Norwegian University
of Life Sciences

Master's Thesis 2019 60 ECTS
Faculty of Chemistry, Biotechnology and Food Science

Solvent-free quantification for selected volatile organics in Arctic air

Application of thermal desorption-gas chromatography-mass spectrometry

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Preface

This master thesis in organic analytic chemistry was written at the Faculty of Chemistry, Biotechnology and Food Science at the Norwegian University of Life Sciences (NMBU) in Ås, Norway from January 2019 to December 2019.

The sampling was conducted while attending a course at The University Centre at Svalbard from April 2019 through May 2019.

The Research Council of Norway founds this thesis under the project “Reducing the impact of fluorinated compounds on the environment and human health”, PFOslo; RCN: 268258

Acknowledgments

I would like to thank my supervisor Professor Roland Kallenborn for giving me the opportunity to work with such a fun and challenging thesis. Thank you for believing in me and being supportive and motivational since day one.

Secondly, my greatest appreciations go to Post Doc. Aasim M. M. Ali for always lending out a hand when the ATD instrument or the GC gave me a hard time. Thank you for all the supportive and motivational talks and, last but not least, for all the knowledge about everything you have shared with me.
Thank you to both of you for always having an open door for questions and, especially, for valuable feedback in the writing process.

To all the amazing people I have met during my years at NMBU, thank you for the fun memories and hopefully lifelong friendships. To family and friends for being patient and supportive throughout this year.

Ås, December 2019
Lina B. Aarsbog

Abstract

Perfluorocarbons (PFCs) are a group of human-made fluorinated organic chemicals, which have been used in the industry since the 1950s. The group holds a variety of structures, and the stable CF-bond makes them thermal and chemically stable, but also hydrophobic and lipophobic. Many are persistent and have the potential to bioaccumulate. Some of these compounds have since the 2000s been detected in various matrices around the world. The detection of these compounds in remote locations like the Arctics suggests that long-range transport of these compounds is possible.

Because of this fate, screening programs focus on new contaminants detected in the Arctic. A list of 13 volatile PFCs was selected as target analytes based on previous screening studies. Also, eight biogenic volatile organic compounds were included as target analytes. Emissions from volatile organics have been studied for decades. Biogenic VOCs are mainly vegetation based emission, unlike the PFCs.

Thermal desorption- gas chromatography coupled with tandem mass spectrometry (TD-GC-MS/MS) method was successfully developed for six PFC in electron capture negative ion chemical ionization (ECNICI). Further, a TD-GC-MS/MS method for three PFCs and three VOCs were validated with electron ionization (EI).

The limit of quantification (LOQ) ranged from 0.06 to 0.69 ng/m^3 for the PFCs and from 1.81 to 16.09 ng/m^3 for the VOCs. Contamination issues in the instrumental blanks elevated the LOQs. Apparent recoveries, at 500 pg, ranged for PFCs from 40.4 to 71.8%, and for VOCs from 86.7 to 103.7%.

Low volume air samples were collected indoor and outdoor in the settlements of Barentsburg and Longyearbyen, Svalbard, Norway. All validated compounds were detected from below the LOQ to above the upper limit of quantification. There were detected higher levels of all compounds in indoor samples than in outdoor samples. Because of field blanks left open during the time of sampling, the possibility of contamination during transport and storage is present.

Sammendrag

Perfluorinerte karboner er en gruppe menneskeskapte fluoriserte kjemikalier, som har vært brukt i industrien siden begynnelsen på 1950-tallet. Disse forbindelsene kan ha mange strukturer. Karbon-fluor båndet gir de egenskaper som termisk og kjemisk stabilitet, i tillegg til å være vann og fett avstøtende. På grunn av dette kan de opptre som vedvarende forbindelser i miljøet. Noen slike perfluorinerte forbindelser har vært detektert siden 2000-tallet i en mengde forskjellig prøvemateriale. Identifisering av vedvarende forbindelser i utenforliggende områder foreslår at disse forbindelsene kan transporteres over lange avstander i atmosfæren.

På grunn av dette, fokuserer screeningprogram å identifisere nye perfluorinerte forbindelser i avsidesliggende områder som Arktis.

Tretten forbindelser ble valgt på bakgrunn av tidligere screeningundersøkelser. I tillegg ble åtte biogene flyktige forbindelser lagt til i målforbindelsene. Utslipp fra flyktige forbindelser har blitt studert i tiår og biogene utslipp kommer stort sett kun fra vegetasjon i motsetning til perfluorinerte forbindelser.

En metode basert på termo desorpsjon-gass kromatografi koblet med tandem massespektrometer ble utviklet for seks perfluorinerte forbindelser i electronfangende kjemisk ionisering. Videre ble metoden utviklet og validert for tre perfluorinerte forbindelser og tre biogene flyktige forbindelser med elektron ionisering.

Resultatene fra validering ble en kvantifiseringsgrense fra 0.06 til 0.69 ng^3 for fluorinerte forbindelser og fra 1.81 til 16.09 ng^3 for biogene flyktige forbindelser. Det var forurensningsproblemer i blanke prøver som hevet kvantifiseringsgrensene. Tilsynelatende gjennvinning ble regnet ut til å variere fra 40.4 til 71.8% for fluorinerte forbindelser og fra 86.7 til 103.7% for de biogene flyktige forbindelsene.

Luftprøver av lavt volum ble samlet innendørs og utendørs i bosetningene Barentsburg og Longyearbyen, Svalbard, Norge. Alle de validerte forbindelsene ble detektert fra under kvantifiseringsgrensen til over den konsentrasjoner utenfor den lineære kurven. Gjennomsnittlig var det høyere nivåer innendørs enn utendørs. Felt prøver ble etterlatt åpne under hele prøvetakningsperioden som gjør det vanskelig å utelukke forurensninger fra transportering og lagring av prøvene.

Abbreviations

AFFF Aqueous film-forming foam

AMAP Arctic Monitoring and Assessment Programme

BTV Breakthorugh volume

CAS Chemical Abstract services

CE Collision energy

CI Chemical ionization

DMAPP Dimethylallyl phosphate

DWR Durable water repellent

ECF Electrochemical fluorisation

ECHA The European Chemical Agency

ECNICI Electron capture negative ion chemical ionization

EI Electron ionization

eV electron Volt

FASA Fluoroalkyl sulfonamide

FDA Food and Drug Administration

FOSE Fluoroalkyl sulfonamide ethanols

FTOH Fluorotelomer alcohols

GC Gas chromatography

GFF Glass fiber filter

GFF Quartz fiber filter

IDL instrumental detection limit

IPP isopentyl phosphate

IQL instrumental quantification limit

ISTD Internal standard

kPa kilo Pascal

LOD Limit of detection

LOQ Limit of quantification

LRAT Long range atmospheric transport

MEP Methylerythritol posphate

MS Mass spectrometer

MS/MS Tandem mass spectrometry

NCI Negative chemical ionisation

PCI Postive chemical ionisation

PFAA perfluoroalkyl acid

PFAS Perfluorinated alkylated substances

PFC Perfluoro carbons

PFCA Perfluoroalkyl carboxylates

PFOA Perfluorooctane sulfonamide

PFOS Perfluorooctane sulfonic acid

POP persistent organic pollutant

ppb parts per billion

PUF Polyurethane foams

QqQ Triple quadrupole

REACH Registration, Evaluation, Authorisation and restriction of Chemicals

SIM Selected ion monitoring

SRM Multiple reaction monitoring

SSV Safe sampling volume

t/year tons per year

TgC/year Tera grams of carbon per year

UNIS University centre in Svalbard

US EPA United States Environmental Protection Agency

VOC Volatile organic compound

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Chapter 1

Introduction

1.1 Perfluorocarbons

Perfluorocarbons (PFCs) are a broad group of human-made fluorinated organic compounds. The CF-bond is the most stable bond in organic chemistry, resulting in chemically and thermally stable compounds capable of resisting hydrolysis, photolysis, basic and acidic attacks, as well as stability against oxidizing and reducing agents (Lange et al., 2006). The perfluorinated carbons give PFCs the properties of being hydrophobic and lipophobic. Combined with functional groups, their properties can be altered to makes them desired in polymer coatings and film-forming foams, metal plating industries, textile industries and paper production (Buck et al., 2011).

The PFCs have been recognized as one of the emerging issues in environmental chemistry. Per- and polyfluoroalkyl substances (PFASs) are a large group of PFCs, which environmental levels and fate have been studied since the early 2000s. For PFASs, the common characteristic is the backbone structure of C_nF_{2n+1}. PFASs have been used since the 1950s in numerous industrial and commercial applications.

The earliest and most frequently detected PFAS are perfluoroalkyl sulfonates and perfluoroalkyl sulfonic acid. Both are containing an eight fluorinated carbon backbone.

According to Buck et al. (2011), polyfluorinated carboxylic acids containing eight fluorinated carbons or greater and perfluoroalkyl sulfonates containing six or more fluorinated carbons are termed long-chained. This terminology is adopted in this thesis.

1.1.1 Synthesis

There are two main manufacturing processes for the PFCs: Electrochemical fluorination (ECF) and telomerization.

In ECF, an organic raw material, e.g. octane sulfonyl fluorine ($C_8H_{17}SO_{2F)}$), undergoes electrolysis in anhydrous hydrogen fluoride. This leads to the replacement of all hydrogen atoms with fluorine atoms. This reaction yields free radicals, which can make the carbon-chain to rearrange and break, resulting in a mixture of linear and branched isomers and homologs of the raw material. In the case of octane sulfonyl fluoride, the reaction yields the primary raw material to produce perfluorooctane sulfonyl fluoride ($C_8F_{17}SO_2F$). For perfluorooctanyl acid (PFOA), the raw material octanoyl fluoride ($C_7H_{15}COF$) undergoes ECF. This process has been used to produce 4-,6-,8- and 10-carbon perfluoroalkane sulfonyl derivates (Buck et al., 2011).

In the telomerization process, perfluoroalkyl iodine, $C_nF_{2n+1}I$, reacts with tetrafluoromethylene, CF_2=CF_2, creating perfluorinated chains, $C_nF_{2n+1}(CF_2CF_2)_nI$. This product can react with tetrafluoroethylene again, to produce longer chains. This process produces some of the same classes of PFAS as ECF. For instance, PFOA and perfluoroalkyl carboxylates (PFCA), in addition to other classes like fluorotelomer alcohols (FTOH), sulfonic acids, acrylates and fluorinated phosphates (Buck et al., 2011).

1.1.2 Sources and transport

PFCs are emitted to the environment either by direct or indirect sources. Direct sources are when compounds are emitted to the environment from manufacturing, use or disposal. Indirect sources are when emitted PFCs are precursors for other substances in the environment or as impurities in emissions (Prevedouros et al., 2006).

Since PFCs are used in fire fighting foams as aqueous film-forming foams (AFFFs). PFCs used in AFFFs have ionic functional groups and, therefore, amphiphile. Because of this they are added to the foams to reduce the surface tension, which ensures a better spreading of the AFFFs on both water and oil (Hale et al., 2017). As a consequence, fire fighting training sites have been investigated as a hot-spot for direct sources of PFCs to both water and soil. Hale et al. (2017) conducted a study on soil-samples at the airport at Gardermoen, the biggest airport in Norway. The result showed that perfluorooctyl sulfonate (PFOS) was the dominant PFAS with a concentration between 9-2600 µg/kg in all soil samples. In the Arctic, Skaar et al. (2019) sampled run-off water from the airports located in Longyearbyen, Svalbard, and soil-samples near the airport in Ny-Ålesund, Svalbard. In run-off water collected near the airport in Longyearbyen, the sum of PFASs were in the range of 110-120 ng/L, where PFOS was the predominant compound with 55-58 % of the ∑PFAS. PFOS was also the predominant compound in soil-samples from Ny-Ålesund, ∑PFASs ranged from LOQ up to 800 ng/g dw.

Compared to background site concentration in soil ranged from below LOQ to 7.06

ng/g dw. Background concentrations of freshwater ranged from 0.2 to 0.78 ng/L. As mentioned earlier, PFCs are used in coating industries because of its properties to be water repellant. Gremmel et al. (2016) investigated the PFC-concentrations in outdoor jackets and found the presence of a range of PFCAs and FTOHs. The sum of PFAS ranged from 0.03 to 719 $\mu g/m^2$. This analysis illustrates that also water-repellant outdoor wear is a source of emissions to the environment.

Barber et al. (2007) presented four hypotheses on how it is possible to detect PFCs in remote locations like the Arctic or the Antarctic. The first is the precursor' hypothesis. PFOS and PFCA are degradation products/metabolites of neutral PFCs. These neutral molecules are more volatile and are, therefore, more likely to undergo long-range atmospheric transport (LRAT) (Barber et al., 2007). This hypothesis is supported by smog chamber studies performed by Ellis et al. (2004) and Martin et al. (2006). These studies found that the neutral fluorotelomer alcohols (FTOHs) had a lifetime of 10-20 days and 20-50 days for fluoroalkyl sulfonamides (FASAs). If the transport only were dependent on wind speed, a FTOH would travel 7000 km in 20 days with a wind speed of 4 m/s.

The second hypothesis predicts that the atmospheric transport suggested above is insignificant compared to direct oceanic transport. A modeling study performed found that oceanic transport is the dominant pathway for PFOA with emission from direct sources (Armitage et al., 2009).

The third hypothesis concerns particular matter and that PFOS and PFCAs are emitted with particles from primary sources, and then directly are transported over long ranges in the atmosphere, this is supported by studies from Boulanger et al. (2005) and Harada et al. (2006). The last hypothesis is that PFAS are concentrated at river and ocean surfaces and gets transported into the air by marine aerosols (Prevedouros et al., 2006). This hypothesis is not supported by any studies yet.

Exactly the mechanism of LRAT for PFCs is not entirely understood.However, it is indicated that neutral PFAS get transported by air and then undergo degradation, based on both the smog chamber studies by Ellis et al. (2004) and Martin et al. (2006).

Kwok et al. (2013) conducted a study on the transport of PFAS from Arctic glaciers to downstream locations in Longyearbyen, Svalbard. An illustration of their result is presented in Figure 1.1, included PFOS and PFOA concentrations. They found both PFOS and PFOA concentrations to be highest in surface snow and lowest in ice cores, which support a theory about LRAT. The figure is an illustration of the direct and indirect sources for PFCs in an Arctic environment.

The first of the hypothesis presented by Prevedouros et al. (2006) was that neutral PFCs are precursors for ionic PFCs, and in that way are indirect sources for these ionic PFCs. For instance, the fate of fluorotelomer alcohols is suggested to be degraded to PFCA in remote locations (Ellis et al., 2004).

Smog chamber studies have been conducted by Martin et al. (2006) on N-ethyl perfluorobutane sulfonamide (N-EtFSBA). The reaction pathway suggested was atmospheric

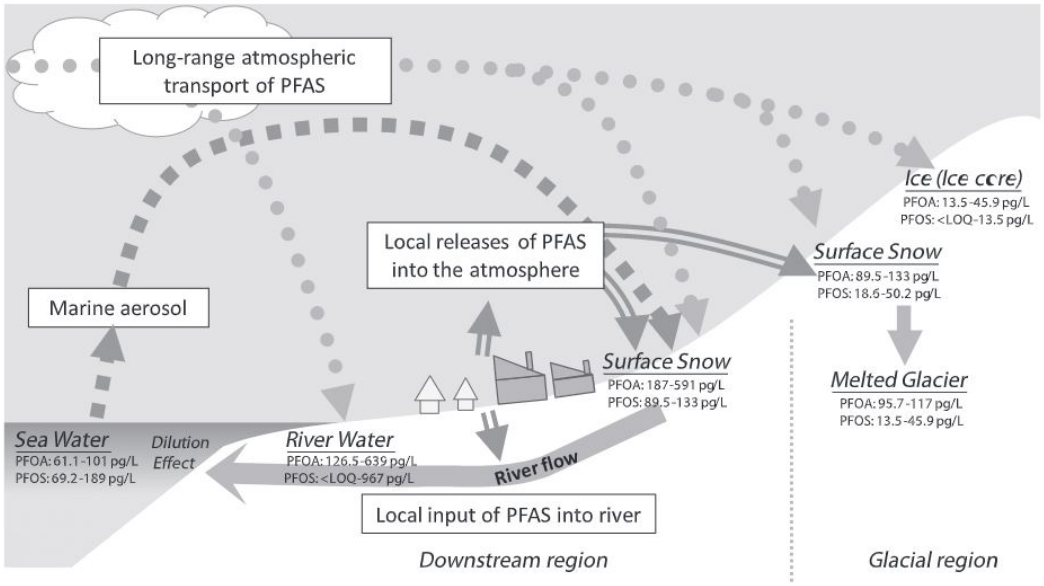


Figure 1.1: Schematic illustration of sources of PFAS in the Arctic. Figure reprinted from Kwok et al. (2013), with permission from Elsevier.

oxidation by chlorine-atoms or hydroxy-radicals. Results suggested that oxidation of N-EtFBSA yields PFCAs and both SO_2 and COF_2. They suggested the same environmental degradation pathway, for N-ethyl fluorooctane sulfonamid (N-EtFOSA), which have the same reactive moiety as N-EtFBSA.

D'Eon et al. (2006) also conducted smog chamber studies, but on N-methyl perfluorobutane sulfonamidethanol (N-MeFBSE). They observed both the formation of sulfonates and carboxylates as products when exposed to hydroxy-radicals.

1.1.3 Target compounds

Some of the target analytes in this study do not have the conventional C_nF_{2n+1} backbone, but rather other perfluorinated structures. Therefore are the target analytes addressed as perfluorinated carbons (PFCs), even when some of the target analytes actually are true PFAS. These analytes are N-methyl perfluorohexane sulfonamide (TDFMS), N-methyl perfluorobutane sulfonamide (MeFBSA), N-ethyl-N-(2-hydroxyethyl)-perfluorohexane sulfonamide (N-EtFHxSE), and the more well-known 8:2 FTOH. Target analytes are presented in Table 1.1, with the CAS-number and acronym. Table A.2 in Appendix A contains the structures of the target compounds.

New contaminants are introduced in screening studies. Arctic Monitoring and Assessment Programme (AMAP) are a reporting program, which provides both reliable and sufficient information about the Arctic environment, its status, and the threats (AMAP, 2017). In AMAP (2017), some new PFCs are mentioned as a future focus for screening studies. These compounds are obtained from agencies that work with chemical regulations. In Europe, the European Chemical Agency (ECHA), under the European Union

(EU), controls which chemicals companies are using and importing, whether it is used in production, exporting, as solvents, or as intermediates. From this, the database REACH is formed. REACH stands for Registration, Evaluation, Authorisation and restriction of Chemicals and the goal is to protect human health and the environment from potentially dangerous chemicals (European Chemicals Agency, 2019). Compounds with a distribution of over 1 t/year are included in the REACH list. However, compounds with a distribution under 1 t/year are included in the pre-register list. All target PFCs, except N-EtFHxSE and perfluorotripropylamine (PFTPA), are listed in the pre-registered list of REACH. N-EtFHxSE is not found in the register and PFTPA is imported to the European economic area at a rate of 1000-10000 t/year.

In the screening program from Schlabach et al. (2018), 8 of the 13 target PFCs in this study were selected for screening. In air perfluoroperhydrophenanthrene (PFPHP), perfluorotributylamine (PFTBA), 1,2,3,4-tetrachlorohexafluorobutane (TCFB) were identified. The latest study was completed by the Nordic Council of Ministers, where all the 14 PFCs were target compounds. The compounds 1,3-bis(trifluoromethyl)-5-bromo-benzene (FMBrBz), Bromopentafluorobenzene (BrFBz), 1,3,5,7-tetrakis(3,3,3)-trifluoropropyl)-1,3,5,7- tetramethylcyclosiloxanes (TTFMCS) and N-EtFHxSE were identified and quantified (Kärrman et al., 2019).

Because of the structure deviation from PFAS, some of these compounds can, therefore, have some other applications. Schlabach et al. (2018) listed seven of the target compounds as solvents, FMBrBz, PFPHP, TCFB, undecafluoro(nonafluorobutyl)cyclohexane (UDFBC), PFTBA, PFTPA and perfluoro-(2,3-dimethyl)-3-ethyl pentane (DTFMP). While BrFBz is listed as an intermediate.

In addition to being a solvent PFPHP, has been used since the early 1990s in eye surgery under the acronym Vitreon (Blinder et al., 1991). Another acronym for the same compound is Flutec PP 11, which has been tried as, e.g. a tracer compound for the direction and speed of oils in groundwater (Mccarville et al., 1995). In more recent years, Flutec PP 11 has been included in a patent for razor blade coating of the cutting edge, but the patent is still under consideration (Chadwick and Sonneberg, 2017).

The two structural alike molecules PFTBA and PFTPA, have both been used in emulsion-based blood substitutes. A mixture of PFTPA and perfluorodecalin was the first generation blood substitutes called Fluorosol approved by the Food and Drug Administration (FDA) in 1989. Nevertheless, in 1993, it was discarded due to its low oxygen-carrying capacity, poor stability and the need for the stem emulsion to be frozen until the application (Lowe, 2000). Another blood substitute was made by mixing PFTBA in methanol and was called Oxypherol. This product was never used in the medicinal market because PFTBA has a half-time of 500 days in the body (Lowe, 2000).

PFTBA has, in later years, been used as a calibrate liquid for mass spectrometers due to the fragmentation pattern.

UDFBC has been used as an oxygen carrier in surgeries under the name Oxycyte (Ya-

coub et al., 2014). It has also been used in cosmetics, but in 2019 the multinational clothing-retail company H&M banned UDFBC from their cosmetics products (H&M Group, 2019).

Table 1.1: Target PFCs and VOCs, including their chemical abstract service (CAS) number and acronym

Name	CAS-number	Acronym
PFCs		
1,3-bis(trifluoromethyl)-5-bromo-benzene	328-70-1	FMBrBz
Perfluoroperhydrophenanthrene	306-91-2	FPPPH
Bromopentafluorobenzene	344-04-7	BrFBz
1,2,3,4-tetrachlorohexafluorobutane	375-45-1	TCFB
Undecafluoro(nonafluorobutyl)cyclohexane	374-60-7	UDFBC
1,3,5,7-tetrakis(3,3,3)-trifluoropropyl) -1,3,5,7- tetramethylcyclosiloxanes	429-67-4	TTFMCS
Perfluorotributylamine	311-89-7	PFTBA
Perfluorotripropylamine	338-83-0	PFTPA
Perfluoro-(2,3-dimethyl)-3-ethyl pentane	50285-18-2	DTFMP
N-methyl perfluorohexane-sulfonamide	68259-15-4	TDFMS
N-methyl perfluorobutane sulfonamide	68298-12-4	MeFBSA
N-ethyl-N-(2-hydroxyethyl) -perfluorohexane sulfonamide	3445-03-3	N-EtFHxSE
1H,1H,2H,2H-perfluoro-1-decanol	678-39-7	8:2 FTOH
VOC		
7-methyl-3-methylideneocta-1,6-diene	123-35-3	β-myrcene
6,6-dimethyl-2-methylidenebicyclo[3.1.1]heptane	127-91-3	β-pinene
2,6,6-trimethylbicyclo[3.1.1]hept-2-ene	80-56-8	α-pinene
2,2-dimethyl-3-methylidenebicyclo[2.2.1]heptane	79-92-5	Camphene
3,7,7-trimethylbicyclo[4.1.0]hept-3-ene	13466-78-9	3-Carene
Hexanal	66-25-1	
1-methyl-4-prop-1-en-2-ylcyclohexene	138-86-3	Limonene
Pentanal	110-62-3	

1.1.4 Changes around perfluorocarbons

The properties which make PFCs desirable in products also result in undesired environmental properties such as bio-accumulation potential, persistence and toxicity. The long-chained perfluoroalkyl acids (PFAAs), PFCA and perfluoro sulfonates were the first PFCs to have been recognized as global environmental contamination (Gomis et al., 2018). With the enlarged field of research, restrictions were made for these legacy contaminants.

The United States Environmental Protection Agency (US EPA) and eight PFC-leading manufacturers agreed in 2006 to first reduce and then eliminate the emission of PFOA and related chemicals in their fluorinated polymers by 2015 (EPA, 2015). Also, the Stockholm convention announced in June 2017 in annex B that PFOS, and its salts, is mentioned as a restricted chemical (Stockholm-Convention, 2019b). The Stockholm Convention is a treaty to protect human health and the environment from persistent organic pollutants (POPs). This treaty was adopted in 2001 and was set into force in 2004. As of May 2017, there are 181 participating countries. The aim is to reduce or eliminate the production and emission to the environment of hazardous and persistent chemicals. POPs are carbon-based organic chemicals with a combination of physical and chemical properties that make them, when emitted to the environment, remain stable over long periods, and therefore be distributed throughout the environment to soil, biota, water, humans and air. For living organisms, including humans, POPs accumulate in fatty tissue and are toxic to humans and wildlife (Stockholm-Convention, 2019a).

Since PFOS is listed in Annex B, there are some acceptable purposes and specific exceptions due to not having suitable substitutes. These purposes are in the industry; photo imaging, semi-conductor industries, liquid crystal display (LCD) industries and certain medical devices (Stockholm-Convention, 2019b).

Due to the PFOA stewardship program in 2006 and the listing of PFOS in Annex B in the Stockholm Convention the production and emissions of PFOS, PFOSA and some precursors the production have been phased out or decreased in the US and Europe, leaving China to increase the production to meet the demands from Europe and the US (Meng et al., 2017).

Restrictions lead the industry to replace the legacy fluorinated compounds. For instance, the textile industry needed to replace the perfluorooctyl chain polymers used in durable water repellent (DWR). Since the phase-out, four- and six-chained perfluoroalkyls have been the replacement chemicals (Holmquist et al., 2016). Information about the replacement chemicals are limited and poses an enlarged field of research. The development of more information enlarges the field to research other perfluorinated carbons.

1.2 Selected volatile organic compounds

Volatile organic compounds (VOC) are a group of carbon-containing low molecular weight compounds being volatile at ambient temperatures. This group of compounds is classified into two groups; biogenic and anthropogenic, where compounds produced and emitted by living organisms are biogenic, and compounds that are emitted to the environment through industries, fossil fuels and household waste are anthropogenic VOCs (Hanks and Louglin, 2011). The anthropogenic emission is estimated to be around 200 TgC/year, while the biogenic emission is around 400-1200 TgC/year. The variation in the biogenic emissions is due to seasonal and geographical variations since the primary emissions are from vegetation, and minor emissions are from soil and ocean (Sindelarova et al., 2014).

VOCs are used in products like food, flavor, fragrances, in medical, pharmaceutical and forensic science and in environmental science. It is a diverse group of chemicals consisting of terpenes, aldehydes, ketones, alcohols, aromatic hydrocarbons, acids and esters.

Most monoterpenes are optically active. The enantiomers can produce different biological responses, for instance, the olfactory response in the nose of humans. E.g. (+)-limonene smells like oranges and (-)-limonene smells like lemon (Dewick, 2009).

VOCs can be defined as compounds having a vapor pressure greater than 0.1 torr at 25 °C and 1 atm and that these compounds contribute to the photochemical ozone creation (EPA, 1999a).

The VOCs in this study are monoterpenes and aldehydes. These are mostly emitted from biogenic sources. Monoterpenes are a group of natural products that are made up of two isoprene units. This gives them a C_{10} skeleton. In nature, the isoprene units can be derived from two pathways: the mevalonic acid pathway and the methylerythritol phosphate (MEP) pathway. The latter pathway is believed to be the most utilized in nature. From both pathways, two intermediates are produced: isopentyl pyrophosphate (IPP) and dimethylallyl pyrophosphate (DMAPP). An enzyme-catalyzed combination of these gives geranyl diphosphate (GPP). With the elimination of phosphate and a combination of other reactions, the GPP can form a range of linear monoterpenes, e.g. target analytes in this study: β-Myrcene, limonene, α-pinene, β-pinene and camphene (Dewick, 2009).

1.3 Gas chromatography/mass spectrometry (GC/MS)

Chromatography is a widely used separation technique based on distribution between two phases, the stationary and the mobile phase. It is an important method for isolating and purifying chemicals. A chromatograph is usually coupled with a detector, a system that can be used for both identification and quantification. Gas chromatography (GC) has from 1952 been a high-performance chromatography technique, and are a preferred technique for separating volatile organic compounds (Miller, 2009). The main parts of a

gas chromatograph are the injector, the column and the detector.

Most often in GC-systems the sample introduction is accomplished with the use of a microsyringe through a rubber septum or from gas sample valves. The goal for the injector is to get the sample into the column fast. For the GC it is important that the sample enters the column vaporized. This is achieved by devices that lower the pressure or increases the temperature, or a combination of both (Miller, 2009).

The mobile phase for gas chromatography is an inert gas, usually helium, nitrogen or hydrogen. The inertness is essential since the only purpose of the gas is to carry the sample through the column. The most used gas is helium due to its higher efficiency at faster flow rates (Miller, 2009).

The stationary phase is placed inside the column. Most commonly, the column is either capillary column with the stationary phase coated on the wall or a packed column. Capillary columns gives higher sensitivity and selectivity compared to packed columns (Miller, 2009).

1.3.1 Automated thermal desorption (ATD)

Thermal desorption is a powerful and versatile sample introduction technique because of its ability to combine sampling and sample preparation. It is also an efficient GC-injection system (Wolfenden, 2012).

The principle in thermal desorption is that gas molecules are retained by adsorption to a sorbent media. Adsorption is a surface phenomenon and mainly depends on the surface area of the sorbent and the interaction between sorbent and analyte (Wu and Chang, 2012). To elute these retained gas molecules the sorbent media are heated and an inert carrier gas flow is purged through, taking the gas molecules into the GC-column. Thermal desorption as sampling technique are a two staged desorption process. First analyte molecules are adsorbed to the sorbent media in sample tubes, before the molecules are eluted and concentrated in a trap before introduction to the GC-column. This two-staged technique enhances the sensitivity and lower the detection limits (Wolfenden, 2012).

In this study, an ATD-400 is used. For this process the sorbent media are placed in stainless steel tubes. The molecules are introduced to the sorbent media either by injection of liquid into the tubes, pumping contaminated air through the tubes or the use of gas standards. The volatile compounds will be retained on the sorbent media. These tubes are then introduced one by one into the thermal desorption unit where they are locked into the gas flow. Figure 1.2 illustrates the thermal desorption layout of the ATD-400 used in this study. The wheel in the middle is a heated valve, which rotates so that the gas flow is connected to the right path according to the program settings.

Two settings are essentially used. Tube conditioning and two-stage desorption. Conditioning of the tubes is an important step where the tube is sealed into the gas flow and purged at high temperature for a given time. This is done to get rid of lower molecular impurities and remaining volatile compounds, but also to activate the sorbent media. The

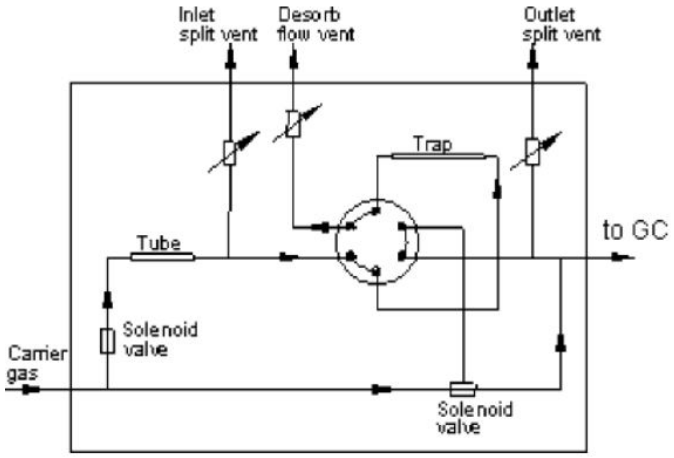


Figure 1.2: Schematic illustration of the ATD-400. Figure reprinted from (Massold et al., 2005), with permission from Springer Nature

two-staged desorption is the analysis mode, where the sample is injected to the GC.

In both modes, the system is always checking for leaks when tubes are locked into the gas flow. Each tube has to pass two leak test. These test are conducted at ambient temperature and zero-flow conditions and the pressure across the ATD should be at column head pressure (1.4 kPa). The first leak test happens by pressurizing the sample tube, by opening the first solenoid valve for 5 seconds (the valve left in Figure 1.2), and the heated valve is turned so that the flow path is connected to the desorbed flow vent. There is a differential pressure transducer measuring the pressure at each sides of the valve, which is not illustrated in the figure. If the pressure difference across the transducer fails to fall down to 6.9 kPa it indicates a major leak in the system, and the tube will be loaded back into the sample carousel. If the tube passes the first leak test, the second test consist of closing the first solenoid valve while the flow path is still connected to the desorb flow vent. If the pressure difference exceeds the column head pressure, the system will identify a leak and the tube is loaded back into the sample carousel, and the ATD will stop the run.

In the two-stage desorption, used for sample introduction, the cold trap also undergoes a leak test. For the cold-trap leak test, the heated valve is rotated so that the gas flow path from the tube includes the cold trap. The leak test is the same as the first one, where the first solenoid valve is opened for five seconds, and the transducer measures the pressure difference. The system passes again the leak test if the pressure drops to 6.9 kPa. After the leak tests, in the two-staged desorption mode, the tubes are purged at ambient temperature with the carrier gas to get rid of contaminants like water. When the selected time of purging is finished, the tube is heated. The retained molecules are desorbed and carried by the gas flow to the cold trap for a given time. Here the temperature are set low, down to -15°C, and the molecules will again be retained. In the ATD-400 the cold trap is a straight tube 165 mm long with an internal diameter of 3mm, filled with sorbent material. The cold trap is kept cold until the desorption time is finished. Then the trap is heated at a fast

rate of 40 °C/sec while the gas flow is reversed. The valve into the GC-column opens at this stage, introducing the molecules to the GC-column (Perkin-Elmer, 1998). Figure 1.2 illustrates that it is possible to split the sample before and after the refocusing on the cold trap. On the ATD-400 system, splitting a sample destructs the part that goes to the waste. In newer thermal desorption units, the split sample can be collected for further analysis.

1.3.2 Mass spectrometry

A mass spectrometer (MS) is often used as a detector for chromatographic systems. A important advantage of the MS is the capability to give structural information, like the molecular weight and fragmentation pattern, about the peaks separated by the GC. The principle is that the molecules get ionized in an ion source, further, the ions are analyzed in the mass analyzers based on their mass-to-charge ratio (m/z). At last the ions are detected in a detector. This happens under high vacuum conditions (Gross, 2011). The information in this section are based on de Hoffmann and Stroobant (2007), if nothing else is stated.

Ionization techniques

There are many techniques for ionization of molecules. For a GC/MS system the most common ionization techniques are electron ionization (EI) and chemical ionization (CI).

A schematic illustration of an EI-source is given in Figure 1.3. The sample are introduced in gas-form into the ionization chamber. In the chamber a heated filament emits electrons at a given voltage. Most commonly, this voltage is 70 eV. This is because organic molecules produce a maximum of ions at 70 eV. However, it also leads to, in many cases, extensive fragmentation. The ionization space maintains an electric potential and the extraction lenses are kept at ground potential, which extracts the ions out from the ionization space and into the mass analyzer. A feature not included in Figure 1.3, is the repeller-electrode, which can retain or push ions out of the ion source.

CI is a softer ionization technique than EI. For a schematic illustration, it looks almost the same as the EI-source illustrated in Figure 1.3. The initial changes are that both the inlet and outlet holes are much narrower. This is to keep the reagent gas inside the ionization space. There is no anode to capture the electron beam. At last, there is also a reagent gas introduction port. The ions that are produced by CI have little to no excess energy, which leads to less fragmentation than with EI. The molecular ion is, therefore, easily recognized. This can be achieved by proton or electron transfer. The analyte molecules collide with primary ions produced by a series of reactions by a reagent gas e.g. methane, isobutane or ammonia. Isobutane and ammonia are more selective, but methane gives better fragmentation. In positive chemical ionization (PCI) there is a proton transfer between the primary ions and the analyte molecules resulting in the ionization of the analyte molecule.

In negative chemical ionization (NCI), the formation of analyte ions are slightly dif-

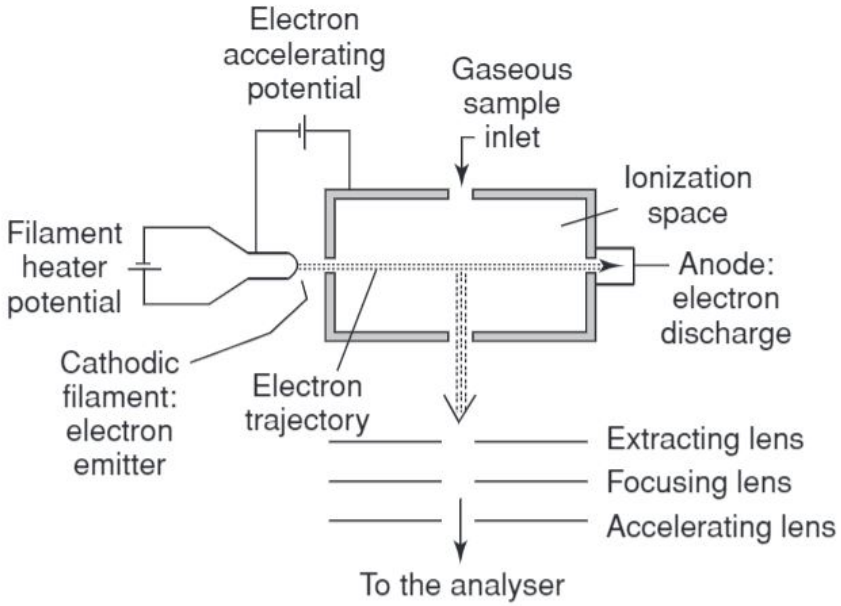


Figure 1.3: Schematic illustration of an EI-source. Figure reprinted from de Hoffmann and Stroobant (2007), with permission from John Wiley & Sons Ltd.

ferent because almost all neutral molecules are able to form positive ions but to form negative ions, the molecule requires the presence of either a acidic group or electronegative elements. The primary negative ion formation is by electron capture negative ion chemical ionization (ECNICI). In both NCI and PCI the ionization space contains electrons with low energy formed by primary ionization reactions (The same primary reactions as in PCI), in addition to the molecules formed of the methane gas. These electrons can be captured by a molecule, resulting in a radical molecule with negative charge.

Mass analyzer

The quadrupole is a frequently used mass analyzer. In a quadrupole, the m/z-ratios are separated by the stability of the trajectories in oscillating electric fields. A quadrupole consists of four parallel rods, aligned as shown in Figure 1.4. The rods placed opposites another holds the same charge at the same time, oscillates with Equation 1.1, where U is the direct potential, V is the amplitude of the radio-frequency voltage and ω is the angular frequency.

$$U - V \cos \omega t \tag{1.1}$$

For an ion entering the field between the rods, it will be drawn to the rod with the same charge as itself. The ion will change direction if the potential in the rods changes before it gets discharged on the rod. Based on this principal, it is possible to adjust which ions-masses gets through the analyzer without being discarded. It is possible to operate in

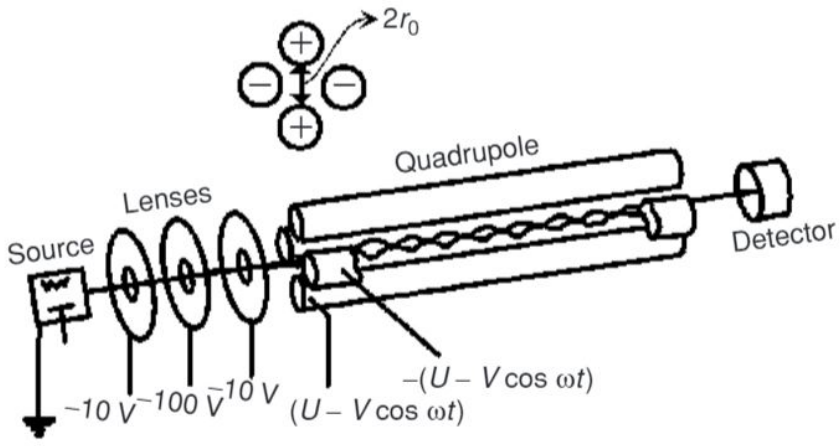


Figure 1.4: An illustration of a quadrupole. Figure reprinted from de Hoffmann and Stroobant (2007), with permission from John Wiley & Sons Ltd.

multiple mass analyzers in tandem, creating MS/MS systems. A triple quadrupole (QqQ) is an example of a MS/MS system. In a triple quadrupole, the first and the last quadrupole serve as mass analyzers, but the middle one, q, is a radio frequency-only quadrupole.

Here it is possible to introduce a gas, making this quadrupole a collision cell. A system with a QqQ can be run in six different modes, illustrated in Figure 1.5. It can be used as a single quadrupole in full scan mode and selected ions monitoring (SIM) mode. The combinations of scan and selecting ions give four possibilities in the QqQ; product ion scan, precursor ion scan, neutral loss scan and selected reaction monitoring (SRM), illustrated in Figure 1.5.

Collision-induced dissociation (CID) can occur when an inert gas is introduced into the collision cell. Ions are accelerated in the collision cell and collisions occur between the ions and the collision gas. This will partly change the translational energy into internal energy. This increase in the internal energy can lead to dissociation of the ion. If the ion dissociates into smaller fragments of charge, they can be analyzed by the second mass analyzer (Niessen and Falck, 2015).

The combination of scan and selecting ions makes a QqQ more sensitive and selective than a single quadrupole. This is because by increasing the criteria of detection the S/N ratio gets higher resulting in quantification with lower detection limits. This gives better accuracy at low concentrations. It also gives more reliable identification with SRM compared to SIM, because there are more detection criteria. This can also be used as a drawback for SRM. Some molecules are not capable of fragmenting to the level which is needed to create SRMs. For these molecules, SIM will give better sensitivity.

The electron multiplier detector

A very widely used ion detector is the electron multiplier. The principle is that ions from the detector are accelerated to high velocity. This enhances the the detection efficiency

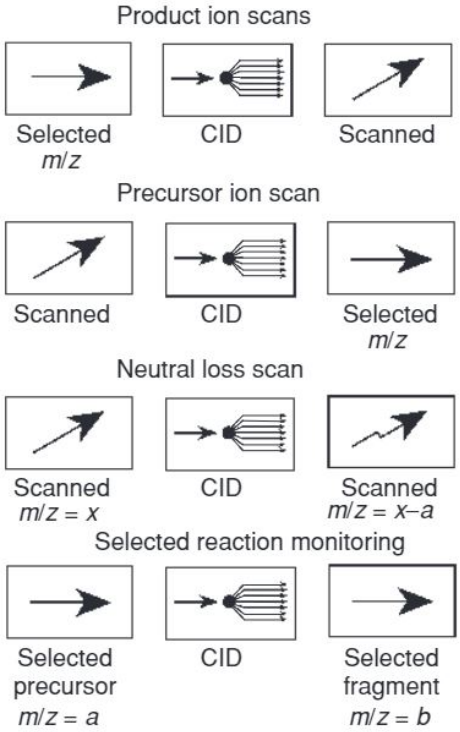


Figure 1.5: Illustration of the MS/MS set-up for the four possibilities. Figure reprinted from de Hoffmann and Stroobant (2007), with permission from John Wiley & Sons Ltd.

and Figure 1.6 illustrates the process.

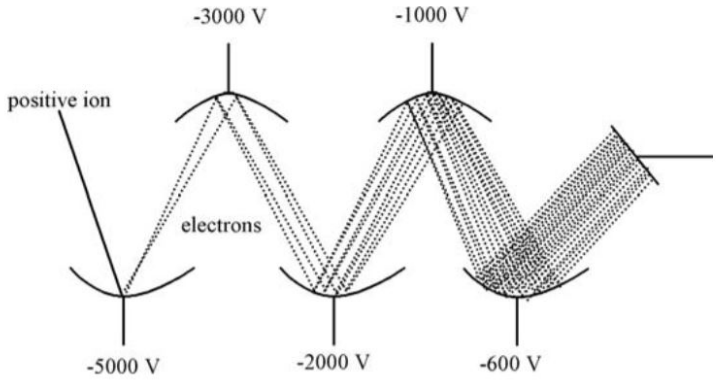


Figure 1.6: A simplified illustration of an electron multiplier. Figure reprinted from de Hoffmann and Stroobant (2007), with permission from John Wiley & Sons Ltd.

The first electrode is called a conversion dynode. It holds either positively or negatively a high voltage. The charge of the dynodes are opposite the charge of the detected ions. In Figure 1.6 the detected ion is positive, while the dynodes then are negative. When the ion strikes the conversion dynode, it emits secondary particles like positive and negative ions, electrons and neutrals. The secondary particles depend on the charge of the initially detected ion. When these secondary particles hits the next dynode they are all

converted to electrons. Further, these are amplified in a cascade effect producing a electron current accelerated by the decreasing potential at the dynodes. At the output of the electron multiplier there is an electrometer.

1.4 Air sampling and analytical method

Air is a complicated matrix to analyze. It is complicated as its many compounds occur in the ppm-ppb concentration range (Dettmer and Engewald, 2002). Therefore it is essential to have sampling and analytical methods that are selective and sensitive enough for the target analytes in this range. Thermal desorption is a recognized method for VOCs and terpenes since the early 2000s (Hodgson and Levin, 2003; Wolkoff and Nielsen, 2001).

A recognized method for air sampling are sample collection on foams and filters. E.g. quartz fiber filters (QFF), glass fiber filters (GFF), polyurethane foams (PUF) and XAD resins. After sampling, it is necessary to apply a liquid extraction method before injection into the GC/MS-system (e.g. Barber et al. (2007); Martin et al. (2002)).

Thermal desorption is a solvent-free transfer of analytes, compared to the extraction needed when sampling with filters and foams. The reducing of steps of sample preparation also reduces the chances of errors conducted by the researcher. But to have a thermal desorption method to perform well, the adsorbent material in the tubes needs to fulfill different criteria. The desorption process needs to be fast, and the desorption of analytes complete. To be able to do this, the sorbent media should have an inert surface, be mechanical and thermal stable, have a low affinity for water and other inorganic constituents in the air (O_3, NO_2, CO_2 and SO_2) (Dettmer and Engewald, 2002). The surface area and the porous structure gives a rough indication of the strength of the adsorbent media. A closer characterization is given by the specific breakthrough volume (BTV) (Dettmer and Engewald, 2002).

BTV is defined as the volume of gas that can migrate a compound through an adsorbent bed of one gram and estimates the maximum sampling volume that secures quantitative sampling (Engewald, 2003).

The determination of BTV can be done by calculation based on adsorption isotherms or experimentally. When determining the BTV experimentally, a tube of a defined amount of sorbent media is placed in a GC-oven, connected to the injector and detector. The determination can be done either by the frontal technique, or the elution technique. In the frontal technique, a gas containing the model substance will be led through the sorbent bed at a defined temperature. In the elution technique, a model substance get pulsed into the sorbent bed. In both cases, the acquired chromatogram can be used to calculate the BTV. The big difference of the two experimental techniques are that frontal technique will also account for capacity overload of the sorbent bed (Engewald, 2003).

To calculate the safe sampling volume (SSV), a direct method proposed by EPA (1999b) are to take two-thirds of the breakthrough volume.

In the same guidelines, the EPA provided a method for determination of VOCs in ambient air with the use of active sampling onto sorbent tubes. There is the determination and validation of the SSV described. Six pairs of linked sorbent tubes are prepared, connected with Swagelok-type 1/4 inch metal unions PTFE fittings. The pairs are then connected to pumps, and simultaneously are three different air volumes tested with two replicates. If more than 5% of any of the analytes is observed in the backup tube, breakthrough is observed. The SSV is then the two-third of the volume where breakthrough is observed.

The sorbent media used in this study are Tenax TA. A hydrophobic and thermally stable sorbent. It is a poly-(2,6)-p-phenyl-oxide polymer with a specific surface area of 35 m^2/g. There are some drawbacks because it can form compounds like benzaldehyde, acetophenone and higher aldehydes (octanal, nonanal and decanal)(Dettmer and Engewald, 2002).

Artifact generation usually happens when tubes are not properly conditioned or if they are used over 100 times, which is the ”hold” time for tenax TA in tubes.

Tenax TA has a low specific surface area, and are, therefore, not suitable for sampling highly volatile organic molecules. Tenax TA are frequently used for compounds with more than five carbons. From the manufacture the sampling range is noted as C7-C26 (Dettmer and Engewald, 2002).

1.5 Aim of the study

The aim of this study was to develop, optimize and validate a thermal desorption- gas chromatography-mass spectrometry method for selected volatile organic compounds, including perfluorocarbons. Kärrman et al. (2019); Schlabach et al. (2018) detected new perfluorocarbons in air in remote locations. Selected neutral perfluorocarbons from these studies were selected as target compounds for this study (table 1.1 in the appendix). The emphasis in this study were on the development, optimization and validation of a solvent-free analytical method for neutral compounds in air. Sampling in Arctic air were also conducted to test the method on environmental samples.

Chapter 2

Method

All the laboratory work was conducted in the group of Natural Product Chemistry and Organic Analysis at the Faculty of Chemistry, Biotechnology and Food Science at the University of Life Sciences (NMBU) in Ås, Norway. The work was carried out on an Agilent 7890B GC-system connected to a 7000C Triple Quadrupole Mass Spectrometer (Agilent Technologies, Santa Clara, USA). As injector an ATD-400 automated thermal desorption unit (Perkin Elmer, Norwalk, USA) was used. The ATD-400 was connected to the GC oven by a deactivated fused silica capillary transfer line which can be heated to between 50-225 °C (Perkin Elmer, Norwalk, USA).

The column was a HP-VOC, which are designed for volatile organic compounds (HP-VOC, 60m X 0,2 mm, 1,1 µm, J&W Scientific, Agilent Technologies, Santa Clara, USA). Helium (6,0 quality, AGA, Porsgrunn, Norway) was used as the carrier gas and methane (6,0 quality, AGA, Porsgrunn, Norway) was used as the reaction gas in chemical ionization. All glass equipment was rinsed at least three times with *n*-hexane prior to use. The gas flow was selected to be around 1 mL/min based on optimum flow calculations provided by Perkin Elmer's user manual for the ATD-400 (Perkin-Elmer, 1998). All tubes in this study were prepacked Tenax TA stainless steel tubes, approximately 90 mm long, and had an outside diameter of 6.35 mm (Perkin-Elmer, 1998). List of chemicals and materials are rendered in Appendix A. All standards used are listed in Table A.1 in Appendix A.

2.1 Method development

First, an already published method was adapted on a mixture of the PFCs target analytes. Wu and Chang (2012) have published a method for neutral PFAS using TD-GC-PCI-MS. Their temperature program for the ATD and GC-MS system was used as a template for further optimization, shown in Table 2.1. Some initial changes were made. In the first trials the source configuration was changed to NCI-mode, due to some tuning troubles in PCI-mode. The MS source temperature was lowered from 300 °C to 250 °C to avoid pos-

sible degradation. Also, in other studies where PFAS was target compounds, the source temperature was reported consistently at a lower source temperature (Barber et al., 2007; Dreyer et al., 2008; Martin et al., 2002).

The cold trap high temperature was also lowered to 250 °C because of the maximum temperature in the transfer line (225°C).

The Tenax TA tubes were spiked using Hamilton syringes, 5 µL from a stock solution of 100 pg/µL were added into the tubes. The tubes were first analyzed in full scan mode. From these initial MS-spectra, the compounds that were identified were assigned retention time and two ions for using SIM-mode during the optimization. The optimized parameters were ATD temperatures, GC temperature program, ion source temperature, ionization voltage and quadrupole temperature. The method was then tried in full-scan PCI-mode but was not possible to obtain due to tuning errors and high background noise. Finally, the method was developed and used in EI-mode. The method was optimized with SRM transitions. This was achieved by selecting high abundant ions, and doing a product ion scan at different collision energies for the selected ions. The highest abundant transitions were selected for the final SRM method. The Wu and Chang (2012) method and the final method for NCI and EI are presented in table 2.1.

Table 2.1: Comparison from the first adapted method and the final NCI and EI method

		Wu and Chang[1]	NCI	EI
ATD	Primary temp	320 °C	250 °C	250 °C
	Time	10 min	30 min	30 min
	Cold trap low		-15 °C	-15 °C
	Cold trap high	335 °C	250 °C	250 °C
GC	Initial	50 °C held for 2 min	50 °C held for 0 min	
	Ramp 1	2 °C/min to 80°C held for 0 min	5 °C/min to 150 °C held for 5 min	
	Ramp 2	10°C/min to 230 °held for 5 min	50 °C/min to 290 °C held for 10 min	
MS	Source temperature	300°C	250 °C	200 °C
	Collision energy		-100 eV	70 eV
	Quadrupole temperature		200 °C	200 °C

[1]- From Wu and Chang (2012)

Blank spaces where not included in either publication or in supplementary information

2.2 Validation

Quantification was done by adding 1,2,3,4,5-pentadeuterio-6-(trideuteriomethyl)benzene (toluene-D8) as an internal standard. Calibration curves were established by spiking tubes with 200 pg of toluene-D8 (ISTD) and with a mixture of natives at 1, 10, 50, 100, 200,

400, 800 and 1000 pg. Between every spiked tube, a conditioned blank tube was used as an instrumental blank. To account for carry-over in the tubes, another desorption cycle was completed right after the first analysis was done.

Due to time limitations, it was not possible to find a suitable recovery standard or more than one internal standard. All internal standards tested are listed in Table A.1 in the appendix.

For quality control, replicates spiked at 10, 200 and 500 pg was analyzed. Besides, a desiccator was used to conduct recovery and breakthrough tests using the same pump as under sampling.

2.3 Sampling at Svalbard

Two Pocket Pump Touch Sample Pumps (SKC, Blandford Forum, United Kingdom) were used for sampling at a flow rate of 125 ml/min.

Five low volume samples were collected in Longyearbyen and Barentsburg at Svalbard, Norway, in April and May 2019. Site, abbreviation, coordinates and sampling date are presented in Table 2.2. Additional sampling information are presented in Table D.1 in Appendix D. Both indoor and outdoor sites were selected due to testing the sampling method and the analytical method. One indoor and one outdoor sample were collected in Barentsburg, a small settlement approximately 60 km west for Longyearbyen. While the remaining indoor and outdoor sample was collected in Longyearbyen.

(a) Outdoor sampling at the firefighting training site

(b) Indoor sampling at the logistic department, UNIS

Figure 2.1: Examples of sampling set-up at two of the five sites

In Barentsburg, the indoor sample was collected at the Promor Hostel, second floor in the hallway. The outside sample was collected 1 km south for the main center, closer to the power plant.

In Longyearbyen, one sample was collected at the airport fire-training site a couple of hundred meters south of Svalbard Airport. The second beside the waste station within

Table 2.2: The different sampling sites and their abbreviation

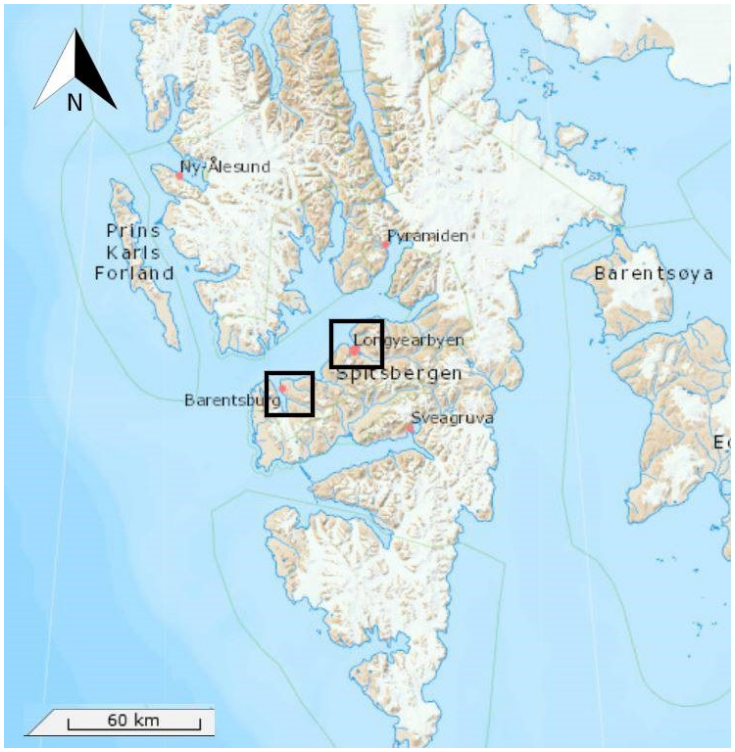
Abbreviation	Site	Coordinates [Lat. /long. dd°mm'ss. s"]	Sampling date
H	Promor Hostel, Barentsburg	N78°03'46.3" E14°13'06.8"	2019.04.30
PP	South for main road, Barentsburg	N78°03'21.1" E14°13'16.4"	2019.05.02
FF	Fire Fighting training site, Longyearbyen	N78°14'22.7" E15°30'25.8"	2019.05.14
UNIS	Logistic department at UNIS, Longyearbyen	N78°13'21.5" E15°29'16.9"	2019.05.23
WS	Waste station, Longyearbyen	N78°13'24.1" E15°39'40.8"	2019.05.27

the city and the third, indoor sample, were collected in the equipment room at the logistic department at UNIS. Figure 2.1a and 2.1b show the sampling set-up at an outdoor and an indoor site. All sites are marked in Figure 2.2. All abbreviations used in Figure 2.2 are explained in Table 2.2.

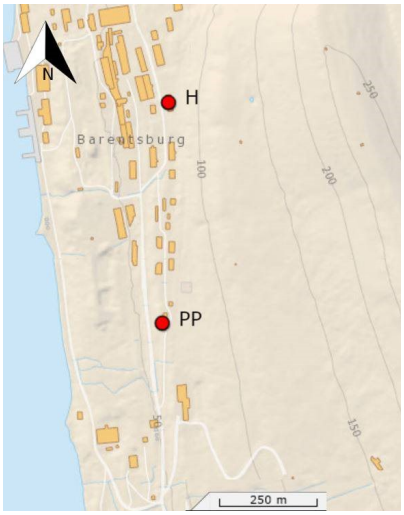
Two replicates were collected simultaneously at all sampling stations. A blank tube was exposed to the environment during sampling.

2.4 Data-analysis

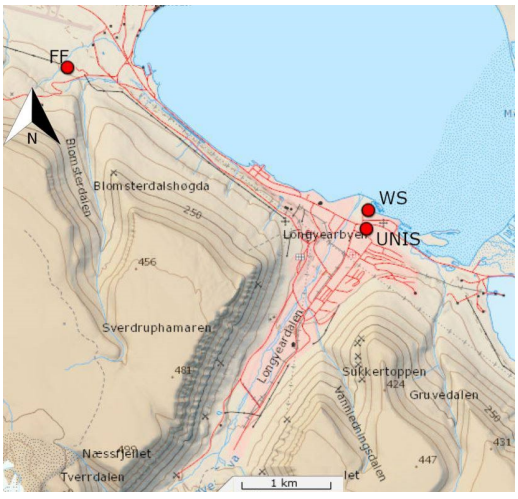
The computer software "Agilent MassHunter Qualitative Analysis B.06.00" was used for investigation of chromatograms and conformation of retention times and qualifier/quantifier ions during method optimization. The software "Agilent MassHunter Quantitative Analysis B.07.00" was used for setting up the validation method and calculation of quantification. The latter software automatically integrated the peaks with the algorithm "Agile2". The integration of all peaks were manually checked, and the integration was corrected where it was necessary. The signal-to-noise ratios (S/N) were calculated by MassHunter and the algorithm "RMS". This algorithm has a standard deviation multiplier of 5. The data were exported to Microsoft Excel, where further analysis was carried out.



(a) An overview of Svalbard, Norway, with the settlements of sampling marked



(b) Barentsburg



(c) Longyearbyen

Figure 2.2: Overview of Svalbard, and the sampling sites in Barentsburg and Longyearbyen. Maps adapted from Topo Svalbard (NPI, 2019)

Chapter 3

Quality assurance and quality control

It has become essential with a quality assurance and control policy over the years with the development of good laboratory practice.

It is to have a quality assurance and control policy to ensure results that are reliable, consistent and reproducible. Precision and accuracy should be in mind from sampling to final results. The importance of reliable results in all fields of research is present. Some field requires more in-depth validation than others. Environmental research most often results in samples with trace amounts of the target compound and, therefore, need analysis, which produce reliable results. In other fields, for instance, in doping control, it is still in the range of trace amounts, but the correct identification and concentration is even more critical than in environmental analysis.

Quality control is a part of quality assurance. The latter is more the overall procedures when working for instance in the laboratory, while quality control is more based on each qualitative or quantitative method.

Before starting a validation process, it is essential to define which parameters the performance of the method should be investigated. Different guidelines have different criteria (Kalra, 2011). This chapter will set the validation parameters and what results are acceptable based on 'Quality control in organic trace analysis' by Oehme (2007).

3.1 Contamination control

All tubes were conditioned at 300 °over 30 minutes, sealed and stored individually wrapped in aluminum foil. Each tube was assigned a number so that it was possible to follow tubes through sampling and analysis. Nitrile gloves were used during all handling of tubes. After sampling, tubes were stored at UNIS in a freezer at -20 °before transportation to a -20 °C freezer at NMBU.

When preparing standard solutions, all glassware was cleaned initially in the department's dishwasher. Prior to use, all glassware was rinsed at least three times with n-hexane, the solvent used in making the standards.

Fume hoods and other working surfaces were cleaned and covered in aluminum foil.

3.2 Identification criteria

The first step of establishing a quality control set-up is to identify and decide the identification criteria. This will provide evidence that the signal from the sample is from the analyte. For environmental analysis, it is acceptable to have three identification criteria to identify a compound successfully (Oehme, 2007).

The most frequently used identification criteria are retention time, detection limits and detector-specific information. Retention times and peak shape should be the same as in external standard solutions. For a compound to be distinguishable from background noise, the signal-to-noise ratio needs to be above 3:1 for the analyte signal. This response will set the detection limits. The detector specific criteria are based on the response from the detector, depending on which kind of detector. With a mass spectrometer, it will be based on specific fragment ions and the ratio between them, either in SIM or in SRM mode. Or the exact mass by operating a high resolution mass spectra (Oehme, 2007).

In this thesis, retention time, detection limits, and two SRM transitions, and their ratio with a tolerance of 20% are emphasized as identification criteria for the EI-SRM-method.

3.3 Quantification method

The most used quantification methods are the external standard method, internal standard method and standard addition method. Both the external standard method and the standard addition method depend on only the standard solution of the natives. The internal standard method, on the other hand, uses one or multiple compounds with similar structure and properties as the natives but should not be present in any samples.

The selected quantification method in this study was to add an internal standard to both validation tubes and sample tubes. Then calculate calibration curves based on the chromatographic response to both the analyte and its internal standard (equation 3.1). The advantages of this method compared to, e.g. the external standard method is that changes due to matrix effects are considered, and small volume losses of the solution containing the ISTD are of no concern (Skoog et al., 2014).

$$y = ax + b \tag{3.1}$$

$$Where: \qquad y = \frac{A_{\mathrm{i}}}{A_{\mathrm{ISTD}}} \qquad x = \frac{M_{\mathrm{i}}}{M_{\mathrm{ISTD}}} \qquad b = constant$$

$A_{i/ISTD}$ = Area of chromatography peak of native compound (i) or internal standard (ISTD)

$M_{i/ISTD}$ = Amount of native compound (i) or internal standard (ISTD)

3.4 Linearity

The calibration curve describes the relationship between the signal response and the concentration of the analyte. This relationship is most commonly linear over a dynamic range. Then equation 3.1 can be used to predict the concentrations of analyte in samples.

Another term to be drawn from the calibration curve is sensitivity. Which are defined as the change in the response signal per unit change in analyte concentration (Skoog et al., 2014).

3.5 Recovery

Apparent recovery is presented as the ratio between the measured amount and the added amount, equation 3.2. In this study the terms apparent and absolute recovery are used. IUPAC recommends that that apparent recovery is used when the the recovery is not based on the extraction efficiency or a pre-concentration stage of a analytical process (Gohshi et al., 2002).

The apparent and absolute recovery are both calculated by Equation 3.2, but in apparent recovery the measured amount is corrected by the response of an internal standard. In absolute recovery concentration is not corrected by the response of an internal standard.

$$\%\ Apparent\ recovery = \frac{Measured\ amount}{Added\ amount} \times 100 \tag{3.2}$$

3.6 Limits of detection and quantification

Limit of detection (LOD) and limit of quantification (LOQ) are calculated to be sure that the analyte signal is significantly higher than the noise in the chromatograms. There is no standard method to calculate these limits, but The IUPAC definition states that "the limit of detection, expressed as a concentration, c_L, is derived from the smallest measure, x_L, that can be detected with reasonable certainty for a given analytical procedure" (Long and Winefordner, 1983).

The limit of quantification and detection for the method is, therefore, based on these levels in the blanks and are calculated according to equation 3.3. Where cL is the limit of detection, cB is the average of the analyte signal in the blanks, sB is the standard deviation of the signal in the blanks and k is a factor to be defined. k is defined as three for detection limits and ten for quantification limits.

$$cL = cB + k \times sB \tag{3.3}$$

In this study, there were detected peaks with a S/N above ten or all analytes in the instrumental blanks. cB was estimated by converting the S/N to concentration by dividing them on the slope of the linear curve. The slopes for each analyte were obtained by S/N from the three to four lowest calibration samples. The average concentration calculated represents cB in Equation 3.3. sB were then the deviation between these estimated concentrations.

The instrumental detection limit (IDL), the instrumental quantification limit (IQL) was calculated based on what response that gave a S/N equal three and ten. Based on the same S/N calibration curves mentioned.

3.7 Breakthrough and carry-over

The ideal when sampling is that the adsorption material is able to retain all analytes of interest so that there are no losses or carry over in the tubes. To , breakthrough and carry over was tested. Breakthrough and carry-over were tested, to indicate the performance of the tubes. Breakthrough is identified if the concentration in the second tube exceed 5 % of the concentration in the first tube, according to the EPA guidelines on sampling VOCs onto sorbent tubes (EPA, 1999b). Equation 3.4 illustrates the calculation.

$$Breakthrough\ = \frac{Amount\ in\ second\ tube}{Amount\ in\ first\ tube} \times 100 \tag{3.4}$$

Carry-over in the tubes was investigated by doing another desorption cycle after the initial analysis. The same calculation as for breakthrough, equation 3.4, was used to determine how much of the added analytes was actually desorped by the ATD.

Chapter 4

Results and discussion

A TD-GC-MS method was developed and optimized for both ionization techniques EI and ECNICI. Due to the lack of internal standard, only the method with EI as the ionization technique was validated with one internal standard.

It was possible to optimize the TD-GC-EI-MS method for eight out of twenty-one target compounds listed in Table 1.1. These 21 compounds included 13 PFCs and eight VOCs. The 13 PFCs were also tested in GC-ECNICI-MS, where the a method were optimized for six compounds.

The validated TD-GC-EI-MS method was tested on three outdoor and two indoor samples. Three sampling sites were located in Longyearbyen, Svalbard, and two samples were located in Barentsburg, Svalbard.

4.1 Singel ion monitoring with electron capture negative ion chemical ionization

Out of 13 volatile PFC, a ECNICI-SIM method was optimized for six PFCs.

The VOCs were not tried in ECNICI-mode because previous research states that ionization with EI is the best technique for these compounds (EPA, 1999a; Ribes et al., 2007; Rodríguez-Navas et al., 2012). The method was developed and optimized for the volatile PFC with SIM in ECNICI-configuration. The method parameters are shown in Table 2.1. Because it was not possible to optimize the method with SIM of any of the seven internal standards tested in ECNICI-configuration, validation could not be concluded.

The PFC compounds are presented in Table 4.1 with their retention time, the quantitative and qualitative ion. A chromatogram showing the peaks is presented in Figure 4.1. The injected concentration for the chromatogram was 500 pg.

Table 4.1: Retention time, quantitative and qualitative ion for the seven optimized PFC-compounds with ECNICI-SIM method

Acronym	Retention time [min]	Quantitative ion	Qualitative ion
FMBrBz	21.0	246.0	167.0
PFPHP	18.5	624.0	586.0
BrFBz	20.2	212.9	292.0
TDFMS	25.2	282.2	250.7
MeFBSA	28.1	382.9	300.0
N-EtFHxSE	33.9	249.5	262.0

The peak shape for PFPHP is not as sharp and symmetric as desired. From individual chromatograms of standards solution, PFPHP shows two peaks, at retention time 17.7 and 18.5, with the same peak shape as in Figure 4.1. According to the producer of PFPHP, the standard is a mixture of isomers. This could explain the compound having two peaks.

The rest of the compounds have acceptable peak shapes. PHPFP, TDFMS and N-EtFHxSE all have smaller areas, and will then have higher detection limits than the other if this method were to be validated.

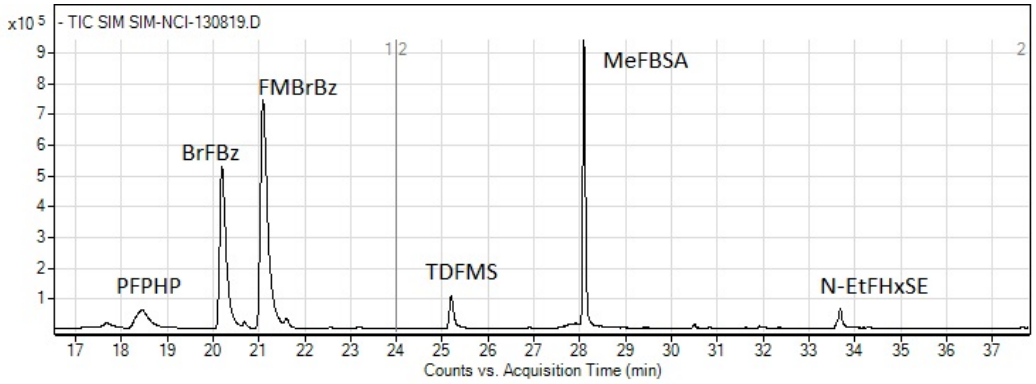


Figure 4.1: Total ionic chromatogram for ECNICI-SIM method.

The ECNICI-technique is a soft ionization technique. Soft techniques, like ECNICI and PCI, are often the preferred techniques to ionize and obtain the molecular ion. As for ECNICI, the molecular ion is only obtained for FMBrBz and PFPHP as the quantitative ion and as qualitative ion for BrFBz.

When developing a SIM-method, it is important to select the ions which gives the highest abundance. For both BrFBz and N-EtFHxSE a lower weighted ion were more abundant. This is important because of sensitivity for the method. The optimization was carried out mainly at a 500 pg level of spiking. The fragmentation pattern will be the same at lower concentrations but the generation of certain ions could become under the detection limit for the MS.

4.2 Selected reaction monitoring with electron ionization

Out of the 21 compounds, shown in Table 1.1, eight were identified in SRM-mode, in addition to the internal standard, 1,2,3,4,5-pentadeuterio-6-(trideuteriomethyl)benzene (toluene-D8). All nine compounds are presented in table 4.2 with assigned retention time and quantitative and qualitative SRM transitions, the collision energy (CE) is given for each SRM-transition. Out of the eight native compounds, three were PFCs, and 5 were VOCs. The three monoterpenes β-pinene, Camphene and β-myrcene were very close in retention time but in chromatograms, they are distinguishable, as shown in Figure 4.2. Hexanal shows, in the same figure, a very high intensity, and the three PFCs, therefore, barely are distinguishable from background noise, even when they had a S/N ratio above 10. In Figure 4.3, the transitions for BrFBz are extracted. The black lines in the figure represent the quantitative transitions and the red line the qualitative transitions. The peak shape and intensities are acceptable when the transitions are extracted.

Table 4.2: Retention time, quantitative and qualitative SRM and the expected ratio between quantitative and qualitative SRM for the EI-SRM method. The collision energy (CE) are given for each SRM-transition

Analyte	Rt [min]	Quantitative SRM (CE)	Qualitative SRM (CE)	Quant/Qual
BrFBz	20.4	292.0 → 213.0 (20)	213.0 → 163.0 (15)	46.9
FMBrBz	21.3	246.0 → 167.0 (20)	167.0 → 117.0 (10)	97.5
N-EtFHxSE	33.9	440.0 → 348.0 (10)	348.0 → 328.0 (15)	21.7
α -Pinene	24.9	136.0 → 93.0 (10)	136.0 → 77.0 (10)	7.8
Camphene	25.8	121.0 → 77.0 (20)	136.0 → 79.0 (15)	39.5
β -Pinene	26.4	93.0 → 77.0 (10)	93.0 → 91.0 (10)	39.1
β -Myrcene	26.7	93.0 → 77.0 (20)	136.0 → 51.0(25)	0.2
Hexanal	18.3	82.0 → 67.0 (10)	72.0 → 57.0 (10)	13.4
Toluene-D8 (ISTD)	17.0	100.0 → 98.0 (5)	100.0 → 70.0 (20)	11.6

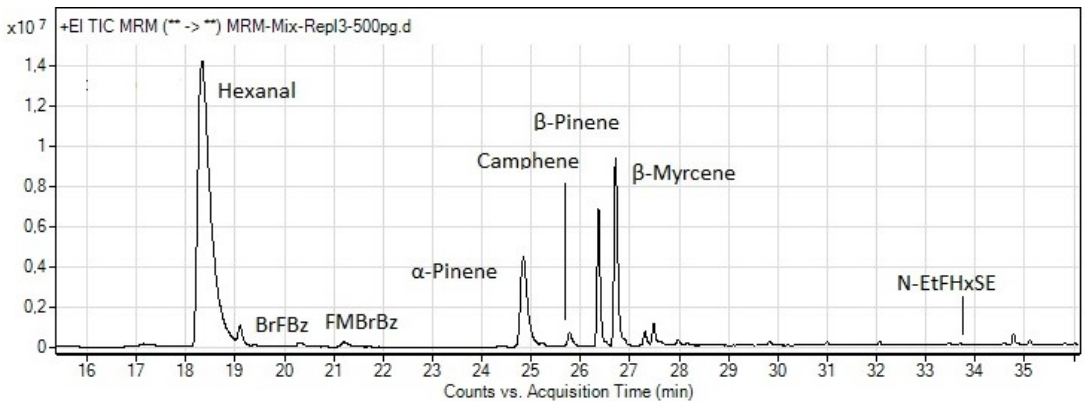
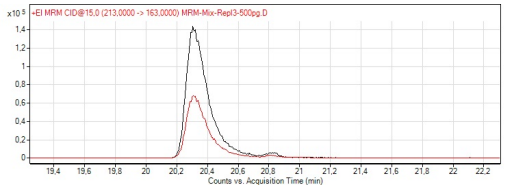
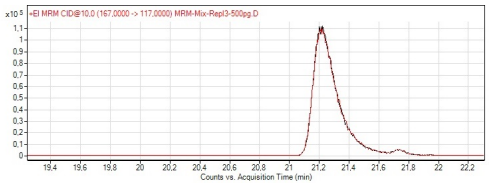


Figure 4.2: Chromatogram at 500 pg with the EI-SRM method.

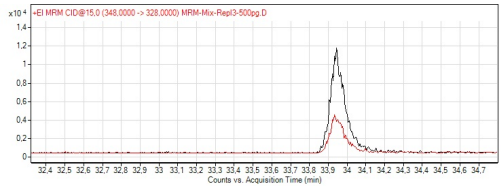
The monoterpenes have the same molecular mass and, therefore, have similar transitions. β-pinene and β-myrcene have the same quantitative SRM transition, which is not ideal, but acceptable as long as do not co-elute and have separate retention times. Under the validation process, the MassHunter software suggested 93.0 $\rightarrow$ 77.0 as the quantitative SRM for both. Since the method was set-up with four identification criteria, retention time, quantification and qualification SRM and the ratio within the accepted range of 20%, this was accepted.



(a) BrFBz



(b) FMBrBz



(c) N-EtFHxSE

Figure 4.3: The extracted SRM transitions for PFCs

When developing SRM-transitions, the same principle as discussed for the SIMs in the ECNICI-method applies. Preferably the quantititaive SRM-transition should have the molecular ion as precursor ion. This was true for BrFBz, FMBrBz, α-pinene, hexanal and toluene-D8. α-pinene, camphene and toluene-D8 have their molecular ion as qualitative SRM-transition. Since monoterpenes have the same molecular weight, SRM-transitions will give more reliable identification than SIM. The issue with creating SRM-transitions for molecules with the same molecular weight is that with a transition can be true for multiple compounds. As long as there is a difference in retention time, this is not an issue.

4.3 Comparison of chemical ionization and electron ionization

Table 4.3 shows the difference in area response at 500 pg for the three molecules, BrFBz, FMBrBZ and N-EtFHxS, which was developed with both EI and ECNICI methods. The response from ECNICI obtained from SIM, while the response from EI is obtained from SRM. The mode with highest area gives the best response for each analyte. Both areas for quantitative and qualitative SIM/SRM are included.

Table 4.3: Comparison of EI-SRM and ECNICI-SIM for the three PFC compounds at 500 pg

	EI		ECNICI	
	quant. SRM	qual. SRM	quant. SIM	qual. SIM
BrFBz	11437780	5444933	510425	27467
FMBrBz	1041925	1023194	4509315	891055
N-EtFHxSE	52116	1987	46402	38292

BrFBz and N-EtFHxSE have larger areas for both quantitative and qualitative SRM in EI, while FMBrBz has the largest area in ECNICI. The difference between EI and ECNICI for BrFBz is big, but for the two others, the difference is not that significant. N-EtFHxSE has a small area for the EI qualifier ion, which may result in no qualifier confirmation in lower concentrations. This could result in a more difficult quantification because of the lower sensitivity. In the raw data for, e.g., the apparant recovery, the S/N ratio-ratio for 200 pg and 500 pg are above 10, but for 10 pg, it is lower, resulting that N-EtFHxSE has a instrumental detection limit (IQL) about 10 pg.

In respect of optimized PFCs, the ECNICI-SIM method successfully optimized the method for six PFCs, while the EI-SRM method only optimized the method for three PFCs. The only way of optimizing the method for more compounds was to increase the concentration. The method was set-up to work in trace-levels, when increasing the concentration range, it is a possibility to lose sensitivity in the lower concentration range. As mentioned in section 4.4.2, the highest calibration level, 1000 pg, was excluded because saturation was indicated with a flattening of the curve. If this is true for higher concentrations as well, the slope of the curve will decrease, resulting in a decreased sensitivity.

Last, there are advantages and disadvantages with using both SIM and SRM methods. There is a sensitivity gain changing from a scan-method to a SIM-method. This is due to the signal-to-noise ratio. The background will decrease, and therefore the sensitivity will increase. From SIM to SRM, the same happened. The background will decrease even more since the detection criteria get narrower. The drawback of this sensitivity change from SIM to SRM is that it also gets more difficult to successfully identify a compound. From selecting a few ions to search for in each chromatogram to yield a reaction at the

exact collision energy could make the SRM too selective (de Hoffmann and Stroobant, 2007).

Both the ECNICI-SIM and the EI-SRM method do not have eluting compounds before over 17 minutes into the temperature-program, illustrated by the x-axis in Figure 4.1 and 4.2 The temperature program was altered to try and shorten the analysis time. Any changes made the three monoterpenes, α-pinene, β-pinene and camphene to co-elute, which made it impossible to distinguish them.

4.4 Validation results

Validation was carried out for eight analyte compounds with the EI-SRM method. The validation criteria were set by information given in Oehme (2007). Identification criteria were set to retention time (Rt), quantitative SRM and Qualitative SRM, and the ratio between then were within 20% of the set ratio. However, for a peak to be detected, it needs to have a S/N ratio three times the background S/N ratio, and ten times for quantification.

For the calibration curves, it needed to have at least five measuring points, over two orders of magnitude. The linearity of the measuring range, represented by the coefficient of determination, mustt be above 0.95.

Recoveries were accepted in the range from 40-120% with a RSD limit of 20%. Breakthrough were established if it exceeded 5% based on EPA (1999b)-method for sampling VOCs in sorbent tubes.

4.4.1 Identification criteria

The identification criteria for the compounds are presented in Table 4.2. The column denoted with quant/qual in Table 4.2 is calculated by the expected qualifier ion response as the percentage of the quantitative SRM.

When developing multiple SRM transitions for each compound, preferably, both the quantitative and qualitative precursor ion are the same. In this case, many of them have different precursor ions. This is because, under the development of SRM transitions, the SRM transitions with the highest abundance was selected. This will increase the sensitivity for the method.

4.4.2 Calibration curves

All calibration curves can be seen in the Appendix C, Figure C.1 with the associated raw data in Table C.1 in Appendix C. Camphene had a S/N ratio less than three for almost all calibration solutions except 800 and 1000 pg. Therefore, Camphene was excluded from further validation.

For all the other compounds, the highest calibration standard was excluded to obtain a better coefficient of determination (R^2) and to ensure a better fitted curve for the lower

concentrations. The coefficient of determination measures the variation in y which are explained by the linear relationship. The closer R^2 is to unity, the better the linear model explains the variations in y (Skoog et al., 2014).

Mid concentration solutions were sometimes excluded for the same reason. All calibration parameters like linear range, coefficient of determination, origin treatment, weight and equation are presented in table 4.4. The lowest value for R^2 was 0.97, which are within the acceptable range. No curve was forced through the origin, and almost all compounds except hexanal had y-intercepts (b) close to zero. Also, no weight was added to the curves. In terms of sensitivity, explained in section 3.4, the steeper the slope of the curve is, the better the sensitivity is. Therefore, the most sensitive compound is Hexanal, followed by β-Myrcene and β-Pinene.

Table 4.4: Calibration parameters

Analyte	Linear range [pg]	R^2	Origin treatment	Weight	y=ax+b a	b
FMBrBz	1-800	0.9944	ignore	none	1.9×10^{-3}	0.0207
BrFBz	10-800	0.9961	ignore	none	8.15×10^{-4}	0.154
α-Pinene	1-800	0.9884	ignore	none	1.5×10^{-3}	0.024
β-Pinene	1-800	0.9972	ignore	none	1.5×10^{-2}	0.033
β-Myrcene	1-800	0.9996	ignore	none	2.5×10^{-2}	0.136
N-EtFHxSe	1-800	0.9718	ignore	none	8.36×10^{-5}	0.0031
Hexanal	1-800	0.9931	ignore	none	9.4×10^{-2}	3.99

As explained earlier, the 1000 pg calibration-level was excluded for all analytes. This was to improve the fitting of the curve (R^2 above 0.95) at the lowest concentrations, in addition to that the 1000 pg level showed a tendency to be more saturated as it had a lower response than the 800 pg level.

4.4.3 Limits of detection

All limits were calculated based on the level of analytes in the instrumental blanks, which were described section 3.6. The calculated result are presented in Table 4.5, and the raw data are presented in Table B.3 in Appendix B. The instrumental limit of detection (IDL) ranged from 0.05-0.79 pg for PFCs and 1.22-22.8 pg for VOCs. The method LOQ ranged from 0.06-0.69 ng/m^3 for PFCs and 1.81-16.1 ng/m^3 for VOC.

For conditioning of tubes EPA (1999b) recommends prepacked tubes to be conditioned for 30 minutes at 350°C while at least 50 mL/min carrier gas flow through. But for this study, each tube was conditioned at 300 °C over 30 minutes before used as blanks or sample tubes. The temperature was lowered to 300 °C because of the maximum temperature for Tenax TA, 350°C (Dettmer and Engewald, 2002). This should be sufficient for conditioning of the tubes and minimize the contamination issues.

Table 4.5: Limit of detection and quantification

Analyte	IDL [pg]	IQL [pg]	LOQ [ng/m^3]
FMBrBz	0.05	0.17	0.06
BrFBz	0.55	1.84	0.38
N-EtFHxSE	0.79	2.63	0.69
α-Pinene	22.80	75.99	16.09
β-Pinene	3.56	11.85	1.88
β-Myrcene	2.21	7.38	1.81
Hexanal	1.22	4.08	1.87

The VOCs had all a higher level of blank contamination and this could be explained by that these compounds exist around because of origin of emissions.

4.4.4 Recovery

Apparent recoveries for 500 pg, 200 pg, and the absolute recovery for the desiccator-test at 500 pg are presented in Table 4.6. Numbers for apparent recovery are corrected with the response of the ISTD, while absolute recoveries are not corrected with the response of the ISTD, calculated as described in the Section 3.2.

Apparent recoveries were also tested at 10 pg. There results were rejected because the recoveries ranged from 311.3 to 1099.5%, numbers presented in B.4. For the compounds α-pinene and β-pinene, 10 pg are below the IQL. At low concentrations the reliability of the results is low. Skoog et al. (2014) explains that "at ultratrace levels of 1 ppb, interlaboratory error (%RSD) is nearly 50%. At lower levels, the error approaches 100%." This could be the explanation of the very high recoveries at 10 pg.

One replicate was an obvious outlier for both 500 and 200 pg, and where because of that ignored when recoveries were determined. This resulted in apparent recoveries at 500 and 200 pg only have two replicates. The raw data for all the replicates is shown in Table B.4, where replicate named mix-200 and mix3-500 were excluded. This was because the signal from the ISTD was high compared to the ISTD signal in the other replicates resulting in minimal concentrations for the analytes, as these areas held the same order of magnitude as in the other replicates. This could be caused by a volume error during the spiking of these tubes, since they were manually spiked with Hamilton syringes.

Hexanal was excluded from sample results due to recoveries for 500 pg at 30.0 $\pm$ 141% and for 200 pg, 240 $\pm$ 4%. There is no other compound that deviates this much in the 500, 200 pg replicates. As explained earlier, biogenic VOCs i are compounds that are around us at any time. The unaccepted recoveries for hexanal could be attributed to contamination issues as this compound most probably occurs in the lab atmosphere. Jiang et al. (2017) found that hexanal were the major odorous compounds emitted from

particleboard, which are a common building material in the lab as well. Further, hexanal had, according to the calibration curves, the best sensitivity of all compounds. This can contribute to higher sensitivity for low contamination levels.

Table 4.6: Apparent recovery and RSD [%] for 500 pg and 200 pg, and absolute recovery and RSD [%] at 500 pg spiked in a desiccator

Analyte	Recovery ± RSD [%] 500 pg n=2	Recovery ± RSD [%] 200 pg n=2	Recovery-desiccator ± RSD [%] 500 pg n=3
FMBrBz	50.2 ± 14.4	87.2 ± 21	43.4 ± 33.6
BrFBz	71.8 ± 19.6	82.0 ± 12.7	140.6 ± 55.6
N-EtFHxSE	40.4 ± 22.7	47.7 ± 2.2	15.6 ± 173.2
α-Pinene	86.7 ± 9.0	126 ± 4.6	239.1 ± 37.8
β-Pinene	103.7 ± 9.4	151 ± 4.6	432.4 ± 19.7
β-Myrcene	99.5 ± 9.5	149.8 ± 4.6	155.1 ± 17.6
Hexanal	30.0 ± 141	240 ± 4	185.1 ± 6.4

At 500 pg, all the other compounds showed acceptable recoveries. N-EtFHxSE had an average apparent recovery at 40.4 ± 22.7%. This is on the edge of the validation limits set for this method. However, the result is an average of just two replication,

α-pinene, β-pinene and β-myrcene all had apparent recoveries above the acceptable limit at 200 pg. Again, this could be caused by contamination in the lab or the instrument room. These levels of contamination are quite challenging to control because of the natural emissions of the VOCs.

The desiccator experiment was conducted with spiking a desiccator at ambient temperature, waiting at least 30 minutes, and then withdrawal of the air with the sampling pump. It was not possible to connect this system to clean nitrogen gas or another clean gas. This caused the pump to stop after few seconds because of under-pressure in the system. The valve, closing the desiccator, needed to be slightly open so that the pressure was constant in the desiccator. This causes potential errors. First of all, there is the potential that the volatile analytes evaporates through the slightly open valve, because of their vapor pressure.

Toluene-D8 have a high vapor pressure, evaporation out of the desiccator could cause the areas to be much lower than for the tubes spiked with liquid at the same concentration. Because of this, the recoveries were calculated as absolute recovery, without correcting them for the response of the ISTD. The absolute recovery for all compounds, except for FMBrBz and N-EtFHxSE, is much higher than the accepted range. This indicates that the air in the lab environment actually are contaminated with biogenic compounds as suggested earlier.

4.4.5 Breakthrough and carry-over

In the spiked desiccator, the breakthrough was tested by having two tubes in tandem when sampling.This was done in three replications. The results are presented in figure 4.4.

In the desiccator test, all tubes were analyzed beforehand to be sure that target analyte levels were low to zero. The raw results are included in B.2 in Appendix B. There were reported levels in almost all tubes, as for other lab blanks. These levels were not corrected in the breakthrough test, and therefore, could contribute to higher breakthrough.

The calculated breakthrough showed that only BrFBz was below 5 % with 0.0 $\pm$ 0.0 %, followed by Hexanal with 6.64 $\pm$ 34.22 %. The remaining analytes varied from 10.37 $\pm$ 17.27 % to 50.36 $\pm$ 173.21 %. As described for the recoveries for the desiccator, the set-up of the sampling could cause contamination of the samples because air were let in the desiccator. Since the SSV was not calculated and the order of the potential contamination is unknown, it is not possible to know if the sorbent media in the first tube was saturated, causing the analyte molecules to be collected in the second tube. This could explain the high breakthrough for the monoterpenes.

N-EtFHxSE has not only a considerable high breakthrough, but also a very high RSD. Compared to the absolute recovery for N-EtFHxSE, which only were at 15.6 %, with a RSD at 173.2%. There is a high variation in both tubes in tandem, within all three replicates. These variations can be explained that N-EtFHxSE were detected in all sample tubes, but had low response, resulting a calculated concentration of zero for two of the replicates. This result indicates that the sampling of N-EtFHxSE war not compleeted, and that N-EtFHxSE either evaporized out of the chamber or did not vaporize in the chamber.

These variations could also be caused by contamination. However, N-EtFHxSE is not a compound that have been frequently detected in indoor air, which make a contamination issue less plausible.

When checking the carry-over, the calibration tubes were re-analyzed. In Table 4.7, the results are presented.

At higher concentrations there is no carry-over. But for the lower concentrations, especially the 1 pg, there is some carry-over. The results marked with superscript 1 had concentrations in the second round of analysis exceed the concentration in the first analysis. As explained earlier, this could be caused by contamination of the tubes. When conducting these analyses, all tubes were loaded into the carousel of the ATD. One by one, the tubes were analyzed and then loaded back into the carousel while the rest of the analysis was run. Between 12 to 16 tubes were analyzed in one run, resulting in an analysis time around 12-14 hours before the analysis was started again to check for carry-over in the tubes. This causes the tubes to be stored in an environment with no control over possible contamination. As explained earlier, at low concentrations, a small change in response can cause then give significant concentration changes.

When excluding the internal standard, new calibration curves needed to be made for all analytes. For many compounds, these were less linear. These calibration curves are

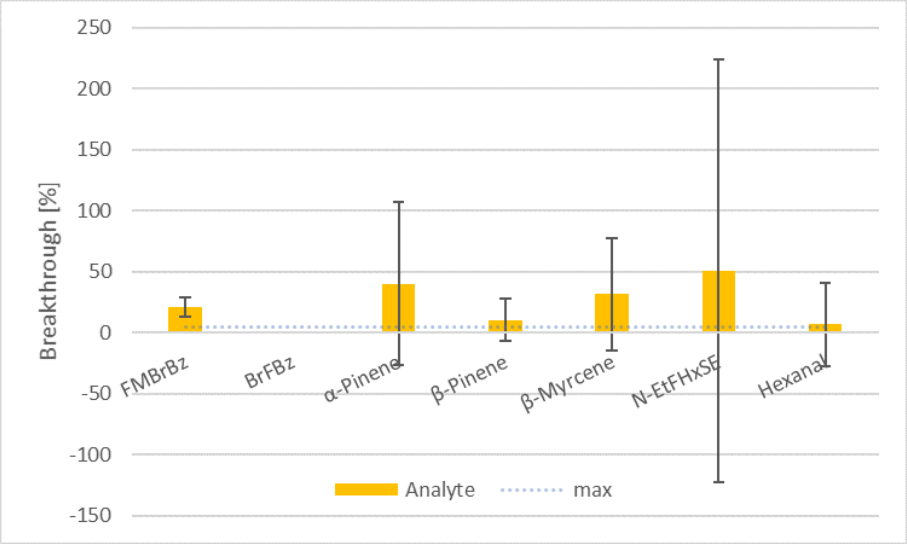


Figure 4.4: Breakthrough [%] in the desiccator-test. The error-bars represents the RSD [%]. The max line are at 5%.

Table 4.7: The ratio [%] between first and second adsorption for the calibration curve standards

	1 pg	10 pg	50 pg	100 pg	200 pg	400 pg	800 pg	1000 pg
BrFBz	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
FMBrBz	0.5	0.18	0.0	0.0	0.0	0.0	0.0	0.0
α-Pinene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
β-Pinene	1423.5[1]	0.0	0.0	0.0	0.0	0.0	0.0	0.0
β-Myrcene	2688.5[1]	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N-EtFHxSE	0[1]	0.0	0.0	0.0	0.0	0.0	0.0	0.0

listed in Figure C.2 in Appendix C. This will then make the test results without correction of the response of the ISTD less reliable. However, it will still indicate whether there was breakthrough or not.

The carry-over test showed that the ATD successfully desorbed the analytes retained in each tube. There were some inconclusive results for 1 pg, but since this was the lowest calibration level, its also the level with the highest uncertainties (Skoog et al., 2014).

4.4.6 Comparison with other validated methods

Poly-and perfluoro carbons

Kärrman et al. (2019) is the only published work that has quantified the three PFCs validated in this study. The samples were taken with GFF and PUF/XAD-2/PUF sandwiches and analyzed with GC-MS/MS with an automated liquid sampler. The specific recovery was between 35 and 105 % for all compounds in the analysis. Compared to the recovery

calculated from the 500 pg spiking, they are at the same level. Some of the recoveries at 200 pg are higher than 105 %, but this applies to the monoterpenes and hexanal, which was not a part of Kärrman's study. It is possible to compare the recoveries, even though they are calculated different ways. The comparison will, therefore, just give a indication about how the performance of the methods that are compared.

The big difference is that the Kärrman's have used, probably, better suited internal standards, 2-perfluorohexyl- [1,1-$^{2}H_{2}$]-[1,2-$^{13}C_{c}$]-ethanol and N-methyl-$^{2}H_{3}$-perfluoro-1-octanesulfonamide, which will account for volume losses or matrix effects better for PFAS, and most target PFCs, then toluene-D8.

Further, a comparison between the IDL, IQL and LOQs for the methods are complicated. This is because the limits from Kärrman's study are reported in pg/m^3, while this study reports IDL and IQL in pg, while the LOQ is reported in pg/m^3. Kärrmann have also split the LOQ into the LOQ for the PUF and the GFF. For BrFBz the LOQ in PUF was 5 pg/m^3 and in GFF 12 pg/m^3. The result of this study was 0.38 ng/m^3. FMBrBz have here a LOQ at 0.06 ng/m^3 and in Kärrman et al. (2019); 200 pg/m^3 in PUF and 900 pg/m^3 in GFF. Last are the N-EtFHxSE with a LOQ in PUF and GFF at 4 pg/m^3, compared to 0.69 ng/m^3 in this study. Overall, the Kärrman et al. (2019) study have lower limits for the same compounds. This could be because of the blank issues in this study or that the methods sensitivity relies on the non-ideal introduction of liquid to the Tenax TA.

This comparison primarily indicates the difference in injection with an automatic liquid sampler (ALS) and a thermal desorption unit for the three validated PFCs. The ALS gives lower limits for both BrFBz and N-EtFHxSE in comparison with this study. As will be more discussed in Section 4.6, the spiking method with a hamilton syringe, is not optimal for volatiles. Further, the sorbent media could not be optimal for fluorocarbons. Still, a drawback of the ALS is the amount of sample preparation and the fact that only a small amount of the sample is injected.

Wu and Chang (2012) have conducted a study on neutral PFAS with TD-GC/MS. Target analytes in the Wu-study were 4:2,6:2,8:2 and 10:2 FTOHs, FOSAs and FOSEs. The Et-FOSE is the 8-chained equivalent to the target analyte, N-EtFHxSE (6-chained) in this study. Structurally they have the same reactive moiety, but differ in chain-lenght. The acceptable range for recoveries in the Wu-study was between 86 to 138% and was tested at both 60 pg and 500 pg spiking levels. The same applies to this study as for the Kärrman et al. (2019), they have used a recovery standard to calculate the recoveries. The FTOHs had recoveries between 94 to 120%, the MeFOSA 95%, EtFOSA 103 %, MeFOSE 183% and the EtFOSE 166%.

The FOSE shows higher recoveries than the accepted value by Wu and Chang (2012). While the structure equivalent N-EtFHxSE had recoveries at 40.4% at 500 pg and 47.7%. The difference between this method and the Wu and Chang (2012) method, is that they used recovery standard, that the analysis was run in PCI-configuration and the tubes was filled with both Tenax TA and Carbograph 1TD as sorbent media.

The IDL and IQL are in Wu and Chang (2012) reported in pg, while the LOQ are reported in pg/m^3, the same as for this study. For Et-FOSE, the IDL was 0.8 pg, the IQL was 3.0 pg and the LOQ was 65 pg/m^3. The IDL in this study was 0.79 pg, the IQL was 2.63 pg and the LOQ was 0.69 ng/m^3. Regarding the IDL and IQL the methods are at the same levels, but for the method LOQ the Wu and Chang method, is more sensitive. Again, this difference can be explained by the fact that there were blank issues in this study.

Volatile organic compounds

VOCs have been investigated with thermal desporption earlier. Ribes et al. (2007) analyzed, among others, the compounds hexanal, pentanal, α-pinene, β-pinene and limonene. LOD for α-pinene was 0.01 ng, for β-pinene 0.3 ng and for hexanal 2.0 ng. The IDL and IQLs in this study are much lower for these compounds. They did not report any recoveries, but instead their precision, with calculating the RSD for five replicates of 500 ng spiked tubes. Hexanal had a RSD of 8%, α-pinene 10% and β-pinene 16%. In this study the RSD is lower for α-pinene and β-pinene at both 500 and 200 pg concentrations.

4.5 Occurrence of VOCs and PFCs in indoor and outdoor samples collected at Svalbard

Both camphene and hexanal were rejected in the validation process as a result of the validation criteria set in Section 4.4 . Results from the six validated analytes are presented in Table 4.8. Since there were only two replicates, they are presented individually. The raw data is presented in Table B.1 in Appendix B. Abbreviations are explained in Table 2.2. The field blanks were left exposed to air during the time of sampling. This is not the recommended technique for blank sampling. Because of this, any contamination in the blank samples can not be explained by storage and transportation, as a field blank should. They are included in Table 4.8 named as blanks.

Table 4.8: Results from samples in both Barentsburg and Longyearbyen [ng/m^3].

Sample	FMBrBz	BrFBz	N-EtFHxSE	α-Pinene	β-Pinene	β-Myrcene
H1	ND	8.92	ND	>ULOQ	6.77	14.58
H2	39.78	>ULOQ	>ULOQ	>ULOQ	>ULOQ	>ULOQ
H-blank	ND	9.4	ND	<16.09	<1.88	<1.81
PP1	<0.06	>ULOQ	ND	<16.09	<1.88	<1.81
PP2	ND	12.07	ND	<16.09	<1.88	<1.81
PP-blank	ND	>ULOQ	ND	9.81	2.70	<1.81
FF1	ND	ND	ND	<16.09	<1.88	ND
FF2	0.06	>ULOQ	ND	<16.09	2.13	<1.81
FF-blank	ND	8.39	ND	<16.09	0.89	<1.81
UNIS1	5.34	>ULOQ	>ULOQ	>ULOQ	6.27	8.62
UNIS2	0.92	>ULOQ	>ULOQ	>ULOQ	>ULOQ	13.84
UNIS-blank	ND	>ULOQ	ND	<16.09	0.89	<1.81
WS1	ND	>ULOQ	ND	>ULOQ	1.01	3.13
WS2	6.33	>ULOQ	8.15	>ULOQ	0.87	3.28
WS-blank	<0.06	>ULOQ	ND	5.70	1.12	<1.81

Analytes not detected are noted ND, and some analytes were detected above the linear range, which is noted as >ULOQ. These results are quite variated. For instance, N-EtFHxSE are not detected in one replicate from the Promor hostel, but above the linear range in the second replicate. For the replicates from the Promor Hostel, this seems to be the trend. The second replicate are more concentrated for all analytes. The blank sample here showed lower than replicates, except for BrFBz.

For the samples taken outside in Barentsburg, the replicates are at the same level. The three monoterpenes, were all under the LOQ. BrFBz was detected at 12.07 ng/m^3 for one replicate, and above the linear range for the second. The LOQ for BrFBz was 0.38 ng/m^3, and the concentration was above the upper limit of quantification, 800 pg, before it was

converted to ng/m^3. The blank sample at this location had a higher concentration than the replicates for BrFBz, α-pinene and β-pinene. The sampling devices were attached to a steel railing. Which do not give a clear contamination source at the sampling site. The firefighting training site tubes were attached to a wooden log during sampling, as illustrated in Figure 2.2. This could lead to contamination of the tubes regarding monoterpenes. Since their natural emissions is from wood. Almost all concentrations for monoterpenes were below the LOQ, except for β-pinene in one of the replicates and in the blank-sample.

At the logistic department at UNIS the expectation of PFCs were highest because of the equipment storage in the room. In these samples, all compounds were detected in both replicates. N-EtFHxSE were detected above the upper limit of quantification in both replicates and not detected in the blank. Smog chamber experiments done by Martin et al. (2006), indicates that four-chained perfluoro sulfonamides are precursor for both carboxylic acids and sulfonates. PFHxS is the sixcarbon sulfonates, and are detected in amounts under the LOQ in outdoor jackets by Gremmel et al. (2016). Based on the precursor theory, N-EtFHxSE is a potential precursor for the sulfonate PFHxS.

BrFBz, N-EtFHxSE and α-pinene had both replicates above the upper limit of quantification. FMBrBz was quantified in both replicates. All three PFCs were identified in the samples from the logistic department at UNIS, but BrFBz and N-EtFHxSE were not quantifiable because they were above the upper limit of quantification. The results indicate that the linear range should have been much higher to be able to quantify these amounts detected. Another possibility would have been to split the sample in the ATD-injector. This could then have led to the samples which were detected under the LOQ, were not detected instead. The expectation was that for the volume collected for the samples, it would result in lower pg/m^3 range. Issues like these, is one drawback from using the ATD and the tubes, because when the sample have been analysed it is destructed.

Samples taken besides the waste station, had detection in the blank sample for all compound expect from N-EtFHxSE, but lower than the sample-replicates.

For Figure 4.5 numbers below the limit of detection were set to half of the LOQ and numbers higher than the upper limit of quantification were kept. There are in Figure 4.5 a clear difference between the indoor and the outdoor samples. The abbreviations are explained in Table 2.2. α-pinene being the most abundant compound, followed by BrFBz.

Representative samples

The goal with the sampling were to test the method. In the introduction, there is mentioned out places that there have been detected PFCs before. When the sample set up was design, it was important that both remote locations and locations with potentially higher concentrations was selected. The firefighting training site is a known source for some PFASs, due to the use of aqueous film-forming foams (Hale et al., 2017). In the logistic department at UNIS all outdoor equipment for employees and students are stored. For instance, different outdoor clothing, that are water and grease repellent. At last, the

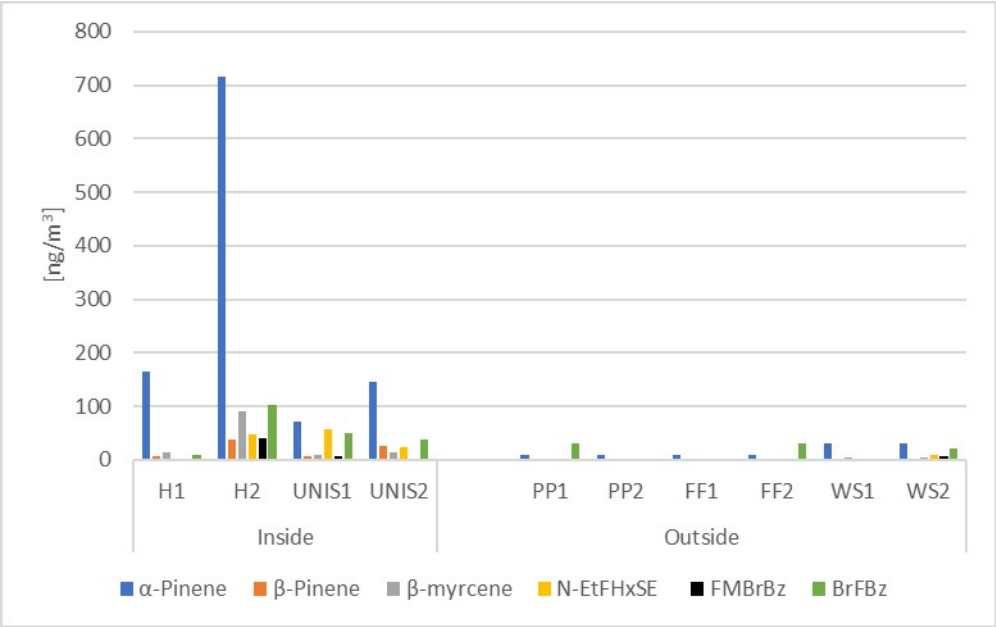


Figure 4.5: Indoor and outdoor samples compared.

waste station was also chosen to be a more contaminated source, due to earlier studies investigating landfills (Ahrens et al., 2011).

The sampling space at the Promor Hostel in Barentsburg were surrounded by wood paneling, so this would possible be a more contaminated indoor sample with regards to the VOCs than the logistic department. The latter had also much wood paneling, but the room was much bigger, big gates, and probably a better ventilation system in place. From Table 4.8 and Figure 4.5 it seems to be that the trend is that there are more VOCs in the Promor Hostel samples, and more PFCs in the logistic department.

Emissions from VOCs in Arctic air are low, due to the lower amount of vegetation. Sindelarova et al. (2014) illustrates by modeling the emissions that the emissions in the Arctic are calculated to be around 1% of the total emission of monoterpenes. α-pinene, β-pinene and β-myrcene was overall detected but more rare quantified in outdoor samples than in the indoor samples.

4.6 Analytical method

The target analytes are expected to be volatile, and therefore a separation technique like gas chromatography is suitable. There are many parts of an analytical system, like the TD-GC-MS/MS, that needs to be optimized for the best analytical performance.

In this section, the column, detector, injector and sorbent media will be discussed.

It is essential to have a column that are able to separate the compounds from each other with desired resolution. The column should suit the polarity of the compound, based on the basic chemistry of like dissolves like. The HP-VOC column is a mid-polar column, and the majority of the target analytes are non-polar compounds. For non-polar compounds the optimal would be a non-polar column (Miller, 2009).

EPA (1999a) are one set of guidelines for the determination of volatile organic compounds in air collected by canisters and analyzed with GC/MS and EPA (1999b) are another set of guidelines for the determination of volatile organic compounds in ambient air with sampling onto sorbent tubes. In the EPA (1999a), it is recommended that the chromatography column for VOCs is either 100% methyl silicone or 95% methyl silicone and 5% phenyl with an inner diameter from 0.25 to 0.53 mm. These types of columns separate non-polar compounds. In Volden et al. (2005), a CP-SIL8 CB column (30m, 0.25mm i.d. and 0.25 µm film) was used, which consist of 5% phenyl and 95% methyl silicone, on separating target analytes like α-pinene, β-pinene and limonene. Furthermore, Ribes et al. (2007) used a DB-624 (60m, 0.25 mm i.d. and 1.4 µm film), containing 6% phenyl and 94% siloxane on target analytes pentanal, hexanal, α-pinene, β-pinene and limonene. Both of these columns are non-polar columns.

In analyses of neutral PFAS the columns most often used are polar to highly polar. For instance, Dreyer et al. (2008); Wang et al. (2015), used supelcowax10 (60m, 0.25 mm i.d. and 0.25-1 µm film) on target analytes 4:2-12:2 FTOHs, FOSEs, FOSAs and MeFBSA. Wu and Chang (2012) used a HP-INNOWAX column (60m, 0.25 mm i.d. and 0.25 µm film) in the analysis of 4:2-8:2 FTOHs, FOSAs and FOSEs with thermal desorption GC/MS. Compounds like the FTOHs and FOSEs have an OH-group, which makes them more polar than the FOSAs, which only have the methyl or ethylated sulfonamide group. the majority of compounds in the target list of this study are non-polar. The mid-polar column used in this study are suited, based on this, a joint analysis of PFCs and VOCs.

A mass spectrometer is a well-suited detector for the GC, due to its capacity to detect a variation of molecules (Miller, 2009). The most recognized method for neutral PFAS analysis is with GC-PCI-MS, used in, e.g., Barber et al. (2007); Del Vento et al. (2012); Stock et al. (2004). PCI is a technique based on proton affinity. The molecule will be protonated as long as it has a higher proton affinity than the reagent gas. This makes PCI a universal technique capable of ionizing many neutral molecules, explaining the popularity of the GC-PCI-MS methods. ECNICI, on the other hand, only ionize compounds with electronegative elements or acidic groups. This provides some selectivity for detection in

mixtures (de Hoffmann and Stroobant, 2007). Based on this ECNICI could be favorable with neutral PFCs because of the high number of fluor-atoms. Dreyer et al. (2008); Martin et al. (2002) used both PCI and ECNICI in the quantification of neutral PFAS.

For monoterpenes, the most used ionization technique is EI. Hackenberg et al. (2017) used TD-GC/MS with EI for monoterpenes like α-pinene, β-pinene, β-myrcene, carene and limonene in Arctic air. The same compounds plus hexanal was identified by GC-EI-MS in odor from landfills by Davoli et al. (2003).

The big difference between EI and CI is the amount of excess energy they add to a molecule. This excess energy often results in fragmentation. According to de Hoffmann and Stroobant (2007), most organic molecules are ionized by a electron energy at 10 eV. The electron energy in EI is most commonly set to 70 eV, because this produces the maximum amount of ions. The energy difference will go to extensive fragmentation of the ions. In ECNICI the collision energy and the pressure together induces the ionization of the molecules in the soucre.

Based on this, and the knowledge that ECNICI are a soft ionization technique and EI are a harder technique, theoretically in ECNICI all target analytes could yield the molecular ion. This is not true for compounds like, MeFBSA, TDFMS and N-EtFHxSE. For N-EtFHxSE, EI yielded higher weighted molecules in the SRM-transition.

The choice of sorbent media is also something that should suite the target compounds. Tenax TA is a well-known adsorbent for monoterpene-analysis. However, it has been reported some issues regarding losses and decomposing. According to Hoffmann (1995), up to 50 % of limonene and myrcene was lost if ozone is present in the sample. This was done by ozone scrubbers prior to the preconcentration step, if not, the concentrations were an underestimation. This is supported by Klenø et al. (2002), which identified degradation products for mixtures of ozone and limonene. Ozone exist in the troposphere at low trace levels. This could have underestimated the concentrations of the monoterpenes in the samples.

Sunesson et al. (1999) conducted experiments that showed that Tenax TA gave a lower uptake rate than chromosorb 106 for the terpenes α-pinene, β-pinene and carene in diffuse sampling. All three terpenes had a good storage stability on both adsorbents. In addition, Chromosorb 106 has higher blank levels, which are impractical in trace analysis (Dettmer and Engewald, 2002).

A combination of adsorbents could be the solution for losses and underestimation of concentration, based on multiple studies (e.g. (Mochizuki et al., 2015; Rodríguez-Navas et al., 2012; Wu and Chang, 2012).

The most used sampling technique for PFAS is the PUF/XAD/PUF cartridges for high volume air sampling. Compared to Tenax TA, the surface area of the PUF/XAD combination is much higher, and are therefore capable of sampling higher amounts of analytes. Wu and Chang (2012) concluded that their combination of Tenax TA and Carbograph 1TD tubes provided sufficient sorption capacity for their target PFAS.

The determination of BTV and SSV for the analytes on Tenax TA were not done. This contributes to uncertainties about the maximum load for the sorbent media. The sampling volume were kept low because of this, average of 0.04 m^3. Compared to Wu and Chang (2012), which had sampling volumes between 0.36-0.72 m_3 for Tenax TA and Carbograph 1TD tubes.

There are no direct structural matches with the tested target list of EPA (1999b), but some similar structures have SSV on Tenax TA of 6L for benzene, 1800L 1,3,5-trimethyl benzene and butanal have a SSV of 50L. This shows the importance of calculating the BTV and SSV, and that even with a volume of 40L, the sorbent media can be saturated. However, based on the carry-over test, Table 4.7, it is reasonable to believe that all the compounds adsorbed by the Tenax TA in each tube are desorbed again.

The spiking method could cause the variation in recoveries; Harper (2000) used reference standards in pre-spiked tubes or gas standards. EPA (1999b) recommends that the optimum approach, when using liquids is to use a GC packed column injector, which completely vaporizes the liquid onto the sorbent bed. When spiking with liquid, there is always uncertainties that the liquid does not fully vaporize, and therefore, in the thermal desorption can get purged out before the desorption.

Comparison of thermal desorption and liquid extraction

Król et al. (2010) summarized the advantages and disadvantages for both thermal desorption and solvent extraction

Conventional PFAS sampling onto sorbent beds followed by solvent extraction is a cheap method and not much extra equipment is needed to perform the extraction. On the other side, a liquid extraction will dilute the sample. For some compounds the extraction is most effective with the use of solvents which are toxic. Solvent can also cause interference and the sorbent bed used for sampling need regeneration before reuse.

Sampling and injection by thermal desorption is more expensive because of the instrument which are needed. Thermal unstable compounds may decompose because thermal desorption requires high temperatures, and the technique can lose non-volatile compounds. On the other side it requires no sample preparation step and the sorbent are reusable.

An optimized sampling and instrumental analysis with thermal desorption is a fast technique which requires minimal sampling preparation and can sample low levels of VOCs. Sampling with pocket pumps are an easy sampling instrumentation, which makes it possible to actively sample, for instance, attached to humans or stagnant sample set-ups.

4.6.1 internal standards

The quantification method here was done by adding known amounts of internal standard to each sample and validation tubes. Compounds used as internal standard shall not be

present in the sample, bbut elute near peaks of interest and still be resolved from them, it should be chemically similar to the analytes and not react with any component in the sample. At last, it must be available in pure form (Miller, 2009). Isotope-labeled versions of the target analytes are, because of this, preferred compounds as internal standards.

In this study, six internal standards were tested in both ECNICI and EI-mode, listed in Table A.1 in Appendix A. Some of them were selected based on similar structures as the analytes and have been used in other studies. N-trideuteriomethyl-perfluoro-1-octanesulfonamide (d-N-MeFOSA-M) has been used as an internal standard in, for instance, Barber et al. (2007); Jahnke et al. (2007) in both PCI and ECNICI mode and 2-perfluorohexyl-[1,1$^{2}H_{2}$]-[1,2-$^{13}C_{2}$]-ethanol (MFHET) and 2-perfluorooctyl-[1,1$^{2}H_{2}$]-[1,2-$^{13}C_{2}$]-ethanol (MFOET) were also used as ISTDs in these studies.

d-N-MeFOSA-M, 2-perfluorohexyl-[[1,2-$^{13}C_{2}$]-ethanol (M2FHET), 2-perfluorooctyl-[2-perfluorooctyl-[1,2-13C2]-ethanol]-ethanol (M2FOET) and 2-(N-methyl-d3-perfluoro-1-octane-sulfonamido)ethan-d4-ol were selected based on trying to suite the perfluoro compounds, and toluene-D8 for the VOCs and fluorobenzene rings.

Toluene-D8 were the only internal standard possible to optimize a method for. This compound will not be an effective internal standard for all compounds because of structural similarity. In addition, toluene-D8 elutes at 17.0 minutes and N-EtFHxSE elutes at 33.9 minutes. Because of both structural differences and retention times far apart, toluene-D8 is not a suitable internal standard for all the validated compounds. A better suited internal standard will account for volume losses and matrix effects better.

Chapter 5

Conclusion

The development of a solvent-free analytical procedure was the main motivation in this project. The use of sorbent media and thermal desorption have been a long recognized method for biogenic volatile compounds, but are a new field of sampling and sample introduction for GC-MS analysis for perfluorocarbons. Compared to sampling that need sample preparation by solvent extraction, a TD-GC-MS analysis is fast, selective and sensitive method, which also reduces the chance of random and systematical errors which can occure during sample preparation.

A method was successfully optimized with TD-GC-ECNICI-MS for six PFCs. And further, optimized and validated with TD-GC-EI-MS for three PFCs and three biogenic VOCs. During the validation process two biogenic VOCs were excluded. Camphene because of S/N ratios below three in the calibration curve and hexanal was excluded due to apparent recoveries outside the validation criteria.

Samples were collected with two replicates outdoor and indoor in Barentsburg and Longyearbyen, Svalbard, in the period from April 2019 to May 2019. Sites were selected based on the expectation of both low and higher levels of contamination. The total level of PFCs varied from not detected to above the upper limit of quantification. BrFBz was the most abundant PFC detected, with levels above the quantification limits at all sampling sites. The concentration of VOCs ranged from below the LOQ to above the upper limit of quantification. The results show a higher contamination level of both PFCs and VOCs in indoor air. Overall, α-pinene was the most abundant compound in both indoor and outdoor samples. A draw back from the sampling were that field blanks were left open during the time of sampling. Because of this it it not possible to dismiss that no contamination could have occurred during transportation and storage.

Monoterpenes are compounds which are around us at all times, and are, therefore, difficult compounds to analyze. Contamination from the lab environment can not be ruled out since there were instrumental blank issues.

Based on the quality control set by the validation the method performed sufficient for the optimized compounds. Drawbacks of the instrumental analysis is the absence

of a technique to introduce volatile compounds to the sorbent bed for optimization and validation.

Drawbacks from the analysis of volatile compounds in Arctic air were that sampling method was not validated for the compounds by determine the SSV for the compounds on the sorbent media.

5.1 Future perspective

The aim of future research should be about further optimize the method for PFCs in either ECICI or PCI. Based on the result in this study, ECINI were optimized for more fluorocarbons than EI, which indicates that softer ionization techniques are better suited for fluorocarbons. However, there is the need to find suitable internals standards and recovery standards for the PFC-compounds first.

It could be advantageous to split the VOCs and PFCs into two separate methods. Which are separately optimized include more of the target compounds. For the PFCs-method it should also be expanded to include more of the non-PFAS structures registered in the REACH-list.

Further a suitable method for spiking the stainless-steel tubes should be developed and validated. For instance, with a packed column GC-injector, recommended by EPA (1999b). At last, validation of the sampling method by estimating the SSV for each compound on the sorbent media should be a focus-point for further development of the analytical method.

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Appendix A

Standards, chemicals and materials

Chemicals

n-hexane, Supratrace grade, VWR International, Oslo, Norway
n-hexane, Normapur grade, VWR International, Oslo, Norway
Helium, 5.0, AGA AS, Porsgrunn, Norway
Methane, AGA AS, Porsgrunn, Norway
Standards listed in Table A.1.

Materials

Glass pasteur pippettes, 150 mm, VWR International, Oslo, Norway
Beakers and Erlenmeyer flasks of various volumes
8 mL vials with caps in Amber, (8-SVA-CP) Thermo Fisher Scientific, Teknolab, Ski, Norway
Hamilton syringe, 5 µL, Perkin-Elmer, Norwalk, USA
Hamilton syringe, 25 µL, SGE Analytical Science, Melbourne, Australia
Stainless Steel ATD Prepacked Sample Tube with Tenax TA 60/80, Perkin Elmer, Norwalk, USA
Automatic pipetts, Finnpipette 5-1000 µL, Thermo Fisher Scientific, Teknolab, Ski, Norway
Microweight, CP2P Sartorius, VWR International, Oslo, Norway

Instrumentation

7890B Gas chromatograph, Agilent Technologies, Santa Clara, CA, USA
7000C Triple Quadrupole mass spectrometer, Agilent Technologies, Santa Clara, CA, USA

ATD-400, Perkin Elmer, Norwalk, USA
HP-VOC (60m X 0,2 mm, 1,1 µm), J & W Scientific, Agilent Technologies, Santa Clara, USA
Pocket Pump Touch Sample Pumps, SKC, Blandford Forum, United Kingdom

Computer software

Agilent Masshunter Qualitaitve Analysis B.06.00
Agilent MassHunter Quantitative Analysis B.07.00
Microsoft Excel, Office 365
ChemDraw Professional (version 15.0.0.106), PerkinElmer Informatics, Inc. (Boston, Massachusetts, USA)

Table A.1: List of standards, acronym, concentration, purity producer and LOT-number

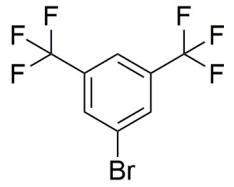
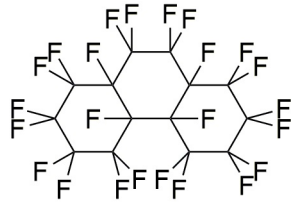
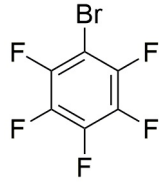
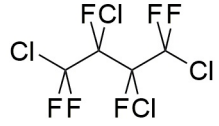
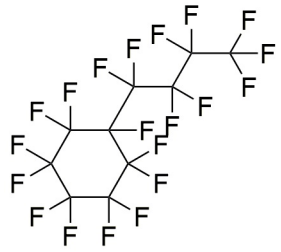
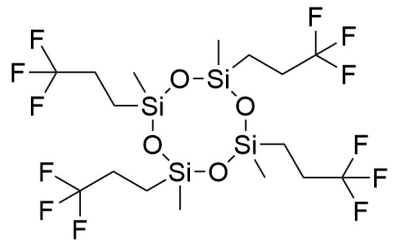
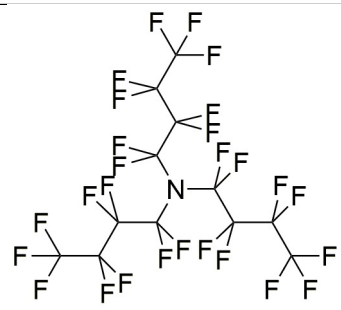
Acronym	Compound	Concentration[a]	Purity[%]	Producer	LOT#
PFC					
FmBrBz	1,3-bis(trifluoromethyl)-5-bromo-benzene		99	Sigma Aldrich	MKBV7369V
PFPHP	Perfluoroperhydrophenanthrene		80	Chemsupport AS	AS462333
BrFBz	Bromopentafluorobenzene		99	Sigma Aldrich	STBF8772V
TCHFB	1,2,3,4-tetrachlorohexafluorobutane			Chemsupport AS	T820751701[2]
UDFBC	Undecafluoro(nonafluorobutyl)cyclohexane			Chemsupport AS	FU853641701[2]
TTFMCS	1,3,5,7-tetrakis(3,3,3)-trifluoropropyl) -1,3,5,7- tetramethylcyclosiloxanes			Sigma Aldrich	CD5011366
PFTBA	Perfluorotributylamine			Chemsupport AS	LC23033V
PFTPA	Perfluorotripropylamine			Chemsupport AS	FCB012222
DTFMP	Perfluoro-(2,3-dimethyl)-3-ethyl pentane			Chemsupport AS	00008285
TDFMS	N-methyl perfluorohexane-sulfonamide			Chemsupport AS	AS471408
MEFBSA	N-methyl perfluorobutane sulfonamide			Chemsupport AS	AS471151
N-EtFHxSE	N-ethyl-N-(2-hydroxyethyl) -perfluorohexane sulfonamide			Chemsupport AS	AS472540
8:2 FTOH	1H,1H,2H,2H-perfluoro-1-decanol		97	Wellington Laboratories	MKBL4812V
VOC					
β-myrcene	7-methyl-3-methylideneocta-1,6-diene		>90	Chiron AS	TR-M875300-500MG[1]
β-pinene	6,6-dimethyl-2-methylidenebicyclo[3.1.1]heptane		94	Chiron AS	11306.10-100MG[1]
α-pinene	2,6,6-trimethylbicyclo[3.1.1]hept-2-ene		99	Chiron AS	10180.10-100MG[1]
Camphene	2,2-dimethyl-3-methylidenebicyclo[2.2.1]heptane	1000 µg/mL		Chem Service Inc.	8077900
3-carene	3,7,7-trimethylbicyclo[4.1.0]hept-3-ene	1000 µg/mL		Chiron AS	1184910-k-10
	Hexanal			Chiron AS	10010.6-1ML[1]
Limonene	1-methyl-4-prop-1-en-2-ylcyclohexene	100 µg/mL	98.6	Chiron AS	
	Pentanal	1000 µg/mL		Chem Service Inc.	2257.7-1ML[1]
Internal standards					
Toluene-D8	1,2,3,4,5-pentadeuterio-6-(trideuteriomethyl)benzene	100 µg/mL		Chiron AS	2253.7-100ML[1]
M2FHET	2-perfluorohexyl-[1,2-13C2]-ethanol	50 µg/mL		Wellington Laboratories	M2FHET[1]
M2FOET	2-perfluorooctyl-[1,2-13C2]-ethanol	50 µg/mL		Wellington Laboratories	M2FOET[1]
d9-N-MeFOSA-M	2-(N-methyl-d3-perfluoro-1- octane-sulfonamido)ethan-d4-ol	50 µg/mL		Wellington Laboratories	d9-N-EtFOSE-M[1]
d-N-MeFOSA-M	N-methyl-d3-perfluoro-1-octanesulfonamide	50 µg/mL		Wellington Laboratories	d-N-MeFOSA-M[1]
Hexamethyl-d18-disiloxane	tris(trideuteriomethyl)-[tris(trideuteriomethyl)silyloxy]silane		99.7	CDN Isotopes Inc.	G-243

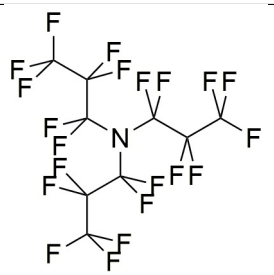
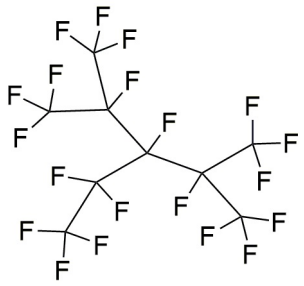
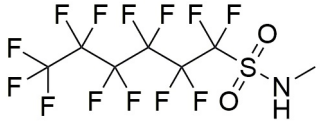
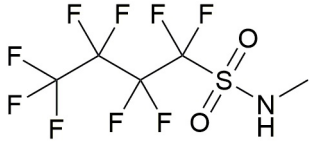
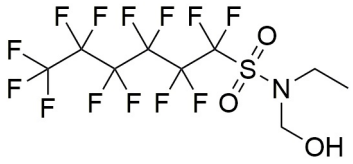
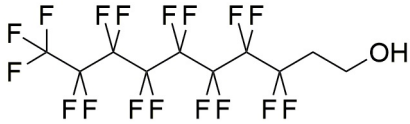
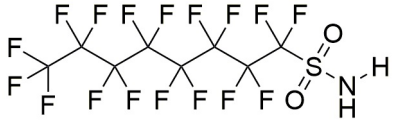
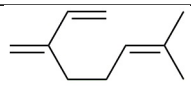
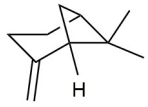
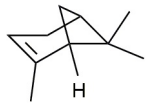
[a]- Compounds without a value were either crystalized or stated in amount

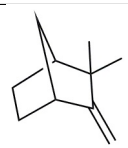
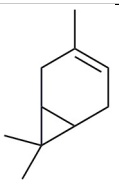
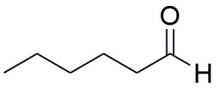
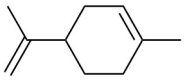
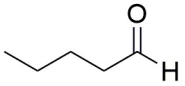
[1]- Catalouge number

[2]- Batch number

Table A.2: Sructures and acronyms for all target analytes. Structures are prepared with ChemDraw Professional.

Analyte	Acronym	Structure
1,3-bis(trifluoromethyl)-5-bromo-benzene	FMBrBz	
Perfluoroperhydrophenanthrene	PFPHP	
Bromopentafluorobenzene	BrFBz	
1,2,3,4-tetrachlorohexafluorobutane	TCHFB	
Undecafluoro(nonafluorobutyl)cyclohexane	UDFBC	
1,3,5,7-tetrakis(3,3,3)-trifluoropropyl) -1,3,5,7- tetramethylcyclosiloxanes	TTFMCS	
Perfluorotributylamine	PFTBA	

Perfluorotripropylamine	PFTPA	
Perfluoro-(2,3-dimethyl)-3-ethyl pentane	DTFMP	
N-methyl perfluorohexane-sulfonamide	TDFMS	
N-methyl perfluorobutane sulfonamide	MeFBSA	
N-ethyl-N-(2-hydroxyethyl) -perfluorohexane sulfonamide	EDTHS	
1H,1H,2H,2H-perfluoro-1-decanol	8:2 FTOH	
Perfluoroocante sulfonamide	PFOSA	
7-methyl-3-methylideneocta-1,6-diene	β-myrcene	
6,6-dimethyl-2-methylidenebicyclo[3.1.1]heptane	β-pinene	
2,6,6-trimethylbicyclo[3.1.1]hept-2-ene	α-pinene	

2,2-dimethyl-3-methylidenebicyclo[2.2.1]heptane	Camphene	
3,7,7-trimethylbicyclo[4.1.0]hept-3-ene	3-Carene	
Hexanal		
1-methyl-4-prop-1-en-2-ylcyclohexene	Limonene	
Pentanal		

Appendix B

Raw data

Table B.1: Raw data from samples in both Barentsburg and Longyearbyen [ng/m^3]

Sample name	FMBrBz			BrFBz			α-pinene			β-pinene			β-myrcene			N-EtFHxSE			
	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	
Range			[37.5,56.3]			[78.0,117]			[6.2,9.3]			[31.2,46.9]			[0.1,0.2]			[17.4,26.1]	[77.2,115.8]
H1	25.9	0.0	56.1	50270.6	200.1	121.7	5.6	3704.5	7.1	1.86	152.4	38.7	6.17	327.00	0.1	20270	0.0	41	
H2	∞	895.1	55.3	2801.8	2290.7	117.2	3.5	16079.4	8.4	1.9	831.6	39.9	8.58	2041.9	0.1	149.1	1049.9	44.1	
H-blank	20.3	0.0	57.1	25.4	188.3	117.1	7.9	156.6	5.4	9.3	25.01	35.0	7.0	5.7	0.1	∞	0.0	42.8	
PP1	26.3	0.46	59.6	25.2	1154.7	127.9	11.9	169.7	5.6	4.1	65.5	36.2	1.6	8.9	0.1	11.4	0.0	54.5	
PP2	28.8	0.0	58.9	21.9	466.1	128.7	11.2	89.8	5.6	11.4	34.9	38.6	4.8	2.4	0.0	11.1	0.0	42.7	
PP-blank	570.2	0.0	56.0	25.4	858.8	127.5	8.9	392.2	5.4	3.5	107.8	36.8	1.3	19.2	0.1	7.2	0.0	51.9	
FF1	24.3	0.0	58.7	25.2	0.0	126.9	80.5	12.9	5.3	10.4	8.4	36.6	3.6	0.0	0.1	15.4	0.0	41.8	
FF2	14.6	2.3	57.4	25.5	1257.1	128.3	163.6	216.5	5.4	14.5	86.3	36.4	5.9	11.5	0.2	15.2	0.0	48.9	
FF-blank	28.2	0.0	57.1	25.2	335.5	129.1	10.2	88.4	5.7	5.6	35.2	35.2	2.8	2.93	0.1	∞	0.0	45.0	
UNIS1	24.1	231.8	53.5	34.7	2127.5	122	10.1	3126.5	5.3	1.9	272.2	107.5	1.8	374.3	0.1	50.9	2494.7	42.7	
UNIS2	18305.9	39.9	58.0	29.4	1670.8	124.6	13.0	6261.6	5.6	2.8	1117.6	38.1	2.5	598.6	0.1	83.9	1008.1	38.8	
UNIS-blank	24.09	0.0	59.4	21.6	901.1	129.7	102.1	157.2	5.7	3.0	35.9	40.6	1.7	5.81	0.1	48.8	0.0	43.1	
WS1	22.9	0.0	61.9	19.9	896.5	124.9	16.7	1974.9	6.1	2.6	66.6	38.7	19.1	205.9	0.1	13.7	0.0	44.4	
WS2	67451.4	410.6	55.4	8918	1419.4	123.3	835.5	2038.9	6.0	2.5	56.7	37.5	23.78	207.4	0.1	∞	528.9	44.0	
WS-blank	25.6	0.82	55.8	22909.5	1053.8	130.0	106.1	370.4	5.9	3.1	72.9	36.6	2.9	24.4	0.1	22.6	0.0	39.1	

Table B.2: Breakthrough results including level in tubes before analysis of breakthrough.

Sample name	FMBrBz			BrFBz			α-pinene			β-pinene			β-myrcene			N-EtFHxSE			Hexanal		
	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual
Range			[37.5,56.3]			[78.0,117]			[6.2,9.3]			[31.2,46.9]			[0.1,0.2]			[17.4,26.1]			[77.2,115.8]
Blank1	∞	19.1	47.8	∞	728.4	92.9	0.6	0.0	2.3	1.1	0.0	31.1	0.5	0.0	1.8	5.7	11.4	42.6	2.2	0.0	81.1
ch-test-blank1	∞	62.9	51.9	937.2	0.0	82.9	128.8	1347.7	5.1	314.3	1751.4	30.2	214.3	765.9	0.1	14.5	0.0	51.8	83.7	16.3	110.9
Blank2	11.6	0.0	39.0	480.3	268.2	85.1	0.1	0.0	8.9	12.5	157.9	34.2	25.8	90.4	0.7	425.7	7.9	32.7	9.7	0.0	87.9
ch-test-Repl-500pg	∞	224.7	55.7	13211.9	531.4	124.9	126.9	1636.4	5.8	12.6	2704.7	33.9	239.2	1374.0	0.1	8.2	0.0	32.6	240.9	831.4	102.6
Blank3	7.8	0.0	40.6	13.0	0.0	96.4	0.9	0.0	7.2	10.1	0.0	36.4	10.2	0.0	0.4	14.1	0.0	34.8	16.0	0.0	99.4
ch-test-Repl-brth-500pg	424.6	43.0	49.6	11.9	0.0	101.0	78.2	1152.8	5.7	60.9	333.4	32.4	397.4	659.6	0.2	12.2	0.0	47.0	164.5	70.9	108.5
Blank4	21.8	9.9	49.9	7485.4	0.0	108.2	1.7	0.0	4.9	4.5	0.0	34.5	4.5	0.0	0.7	10.6	0.0	29.9	60.4	0.0	99.6
ch-test-blank2	5169.8	52.0	51.0	18.8	967.1	106.9	112.9	1291.9	3.4	335.0	2174.9	31.1	86.5	349.5	0.1	4.5	0.0	53.6	90.8	15.1	106.7
Blank5	345.0	0.0	46.1	10.5	0.0	103.9	2.2	0.0	8.5	10.5	0.0	38.1	11.4	0.0	0.2	58.5	46.5	26.5	122.8	34.9	101.4
ch-test-Repl2-500pg	25059.8	283.1	51.5	24.9	977.2	105.6	160.7	2110.3	3.6	330.7	2461.8	33.5	239.2	858.2	0.1	10.0	0.0	42.6	15.0	506.0	108.2
Blank6	16.7	0.0	47.8	21.4	0.0	101.9	2.6	0.0	2.8	12.0	0.0	37.9	2.8	0.0	ND	648.1	34.1	31.1	103.8	6.8	105.5
ch-test-Repl2-brth-500pg	1652.2	62.7	44.3	19.8	0.0	97.6	68.9	667.2	3.5	83.9	246.2	31.8	128.7	220.1	0.1	108.6	0.0	29.6	126.1	36.8	104.3
Blank7	1848.2	12.5	46.8	16.6	0.0	103.0	5.4	0.0	6.7	22.4	9.5	38.7	2.6	87.5	0.1	325.4	0.0	29.3	13.2	0.0	87.7
ch-test-blank3	11.9	0.0	52.1	7856.1	44.5	113.4	15.9	143.8	3.3	346.2	811.3	30.2	24.8	6.4	ND	12.5	0.0	33.4	105.9	4.1	103.6
Blank8	13677.0	199.1	51.2	∞	3810.3	111.3	24.4	33.0	3.9	24.7	22.6	37.4	81.9	76.9	0.1	41.0	0.0	37.3	154.9	28.9	87.9
ch-test-Repl3-500pg	343.9	185,1	50.4	51.0	640.5	98.7	41.9	550.3	3.3	280.9	1708.1	32.2	108.1	399.5	0.1	∞	114.9	42.8	373.1	277.3	102.7
Blank9	21.5	219.7	52.0	∞	168.7	111.6	14.3	16.3	4.3	30.2	35.4	37.5	75.6	80.8	0.1	32.8	281.4	36.9	163.5	63.6	102.4
ch-test-Repl3-brth-500pg	22.7	40.3	43.9	22.3	0.0	102.3	23.6	102.3	4.3	56.2	150.4	31.0	42.9	82.9	0.1	24.3	173.6	44.4	78.7	11.4	102.6

Table B.3: Signal-to-noise ratios for blank samples, included slope of the S/N calibration curve

Sample name	FMBrBz	BrFBz	α-pinene	β-pinene	β-myrcene	N-EtFHxSE	Hexanal
Slope	59.70	5.45	0.13	0.84	1.56	3.80	2.45
Blank1	23.5	14.6	4.5	1.3	7.0	10.7	2.3
Blank2	21.1	15.9	8.1	4.9	1.9	6.2	9.7
Blank3	14.2	12.5	2.6	3.4	3.5	12.6	16.0
Blank4	16.2	18.9	8.7	4.7	4.5	3.8	13.2
Blank5	14.2	14.4	10.3	0.3	5.3	14.0	2.5
Blank6	7.6	11.3	3.7	0.9	12.3	1.2	26.4
Blank7	22.1	9.3	11.5	0.8	3.1	3.4	20.6
Blank8	21.6	11.6	10.8	8.1	10.3	0.6	19.9
Blank9	17.7	12.4	12.0	5.9	5.8	5.9	9.7
Blank10	18.7	16.1	5.5	6.9	14.6	5.5	9.2

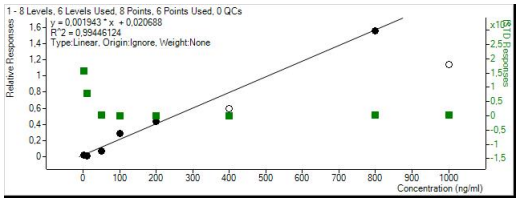
Table B.4: Results from recovery test at 500 pg, 200 pg and 10 pg

Sample name	FMBrBz			BrFBz			α-pinene			β-pinene			β-myrcene			N-EtFHxSE			Hexanal		
	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual
Range			[37.5,56.3]			[78.0,117]			[6.2,9.3]			[31.2,46.9]			[0.1,0.2]			[17.4,26.1]			[77.2,115.8]
Mix-10pg	1061.3	14.6	46.0	∞	0.0	102.6	12.9	126.8	3.5	15.6	46.7	35.66	40.9	73.0	0.1	∞	126.9	40.2	691.1	0.0	91.9
Mix2-10pg	6054.6	186.9	48.2	1854.4	0.0	94.3	2.9	6.6	3.4	11.1	19.8	38.9	17.3	27.8	0.3	∞	50.8	31.8	391.0	9.6	87.3
Mix3-10pg	2673.3	21.1	46.5	15.1	0.0	95.8	2.6	11.8	1.8	14.4	26.9	37.0	23.4	36.7	0.1	9.4	3.3	39.1	418.8	320.2	100.8
Mix-200pg	1560.7	2.3	47.9	459.4	414.7	98.8	33.1	6.7	4.3	150.0	20.9	39.7	230.8	26.8	0.1	234.1	0.0	35.1	84.4	21.6	100.8
Mix2-200pg	15752.6	201.1	44.3	8936.2	149.1	98.8	68.3	249.9	4.1	264.3	291.5	39.6	368.8	289.8	0.1	487.9	96.8	34.4	1196.7	495.7	100.3
Mix3-200pg	1418.6	147.8	48.1	1408.7	178.5	91.9	34.0	254.1	3.3	126.7	311.4	40.4	184.9	309.4	0.1	771.9	93.8	38.1	553.9	468.1	100.1
Mix-500pg	3272.0	225.4	47.7	380.5	309.3	101.0	46.3	405.6	4.0	409.3	483.8	39.3	494.2	464.0	0.1	1090.1	169.4	33.2	57.7	0.0	101.9
Mix2-500pg	17837.1	276.3	45.1	22392.5	408.8	96.1	76.2	461.7	3.8	311.2	552.9	40.4	413.9	531	0.1	149.3	234.3	38.2	16.3	293.7	103.9
Mix3-500pg	42425.9	71.1	47.5	1307.0	0.0	97.2	88.6	0.0	4.0	220.6	11.8	40.3	317.6	18.5	0.1	∞	0.0	38.3	88.1	0.0	100.4

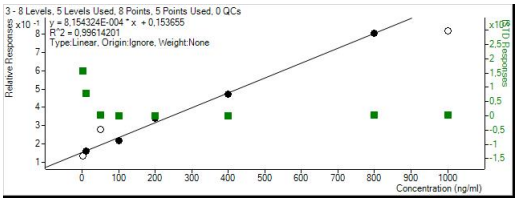
Appendix C

Calibration curves

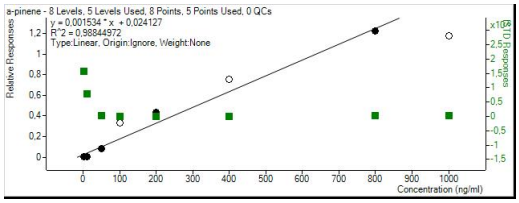
C.1 Calibrationcurves with ISTD



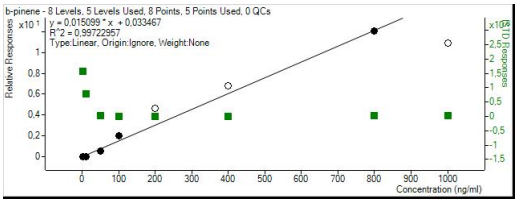
(a) FMBrBz



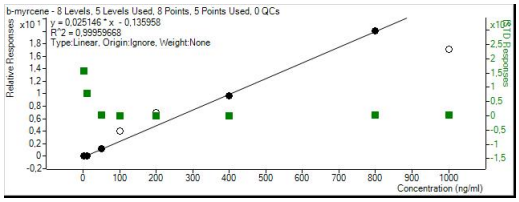
(b) BrFBz



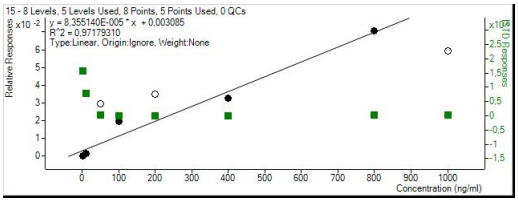
(c) α-Pinene



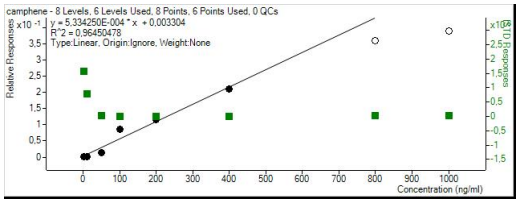
(d) β-Pinene



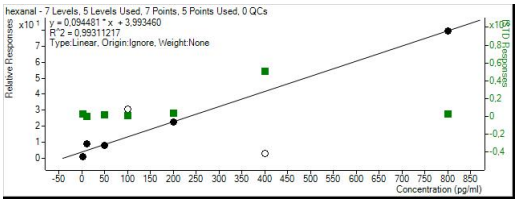
(e) β-Myrcene



(f) N-EtFHxSE

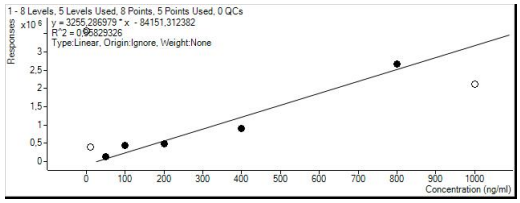


(g) Camphene

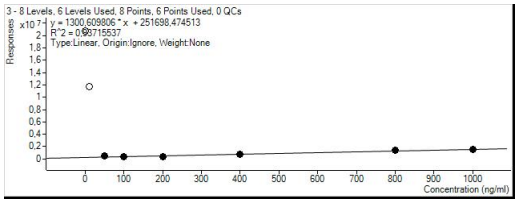


(h) Hexanal

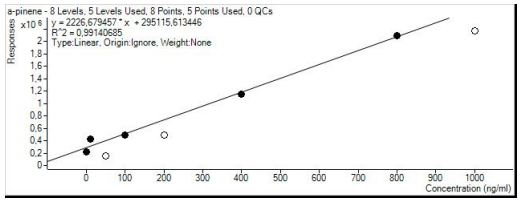
Figure C.1: Calibration curves for analytes with ISTD



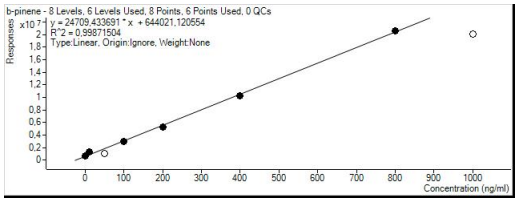
(a) FMBrBz



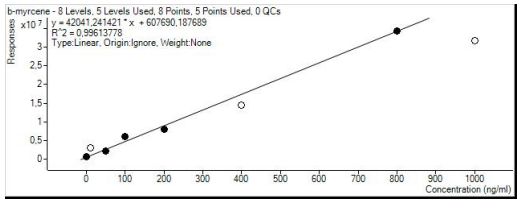
(b) BrFBz



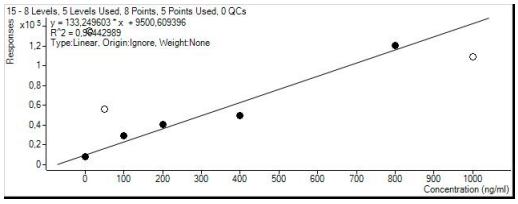
(c) α-Pinene



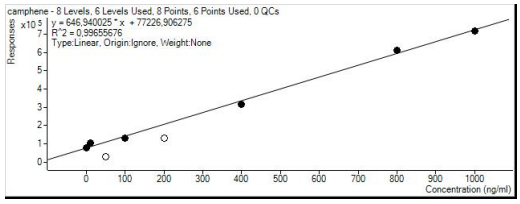
(d) β-Pinene



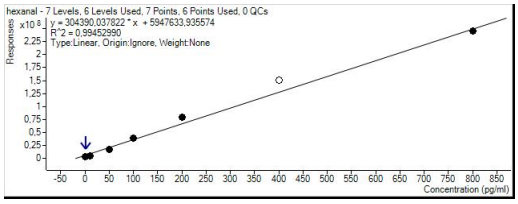
(e) β-Myrcene



(f) N-EtFHxSE



(g) Camphene



(h) Hexanal

Figure C.2: Calibration curves for analytes without ISTD

Table C.1: Calibration results, Concentrations corrected to the area of ISTD.

Sample name	FMBrBz			BrFBz			α-pinene			β-pinene			β-myrcene			N-EtFHxSE			Camphene			Hexanal		
	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual	S/N	Conc.	quant/qual
Mix-1pg	35609.2	1.1	48.1	128664.4	0.0	97.6	10.8	0.0	5.5	16,64	0,00	35,4	14,908	5,77	0,17	357,13	0,00	26,63	2,62	0,00	12,65	55.9	0.0	102.3
Mix-10pg	1109.7	0.0	43.9	160385.5	18.5	97.3	23.3	0.0	5.3	25.7	0.0	33.9	66.5	6.9	0.2	859.4	0.0	31.5	3.4	0.0	14.4	94.6	53.8	101.5
Mix-50pg	1263.2	24.1	43.6	10761.8	162.1	98.9	8.3	38.1	4.4	26.8	35.9	38.9	62.6	53.9	0.3	12.7	318.6	34.0	1.2	0.0	4.5	186.5	42.8	97.7
Mix-100pg	3426.2	137.9	48.6	∞	86.1	93.3	20.6	200.6	6.5	53.4	131.0	38.4	199.7	167.2	0.2	82.4	197.2	31.4	3.5	106.7	12.8	17.4	280.2	109.1
Mix-200pg	13616.4	211.7	47.6	∞	235.6	97.3	17.7	265.1	5.8	187.1	304.8	39.3	237.6	282.0	0.2	∞	380.9	28.8	5.9	180.1	14.8	584.9	197.5	100.4
Mix-400pg	1134.7	294.6	43.3	2253.3	390.7	92.1	31.7	479.2	6.6	255.1	447.9	39.0	340.7	389.1	0.2	59.3	356.2	32.3	9.2	418.1	15.2	351.0	0.0	99.3
Mix-800pg	177.1	794.2	47.5	3666.2	797.4	102.9	116.6	784.8	7.3	550.9	797.2	40.3	756.3	805.3	0.2	∞	810,12	31.2	25.9	795.1	14.3	280.7	800.6	96.5
Mix-1000pg	∞	579.1	46.2	118.3	814.1	95.2	98.1	752.7	6.4	289.5	720.2	38.9	833.6	688.4	0.2	4421.2	672.1	31.6	19.9	872.3	14.4	-	-	-

Appendix D

Sample information

Table D.1: Sample information

	Site	Abbreviation	Date	Latitude [dd°mm'ss. s" N]	Longitude [dd°mm'ss. s"E]	Volume [m^3]	Temperature [°C]	Weather
Inside	Hostel	H	30.04.2019	78°03'46.3"	14°13'06.8"	0.02	22	
	Logistic department	UNIS	23.05.2019	78°13'21.5"	15°29'16.9"	0.04	22	
Outside	Power plant	PP	02.05.2019	78°03'21.1"	14°13'16.4"	0.04	-5	Wind: 5-14m/s ↙ 60 % humidity
	Firefighting training site	FF	14.05.2019	78°14'22.7"	15°30'25.8"	0.04	2	Wind: 1-4 m/s ↖ 85-99 % humidity
	Waste station	WS	27.05.2019	78°13'24.1"	15°39'40.8"	0.07	-2	Wind: 5-9 m/s ↖ 60 % humidity

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