higher in comparison to lower concentrations. The lower decomposition rates of PFCAs at low PFCAs concentrations were explained based on the higher percentage absorption of PFCAs onto pump tubes and glass coils under these conditions. For studying the effects of temperature in the UV/heating unit, we used 24 (= 6 × 4) different experimental conditions for the decomposition of PFCAs. We observed that, when the temperature was increased from 55 to 80 °C, the irradiation time was reduced from 20 min to 4.4 min. This led to the reduction in the decomposition rates of the PFCAs. We suspected that the decrease in irradiation time was the main factor contributing to the lower decomposition rates of PFCAs in this case. We recommend 65 °C to be the optimum heating temperature of the UV/heating unit.

The developed experimental system for the continuous decomposition of PFCAs and quantification of released fluoride was then applied to assess the effects of organic and inorganic interferences. Dissolved organic compounds (DOC) may compete with PFCAs in terms of using up oxidant and energy of UV light leading to a decrease in the decomposition rates of PFCAs. Besides, the decomposition reactions of DOC will form gases. The formation of gases would increase the pressure in the system and cause the tubes to unplug. Therefore, we selected glucose, humic acid, and methanol for studies on the effects of DOC interferences on the development of continuous flow analysis for PFCAs. The results show that glucose at concentrations of 1–30 mg/L did not affect the decomposition rates of PFCAs significantly. However, the decomposition rates were slightly decreased when we increased the concentration of glucose from 30–100 mg/L. HA (1–100 mg/L) and methanol (0.1%–1.0% v/v) did not have any significant effect on the decomposition rates of the PFCAs.

Chloride is available in many different types of wastewater and surface water. Our primary research showed that the chloride ion had negative effects on the recorded fluoride signals. These negative effects occurred only when a combination of $UV_{254+185}$ light or/and temperature of 65 °C was used. Ascorbic acid at a concentration of 1,500 mg/L in the absorption reagent successfully eliminated the effects of chloride interference at high chloride concentrations (500 mg/L). The results suggested that the use of ascorbic acid at a concentration of 1,500 mg/L in the absorbance reagent did not affect the continuous flow analysis of PFCAs (PFHxA, PFOA, and PFNA). This condition was recommended for future research for improving the CFA for PFCAs.

Since the fluoride ion may be present in water samples, especially in wastewater sources, a study on the methods for quantification of total organic fluoride (TOF), inorganic fluoride (IF), and total fluoride (TF) is important. Therefore, we developed an analytical method for the detection of IF (Method A) by modification of the above methods. The data showed that no signals of fluoride were detected in the case of *Milli-Q* sample and PFCAs samples at concentration of 3 mg/L. When we spiked 1 mg/L of fluoride to *Milli-Q* water and PFCA samples, fluoride concentrations were measured from 0.97–1.03 mg/L with a SD of 0.02 and CV of 2.43%. For PFCA samples spiked with 1 mg/L of fluoride, our analytical methods gave fluoride concentration values of 1.03–1.07 mg/L. These methods were successfully applied for examining the effects of interferences from WWTPs for the determination of TOF, TF and IF. In the case of wastewater samples spiked PFCAs (3 mg/L) and F^- (1 mg/l), the calculated IF concentrations were 0.93–1.0 mg/L (PFHxA), 0.97–1.07 mg/L (PFOA), and 0.94–0.99 mg/L (PFNA), respectively. These results were acceptable and our developed methods can be recommended for further research.

Keywords

Perfluorinated compounds, perfluorocarboxylic acids, UV decomposition, colorimetric method, continuous flow analysis, total organic fluoride, inorganic fluoride, total fluoride.

TABLES OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Abbreviations

CFA	continuous flow analysis
DOC	dissolved organics carbon
HPLC	high-performance liquid chromatography
IF	inorganic fluoride
IZ	industrial zone
LC	liquid chromatograph
LOD	limits of detection
LOQ	limits of quantification
MS/MS	tandem mass spectrometer
PFASs	perfluoroalkyl sulfonates
PFBA	perfluorobutanoic acid
PFCAs	perfluorocarboxylates
PFCs	perfluorinated compounds
PFHpA	perfluoroheptanoic acid
PFHxA	perfluorohexanoic acid
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoate
PFOS	perfluorooctane sulfonate
PFPA	perfluoropentanoic acid
TF	total fluoride
TOF	total organic fluoride
WTP	water treatment plant
WWTP	wastewater treatment plant
UV	ultra violet
VUV	vacuum ultra violet

Chapter 1 Introduction

1.1 Research background

Water contamination by persistent organic pollutants (POPs) such as perfluorinated compounds (PFCs) is a major environmental issue. PFCs have been widely used in industrial and commercial applications for over 50 years (Olsen *et al.* 2005). Prevedouros *et al.* (2005) estimated the global historical industry-wide emissions of total PFCAs from direct (manufacture, use, consumer products) and indirect (PFCA impurities and/or precursors) sources to be about 3,200–7,300 ton. They are now considered as persistent, toxic, bio-accumulated chemicals and are widespread in the environment (Harada and Koizumi 2009, Tanaka *et al.* 2008, Saito *et al.* 2004). The stability of these chemicals makes them difficult to be treated by conventional wastewater and water treatment processes (Schultz *et al.* 2006, Sinclair and Kannan 2006).

PFC contamination of water has been found not only in developed countries but also in developing countries (Sinclair and Kannan 2006, Tanaka *et al.* 2008). High levels of PFOA (14.8–402.3 ng/L) and PFOS (3.1–36.9 ng/L) were detected in rivers near the industrialized areas in Eastern Thailand (Kunacheva *et al.* 2009).

However, reports on PFCs in water environment and industries related to PFCs are limited since the current analytical methods were extremely expensive and complicated (Kunacheva *et al.* 2012). Furthermore, the lack of appropriate analytical methods, instruments and the unavailability of standards have prevented the determination of PFCs in water samples. Although, current analytical methods can measure 41 types of PFCs in water samples (Kunacheva *et al.* 2009, Taniyasu *et al.* 2005, Taniyasu *et al.* 2008), it is still a major challenge to determine of all PFCs in water. An analytical method for total organic fluoride (TOF) in water samples would provide important information of TOF load and complete detection of all organic fluoride compounds in a sample. The determination of TOF is an important step for faster identification of PFC pollution sites or to indicate the pollution levels in the specific industrial processes

related to PFCs. The current standard method for the determination the determination of absorbable organic halogen (AOX) (American Public Health Association 2005) is the Wickbold method which uses an oxygen-hydrogen flame combustion (Čápka *et al.* 2004), or combustion ion chromatography (CIC) (Miyake *et al.* 2007, Wagner *et al.* 2013). These methods are still complicated and not fully automated since they use solid phase extraction (SPE) for extracting organofluoride from water and minimization of interferences.

Therefore, there is a great demand for the development of fast and easy measurement protocols. Our targeted wastewaters were from some specific industrial processes which have the potential of high concentration of PFCs at mg/L level. A possible method in our case is a continuous flow analysis of fluoride ions by a colorimetric method after PFC decomposition, using AutoAnalyzer 3. Six types of PFCAs (perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), and perfluorononanoic acid (PFNA) were selected for this research.

Previous studies show that PFCs were decomposed by direct photolysis, or photocatalysis (Hori *et al.* 2004 , Hori *et al.* 2005, Chen *et al.* 2007, Cao *et al.* 2010, Wang *et al.* 2010, Panchangam *et al.* 2009, Estrellan *et al.* 2010); sonolysis (Cheng *et al.* 2008, Campbell *et al.* 2009, Cheng *et al.* 2009). Among these processes, photolysis methods would be a suitable choice for the breaking of C-F bonds in PFCAs. Distillation and absorption units were applied for the separation of fluoride ions and other interfering species before detection by a colorimetric unit (**Fig. 1.1**).

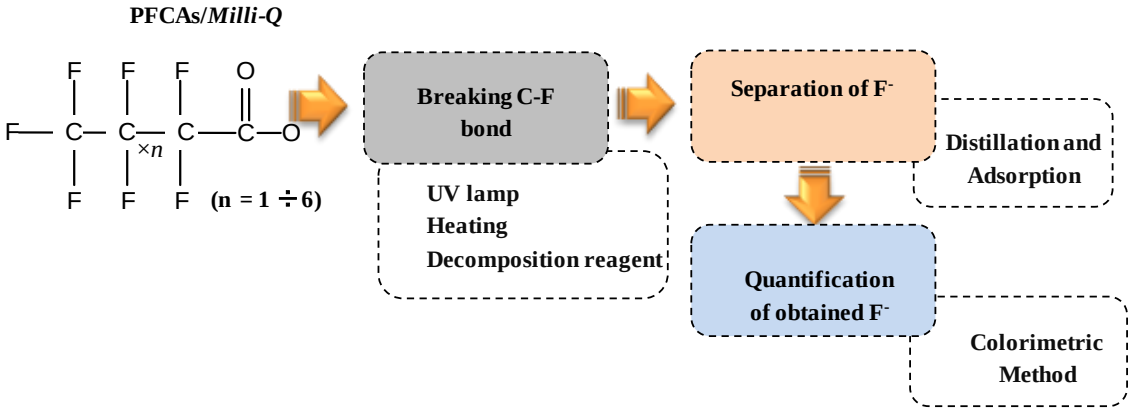


Figure 1.1 Research outline for the CFA of PFCAs by a colorimetric method.

1.2 Research objective

The main objective of this study was to develop a fast and easy measurement protocol for PFCAs in industrial wastewater by a continuous flow analysis. Our specific aims towards achieving the main objective specific are given below:

- To determine the PFCs contamination in drinking water, surface water and wastewater in Da Nang, Vietnam.
- To develop method for PFCA decomposition by continuous experiment and a study on the effects of UV light and irradiation time on the decomposition of PFCAs.
- To develop an experimental system for the continuous decomposition of PFCAs and the quantification of released fluoride by a colorimetric method followed by a study on the experimental conditions for the decomposition of these compounds.
- To study the effects of interferences on the continuous flow analysis of PFCAs by the colorimetric method.
- To develop a method for the determination of TOF from PFCAs through the measurement of TF and IF.

Based on previous research, this study focused on the development of a fast and easy measurement protocol for PFCAs. Initially, surveys were conducted to find the PFC levels in surface water and wastewater (drinking water, domestic wastewater, wastewater from landfill site and industrial wastewater treatment plants) in Da Nang, Vietnam (Chapter 3). Next, a continuous decomposition experiment for the PFCAs was developed. The studied experimental conditions for breaking C-F bonds of PFCAs included irradiation with UV lights (Chapter 4). Subsequently, a continuous flow analysis for PFCAs by a colorimetric method was developed. The effects of the experimental conditions (acid and oxidant, initial concentration of PFCAs and heating temperature) on the decomposition of PFCAs were considered (Chapter 5). This was followed by a study on the effects of interferences which included organic and inorganic species (Chapter 6). Finally, a method for the determination of PFCAs through the measurement of TOF was developed via a study of TF and IF (Chapter 7).

This dissertation consists of eight chapters are shown in **Fig. 1.2**.

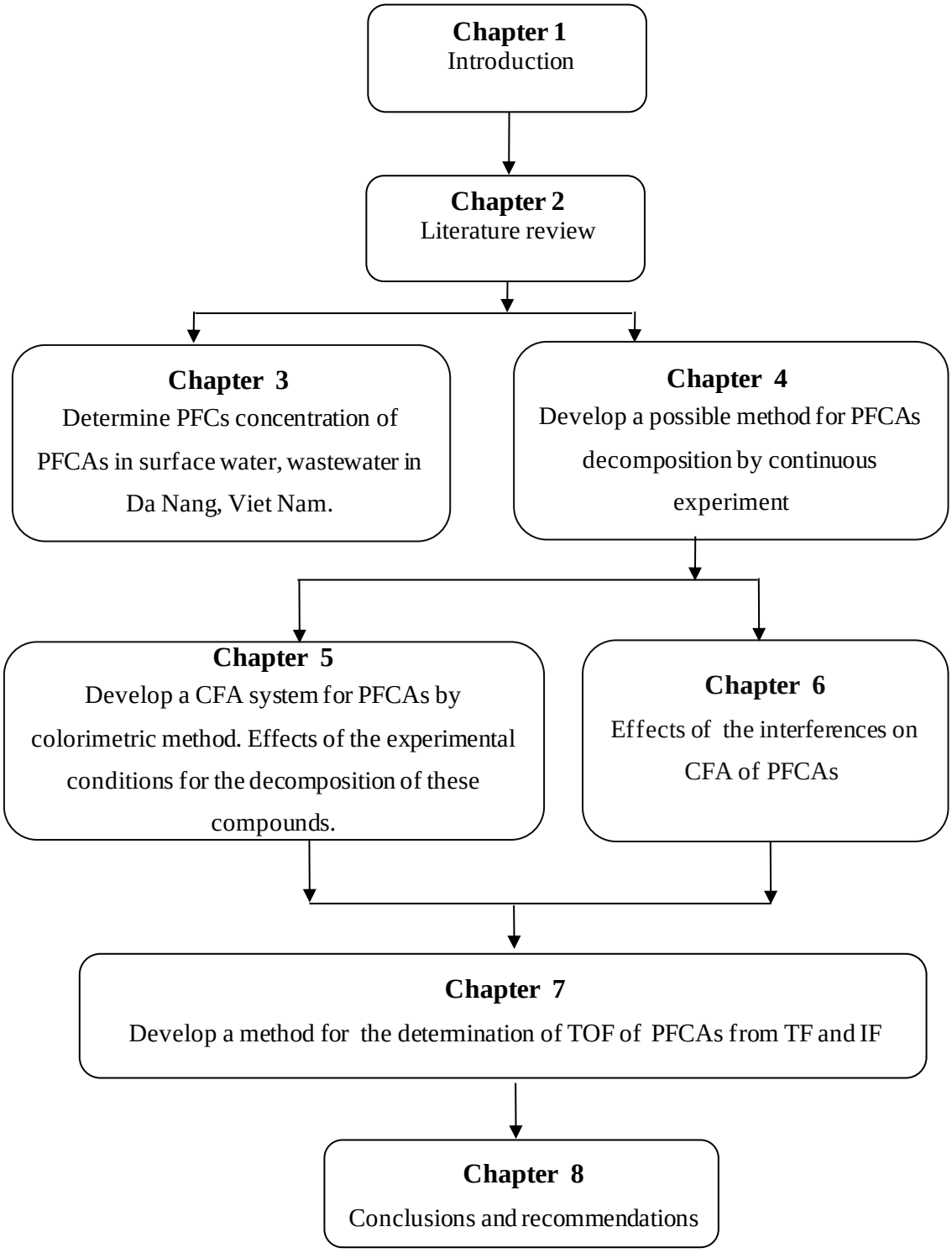


Figure 1.2 Structure of the dissertation.

Chapter 2 Literature review

2.1 Introduction to perfluorinated compounds (PFCs)

2.1.1 Properties of PFCs

Perfluorinated compounds (PFCs) are man-made chemicals, which are formed by the replacement of hydrogen atoms in the hydrocarbon chain by fluorine atoms. The C-F bond is one of the strongest in organic chemistry (an average bond energy around 480 kJ/mol (Kirsch 2013) which makes them highly stable against extreme physical, chemical and biological conditions (O'Hagan 2008, 3M 1999). The stability of these chemicals has made them widely applicable in industry for over 50 years (Björklund *et al.* 2009). PFCs are used in products to resist grease, oil, stains, and water. They are also used in fire-fighting foam (Minnesota Department of Health 2012). PFC-coated products may include non-stick cookware, Teflon®, GORE-TEX®, water-proof clothing, fast food wrappers, pizza boxes, popcorn bags, stain-resistant carpet, and paint (Environmental Working Group 2003).

PFCs are divided in two major groups: perfluorocarboxylates (PFCAs) and perfluoroalkyl sulfonates (PFASs). Their chemical structures are shown in **Fig. 2.1**. Fully fluorinated carbons chain of the PFCs makes them hydrophobic while the presence of polar functional groups at the end makes PFCs hydrophilic. Different

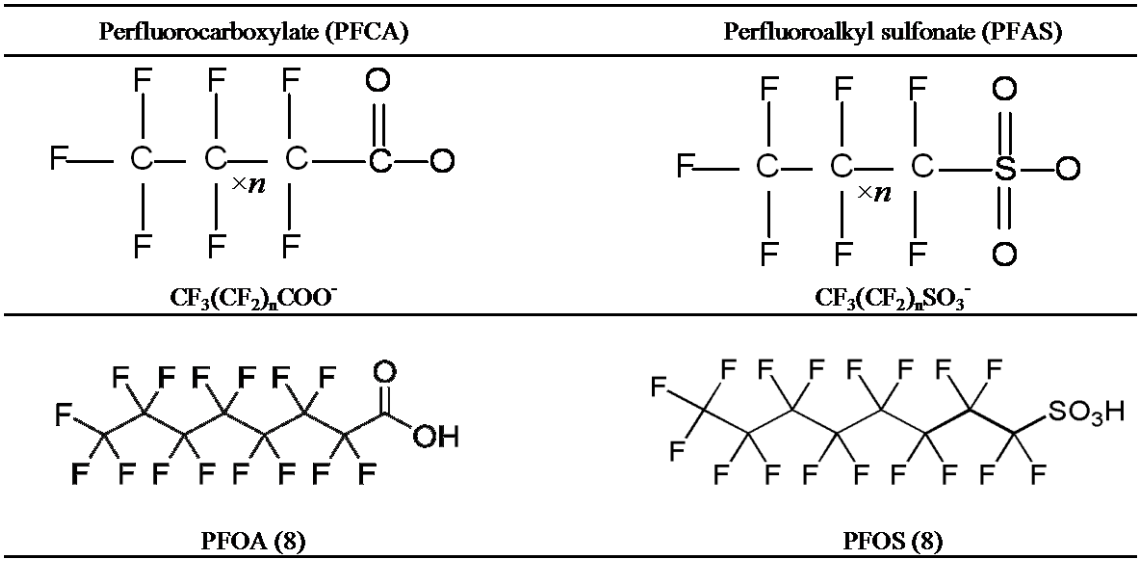


Figure 2.1 Structures of PFCA and PFAS.

hydrophilic functional groups show diverse behaviour in aqueous environments. The longer the carbon chain length, the more strongly hydrophobic is the PFC molecule. The most commonly used PFCs are perfluorooctane sulfonate (PFOS) and perfluorootanoic acid (PFOA). PFOS and PFOA have eight carbons each and the chemical formulas of these compounds are $C_8F_{17}SO_3^-$ and $C_8F_{15}COO^-$, respectively. **Table 2.1** shows the physiochemical properties of PFCAs used in this study. (The number following the abbreviation in brackets refers to the carbon chain length)

Table 2.1 Basic physicochemical properties of PFCAs used in this study.

Type of PFCAs	Molecular weight	pKa[a]	Melting point[b], °C	Boing point[c] °C	Specific gravity	Standard reaagent		
						Supplier	Appearance	Purity, %
PFBA (4)	213			120.8 - 121	1.65	TCI	Yellow liquid	95
PFPA (5)	263			70 (40 mm)	1.71	TCI	Yellow liquid	> 98
PFHxA (6)	313			159-160	1.76	TCI	Clear liquid	> 98
PFHpA (7)	363			175 (742) mm	1.79	TCI	Crystalline	> 96
PFOA (8)	413	2.5[a]	55-56, 37-50	189 (736 mm)	1.70	Wako	White powder	> 95
PFNA (9)	463		63-66, 65	122 (30 mm)		TCI	White powder	> 95

Note: *a* = PFOA (OECD 2002) PFOS (EPA 2002); *b* = melting point, data from material safety data sheet (MSDS) of Wako Company and ExFluor Company; *c* = boiling point, from ExFluor MSDS.

2.1.2 PFCs and Stockholm Convention

The Stockholm Convention on Persistent Organic Pollutants (POPs) is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, and accumulate in the fatty tissue of humans and wildlife. This convention was adopted in 2001 and entered into force in 2004. By signing this convention, the parties agree to take measures to eliminate or reduce the release of POPs into the environment. The Convention is administered by the United Nations Environment Program and is based in Geneva, Switzerland. A separate committee has been established (POPRC) as a subsidiary body to the Stockholm Convention for reviewing new chemicals proposed for listing in a suitable category. One of the known PFCs, namely PFOS, was reviewed

by the 4th POPs review committee which recommended to categorize it as a POP (Stockholm Convention 2009). This recommendation was seriously considered at the fourth meeting of the Conference of the Parties (COP4) to the Stockholm Convention and it was decided to amend part I of Annex B of the Convention to list perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride as a POP with acceptable purposes and specific exemptions.

2.1.3 Occurrence of PFCs in the environment

Historic emissions of perfluorocarboxylates (PFCAs) were estimated at 3,200–7,300 ton (1951–2004) (Prevedouros *et al.* 2005). The OECD estimated the historic production volume of perfluorooctane sulfonate (PFOS) and related compounds at 4,500 tons/year (OECD 2002). Environmental water and tap water in many countries were found to be contaminated with PFCs.

Saito *et al.* (2003) reported that the concentration of PFOS in surface water in Osaka, Japan ranged from 0.3 to 157 ng/L. For tap water, in Italy, PFOS was detected at 6.2–9.7 ng/L and PFOA at 1.0–2.9 ng/L (Loos *et al.* 2007). The concentrations of PFOA in water from Italy were lower than the concentrations found in Osaka. PFOA was detected at 22–519 ng/L in Germany where, over 100 ng/L of PFOA was detected in six out of 11 samples (Skutlarek *et al.* 2006).

Not only in water environments, PFOA and PFOS have also been detected in livers, bladders, and blood samples of humans and many kinds of animals, including fishes, birds, and marine mammals (Renner 2001).

2.2 Treatment of PFCs

2.2.1 Conventional water and wastewater treatments

Conventional treatment processes for water and wastewater have been reported but these are not sufficient to remove PFCs (Schultz *et al.* 2006). Thus, studies on effective treatment techniques are necessary. Many researchers have reported several PFCs

removal techniques which were useful for developing further effective techniques applicable to the real world. These removal techniques can be classified as (1) advanced oxidation processes, photolysis and/or photocatalysis, thermal degradation and sonochemical processes; and (2) separation (membrane filtration and adsorption).

2.2.2 Advanced oxidation process

2.2.2.1 Direct UV photolysis

Photolysis is a chemical bond-breaking process driven by light. Simulated sunlight applied to aqueous solutions of PFOS and N-EtFOSE for 30 days had no effect on their concentrations while the 8:2 fluorotelomer alcohol also does not significantly degrade under direct photolysis (Gauthier and Mabury 2005). Therefore, direct photolysis of PFCs is not expected to be useful under natural environment conditions.

Hori *et al.* (2004) reported on the decomposition of aqueous PFOA (560 mg/L, 22 mL) under the irradiation of 254 nm UV light (200W Xe-Hg lamp, 4.8 atm of O_2). Under these conditions, 44.3% of initial PFOA degraded after 24 h of irradiation and 89.5% after 72 h. **Figure 2.2** shows the decomposition products of PFCAs. The primary photoproducts were shorter chain carboxylic acids and fluoride (Hori *et al.* 2004). This result is similar to that reported by Chen *et al.* (2006).

$$C_X F_{2X+1} COOH \xrightarrow{hr,-COOH} C_X F_{2X+1}\bullet$$
$$\xrightarrow{H_2O} C_{X-1} F_{2X-1} CF_2 OH \xrightarrow{-HF} C_{X-1} F_{2X-1} CFO$$
$$\xrightarrow{H_2O,-HF} C_{X-1} F_{2X-1} COOH \xrightarrow{hr} \cdots$$
$$\xrightarrow{H_2O,-2HF} CF_3 COOH \rightarrow \cdots \rightarrow CF_3 + CO_2$$

Figure 2.2 Degradation mechanisms of PFCAs.

Furthermore, PFOA degraded faster under the irradiation of $UV_{285+185}$ light (Chen *et al.* 2007). The results showed that, 61.7% of initial PFOA (25 mg/L, 800 mL, pH 3.7, 40 °C) degraded after 2 h of irradiation using a UV lamp which mainly emitted 254 nm light along with a small amount of 185 nm light (15 W, N_2). The primary photoproducts

were shorter chain carboxylic acids with a defluorination ratio of 17%. Degradation of PFOS has been reported by Yamamoto *et al.* (2007). Aqueous PFOS (20 mg/L, 750 mL) in both media was irradiated with a low-pressure mercury lamp (254 nm, 32 W). PFOS was degraded by 8% after 24 h and by 68% after 240 h irradiation compared to the initial concentration in deionised water. In alkaline 2-propanol, 76% and 92% of PFOS was degraded after one and ten days' irradiation, respectively. Photo degradation of PFOS in alkaline 2-propanol was much faster and effective than in water. From an observation of the degradation products, two major degradation pathways of PFOS were considered via C_8HF_{17} and $C_8F_{17}OH$, respectively, resulting in short-chain fluorinated compounds such as C_7HF_{15} and $C_7F_{15}OH$ by stepwise removal of CF_2 groups. Formation of short-chain fluorocarbons such as CF_4, C_2F_6, and C_3F_8 were also confirmed. Direct photolysis of PFCs will be negligible under natural environmental conditions. Higher energy UV and VUV photolysis can degrade PFCs. However, competitive UV light absorption by solvent and other matrix components will limit the photolysis rates.

2.2.2.2 Persulfate photolysis: Sulfate radical oxidation

Persulfate photolysis has been utilized for the oxidative degradation of a number of organics. Persulfate photolysis generates two sulfate radicals, $SO_4^{\cdot -}$, (Eqn. (2.1)). The sulfate radical is an oxidizing radical that reacts by a direct one-electron transfer to form a sulfate (Eqn. (2.1)). The sulfate radical has a one-electron reduction potential of 2.3 V, making it a stronger direct-electron transfer oxidant than the hydroxyl radical.

$$S_2O_8^{2-} + h\nu\,(<270\text{ nm})/\Delta \rightarrow 2SO_4^{\cdot} \quad (2.1)$$

$$SO_4^{\cdot} + e^- \rightarrow SO_4^{2-} \quad (2.2)$$

Persulfate photolysis has been utilized to degrade a number of perfluoro-alkylcarboxylates of various chain lengths (Hori *et al.* 2005). An aqueous solution (22 mL) containing PFOA (560 mg/L) and $K_2S_2O_8$ (13,500 mg/L) was irradiated with a xenon-mercury lamp (254 nm, 200 W). PFOA was degraded by 100% after 4 h irradiation. The primary products were shorter chain carboxylic acids, F^- and CO_2. However, the observation of the product showed that the formation of F^- and CO_2 were continued after 4 h, indicating that compounds other than PFOA continued to produce F^- and CO_2.

The detection of shorter-chain PFCAs in the liquid phase such as $C_6F_{13}COOH$, $C_5F_{11}COOH$, C_4F_9COOH, and C_3F_7COOH suggested the reaction mechanism for the sulfate radical-mediated degradation of perfluoroalkylcarboxylates. The initial degradation is postulated to occur through an electron transfer from the carboxylate terminal group to the sulfate radical (Eqn. 2.3). The oxidized PFOA subsequently decarboxylates to form a perfluoroheptyl radical (Eqn. 2.4) which reacts quantitatively with molecular oxygen to form a perfluoroheptylperoxy radical (Eqn. 2.5). The perfluoroheptylperoxy radical will react with another perfluoroheptylperoxy radical in solution, since there are no reductants present, to yield two perfluoroalkoxy radicals and molecular oxygen (Eqn. 2.6). The perfluoroheptyloxy has two branching pathways: unimolecular decomposition to yield the perfluorohexyl radical and carbonyl fluoride (Eqn. 2.7) or an H-atom abstraction from an acid such as HSO_4^- to yield perfluoroheptanol (Eqn. (8)). The perfluorohexyl radical formed in Eqn. 2.7 will react with O_2 (Eqn. 2.6) and resume the radical unzipping cycle. COF_2 will hydrolyse to yield CO_2 and two HF molecules (Eqn. 2.8). The perfluoroheptanol from Eqn. 2.9 will unimolecularily decompose to give the perfluoroheptylacyl fluoride and HF (Eqn. 2.10). Perfluoroheptyl acyl fluoride will hydrolyse to yield perfluoroheptanoate (Eqn. 21).

$$CF_3(CF_2)_6COO^- + SO_4^{\cdot -} \rightarrow CF_3(CF_2)_6COO^{\cdot} + SO_4^{2-} \quad (2.3)$$

$$CF_3(CF_2)_6COO^{\cdot} \rightarrow CF_3(CF_2)_5CF_2. + CO_2 \quad (2.4)$$

$$CF_3(CF_2)_5CF_2^{\cdot} + O_2 \rightarrow CF_3(CF_2)_5CF_2OO^{\cdot} \quad (2.5)$$

$$CF_3(CF_2)_5CF_2OO^{\cdot} + R_FOO. \rightarrow CF_3(CF_2)_5CF_2O^{\cdot} + R_FO. + O_2 \quad (2.6)$$

$$CF_3(CF_2)_5CF_2O^{\cdot} \rightarrow CF_3(CF_2)_4CF_2^{\cdot} + COF_2 \quad (2.7)$$

$$COF_2 + H_2O \rightarrow CO_2 + 2HF \quad (2.8)$$

$$CF_3(CF_2)_5CF_2O^{\cdot} + HSO_4^- \rightarrow CF_3(CF_2)_5CF_2OH + SO_4^{\cdot -} \quad (2.9)$$

$$CF_3(CF_2)_5CF_2OH \rightarrow CF_3(CF_2)_5COF + HF \quad (2.10)$$

$$CF_3(CF_2)_5COF + H_2O \rightarrow CF_3(CF_2)_5COO^- + HF + H^+ \quad (2.11)$$

During photolysis, Hori has observed that the pH of the solution declined to values lower than 3 due to the formation of HF (Eqn. 2.11).

2.2.2.3 Phosphotungstic acid photocatalysis

PFOA has been reported to be decomposed by $H_3PW_{12}O_{40}$ photocatalysis (Hori *et al.* 2004). 100% of PFOA (560 mg/L, 22 mL) degraded during phosphotungstic acid photolysis ($H_3PW_{12}O_{40}\cdot 6H_2O$ = 20,113 mg/L, pH < 2.9, 4.8 atm of O_2) after 24 h. In this process, fluoride accounted for 20% of the total fluorine. The extent of fluoride production is similar to that observed during persulfate photolysis suggesting a similar degradation mechanism where the carboxylate headgroup is oxidatively removed and a shorter-chain perfluoroalkyl-carboxylate is formed. Reaction mechanisms were proposed in Eqn. (2.13)–(2.15) PFOA first complexes with $PW_{12}O_{40}^{3-}$ (Eqn. (2.13)) and upon photon adsorption, an electron is directly transferred from PFOA to $PW_{12}O_{40}^{3-}$ (Eqn. (2.14). Similar to the sulfate radical mechanism, PFOA will decarboxylate to form the perfluoroheptyl radical. Oxygen is essential for the photocatalytic cycle since it accepts an electron from the reduced phosphotungstic acid, $PW_{12}O_{40}^{4-}$, (Eqn. (2.14) returning it to its photoactive state. The reaction using phosphotungstic acid can show the possibility in decomposition of PFOA in water. However, the reaction time for this process was very long.

$$CF_3(CF_2)_6COO^- + PW_{12}O_{40}^{3-} \rightarrow CF_3(CF_2)_6COO^- \ldots\ldots PW_{12}O_{40}^{3-} \quad (2.13)$$

$$CF_3(CF_2)_6COO^- \ldots PW_{12}O_{40}^{3-} + h\nu\ (\lambda < 390\ nm) \rightarrow CF_3(CF_2)_5CF_2^{\cdot} + CO_2 + PW_{12}O_{40}^{4-} \quad (2.14)$$

$$PW_{12}O_{40}^{4-} + O_2 \rightarrow PW_{12}O_{40}^{3-} + O_2^{\cdot -} \quad (2.15)$$

2.2.2.4. TiO_2 photocatalysis

TiO_2 photocatalysis has been shown to degrade a large number of pollutants through oxidative and reductive pathways (Hoffmann *et al.* 1995). Degradation of PFOA (25 mg/L, 250 mL) under UV wavelength at 254 nm (low-pressure mercury lamp, 23 W) by using TiO_2 with a sub-monolayer Ni-Cu coating (TiO_2/Ni-Cu) was reported (Chen *et al.* 2006). PFOA decomposed significantly in the presence of TiO_2/Ni–Cu: it almost disappeared after 6 h. And at the same time, fluoride ions in aqueous solution were detected. After the reaction was run for 6 h, defluorination was up to 40%. Furthermore,

the decomposition of PFOA was greatly enhanced by using TiO_2/Ni–Cu with -0.1 V bias potential along with 0.1 $mol \cdot L^{-1}$ Na_2SO_4. The results showed that 92.5% PFOA was decomposed within 2 h, and it completely decomposed after 4 h. The defluorination rate was also greatly enhanced after 6 h of reaction and became 85.6%. The main decomposition products of PFOA were shorter perfluorinated carboxylic acids containing 4–7 carbon atoms, including perfluorobutyric acid (PFBA), perfluoropentanoic acid (PFPeA), per-fluorohexanoic acid (PFHxA), and perfluoroheptanoic acid (PFHpA). Small amount of trifluoroacetic acid (TFA) and pentafluoropropionic acid (PFPA) were also detected.

2.2.3 Thermal degradation process

Thermal degradation of a polyester/cellulose fabric substrate treated with a fluorotelomer-based acrylic polymer has been reported under laboratory conditions conservatively representing typical combustion conditions of time, temperature, and excess air level in a municipal incinerator. The average temperature was 1000 °C or greater over approximately 2 s of residence time. The results of these experiments demonstrate that the polyester/cellulose fabric treated with a fluorotelomer-based acrylic polymer is destroyed and no detectable amount of perfluorooctanoic acid (PFOA) is formed under typical municipal incineration conditions (Yamada *et al.* 2005).

2.2.4 Sonochemical process

Sonochemistry is the application of ultrasound to chemical reactions and processes. The mechanism causing sonochemical effects in liquids is based on the phenomenon of acoustic cavitation. Sonochemical degradations of PFOS and PFOA were observed and the half-life times of PFOS and PFOA degradations under an argon atmosphere were determined to be 43 and 22 min, respectively (Moriwaki *et al.* 2005). Sonolysis for decomposition of PFOS and PFOA present in groundwater beneath a landfill was also reported (Cheng *et al.* 2008). However, the presence of organic matrixes was affecting the decomposition rates of the PFCs. The pseudo first-order rate constant for the sonochemical degradation in the landfill groundwater is reduced by 61% and 56% relative to *Milli-Q* water for PFOS and PFOA.

2.2.5 Membrane filtration

Semiconductor wastewater containing PFOS concentrations of 0.5–1500 mg/L was treated using commercial reverse osmosis (RO) (Tang *et al.* 2006). The RO membranes generally rejected 99% or more of the PFOS.

RO membranes were also reportedly installed in a drinking water treatment plants for the removal of PFOS and PFOA (Flores *et al.* 2013). The treatment system was able to remove ≥ 99% of both compounds.

2.2.6 Adsorption

Adsorption of PFOS by using granular activated carbon, ion-exchange polymers and non-ion exchange polymers were studied (Senevirathna *et al.* 2010). GAC and ion exchange polymers reached the equilibrium concentration faster than non-ion exchange. The sorption capacity at 1 µg/L equilibrium concentration decreased from ion exchange polymer, non-ion exchange polymer, and GAC respectively. Adsorption isotherms and adsorption kinetics indicated that non-ion exchange (XAD4) and ion exchange polymer (Dow Marathon A) could be recommended to eliminate PFOS at ng/L equilibrium concentration. Moreover, a column test found that XAD4 removed 99.99% of PFOS (10 µg/L) with 23,000 bed volumes at 15 mL/min flow rate (0.75 bed volume/min).

2.3 Analytical methods for PFCs

2.3.1 Non-specific quantification methods

The historical method in the literature for the measurement of organic fluorine compounds is the Wickbold method (Čápka *et al.* 2004), where organic fluorine is converted to hydrogen fluoride via combustion. In this context, an analytical method for total organic fluoride (TOF) in samples provides important information of TOF load and complete detection of all organic fluoride compounds of a sample. However, this method does not provide information about specific PFCs.

2.3.1.1 Combustion ion-chromatography for the determination of total fluorine and extractable organic fluorine

A method for the determination of trace levels of TF in the environmental samples has been developed by Miyake *et al.* (2007). In this mass balance approach, TF in a sample is measured using CIC. The sample is fractionated into organic and inorganic fractions using solvents, and each fraction is analysed for TF, TOF, and IF. This method has been applied for both seawater and human blood samples. The analysed liquid samples are combusted on a quartz boat in an oxygen atmosphere in a furnace at 900–1000 °C. The hydrogen fluoride is absorbed in a sodium hydroxide solution and determined by ion-chromatography with conductivity detection. Prior to the CIC determination, samples of seawater were pre-treated with OnGuard Dionex cartridges to remove interfering sulfate and chloride. Blood samples were directly introduced to the silica boat and were placed directly in the furnace of CIC. LC-MS/MS was applied for PFC determination which enabled the calculation of the fraction of TF contributed by PFCs. Perfluorinated compounds detected with LC-MS/MS in blood samples accounted for >80% of total fluorine in the organic fraction. Similar measurements carried out with human blood samples from different regions of China indicate that known PFCs account only for 30 to >70% of EOF depending on the region. In both cases again, the mass balance analysis based on the LC-MS/MS determination of individual PFCs suggests the presence of other forms of organic fluorine in addition to known PFCs.

2.3.1.2 Determination of TOF by HPLC with UV detection

The application of CIC in the determination of the total amount of fluoroorganic compounds requires the use of a dedicated combustion unit, removal of anions interfering in ion-chromatographic determination and two steps of solvent extraction. A defluorination procedure using the reaction with an SBP reagent is instrumentally a much simpler procedure (Musijowski *et al.* 2010). Because of the ultra-trace level of analytes present in the environmental and biological samples it is essential to be able to detect of fluoride at much lower limits of detection. The method consisted of the following steps: (1) pre-concentration of perfluorinated substances from a large sample

volume (1 L) using the solid-phase extraction with an activated carbon sorbent. (2) Defluorination with SBP reagent after extraction of analytes from the sorbent and solvent evaporation. (3) Derivatisation of obtained fluoride with TPSiOH and finally (4) RP-HPLC quantitation of the reaction product, TPSiF. The LOD value established for the developed procedure was 14 ng/L fluoride (corresponding to 20 ng/L of PFOA). The major hindrance in achieving an even lower detection limit was a relatively high fluoride blank originating from the SBP reagent. The developed procedure has been applied to analysis of different samples of natural waters, where determined TOF values have been compared to results of determination of PFOS and perfluorinated carboxylic acids using the LC/MS/MS method under conditions reported earlier for the determination of fluorotelomer alcohols (Szostek *et al.* 2006). The results indicate that in each case there is a fraction of unidentified fluorinated organic compounds besides the species identified and determined by LC/MS.

2.3.1.3 Flow injection methods for determination of TOF

Flow analysis is a valuable and widely used methodology for analytical measurements with different detections techniques and online methods of sample pre-treatment. A continuous flow analysis mode is used mainly in process analysis in industrial and environmental laboratories, while flow injection techniques, which use small volumes of sample, are employed mostly in research laboratories. The simplest version of the latter flow methods was employed with two detection methods for the determination of fluoride as the final step of TOF analysis.

In both methods, the first step involved offline sorption of PFCAs, which were used as model perfluorinated organic compounds, on an activated carbon sorbent in order to separate them from the sample solution. Then, defluorination with the sodium biphenyl (SBP) reagent was carried out directly on a dried sorbent bed. The use of SBP was earlier reported for the determination of covalently bound fluorine in organic compounds and biological matrices by a manual procedure spectrophotometrically and with the fluoride ion-selective electrode (Venkateswarlu 1982). As a result of radical reduction reaction of organic fluorine with SBP, the fluoride ions are released, which is then, transferred to the aqueous solution as a result of hydrolysis of the SBP reaction

products. The main obstacle in the determination of fluoride with the potentiometric detection in FIA is a slow response of the indicating electrode and limited concentration range of response (Musijowski *et al.* 2007). In order to be applicable for determination of TOF in environmental samples, it would require a large pre-concentration factor.

The developed flow-injection methods are instrumentally simple and can be employed for determination of TOF without complex and expensive instrumentation. The majority of determinations of perfluorinated compounds are carried out at trace and ultra-trace levels of concentrations. There are also practical situations, however, where a very low delectability is not required, such as determination in specific industrial wastes, control of surface water samples from fire-fighting foam spills or other environmental accidents. In such cases simple FIA methods with different detections may be sufficient for the preliminary screening based on the established action level.

2.3.2. Specific quantification methods

The environmental importance of perfluorinated compounds and the complexity of PFC interactions with living organisms, including humans, is a reason for very intense efforts to develop reliable analytical methods for PFCs quantification in various materials and sample matrices. These efforts have been documented in hundreds of original research papers, review papers, and presentations at specialized scientific conferences.

The methods which have been widely used in the last decade for the determination of specific PFCs involve HPLC separation and mass spectrometric detection. LC-MS/MS is considered a standard method for the determination of PFCs (Voogt and Sáez 2006). Depending on the type of MS detector used, different selectivity and limit of detection is obtained. Hence there are different requirements for cleanup procedures and pre-concentration of analytes with different instrumental preferences reported for various types of perfluorinated compounds.

Chapter 3 Perfluorinated compounds (PFCs) contamination in tap water, surface water, and wastewater in Da Nang

3.1 Introduction

PFCs have been found in tap water, surface water, municipal and domestic WWTPs in many developed countries (Tanaka *et al.* 2008, Kunacheva *et al.* 2011, Kim *et al.* , 2012). Recent trends in industrial production indicate that many manufacturing industries are moving from developed countries to the developing countries. Kunacheva *et al.* (2009) have reported high concentrations of PFOA (14.8–402.3 ng/L) and PFOS (3.1–36.9 ng/L) in rivers near the industrialized areas in Eastern Thailand. Very high concentration of total PFCs (647–1,383 ng/L) was found in the effluents of WWTPs of industrial zones (Kunacheva *et al.* 2011). Vietnam, like many other developing countries in Southeast Asia, will be facing water pollution issues related to PFCs. Therefore, an accurate estimation of the levels of PFCs contamination in the water environment, both municipal and wastewater, is very important.

Da Nang city is directly governed by the central government of Vietnam with an area of 1,257 km^2 and a population of 940,000 (as of 2011). Da Nang is a central key economic region and a nucleus linking different localities in the country. It is an industrial and commercial city with great potential for tourism. The high economic growth of Da Nang raises the possibility of PFC contamination of the water environment of the city. Therefore, this chapter focuses on a study of the occurrence and distribution of PFCs contamination in Da Nang, Vietnam.

3.2 Objectives

The detailed objectives of this study are shown as follows.

1. To investigate PFCs contamination in drinking water sources.
2. To investigate PFCs contamination of surface water.
3. To investigate PFCs contamination in domestic and industrial WWTPs

3.3 Materials and Methods

3.3.1 Chemicals and reagents

In this study, eleven PFCs were selected as target chemicals. Standard reagents were obtained from Wellington Laboratories, Canada, with purities of >99%. PFCs stock solutions were prepared by dissolving perfluorocarboxylic acids-mixed solution (PFCs-MXA) and perfluorosufonate-mixed solution (PFS-MXA) into 100 mL acetonitrile (LC/MS grade) and were stored in polypropylene (PP) bottles at 4 °C. PFCs standard solutions were prepared by diluting different volumes of the stock solutions with 40% acetonitrile. These multicomponent standards contained the same concentration of each PFC. All targeted PFCs are shown in **Table 3.1**.

Table 3.1 Analytical parameters of analysed PFCs by HPLC-MS/MS

Compounds	Abbreviation	Parent ion (*m/z*)	Daughter ion (*m/z*)	CE (eV)	Retention time (min)	*LOD* (ng/L)	*LOQ* (ng/L)
Perfluorobutane sulfonate	PFBuS	299	80	55	2.7	0.03	0.11
Perfluorohexane sulfonate	PFHxS	399	80	55	7.9	0.04	0.12
Perfluorooctane sulfonate	PFOS	499	80	55	13.8	0.04	0.16
Perfluoropentanoic acid	PFPA	263	219	5	1.9	0.08	0.20
Perfluorohexanoic acid	PFHxA	313	269	5	2.8	0.04	0.08
Perfluoroheptanoic acid	PFHpA	363	319	5	4.7	0.04	0.12
Perfluorooctanoic acid	PFOA	413	369	5	7.2	0.04	0.12
Perfluorononanoic acid	PFNA	463	419	5	9.9	0.04	0.08
Perfluorodecanoic acid	PFDA	513	469	5	12.7	0.04	0.16
Perfluoroundecanoic acid	PFUnDA	563	519	5	15.4	0.28	0.88
Perfluorododecanoic acid	PFDoDA	613	569	5	18.0	0.28	0.88

Note: CE = Collision Energy
LOD = Limit of Detection
LOQ = Limit of Quantification

3.3.2 Sampling site

A field survey was carried out in Da Nang from July 30 to August 3, 2011. Samples were collected from the rivers, lakes and domestic and industrial WWTPs. **Figure 3.1** and **Table 3.3** show the sampling site location and information in Da Nang. A total of 34 samples were collected where 18 samples were river and lake water, 11 samples were from effluents of domestic and industrial WWTPs, while five samples were from tap water.

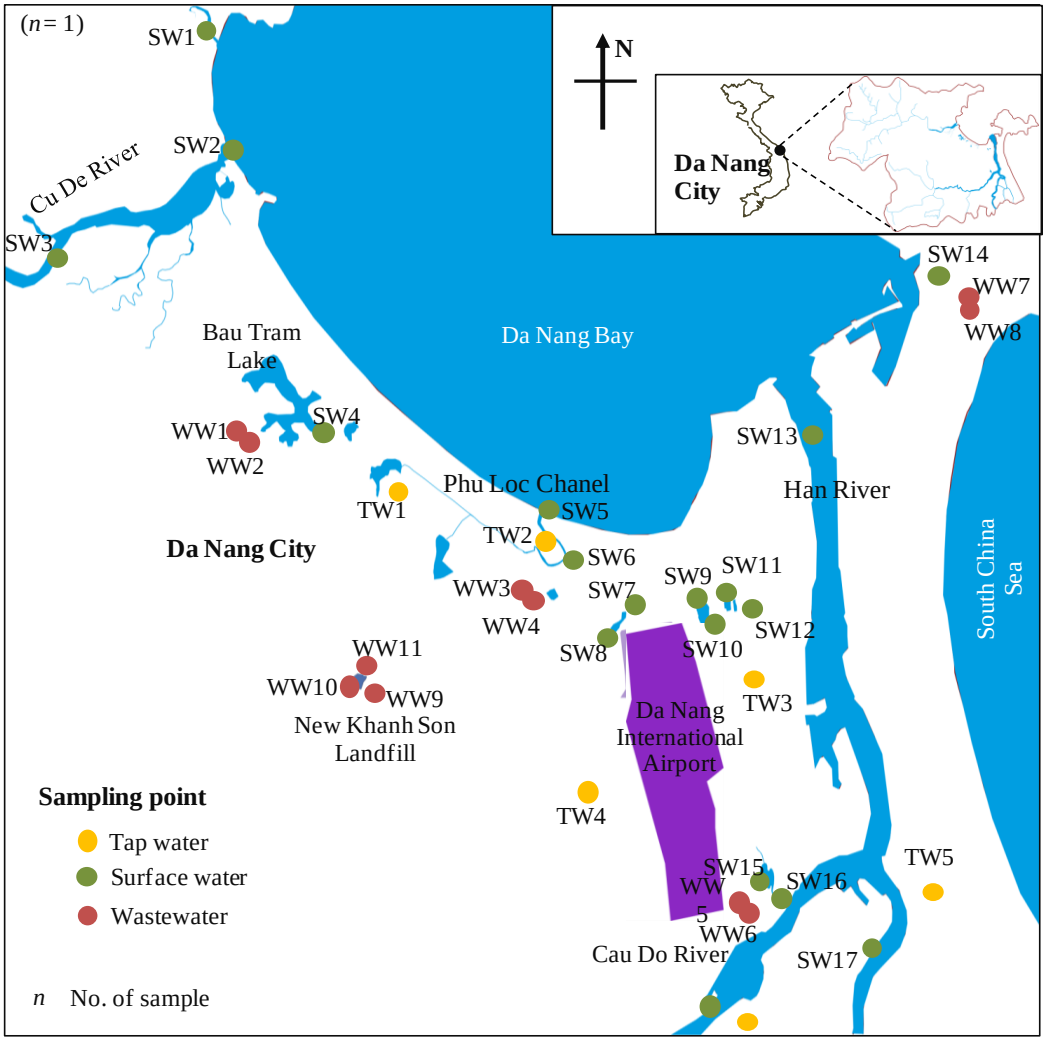


Figure 3.1. Location of the sampling site in Da Nang, Vietnam

The use of TEFLON and glass materials was minimized in the whole procedure of sampling, storage, pre-treatment and measurement to avoid possible contamination or adsorption. Samples were collected by direct grab-sampling using polypropylene container. New 1.5 L narrow-neck polyethylene terephthalate (PET) bottles with screw caps were used as sampling containers. Containers were rinsed three times with the sample before collection. After sampling, the samples were brought back to the laboratory and were pre-treated on the same day

3.3.3 Pre-treatment and extraction

All samples collected in Da Nang were processed following the procedure shown in **Fig. 3.2**. The collected samples were filtered through dry GF/B filter papers (1 µm, Whatman, Japan), which were washed with methanol and dried. The filtrates (250–1000 mL) were passed through a PresepC-Agri (C_{18}) cartridge (Wako, Japan)

Table 3.2 Type of samples and information of the sampling sites in Da Nang

Sample type	Sample No.	Site name
Tap water	TW1	Lien Chieu District, Hoa Ninh Ward
	TW2	Ngu Hanh Son Distric, Khue My Ward
	TW3	Thanh Khe District
	TW4	Hai Chau District
	TW5	Cam Le District, Cam Le Ward
Surface water	SW1	Cu De River (water source for WTP)
	SW2	Cau Do River (water source for WTP)
	SW3	Thac Gian Lake
	SW4	Vinh Trung Lake
	SW5	29/3 Lake
	SW6	29/3 Lake
	SW7	Xuan Hoa Lake (Northern part of DaNang Airport)
	SW8	Xuan Hoa Lake (Southern part of DaNang Airport)
	SW9	Phu Loc River Estuary
	SW10	Phu Loc River (Near discharge point of March 29 Textile-Garment JSC
	SW11	Do Xu Lake: Do Xu Bridge
	SW12	Do Xu Lake: midle of lake
	SW13	Bau Tram River: Near discharge point of Hoa Khanh Industrial WWTP
	SW14	Au Thuyen -Tho Quang River: Near Thuan Phuoc Fishing port
	SW15	Au Thuyen -Tho Quang River: Near May Quang Bridge
	SW16	Cau Trang River:Near discharge point of Lien Chieu Industrial WWTP
	SW17	Cu De River Estuary
	SW18	Downstream Co Co River
Wastewater	WW1	Phu Luc Domestic WWTP: input wastewater
	WW2	Phu Luc Domestic WWTP: treated wastewater
	WW3	Hoa cuong Domestic WWTP: input wastewater
	WW4	Hoa Cuong Domestic WWTP: treated wastewater
	WW5	Hoa Khanh industrial WWTP: treated wastewater
	WW6	Hoa Khanh industrial WWTP: discharge chanel
	WW7	Tho Quang Industrial WWTP: Input wastewater
	WW8	Tho Quang Industrial WWTP: treated wastewater
	WW9	Leachate in New Khanh Son's Landfill
	WW10	Leachate iffluent in New Khanh Son's Landfill
	WW11	Treated leachate in New Khanh Son's Landfill

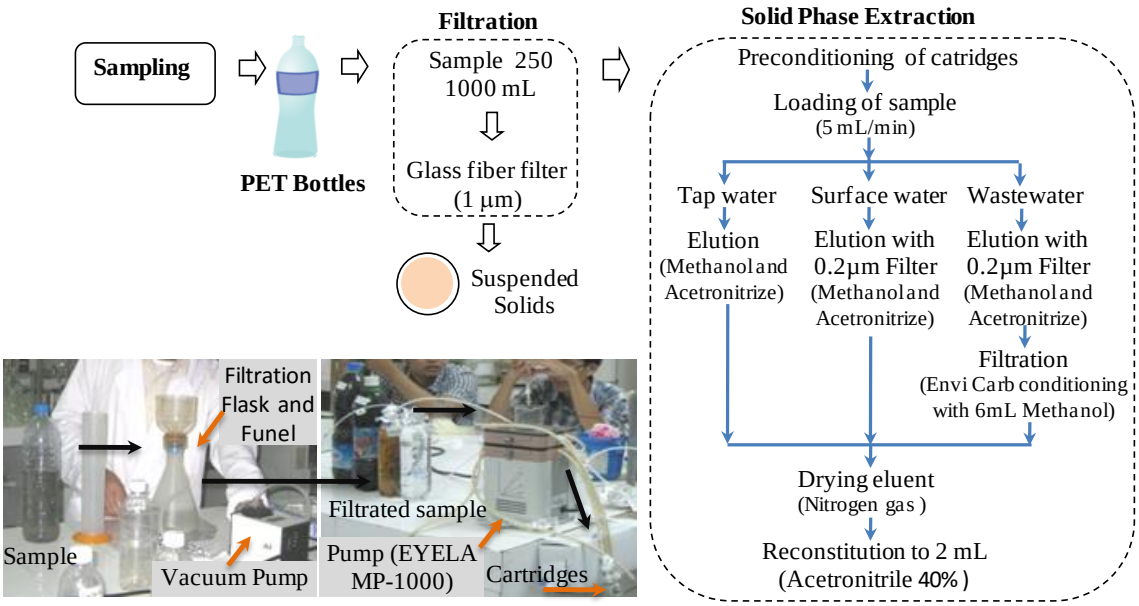


Figure 3.2 Procedure for sample treatment

connected with Oasis®HLB (Water, Japan). The cartridges that were used for loading were preconditioned with 10 mL of methanol followed by 20 mL de-ionized water manually. The filtered samples were loaded onto two cartridges at 5 mL/min. The concentrator pump was pre-washed with methanol for 5 min at 5 mL/min followed by ultrapure water for 15 min at 10 mL/min before concentrating each sample.

The above procedures were conducted in Da Nang and all the cartridges were brought back to Japan for further treatment and analysis. In Japan, the cartridges were dried in a vacuum manifold (Water, USA) for two hours. The target compounds in the dry cartridges were eluted by 2 mL methanol (LC/MS grade) followed by 2 mL of acetonitrile into a PP tube. They were then evaporated until dry using nitrogen gas and then, reconstituted with 2–10 mL of 40% acetonitrile in ultrapure water, which was analysed by HPLC-MS/MS. PFCs in the filtrates were concentrated by a factor of 25–500 times.

3.3.4 Analytical techniques using HPLC-MS/MS

Separation of the PFCs was performed using Agilent 1200SL high performance liquid chromatography (HPLC), (Agilent, Japan). Ten µL of the extracted sample was injected to a 2.1 × 100 mm (5 µm) Agilent Eclipse XDB-C18 column. The mobile phase consisted of (A) 5 mM ammonium acetate in ultrapure water (LC/MS grade) and (B) 100% acetonitrile (LC/MS grade). At a flow rate of 0.25 mL/min, the separation process began with initial conditions of 30% (B), which was increased to 50% (B) at 16.5 min, then went to 70% (B) at 16.6, was held at 70% (B) for 3.4 min, then went up to 90% (B) at 21 min, and finally was kept at 90% (B) for 1 min, for each sample. The mass spectrometer was operated in the electrospray ionization (ESI) negative mode. The analyte ions were monitored by using the multiple reactions monitoring (MRM) mode.

The calibration curves for quantification, consisted of six points ranging from 0.05 to 10 µg/L. The determination coefficient (R^2) of the linear calibration curve was more than 0.99. Limit of detection (LOD) was defined as the concentration with signal to noise ratio (S/N) 3:1. Limit of quantification (LOQ) defined as 10:1 of *S/N*, was used for quantifying the analytes. The analysis was replicated on all samples and the coefficients of variations (CV) of concentrations were below 20%.

3.4 Results and discussion

3.4.1 PFCs concentration in tap water

Several types of PFCs were found in most tap water samples in Da Nang. The PFCs concentrations of five sampling points are shown in **Table 3.3**.

The total PFC concentration in tap water samples was found to be 110.8 ng/L. The total PFC concentration in five samples ranged from 1.2 to 52.0 ng/L. Among five tap water samples, TW1 (52.0 ng/L) had the highest PFCs concentration followed by TW5 (37.2 ng/L), TW2 (8.0 ng/L), TW3 (3.3 ng/L), and TW4 (1.2 ng/L). PFOA was predominant and it`s concentration ranged from 1.7 to 40.3 ng/L.

Table 3.3 Concentrations of PFCs (ng/L) in tap water in Da Nang

Type of PFCs	PFCs concentration, ng/L					Average concentration, ng/L
	TW1	TW2	TW3	TW4	TW5	
PFPeA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ
PFHxA	0.3	<LOQ	<LOQ	<LOQ	3.8	0.8
PFHpA	3.0	0.0	0.2	<LOQ	2.0	1.0
PFOA	40.3	1.9	1.7	<LOQ	12.9	11.4
PFNA	2.7	0.7	0.9	1.0	1.5	1.4
PFDA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ
PFUnDA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ
PFDoDA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ
PFBuS	2.4	3.4	N.D	N.D	3.6	1.9
PFHS	0.5	0.2	<LOQ	<LOQ	0.5	0.3
PFOS	2.7	1.7	0.4	<LOQ	3.7	1.7
Total PFCs, ng/L	**52.0**	**8.0**	**3.3**	**1.2**	**27.9**	**18.5**

3.4.2 PFCs concentration in surface water

Several types of PFCs were found in most of the samples. PFCs concentration in the lakes and rivers (n = 18) of Da Nang are shown in **Table 3.4**. Total PFCs concentration was 492.2 ng/L. The high PFCs concentration was found at SW8 (132.2 ng/L) followed by SW7 (126.7 ng/L) and SW17 (65.1 ng/L). Other sampling points had a PFCs concentration of lower than 50 ng/L. Among the investigated PFCs, PFOA (304.6 ng/L) was found as the highest concentration, following by PFPA (69.8 ng/L), PFHxS (43.9 ng/L), and PFBuS (39.3 ng/L). Other PFCs had concentrations less than 15 ng/L. The results also showed that concentration of PFCA (396 ng/L) was much higher than the concentration of PFAS (96 ng/L).

Table 3.4. Concentrations of PFCs (ng/L) in surface water in Da Nang

Sampling point	PFCs concentration, ng/L											Total, ng/L
	Perfluorocarboxylate (PFCA)								Perfluoroalkyl sulfonate (PFAS)			
	PFPA C5-A	PFHxA C6-A	PFHpA C7-A	PFOA C8-A	PFNA C9-A	PFDA C10-A	PFUnDA C11-A	PFDoDA C12-A	PFBuS C4-S	PFHxS C6-S	PFOS C8-S	
SW1	< *LOQ*	< *LOQ*	1.5	3.1	< *LOQ*	< *LOQ*	< *LOQ*	< *LOQ*	2.1	0.7	< *LOQ*	7.6
SW2	*N.D.*	*N.D.*	< *LOQ*	< *LOQ*	*N.D.*	<LOQ	< *LOQ*	< *LOQ*	*N.D.*	*N.D.*	< *LOQ*	0.2
SW3	< LOQ	< *LOQ*	<LOQ	1.1	*N.D.*	<LOQ	< *LOQ*	< *LOQ*	*N.D.*	*N.D.*	< *LOQ*	1.3
SW4	1.1	*N.D.*	1.3	19.8	*N.D.*	0.1	< *LOQ*	< *LOQ*	4.5	0.9	3.8	31.6
SW5	0.1	*N.D.*	<LOQ	0.1	*N.D.*	<LOQ	< *LOQ*	< *LOQ*	2.5	0.6	< *LOQ*	3.4
SW6	14.8	< *LOQ*	0.9	6.5	< *LOQ*	1.7	< *LOQ*	< *LOQ*	2.2	0.1	< *LOQ*	26.3
SW7	7.2	< *LOQ*	1.4	99.5	< *LOQ*	0.1	< *LOQ*	< *LOQ*	0.6	15.1	2.6	126.7
SW8	8.2	0.2	1.8	104.5	< *LOQ*	< *LOQ*	< *LOQ*	< *LOQ*	0.7	15.1	1.6	132.2
SW9	14.2	< *LOQ*	< *LOQ*	2.3	< *LOQ*	< *LOQ*	< *LOQ*	< *LOQ*	4.7	3.1	< *LOQ*	24.6
SW10	15.5	< *LOQ*	< *LOQ*	2.4	< *LOQ*	< *LOQ*	< *LOQ*	< *LOQ*	4.9	3.0	< *LOQ*	26.0
SW11	2.8	< *LOQ*	0.4	3.7	< *LOQ*	< *LOQ*	< *LOQ*	< *LOQ*	5.1	1.3	0.2	13.5
SW12	1.6	< *LOQ*	0.9	5.9	0.1	0.1	< *LOQ*	< *LOQ*	1.5	1.2	0.9	12.3
SW13	< *LOQ*	*N.D.*	< *LOQ*	0.3	*N.D.*	< *LOQ*	< *LOQ*	< *LOQ*	0.1	0.0	< *LOQ*	0.5
SW14	<LOQ	*N.D.*	< *LOQ*	< *LOQ*	*N.D.*	< *LOQ*	< *LOQ*	< *LOQ*	0.3	< *LOQ*	< *LOQ*	0.5
SW15	< *LOQ*	< *LOQ*	1.0	< *LOQ*	< *LOQ*	< *LOQ*	< *LOQ*	< *LOQ*	2.5	0.7	1.2	5.6
SW16	*N.D.*	< *LOQ*	0.4	< *LOQ*	*N.D.*	< *LOQ*	< *LOQ*	< *LOQ*	7.2	1.9	0.8	14.6
SW17	< *LOQ*	< *LOQ*	3.7	55.4	4.5	0.1	< *LOQ*	< *LOQ*	*N.D.*	< *LOQ*	1.3	65.1
SW18	< *LOQ*	*N.D.*	< *LOQ*	< *LOQ*	*N.D.*	<LOQ	< *LOQ*	< *LOQ*	0.1	< *LOQ*	< *LOQ*	0.3
Total , ng/L	**69.8**	**0.6**	**13.7**	**304.6**	**4.9**	**2.4**	**0.2**	**0.2**	**39.3**	**43.9**	**12.6**	**492.2**

3.4.3 PFCs in domestic wastewater treatment plants

Several types of PFCs were found in samples from DWWTPs. PFC concentration in the influent (n = 1) and effluent (n = 1) of two DWWTPs are shown in **Table 3.5**.

The total PFC concentration in influents ranged from 27.6 to 166 ng/L while PFCs concentrations in effluents were from 42.6 to 53.3 ng/L. Hoa Cuong DWWTP (52.3 ng/L) had higher PFC concentration in the effluent. PFOA, PFHxS, and PFBuS were predominant and their concentrations were high in both the influent and effluent.

The concentration levels of other PFCs were mostly lower than PFOA, PFHxS, and PFBuS. Increase in short carbon-chain PFCs such as PFHxS and PFBuS concentration

Table 3.5 Concentrations of PFCs (ng/L) in two DWWTPs in Da Nang

Sampling site	Sample type /Sample code	PFCs concentration, ng/L											
		PFPeA C5-A	PFHxA C6-A	PFHpA C7-A	PFOA C8-A	PFNA C9-A	PFDA C10-A	PFUnDA C11-A	PFDoDA C12-A	PFBuS C4-S	PFHxS C6-S	PFOS C8-S	Sum of PFCs
Phu Loc DWWTP, n = 1	Influent (WW1)	<LOQ	<LOQ	0.8	18.6	<LOQ	<LOQ	<LOQ	<LOQ	22.1	43.2	3.5	27.6
	Effluent (WW2)	<LOQ	<LOQ	0.8	21.8	<LOQ	<LOQ	<LOQ	<LOQ	11.3	5.5	<LOQ	42.6
Hoa Cuong DWWTP, n = 1	Influent (WW3)	<LOQ	83.1	14.2	55.5	4.9	<LOQ	<LOQ	<LOQ	6.6	1.5	<LOQ	166.0
	Effluent (WW4)	<LOQ	<LOQ	1.2	31.1	<LOQ	<LOQ	<LOQ	<LOQ	18.5	1.3	<LOQ	52.3
New Khanh Son's Landfill, n = 1	Leachate (WW9)	<LOQ	<LOQ	2.6	45.1	6.2	1.6	1.7	<LOQ	134.9	7.7	<LOQ	199.8
	Leachate + Septic Wastewater (WW10)	<LOQ	<LOQ	22.7	254.6	21.9	19.7	4.0	<LOQ	179.5	11.7	1.9	516.1
	Treated leachate (WW11)	N.D.	1.4	4.9	38.2	2.5	0.6	0.4	<LOQ	23.4	2.4	1.2	75.0

in wastewater was due to substitution for PFOS. In addition, samples from landfill site were collected to assess the possible source of PFCs from domestic activities. **Table 3.5** shows the PFCs in leachate, mixture of leachate and septic wastewater and treated effluent from landfill site. Total PFCs concentrations were 200 ng/L, 516 ng/L, and 75 ng/L, respectively.

Since PFCs in domestic wastewater and treated effluent from landfill site were detected, the current wastewater treatment processes were not been able to remove the PFCs completely. PFCs have been used in several products, including protective coatings for food packaging, textiles, carpets, paper, coats, fabrics, leather, and non-stick cooking material (Giesy and Kannan 2002). Daily domestic activities using PFC-containing products could be possible sources of PFCs in DWWTP and landfill sites. Therefore, DWWTPs and landfill sites have the potential of the sources of PFCs contamination in water environment.

3.4.4 PFC contamination in industrial wastewater

Industrial wastewater is the major source of PFCs discharged into the water environment. In Da Nang, there are many industries which are located in particular areas called industrial zones (IZ). All industries discharge wastewater into the central WWTP in IZ. In this study, two IWWTPs which have not reported PFC concentrations were selected. Influent and effluent of each IWWTP was collected to examine the

removal of PFCs in wastewater treatment process. All PFCs were detected in most samples above *LOQ* except for PFDoDA.

Table 3.6 shows PFCs concentration of each IWWTP. Total PFCs concentration in effluent of Tho Quang IWWTP was 72.6 ng/L, which was lower than influent (152 ng/L). The same total PFCs concentration was found in the effluent of Hoa Khanh IWWTP (42.1 ng/L). However, our survey in the Khoa Khanh IZ showed that total PFCs concentration in effluent of IWWTP (42.1 ng/L) was seven times smaller than the samples collected from the discharging channel of this IZ (191 ng/L). This result indicated that some factories located in site Hoa Khanh' IZ were discharging their wastewater, which contained high PFCs concentrations, into the discharging channel without going to the central WWTP of IZ.

Table 3.6 Concentrations of PFCs (ng/L) influent and effluent from IWWTPs

Sampling site	Type of sample (Sample code)	PFCs concentration, ng/L											
		PFPeA C5-A	PFHxA C6-A	PFHpA C7-A	PFOA C8-A	PFNA C9-A	PFDA C10-A	PFUnDA C11-A	PFDoDA C12-A	PFBuS C4-S	PFHxS C6-S	PFOS C8-S	Sum of PFCs
Hoa Khanh IWWTP, n = 1	Effluent (WW5)	<LOQ	17.9	3.7	15.4	1.5	0.3	0.2	<LOQ	2.7	0.3	<LOQ	42.1
	Discharge channel (WW6)	0.6	19.5	6.6	41.8	7.6	0.7	0.3	<LOQ	5.6	0.4	209.4	292.4
Tho Quang IWWTP, n = 1	Influent (WW7)	<LOQ	5.6	9.3	153.7	7.4	0.5	0.8	<LOQ	54.2	1.7	19.2	252.5
	Efluent (WW8)	1.5	0.1	2.3	53.2	4.4	0.4	0.6	<LOQ	5.4	3.4	1.2	72.6

3.5 Summary

PFCs concentrations were investigated in tap water, river and lake water, two domestic and two industrial WWTPs, and landfill sites in Da Nang.

1. Among five tap water samples, TW1 (52.0 ng/L) had the highest PFCs. PFOA was predominant and it`s concentration ranged from 1.7 to 40.3 ng/L.
2. Among 18 surface water samples, SW8 had the highest concentration (132.2 ng/L) followed by SW7 (126.7 ng/L). The major PFCs were PFOA (304.6 ng/L), PFHpA (69.8 ng/L), PFHxS (43.9 ng/L), and PFBuS (39.3 ng/L).
3. PFCs were found in two DWWTPs (Phu Loc and Hoa Cuong), two IWWTPs (Hoa Khanh and Tho Quang) and at a landfill site (Khanh Son). Highest PFC

concentration was founded at the landfill site. The major PFC contaminations in the effluent were PFOA, PFHpA, PFBuS, and PFHxS

4. Wastewater treatment facilities at the WWTPs were not able to completely remove PFCs present in the wastewater. Therefore, effective removal techniques should be applied to minimize environmental impact.
5. High PFCs (292 ng/L) found in the discharging channel of IZ indicates the limitations in the management of industrial wastewater in IZ.

Chapter 4 Development of a possible method for the decomposition of PFCAs by continuous experiment

4.1 Introduction

UV photolysis had shown great potential in the decomposition of PFCs by breaking C-F bonds present in these compounds. Hori *et al.* (2004) have reported on the decomposition of aqueous PFOA (560 mg/L, 22 mL) under irradiation of 254 nm UV light (200W Xe-Hg lamp, 4.8 atm of O_2). Under these conditions, 44.3% of initial PFOA degraded after 24 h of irradiation and 89.5% after 72 h. Furthermore, PFOA decomposed faster under irradiation of VUV light. Chen *et al.* (2006) showed that 61.7% of initial PFOA (25 mg/L, 800 mL, pH 3.7, 40 °C) decomposed after 2 h of irradiation with a UV lamp which mainly emitted 254 nm light with a small amount of 185 nm light (15 W, N_2). However, these studies were conducted under batch conditions with high volumes of samples (22–3000 mL), and long irradiation times (2–72 h). Therefore, a system for the decomposition of PFCAs under continuous conditions using small volume of samples and short irradiation times was sought to be developed.

In this chapter, we focused on the application of UV irradiation in the decomposition of PFCAs by continuous experiments. The main objective was to study the effects of irradiation times and wavelengths on the decomposition of PFOA and PFNA dissolved in *Milli-Q* water at a concentration of 10 μg/L.

4.2 Materials and methods

4.2.1 Materials

PFOA (>95%) was purchased from Wako Pure Chemical Industries (Osaka, Japan). PFNA (>95%) was purchased from TCI (Tokyo Chemical Industry), Japan. Standard PFC solutions were obtained from Wellington Laboratories, Canada, with purities of more than 99%. PFCs stock solutions were prepared by dissolving the single standard PFC into acetonitrile (LC/MS grade) and storing in polypropylene (PP) bottles at 4 ºC.

PFC standard solutions were prepared by diluting different volumes of the single stock solutions together into 40% acetonitrile solvent.

4.2.2. Apparatus

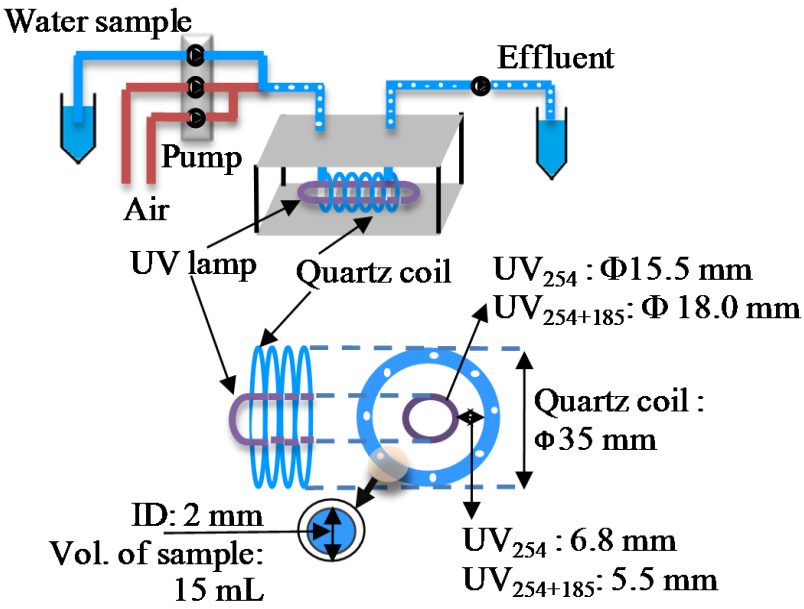


Figure 4.1 Schematic view of the apparatus system

A schematic diagram of the apparatus system is illustrated in **Fig. 4.1**. Two modules of Auto Analyzer 3 (BLTEC Ltd., Japan): UV reactor and peristaltic pump were used. Two types of lamps were used: One mainly emitted 254 nm UV light (8W, GL-8, Panasonic Co., hereafter referred to as UV_{254}), while the other emitted mainly 254 nm and a small amount (1%) of 185 nm UV light (6 W, UL0-6DQ, Ushio Co., hereafter referred to as $UV_{254+185}$). The lamp was placed in the centre of the quartz coil (external diameter 35 mm) in the apparatus.

4.2.3. Experimental conditions

Stock solutions of single standard PFCAs (PFOA, PFNA) were used for preparing sample solutions at concentrations of 10 μg/L in *Milli-Q* water for the photodecomposition experiments. All polypropylene (PP) tubes were rinsed three times with methanol and dried prior to use. Pump tubes were rinsed using 30 mL of methanol

followed by 50 mL of *Milli-Q* water before being used to minimize PFC background contamination.

Sample solutions were pumped continuously through the quartz coil. The sample solutions were irradiated and heated at different time intervals of 10 min, 20 min, 30 min, and 60 min by controlling the changing of pump tubes with different diameters. The reaction temperature was maintained at 65 °C. The pH values of the sample solutions were not adjusted in any of the cases.

4.2.4. Sample pre-treatment

The collected effluent (2 mL) after UV decomposition was loaded onto two cartridges (PresepC-Agri and Oasis®HLB), which were used for concentrating the PFCs at a flow rate of 5 mL/min (Kunacheva *et al.* 2009). The cartridges were pre-conditioned using 10 mL of methanol (LC/MS- grade) followed by 2×10 mL of *Milli-Q* water prior to use. The cartridges were dried for one hour and were eluted with 2 mL methanol and 2 mL acetonitrile (LC/MS-grade). The elutes were evaporated to dryness with nitrogen gas and were reconstituted using 40% LC/MS-grade acetonitrile to a final volume of 2 mL.

4.2.5. Sample analysis

Separation of the PFCs was performed by using Agilent 1200SL high-performance liquid chromatography (HPLC), (Agilent, Japan). 10 µL of the analyte was injected into a 2.1×100 mm (5 µm) Agilent Eclipse XDB-C18 column. The mobile phase consisted of (A) 5 mM ammonium acetate in ultrapure water and (B) 100% acetonitrile (LC/MS grade). The flow rate was 0.25 mL/min. For quantitative determination, the HPLC was interfaced with an Agilent 6400 Triple Quadrupole (Agilent, Japan) mass spectrometer (MS/MS) which was operated in multimode with electrospray ionization (MMI-ESI) negative ionisation. The total running time was 34 min for each sample.

4.3 Results and Discussion

4.3.1 Photodecomposition of PFOA

The decomposition rates of PFOA (10 μg/L) under four different irradiation times (10, 20, 30, and 60 min) and two types of UV lamps are shown in **Fig. 4.2(a)**.The decomposition rate was 0% after 10, 20, and 30 min irradiation in case of UV_{254} light. Nearly 96% of PFOA was decomposed at 60 min of irradiation. However, PFOA was decomposed faster under irradiation of $UV_{254+185}$ light. As shown in **Fig. 4.2(a)**, 76% of PFOA was decomposed after 10 min of irradiation. The decomposition amount increased to 78%, 94%, and 100% corresponding to 20, 30, and 60 min of irradiation, respectively. This decomposition of PFOA is explained by the ability of UV light to excite PFOA, leading to the cleavage of the C-C or C-F bonds (Chen *et al.*, 2007, Hori *et al.*, 2004) in the molecule.

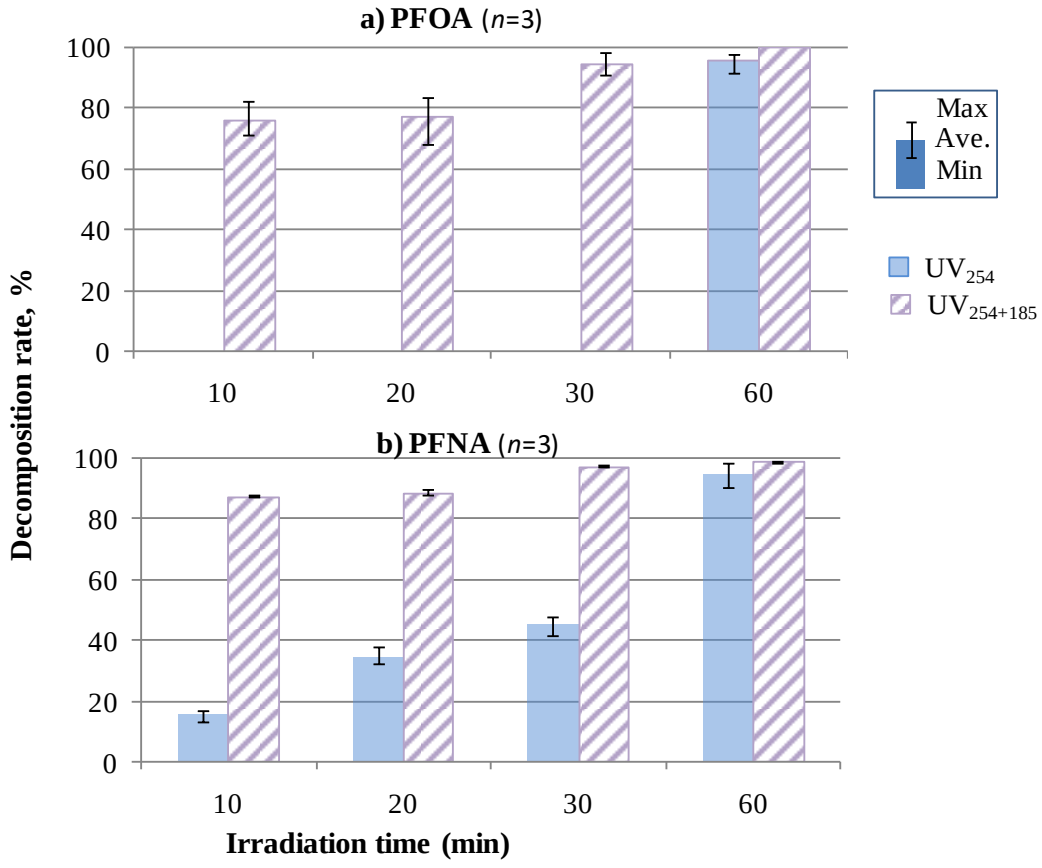


Figure 4.2 Decomposition rates of PFOA and PFNA under UV_{254} and $UV_{254+185}$

Decomposition rates of PFOA are similar to those reported by Hori *et al.* (2004) and Chen *et al.* (2007). Under irradiation of UV_{254} (200 W), 44% of initial PFOA (560 mg/L, 22 mL) was decomposed after 24 h and 89% after 72 h. In the case of $UV_{254+185}$ (15W), 61.7% of initial PFOA (25 mg/L, 800 mL, pH 3.7, 40 °C) was decomposed after 2 h. However, the decomposition rates of PFOA in our research were significantly higher than theirs. The higher decomposition rates were explained based on the low initial concentration of PFOA (10 μg/L) and low sample flow rates (0.1–0.32 mL/min) in our studies.

4.3.2 Photodecomposition of PFNA

Figure 4.2(b) shows the decomposition rates of PFNA (10 μg/L) under four different irradiation intervals (10, 20, 30, and 60 min) and two types of UV lamps. Under

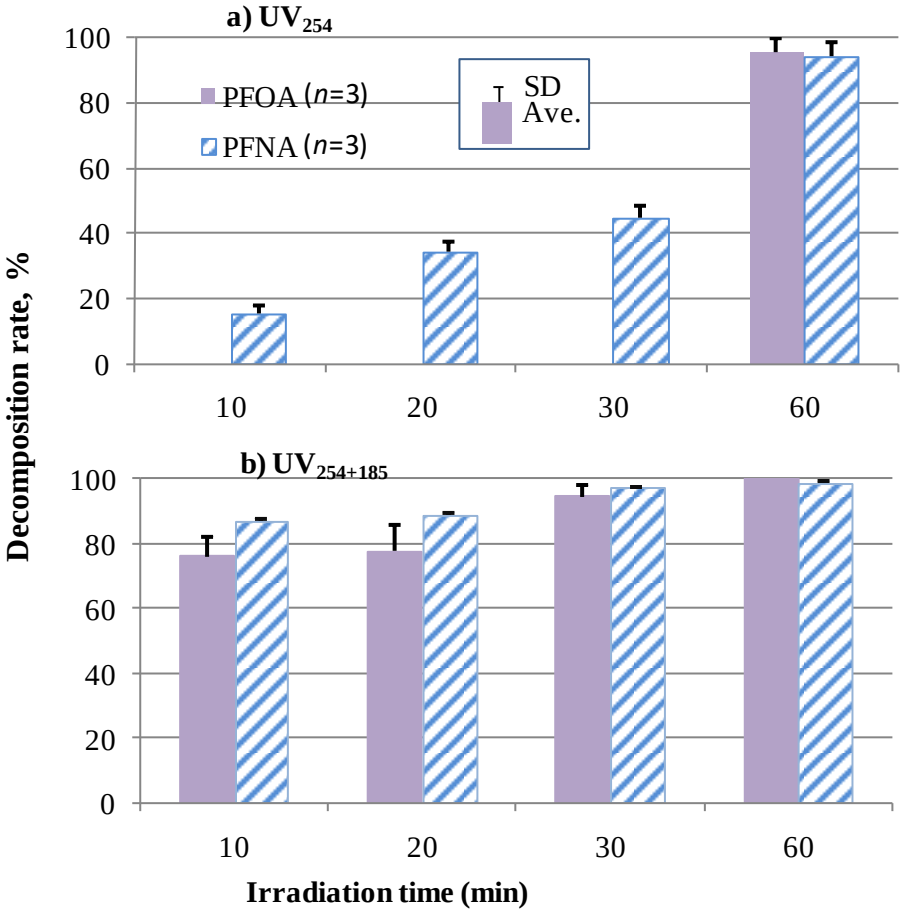


Figure 4.3 Comparison of the decomposition rates of PFOA and PFNA under UV_{254} and $UV_{254+185}$ light irradiation

irradiation of UV_{254} light, the decomposition rates were 16%, 34%, 45%, and 94% corresponding to 10, 20, 30, and 60 min of irradiation, respectively. Under irradiation of $UV_{254+185}$ the decomposition rates of PFNA showed a tendency similar to the case of PFOA. As shown in **Fig. 4.2(b)**, 87% of PFNA was decomposed after 10 min of irradiation. The decomposition rate increased to 89%, 97%, and 99% corresponding to 20, 30, and 60 min of irradiation, respectively.

Figure 4.3 shows a comparison of the decomposition rates among targeted PFCs under two different types of UV lamps. Higher decomposition rates of PFOA and PFNA were observed under irradiation of $UV_{254+185}$ light in comparison with those of UV_{254} light. These results seem to indicate that the energy of $UV_{254+185}$ were higher than that of UV_{254} and thus more effective for decomposition of PFCs.

4.4 Summary

The possibility of decomposition of PFOA and PFNA by continuous experiments was shown in this study. The decomposition experiments were conducted under irradiation of UV light. It was observed that, the target PFCs were decomposed faster under irradiation of $UV_{254+185}$ light in comparison to UV_{254}. The results showed that 100% of PFOA was decomposed under irradiation of $UV_{254+185}$ light in 60 min. Under the same conditions of 60 min irradiation, lower decomposition rates were observed in the case of PFNA (99%).

Chapter 5 Development of a continuous analytical system for the decomposition of PFCAs and the quantification of released fluoride by a colorimetric method. Effects of experimental conditions for PFCA decomposition

5.1 Introduction

In the previous chapter, a possible continuous system was developed for the decomposition of PFCAs. The experimental system consisted of a UV/heating unit (glass coils, UV lamp, heater), and a peristaltic pump. Irradiated effluents were collected for PFCA analysis by HPLC-MS/MS. The decomposition rates of PFCAs were 100% for PFOA and 99% for PFNA in 60 min under irradiation of $UV_{254+185}$ light. In this chapter, we continue to develop a system which combines the on-line decomposition of PFCAs, fluoride separation, and spectrophotometric detection for the continuous quantification of these compounds. The studied experimental conditions were first focused on the effects of acid (H_2SO_4) and oxidant ($K_2S_2O_8$) concentrations. Since the concentration of $K_2S_2O_8$ (0.16 mol/L) used in this study was the maximum possible, the effects its concentration on PFCA decomposition should be studied to optimise the amount of $K_2S_2O_8$ which should be used for the decomposition of PFCAs at different concentrations

Previous reports have dealt with batch experiments on heat-activated persulfate oxidation (20–150 °C) (Hori *et al.* 2008, Lee *et al.* 2009, Lee *et al.* 2012) or photo-activated persulfate oxidation on PFCAs (Hori *et al.* 2007). However, there are no reports on the combined effects $UV_{254+185}$ and heating temperature on the continuous decomposition of PFCAs. Therefore, this chapter focused on the effects of temperature combined with $UV_{254+185}$ irradiation on the decomposition rates of PFCAs.

Three-way analysis of variances (ANOVA) with interaction methods were applied to assess the contributions of H_2SO_4, $K_2S_2O_8$, types and concentration of PFCAs, and heating temperature, as well as the combined effects of these factors on the

decomposition rates of PFCAs. The results reported here are important for selecting the optimum experimental conditions for this process.

The objectives of this study were:

1. To develop a feasible experimental system for the continuous decomposition of PFCAs and the quantification of released fluoride by a colorimetric method.
2. To study the effects of acid (H_2SO_4) and oxidant ($K_2S_2O_8$) concentrations.
3. To study the effects of PFCAs concentrations.
4. To study the effects of temperature in the UV/heating unit

5.2 Materials and methods

5.2.1 Materials

All chemicals used were of analytical reagent grade. PFCAs (PFBA, PFPA, PFHxA, PFHpA, PFOA, and PFNA) were purchased from Wako Pure Chemical Industries (Osaka, Japan) and TCI (Tokyo Chemical Industry), Japan. PFCA stock solutions were prepared by dissolving single standard PFCA into *Milli-Q* water and storing in polypropylene (PP) bottles at 4 ºC. Standard fluoride (NaF) was purchased from Wako Pure Chemical Industries (Osaka, Japan). The working standard solutions were prepared by dissolving the standard solution with *Milli-Q* water. The decomposition reagent was prepared by dissolving $K_2S_2O_8$ and H_2SO_4 in *Milli-Q* water. A mixture of 15% (v/v) sulphuric acid and 0.1 mg/L fluoride was used as the distillation solution. The absorption reagent was prepared by adding 3.4 g of imidazole to 100 mL of *Milli-Q* water and 10 mL of acetic acid. The solution was made up to 1000 mL with *Milli-Q* water and then 10 mL solution of tritonX-100 and ethanol (50% v/v) was added. The colour reagent was prepared by mixing together 10 g of alfusone, 155 mL of acetic acid, 38.5 g of imidazole, and 480 mL of acetone. The solution was made up to 1000 mL with *Milli-Q* water to which a 25 mL solution of triton X-100 and ethanol (50% v/v) was added.

5.2.2 Apparatus and procedure

Initially, we developed the experimental system for the continuous decomposition of PFCAs and the quantification of fluoride released from the PFCAs. The original system is shown in **Fig. 5.1**. The system consisted of five parts: an auto sampler, a decomposition unit, a distillation unit, a detection unit and a peristaltic pump. The RAS-8000 auto sampler was controlled by software which enables an automatic sampling mode. The decomposition unit (UV/heating unit) consisted of a UV lamp which emitted mainly 254 nm with a small amount (1%) of 185 nm UV light (6 W, UL0-6DQ, Ushio Co., hereafter referred to as $UV_{254+185}$), a heater and a quartz coil (internal diameter 2 mm, volume 15 mL). The distillation unit consisted of a heater, an oil bath, a heating glass coil and cooling units. The detection unit consisted of a reaction coils, a colorimeter with a flow cell (30 mm path length) and a wavelength filter (620 nm). The change in the absorbance at 620 nm was measured by the spectrophotometer. The signal was recorded using a data-processing computer with ACCE software. The system was operated using a peristaltic pump and its several flow rates were adjusted with calibrated pump tubes having different diameters (Tab. 5.1).

In this system, the sample and together with the decomposition reagent were continuously pumped through an analytical manifold with a flow rate of 0.16 mL/min. The reaction stream was then made to flow sequentially to the UV/heating unit for breaking up the C-F bonds of PFCAs, and then to the distillation unit (150 °C) to recover fluoride, followed by the colorimetric unit for fluoride detection. The heating temperature in the UV/heating unit was maintained at 65 °C. The time for heating and irradiation was identified based on time of mixture of sample and decomposition reagent going in and out from the UV/heating unit.

We then proceeded to study the experimental conditions for the decomposition of PFCAs using our experimental system (Tab. 5.2). The experimental conditions were as follows:

(1) Study on effects of H_2SO_4 and $K_2S_2O_8$ concentrations:

This study used 42 (6 × 7) different concentrations of the decomposition reagent. Six levels of H_2SO_4 (0, 0.02, 0.1, 0.4, 1.0, and 2.0 mol/L) and seven levels of $K_2S_2O_8$ (0, 0.01, 0.02, 0.04, 0.08, 0.12, and 0.16 mol/L) were used to assess their effects on the breaking of C-F bonds of six PFCAs (3 mg/L).

(2) Study on the effects of PFCA concentrations:

This study used four (1 × 4) different conditions for the decomposition reagent: One level of H_2SO_4 (0.4 mol/L) and four levels of $K_2S_2O_8$ (0.02, 0.04, 0.08, and 0.16 mol/L) to investigate their effects on the breaking of C-F bonds in the

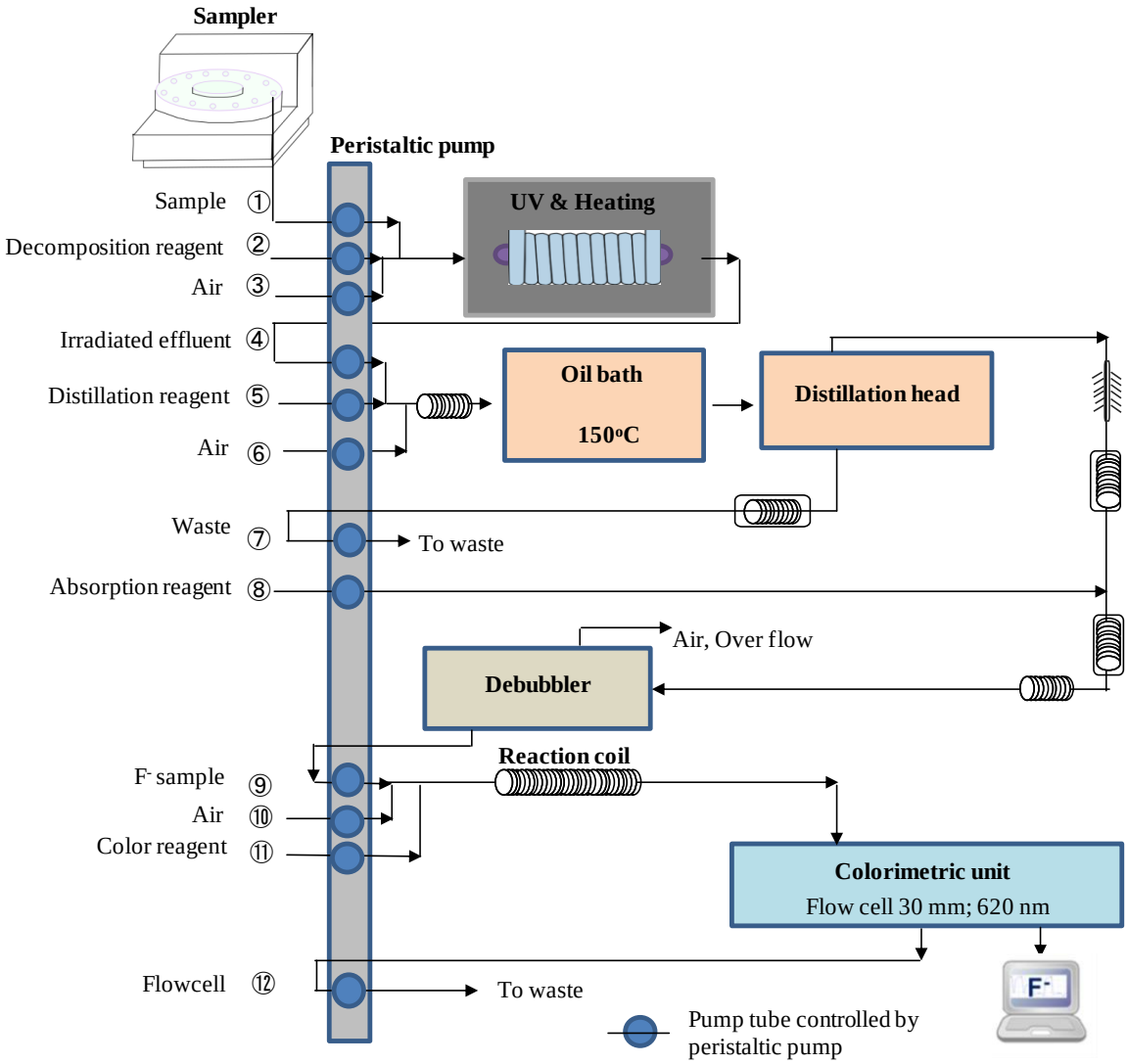


Figure 5.1 Experimental setup for the continuous flow analysis of PFCAs by a colorimetric method

PFCAs (3, 4, 5, 6, and 10 mg/L).

(3) A study of the effects of temperatures on the decomposition.
This study used six different temperatures (55, 60, 65, 70, 75, and 80 °C) to investigate its effect on the breaking of C-F bonds in the PFCAs (3 mg/L).

Figure 5.2 shows the sample procedure for one experiment in this research. A primer sample was entered at the beginning of each tray protocol with the same concentration the highest concentration of the standards. A drift standard is a solution of known concentration and was used to measure and correct the sensitivity drift. Since pump tubes were heating up during the operation and their flow rate fell slightly, a small increase in reaction time was observed. To correct for this drift and baseline samples were added. In this research, we selected a sampling time of 6 min and the interval time (washing time) was 4 min which would help to reduce the carryover.

Fluoride standards (0.5–4.0 mg/L) were measured in every run under the same conditions as the samples for the calculation of recovery fluoride concentration. The decomposition rates of these PFCAs were calculated using a comparison of the concentration of recovered fluoride with the theoretical fluoride contained in the PFCA samples (Eqn. 5.1).

$$\text{Decomposition rate} = (C/C_0) \times 100 \quad (5.1)$$

where C denotes the measured F^- concentration (mg/L) and C_0 denotes the theoretical F^- concentration (mg/L) in the case where 100% of the PFCAs was decomposed.

For all the cases, the temperature of the UV/heating unit was controlled at 65 °C.

Table 5.1 Theoretical flow rates of pump tubes

Tube name	Tube number	Theoretical flow rate, mL/min	Pump tube material
Sample	①	0.16	Solvaflex
Decomposition reagent	②	0.16	Tygon
Air	③	0.05	Tygon
Irradiated effluent	④	0.60	Solvaflex
Distillation reagent	⑤	0.05	Tygon
Air	⑥	0.42	Tygon
Waste	⑦	0.42	Tygon
Absorption reagent	⑧	2.50	Tygon
F- sample	⑨	0.32	Tygon
Air	⑩	0.32	Tygon
Color reagent	⑪	0.60	Silicon
Flowcell	⑫	0.32	Solvaflex

Table 5.2 General experimental conditions for the determination of fluoride obtained from the decomposition of PFCAs

Paramerters		Effect of acid and oxidant concentration	Effect of PFCAs concentration	Effect of heating temperature
Sample type: PFCAs/*MilliQ*		PFCAs (PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA): 3 mg/L	PFCAs (PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA) : 3; 4; 5; 6; 10 mg/L	PFCAs (PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA): 3 mg/L
Decomposition reagents	H_2SO_4	0; 0.02; 0.1; 0.4; 1; 2 mol/L	0.4 mol/L	
	$K_2S_2O_8$	0; 0.01; 0.02, 0.04, 0.08, 0.12, 0.16 mol/L	0.02; 0.08; 0.12; 0.16 mol/L	0.04; 0.08; 0.12; 0.16 mol/L
UV lamp		254 nm (mainly), 185 nm (1%), 6W		
Heating temperature		65 ^oC		55; 60; 65; 70; 75; 80 ^oC
Sampling time		6 minutes		
Interval time		4 minutes		
Distillation temperature		150 ^oC		

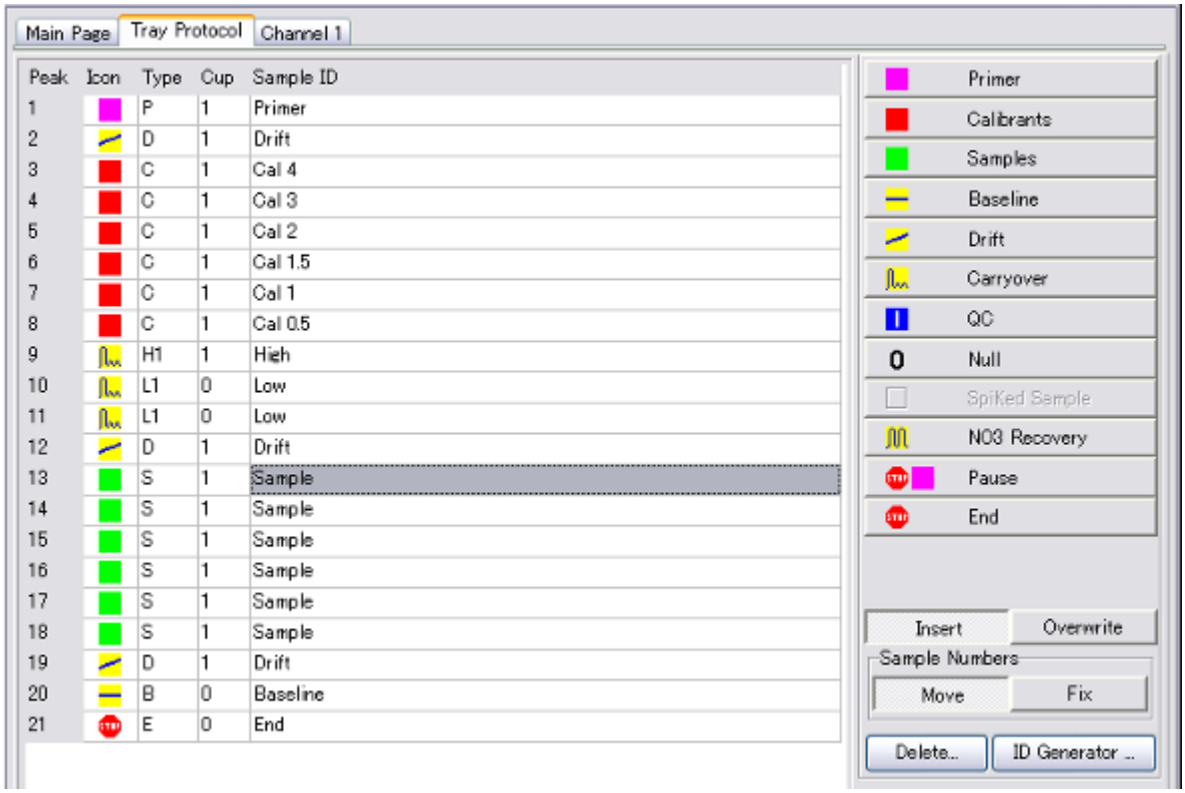


Figure 5.2 Experimental procedures

5.2.3 Three-way ANOVA method for the evaluation of the effects of experimental factors on the decomposition rates of PFCAs

Three-way ANOVAs were introduced to evaluate the effects of experimental factors and their interactions on the decomposition of PFCAs.

(1) Study on the effects of H_2SO_4 and $K_2S_2O_8$

The evaluation factors were the concentration of H_2SO_4 (factor A, i = 1–6), concentration of $K_2S_2O_8$ (factor B, j = 1–7), and types of PFCAs (factor C, k = 1–6).

(2) Study on the effects of the PFCA concentrations

The evaluation factors were the concentration of $K_2S_2O_8$ (factor A, i = 1–4), concentration of PFCAs (factor B, j = 1–5), and type of PFCAs (factor C, k = 1–6).

(3) Study on the effects of temperature

The evaluation factors were the concentration of $K_2S_2O_8$ (factor A, j = 1–4), heating temperature (factor B, j = 1–6), and type of PFCAs (factor C, k = 1–6).

A decomposition rate X_{ijk} is modelled by the following equation (Eqn. 5.2):

$$X_{ijk} = X_o + a_i + b_j + c_k + (ab)_{ij} + (ac)_{ik} + (bc)_{jk} + e_{ijk} \quad (5.2)$$

where X_o : average level of X_{ijk}; a_i, b_j, c_k : parameters for main effects; $(ab)_{ij}$, $(ac)_{ik}$, $(bc)_{jk}$: parameters for interaction effects of their combinations; e_{ijk}: residual factor which is a part of variation that cannot be explained by these parameter values.

All parameter values except X_o have conditions that all their partial sums must be zero, so that the degree of freedoms is given by the compound of each level number minus one. The parameter value of each factor reflects the magnitude of its effect on the decomposition rates and its sum of squares (SS) gives the contribution percentage of the parameter on the sample variance of the decomposition rates.

5.3 Results and discussion

5.3.1 Development of an experimental system for the continuous decomposition of PFCAs and the quantification of fluoride obtained from PFCAs

Under the experimental conditions, fluoride signals recorded by ACCE software and the data-processing computer were in an unsteady state (**Fig. 5.3**). This was leading to errors in the quantification of the fluoride concentration. Observation of the experimental system showed that the unsteady state of fluoride signals was caused by the intermittent state of the irradiated effluent ④ **Fig. 5.4**.

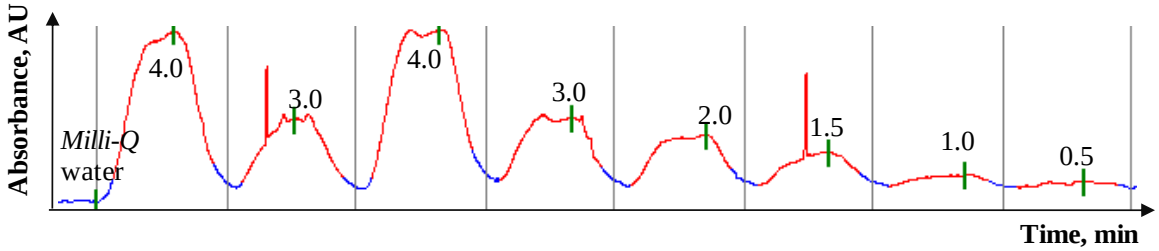


Figure 5.5 Recording fluoride standard signals. The numbers on the peaks are fluoride concentrations in mg/L.

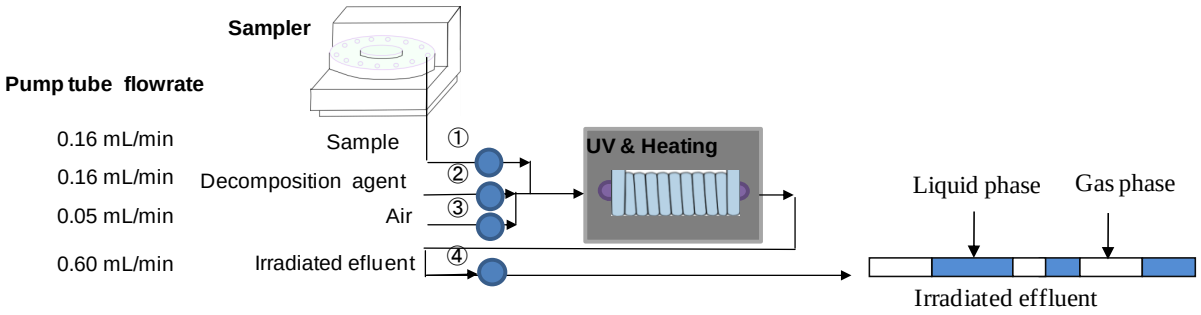


Figure 5.4 Flow pattern of the irradiated effluent.

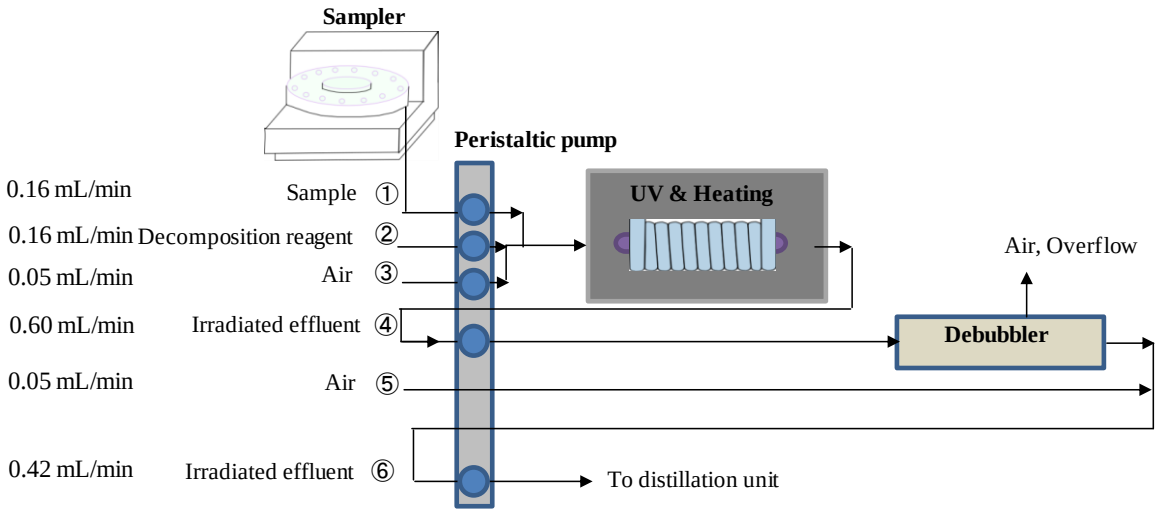


Figure 5.3 Modification of the manifold with the debubbler/rebubbler unit after the UV/heating unit.

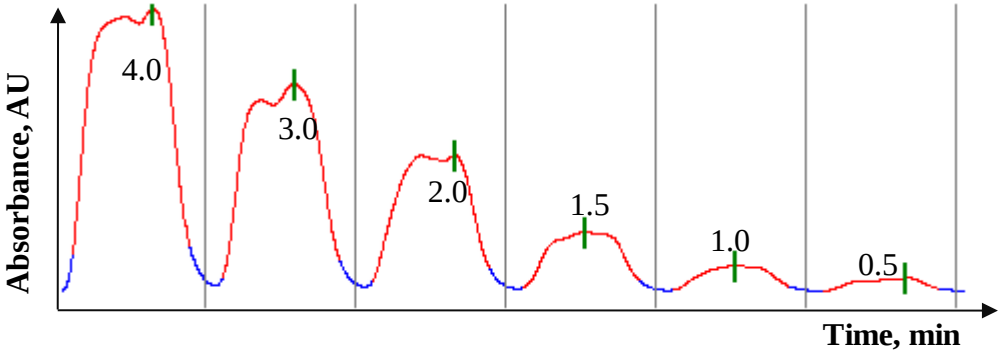


Figure 5.6 Recording fluoride standard signals in case of installation of the debubbler/rebubbler unit after UV/heating unit. The numbers on the peaks are the fluoride concentrations (mg/L)

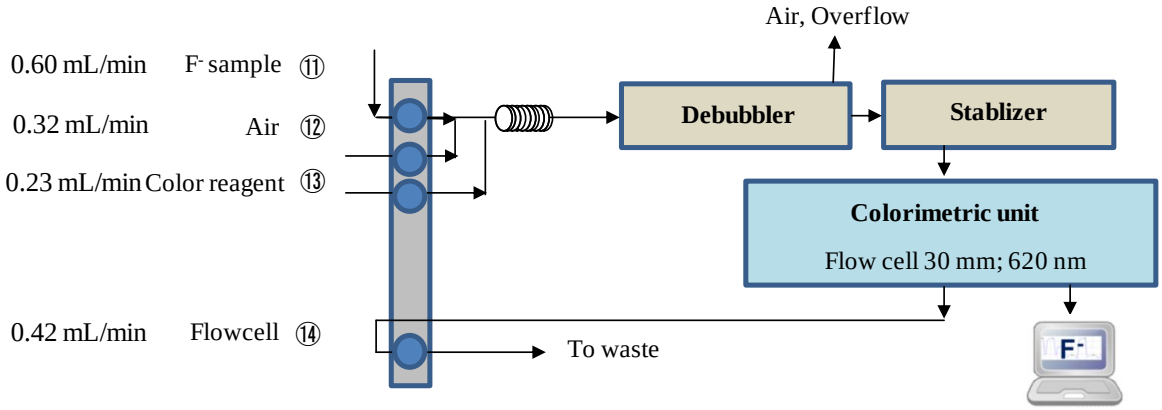


Figure 5.6 Modification of the manifold with the debubbler and reaction coil before the colorimetric unit.

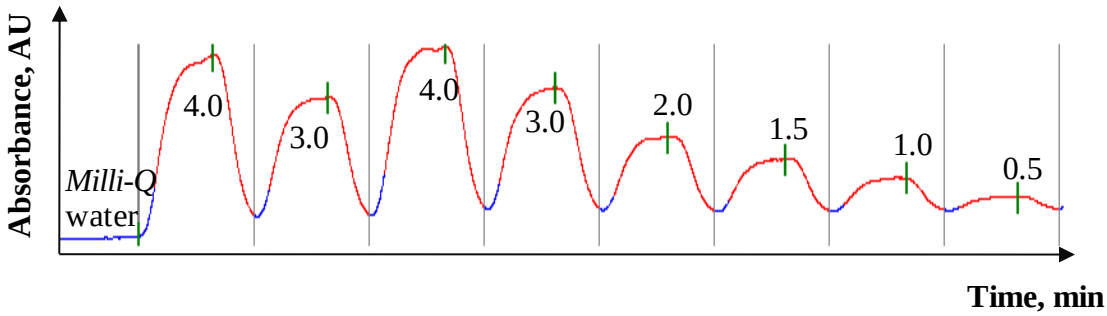


Figure 5.7 Recording of the fluoride standard signals in experiments with the combined modification of manifold with the debubbler/rebubbler after the UV/heating unit and debubbler/stabilizer before the flow cell (30 mm). The numbers on the peaks are fluoride concentrations (mg/L).

To solve the problem, the experimental system was modified by installing a debubbler/rebubbler unit after the UV/heating unit. **Figure 5.5** shows the design of the modified system with the debubbler/rebubbler unit. Irradiated effluent ④ after the UV/heating unit was pumped to the debubbler unit for separation of the air phase from overflow of the liquid phase. The effluent after the debubbler unit was then mixed with air at a flow rate of 0.05 mL/min to prevent each sample from diffusing into the following one. The irradiated effluent ⑤ was controlled with a flow rate of 0.42 mL/min before going into the distillation unit.

Figure 5.6 shows that better fluori**d**e signals were recorded in the presence of the debubbler/rebubbler unit after the UV/heating unit. However, the signals were not in steady state and needed further improvement. This led us to modify the system before the flow cell (**Fig. 5.7**). As the results show, better fluoride signals were observed (**Fig. 5.8**). These modifications in the systems were used for later experiments in our research.

5.3.2 Analytical performance

Under the experimental conditions of a temperature of 65 °C, six known concentrations of fluoride (0.5–4 mg/L) were used for the quantification with a correlation coefficient of 0.995 and standard deviation of 0.03 (based on 42 runs). We observed that, all the experiments had a low carry over (less than 0.5%). Typical recoded signals for fluoride analysis are shown in **Fig. 5.9**. The modified experimental setup is shown in **Fig**. **5.10**. In this system, the decomposition reagent stream was segmented with air bubbles at a flow rate of 0.05 mL/min before being mixed with the samples: these prevent each

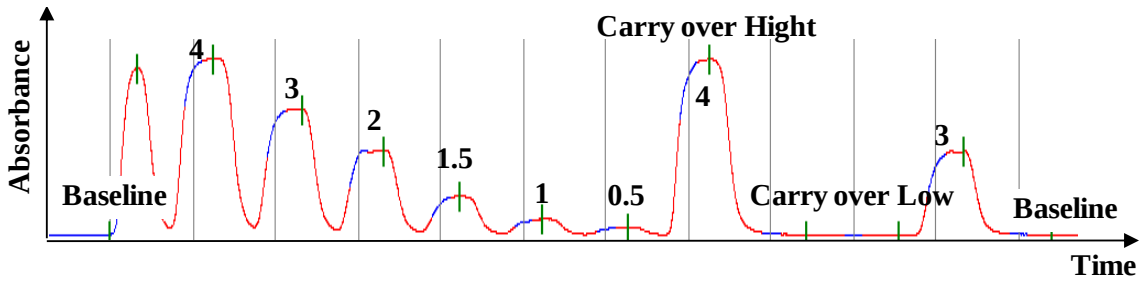


Figure 5.8 Typical recorded signals for fluoride standards under recommended condition. Numbers on the peaks are fluoride concentration (mg/L).

sample from diffusing into the following one, and make it easier to observe the flow of the liquid in the glass coils.

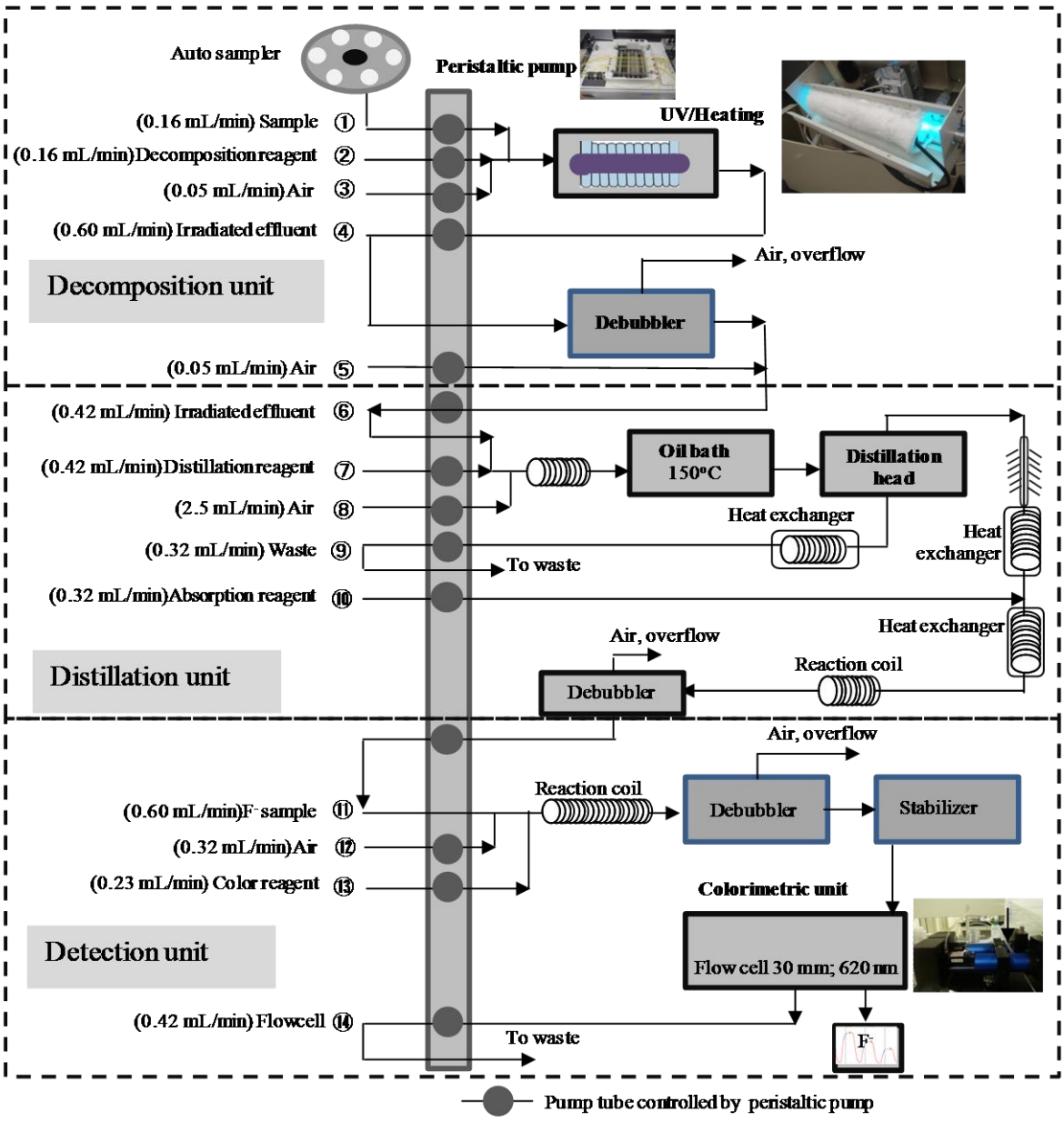


Figure 5.9 Modified experimental setup for a continuous flow analysis of PFCAs by a colorimetric method.

5.3.3 Effects of acid (H_2SO_4) and oxidant ($K_2S_2O_8$) concentration

We used 42 different decomposition reagents of an acid (H_2SO_4, six levels: 0–2 mol/L) and oxidant ($K_2S_2O_8$, seven levels: 0–0.16 mol/L) to investigate their effects on the

decomposition rates of six PFCAs at a concentration of 3 mg/L. Samples were irradiated with $UV_{254+185}$ at 65 °C. The irradiated/heating time was 12 min. **Figure 5.11** shows the decomposition rates of the PFCAs. We observed that the PFCAs were slowly decomposed under irradiation of $UV_{254+185}$ light and a temperature of 65 °C in 12 min. The decomposition rates of the PFCAs were 18.3% (PFBA), 16.4% (PFPA), 16.5% (PFHxA), 15.5% (PFHpA), 14.9% (PFOA), and 12.7% (PFNA). These results are similar to that reported by (Chen *et al.* 2007). They showed that 11% of initial PFOA (41.4 mg/L; 0.1 mmol/L) decomposed under 30 min irradiation of $UV_{254+185}$ (15W) at a temperature of 40 °C. The PFCA decomposition mechanisms were reported previously (Hori *et al.* 2004, Hori *et al.* 2005, Chen *et al.* 2007, Moriwaki *et al.* 2005), and are known to form shorter-chain PFCAs besides the fluoride ions, losing CF_2 units in a stepwise mechanism.

Our results showed that the use of H_2SO_4 (0.02–2 mol/L) as the decomposition reagent has not clearly contributed to any increase in the decomposition rates of the PFCAs. However, the use of $K_2S_2O_8$ (0.01–0.16 mol/L) as the decomposition reagent contributed to the higher decomposition rates of PFCAs. Under the conditions of 0.16 mol/L of $K_2S_2O_8$, depending on the type of the PFCAs, the decomposition rates were increased from 2.1 to 3.3 folds in comparison with direct photolysis.

The increase in the decomposition rates of the PFCAs was explained based on the formation of oxygen-free radicals ($O^{\cdot}$), as shown in Eqn. (5.2). Oxygen-free radicals react with the PFCAs to form CO_2 and HF, as shown in Eqn. (5.3)–(5.8).

$$S_2O_8^{2-} + H_2O \xrightarrow{h\nu,\ \text{heat}} 2SO_4^{2-} + 2H^+ + O^{\cdot} \quad (5.2)$$

$$C_3F_7COOH + 3H_2O + 3O^{\cdot} \longrightarrow 4CO_2 + 7\,HF \quad (5.3)$$

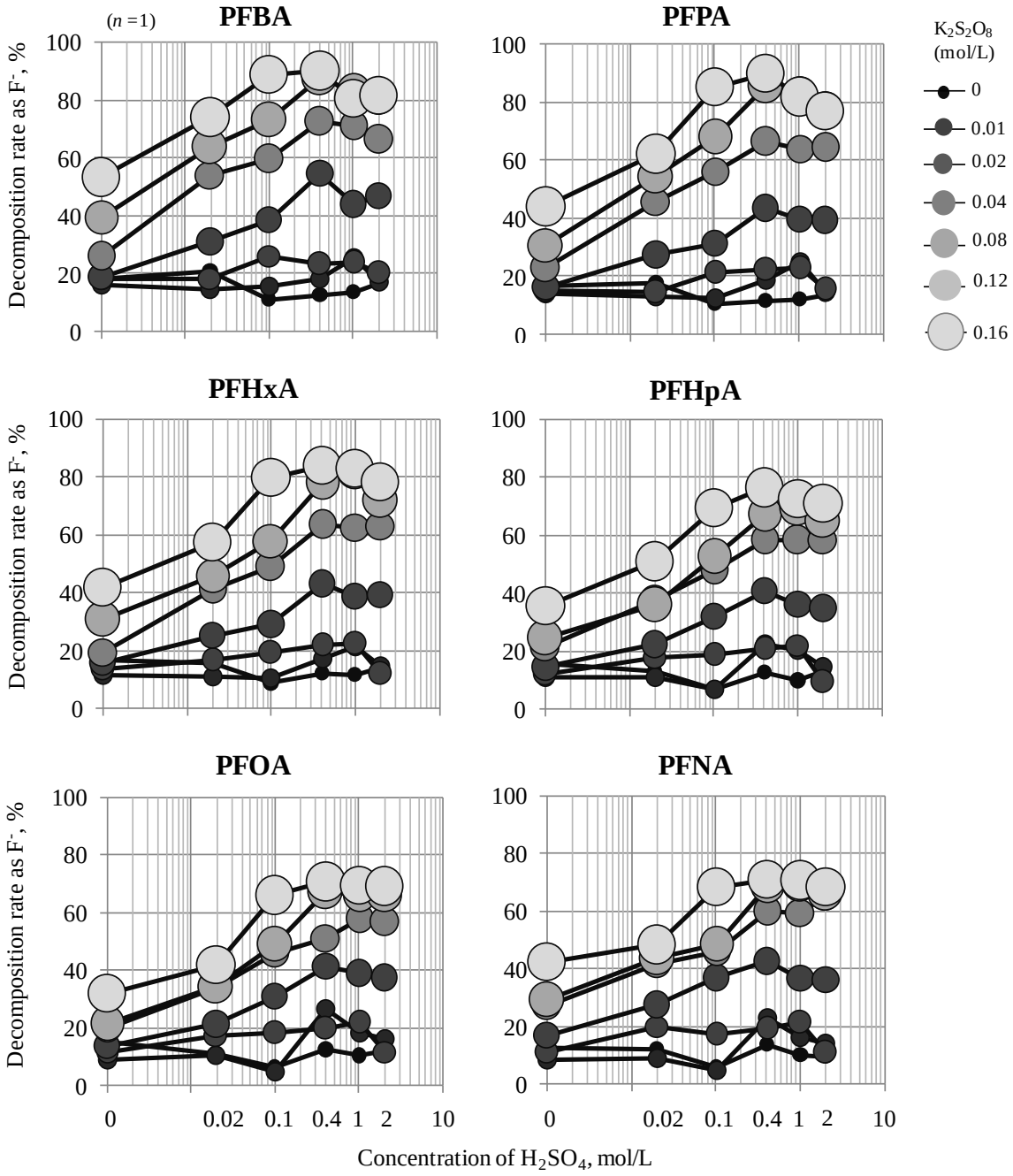


Figure 5.10 Decomposition rates of PFBA (14 μmol/L, 3 mg/L), PFPA (11.4 μmol/L, 3 mg/L), PFHxA (9.6 μmol/L, 3 mg/L), PFHpA (8.2 μmol/L, 3 mg/L), PFOA (7.2 μmol/L, 3 mg/L), and PFNA (6.5 μmol/L, 3 mg/L) with H_2SO_4 (0–0.4 mol/L) and $K_2S_2O_8$ (0–0.16 mol/L) under $UV_{254+185}$, 65 °C and irradiation time of 12 min.

$$C_4F_9COOH + 4H_2O + 4O^{\cdot} \longrightarrow 5CO_2 + 9\,HF \quad (5.4)$$

$$C_5F_{11}COOH + 5H_2O + 5O^{\cdot} \longrightarrow 6CO_2 + 11\,HF \quad (5.5)$$

$$C_6F_{13}COOH + 6H_2O + 6O^{\cdot} \longrightarrow 7CO_2 + 13\,HF \quad (5.6)$$

$$C_7F_{15}COOH + 7H_2O + 7O^{\cdot} \longrightarrow 8CO_2 + 15\,HF \quad (5.7)$$

$$C_8F_{17}COOH + 8H_2O + 8O^{\cdot} \longrightarrow 9CO_2 + 17\,HF \quad (5.8)$$

The use of a combination of H_2SO_4 and $K_2S_2O_8$ as the decomposition reagent enhanced the decomposition rates of the PFCAs (**Fig. 5.11**). Our results show that the PFCA decomposition rates increased with increasing concentrations of H_2SO_4 (from 0.02–0.4 mol/L) and $K_2S_2O_8$ (from 0.01–0.16 mol/L). The highest decomposition rates of the PFCAs were observed under the conditions of 0.4 mol/L of H_2SO_4 and 0.16 mol/L of $K_2S_2O_8$. The decomposition rates of the PFCAs were 90% (PFBA), 89% (PFPA), 83% (PFHxA), 76% (PFHpA), 71% (PFOA), and 71% (PFNA), respectively. The rates were increased 4.9 times (PFBA), 5.5 times (PFPA), 5.1 times (PFHxA), 4.9 times (PFHpA), 4.7 times (PFOA), and 5.6 times (PFNA), respectively. However, increasing the concentration of H_2SO_4 from 0.4 to 2.0 mol/L did not contribute to any increase in the decomposition rates of the PFCAs. Under the conditions of 2 mol/L of H_2SO_4 and 0.16 mol/L of $K_2S_2O_8$, the decomposition rates of PFCAs were 82% (PFBA), 77% (PFPA), 78% (PFHxA), 71% (PFHpA), 69% (PFOA), and 68% (PFNA), respectively. The decomposition rates of the short-chain PFCAs were higher than that of long chain PFCAs.

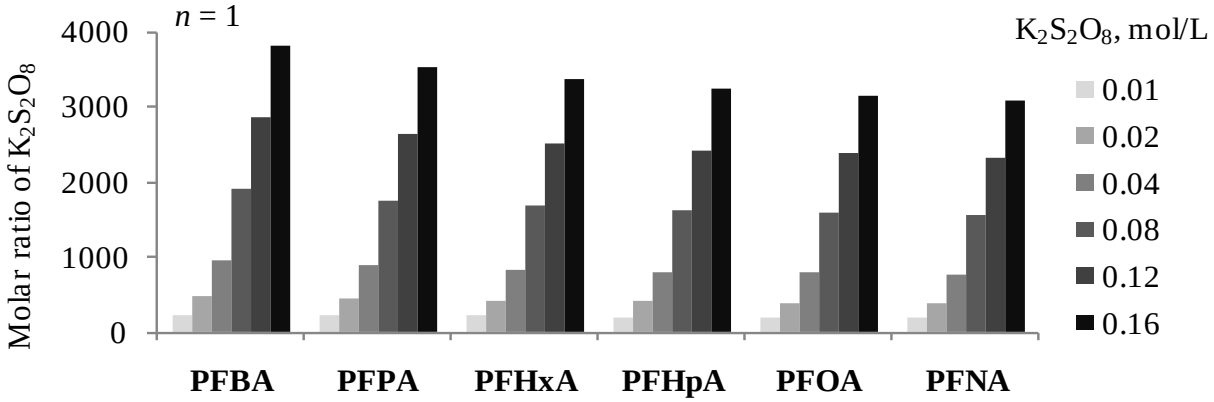


Figure 5.11 Comparison of the molar ratio of input $K_2S_2O_8$ (0.01–0.16 mol/L) with theoretical number of moles of $K_2S_2O_8$ for the complete decomposition of PFCAs (3 mg/L).

We assumed that the theoretical amounts of $K_2S_2O_8$ required for the complete decomposition of PFCAs (3 mg/L) were calculated based on the Eqn. (3.2)–(3.7). **Figure 5.12** shows the comparison of the molar ratios of input concentrations of $K_2S_2O_8$ (0.01–0.16 mol/L) with theoretical number of moles of $K_2S_2O_8$ for the complete decomposition of the PFCAs (3 mg/L). For all the cases, the amount of input $K_2S_2O_8$ was much higher than the theoretical amount required for the complete decomposition of PFCAs by about 193–3520 times. However, the decomposition rates of the PFCAs were increased clearly only at molar ratios higher than 1500 times ($K_2S_2O_8$ > 0.08 mol/L).

In order to evaluate the effect of each parameter and their interactions, three-way ANOVA was applied. **Table 5.3** summarises the ANOVA results for evaluating the effects of H_2SO_4, $K_2S_2O_8$ and type of PFCAs on the decomposition. The calculated results showed that all the *F*-values are higher than *F crit* (*F* critical value) and the *p*-values are obviously less than 0.05 (α). This indicates that all the effects are statistically significant but this inference does not mean that all the factors are practically influential. Therefore, the contribution percentage was calculated to understand the practical impacts of the factors the decomposition rates of PFCAs.

Table 5.1 Results of three-way ANOVA analysis of variance for the concentration of H_2SO_4 and $K_2S_2O_8$, type of PFCAs, and interaction terms. Statistically significant difference was set at $p < 0.05$.

Source of varience	Varience	*TSS*	*df**	*MS**	*F*	*p-value*	*F crit***	Adjusted *TSS*	% Cont*
Concentration of H_2SO_4 (A)	68.8	17331.7	5.0	3466.3	555.6	7.6E-95	2.27	17300.5	11.8
Concentration of $K_2S_2O_8$ (B)	436.2	109919.7	6.0	18320.0	2936.3	8.8E-153	2.16	109882.3	75.2
Types of PFCAs (C)	14.3	3595.7	5.0	719.1	115.3	1.5E-49	2.27	3564.5	2.4
AxB	48.7	12274.9	30.0	409.2	65.6	1.6E-71	1.54	12087.7	8.3
AxC	6.9	263.1	25.0	10.5	1.7	0.03	1.58	107.2	0.1
BxC	1.0	1726.5	30.0	57.6	9.2	1.7E-21	1.54	1539.4	1.1
Errors	3.7	935.9	150.0	6.2	-	-		1566.0	1.1
Total	579.6	146047.5	251.0	581.9	-	-		146047.5	100

* *TSS* : Total Sum of Squares, *df* : degree of freedom,, *MS* : Mean Square, % Cont: % Contribution

** *F* critical value, α = 0.05

As shown in **Table 5.3**, the most important factor affecting the decomposition rates of the PFCAs was the concentration of $K_2S_2O_8$, which contributed 75.2%. The second important factor was the concentration of H_2SO_4 (11.8%). The interaction effect (factor A × factor B) shows that the contribution percentage was 8.3%, indicating the interdependence of H_2SO_4 and $K_2S_2O_8$ on the decomposition of the PFCAs. Besides, the contribution percentage of interaction effects of (A × C) and (B × C) was less than 1.2%, indicating the interaction effects of the concentration of $K_2S_2O_8$ and the type of PFCAs when the concentration of $K_2S_2O_8$ or the PFCAs were not negligible. The analysis could not explain 1.1% of the data.

5.3.4 Effects of PFCA concentrations

We used three different decomposition reagents (H_2SO_4: 0.4 mol/L and $K_2S_2O_8$: 0.04, 0.08, 0.16 mol/L) to find the effects on the decomposition of the PFCAs at five concentration levels (3–10 mg/L; 9–32 μmol/L). **Figure 5.13** shows the effects of initial concentration of PFCAs on their decomposition rates.

In all the cases, $K_2S_2O_8$ at a concentration of 0.16 mol/L contributed to the highest decomposition rates of the PFCAs. Decomposition rates of the PFCAs at higher concentrations were higher in comparison to lower concentrations. At concentrations of H_2SO_4 (0.4 mol/L) and $K_2S_2O_8$ (0.16 mol/L), the decomposition rates of PFCAs at 10 mg/L were 98.8% (PFBA), 98.8% (PFPA), 94.2% (PFHxA), 92.2% (PFHpA), 86.2% (PFOA) and 88.2% (PFNA), respectively. The decomposition rates of PFCAs were increased by 1.1–1.25 folds in comparison to conditions with 3 mg/L of the PFCAs. The lower decomposition rates of PFCAs at low concentrations could be explained based on the higher percentage absorption of PFCAs onto pump tubes and glass coils in comparison with that of higher concentration of PFCAs.

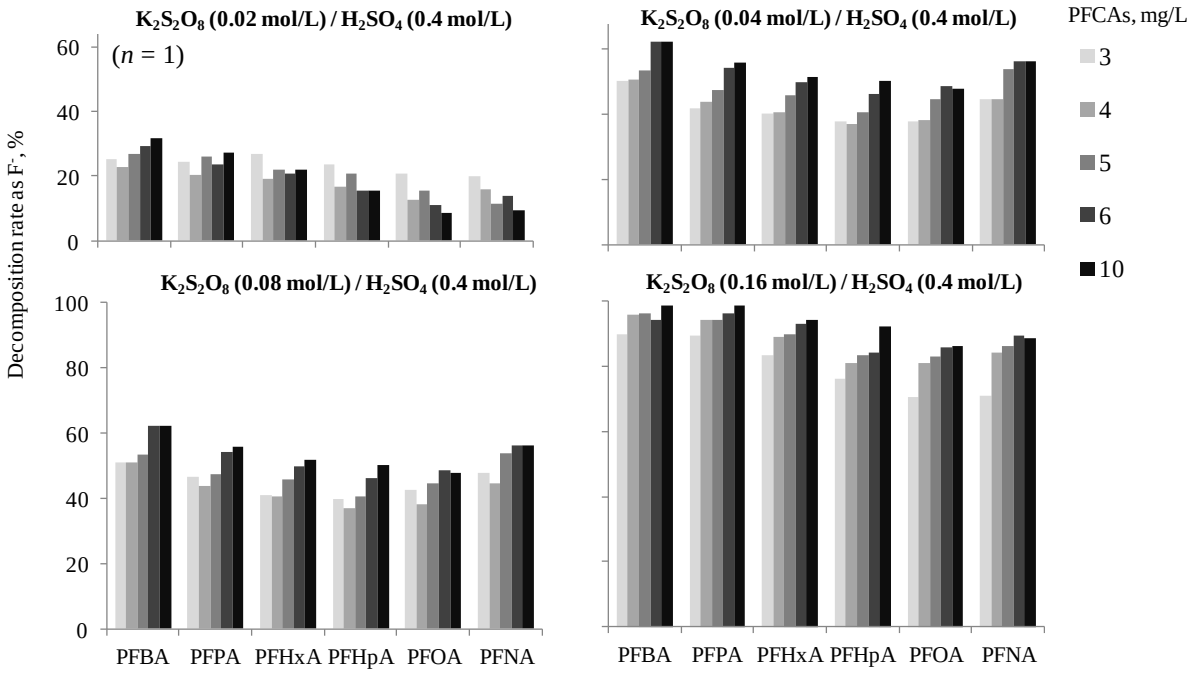


Figure 5.12 Effects of the initial PFCA concentrations on the decomposition rates of these compounds.

Table 5.2 Results of three-way ANOVA analysis of variance for the concentration of $K_2S_2O_8$, concentration and type of PFCAs, and interaction terms. Statistically significant difference was set at $p < 0.05$.

Source of varience	Varience	*TSS*	*df**	*MS**	*F*	*p-value*	*F crit***	Adjusted *TSS*	% Cont*
Concentration of $K_2S_2O_8$ (A)	587.3	70473.8	3	23491.3	2720.6	4.9E-64	2.8	70447.9	92.5
Concentration of PFCAs (B)	10.4	1252.9	4	313.2	36.3	2.1E-15	2.5	1218.3	1.6
Type of PFCAs (C)	62.7	7526.5	5	1505.3	174.3	2.2E-34	2.4	7483.3	9.8
A × B	8.2	987.1	12	82.3	9.5	5.5E-10	1.9	883.4	1.2
A × C	21.8	2612.6	15	174.2	20.2	5.3E-18	1.8	2483.1	3.3
B ×C	16.6	1991.1	20	99.6	11.5	8.0E-14	1.7	1818.4	2.4
Errors	4.3	518.1	60	8.6	-	-	-	1027.5	1.3
Total	634.4	76133.7	119	639.8	-	-	-	76133.7	100

* *TSS*: Total Sum of Squares, *df*: degree of freedom,, *MS*: Mean Square, % Cont: % Contribution

** *F* critical value, $a = 0.05$

Table 5.4 shows the results of three-way ANOVA used for evaluating the efficiency of concentration of PFCAs (five levels), type of PFCAs (six level) and concentration of

$K_2S_2O_8$ (four levels) and interactions on the decomposition rates of PFCAs. The calculated results showed that all *F*-value are higher than *F crit* (*F* critical value) and *p*-value are obviously less than 0.05 (α). This meant that all of the effects statistically significant but this does not support all factors are practically influential. Therefore, the contribution percentage was calculated to show the practical meaning of factor effects, how many contribution percentages of factors on the whole variation of decomposition rates of PFCAs. The calculated results showed the most important contribution factor to the change of the decomposition rates of PFCAs was the concentration of $K_2S_2O_8$ (92.5%). The second important factor was the types of PFCAs (9.8%). The effect of PFCAs concentration was contributed about 1.6%. The interaction effects contributed about 6.9% to the changes in the decomposition rates of PFCAs. The analysis could not explain 1.3% of the data.

5.3.5 Effects of heating temperature

Figure 5.14 shows the effect of the temperature on the PFCA decomposition rates. When we increased the temperature from 55 to 80 °C, the irradiation time was reduced from 20 min to 4.4 min, thus leading to changes in the decomposition rates of the PFCAs.

In case of PFOA with 0.16 mol/L of $K_2S_2O_8$, the decomposition rates of PFOA increased by 1.2 times when the temperature was increased from 55 to 65 °C, even as the irradiation time reduced by 1.7 times. However, when we increased the temperature from 65 to 80 °C, the decomposition rate of PFOA reduced 2.1 times while the irradiation time reduced 2.7 times. The same trend was observed in the cases of PFBA, PFPA, PFHxA, PFHpA, and PFNA at different concentrations of $K_2S_2O_8$. We suspect that the reduction in irradiation time was the main factor which contributed to the lower decomposition rates of the PFCAs in this case.

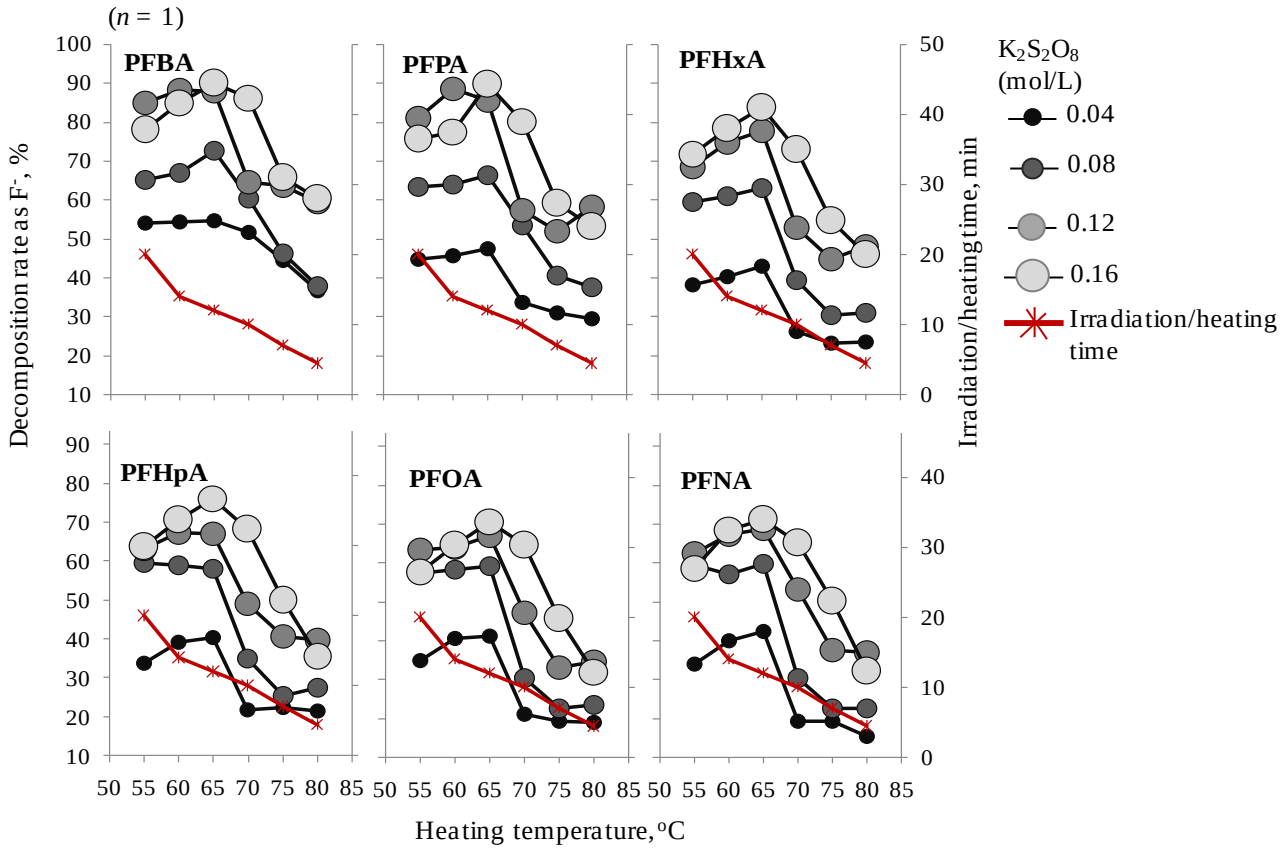


Figure 5.13 Effects of the temperature on the decomposition rates of PFCAs.

Table 5.5 shows the results of three-way ANOVA used for evaluating the efficiency of $K_2S_2O_8$ (four levels) concentrations, temperature (six levels), types of PFCAs (six levels), and the combined interaction of these factors on the decomposition rates of the PFCAs. It can be interfered from the table that the concentration of $K_2S_2O_8$, temperature, types of PFCAs, $K_2S_2O_8$×temperature interaction, and $K_2S_2O_8$×type of PFCA interactions were statistically significant ($p < 0.05$). However, among the statistically significant factors and interactions, only the concentration of $K_2S_2O_8$, temperature, and type of PFCAs were shown to be practically significant. The calculated results show that the most important contributing factor to the change in the decomposition rates of the PFCAs was the concentration of $K_2S_2O_8$ (40.21%). The second important factor was the temperature (37.39%) and the third factor was the type of PFCAs (15.38%). The $K_2S_2O_8$×temperature factor affected to the decomposition rates of PFCAs to a small extent (4.07%).

Table 5.3 Results of three-way ANOVA analysis of variance for the concentration of $K_2S_2O_8$, heating temperature, and type of PFCAs, and their interaction terms. Statistically significant difference was set at $p < 0.05$.

Source of varience	Varience	*TSS*	*df**	*MS**	*F*	*p-value*	*F crit***	Adjusted *TSS*	% Cont*
Concentration of PFCA (A)	55.7	8019.2	5.0	1603.8	183.9	1.3E-40	2.28	7975.6	15.4
Concentration of $K_2S_2O_8$ (B)	145.0	20882.2	3.0	6960.7	798.2	8.5E-57	2.67	20856.0	40.2
Heating temp. (C)	135.0	19437.4	5.0	3887.5	445.8	2.9E-54	2.28	19393.8	37.4
AxB	2.4	352.0	15.0	23.5	2.7	2.5E-03	1.74	221.2	0.4
AxC	1.9	278.5	25.0	11.1	1.3	2.1E-01	1.58	60.5	0.1
BxC	15.6	2242.2	15.0	149.5	17.1	2.0E-18	1.74	2111.4	4.1
Errors	4.5	654.0	75.0	8.7	-	-		1247.0	2.4
Total	360.2	51865.5	143.0	362.7	-	-		51865.5	100

* *TSS* : Total Sum of Squares, *df* : degree of freedom,, *MS* : Mean Square, % Cont: % Contribution

** *F* critical value, α = 0.05

5.4 Summary

Continuous flow analysis of PFCAs after decomposition by a colorimetric method was developed. This chapter dealt with our investigations on the effect of acid (H_2SO_4) and oxidant ($K_2S_2O_8$) concentrations, the initial concentration of the PFCAs and the temperature on the breaking of C-F bonds in these chemicals.

- The modifications of the analytical system have been made with the installation of a debubbler/rebubbler after the UV/heating unit and debubbler/stabilizer before the flow cell (30 mm length for) achieving better signals for the fluoride ions.

- Very low decomposition rates of PFCAs were observed in the absence of H_2SO_4 and $K_2S_2O_8$. Combined use of H_2SO_4 and $K_2S_2O_8$ contributed to higher decomposition rates of the PFCAs. The highest decomposition rates of the PFCAs were observed under conditions of 0.4 mol/L of H_2SO_4 and 0.16 mol/L of $K_2S_2O_8$. The decomposition rates of PFCAs were 90% (PFBA), 89% (PFPA), 83% (PFHxA), 76% (PFHpA), 71% (PFOA), and 71% (PFNA). Increasing the

concentration of H_2SO_4 from 0.4 to 2.0 mol/L did not contribute to any increase in the decomposition rates of the PFCAs. Under the conditions of 2 mol/L of H_2SO_4 and 0.16 mol/L of $K_2S_2O_8$, the decomposition rates of PFCAs were 82% (PFBA), 77% (PFPA), 78% (PFHxA), 71% (PFHpA), 69% (PFOA), and 68% (PFNA), respectively. The use of three-way ANOVA analysis gave statistically significant information on the effects of concentrations of acid and oxidant and types of the PFCAs by their contribution percentage. The most importance factor was the concentration of $K_2S_2O_8$ with a contribution of 75.2%. In addition, the ANOVA results indicated that the interaction effect of $H_2SO_4 \times K_2S_2O_8$ contributed to the change in the decomposition rates of PFCAs was about 8.3%.

- Concentrations of PFCAs (3–10 mg/L) had smaller effects on the decomposition rates of these chemicals. The decomposition rates of PFCAs at 10 mg/L were increased 1.1–1.25 times in comparison to the case where the concentration of the PFCAs was 3 mg/L. The lower decomposition rates of PFCAs at low concentrations could be explained based on the higher percentage absorption of PFCAs onto pump tubes and glass coils in comparison with that of higher concentration of PFCAs. The use of three-way ANOVA analysis gave statistically significant information on the effects of experimental factors by their contribution percentage. The results of the ANOVA calculation showed that the concentration of PFCAs contributed about 1.6% to the change in the decomposition rates of these chemicals.

- The changes in temperature in the UV/heating unit contributed to the changes of irradiation time and decomposition rates of the PFCAs. The irradiation time was reduced from 20 min to 4.4 min when we increased the temperature from 55 to 80 °C. The decomposition rates of PFCAs increased when the temperature was increased from 55 to 65 °C. However, they were reduced when we increased the temperature from 65 to 80 °C. The reduction of irradiation time was the main factor which contributed to the lower decomposition rates of PFCAs in this case. Results of the three-way ANOVA analysis show that temperature contributed about 37.39% to the changes in the decomposition rates of PFCAs.

Chapter 6 Study on the effects of interferences on CFA of PFCAs by a colorimetric method

6.1 Introduction

Previous chapters have shown that under irradiation with $UV_{254+185}$ light and a temperature of 65 °C, the optimum concentrations of acid and oxidant comprising the decomposing reagent were 0.16 mol/L of $K_2S_2O_8$ and 0.4 mol/L of H_2SO_4. The reaction time observed in those experimental conditions was 12 min. The obtained conditions were applied to more complex systems as reported in this chapter. Previous chapters had reported experiments with pure PFCA solutions. However, actual wastewater samples also contain many types of dissolved organic compounds (DOC). These compounds may compete with PFCAs in using up the oxidant and energy of UV light which may lead to a reduction in the decomposition rates of the PFCAs. Besides, the decomposition reactions of DOC will form gases. The formation of gases would increase the pressure in the system and cause the tubes to unplug. Therefore, a study on the effects of DOC interferences on PFCA decomposition is necessary for the development of this analytical method.

Spectrophotometric methods with a flow-injection procedure have been achieved with high sensitivity as reported previously. These are based on the use of ternary fluoride complexes such as the La(III)-alizarin complex(La-ALC) (Li and Xu 1999, Wada *et al.* 1985). Shimada *et al.* (Shimada *et al.* 2005) reported a distillation flow-injection spectrophotometric method for the determination of fluoride using the formation of the La-ALC complex. Interfering ions such as aluminium(III) and iron(III) were effectively eliminated. Chloride ions at a concentration of 142 mg/L did not affect the determination of fluoride at 0.4 mg/L (Wada *et al.* 1985). The American Public Health Association reported that the only common volatile constituent likely to cause interference with colorimetric analysis of the distillate is chloride (American Public Health Association 2005).

In this chapter, we selected glucose, humic acid, methanol, and chloride for our studies on the effects on CFA of PFCAs by the colorimetric method

6.2 Objective

The detailed objectives of this chapter were:

1. Study on the effect of glucose interference,
2. Study on the effect of humic acid interference,
3. Study on the effect of methanol interference,
4. Study on the effect of chloride interference.

6.3 Methodology

6.3.1 Effect of glucose interference

Glucose purchased from Wako Pure Chemical Industries (Osaka, Japan) was used as an organic interference in this study. Glucose stock solution was prepared by dissolving glucose in *Milli-Q* water at a concentration of 1000 mg/L. This stock solution was used up

Table 6.1 Experimental conditions for the effect of glucose interference.

Sample	PFCAs (PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA)	3 mg/L
	Glucose	0, 1, 3, 10, 30, 100 mg/L
Decomposition reagents	H_2SO_4	0.4 mol/L
	$K_2S_2O_8$	0.16 mol/L
UV lamp		254 nm (mainly), 185 nm (1%), 6W
Heating temperature		65 °C
Sampling time		6 minutes
Interval time		4 minutes
Distillation temperature		150 °C

during the day of preparation. **Table 6.1** shows the experimental conditions for the study on the effect of glucose interference on the decomposition of PFCAs. Samples were prepared by spiking the glucose stock solution with pure PFCA standard solutions to make up the final solutions with the concentration of glucose varying from 1 to 100 mg/L. The PFCA concentration was kept at 3 mg/L. The experimental setup and conditions were kept the same as reported in previous chapters.

6.3.2 Effect of humic acid interference

Standard humic acid (HA) purchased from Wako Pure Chemical Industries (Osaka, Japan) was used as an organic interference in this study. The HA solution was prepared by dissolving HA in *Milli-Q* water. This solution was then filtered followed by the addition of *Milli-Q* water to make a stock solution of HA with a concentration of 250 mg/L. **Table 6.2** shows the experimental conditions for our studies on the effect of HA interference on the decomposition of PFCAs. The samples were prepared by spiking the HA stock solution with pure PFCA standard solutions to make the final solutions with the concentration of HA ranging from 1 to 100 mg/L. The PFCA concentration was kept at 3 mg/L. The experimental setup and conditions were kept the same as in previous chapters.

Table 6.2 Experimental conditions for the effect of HA interference.

Sample	PFCAs (PFBA, PFHxA, PFOA)	3 mg/L
	Humic acid	0, 1, 3, 10, 30, 100 mg/L
Decomposition reagents	H_2SO_4	0.4 mol/L
	$K_2S_2O_8$	0.16 mol/L
UV lamp		254 nm (mainly), 185 nm (1%), 6W
Heating temperature		65 ^oC
Sampling time		6 minutes
Interval time		4 minutes
Distillation temperature		150 ^oC

6.3.3 Effect of methanol interference

Methanol purchased from Wako Pure Chemical Industries (Osaka, Japan) was used as organic interference in this study. **Table 6.3** shows the experimental conditions for the study on the effect of methanol interference on the decomposition of PFCAs. Samples were prepared by spiking the methanol solution with pure PFCA standard solutions to make the final solutions with the concentration of methanol ranging from 0.1% to 1% v/v. The PFCA concentration was kept at 3 mg/L. The experimental setup and conditions were kept the same as in previous chapters.

Table 6.3 Experimental conditions for the effect of methanol interference.

Sample	PFHxA	3 mg/L
	Methanol	0, 0.1, 0.5, 1.0 % v/v
Decomposition reagents	H_2SO_4	0.4 mol/L
	$K_2S_2O_8$	0.16 mol/L
UV lamp		254 nm (mainly), 185 nm (1%), 6W
Heating temperature		65 °C
Sampling time		6 minutes
Interval time		4 minutes
Distillation temperature		150 °C

6.3.4. Effect of chloride interference

Sodium chloride (NaCl) purchased from Wako Pure Chemical Industries (Osaka, Japan) was used as interference in this study. NaCl solution was prepared by dissolving it in *Milli-Q* water to make a stock solution at a concentration of 1000 mg/L. Five types of samples

(effluents from WWTPs, surface water samples, *Milli-Q* spiked chloride, *Milli-Q*) were used for studying the effect of chloride interference. **Tables 6.4** and **6.5** show the five types of samples used for the study and their characteristics. The experimental setup was kept the same as in the previous chapter.

Table 6.4 Experimental conditions of the UV/heating unit and decomposition reagent for screening the effect of chloride.

Sample	Type of sample	Characteristic of sample				
		TOC, mg/L	pH	Turbidity, NTU	F^-, mg/L	Cl^-, mg/L
S1	*Milli-Q*	-	-	-	0	0
S2	Wastewater (Efluent of WWTP)	5.6	6.5	0.77	0.05*	41.23*
S3	Wastewater (Efluent of WWTP)	6.6	6.5	0.93	0.04*	54.03*
S4	Surface water (downstream of WWTP)	4	6.6	1.69	0.05*	54.83*
S5	Chloride /*Milli-Q*	-	-	-	0	50

* The results were measured by ion chromatography ICS-2000

Table 6.5 Characteristics of samples used for the study on the effect of chloride interference.

Input samples		Experimental conditions		
		Decomposition agent	UV&Heating unit	
			$UV_{254+185}$	Heating at 65°C
S1, S2, S3, S4, S5	Case 1	None	Used	Used
	Case 2		None	None
	Case 3	Used	Used	Used
	Case 4		Used	None
	Case 5		None	Used
	Case 6		None	None

6.4 Results and discussion

6.4.1 Effect of glucose interference

Figure 6.1 shows the effect of glucose concentrations (1–100 mg/L) on continuous flow analysis of PFCAs at concentration of 3 mg/L by the colorimetric method. It can be inferred from the table that increasing the concentration of glucose from 1 to 100 mg/L had a small effect on the decomposition rates of the PFCAs at a concentration of 3 mg/L. At a glucose concentration of 100 mg/L, the PFCA decomposition rates were reduced by 1.09–1.15 times in comparison with the case of non-spiked glucose. The reduction in the PFCA decomposition rates were explained based on (1) competition in using up the decomposition reagent between PFCAs and glucose; (2) the formation of CO_2 from glucose decomposition which would lead to a slight change in the irradiation and heating times.

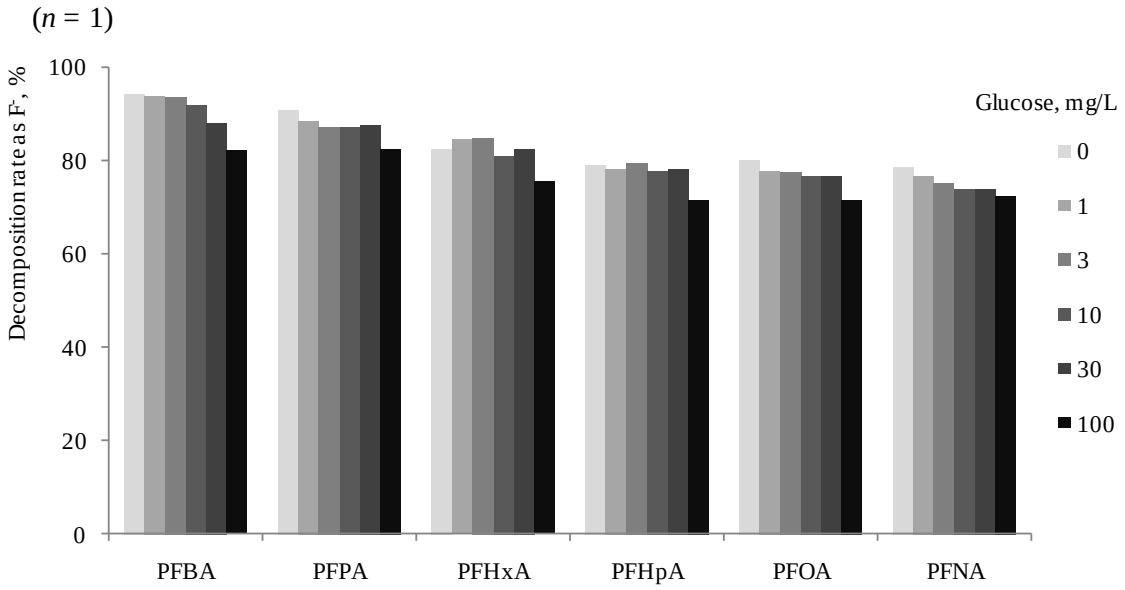


Figure 6.1 Effects of glucose interference.

Table 6.6 Results of two-way ANOVA analysis of variance for glucose concentrations and types of PFCAs. Statistically significant difference was set at $p < 0.05$.

Source of variance	Variance	*SS*	*N*	*df*	*MS*	*F*	*p* value	*SS'*	Contribution, %
Total	42.2	1517.6	36	35	43.4	-	-	1517.6	100
Concentration of Glucose	43.8	262.6	6	5	52.5	25.5	4.6E-09	261.2	17.21
Type of PFCAs	200.6	1203.4	6	5	240.7	116.8	1.7E-16	1201.9	79.20
Error	2.4	85.8	36	25	3.4	-	-	120.1	7.92

Table 6.6 shows the results of two-way ANOVA used for evaluating the efficiency of concentration of glucose (six levels) and type of PFCAs (six levels) on the decomposition rates of the PFCAs. It can be inferred from the table that all the factors were statistically significant ($p < 0.05$). The most important contributing factor to the change in the decomposition rates of PFCAs was the type of PFCAs (79.20%). The concentration of glucose had a lower contribution (17.21%) to the change in the decomposition rates of PFCAs.

We assumed 100% glucose was decomposed by $K_2S_2O_8$ as indicated in the Eqn. (6.1) and (6.2).

$$S_2O + H_2O \xrightarrow{h\nu,\ h} 2SO + 2H^+ + O^{\cdot} \quad (6.1)$$

$$C_6H_{12}O_6 + 12O^{\cdot} \rightarrow 6CO_2 + 6\,H_2O \quad (6.2)$$

The highest percentage of $K_2S_2O_8$ used for completely decomposing glucose (100 mg/L–0.556 mmol/L) was 4.17% of the total amount of $K_2S_2O_8$. The total percentage of $K_2S_2O_8$ used for the complete decomposition of glucose at the highest concentration of PFCAs was less than 4.2%. It means that, glucose at a concentration of 100 mg/L did not affect the required amount of $K_2S_2O_8$ for complete decomposition of the PFCAs. The reduction in the

PFCA decomposition rates can be explained based on the formation of CO_2 from the decomposition of glucose which led to the reduction in irradiation time.

6.4.2 Effect of humic acid (HA) interference

Photodecomposition rates of PFCAs (3 mg/L) with different concentrations of HA under irradiation of $UV_{254+185}$ light for 12 min at a temperature of 65 °C are shown in **Table 6.7**. HA was added at concentrations of 1, 20, 50, and 100 mg/L. PFCA samples without HA were used in the same runs for comparing the effect of HA on our analytical method. The decomposition rates of PFCAs were 88.1%–91.7% (PFBA), 77.2%–77.9% (PFHxA), and 66.7%–72.9% (PFOA), respectively. Coefficient variations for each group of PFCAs were 1.5 (PFBA), 1.3 (PFHxA) and 4.4 (PFOA), respectively. These data show that the used of HA at a concentration of 100 mg/L as the interference had no effect on the decomposition rates of PFBA, PFHxA, or PFOA.

Table 6.7 Effect of humic acid interference on the CFA of PFCAs at 3 mg/L by our method. The heating temperature was 65 °C.

Humic acid, concentration, mg/L	Decomposition rate, %		
	PFBA: 3 mg/L	**PFHxA: 3 mg/L**	**PFOA: 3 mg/L**
0	88.1	77.8	74.8
1	90.4	77.2	68.7
5	90.8	75.5	77.4
20	91.7	76.5	74.6
100	90.7	77.9	72.9
Mean	90.3	77.0	73.7
Standard deviation (SD)	1.3	1.0	3.2
Coefficient of variation (CV), %	1.5	1.3	4.4

6.4.3 Effect of methanol interference

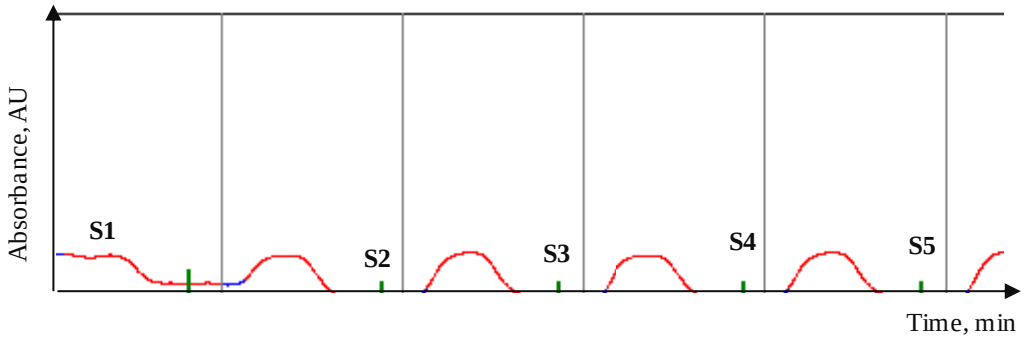
Photodecomposition rates of PFHxA (3 mg/L) with different concentrations of methanol under irradiation/heating of UV/heating unit for 12 min and a temperature of 65 °C are shown in **Table 6.8**. Methanol was added at concentrations of 0.1, 0.5, and 1.0 v/v (0.02–0.25 mol/L), respectively. A PFHxA sample without added methanol was used in the same run for a comparison of the effect of methanol on our analytical method. The decomposition rates of PFHxA were 77.8%–83.1% while the coefficient of variation was 2.8%. These data showed that methanol at the spiked concentration of 0.1%–1% v/v had no effect on the decomposition rates of PFHxA.

Table 6.8 Effect of methanol interference on the continuous flow analysis of PFHxA by a colorimetric method.

Characteristic of input sample			Decomposition rate , %	Mean	Standard deviation	Coefficient of variation (CV), %
Concentration of PFHxA, mg/L	Methanol		PFHxA			
	% v/v	mol/L				
3 (0.01 mol/L)	0	0	79.6	80.0	2.2	2.8
	0.1	0.02	79.5			
	0.5	0.12	77.8			
	1	0.25	83.1			

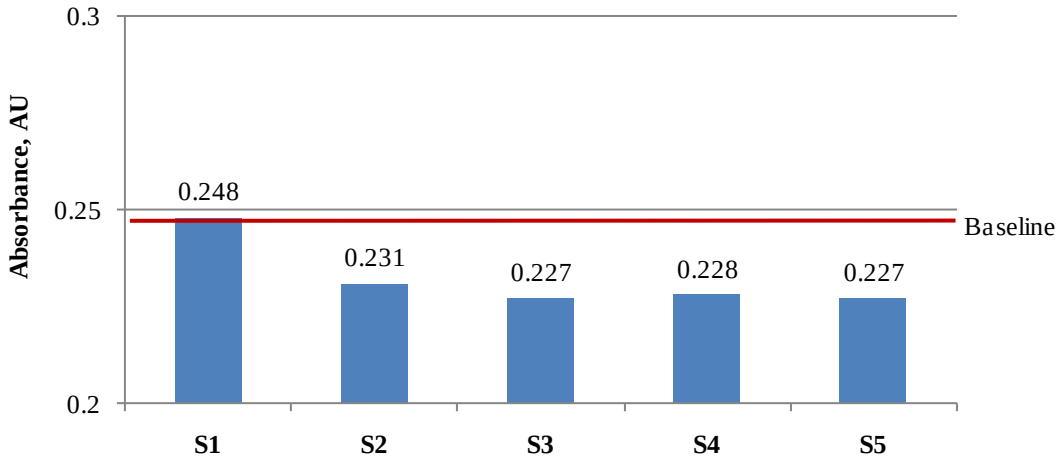
6.4.4 Effect of chloride interference

Figure 6.2 shows the recorded fluoride signals of five samples. The results showed that fluoride signals of all the samples (S2, S3, S4, and S5) except S1 were negative in comparison with that of *Milli-Q* water.



S1 : *Milli-Q* water
S2 : Wastewater (Effluent of WWTP)
S3 : Wastewater (Effluent of WWTP)
S4 : Surface water (downstream of WWTP)
S5 : Chloride / *Milli-Q*

Figure 6.2 Recorded signals of five samples.



S1 : *Milli-Q* water
S2 : Wastewater (Effluent of WWTP)
S3 : Wastewater (Effluent of WWTP)
S4 : Surface water (downstream of WWTP)
S5 : Chloride / *Milli-Q*

Figure 6.3 Absorbance results of collected effluents after flowing through the colorimetric unit. The numbers on the figure are absorbance units.

Table 6.9 Effect of experimental conditions in the UV/heating unit on chloride interference

Input samples		Experimental conditions			Effected to signal Yes/No
		Decomposition agent	UV&Heating unit		
			$UV_{254+185}$	Heating at 65°C	
S1, S2, S3, S4, S5	Case 1	None	Used	Used	No
	Case 2		None	None	No
	Case 3	Used	Used	Used	**Yes**
	Case 4		Used	None	**Yes**
	Case 5		None	Used	**Yes**
	Case 6		None	None	No

The same experiments were repeated for all five samples. However, effluents flowing out of the UV/heating unit were collected for measurement of absorbance by ultraviolet-visible spectrophotometry (UV-VIS). **Figure 6.3** shows the absorbance results of the collected effluents which show that the absorbance of effluent corresponding to *Milli-Q* water sample (S1) was 1.07–1.09 times higher than that of S2, S3, S4, and S5. We suspect that chloride interference caused the lower absorbance levels of samples (S2–S5) in comparison with that of *Milli-Q* water sample (S1). However, we found out that the negative effects of chloride were occurring only under conditions where $UV_{254+185}$ light or/and heating temperature of 65 °C were used (**Table 6.9**).

Under the experimental conditions, chloride reacted with persulfate ions to form hypochlorite ion (OCl^-), as shown in Eqn. 6.3. The hypochlorite ion then reacted with the colour reagent which led to the lower absorbance of S2, S3, S4, and S5 compared to S1.

$$5Cl^- + S_2O_8^{2-} \xrightarrow{hv,\ heating} S_2O_3^{2-} + 5\ OCl^- \quad (6.3)$$

Ascorbic acid is a non-hazardous chemical and has been widely used for dechlorination of water (Wang *et al.* 2007, Tikkanen 2001). This compound reacts with hypochlorite to form dehydroascorbic acid and chloride, as shown in Eqn. 6.4.

$$C_5H_5O_5CH_2OH + OCl^- \rightarrow C_5H_3O_5CH_2OH + Cl^- + H_2O \quad (6.4)$$

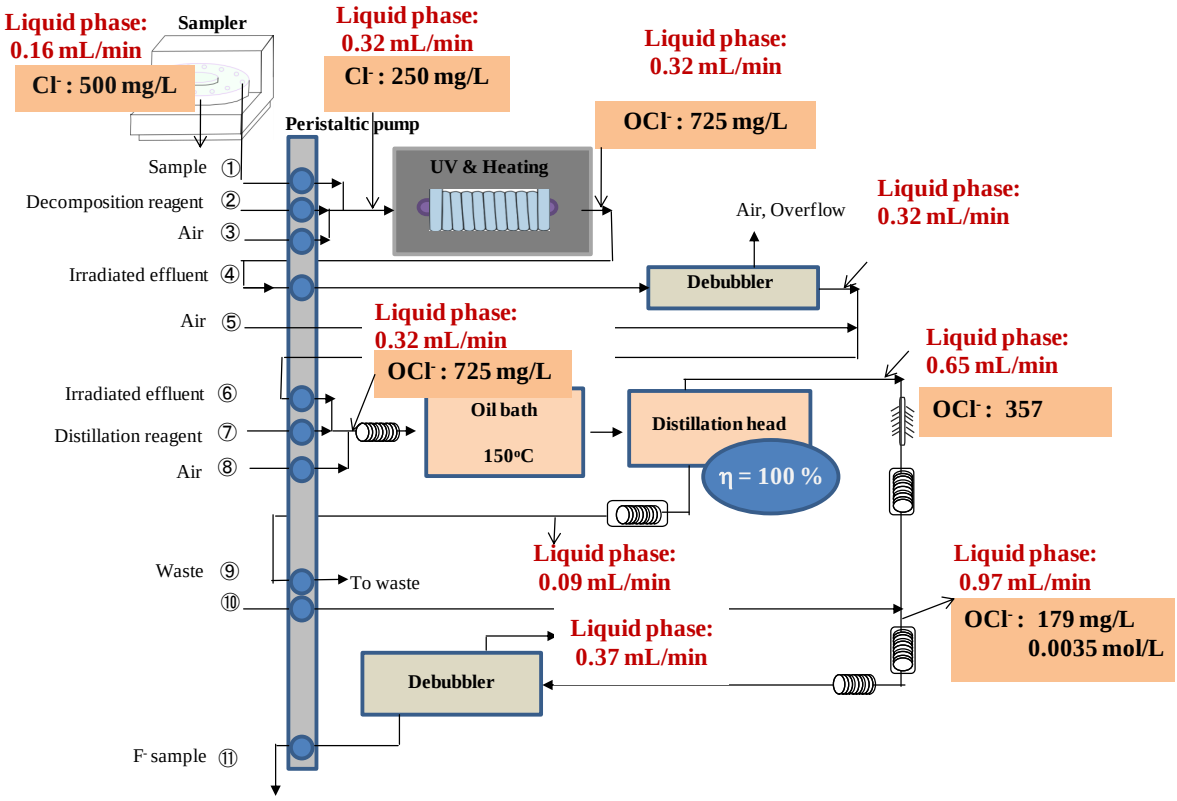


Figure 6.4 Calculated OCl^- balance. Concentration of Cl^- in sample was 500 mg/L. We assumed that 100% Cl^- was converted to OCl^- and 100% OCl^- was evaporated in the distillation unit.

In this study, ascorbic acid ($C_6H_8O_6$) was purchased from Wako Pure Chemical Industries (Osaka, Japan). An ascorbic acid standard solution was prepared by dissolving ascorbic acid in *Milli-Q* to make the stock solution at a concentration of 1000 mg/L. In our method, ascorbic acid was spiked with the absorption reagent to neutralize OCl^- formation at the UV/heating unit. **Figure 6.4** shows the concentration of OCl^- of each unit of input Cl^- concentration in the sample was 500 mg/L. In our calculation, we assumed that 100% Cl^- was converted to OCl^- following Eqn. (6.3) and 100% OCl^- was evaporated and separated in the distillation unit. Concentration of OCl^- after distillation unit was 0.0035 mol/L (~179 mg/L).

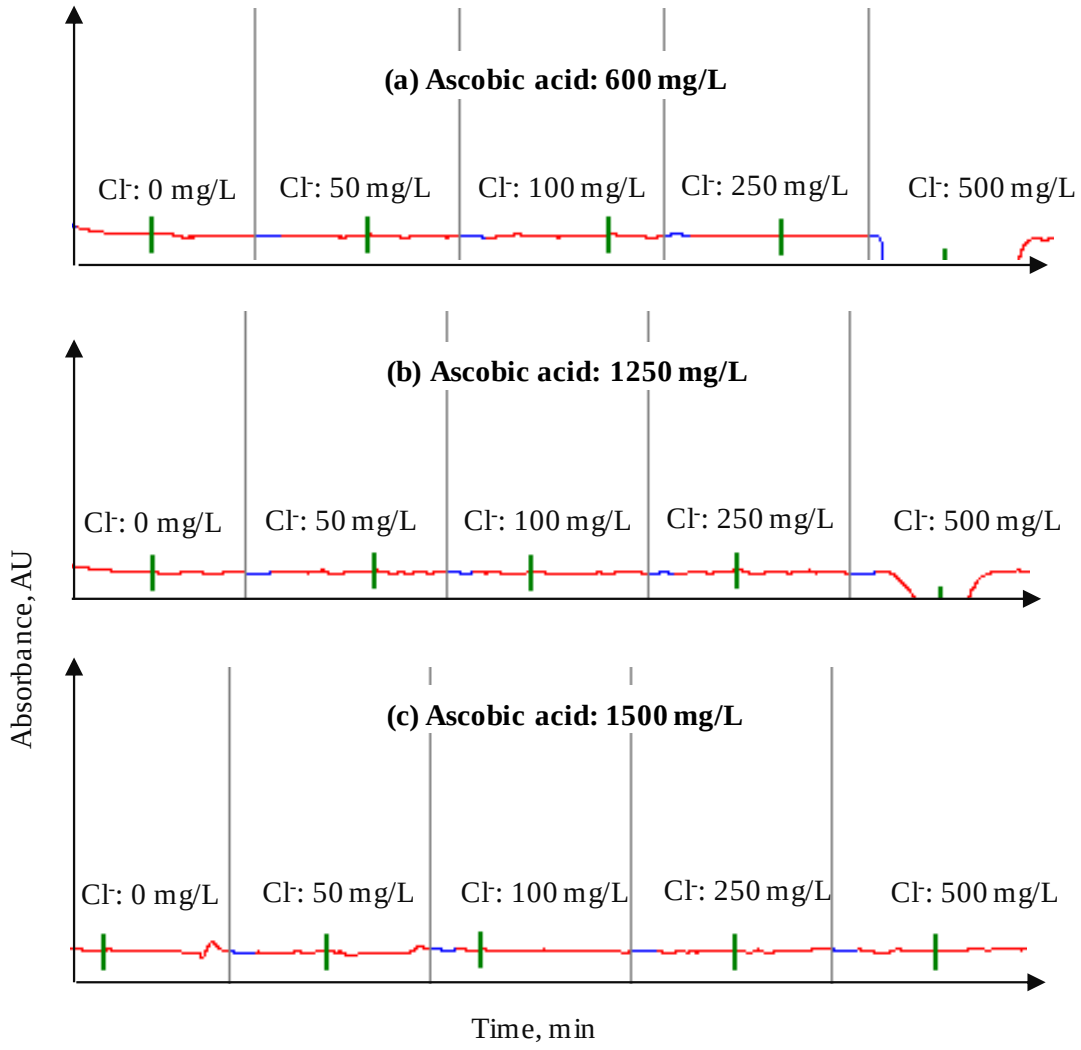


Figure 6.5 Recorded signals for the study on the effect of ascorbic acid in eliminating the effect of chloride.

Therefore, the theoretical concentration of ascorbic acid in the absorption reagent for eliminating the effect of chloride was 1232 mg/L. In our research, we conducted experiments with the concentrations of ascorbic acid at 600, 1,250, and 1,500 mg/L, respectively. Five concentrations of chloride (0, 50, 100, 250, and 500 mg/L) in the samples were used to assess the efficiency of ascorbic acid. Recorded signals (**Fig. 6.5**) show that ascorbic acid at a concentration of 1250 mg/L had completely eliminated the effect of chloride ion at concentrations of 0 to 250 mg/L, but not for a higher chloride concentration

Table 6.10 Experimental conditions for the study on the effect of chloride interference on CFA of PFCAs with the use of ascorbic acid in the absorption reagent

Parameter			Interferences
Samples		Fluoride : 1 mg/L	Chloride : 0, 50, 100, 250, 500 mg/L
		PFCAs (PHFxA, PFOA, PFNA) : 3 mg/L	
Decomposition reagents	H_2SO_4		0.4 mol/L
	$K_2S_2O_8$		0.16 mol/L
UV lamp			254 nm (mainly), 185 nm (1%), 6W
Heating temperature			65 °C
Sampling time			6 minutes
Interval time			4 minutes
Distillation temperature			150 °C

of 500 mg/L. However, when we increased concentration of ascorbic acid to 1500 mg/L, the negative impact of chloride ion at chloride concentration of 500 mg/L was also eliminated.

This experimental condition was recommended for the study on effects of samples (fluoride: 1 mg/L; PFBA, PFHxA, PFOA: 3 mg/L) spiked with different concentrations of chloride (0–500 mg/L). These experimental conditions are shown in **Table 6.10**.

Table 6.11 Effect of ascorbic acid in the removal of chloride interference during continuous flow analysis of PFCAs by a colorimetric method.

Type of sample	Detected fluoride concentration, mg/L					Mean, mg/L	Standard deviation	Coefficient of variation (CV), %
	Cl^- : 0 mg/L	Cl^- : 50 mg/L	Cl^- : 100 mg/L	Cl^- : 250 mg/L	Cl^- : 500 mg/L			
Fluoride/*Milli-Q*: 1 mg/L	0.90	1.12	0.99	0.98	1.06	1.01	0.08	8.06
PFHxA/*Milli-Q*: 3 mg/L	1.56 (78.1%)*	1.60 (80.2%)	1.58 (79.4%)	1.64 (82.0%)*	1.59 (79.6%)*	1.59 (79.8 %)*	0.03 (1.4)	1.89
PFOA/*Milli-Q*: 3 mg/L	1.68 (81.4%)*	1.73 (83.8%)*	1.77 (85.7%)*	1.77 (85.7%)*	1.73 (83.7%)*	1.74 (84.1)*	0.04 (1.7)	2.30
PFNA/*Milli-Q*: 3 mg/L	1.79 (85.8%)*	1.74 (83.3%)*	1.78 (85.3%)*	1.83 (87.8%)*	1.83 (87.7%)*	1.8 (86.0%)*	0.04 (1.87)	2.22

Table 6.11 shows the results on the effect of ascorbic acid in the removal of chloride interference. In the case of fluoride ions in *Milli-Q* at a concentration of 1 mg/L, the detected fluoride concentration was 0.9–1.06 mg/L with a standard deviation of 0.08 and CV of 8.06. These results showed that ascorbic acid at a concentration of 1,500 mg/L can eliminate the effect of chloride ions up to a concentration of 500 mg/L. The use of ascorbic acid did not affect the quantification of fluoride ions by this method.

In case of the samples where the PFCAs (PFHXA, PFOA, and PFNA) in *Milli-Q* water at a concentration of 3 mg/L were used, the average decomposition rates of these PFCAs were 79.8% (PFHxA) with a standard deviation of 1.4, 84.1% (PFOA) with standard deviation of 1.7%, and 86.0% (PFNA) with a standard deviation of 1.9, respectively. The calculated CVs were from 1.9% to 8.0%. These results suggested that the use of ascorbic acid at concentration of 1500 mg/L did not effect to the continuous flow analysis of fluoride and PFCAs (PFHxA, PFOA, and PFNA) by our method.

6.5 Summary

Dissolved organic compounds (DOC) may compete with PFCAs in terms of using oxidant and energy of UV light leading to a reduction in the decomposition rates of the PFCAs. Besides, the decomposition reactions of DOC will form gases. The formation of gases would increase the pressure in the system and cause unplugging of the tubes as well as a reduction in the irradiation and heating time. In this chapter, we selected glucose, humic acid, and methanol for studies on the effects of DOC interferences.

- Glucose at concentrations of 1–100 mg/L affected the decomposition rates of PFCAs (3 mg/L) slightly. At a glucose concentration of 100 mg/L, the PFCA decomposition rates were reduced by 1.09–1.15 times in comparison with the cases of non-spiked glucose.
- HA (1–100 mg/L) and methanol (0.1%–1.0% v/v) did not clearly affect the decomposition rates of the PFCAs.

For chloride, our results show that it was clearly affecting the fluoride signals of all the tested samples (wastewater, surface water, and *Milli-Q* water). The negative effects of chloride were occurring only when $UV_{254+185}$ light or/and temperature of 65 °C were used.

Our research suggests the use of ascorbic acid in eliminating effect of chloride. The results show that ascorbic acid at a concentration of 1,500 mg/L in the absorption reagent would successfully eliminate the negative impact of chloride ion which is at a concentration of 500 mg/L. The use of ascorbic acid at a concentration of 1,500 mg/L did not effect to the continuous flow analysis of samples containing fluoride (1 mg/L) or the PFCAs (PFHxA, PFOA, and PFNA).

Chapter 7 Development of a method for the determination of total organic fluoride (TOF) from samples containing PFCAs through the measurement of total fluoride (TF) and inorganic fluoride (IF)

7.1 Introduction

Previous chapters suggested experimental conditions for the determination of TOF from PFCAs after decomposition by a continuous flow analysis using a colorimetric method. The original analytical system was modified to develop our experimental system: we added a debubbler/rebubbler unit after the UV/heating unit, a debubbler, and a stabilizer before the flow cell 30 mm to achieve better signals for the quantification of fluoride concentrations. Effects of DOC such as HA and methanol were negligible except in the case of glucose concentrations as high as 100 mg/L. A negative effect of chloride interference at a concentration of 500 mg/L was eliminated by adding ascorbic acid to the absorption reagent at a concentration of 1,500 mg/L. This modified analytical system can be used for further research and applications in the field.

In order to determine the TOF from PFCAs in wastewater, the development of a simple method for determining the total fluoride (TF) and inorganic fluoride (IF) is necessary. The TOF can then be calculated from the TF and IF values.

7.2 Objective

The detailed objectives of this chapter are:

1. A study on a method for the determination of IF by CFA using a colorimetric method
2. Application of the developed methods for the determination of TF, IF, and TOF for fluoride ions and PFCAs in *Milli-Q* water
3. Application of the developed methods for the determination of TF, IF, and TOF for fluoride ions and PFCAs in the effluent of WWTP.

7.3 Methodology

7.3.1 Study on a method for the determination of IF by CFA using colorimetry

Analytical method for IF (Method A) was developed based on the method for

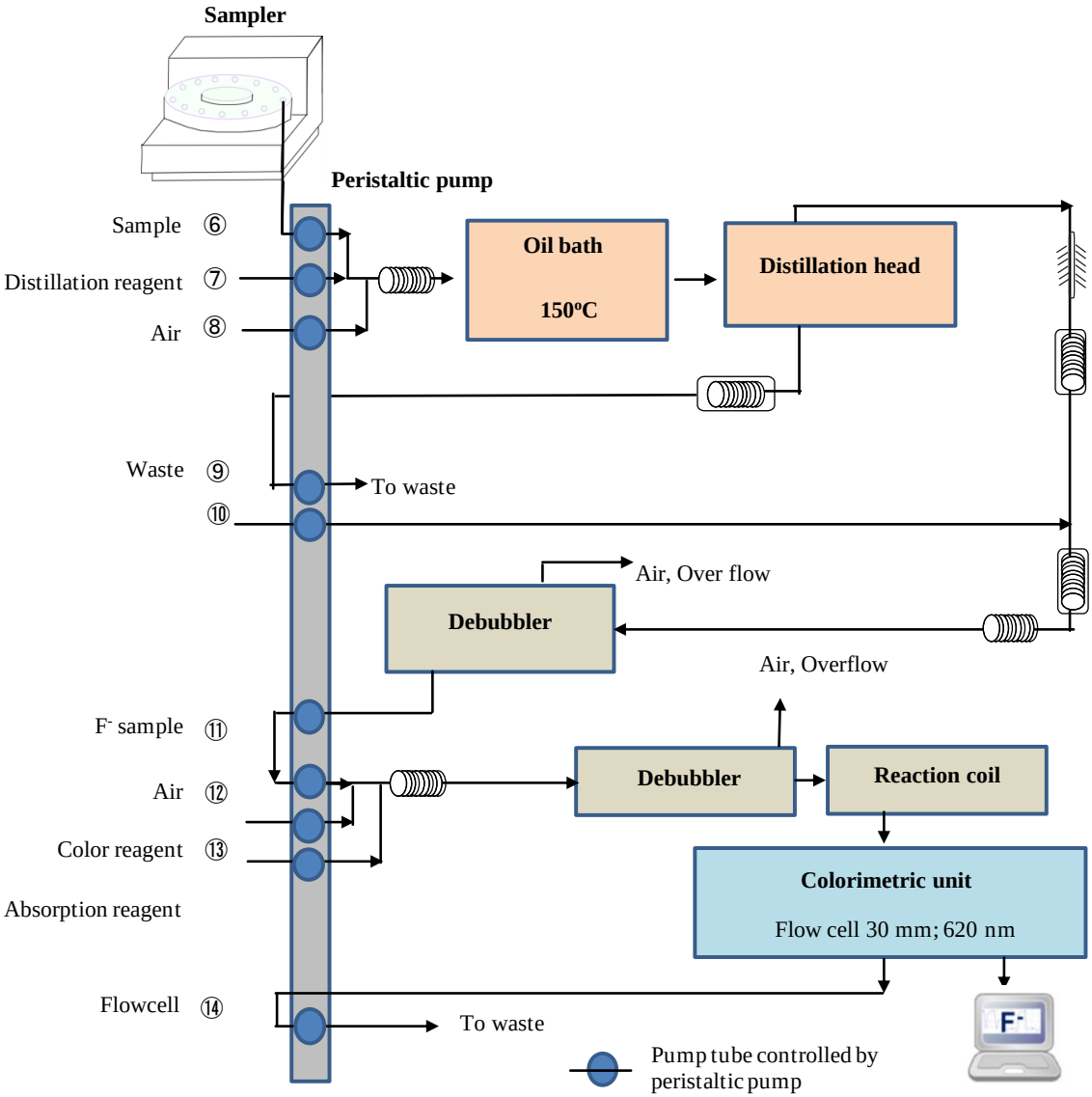


Figure 7.1 Schematic view of analytical manifold for the determination of IF by CFA with a colorimetric method

determination of TOF from PFCAs after decomposition by CFA using colorimetric method. **Figure 7.1** shows the analytical manifold for determination of IF.

The analytical system was almost the same as the system for the determination of TOF from PFCAs. The only difference was the eliminated of the UV/heating unit. Samples were continuously pumped to make a mixture with the distillation reagent using a flow rate of 0.42 mL/min. The mixture was then segmented with air bubbles with a flow rate of 2.5 mL/min before sending it to the distillation unit to recover fluoride followed by the colorimetric unit for fluoride detection. The flow cell type was 10 mm long. The change in the absorbance at 620 nm was measured by the spectrophotometer. The signal was recorded using ACCE software and a data-processing computer. Fluoride standards (0.5–4.0 mg/L) were measured in every run under the same conditions as the samples for calculation of recovered fluoride concentration. **Table 7.1** shows the types of sample and experimental conditions used for the determination of IF. For better quantification of the fluoride concentration, the sampling time was increased to 8 min instead of 6 min.

Table 7.1 Experimental conditions for the determination of IF by method A.

Sample	**Interference**
Milli-Q	F^- (1.0 mg/L)
PFCAs (PFHxA, PFOA, PFNA)/*Milli-Q* at 3 mg/L	
Distillation	
Sampling time	8 minutes
Interval time	4 minutes
Distillation reagent	H_2SO_4 (15% v/v), F^- (0.1 mg/L)
Distillation temperature	150 °C
Detection	
Absorption reagent	Imidazole (0.34% w/v), Acetic acid (0.006% v/v), Ascobic acid (1500 mg/L)
Color reagent	Alfusone (1% w/v), Imidazole (3.85% w/v)
Flow cell path length	10 mm
Glass filter	620 nm

7.3.2 Application of the developed method for the determination of TF, IF, and TOF

TOF from PFCAs samples was determined by Eqn. 7.1.

$$TOF = TF - IF \quad (7.1)$$

Table 7.2 shows the types of samples and the application method for the determination of TF. *Milli-Q* water and *Milli-Q* water-spiked fluoride at a concentration of 1 mg/L were used to assess the possibility of applying CFA for PFCAs by the colorimetric method that was developed in the previous chapters (method B). PFCA samples with non-spiked and spiked fluoride at 1 mg/L were analysed using method B for the determination of total TOF and TF. IF was then calculated from the TF and TOF values.

Table 7.2 Type of samples and analytical method for TOF determination

Type of sample	Interference	Type of fluoride measurement , mg/L
Milli-Q	None	TOF
	F^-, 1mg/L	TF
PFHxA: 3 mg/L	None	TOF
	F^-, 1mg/L	TF
PFOA: 3 mg/L	None	TOF
	F^-, 1mg/L	TF
PFNA: 3 mg/L	None	TOF
	F^-, 1mg/L	TF

7.3.3 Effect of interferences from domestic WWTPs in the determination of TF, IF and TOF

In this part, effluents from domestic WWTPs were used to examine the effects of matrices to our developed methods. **Table 7.3** shows the types of samples used. Experimental conditions and the experimental setup were kept the same as described above.

Table 7.3 Types of samples for the study on the effect of interferences from WWTPs for the determination of TOF, TF, and IF.

Type of samle	Spiked substance	Analytical method
S1 (Toba WWTP) S2 (Kisshoin WWTP)	None	Method A Method B
	F- (1mg/l)	
	PFCAs (PFHxA, PFOA, PFNA) at 3 mg/L	

7.4 Results and Discussion

7.4.1 Investigation of a method for the determination of IF by CFA using colorimetry

Six known concentrations of fluoride (0.5–4 mg/L) were used for the quantification with a correlation coefficient of 0.999. **Figure 7.2** shows the recorded signals for the fluoride standards which show that the developed method can be used for the quantification of fluoride ions. **Table 7.4** shows the results of the IF determination by the application of method A. No signals of fluoride concentrations were detected in the case of *Milli-Q* sample and PFCA samples at a concentration of 3 mg/L. However, when we spiked 1 mg/L of fluoride to *Milli-Q* water and PFCAs samples, fluoride concentrations were measured from 0.97–1.03 mg/L with the SD of 0.02 and CV of 2.43%. These results suggest that, the modified method (method A) can be used for the identification of inorganic fluoride.

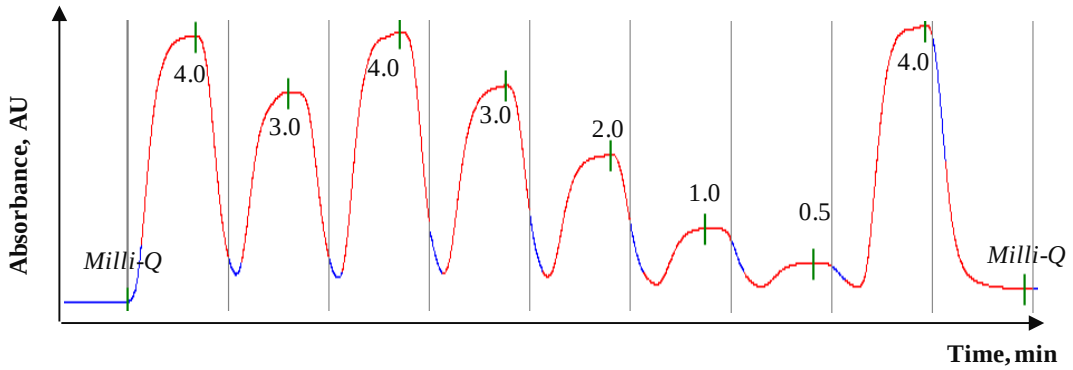


Figure 7.2 Recorded signals of CFA for the determination of fluoride by Method A. Numbers on the figure are fluoride concentrations (mg/L).

Table 7.4 Results of IF concentrations in water samples by method A

Type of sample	Interference	Detected fluoride concentration, mg/L
Milli-Q	None	N.D
	F^-, 1mg/L	1.01
PFHxA: 3 mg/L	None	N.D
	F^-, 1mg/L	1.03
PFOA: 3 mg/L	None	N.D
	F^-, 1mg/L	1.03
PFNA: 3 mg/L	None	N.D
	F^-, 1mg/L	1.01

7.4.2 Determination of TF, IF, and TOF in a *Milli-Q* sample spiked with fluoride or PFCAs

The same types of samples used for determination IF in the above study, were used for the determination of TF and TOF. **Table 7.5** shows the analytical results for TF and IF. Detected fluoride concentration of *Milli-Q* water-spiked fluoride at 1 mg/L was 0.96 mg/L. This result shows that our method can be applied for determination of inorganic fluoride in water samples. In the flowing steps, we measured the concentrations of fluoride in PFCA samples which were non-spiked or spiked with fluoride at 1 mg/L. Using Eqn (7.1), the TOF can be calculated from the TF and IF values. The results in **Table 7.5** show that values of TOF for PFCAs/*Milli-Q* and for PFCAs+F^-/*Milli-Q* were acceptable). The developed methods can be recommended for further research for the identification of TF, IF and TOF from wastewater.

Table 7.5 Analytical results for TF, IF and TOF by application of method B.

Type of sample	Theoretical detected F^-, mg/L	Detected fluoride concentration		TOF, mg/L
		IF, mg/L	TF, mg/L	
Milli-Q water	0	0.07	0.06	-
Milli-Q water / F^- : 1 mg/L	1 .00	1.01	0.96	-
PFHxA (3 mg/L)	1.99	0.11	1.59	1.48
PFHxA (3 mg/L) / F^- (1 mg/L)	2.99	1.03	2.66	1.63
PFOA (3 mg/L)	2.07	0.08	1.61	1.53
PFOA (3 mg/L) / F^- (1 mg/L)	3.07	1.03	2.67	1.64
PFNA (3 mg/L)	2.09	0.09	1.66	1.57
PFNA (3 mg/L) / F^- (1 mg/L)	3.09	1.01	2.69	1.68

7.4.3 Effect of interferences from WWTPs on the determination of TF, IF, and TOF

Table 7.6 shows the results of IF analysis by method A which indicates that IF was not detected in the samples S1 and S2. Analytical results of fluoride in S1 and S2 which were spiked with 1 mg/L of fluoride were 1.01 and 1.07 mg/L. These data shows that interferences from WWTPs were not affecting the measurement of inorganic fluoride using our method (method A).

Table 7.6 Analytical results for inorganic fluoride with the effects of interferences from effluents of domestic WWTPs.

Type of sample	Spiked substance PFCAs : 3 mg/L ; F^- : 1 mg/L				
	None	F^-	PFHxA	PFOA	PFNA
S1	ND	1.01	ND	ND	ND
S2	ND	1.07	ND	ND	ND

ND : None detected

Table 7.7 Analytical results of TF with the effects of interferences from effluents of domestic WWTPs.

Type of sample	Spiked substance PFCAs : 3 mg/L ; F^- : 1 mg/L							
	None	F^-	PFHxA	PFOA	PFNA	PFHxA + F^-	PFOA + F^-	PFNA + F^-
S1	ND	0.96	1.73	1.71	1.70	2.66	2.67	2.69
S2	ND	0.97	1.67	1.61	1.67	2.68	2.68	2.61

ND : None detected

Table 7.7 shows the analytical results of TF and TOF for the samples with the effects of interferences from effluents of domestic WWTPs. The results show that TOF of the PFCA samples were 1.67–1.73 mg/L (PFHxA), 1.61–1.71 mg/L (PFOA), and 1.67–1.70 mg/L (PFNA). The TF of PFCA samples spiked with 1 mg/L fluoride were 2.66–2.68 mg/L (PFHxA), 2.67–2.68 mg/L (PFOA), and 2.61–2.69 mg/L (PFNA). From these results, the calculated IF concentrations were 0.93–1.00 mg/L (PFHxA), 0.97–1.07 mg/L (PFOA), and 0.94–0.99 mg/L (PFNA). These results were acceptable and our developed methods (method A and method B) can be recommended for further research.

7.5 Summary

- A method for the determination of IF by CFA using a colorimetric technique was developed (Method A). The concentration of fluoride was not detected in the case of PFCAs with 3 mg/L.

- Results of TF, IF, and TOF of PFCAs/*Milli-Q* samples with or without spiked fluoride at 1 mg/L were acceptable.

- The methods were successfully applied to examine the effects of interferences from effluents of domestic WWTPs for the determination of TF, IF, and TOF.

Chapter 8 Conclusions and recommendations

8.1 Conclusions

Perfluorinated compounds (PFCs) are man-made chemicals in which the hydrogen atoms in the hydrocarbon chain have been replaced by fluorine atoms. These compounds have been recognized as emerging environmental pollutants in water environments because of their ubiquitous occurrence in the environment, biota, and humans. Reports on PFCs in the water environment and industries related to PFCs are limited since the current analytical methods were extremely expensive and complicated. A fast and easy measurement protocol to solve some of these issues was developed in this research. The conclusions are drawn are as follows: (given chapter-wise)

Chapter 2: We reviewed the available literature on PFCs with a special emphasis on analytical methods used for the PFCs.

Chapter 3: We investigated the PFC concentrations in tap water, river and lake water, two domestic and two industrial WWTPs and a landfill site in Da Nang. This chapter indicated that PFCs were found in surface water, wastewater, and tap water at ng/L concentration levels. Among the 18 surface water samples tested, SW8 had the highest concentration (132.2 ng/L) followed by SW7 (126.7 ng/L). For PFCs from two DWWTPs (Phu Loc and Hoa Cuong), two IWWTPs (Hoa Khanh and Tho Quang) and at the landfill site (Khanh Son), the highest PFC concentration was found at the landfill site. The major PFC contaminants in the effluent were PFOA, PFHpA, PFBuS, and PFHxS. The results of this study show that wastewater treatment facilities at the WWTPs were not able to completely remove the PFCs from wastewater. Therefore, effective removal techniques should be applied to minimize the environmental impact of these compounds. Besides, a high PFC (292 ng/L) level found in the discharging channel of IZ indicated the limitation in the management of industrial wastewater in IZ.

Chapter 4: We developed a method for the continuous decomposition of PFCAs. Experiments focused on the application of UV irradiation for the decomposition of PFCs. Our main objective was to study the effects of irradiation times and wavelengths on the decomposition of PFOA and PFNA dissolved in *Milli-Q* water at a concentration of 10 μg/L. The results showed the possibility of decomposition of PFOA and PFNA by the UV photolysis process. It was observed that, the target PFCs were decomposed faster under irradiation of $UV_{254+185}$ light in comparison to UV_{254}. 100% of PFOA was decomposed under irradiation with $UV_{254+185}$ light in 60 min. Under the same condition of 60 min irradiation, lower decomposition rates were observed in case of PFNA (99%).

Chapter 5: We developed a continuous flow system for the decomposition of PFCAs with quantification of the released fluoride. In this chapter, we installed a debubbler/rebubbler unit for UV/heating unit and a debubbler together with a stabilizer for the flow cell (30 mm length) to achieve better signals for the quantification of the fluoride concentration. The analytical system was developed with a correlation coefficient of 0.995 for six known concentrations of fluoride (0.5–4 mg/L) and a low carry over (less than 0.5%). The flow rate of sample was 0.16 min/L. Sampling time was 6 min while the interval time was 4 min. Subsequently, we studied the effects of experimental conditions (acid and oxidant concentration, initial concentration of PFCAs, heating temperature of UV/heating unit) on the decomposition rate of these chemicals. In this research, we used 42 different decomposition reagents comprised of an acid (H_2SO_4, six levels: 0–2 mol/L) and oxidant ($K_2S_2O_8$, seven levels: 0–0.16 mol/L) to find the effects on the decomposition rates of six PFCAs at a concentration of 3 mg/L. Under irradiation of $UV_{254+185}$ light and a temperature of 65 °C, the highest decomposition rates of PFCAs were observed in conditions of 0.4 mol/L of H_2SO_4 and 0.16 mol/L of $K_2S_2O_8$. The decomposition rates of PFCAs were 90% (PFBA), 89% (PFPA), 83% (PFHxA), 76% (PFHpA), 71% (PFOA), and 71% (PFNA). Increasing the concentration of H_2SO_4 from 0.4 to 2.0 mol/L did not contribute to increasing the decomposition rate of PFCAs. The irradiation time for these experiments was 12 min s. For understanding the effects of concentration on the decomposition rates,

we used 20 (= 4 × 5) different experimental conditions which were a combination of initial PFCAs concentrations (five levels) and concentrations of $K_2S_2O_8$ (four levels). And for studying the effects of temperature in the UV/heating unit, we used 24 (= 6 × 4) different experimental conditions which were a combination of temperature (six levels) and four concentration levels of the oxidant. The results showed that the decomposition rates of PFCAs at higher concentrations were higher in than at low concentrations. The lower decomposition rates of PFCAs at low PFCAs concentrations could be explained based on the higher percentage absorption of the PFCAs onto pump tubes and glass coils in comparison with higher concentration of PFCAs. Besides, when we increased the temperature from 55 to 80 °C, the irradiation time was reduced from 20 min to 4.4 min. This factor also could lead to the changes in decomposition rates of PFCAs. The decomposition rates increased when the temperature increased from 55 to 65 °C, even after irradiation time was reduced by 1.7 folds. When we increased the temperature from 65 to 80 °C, the decomposition rate reduced. We suspect that, the reduction in irradiation time was the main factor which contributed to the lower decomposition rates of PFCAs in this case. We recommend the optimum temperature of 65 °C for the UV/eating unit.

Chapter 6: In this chapter we studied the effects of interferences (DOC, chloride) on the continuous flow analysis of TOF from PFCAs using a colorimetric method. Actual wastewater samples contain many types of dissolved organic compounds (DOC). These compounds may compete with PFCAs for using the oxidant and energy of UV light leading to a reduction in the decomposition rates of PFCAs. Besides, the decomposition reactions of DOC will form gases which would increase the pressure in the system and cause the tubes to unplug. Therefore, a study on the effects of DOC interferences on the development of this analytical method is necessary. In this chapter, we selected glucose, humic acid, and methanol for our studies on the effects of DOC interferences on the development of continuous flow analysis for PFCAs using a colorimetric method. The results show that glucose at concentrations of 1–30 mg/L did not affect the decomposition rates of PFCAs significantly. However, the decomposition rates were slightly decreased when we increased the concentration of glucose from 30–100 mg/L. HA (1–100 mg/L) and methanol (0.1%–

1.0% v/v) did not affect the decomposition rates of PFCAs. Our study showed that chloride ions had negative effects on the recorded fluoride signals. However, these effects occurred only under conditions using a combination of irradiation of $UV_{254+185}$ light and temperature of 65 °C. Ascorbic acid at a concentration of 1500 mg/L in the absorption reagent successfully eliminated the effects of chloride interference at concentrations as high as 500 mg/L. These results suggest that the use of ascorbic acid at a concentration of 1500 mg/L would not affect the continuous flow analysis of PFCAs (PFHxA, PFOA, and PFNA) by this method. This condition was recommended for future research geared towards the improvement of the CFA for PFCAs.

Chapter 7: We developed a continuous flow system for the quantification of total organic fluoride (TOF) for PFCAs through the measurement of inorganic fluoride (IF) and total fluoride (TF) in aqueous solutions using a colorimetric method. In this chapter, we developed an analytical method for IF (Method A). The data showed that no signals of fluoride were detected in the case of the *Milli-Q* and PFCAs samples at a concentration of 3 mg/L. When we spiked 1 mg/L of fluoride to *Milli-Q* water and PFCAs samples, fluoride concentrations were measured from 0.97–1.03 mg/L with a SD of 0.02 and CV of 2.43%. These results suggest that our modified method (method A) can be used for the identification of inorganic fluoride. For PFCA samples spiked with 1 mg/L of fluoride, analysed by the method described in the previous chapter (method B), fluoride concentrations were detected from 1.03–1.07 mg/L. The methods were successfully applied for investigating the effects of interferences from WWTPs for the determination of TOF, TF and IF. In the case of wastewater samples spiked with PFCAs (3 mg/L) and F^- (1 mg/l), calculated IF concentrations were 0.93–1.00 mg/L (PFHxA), 0.97–1.07 mg/L (PFOA), and 0.94–0.99 mg/L (PFNA). These results were acceptable and our developed methods (method A and method B) can be recommended for further research.

8.2 Recommendations

The study results showed that the simple analytical methods developed for inorganic fluoride and for PFCAs by CFA analysis after decomposition were efficient. Some modifications of the analytical system were made. Based on the results of this study, we could make the following recommendations.

1. Since there are many different types of PFCs, future research should include other types of PFCs compounds such a long chain PFCAs, perfluoroalkyl sulfonates (PFASs), and fluorotelomer alcohols (FTOHs).
2. Study on the improvement of PFCs decomposition rates by considering effects of longer irradiation times, higher $UV_{254+185}$ lamp power, as well as the combination method for the decomposition of PFCAs is recommended.
3. Study on improvement of the developed system to achieve lower detection limits of fluoride. This method could also be developed for LOD and LOQ of water samples.
4. Need to study methods to increase the concentration of oxidants ($K_2S_2O_8$) in the mixture with the samples higher than 0.08 mg/L in order to examine the effect of oxidant concentration on the decomposition rates of PFCs
5. Consider the use of catalysts in the system in order to improve the decomposition rates of PFCs.

References

3M, Company. (1999) The science of organic fluorochemistry, p. 12, USEPA docket, EPA-HQ-OPPT- 2002-0043-0006.

American Public Health Association, E.A.D.A.W.W.A.W.E.F. (2005) Standard methods for the examination of water and wastewater, APHA-AWWA-WEF, Washington, D.C.

Björklund, J.A., Thuresson, K. and de Wit, C.A. (2009) Perfluoroalkyl compounds (PFCs) in indoor dust: concentrations, human exposure estimates, and sources. Environmental Science & Technology 43(7), 2276-2281.

Campbell, T.Y., Vecitis, C.D., Mader, B.T. and Hoffmann, M.R. (2009) Perfluorinated surfactant chain-length effects on sonochemical kinetics. The Journal of Physical Chemistry A 113(36), 9834-9842.

Cao, M.H., Wang, B.B., Yu, H.S., Wang, L.L., Yuan, S.H. and Chen, J. (2010) Photochemical decomposition of perfluorooctanoic acid in aqueous periodate with VUV and UV light irradiation. Journal of Hazardous Materials 179(1-3), 1143-1146.

Čápka, V.r., Bowers, C.P., Narvesen, J.N. and Rossi, R.F. (2004) Determination of total fluorine in blood at trace concentration levels by the Wickbold decomposition method with direct potentiometric detection. Talanta 64(4), 869-878.

Chen, J., Zhang, P. and Zhang, L. (2006) Photocatalytic decomposition of environmentally persistent perfluorooctanoic acid. Chemistry Letters 35(2), 230-231.

Chen, J., Zhang, P.-y. and Liu, J. (2007) Photodegradation of perfluorooctanoic acid by 185 nm vacuum ultraviolet light. Journal of Environmental Sciences 19(4), 387-390.

Cheng, J., Vecitis, C.D., Park, H., Mader, B.T. and Hoffmann, M.R. (2008) Sonochemical degradation of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in landfill groundwater: environmental matrix effects. Environmental Science & Technology 42(21), 8057-8063.

Cheng, J., Vecitis, C.D., Park, H., Mader, B.T. and Hoffmann, M.R. (2009) Sonochemical degradation of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in groundwater: kinetic effects of matrix inorganics. Environmental Science & Technology 44(1), 445-450.

Environmental Working Group (2003). PFCs: Global Contaminants.

EPA (2002). Hazard assessment of perfluorooctanoic acid and its salts, p. 107, Office of Pollution Prevention and Toxics - Risk Assessment Division, US.

Estrellan, C.R., Salim, C. and Hinode, H. (2010) Photocatalytic decomposition of perfluorooctanoic acid by iron and niobium co-doped titanium dioxide. Journal of Hazardous Materials 179(1-3), 79-83.

Flores, C., Ventura, F., Martin-Alonso, J. and Caixach, J. (2013) Occurrence of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in N.E. Spanish surface waters and their removal in a drinking water treatment plant that combines conventional and advanced treatments in parallel lines. Science of The Total Environment 461–462(0), 618-626.

Gauthier, S.A. and Mabury, S.A. (2005) Aqueous photolysis of 8:2 fluorotelomer alcohol. Environmental Toxicology and Chemistry 24(8), 1837-1846.

Giesy, J.P. and Kannan, K. (2002) Perfluorochemical surfactants in the environment. Environmental Science & Technology 36(7), 146a-152a.

Harada, K. and Koizumi, A. (2009) Environmental and biological monitoring of persistent fluorinated compounds in Japan and their toxicities. Environmental Health and Preventive Medicine 14(1), 7-19.

Hoffmann, M.R., Martin, S.T., Choi, W. and Bahnemann, D.W. (1995) Environmental applications of semiconductor photocatalysis. Chemical Reviews 95(1), 69-96.

Hori, H., Hayakawa, E., Einaga, H., Kutsuna, S., Koike, K., Ibusuki, T., Kiatagawa, H. and Arakawa, R. (2004) Decomposition of environmentally persistent perfluorooctanoic acid in water by photochemical approaches. Environmental Science & Technology 38(22), 6118-6124.

Hori, H., Nagaoka, Y., Murayama, M. and Kutsuna, S. (2008) Efficient decomposition of perfluorocarboxylic acids and alternative fluorochemical surfactants in hot water. Environmental Science & Technology 42(19), 7438-7443.

Hori, H., Yamamoto, A., Hayakawa, E., Taniyasu, S., Yamashita, N., Kutsuna, S., Kiatagawa, H. and Arakawa, R. (2005) Efficient decomposition of environmentally

persistent perfluorocarboxylic acids by use of persulfate as a photochemical oxidant. Environmental Science & Technology 39(7), 2383-2388.

Hori, H., Yamamoto, A., Koike, K., Kutsuna, S., Osaka, I. and Arakawa, R. (2007) Persulfate-induced photochemical decomposition of a fluorotelomer unsaturated carboxylic acid in water. Water Research 41(13), 2962-2968.

International Institute for Sustainable Development (2009) Earth Negotiations Bulletin.

Kim, S.-K., Im, J.-K., Kang, Y.-M., Jung, S.-Y., Kho, Y.L. and Zoh, K.-D. (2012) Wastewater treatment plants (WWTPs)-derived national discharge loads of perfluorinated compounds (PFCs). Journal of Hazardous Materials 201–202(0), 82-91.

Kirsch, P. (2013) Modern fluoroorganic chemistry: synthesis, reactivity, applications. Wiley-VCH, Weinheim.

Kunacheva, C., Boontanon, S.K., Fujii, S., Tanaka, S., Musirat, C., Artsalee, C. and Wongwattana, T. (2009) Contamination of perfluorinated compounds (PFCs) in Chao Phraya River and Bangpakong River, Thailand. Water Sci Technol 60(4), 975-982.

Kunacheva, C., Fujii, S., Tanaka, S., Seneviratne, S.T., Lien, N.P., Nozoe, M., Kimura, K., Shivakoti, B.R. and Harada, H. (2012) Worldwide surveys of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in water environment in recent years. Water Sci Technol 66(12), 2764-2771.

Kunacheva, C., Tanaka, S., Fujii, S., Boontanon, S.K., Musirat, C., Wongwattana, T. and Shivakoti, B.R. (2011) Mass flows of perfluorinated compounds (PFCs) in central wastewater treatment plants of industrial zones in Thailand. Chemosphere 83(6), 737-744.

Lee, Y.-C., Lo, S.-L., Chiueh, P.-T. and Chang, D.-G. (2009) Efficient decomposition of perfluorocarboxylic acids in aqueous solution using microwave-induced persulfate. Water Research 43(11), 2811-2816.

Lee, Y.-C., Lo, S.-L., Kuo, J. and Lin, Y.-L. (2012) Persulfate oxidation of perfluorooctanoic acid under the temperatures of 20–40°C. Chemical Engineering Journal 198–199(0), 27-32.

Li, H.B. and Xu, X.R. (1999) Separation and determination of fluoride in plant samples. Talanta 48(1), 57-62.

Loos, R., Wollgast, J., Huber, T. and Hanke, G. (2007) Polar herbicides, pharmaceutical products, perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA) and nonylphenol and its carboxylates and ethoxylates in surface and tap waters around Lake Maggiore in Northern Italy. Anal Bioanal Chem 387(4), 1469-1478.

Minnesota Department of Health (2012). Perflorochemicals (PFCs) and health.

Miyake, Y., Yamashita, N., Rostkowski, P., So, M.K., Taniyasu, S., Lam, P.K.S. and Kannan, K. (2007) Determination of trace levels of total fluorine in water using combustion ion chromatography for fluorine: a mass balance approach to determine individual perfluorinated chemicals in water. Journal of Chromatography A 1143(1-2), 98-104.

Moriwaki, H., Takagi, Y., Tanaka, M., Tsuruho, K., Okitsu, K. and Maeda, Y. (2005) Sonochemical decomposition of perfluorooctane sulfonate and perfluorooctanoic acid. Environmental Science & Technology 39(9), 3388-3392.

Musijowski, J., Szostek, B., Koc, M. and Trojanowicz, M. (2010) Determination of fluoride as fluorosilane derivative using reversed-phase HPLC with UV detection for determination of total organic fluorine. Journal of Separation Science 33(17-18), 2636-2644.

Musijowski, J., Trojanowicz, M., Szostek, B., da Costa Lima, J.L.F., Lapa, R., Yamashita, H., Takayanagi, T. and Motomizu, S. (2007) Flow-injection determination of total organic fluorine with off-line defluorination reaction on a solid sorbent bed. Analytica Chimica Acta 600(1–2), 147-154.

OECD (2002) Co-operation on existing chemicals hazard assessment of perfluorooctane sulfonate (PFOS) and its salts, p. 362.

O'Hagan, D. (2008) Understanding organofluorine chemistry. An introduction to the C-F bond. Chemical Society Reviews 37(2), 308-319.

Olsen, G.W., Huang, H.Y., Helzlsouer, K.J., Hansen, K.J., Butenhoff, J.L. and Mandel, J.H. (2005) Historical comparison of perfluorooctanesulfonate, perfluorooctanoate, and other fluorochemicals in human blood. Environ Health Perspect 113(5), 539-545.

Panchangam, S.C., Lin, A.Y.-C., Shaik, K.L. and Lin, C.-F. (2009) Decomposition of perfluorocarboxylic acids (PFCAs) by heterogeneous photocatalysis in acidic aqueous medium. Chemosphere 77(2), 242-248.

Prevedouros, K., Cousins, I.T., Buck, R.C. and Korzeniowski, S.H. (2005) Sources, fate and transport of perfluorocarboxylates. Environmental Science & Technology 40(1), 32-44.

Renner, R. (2001) Growing concern over perfluorinated chemicals. Environmental Science & Technology 35(7), 154A-160A.

Saito, N., Harada, K., Inoue, K., Sasaki, K., Yoshinaga, T. and Koizumi, A. (2004) Perfluorooctanoate and perfluorooctane sulfonate concentrations in surface water in Japan. Journal of Occupational Health 46(1), 49-59.

Schultz, M.M., Higgins, C.P., Huset, C.A., Luthy, R.G., Barofsky, D.F. and Field, J.A. (2006) Fluorochemical mass flows in a municipal wastewater treatment facility. Environmental Science & Technology 40(23), 7350-7357.

Senevirathna, S.T.M.L.D., Tanaka, S., Fujii, S., Kunacheva, C., Harada, H., Shivakoti, B.R. and Okamoto, R. (2010) A comparative study of adsorption of perfluorooctane sulfonate (PFOS) onto granular activated carbon, ion-exchange polymers and non-ion-exchange polymers. Chemosphere 80(6), 647-651.

Shimada, K., Shimoda, T., Kokusen, H. and Nakano, S. (2005) Automatic microdistillation flow-injection system for the spectrophotometric determination of fluoride. Talanta 66(1), 80-85.

Sinclair, E. and Kannan, K. (2006) Mass loading and fate of perfluoroalkyl surfactants in wastewater treatment plants. Environmental Science &Technology 40(5), 1408-1414.

Skutlarek, D., Exner, M. and Farber, H. (2006) Perfluorinated surfactants in surface and drinking waters. Environ Sci Pollut Res Int 13(5), 299-307.

Stockholm Convention (2009). Summary of the Fourth Conference of the parties to the Stockholm Convention on Persistent Organic Pollutants, Switzerland.

Szostek, B., Prickett, K.B. and Buck, R.C. (2006) Determination of fluorotelomer alcohols by liquid chromatography/tandem mass spectrometry in water. Rapid Communications in Mass Spectrometry 20(19), 2837-2844.

Tanaka, S., Fujii, S., Lien, N.P., Nozoe, M., Kunacheva, C., Kimura, K. and Shivakoti, B.R. (2008) Contamination of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in water environment of 21 cities in 10 countries. Journal of Japan Society on Water Environment 31(11), 665-670.

Tang, C.Y., Fu, Q.S., Robertson, A.P., Criddle, C.S. and Leckie, J.O. (2006) Use of reverse osmosis membranes to remove perfluorooctane sulfonate (PFOS) from semiconductor wastewater. Environmental Science & Technology 40(23), 7343-7349.

Taniyasu, S., Kannan, K., So, M.K., Gulkowska, A., Sinclair, E., Okazawa, T. and Yamashita, N. (2005) Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota. Journal of Chromatography A 1093(1–2), 89-97.

Taniyasu, S., Kannan, K., Yeung, L.W.Y., Kwok, K.Y., Lam, P.K.S. and Yamashita, N. (2008) Analysis of trifluoroacetic acid and other short-chain perfluorinated acids (C2–C4) in precipitation by liquid chromatography–tandem mass spectrometry: Comparison to patterns of long-chain perfluorinated acids (C5–C18). Analytica Chimica Acta 619(2), 221-230.

Tikkanen, M. (2001) Guidance manual for disposal of chlorinated water, AWWA Research Foundation and American Water Works Association, Denver, CO.

Venkateswarlu, P. (1982) Sodium biphenyl method for determination of covalently bound fluorine in organic compounds and biological materials. Analytical Chemistry 54(7), 1132-1137.

Voogt, P.D. and Sáez, M. (2006) Analytical chemistry of perfluoroalkylated substances. TrAC Trends in Analytical Chemistry 25(4), 326-342.

Wada, H., Mori, H. and Nakagawa, G. (1985) Spectrophotometric determination of fluoride with lanthanum/alizarin complexone by flow injection analysis. Analytica Chimica Acta 172(0), 297-302.

Wagner, A., Raue, B., Brauch, H.-J., Worch, E. and Lange, F.T. (2013) Determination of adsorbable organic fluorine from aqueous environmental samples by adsorption to polystyrene-divinylbenzene based activated carbon and combustion ion chromatography. Journal of Chromatography A 1295(0), 82-89.

Wang, B.B., Cao, M.H., Tan, Z.J., Wang, L.L., Yuan, S.H. and Chen, J. (2010) Photochemical decomposition of perfluorodecanoic acid in aqueous solution with VUV light irradiation. Journal of Hazardous Materials 181(1-3), 187-192.

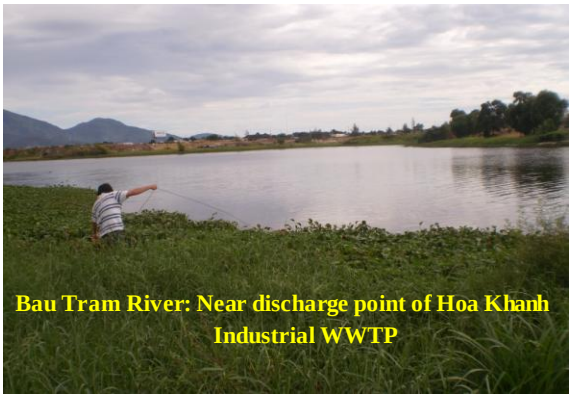
Wang, L.K., Hung, Y.-T. and Shammas, N.K. (2007) Advanced physicochemical treatment processes, Humana Press, Totowa, N.J.

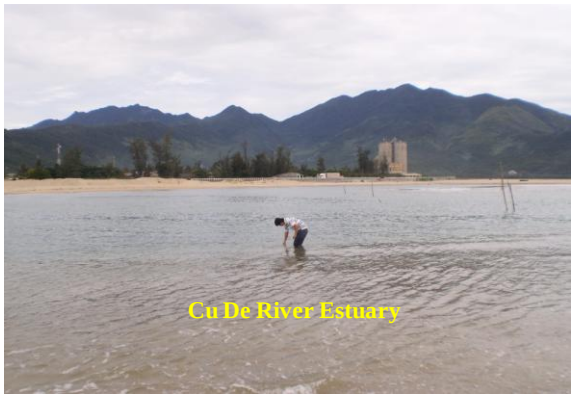
Yamada, T., Taylor, P.H., Buck, R.C., Kaiser, M.A. and Giraud, R.J. (2005) Thermal degradation of fluorotelomer treated articles and related materials. Chemosphere 61(7), 974-984.

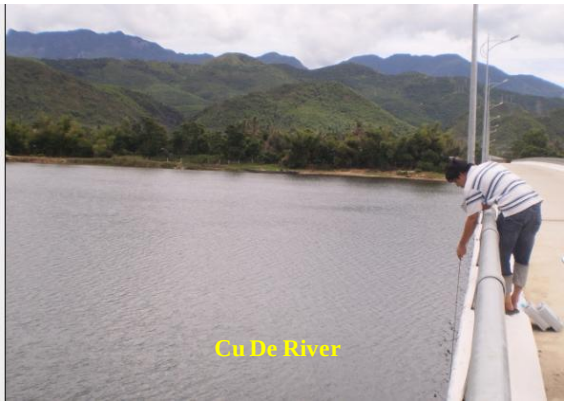
Yamamoto, T., Noma, Y., Sakai, S.-i. and Shibata, Y. (2007) Photodegradation of Perfluorooctane Sulfonate by UV Irradiation in Water and Alkaline 2-Propanol. Environmental Science & Technology 41(16), 5660-5665.

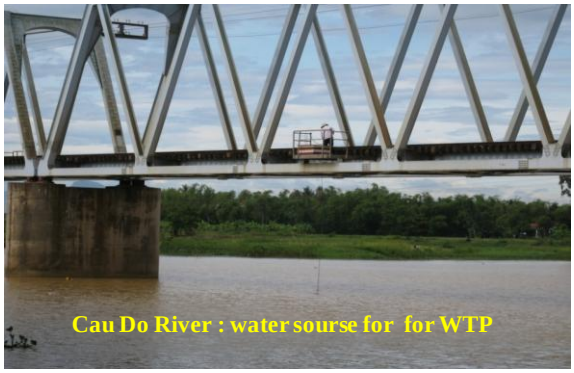
Appendix A

Pictures of field sevey for occurrence of PFCs in Da Nang, Viet Nam










Phu Loc Domestic WWTP: input wastewater


Hoa Khanh Domestic WWTP: treated wastewater


Hoa Khanh Industrial zone: Discharged point


Tho Quang Industrial WWTP: treated wastewater

PFCs concentration (ng/L) in tap water in Da Nang

(Sampling date: July 30 to August 3, 2011)

Type of PFCs	PFCs concentration, ng/L					Average concentration, ng/L
	TW1	TW2	TW3	TW4	TW5	
PFPeA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ
PFHxA	0.3	<LOQ	<LOQ	<LOQ	3.8	0.8
PFHpA	3.0	0.0	0.2	<LOQ	2.0	1.0
PFOA	40.3	1.9	1.7	<LOQ	12.9	11.4
PFNA	2.7	0.7	0.9	1.0	1.5	1.4
PFDA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ
PFUnDA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ
PFDoDA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ
PFBuS	2.4	3.4	N.D	N.D	3.6	1.9
PFHS	0.5	0.2	<LOQ	<LOQ	0.5	0.3
PFOS	2.7	1.7	0.4	<LOQ	3.7	1.7
Total PFCs, ng/L	**52.0**	**8.0**	**3.3**	**1.2**	**27.9**	**18.5**

PFCs concentration (ng/L) in surface water in Da Nang

(Sampling date: July 30 to August 3, 2011)

Sampling point	PFCs concentration, ng/L											Total, ng/L
	Perfluorocarboxylate (PFCA)								Perfluoroalkyl sulfonate (PFAS)			
	PFPA C5-A	PFHxA C6-A	PFHpA C7-A	PFOA C8-A	PFNA C9-A	PFDA C10-A	PFUnDA C11-A	PFDoDA C12-A	PFBuS C4-S	PFHxS C6-S	PFOS C8-S	
SW1	< *LOQ*	< *LOQ*	1.5	3.1	< *LOQ*	< *LOQ*	< *LOQ*	< *LOQ*	2.1	0.7	< *LOQ*	7.6
SW2	*N.D.*	*N.D.*	< *LOQ*	< *LOQ*	*N.D.*	<LOQ	< *LOQ*	< *LOQ*	*N.D.*	*N.D.*	< *LOQ*	0.2
SW3	< LOQ	< *LOQ*	<LOQ	1.1	*N.D.*	<LOQ	< *LOQ*	< *LOQ*	*N.D.*	*N.D.*	< *LOQ*	1.3
SW4	1.1	*N.D.*	1.3	19.8	*N.D.*	0.1	< *LOQ*	< *LOQ*	4.5	0.9	3.8	31.6
SW5	0.1	*N.D.*	<LOQ	0.1	*N.D.*	<LOQ	< *LOQ*	< *LOQ*	2.5	0.6	< *LOQ*	3.4
SW6	14.8	< *LOQ*	0.9	6.5	< *LOQ*	1.7	< *LOQ*	< *LOQ*	2.2	0.1	< *LOQ*	26.3
SW7	7.2	< *LOQ*	1.4	99.5	< *LOQ*	0.1	< *LOQ*	< *LOQ*	0.6	15.1	2.6	126.7
SW8	8.2	0.2	1.8	104.5	< *LOQ*	< *LOQ*	< *LOQ*	< *LOQ*	0.7	15.1	1.6	132.2
SW9	14.2	< *LOQ*	< *LOQ*	2.3	< *LOQ*	< *LOQ*	< *LOQ*	< *LOQ*	4.7	3.1	< *LOQ*	24.6
SW10	15.5	< *LOQ*	< *LOQ*	2.4	< *LOQ*	< *LOQ*	< *LOQ*	< *LOQ*	4.9	3.0	< *LOQ*	26.0
SW11	2.8	< *LOQ*	0.4	3.7	< *LOQ*	< *LOQ*	< *LOQ*	< *LOQ*	5.1	1.3	0.2	13.5
SW12	1.6	< *LOQ*	0.9	5.9	0.1	0.1	< *LOQ*	< *LOQ*	1.5	1.2	0.9	12.3
SW13	< *LOQ*	*N.D.*	< *LOQ*	0.3	*N.D.*	< *LOQ*	< *LOQ*	< *LOQ*	0.1	0.0	< *LOQ*	0.5
SW14	<LOQ	*N.D.*	< *LOQ*	< *LOQ*	*N.D.*	< *LOQ*	< *LOQ*	< *LOQ*	0.3	< *LOQ*	< *LOQ*	0.5
SW15	< *LOQ*	< *LOQ*	1.0	< *LOQ*	< *LOQ*	< *LOQ*	< *LOQ*	< *LOQ*	2.5	0.7	1.2	5.6
SW16	*N.D.*	< *LOQ*	0.4	< *LOQ*	*N.D.*	< *LOQ*	< *LOQ*	< *LOQ*	7.2	1.9	0.8	14.6
SW17	< *LOQ*	< *LOQ*	3.7	55.4	4.5	0.1	< *LOQ*	< *LOQ*	*N.D.*	< *LOQ*	1.3	65.1
SW18	< *LOQ*	*N.D.*	< *LOQ*	< *LOQ*	*N.D.*	<LOQ	< *LOQ*	< *LOQ*	0.1	< *LOQ*	< *LOQ*	0.3
Total , ng/L	**69.8**	**0.6**	**13.7**	**304.6**	**4.9**	**2.4**	**0.2**	**0.2**	**39.3**	**43.9**	**12.6**	**492.2**

PFCs concentrations (ng/L) in two DWWTPs in Da Nang

(Sampling date: July 30 to August 3, 2011)

Sampling site	Sample type /Sample code	PFCs concentration, ng/L											
		PFPeA C5-A	PFHxA C6-A	PFHpA C7-A	PFOA C8-A	PFNA C9-A	PFDA C10-A	PFUnDA C11-A	PFDoDA C12-A	PFBuS C4-S	PFHxS C6-S	PFOS C8-S	Sum of PFCs
Phu Loc DWWTP, $n = 1$	Influent (WW1)	< LOQ	<LOQ	0.8	18.6	< LOQ	< LOQ	< LOQ	< LOQ	22.1	43.2	3.5	27.6
	Effluent (WW2)	< LOQ	<LOQ	0.8	21.8	< LOQ	< LOQ	< LOQ	< LOQ	11.3	5.5	< LOQ	42.6
Hoa Cuong DWWTP, $n = 1$	Influent (WW3)	< LOQ	83.1	14.2	55.5	4.9	< LOQ	< LOQ	< LOQ	6.6	1.5	< LOQ	166.0
	Effluent (WW4)	< LOQ	< LOQ	1.2	31.1	< LOQ	< LOQ	< LOQ	< LOQ	18.5	1.3	< LOQ	52.3
New Khanh Son's Landfill, $n = 1$	Leachate (WW9)	< LOQ	< LOQ	2.6	45.1	6.2	1.6	1.7	< LOQ	134.9	7.7	< LOQ	199.8
	Leachate + Septic Wastewater (WW10)	< LOQ	< LOQ	22.7	254.6	21.9	19.7	4.0	< LOQ	179.5	11.7	1.9	516.1
	Treated leachate (WW11)	N.D.	1.4	4.9	38.2	2.5	0.6	0.4	< LOQ	23.4	2.4	1.2	75.0

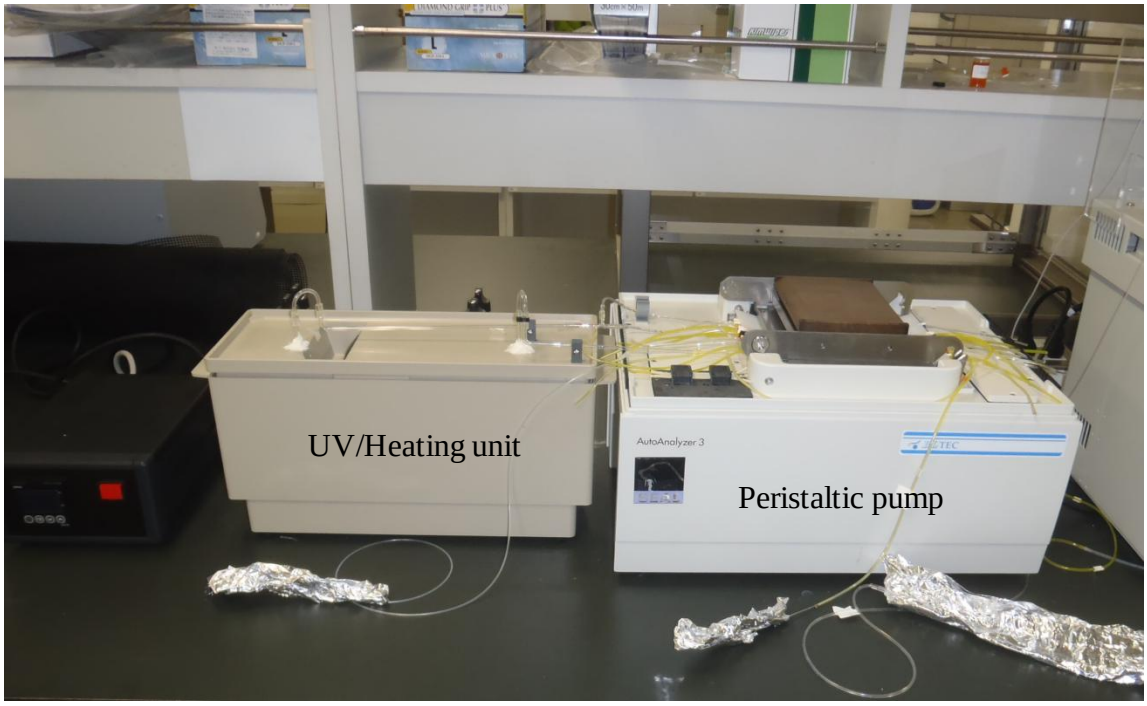
PFCs concentrations (ng/L) in influent and effluent from IWWTPs

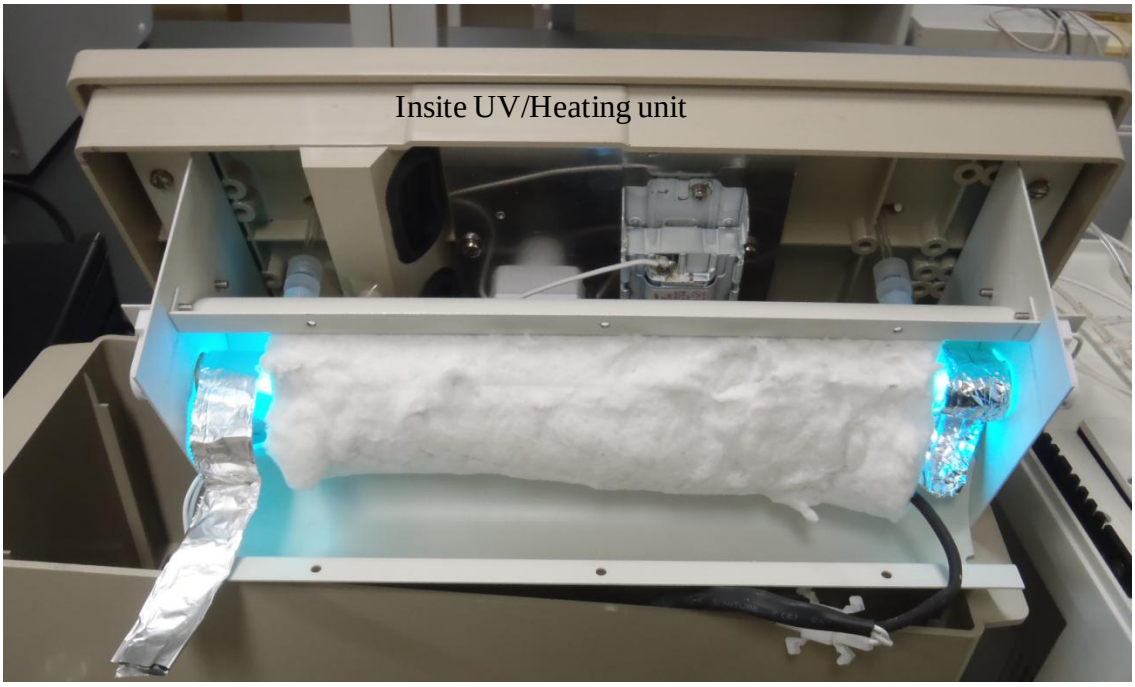
(Sampling date: July 30 to August 3, 2011)

Sampling site	Type of sample (Sample code)	PFCs concentration, ng/L											
		PFPeA C5-A	PFHxA C6-A	PFHpA C7-A	PFOA C8-A	PFNA C9-A	PFDA C10-A	PFUnDA C11-A	PFDoDA C12-A	PFBuS C4-S	PFHxS C6-S	PFOS C8-S	Sum of PFCs
Hoa Khanh IWWTP, n = 1	Effluent (WW5)	<LOQ	17.9	3.7	15.4	1.5	0.3	0.2	<LOQ	2.7	0.3	<LOQ	42.1
	Discharge channel (WW6)	0.6	19.5	6.6	41.8	7.6	0.7	0.3	<LOQ	5.6	0.4	209.4	292.4
Tho Quang IWWTP, n = 1	Influent (WW7)	<LOQ	5.6	9.3	153.7	7.4	0.5	0.8	<LOQ	54.2	1.7	19.2	252.5
	Efluent (WW8)	1.5	0.1	2.3	53.2	4.4	0.4	0.6	<LOQ	5.4	3.4	1.2	72.6

Appendix B

Pictures of experiment system for continuous decomposition of PFCAs



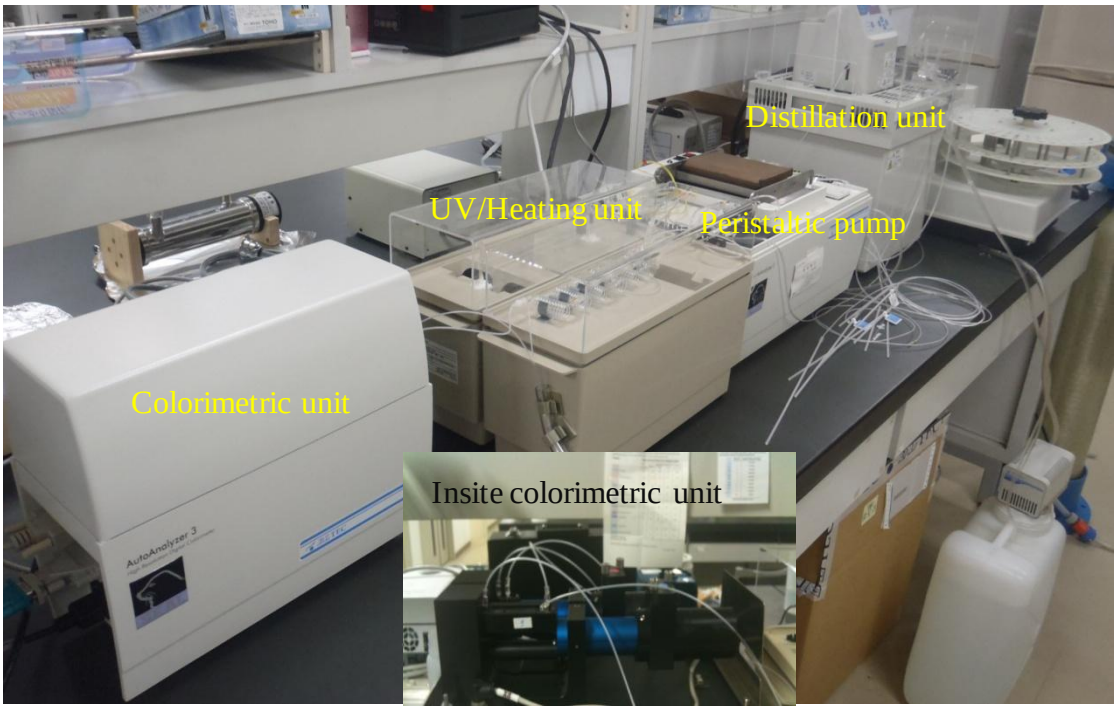


Decomposition rates of PFOA and PFNA (10 μg/L) under irradiation of UV_{254} and $UV_{254+185}$

	Decomposition rate, %							
Type of UV lamp	UV_{254}				$UV_{254+185}$			
Irradiation time	10 min	20 min	30 min	60 min	10 min	20 min	30 min	60 min
PFOA	0	0	0	98.09	82.68	68.27	90.97	100
	0	0	0	98.11	71.48	81.61	93.79	100
	0	0	0	91.38	74.18	83.41	98.61	100
PFNA	13.15	32.88	47.82	98.09	86.96	88.39	97.08	98.33
	16.86	32.31	45.84	95.22	87.94	89.81	96.98	98.72
	16.91	37.72	41.54	89.94	87.00	87.54	97.76	99.05

Appendix C

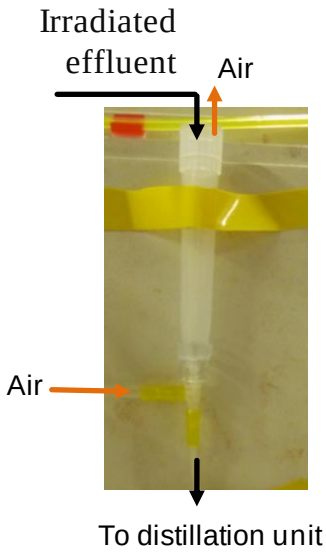
Pictures of experiment system for continuous decomposition of PFCAs and quantification of released fluoride by colorimetric method



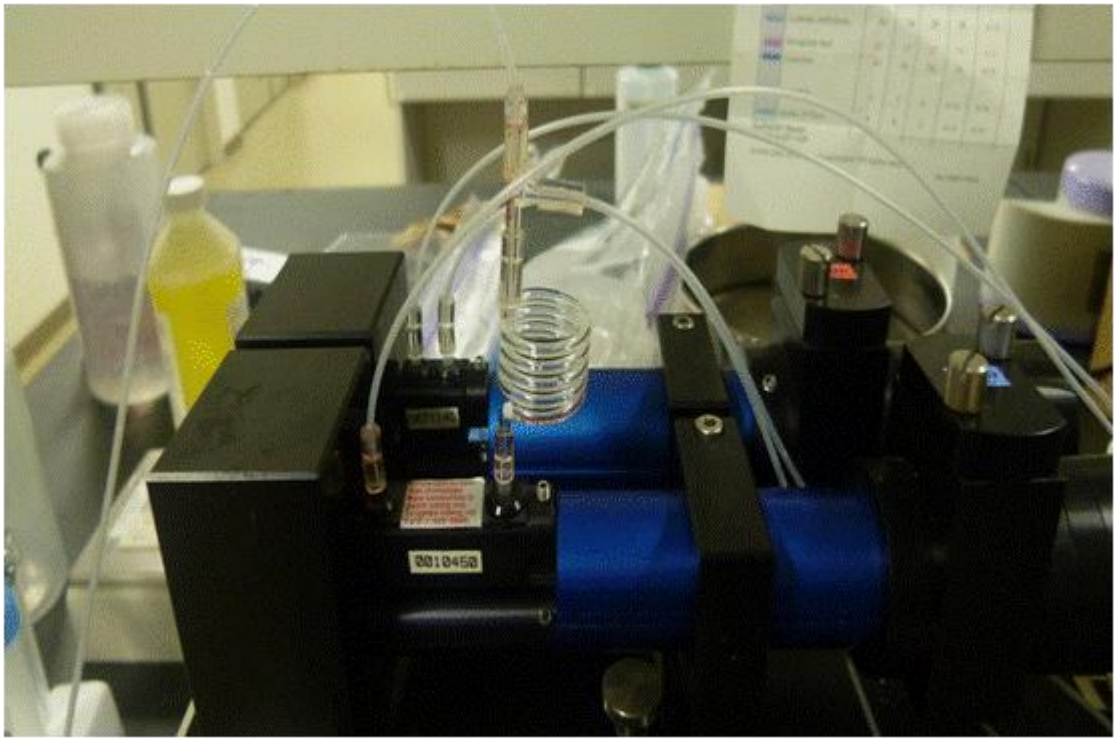
Reaction of fluoride with color reagent in the reaction coils before colorimetric unit

Flow pattern of effluent after UV/Heating unit

Modification of the experimental system with the installation of the debubbler/rebubbler unit after UV/Heating unit



Modification of the experimental system with the installation of the debubbler/stabilizer unit before flow cell of the colorimetric unit



Effects of acid (H_2SO_4) and oxidant ($K_2S_2O_8$) concentration on the decomposition rates of PFCAs at concentration of 3 mg/L. Heating temperature was 65 ^oC and irradiation/heating time was 12 min

Experiment date (Year/Month/Date)	Experiment code	Decomposition reagent, mol/L		Decomposition rate, %					
		$K_2S_2O_8$	H_2SO_4	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA
2012/12/12	121212A	0	0	18.3	16.4	16.5	15.5	14.9	12.7
2012/12/18	121218D	0.01	0	16.0	14.3	11.6	10.8	8.8	8.5
2012/12/19	121219A	0.02	0	18.4	15.0	13.5	11.9	11.5	10.9
2012/12/16	121216A	0.04	0	18.7	16.4	15.7	14.3	13.5	16.8
2012/12/16	121216B	0.08	0	25.9	22.8	19.4	21.5	19.9	26.9
2013/1/7	130107B	0.12	0	39.7	30.8	30.4	24.3	21.3	29.0
2012/12/16	121216C	0.16	0	53.3	44.1	41.5	35.5	31.6	42.2
2012/12/17	121217A	0	0.02	20.7	17.6	15.8	12.9	11.1	11.9
2012/12/19	121219B	0.01	0.02	14.6	13.0	11.1	10.9	10.1	8.7
2012/12/20	121220A	0.02	0.02	18.3	14.4	16.7	17.8	17.2	19.9
2012/12/20	121220B	0.04	0.02	30.9	27.4	24.9	22.1	21.2	27.4
2012/12/23	121223A	0.08	0.02	54.1	46.0	41.0	37.4	34.0	41.6
2013/1/8	130108A	0.12	0.02	63.6	54.8	45.8	35.6	34.5	43.9
2012/12/24	121224C	0.16	0.02	73.9	62.2	57.1	50.7	41.5	48.2
2012/12/25	121225A	0	0.1	10.9	10.4	8.6	6.8	6.0	5.6
2012/12/25	121225B	0.01	0.1	15.6	12.4	10.2	6.6	4.8	4.5
2012/12/26	121226B	0.02	0.1	26.1	21.3	19.1	18.7	18.2	17.1
2012/12/26	121226C	0.04	0.1	38.3	31.2	28.9	31.9	30.7	36.7
2012/12/27	121227A	0.08	0.1	59.6	56.3	48.6	47.8	45.7	45.8
2013/1/9	130109A	0.12	0.1	73.0	68.0	57.8	52.2	48.9	48.4
2012/12/27	121227B	0.16	0.1	88.7	85.1	79.7	69.1	65.7	68.2
2012/12/27	121227C	0	0.4	12.5	11.5	12.2	12.5	12.2	13.7
2012/12/28	121228A	0.01	0.4	18.4	18.6	17.3	22.4	26.6	22.7
2012/12/28	121228B	0.02	0.4	23.1	22.1	21.5	20.6	19.7	19.2
2012/12/28	121228C	0.04	0.4	54.6	43.5	42.9	40.5	41.0	42.5
2013/1/2	130102A	0.08	0.4	72.5	66.3	63.1	58.1	51.1	59.6
2013/1/9	130109B	0.12	0.4	87.9	85.7	77.8	67.0	66.9	68.9
2013/1/2	130102B	0.16	0.4	90.0	89.7	83.6	76.2	70.6	71.0
2013/1/19	130119A	0	1	13.6	12.3	11.4	9.7	10.2	10.1
2013/1/21	130121A	0.01	1	25.3	25.2	21.2	20.1	18.2	16.1
2013/1/21	130121B	0.02	1	23.9	22.9	22.3	21.9	21.6	21.3
2013/1/22	130122A	0.04	1	43.9	39.6	38.7	36.1	38.8	36.4
2013/1/22	130122B	0.08	1	70.8	64.0	62.5	58.2	57.6	59.4
2013/1/23	130123A	0.12	1	83.0	82.4	81.4	69.1	65.8	69.0
2013/1/23	130123B	0.16	1	80.5	81.9	82.6	72.3	69.2	70.6
2013/1/16	130116A	0	2	16.7	13.7	13.8	12.8	12.1	9.6
2013/1/16	130116B	0.01	2	17.0	14.9	14.6	14.6	16.0	13.8
2013/1/3	130103B	0.02	2	20.3	15.7	11.9	9.2	11.6	10.7
2013/1/7	130107A	0.04	2	46.7	39.3	38.9	34.7	37.2	36.0
2013/1/4	130104A	0.08	2	66.4	64.4	63.0	58.3	56.7	65.2
2013/1/10	130110A	0.12	2	80.9	77.2	71.8	65.2	66.2	65.9
2013/1/4	130104B	0.16	2	81.7	76.8	78.0	70.6	69.0	68.1

Effects of initial PFCAs concentrations on the decomposition rates of these chemicals. Heating temperature was 65 ^{o}C and irradiation/heating time was 12 min

Decomposition reagent, mol/L		PFCAs, mg/L	Decomposition rate , %					
$K_2S_2O_8$	H_2SO_4		PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA
0.02	0.4	3	25.2	24.4	26.7	23.6	20.8	20.1
		4	23.0	20.3	19.1	16.6	12.7	15.9
		5	27.0	25.9	22.2	20.6	15.3	11.4
		6	29.3	23.5	20.5	15.3	11.0	13.8
		10	31.8	27.3	22.0	15.3	8.5	9.5
0.04	0.4	3	50.4	41.7	40.1	37.7	37.7	44.7
		4	50.8	43.8	40.5	37.1	38.3	44.7
		5	53.6	47.4	45.9	40.7	44.7	53.8
		6	62.4	54.1	49.9	46.2	48.5	56.1
		10	62.2	55.9	51.6	50.3	47.7	56.3
0.08	0.4	3	51.0	46.4	41.1	39.6	42.7	48.0
		4	56.8	49.8	44.8	42.7	43.9	51.6
		5	59.2	49.0	45.2	42.3	45.6	54.3
		6	61.6	55.2	50.3	48.0	50.0	58.2
		10	68.1	62.7	56.3	54.0	54.1	62.3
0.16	0.4	3	90.0	89.7	83.6	76.2	70.6	71.0
		4	95.8	94.4	89.0	81.2	81.0	84.4
		5	96.3	94.3	90.0	83.5	83.1	86.1
		6	94.5	96.5	93.0	84.4	86.1	89.6
		10	98.8	98.8	94.2	92.2	86.2	88.8

Effects of heating temperature on the decomposition rates of PFCAs at different concentration

Experiment date	Experiment code	Heating Temp., ^{o}C	Irradiation time, min	Decomposition agent, mol/L		Decomposition rate, %					
				$K_2S_2O_8$	H_2SO_4	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA
2013/3/5	130305A	55	20	0.04	0.4	53.9	44.7	38.1	33.9	34.7	34.0
2013/3/5	130305B	60	14	0.04	0.4	54.4	45.5	40.3	39.1	40.4	39.8
2012/12/28	121228C	65	12	0.04	0.4	54.6	47.5	42.9	40.5	41.0	42.5
2012/3/14	130314A	70	10	0.04	0.4	51.5	33.8	26.1	21.9	21.2	19.1
2012/3/14	130314B	75	7	0.04	0.4	44.5	30.9	23.0	22.3	19.1	19.3
2012/3/15	130315A	80	4.4	0.04	0.4	36.6	29.5	23.4	21.5	19.0	15.4
2013/3/1	130301A	55	20	0.08	0.4	65.1	63.2	59.5	59.7	57.3	59.3
2013/2/28	130228B	60	14	0.08	0.4	66.9	64.1	61.0	59.1	58.1	57.1
2013/1/2	130102A	65	12	0.08	0.4	72.5	66.3	63.1	58.1	59.1	59.6
2013/2/28	130228A	70	10	0.08	0.4	60.5	53.3	39.3	35.1	30.3	30.3
2013/2/27	130227B	75	7	0.08	0.4	46.3	40.6	30.2	25.4	22.6	22.4
2013/2/27	130227A	80	4.4	0.08	0.4	37.8	37.7	30.9	27.6	23.4	22.5
2013/2/22	130222A	55	20	0.12	0.4	85.1	81.1	68.5	63.2	63.2	62.5
2013/2/25	130225A	60	14	0.12	0.4	88.2	88.6	74.6	67.5	63.8	67.1
2013/1/9	130109B	65	12	0.12	0.4	87.9	85.7	77.8	67.0	66.9	68.9
2013/2/25	130225B	70	10	0.12	0.4	64.6	57.2	52.9	49.2	47.2	53.3
2013/2/26	130226A	75	7	0.12	0.4	63.7	52.1	44.7	40.6	33.0	37.6
2013/2/26	130226B	80	4.4	0.12	0.4	59.4	58.2	48.0	39.8	34.5	37.0
2013/2/5	130205A	55	20	0.16	0.4	77.9	75.5	71.8	63.8	57.8	58.6
2013/2/14	130214A	60	14	0.16	0.4	85.0	77.5	78.2	70.7	64.5	68.5
2013/1/2	130102B	65	12	0.16	0.4	90.0	89.7	83.6	76.2	70.6	71.0
2013/2/15	130215A	70	10	0.16	0.4	86.3	80.2	72.8	68.4	64.4	65.0
2013/1/31	130131A	75	7	0.16	0.4	65.8	59.2	54.6	50.1	45.6	50.1
2013/2/15	130215B	80	4.4	0.16	0.4	60.3	53.0	45.8	35.7	31.9	32.1

Appendix D

Effect of glucose interference on the decomposition rate of PFCAs

Decomposition agent, mol/L		Characteristic of input sample		Decomposition rate , %					
$K_2S_2O_8$	H_2SO_4	Concentration of PFCAs, mg/L	Concentration of glucose, mg/L	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA
0.16	0.4	3	0	94.5	90.8	82.6	79.3	80.1	78.8
			1	94.2	88.5	84.7	78.2	77.9	76.9
			3	93.7	87.2	84.9	79.3	77.6	75.3
			10	92.2	87.6	81.2	78.1	76.9	74.0
			30	88.2	87.6	82.6	78.3	76.8	74.0
			100	82.5	82.7	75.8	71.5	71.6	72.3

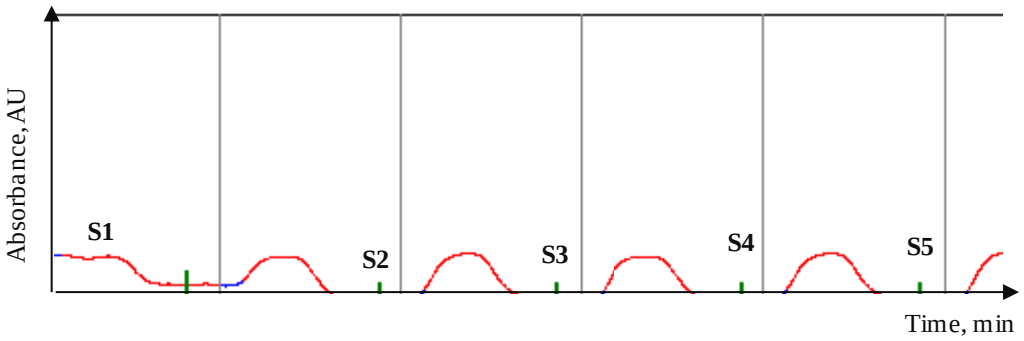
Effect of humic acid interference on the decomposition rate of PFCAs

Decomposition agent, mol/L		Humic acid, concentration, mg/L	Decomposition rate, %		
$K_2S_2O_8$, mol/L	H_2SO_4, mol/L		PFBA: 3 mg/L	PFHxA: 3 mg/L	PFOA: 3 mg/L
0.16	0.4	0	88.1	77.8	74.8
		1	90.4	77.2	68.7
		5	90.8	75.5	77.4
		20	91.7	76.5	74.6
		100	90.7	77.9	72.9

Effect of methanol interference on the decomposition rate of PFCAs

Decomposition agent, mol/L		Characteristic of input sample			Decomposition rate , %
$K_2S_2O_8$, mol/L	H_2SO_4, mol/L	Concentration of PFHxA, mg/L	Methanol		PFHxA
			% v/v	mol/L	
0.16	0.4	3 (0.01 mol/L)	0	0	79.6
			0.1	0.02	79.5
			0.5	0.12	77.8
			1	0.25	83.1

Effect of chloride interference on the recording fluoride signals



S1 : *Milli-Q* water

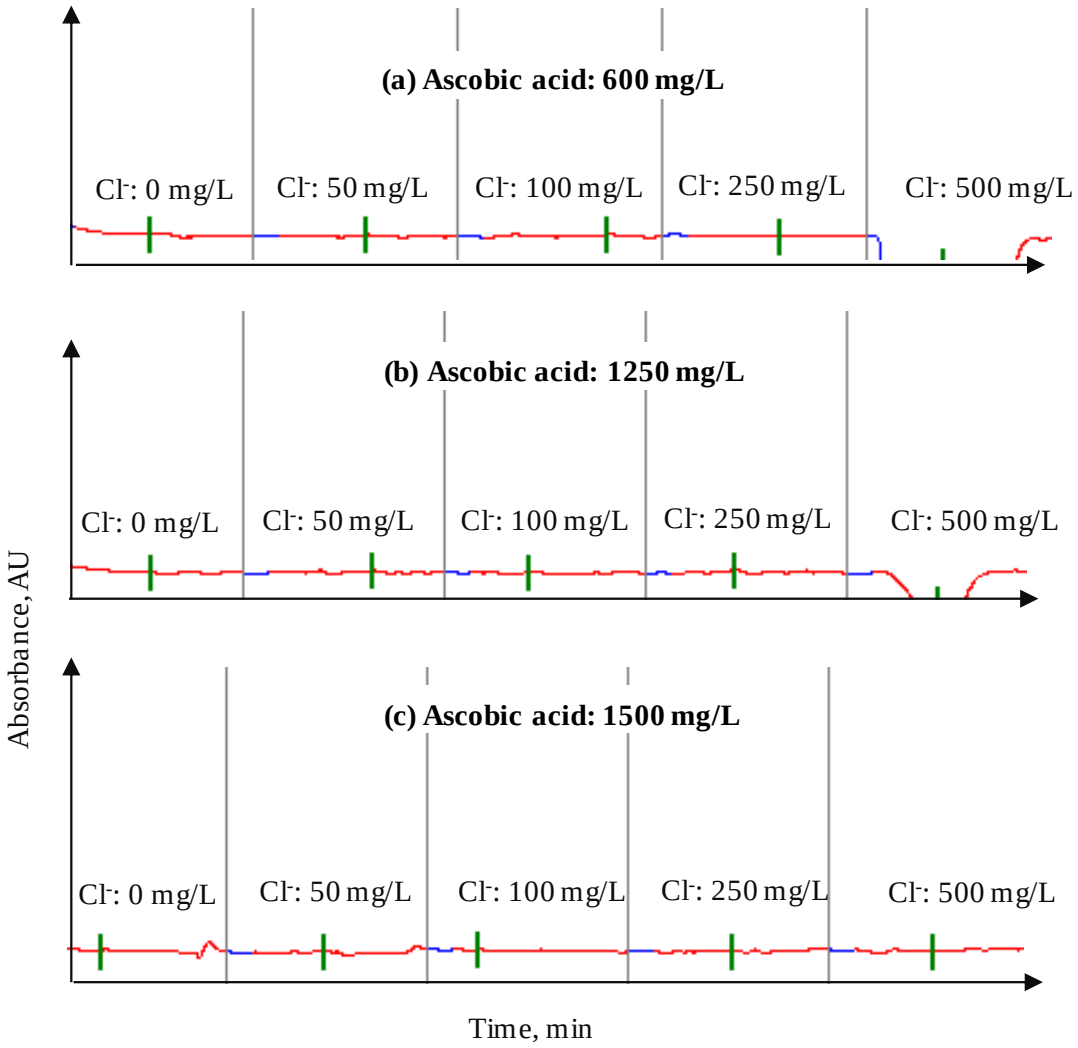
S2 : Wastewater (Effluent of WWTP)

S3 : Wastewater (Effluent of WWTP)

S4 : Surface water (downstream of WWTP)

S5 : Chloride / *Milli-Q*

Effect of ascorbic acid in eliminating effects of chloride

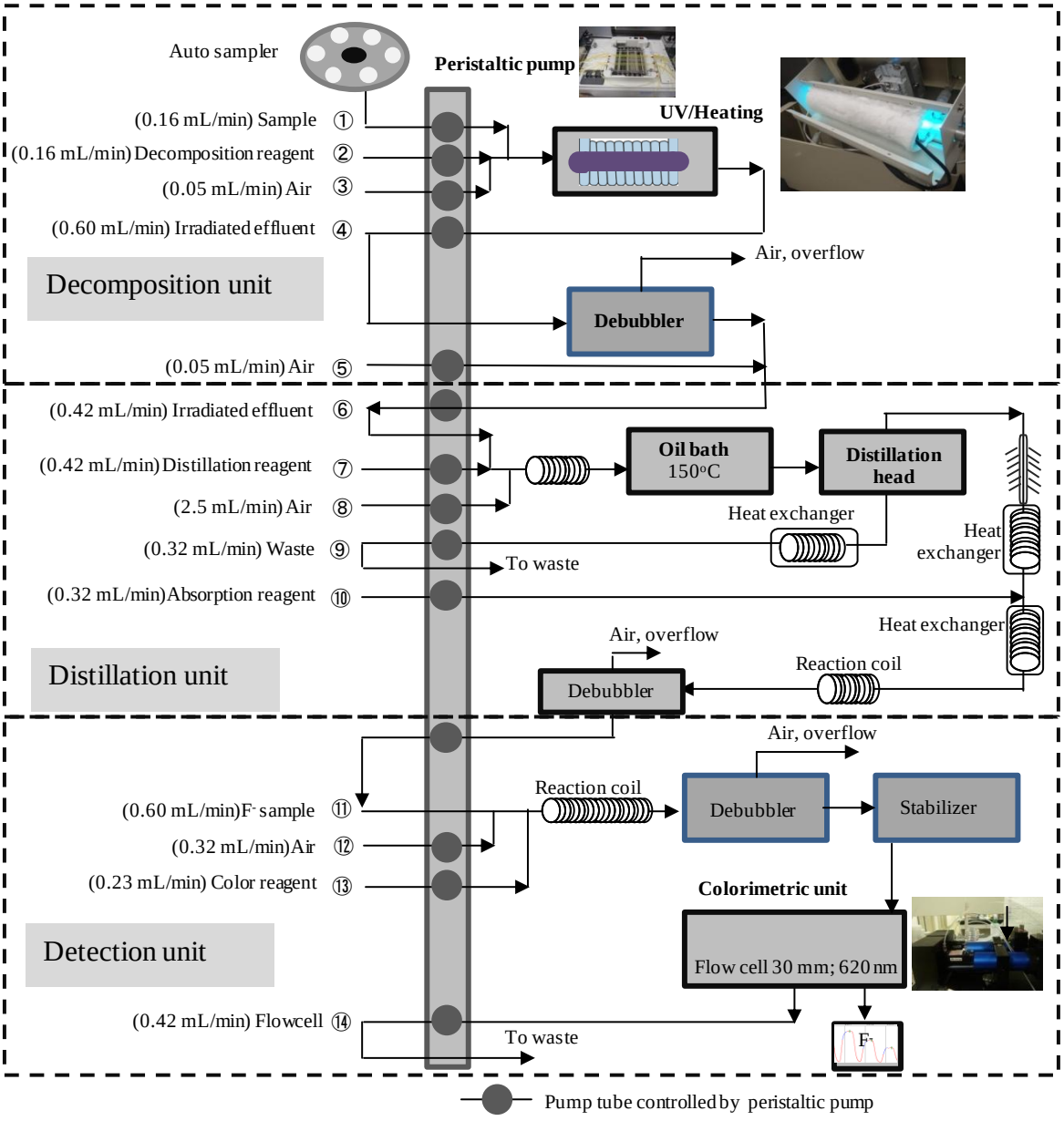


Effect of ascorbic acid at concentration of 1,500 mg/L in the quantification of fluoride from samples spiked chloride at different concentration

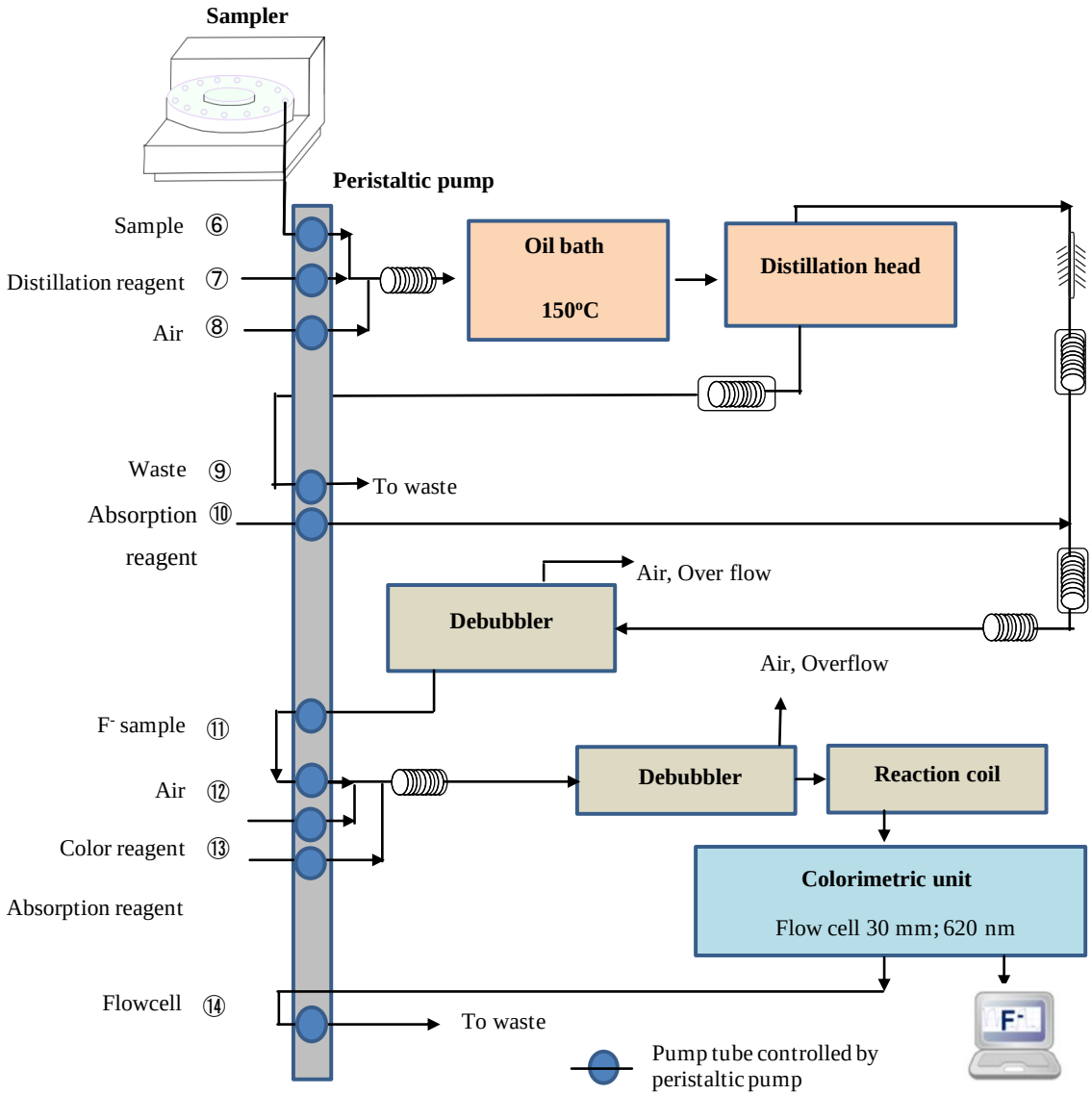
Concentration of spiked fluoride in the sample, mg/L		**0**	**50**	**100**	**250**	**500**
		Detected fluoride concentration, mg/L				
Type of sample	Fluoride/*Milli-Q*: 1 mg/L	0.90	1.12	0.99	0.98	1.06
	PFHxA/*Milli-Q*: 3 mg/L	1.56	1.60	1.58	1.64	1.59
	PFOA/*Milli-Q*: 3 mg/L	1.68	1.73	1.77	1.77	1.73
	PFNA/*Milli-Q*: 3 mg/L	1.79	1.74	1.78	1.83	1.83

Appendix E

Experimental setup for determination of total fluoride (TF) by colorimetric method – Method B



Experimental setup for determination of inorganic fluoride (IF) by colorimetric method – Method A



Measurement of TF and IF of samples by application of method A and method B

Measurement parameter	Interference	Input sample				
	F^-, mg/L	*Milli-Q*	PFBA:	PFHxA:	PFOA:	PFNA:
			3 mg/L	3 mg/L	3 mg/L	3 mg/L
IF, mg/L	0	0	0	0	0	0
	1	1.01	0.97	1.03	1.03	1.01
TF, mg/L	0	0	1.78	1.59	1.61	1.66
	1	0.94	2.84	2.66	2.67	2.69

Effect of interference on determination of IF by method A

Type of sample	Interference	Detected fluoride concentration, mg/L
Milli-Q	None	N.D
	F^-, 1mg/L	1.01
PFHxA: 3 mg/L	None	N.D
	F^-, 1mg/L	1.03
PFOA: 3 mg/L	None	N.D
	F^-, 1mg/L	1.03
PFNA: 3 mg/L	None	N.D
	F^-, 1mg/L	1.01

Effect of interference on determination of TF by method B

Type of sample	Interference	Detected fluoride concentration, mg/L	Inorganic fluoride, mg/L
Milli-Q	None	N.D	
	F^-, 1mg/L	0.94	
PFHxA: 3 mg/L	None	1.59	
	F^-, 1mg/L	2.66	1.07
PFOA: 3 mg/L	None	1.61	
	F^-, 1mg/L	2.67	1.06
PFNA: 3 mg/L	None	1.66	
	F^-, 1mg/L	2.69	1.03