



METHOD DEVELOPMENT TO DETERMINE EXTRACTABLE ORGANIC FLUORINE (EOF) BY COMBUSTION ION CHROMATOGRAHPY (C-IC)

Version 1.0

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List of Abbreviations

Abbreviation	Definition
AOF	Adsorbable Organic Fluorine
C-IC	Combustion Ion Chromatography
EOF	Extractable Organic Fluorine
HPIC	High Pressure Ion Chromatography
IC	Ion Chromatography
IEM	Ion Exchange Membrane
IF	Inorganic Fluoride
MeOH	Methanol
MQ	Milli Q / Ultra-Pure Water
ОСР	Organochlorine Pesticide
OF	Organofluorine / Organic Fluoride
РСВ	Polychlorinated Biphenyl
PFAS	Per- and Polyfluoroalkyl Substance
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctanesulfonic Acid
РОР	Persistent Organic Pollutant
SDG	Sustainable Development Goal
SPE	Solid-Phase Extraction
TF	Total Fluorine
TFA	Trifluoroacetic Acid





Abstract

Per-fluoroalkyl and polyfluoroalkyl substances (PFASs) are persistent organic pollutants and do not degrade in the environment. They contain a carbon-fluorine bond, and these are called organic fluorides. A group of PFASs, which can be extracted from soil samples and be analysed, are called extractable organic fluorides (EOFs) and more attention has been brought to this parameter. SGS is interested in developing a method to determine EOF by combustion ion chromatography (C-IC). However, there is no existing (inter)national frame of reference for this yet. This research is about the development and optimization of EOFs by C-IC and the pre-treatment with methanol. A long-chained PFAS, PFOS, and short-chained PFAS, TFA, were used in this research. Eliminating inorganic fluoride before analysis is important since the technique is not able to differentiate between inorganic and organic fluorides. Optimization had been performed on the method to determine EOF in ground samples where inorganic fluorides are eliminated from the total organic fluoride content. A calibration curve has been made for concentrations ranging from 25 to 1,500 µg L⁻¹ fluoride in methanol and resulted in a correlation of 0.9992. This was performed on another IC instrument since organic fluorides need to be combusted in order to be measured and therefore cannot be determined via this technique. Ten random ground samples measured concentrations between 24 and 1,878 µg kg⁻¹, confirming that there is inorganic fluoride present after extraction. Evaporation after extraction is required to increase the concentration of EOF in the extract. Evaporation of PFOS under a N₂ stream while heating the sample between 40 – 60 °C resulted in the best recovery of 84.9 - 85.6 %. Solid-Phase Extraction (SPE) is used as clean-up method to optimize the elimination of inorganic fluoride where the sorbent is combusted in the C-IC. No inorganic fluoride was recovered after washing the sorbent with a NH₄OH/MQ solution while organic fluoride had a recovery of 66.0 %. Not washing the sorbent gave a recovery of 13.6 % of inorganic fluoride and 61.0 % for PFOS. TFA was not recovered after SPE. Results of the C-IC could be unreliable since soot was formed after combusting the sorbent. Further optimization is required to develop a method for SGS to determine EOF in ground samples by C-IC.





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1. Introduction

In recent years, more and more attention has been brought to the sustainability of the earth. Seventeen sustainable development goals (SDG) have been introduced in 2015 to be achieved by 2030 (United Nations, 2017). One of these goals "6. Clean Water and Sanitation" could helped to be achieved by avoiding certain chemicals in water.

Industrial processes have been the cause of introducing persistent organic pollutants (POPs) into the environment by disposing mostly industrial wastewater containing dye, heavy metals, and pesticides (Ang et al., 2022). POPs are organic chemicals that can remain in the environment for decades due to their non-biodegradability (Aravind et al., 2022). Two well-known POPs are organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). There is a lot of awareness and been put a lot of attention to OCPs and they had been banned in most developed nation during the 1970s and 1980s due to not only their non-degradability, but also due to their mutagenic, teratogenic, or carcinogenic characteristics (Meeker & Boas, 2011; Zhang et al., 2018).

Although plenty of research and information is known about OCPs and PCBs, such as a method development of these compounds by gas chromatography coupled to mass spectrometry and tandem mass spectrometry by De Vos (2022), there is not a lot of research performed on per-fluoroalkyl and polyfluoroalkyl substances (PFASs), which are also part of a group POPs known as organofluorine (OF). PFAS has been discovered and manufactured in the early 1940s. Unlike other POPs, not a lot of attention has been brought to OFs until the early 2000s where Giesy and Kannan (2001) demonstrate that perfluorooctanesulfonic acid was detected in wildlife due to the widespread use of PFASs in recent years. Perfluorooctanoic acid, perfluorohexanesulfonic acid (PFHxS), and PFOS are known to have to highest production volumes of PFAS (Ma et al., 2022).

According to Domingo and Nadal (2019), there had only two papers been published concerning the human exposure to these chemicals, as well as their potential adverse health effects. A more recent study by Anderson et al. (2022) mentions that knowledge of adverse health effect by PFAS on humans is still not fully known, however, it is not sufficient to conclude that PFAS can be assessed for human health risk just because these compounds are persistence in the environment. The continuation to research the adverse health effect of PFAS of humans is important. The increased production of PFAS and increased number of studies about industrial and occupational exposure to chemicals causing cancer and elevated cholesterol have been brought into relation to the possible adverse effects PFAS might have (Blake & Fenton, 2020). The federal public health agency of the department of health and human services in the Unites States, called the "Agency for Toxic Substances and Disease Registry", also states that PFAS might have an increased risk of cancer, affect the immune system, increase cholesterol levels, act as endocrine disruptors, reduce female fertility, and adversely impact early childhood growth and development (Agency for Toxic Substances and Disease Registry, 2022).

Companies have been disposing PFAS in the environment for years now. Such companies are located in Belgium, near the border of the Netherlands and the forever chemicals have been disposed by those companies and ended up in the Western Scheldt (Zeeland, the Netherlands), where a laboratory of SGS is located nearby. According to research by Omroep Zeeland ("Toxicoloog waarschuwt", 2021), PFAS has been determined in fish from the Western Scheldt and it is not recommended to eat the fish from the Western Scheldt anymore. Due to the uncertainty of the effects of PFAS, action already has been taken to reduce the output because PFAS will always remain a chemical persistent to degradation.





SGS is interested in the research of OFs, also known as the sum of all PFAS. As of last year, SGS has been analysing OF in water samples by adsorbing them in activated charcoal and analysing the charcoal containing the OFs by combustion ion chromatography (C-IC). This parameter is called adsorbable organic fluorine (AOF). Another possible method to determine OF is by extraction and is called extractable organic fluorine (EOF) to determine OFs in solid matrices, such as soil and waste samples. However, a method to analyse EOF is still being worked on at SGS and is where this research will be mainly about. Complications occur with the inorganic fluoride content on C-IC as this technique is not able to differentiate between different forms of fluorine, such as inorganic fluorine (IF) (Aro et al., 2021). It is required to set-up a method to eliminate IF via clean-up techniques to determine the OF content measured on C-IC in ground samples. Due to the only recent focus on OF, there is not yet a frame of reference existing as of when this research was performed (R. Herman, personal communication, September 5, 2022).

The main research question of this research will be stated below.

• Can a method be developed with no (inter)national frame of reference at SGS to determine the EOF content in solid matrices using C-IC, while eliminating the interference of the IF content of final EOF concentrations?

Understanding the main aim, some sub-questions can be set-up and determined to provide information for the main aim and possibly additional information to optimize the method. These sub-questions and aims are listed below.

- Is it possible to set-up a method to determine IF in MeOH by IC and could this method be altered to determine lower concentrations?
- \circ What is the concentration of IF in random taken soil samples in the Benelux?
- How can evaporation of the extract be optimized so that the IC and C-IC are able to measure higher concentrations of IF/OF?
- Is pre-treatment by solid-phase extraction a sufficient technique to eliminate all IF from EOF samples and how can this be optimized?
- o Can short-chained PFAS be analysed in the EOF content?





2. Theoretical Background

2.1. Extractable Organic Fluorine (EOF)

Organic compounds containing a carbon-fluorine bond are called OFs and have had a significant impact on the public, such as the use of organofluorine in medicinal chemistry as inhalation anaesthetics or in chrome plating (Glüge et al., 2020; Hori & Honma, 2020; Reddy, 2015). PFASs contain such a bond and are widely used due to their unique chemical properties as they are known to, for example, create a wateror stain-resistant barrier when applied to products. There are currently more than 4500 known substances in the class of PFAS. However, Environmental monitoring focusses on about 30 of them (Kärrman et al., 2021). PFAS is released in the environment in big quantities by travelling through the atmosphere, but mostly through water (Aravind et al., 2022). They are considered relatively stable due to the non-bonding electrons around the fluorine atoms and the persistency of PFAS is caused due to the resistance to degradation by acids, bases, microbes, and more (Kissa, 2001). The disadvantage occurs when the product is not suitable to be used anymore and is disposed in nature, which will not break PFAS down naturally, thus polluting the environment. In this research, perfluorooctanesulfonic acid (PFOS) and trifluoroacetic acid (TFA) are used. Certain chemical properties of these compounds can be found in appendix I, table 1.

2.1.1. PFOS

As already mentioned, the adverse health effects of PFAS in humans is still being studied. However, in massive quantities they have been linked to have negative effects on humans, animals, and plants and regular OFs have also been widely used as pesticides (Davison & Weinstein, 2006; Fujiwara & O'Hagan, 2014). In figure 1 can be seen the structure of the two most abundant manufactured and detected PFAS, which are PFOS and PFOA. According to Johnson (2018), PFOS and PFOA can last up to 8 years in the human body and will lead to accumulation over time. There are courses of actions to take to avoid some PFASs to enter the body. Activated carbon filters could be used to reduce levels of fluorinated chemicals. One could also dust more often in the household or wash hands more often before consuming a meal since PFASs also travel through air.



Figure 1. Structures of the most abundant manufactured and detected PFAS; A: perfluorooctane sulfonate (PFOS), B: perfluorooctanoate (PFOA) (Aro et al., 2020).

2.1.2. TFA

Trifluoroacetic acid (TFA), with a chemical formula of CF₃CO₂H, is also a persistent pollutant but has, unlike PFOS and PFOA, a very short carbon chain of only three carbons (Scheurer & Nödler, 2021). It is a monocarboxylic acid that is the trifluoro derivative of acetic acid. It has been reported that TFA exists naturally, but Joudan et al. (2021) reject this statement after research was performed since there is insufficient evidence that this statement is correct. TFA is also classified as PFAS and is widely used in organic synthesis as solvent, catalyst, and reagent (López & Salazar, 2013).





2.2. Ion Chromatography (IC)

Ion chromatography (IC) makes it possible to separate and determine anions as well as cations in aqueous samples. IC is an important form of liquid chromatography and has always been difficult to detect analyte ions since ionic eluents create a highly conductive ionic background (Dasgupta & Maleki, 2019). An anion exchanger is equipped if the determination of anions is required and a cation exchanger to determine cations. If the IC is equipped with an anion exchanger, it will allow for the analysis of anions, such as fluoride (F⁻), chloride (Cl⁻), Bromide (Br⁻), and more (Fritz, 1987). A simplified explanation of how an anion exchanger works is that the resin takes up a lot of water and consists out of cations which will bind with the anions from the samples. The cations in samples do not bind with the resin and will continue through the system. Then an eluent generator will release a small concentration of salt, such as potassium hydroxide, of which the concentration will increase overtime depending on the method. The cations in the resin will at a certain concentration prefer to bind with the OH⁻ particles and release the anions of interest based on their affinity or ionic strength, causing elution. This process is called "desorption". The F⁻ ion binds weakly to the ion exchanger since it has a lower affinity than other anions and will elute first, followed by chloride, nitrite, nitrate, phosphate, and so on (Zhang et al., 2007). The desorbed analytes finally travel through the suppressor into the detector. The same principle applies in C-IC, but because PFAS is very stable and has a high boiling point until it degrades, a combustion step is required before IC analysis where anions are separated from the PFAS compound.

2.2.1. Combustion Ion Chromatography (C-IC)

Combustion ion chromatography (C-IC) consists of 4 major components. The sampler, shown as "ABC" in figure 2, will transfer the sample into the oven where it is combusted at remarkably high temperature (900-1000 °C) to break down the compounds. The samples are first digested under an Ar atmosphere and then burnt with water (pyrohydrolysis) and O_2 . This means that Ar is used to carry HF after formation from the combustion tube into the absorber solution and the water will humidify it and promote HF formation (Aro et al., 2021). The absorption of by products and combustion products, which in figure 2 takes place in the "Absorption Unit" is brought to the absorbance solution by a syringe. The drain pump will remove excess sample and eluent and is then brought to the injection loop where the sample will then enter the IC for detection.



Figure 2. Schematic overview of combustion ion chromatography. The complete analysis starts from right to left, thus starting at the ABC unit to the combustion unit, then to the absorption unit, and finally the IC (Agustin et al., 2017).

C-IC is regularly used to determine the TF content in samples and has shown to be cost-efficient and has many advantages over other techniques (Gehrenkemper et al., 2021; Li et al., 2021; Miyake et al., 2007a;





Miyake et al., 2007b; Wagner et al., 2013). Liquid chromatography coupled to tandem mass spectrometry can separate individual OF compounds but measures less than the C-IC measurement TF would determine since the TF is a total parameter.

2.2.2. Suppressor & Concentrator Column

The main principle of a suppressor in chromatography is to suppress the eluent conductivity by exchanging influent cations for protons. The suppression takes place after elution of the ion exchanger and before analyses in the detector. The suppressor first converts the salt of the weak acid used in the eluent, to pure water or weakly conducting acids (Maleki et al., 2021). The suppressor is also known as the "second column" or "ion exchange membrane". Not only does the suppressor supress the eluent conductivity, but it also amplifies the anions of interest. According to Dasgupta and Maleki (2019) there are many ion exchange membranes (IEM) which have been used and are still being used today. They can mainly be categorized under chemically regenerated and electrolytically regenerated suppression. According to Moore (2018), chemically regenerated suppression mainly uses chemical solutions to regenerate the suppressor and electrolytically regenerated suppression uses water and a potential applied across two electrodes to regenerate, which eliminates the need to prepare regenerant solutions.

A concentrator column is designed and applied specifically for stripping ions from samples and concentrating the analyte, thus the name concentrator (Tyrrell et al., 2011). In figure 3 is shown where the concentrator column is located in a chromatographic system. The matrix ions are diverted to waste after the injection of a larger volume sample and before the volume is separated over the analytical column, the analyte and other anions are trapped onto the concentrator column (Wagner et al., 2007). The main principle of a concentrator column is to detect lower concentrations of analytes by increasing the injection volume and concentrating the analytes.



Figure 3. Location of a concentrator column in a chromatographic system.





2.3. Solid-Phase Extraction (SPE)

Many liquid-liquid extraction protocols have been replaced by methods which are easier to use. An example of a clean-up method that replaces extractions, due to its versatility and ease of use, is SPE (Ifegwu & Anyakora, 2016). The types of SPE can be categorized under for example reversed-phase and normal phase, or adsorption, ion exchange, and mixed-mode techniques. The difference between the different categories is within the sorbent bed of the extraction method. In normal and reversed-phase, the sorbent bed contains properties which will allow for the analytes to elute based on polarity where the least polar compounds will elute first. Polymer sorbent is, according to Li et al. (2022), a commercial SPE packing for adsorption SPE techniques.

SPE can also be used to separate compounds based on charge and is called ion exchange. This means that the sorbent consists of an ion exchanger resin (Rossi et al., 2017). Similarly, to ion exchange chromatography, ion exchange SPE separates and elutes the compounds by introducing a stronger charged compound over the sorbent bed so that weakly ionized compounds elute first and thus separating the compound.

A combination of an adsorption and ion exchange technique, which is mentioned above, is called mixedmode. Mixed-mode sorbents started to be used more often to isolate target compounds since it allows for selective extractions through dual mechanisms (Blanco-Zubiaguirre et al., 2018). Since IF are required to be eliminated from samples in this research, ion-exchange and reversed-phase mode will form the mixed-mode SPE to achieve the elimination.





3. Materials & Methods

3.1. Chemicals & Samples

Sodium fluoride (NaF) was purchased from J.T.Baker (Deventer, the Netherlands). Ultra-pure water (MQ) was provided by Elix Technology Inside and methanol (MeOH) was purchased from VWR Chemicals (Rosny-sous-Bois, France). Heptadecafluorooctanesulfonic acid (PFOS) >98%, was obtained from Fluka (Buchs, Switzerland). Pentadecafluorooctanoic acid ammonium salt (PFOA) >98 was purchased from Sigma-Aldrich (St. Louis, U.S.A.). Trifluoroacetic acid (TFA) was supplied externally by SGS Belgium – IAC (Antwerpen, Belgium). Ammonium hydroxide, or ammonia solution, 28-30 % (NH₄OH), was obtained from J.T.Baker (Gliwice, Poland). Ten soil samples containing EOF were provided by SGS ('s-Gravenpolder, the Netherlands).

3.2. Instruments

The DionexTM Integrion High Pressure Ion Chromatograph (HPIC), equipped with a DionexTM EGC 500 KOH Eluent Generator Cartridge, a DionexTM ADRS 2 mm suppressor, a Conductivity Detector, and a DionexTM AS-AP autosampler were all purchased from Thermo Scientific (U.S.A.) and were used to analyse IF in the standards and samples. The system was equipped with an IonpacTM AS19 column with a dimension of 2 x 250 mm, an IonpacTM AG19 guard with a dimension of 2 x 50 mm to protect the column and supplied with a DionexTM GM-4 2mm Gradient Mixer (Thermo Scientific, U.S.A). An Ultra Trace Concentrator (UTAC), IonPacTM UTAC-LP2 with a dimension of 4 x 35 mm, was purchased from Thermo (U.S.A.) and was used during the optimization of the method. A Q-sep 3000 centrifuge (Restek, U.S.A.) with a fixed speed of 4,130 rpm, Reacti-Vap evaporating unit (Pierce, Rockford, U.S.A.) SyncorePlus (BUCHI, Hendrik-Ido-Ambacht, the Netherlands), and SuperVap (FMS, U.S.A.) was used to treat and evaporate the samples.

The DionexTM ICS-2100 was used as IC-system for the determination of the OF content and was equipped with a DionexTM Carbonate, Methanesulfonic Acid, and Hydroxide EGC Eluent Generator Cartridge, a DionexTM ADRS 600 suppressor, and a DS6 Heated Conductivity Cell which were all purchased from Thermo Scientific (U.S.A.). The column used was an lonpacTM AS18 with a dimension of 2 x 250 mm, and an lonpacTM AG18 TFIC (Thermo Scientific, U.S.A.) guard, with a dimension of 2 x 50 mm, was used to protect the column. The samples are combusted and absorbed in the AQF-2100H Automatic Quick Furnace, equipped with the ASC-270LS Automatic Sampler Changer (Mitsubishi Chemical Analytech, Chigasaki, Japan). An overview of the instruments can be found in the appendix II, table 2.

3.3. Preparation of Standard Solutions

A standard solution stock of F^- (2.0 g L^{-1}) from NaF in MQ was used to prepare an intermediate stock of 10 mg L^{-1} F^- in MeOH from which calibration dilutions were prepared. Aqueous stock solutions of F^- (1.5 g L^- ¹) from PFOS and F^- (1.0 g L^{-1}) from PFOA were prepared in MeOH.

3.4. Extraction & Clean-Up

A mass of 2.0 grams of sample was weighted. Samples that required spiking were spiked at least 24h before extraction. Blanco sand was spiked with 1.5 g L⁻¹ PFOS. Then, 20 mL of methanol was added to the sample, centrifuged for 5 min and the supernatant was collected afterwards. This was performed a total of three times before the evaporation under nitrogen and heating the extract between 40 - 60 °C to obtain a final extract volume of 1.5 mL.





Before the SPE clean-up is performed, the standard or extract in methanol is diluted 100 times in MQ. Clean-up method used in other studies (Aro et al., 2021; Miyake et al., 2007a; Taniyasu et al., 2005; Young et al., 2022) for EOF by SPE has been applied with few modifications. Agilent Bond Elut (500 mg) (Agilent Technologies, Folsom, U.S.A.) was prior to use treated with 4 mL 0.1% NH₄OH/MeOH and 4 mL MeOH, followed by 4 mL MQ to condition the phase. Then, 100 mL of the 100 times diluted standard or sample were loaded onto the phase and treated by SPE with a flow rate between 2-5 mL min⁻¹. The diluted standards had a concentration of 500 μ g L⁻¹. Then 10 mL of 0.01%, and NH₄OH/MQ was used to remove inorganic fluoride, followed by 10 mL MQ to wash the phase before the analysis onto the C-IC after drying under a N₂ stream for 20 min. The sorbent was collected and measured on IC and C-IC during the optimization of the method to check for loss of analyte. A mass of about 50 mg was measured with each measurement. In some measurements, multiple masses were combusted, and concentrations were added to acquire the final concentration. The expected concentration of F⁻ in PFOS when treating 100 mL of 500 μ g L⁻¹ over 500 mg SPE sorbent is therefore 100 μ g g⁻¹ sorbent . The concentration after washing the F⁻ from NAF with NH₄OH/MQ should be 0.00 μ g g⁻¹ while not having lost a large concentration of F⁻ from PFOS.

3.5. Analysis of Inorganic Fluoride

The liquid extract obtained from SPE containing F⁻ in 1% MeOH was measured by the HPIC unit to confirm if the inorganic fluoride is washed from the SPE phase. The following gradient was used: 9 mM for 4 min to a concentration of 40 mM for 6 min with a rate of 15 mM min⁻¹, and finally decrease back to 9 mM until the total run of 17.5 min is completed using Chromeleon Chromatography Data System software (v 7.2.7, Thermo Scientific, MA, U.S.A.). The suppressor was equipped with a water pump at 0.55 mL min⁻¹, to put the IC in external water mode. The column was kept at 35 °C. Quantification of the IF content was determined using an 8-point calibration curve (25 to 1500 μ g L⁻¹ in pure MeOH and 25 to 500 μ g L⁻¹ in 1% MeOH).

3.6. Analysis of Organic Fluoride

The SPE sorbent was combusted in the C-IC in quantities of 50.0 mg. The temperature of the furnace was between 900 and 1000 °C. The system was equipped with Ar at a rate of 400 mL min⁻¹ and oxygen at a rate of 200 mL min⁻¹. The water supply was 100 mL min⁻¹. The IC pump was set to 0.25 mL min⁻¹ and the column was kept at 30 °C. The settings for the C-IC can additionally be found in appendix II, figure 3 and 4. Quantification of the OF content was determined using an existing calibration of a 6-point calibration curve (25 to 100 μ g L⁻¹) and is currently being used for the analysis of AOF at SGS where activated charcoal is combusted after treating it with 100 mL of sample. The preparation of the calibration curve can be found in appendix III, table 5,





4. Results

4.1. Optimization Inorganic Fluoride on IC

The application of the concentrator column on the IC to achieve a lower detection limit shows severe matrix interference with pure methanol as solvent and is shown in the appendix IV, figure 3. Changing the recycling mode of the suppressor to external water mode while using the concentrator column still resulted into matrix interference with both pure MeOH and 1 % MeOH as shown in appendix IV, figures 4 and 5. By directly injecting the sample onto a regular column instead of using the UTAC resulted into little matrix interference, as shown in figure 4, and therefore the UTAC column is not applied in the method. Peak areas of F^- in pure MeOH were linear, showing an R^2 of 0.9992 between 25 and 1500 µg L⁻¹. Similarly, the calibration curve of 25 to 500 µg L⁻¹ F^- in 1% MeOH had an R^2 of 0.9996. The calibration curves can be found in appendix III, figure 1.



Figure 4. Chromatogram of 500 μ g L⁻¹ fluoride in methanol by IC using 50 μ L direct injection in external water mode. [A] Solvent using pure methanol. [B] Solvent using 1% methanol.





The IF concentration of the samples containing EOF were measured by the calibration curve in pure MeOH after extraction to give an indication if there is IF present to be removed at all before the development of the method. The diluted samples contained concentrations between 0.8 and 62.6 μ g L⁻¹ in 2.0 grams of sample. Evaporation was not performed, but theoretically the concentration would fall between 50.0 and 3755.9 μ g L⁻¹.

4.2. SPE Clean-Up

Sorbents were dried after 100 mL of sample was loaded onto the sorbents and about 50 of 500 mg was taken from the sorbents and combusted in the C-IC. This experiment was performed with MQ, IF, PFOS, and TFA samples separately. The samples were treated by SPE and was washed with and without 0.01% NH₄OH/MQ to compare the elimination of IF. Different percentages of MeOH as solvent was present in the sample were compared to each other. There was no OF present in the MQ samples. There was also no OF in TFA recovered after treatment of SPE. There was OF detected in the PFOS samples. In table 1 is shown the concentrations in µg per gram sorbent. A concentration of 285.6 µg L⁻¹ F⁻ from PFOS was found in 432.7 mg of sorbent after washing the sorbent. There was no F⁻ from NaF found in 201 mg of sorbent after the washing step. Without the washing step, a concentration of 63.21 µg L⁻¹ F⁻ from PFOS in 103.6 mg was found and a concentration of 13.73 µg L⁻¹ F⁻ from NaF in 100.7 mg. In figure 6 and 7 of appendix V can be found the recovered OF per 50 mg combusted sorbent in the PFOS samples and the IF content where the sorbents were washed with and without NH₄OH/MQ.

Table 1. Concentration of F-	from NaF and F ⁻ from PFO	S found per gram sorbent with	and without washing with NH ₄ OH/MQ.
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Component	Concentration without NH ₄ OH/MQ wash (ug g ⁻¹)	Concentration with NH₄OH/MQ wash (ug g ⁻¹)
OF	61.01	66.00
IF	13.63	0.00

4.3. EOF Evaporation

The evaporation of pure methanol was checked with a standard of 50 μ g L⁻¹ F⁻ from about 20 mL methanol to 1.5 – 1.0 mL under N₂ stream, via the SyncorePlus unit, and via the SuperVap unit. The extracts were measured on the IC and calculated by means of the calibration curve. The technique with the greatest recovery was evaporation under N₂ with an average recovery of > 97.1 %. The SyncorePlus and SuperVap had recoveries of about 74.8 % and < 60 %. An overview of recovery standards can be found in appendix VI, table 8.





Table 2. Recovery (%) of the fluoride content in PFOS standards after extraction and evaporation under N_2 while heated between 40-65 °C in triplicate.

	V extract	V after	Concentration	Theoretical	Recovery
	(1112)	(mL)	(µg/ L)	(μg/L)	(70)
F- PFOS I	56	5.3	24.11	28.30	85.2
F- PFOS II	57	4.6	27.68	32.61	84.9
F- PFOS III	58	6.2	20.71	24.19	85.6
STD F- PFOS	20	1.7	35.89	35.29	101.7

PFOS standards were evaporated under N_2 to a certain concentration after finding that evaporation under N_2 resulted into the largest recovery. The evaporation took about 20 hours to complete to evaporate from 20 mL methanol to about 1.0 mL as mentioned above and had a recovery of 101.7 %. The extraction of spiked PFOS concentrations to blank sands were evaporated while being heated to 55 °C to optimize the evaporation step. The recovery of these samples after evaporation were about 85% when evaporating a volume of 60 mL MeOH to about 5 mL and took about 20 hours. In table 2 is shown the recovery of the PFOS samples after evaporating under N_2 while heated.





5. Discussion

5.1. Optimization of IC Method

A method for the quantification of IF in methanol in lower concentrations could not be optimized on IC to match the already existing calibration range on C-IC while using the UTAC column to detect lower concentrations. There is constant and significant matrix interference present at the fluoride peak which is usually not present while using MQ as solvent. An explanation of the interference could therefore be happening due to the methanol solvent. However, according to a scientist at Thermo (E. de Weerdt, personal communication, September 29, 2022) the peak interference is not caused by methanol directly, but instead by methanol which has been electrolyzed back over the membrane of the suppressor. This can be confirmed by research from Rabin et al. (1993) where organic solvents, especially methanol, are not well tolerated in electrolytic modes. Methanol could be oxidized to form ionic by-products. The system used in this research is performed in an electrolytic mode, namely dynamical regeneration mode, and recommended is to use chemical regeneration mode if a validation of the method is required. In this research, the main purpose for the method was to quantify the amount of IF in samples to check if the amount of the IF content after clean-up was eliminated. A validated method was not required.

After creating a calibration curve in pure MeOH, ten ground samples were extracted and measured to give an indication of how much IF there is present in samples from the Benelux. A low concentration was measured in the diluted extract, however, only a small mass of sample was taken and was ultimately diluted sixty times.

5.2. Extraction & Evaporation Techniques

Evaporation under a N_2 stream gives the largest recovery compared to other automated evaporation techniques. It is also one of the most common evaporation techniques currently used. It is used for example with the biological analysis of DNA methylation experiments (LoSchiavo et al., 1989) and chromatographic analysis to determine for example antioxidants (Pezet et al., 1994). In some analyses it is known that evaporation under N_2 stream results into loss of analyte. Chang et al. (2001) demonstrated that losses of polynuclear aromatic hydrocarbons mainly occurred due to coevaporation and based on if the samples were diluted or not.

In this research, the evaporation under N₂ stream takes a lot of time and therefore the extract was heated to just below the boiling point of MeOH to reduce evaporation time. The recovery of the fluoride content was here smaller compared to unheated evaporation. Sample loss due to evaporation usually occurs due to heating the sample too close to the analytes boiling point (Tian et al., 2006). This statement would not apply to this research since PFAS, and in this research PFOS, have very high boiling points. Another possible cause for the smaller recovery when heating the extract could be, according to Castells and Casella (1987), that the evaporation is happening too fast. The evaporation takes a lot of time but is most likely still required to be performed due to the IF and OF content present in samples.

5.3. C-IC Analysis

The expected concentration per gram sorbent OF in the PFOS samples after treatment of SPE was 1000 μ g g⁻¹ on average. The measured concentration per gram sorbent OF in the PFOS samples with and without washing step were lying close to each other, but both do not lay close to the expected value. The SPE cartridges are designed to trap short- and long-chained PFASs, but in this research only 66.00 μ g g⁻¹ was recovered for PFOS, while the expected concentration was 100 μ g g⁻¹. The inorganic fluoride was, as





expected, not recovered after washing the sorbent. It was soon determined that an incomplete combustion occurred after combusting the sorbent in the C-IC and this was most likely the reason for the determined recovery, and not the ability of the sorbent to trap PFASs. The incomplete combustion was clearly visible by the soot that was carried by Ar at the end of the combustion unit and in the absorption unit itself. The measurements for the AOF analysis which is performed at SGS daily were also influenced by this phenomenon since the standards did not match the expected concentration. Standards which should be about 25 μ g L⁻¹ fluoride measured concentrations between 15-18 μ g L⁻¹ instead. Comparing this to the values gained from this research also resulted in concentrations of a factor of about 1.4 lower. The standards still gave the same results after cleaning the system from the soot, which means that there was a problem elsewhere in the system. A logical explanation would be that there is something happening, or is not happening, within the IC. According to Mcnair and Polite (2007), numerous causes can indicate an instrumental problem when problems with peak areas. The peak area can change based on the volume injected, flow rate, pH, leaks, sample stability, integration problems, and loss of sample due to irreversible adsorption on a dirty frit or active column. However, settings of the IC have not been changed so it then could only be irreversible adsorption. But this should not be the cause either since a constant concentration of the standards have been measured. It is most likely that a part in the IC is broken and further investigation for this is required to continue the use of the C-IC at SGS.

No frame of reference yet exists where SPE sorbent is combusted in the C-IC, so an optimized method of the combustion unit is required where the PFAS WAX is combusted. Most studies for the determination of EOF in water samples by C-IC use an elution step of the SPE sorbent so that the extract is measured in a liquid instead of the combustion of the sorbent (Aro et al., 2021; Gehrenkemper et al., 2021; Miyake et al., 2007a). This causes the pre-treatment of the samples to take even longer since another evaporation step is required, which would not be necessary if the method in this research works. Many factors should still be determined to be able to make a reliable method. For example, the exact masses and volumes of the future monsters one would need to measure. This can only be done when a sufficient method on the C-IC has been developed. Aro et al. (2021) also demonstrated that the combustion efficiency for PFASs is not for all components the same and ranged from 66-110%. This can influence the recovery of the experiments performed in this, and possibly in future research.





6. Conclusion & Recommendations

A method to determine IF in MeOH by IC was developed but still has a small amount of interference from the oxidized methanol. Recommended is to further optimize the method to determine even lower concentration which will match the limit of quantification of the C-IC method. The method could be optimized further by using a different kind of suppressor, such as a chemical regeneration suppressor like the Dionex[™] CRS 500 instead of an electrolytic regeneration suppressor used in this research. The recycle mode is not compatible with organic solvents, and thus MeOH, because they tend to oxidize easily. The correlation however was 0.9992 and is considered sufficient. EOF samples contain a high concentration of IF after directly measuring the MeOH extract. The diluted extract concentrations fell between 24 and 1,878 µg kg⁻¹. A better alternative than further optimizing the method to detect lower concentrations is to weigh more samples for the extraction and to evaporate to lower volumes.

The combustion of SPE sorbent caused for the formation of soot which made the concentration measured on the IC unreliable. Concentrations between 22.24 and 46.66 μ g L⁻¹ were recovered from an expected concentration of 50.00 μ g L⁻¹ in the combustion of SPE sorbent. There was no inorganic fluoride detected in sorbent with a spiked concentration of 100 μ g L⁻¹ sorbent after washing with 0.01% NH₄OH/MQ. Recommended is to perform this experiment with a higher concentration of IF, since IF appears in higher concentrations in the environment, to determine whether this is also washed from the sorbent. Another recommendation would be to determine the combustion efficiencies of different PFASs before performing the SPE to avoid any unexpected results after C-IC measurement. The combustion efficiencies have been researched before in literature when using MeOH as solvent.

The method for the combustion unit of the C-IC which is used for the analysis of AOF does not give a proper combustion of the SPE sorbent. To combust the SPE sorbent and thus determine the concentration of TOF, it is recommended to develop a method for the combustion unit where the sorbent is combusted at a slower rate, so no soot is formed. This is done by introducing the quartz boats slower and not immediately to the middle of the tube so that the intense change of temperature difference will not cause for the formation of soot and break the IC. While developing this method, it is also recommended that the combustion unit and the other units are not connected with each other. If in any case the sorbent still causes for the formation of soot, then the other units are not at risk to break, which happened in this research. For the optimization of the SPE experiment, it is recommended to determine which concentration of NH₄OH/MQ results into eliminating all inorganic fluoride while not losing too much analyte. Concentrations between 0.1% and 0.001% of NH₄OH/MQ could be used in different volumes as washing solvent after loading the sample onto the SPE column and determine the most optimal washing concentration where IF is completely eliminated, but where OF will remain on the sorbent.

Evaporation of the EOF extract is most optimal under a N₂ stream while heating the extract. The recovery of evaporating MeOH determining F⁻ was > 97.1 % under N₂ stream, about 74.8 % using the SyncorePlus, and < 60 % while using the SuperVap. Evaporating under N₂ stream took more than 20 hours while the SyncorePlus and SuperVap took less than 2 hours to evaporate. Heating the extract while evaporating under N₂ stream reduced the evaporation time significantly between a temperature of 40 °C and 60 °C (just below boiling point of the solvent, MeOH), but still took more time than the automated evaporation units. Although the automated evaporation units require less time to pre-treat, it is still recommended to use evaporation under a N₂ stream while heating the extract. The SyncorePlus and SuperVap use reusable glassware for other analyses and therefore cross contamination is possible which would influence the final





concentration of OF a lot considering the low concentration of which the OF is, or will be, determined in the C-IC. In order to reduce the evaporation time, it is recommended to let the extract evaporate on a bigger surface. This way, more MeOH is exposed to air and the evaporation time will reduce.





7. References

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Appendices

Appendix I – Chemical Characteristics

Table 1. PFASs used in this research and their chemical characteristics.

PFAS	Molecular Formula	Boiling Point (°C)	Density (g cm ⁻³)	Molecular Weight (g mol ⁻ ¹)	Purity (%)	CAS Number
PFOS	C ₈ HF ₁₇ O ₃ S	260	1.80 ± 0.10	500.13	98	1763-23-1
PFOA	C ₈ HF ₁₅ O ₂	188	1.70 ± 0.10	414.07	98	335-67-1
TFA	C ₂ HF ₃ O ₂	72	1.54	114.02	98	76-05-1





Appendix II – Instruments & Settings

Table 2. Chromatographic instruments used in this research for the analysis of OF and IF. All instruments and equipment for IC was purchased from Thermo Fisher Scientific.

Parameter	OF analysis	IF analysis
Autosampler	ASC-270LS	AS-AP
Ion Chromatograph	ICS-2100	Integrion High Pressure Ion
		Chromatograph
Eluent Generator	Carbonate, Methanesulfonic Acid,	EGC 500 KOH Eluent Generator
	and Hydroxide EGC	Cartridge
Guard Column	AG18 TFIC, 2 x 50 mm	AG19, 2 x 50 mm
Column	AS18, 2 x 250 mm	AS19, 2 x 250 mm
Suppressor	ADRS 600	ADRS 2 mm
Detector	Conductivity	Conductivity

Table 3. C-IC settings.

Parameter	Settings
Combustion Temperature	900-1000 °C
Argon Supply	400 mL min ⁻¹
Oxygen Supply	200 mL min ⁻¹
Water Supply	100 mL min ⁻¹

Table 4. Combustion settings.

Position (mm)	Wait (sec)	Speed (mm sec ⁻¹)
65	30	10
265	420	20
Cool	60	40
Home	10	20
Combustion Time	460 sec	
Ar Time	30 sec	
O ₂ Time	600 sec	





Appendix III – Data Calibration Curves

Table 5. Standard dilutions from a 10 mg/L F⁻ intermediate stock in 1% MeOH/MQ.

Concentration	Intermediate Stock	MeOH	Total Volume
(µg/L)	(mL)	(mL)	(mL)
0	0		
25	0.25		
50	0.50		
100	1		
200	2	1	100
400	4		
500	5		
750	7		
1000	10		



Figure 1. Calibration curves of F⁻ from NaF prepared in MeOH and determined on IC. [A] Calibration curve prepared in a solvent of 1% MeOH and has a correlation of 0.9996. [B] Calibration curve prepared in a solvent of pure MeOH and has a correlation of 0.9992.



Figure 2. Calibration curve of F- which is currently being used at SGS for the analysis of AOF. Has a correlation of 0.9997





Appendix IV – Chromatographic Optimization



Figure 3. Chromatogram of F^- in MeOH with a concentration of 1 mg L^{-1} , injection volume of 100 μ L, and using the UTAC column set in recycling mode.



Figure 4. Chromatogram of F^{-} in MeOH, injection volume of 100 μ L, and using the UTAC column set in external water mode.







Figure 5. Chromatogram of F in MeOH, injection volume of 100 μ L, and using the UTAC column set in external water mode. This measurement was evaporation of 20 times under N₂ stream.





Appendix V – Data SPE

Table 6. SPE treatment followed by C-IC analysis. The samples have not been treated with 0.01% NH₄OH/MQ to remove inorganic fluoride. Concentrations are all the expected amounts from the inorganic fluoride in the component.

Standard and samples	Concentration	Mass
	(µg L⁻¹)	of
		sorbent
		(mg)
Standard 50 µg L ⁻¹ NaF	50.082	-
Standard 50 µg L ⁻¹ PFOS	24.154	-
50 μg L ⁻¹ NAF I	8.6949	50.2
50 μg L ⁻¹ NAF II	5.0334	50.5
50 μg L ⁻¹ PFOS I	39.250	50.2
50 μg L ⁻¹ PFOS II	23.963	53.4
Standard 50 µg L ⁻¹ NaF	40.768	-
Standard 50 µg L ⁻¹ PFOS	25.886	-

Table 7. SPE treatment followed by C-IC analysis. The samples have been treated with 0.01% NH₄OH/MQ to remove inorganic fluoride. Concentration are all the expected amounts from the inorganic fluoride in the component.

Standard and samples	Concentration	Mass
	(µg L ⁻¹)	of
		sorbent
		(mg)
Standard 50 μg L ⁻¹ PFOS	50.007	-
50 μg L ⁻¹ NAF I	0.0000	50.3
50 μg L ⁻¹ NAF II	0.0000	51.4
50 μg L ⁻¹ NAF III	0.0000	48.8
50 μg L ⁻¹ NAF VI	0.0000	50.8
50 μg L ⁻¹ PFOS I	22.241	51.0
50 μg L ⁻¹ PFOS II	31.412	51.1
50 μg L ⁻¹ PFOS III	36.416	49.8
50 μg L ⁻¹ PFOS VI	34.815	49.2
Standard 50 µg L ⁻¹ PFOS	34.302	-
50 μg L ⁻¹ PFOS V	46.662	50.5
50 μg L ⁻¹ PFOS VI	37.879	50.5
50 μg L ⁻¹ PFOS VII	37.474	61.1
50 μg L ⁻¹ PFOS VIII	38.657	69.5





Appendix VI – Data Evaporation

Table 8. Evaporation experiments of a concentration of 50 μ g L⁻¹. Evaporating to about 1000 μ g L⁻¹ in pure MeOH.

Evaporation technique	Begin concentration (μg/L)	Begin volume (mL)	Final volume (mL)	Final concentration (μg/L)	Theoretical final concentration (μg/L)	Recovery (%)
N ₂ stream			1.10	887	909	97.6
			1.44	675	694	97.1
SyncorePlus	50	20	1.28	590	781	75.6
	50	20	1.30	569	769	74.0
SuperVap			1.00	499	1000	49.9
			1.00	577	1000	57.7