

Emissions of Perfluoroalkyl Substances (PFAS) from Thermodegradation – A Pilot Study at Laboratory Scale

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1 Introduction

For about two decades now, perfluoroalkyl substances (PFAS) are known environmental contaminants which may comprise adverse effects such as environmental persistence, bioaccumulation, long-range transport or certain toxicities. PFAS get into the environment by various emission pathways during their production, implementation in PFAS-containing products or during the life cycle of such products. This may also apply to degradation of fluoropolymers disposal (Ellis et al. 2001) or PFAS-contaminated environmental matrices (such as soils from polluted sites) during their thermal disposal. The emission pathway of PFAS directed to the atmosphere from stationary sources may be of importance because it facilitates transboundary air pollution and long-range transport of these compounds. Thus, thermodegradation of PFAS, PFAS containing matrices, or of fluoropolymers, e.g. by waste incineration, may be an important source of PFAS to the atmosphere. However, PFAS emissions to the atmosphere in general and PFAS emissions from stationary sources in special are not well described, yet. Among other reasons, this may be due to the lack of suited, validated and standardized methods for sampling and analysis of such matrices (although the EPA started discussions on that issue with the OTM-45). Thus, only few information is available for PFAS in emission. E.g. Aleksandrov et al. (2019) investigated the potential formation of PTFE in flue gas from combustion of PTFE at typical waste incineration conditions using a pilot plant but did not observe statistically significant evidence that the PFAS studied were created during the incineration of PTFE within procedural limits of the study. From results of laboratory-scale experiments, Taylor et al. (2014) concluded that waste incineration of fluorotelomer-based polymers does not result in the formation of detectable levels of PFOA under conditions representative for typical municipal waste incinerators. Schlummer et al. (2015) investigated emissions of perfluoroalkyl carboxylic acids (PFCA) from heated PTFE surfaces and found indications for the formation of PFCA. The present study was performed in 2017 with the objective to evaluate PFAS emissions from the thermodegradation of fluoropolymers at different temperatures as well as from thermodegradation of PFOS, PFOA and 8:2 FTOH at laboratory scale. The focus was set to investigate the formation of PFCA and perfluoroalkyl sulfonats (PFSA). Additional fluorinated compounds were also investigated. The study was conducted in two steps, 1st preliminary tests on the emission sampling of PFAS and 2nd the thermodegradation experiments.

2 Materials and Methods

The tests were conducted using a VCI pyrolysis apparatus. This apparatus consists of a furnace with two heating areas. Inside of the furnace, there is a quartz glass tube to minimize catalytic reactions with the furnace wall during the tests and to allow for working in a defined environment. The lower part of the quartz glass tube is equipped with an outlet for the connection to devices for the flue gas sampling. The upper part of the quartz glass tube is equipped with an inlet to allow a continuous air flow. During our experiments, synthetic air was used to standardize conditions during thermodegradation. About 0.5 to 0.7 g PTFE, PFOS standard, PFOA standard, or 8:2 FTOH standard were inserted into the quartz glass tube using a valve on top of the tube. Due to strong electrostatic charging, PFOS, PFOA and 8:2 FTOH had to be placed in gelatine capsules. The furnace was heated to 850 °C, 650 °C (PTFE only) and 500 °C (PTFE only). A continuous flow of about 9 L per hour was adjusted to assure an exposure time of at least 2 seconds. The sampling of the flue gas started just before the introduction of the sample and finished 30 minutes after sample introduction. Depending on the target compounds, sampling was finally conducted as follows (also see Figure 1):

1. PFAS (final method): Dust trap followed by absorption of the analytes using 100 mL of basic methanol (7 N MeOH + NH₃; washing bottle 1 and 2) and 100 mL of methanol (washing bottle 3) followed by a back-up-cartridge (Biotage, isolate ENV+, 1g). After sampling, mass-labelled standards were added to the samples. The solvents were combined and, concentrated (as well as filtered and centrifuged if necessary). The back-up SPE cartridge was desorbed with 0.1 % NH₃/methanol and cleaned up. Instrumental detection was performed using LC-MS/MS.
2. Hydrogen fluoride (HF), trifluoroacetic acid (TFA), difluoroacetic acid (DFA), monofluoroacetic acid (MFA): Dust trap followed by absorption of the analytes using 25 mL ultrapure water in washing bottles. Break through was tested by analyzing a second washing bottle filled with 75 mL of water. HF was detected using an ion selective electrode, MFA to TFA were analyzed using ionchromatography. Break through was < 1%.
3. Hexafluoropropene (HFP) other fluorinated VOCs: Adsorption using activated carbon (AC). Samples were extracted by CS₂. Break through was tested by analyzing a second AC tube. HFP was analyzed using GC_MS in the

selected ion monitoring mode. Other fluorinated VOCs were analyzed using the scan mode (screening). A breakthrough was not detected.

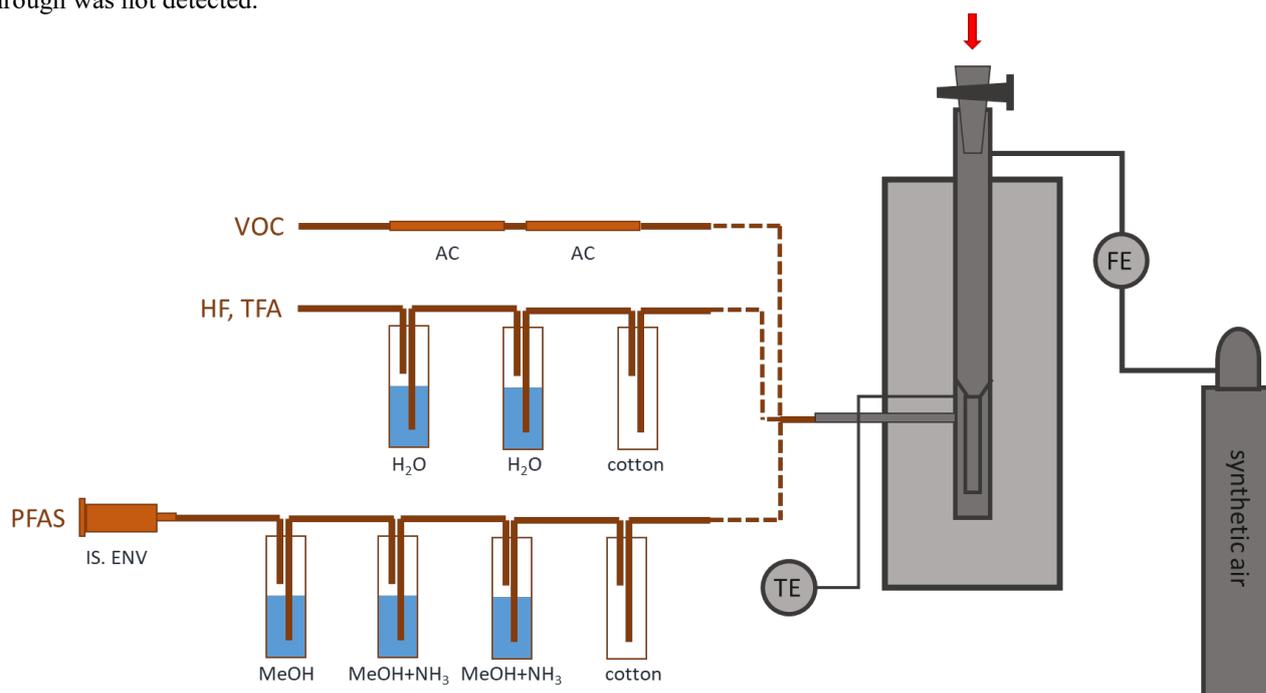


Figure 1: Schematic overview over the tests. Note: VOCs, HF/MFA-TFA, PFAS could not be sampled in parallel. FE: flow element (flow meter). TE: thermo element. AC: activated carbon.

3 Results

3.1 Preliminary tests

During the first attempts to investigate PFAS in flue gas formed during the lab-scale thermodegradation of PTFE we encountered methodological challenges when using pure methanol or water as absorption solutions. These were expressed by a low analytical performance, particularly for perfluorinated carboxylates. In several tests, mass-labelled PFAS standards added prior to the analyses were not recovered (PFCA, Figure 2a) or insufficiently recovered (PFSA, Figure 2c). We observed that this was not due to matrix interferences during chromatography, even though samples were still quite dirty at the time of the instrumental detection. However, if the same mass-labelled standards were spiked directly to the vials, they could satisfactorily be recovered (Figures 2 b, d). We noticed that the solutions in the vials were still very acidic and assumed that this resulted in PFCA becoming protonated during sample processing and were therefore lost due to enhanced volatility as protonated acids. We further assumed, that due to their lower pK_a-values, PFSA were less affected. Alkaline water, e.g. NaOH in water, would principally be able to neutralize the absorption solution. However, well established methods using SPE with anionic exchange resins would have been used afterwards for extraction from such absorption solutions. To our experience, recovery rates of PFAS are very low with high loads of ions in samples when using weak anion exchange resins for SPE. However, elevated loads of ions can be anticipated when using alkaline water as absorption solution. To avoid these problems, we therefore finally applied alkaline methanol (7 N NH₃ MeOH) as it can be evaporated directly without further SPE. During sampling, we observed salts significantly precipitating. In these samples, mass-labelled PFAS standards were not lost and target analytes could be quantified.

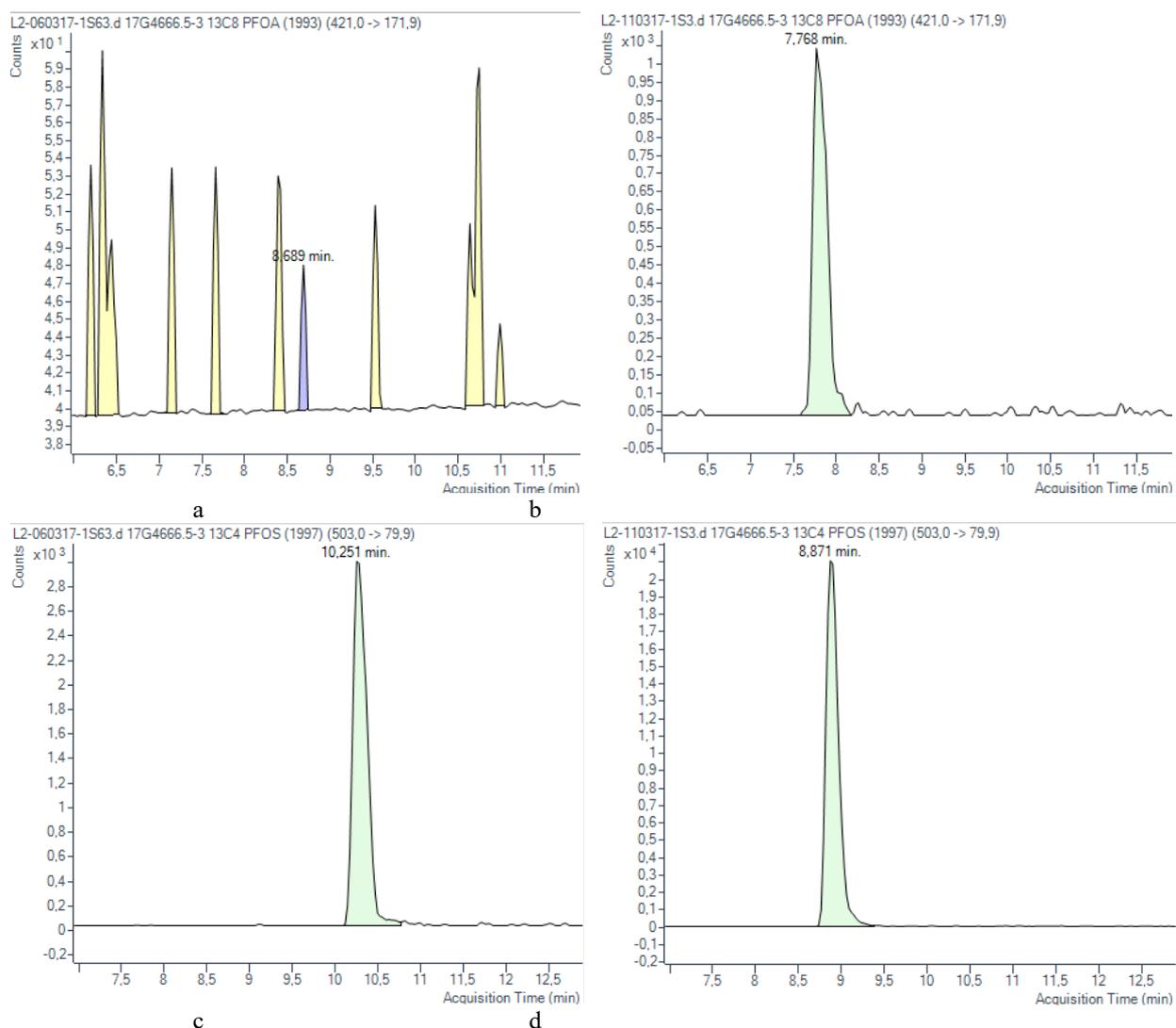


Figure 2: Chromatograms of (a) $^{13}\text{C}_8$ PFOA in the original processed sample (chemically noise only, as the standard was not detectable), (b) $^{13}\text{C}_8$ PFOA spiked to the processed sample prior to the instrumental detection, (c) $^{13}\text{C}_4$ PFOS in the original processed sample, (d) $^{13}\text{C}_4$ PFOS spiked to the processed sample prior to the instrumental detection. Note the different scales.

3.2 Thermodegradation experiments

Results of thermodegradation experiments are given in Table 1 and discussed in the discussion section. PFAS as well as HF and HFP could be observed to different degrees in several samples. Other fluorinated compounds were occasionally identified in screening samples. MFA, DFA were not quantified, TFA was observed in only one sample.

Table 1: Results of thermodegradation experiments.

	PTFE 500°C	PTFE 650°C	PTFE 850°C	PFOA 850°C	PFOS 850°C	8:2 FTOH 850°C	Unit
PFBA	na	3098530	5540	9440	16000	103020	pg/g material used
PFPeA	na	768120	< 570	26460	5400	< 36630	pg/g material used
PFHxA	na	107290	3050	< 8220	4630	< 2610	pg/g material used
PFHpA	na	36270	< 1680	36710	1560	< 20050	pg/g material used
PFOA	na	13790	< 3300	< 9410	13070	< 630	pg/g material used
PFNA	na	11420	< 5030	< 1540	140	< 7820	pg/g material used
PFDA	na	10020	< 1270	< 2670	280	< 3250	pg/g material used
PFUnA	na	7060	< 2460	< 560	< 130	< 590	pg/g material used
PFDoA	na	5310	< 670	< 630	210	< 2200	pg/g material used
PFTTrA	na	3690	< 690	< 600	< 80	< 940	pg/g material used
PFTeA	na	4300	< 1500	< 1090	300	< 2290	pg/g material used
PFBS	na	< 20	< 70	< 810	770	< 13530	pg/g material used

	PTFE 500°C	PTFE 650°C	PTFE 850°C	PFOA 850°C	PFOS 850°C	8:2 FTOH 850°C	Unit
PFHxS	na	< 160	< 340	< 1300	1050	< 320	µg/g material used
PFHpS	na	< 30	< 590	< 430	2260	< 420	µg/g material used
PFOS	na	< 40	< 1190	< 1040	92000	< 1030	µg/g material used
PFDS	na	< 10	< 220	< 540	580	< 420	µg/g material used
HF	568	361	170	149	91	417	mg/g material used
MFA	< 0.6	< 0.3	< 0.03	< 0.75	< 0.4	< 0.4	mg/g material used
DFA	< 0.6	< 0.3	< 0.03	< 0.75	< 0.4	< 0.4	mg/g material used
TFA	< 0.6	< 0.3	2.5	< 0.75	< 0.4	< 0.4	mg/g material used
HEF	< 0.6	48.2	58.1	50.3	< 0.1	54.5	µg/g material used
fluorinated benzenes (di- to penta)	nn	nn	nn	0.52 - 1.03	nn	2.09 - 4.19	µg/g material used
Tetrafluoro ethane	nn	nn	nn	1.0 - 2.1	nn	0.6 - 1.3	µg/g material used
Pentafluor ethane	nn	nn	nn	0.1 - 0.3	nn	0.8 - 1.7	µg/g material used
Pentafluoro propene	nn	nn	0.3 - 0.6	0.1 - 0.3	nn	41.9 - 83.8	µg/g material used
Fluorotri methoxy silane	nn	0.2 - 0.4	0.2 - 0.5	nn	0.05 - 0.1	nn	µg/g material used
TFA-methyl ester	nn	4.8 - 9.6	nn	nn	nn	nn	µg/g material used
Trifluoroacetam ide	nn	nn	nn	nn	nn	nn	µg/g material used
Bis(trifluoromet hyl)acetic acid- methyl ester	nn	nn	nn	nn	nn	nn	µg/g material used

4 Discussion

At 500 °C PTFE could not be sufficiently degraded and thus many analytes could not be analyzed. At 650 °C and 850 °C experiments could be performed without further problems. Particularly at 650°C, PFCA were formed during thermodegradation of PTFE. The shorter the chain length the higher were the yields. At 850 °C PFAS yields were below the MQL except for PFBA and PFHxA indicating that at such temperatures still short chain PFCA may be formed. PFSA were not observed above the MQL. Similarly to PFCA, yields of HF decreased with increasing temperatures.

Thermodegradation of 8:2 FTOH, PFOA and PFOS yielded different amounts of PFAS at a temperature of 850 °C. For the thermodegradation of 8:2 FTOH only PFBA was quantified. PFBA, PFPeA and PFHpA were observed above the MQL when thermodegradation of PFOA was investigated indicating conversion of PFOA to lower chain perfluorinated acids. In contrast to PFOA, the thermodegradation of PFOS yielded multiple PFCA as well as PFSA. Our results indicate that PFSA are not completely thermodegraded and partly converted to other perfluorinated acids. That TFA (as well as MFA, DFA) was not observed above the MQLs in most samples is probably due elevated MQLs as a result of the less sensitive sampling and instrumental method which does not allow for a sample concentration.

5 Conclusions

This pilot study indicates that PFCA may be formed by thermodegradation of fluoropolymers such as PTFE or by thermodegradation of precursor compounds such as 8:2 FTOH. Yields strongly depend on the temperature applied. It is also indicated that PFAS present in samples prior to thermal degradation may not completely be destroyed or will be converted to other fluorinated compounds.

This pilot study also results in suggestions for emission sampling at stationary sources.

We suggest applying an alkaline absorption solution. NH₃-methanol may be used in the laboratory where there are fume hoods, but it is certainly not advised for usage at emission sampling sites without possibilities to avoid the irritating and toxic exhausts. However, applying organic solvents which do not need further SPE clean up may be advantageous. Future studies are needed to find acceptable solutions for collection of flue gasses.

Certainly, sampling standards will be needed for real emission measurements. In our opinion these should not only cover different analyte groups (i.e. PFCA and PFSA) but also different compound chain lengths.

6 References

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