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Application Note 168

PFAS emissions from food contact materials

Summary

This application note outlines the methodology for assessing significant levels of per- and polyfluoroalkyl substances (PFAS) emissions from food contact materials under typical usage conditions. PFAS were detected across a range of temperatures for the items tested, with concentrations varying from 1 pg/g to over 6000 pg/g.

Introduction

PFAS can be found everywhere in our homes, workplaces and vehicles. Since research into the effect of these chemicals on the environment and human health began, three individual PFAS species have been added to the Stockholm Convention on Persistent Organic Pollutants 2001[1] and all long chain perfluorocarboxylic acids (PFCAs) are under review. PFAS as a class contains more than 12,000 chemicals[2] at the time of publication.

The presence of PFAS in materials that come into contact with food is the subject of debate and regulation. Some studies[3] have even found traces of PFAS in materials where they were not intentionally included. This makes a ban difficult to enforce without testing.

PFAS can migrate into food items during storage, transport, and cooking if PFAS coated materials are used. A declaration that no PFAS is present does not guarantee its absence. Consumers will benefit from testing of:

a) Whether food contact materials (packaging, coatings, *etc.*) are emitting significant levels of PFAS;

b) If the emitted PFAS are migrating into the food.

Assessing the release of PFAS from food contact materials

VOC analysis from materials is performed using GC–MS, utilising static headspace or thermal desorption for sample introduction. This study used a large volume, dynamic headspace technique (Markes Micro-chamber/Thermal Extractor) with sample collection onto sorbent tubes. Analysis by thermal desorption–GC–MS enhances detection limits through multiple preconcentration steps. Due to the toxicity of PFAS, it is important to quantify the low concentrations of emitted compounds.

Combining the unmatched concentration power of two-stage thermal desorption with the exceptional sensitivity of GC–MS/MS, provides detection limits that would be within the range for future PFAS levels in food contact regulations.

Developing and validating a method for sampling and analysis

To develop and validate a method for sampling and analysing 19 target PFAS compounds from materials, the study included four different functional groups – perfluoroalkyl carboxylic acids/carboxylates (PFCAs), fluorotelomer alcohols (FTOHs), fluorotelomer carboxylic acids (FTCAs) and perfluorooctane sulfonamides (FOSAs).

Standards

Target species were purchased as individual standards from Wellington Laboratories Inc, Canada, at a concentration of 50 ng/µL. They were combined and diluted to create a 5 ng/µL stock standard. The PFCAs were sourced as a mixture at 2 ng/µL and used as a stock standard. Serial dilution of these stock standards produced the range used in calibration and further tests. PFCAs were later removed from tests; see the results.

To spike sorbent tubes with standards, 1 µL of each standard was injected using a Calibration Solution Loading Rig™ (CSLR™) onto the sorbent tube in a flow of nitrogen at 100 mL/min. Samples were purged for 60 minutes to remove methanol. Markes' TC-20™ unit purged up to 20 tubes simultaneously, expediting the spiking process. The TC-20 was also used to re-condition the sorbent tubes in nitrogen prior to sampling, saving helium.

Samples

Samples included:

- brown paper bags with a clear flexible polymer window designed for storing food;
- food grade “grease proof” paper designed for wrapping burgers;
- silicone cupcake moulds; and
- non-stick BBQ grill mats advertised as BPA and PFOA free.

Material sampling

Emissions chambers enable collection of emitted organic compounds from materials under simulated real-use conditions. A chamber is continuously purged using a gas, which can be dry or humidified. As chemicals are released from the material inside the chamber, they are swept onto tubes packed with sorbents. The trapped compounds are then analysed using thermal desorption with GC–MS according to ISO-16000-6[4], ASTM D6196[5] and other national or international standards. Alternative traps and analytical methods can be used for compounds that are incompatible with GC. The chamber size (114 mL) enables representative portions of packaging and coated materials to be analysed, increasing confidence in results.

Figure 1: The Micro-Chamber/Thermal Extractor large volume, dynamic headspace sampler and TD100-xr automated thermal desorption instrument.

The food contact materials were prepared as described in EN 13682, cut using a stencil, and weighed into aluminium sample boats before being placed in the Micro-Chamber/Thermal Extractor. Once sealed into individual microchambers, the samples were incubated at a user-defined temperature and purged with gas, sweeping evolved vapours into connected sorbent tubes.

Although pure air is often used as the purge gas (dry or humidified) to simulate real-world conditions, in this case nitrogen was chosen to evaluate emissions without oxidation.

Because of the differences between dynamic and static headspace techniques, the base method was taken from ASTM D7706-11.

Micro-Chamber/Thermal Extractor conditions

Temperature:	Varied
Purge flow rate:	50 mL/min
Sampling time:	60 minutes

Analytical conditions

Tubes:	PFAS tubes, C3- AAXX-5424 (stainless steel, conditioned and capped; Markes International)
System:	TD100-xr Advanced
Flow path:	200°C
Automatic dry purge:	1 min at 50 mL/min
Tube desorption:	300°C for 10 min at 50 mL/min
Trap purge:	1 min at 50 mL/min
Focusing trap:	‘PFAS’ focusing trap (U-T24PFAS-2S, Markes International)
Focusing trap low:	-30°C
Elevated trap purge:	25°C
Focusing trap high:	300°C (4 min)
Trap heat rate:	MAX
Outlet split:	6:1
Internal standard:	Toluene D8

GC

Column:	TG-200MS 30 m x 0.25 mm x 1.0 µm
Carrier gas:	Helium
Column flow:	1.2 mL/min, constant flow
GC oven:	35°C for 2 min, 15°C/min to 280°C. Hold for 5 min

MS/MS

Source:	300°C
Transfer line:	280°C
Acquisition mode:	Timed multiple reaction monitoring (MRM) and full scan
Scan range:	m/z 35 –650
MRM/SRM:	MRM/SRM transitions (see Appendix for details).

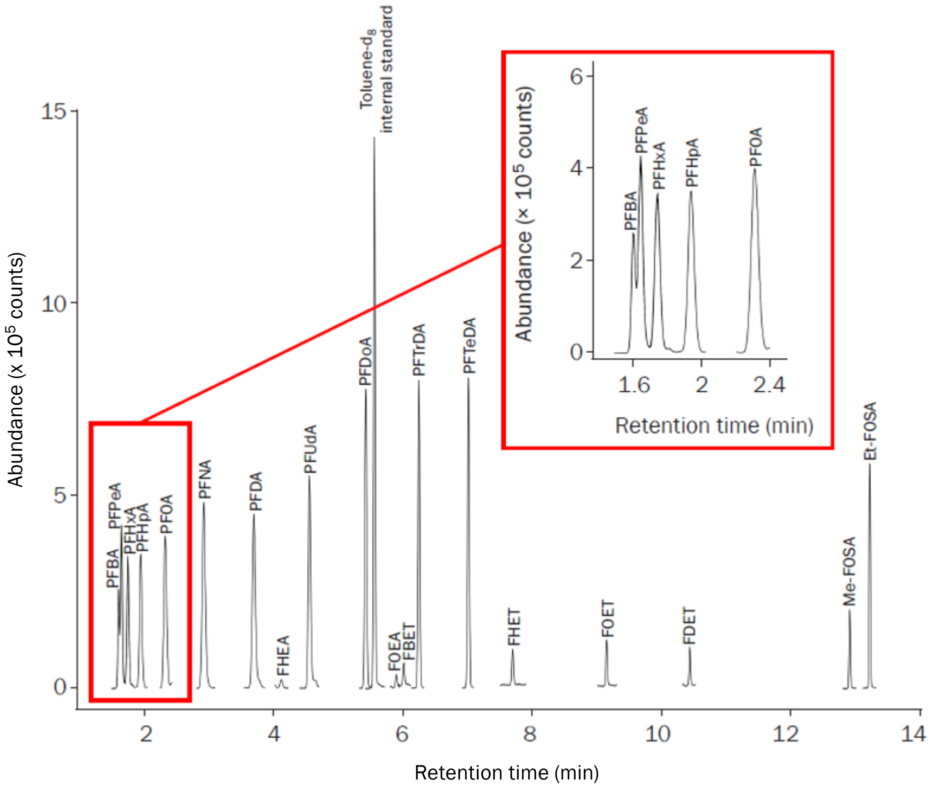

Figure 2: GC–MS chromatogram showing mixed PFAS standard at 500 pg on-tube. The inset shows a close-up view of the chromatogram for the first five compounds, which are perfluoroalkylcarboxylic acids (PFCAs) or their derivatisation products.

Results and discussion

This analysis focuses on characterising emissions from food contact materials. In this study, the average method detection limit (MDL) was 15 pg, with all compounds having MDLs below 65 pg on tube. Figure 2 shows the excellent separation and peak shape achieved for a 500 pg PFAS standard, with calibration and reproducibility metrics detailed in Table 1A. For full details on the validation of TD100-xr for PFAS, please refer to Application Note 166, which demonstrates its performance for ambient air.[6]

Sample results

Samples were prepared and tested using the Markes' Microchamber/thermal extractor operating as described. Each product was sampled at ambient temperature (20°C) and at 30°C. The BBQ grill mat and silicone cupcake moulds were also tested at 200°C to simulate usage temperatures.

Table 2A in the appendix shows which PFAS compounds were detected from the samples, their concentration and the emission rate for each, based on the sampling time and

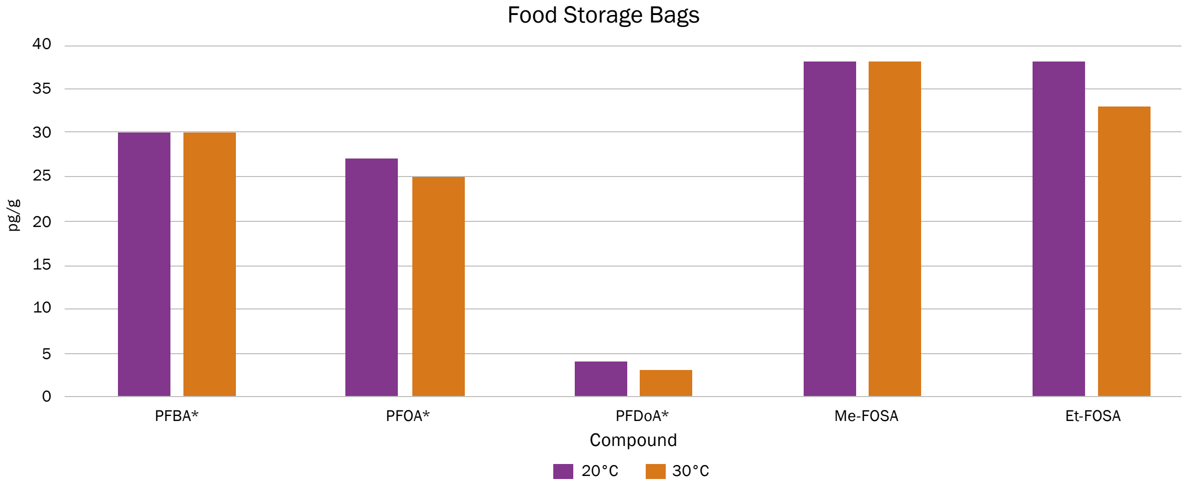

Figure 3: Food storage bags emitted five compounds when tested at ambient (20°C) and slightly elevated (30°C) temperatures. The concentration of the species emitted did not change significantly when the temperature was raised.

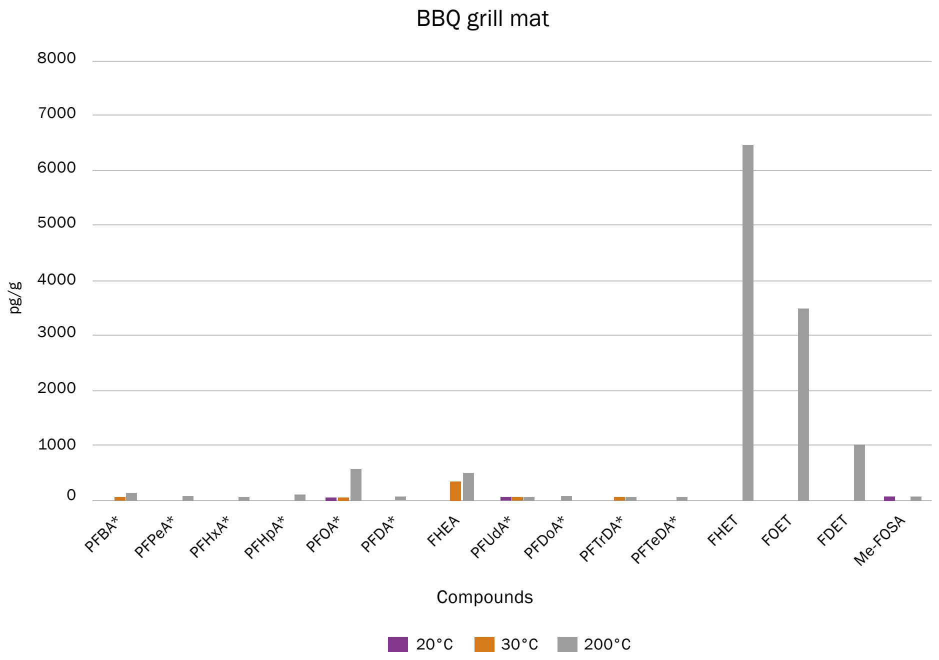

Figure 4a: GC–MS chromatogram showing emissions from the BBQ grill mat. It emitted 15 compounds at 200°C, with the emissions of most compounds much higher at these temperatures. The fluorotelomer alcohols have the highest concentration compounds at 200°C.

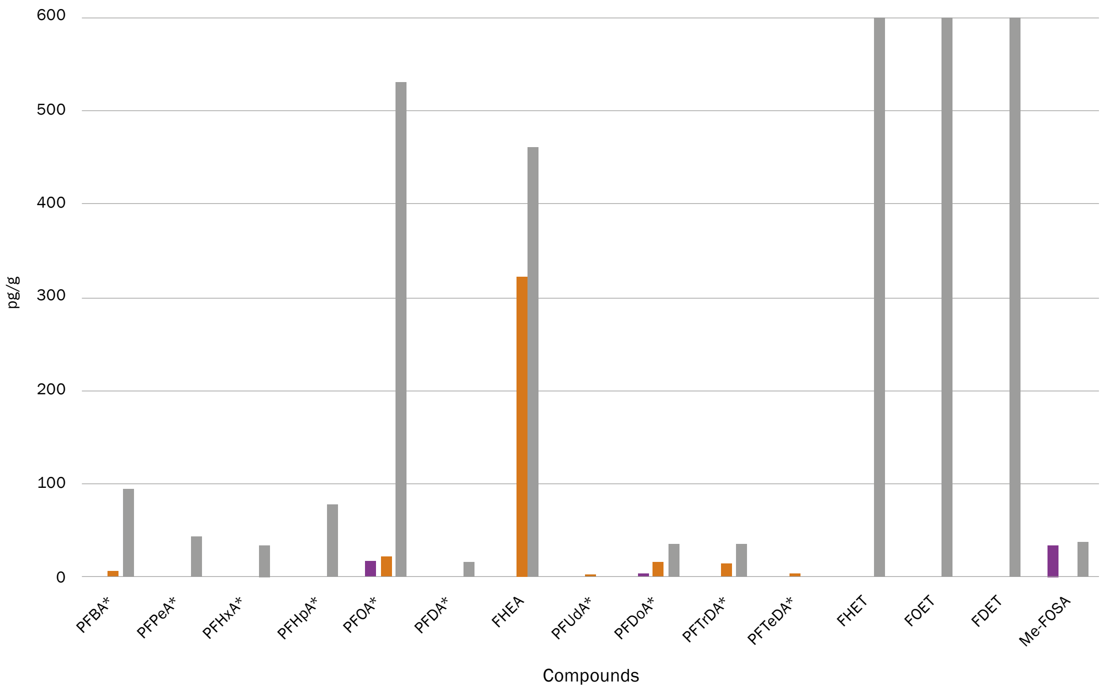

Figure 4b: As above, with the y-axis limited to 600 pg/g. Most compounds emitted to a lower level. In this figure it can be seen that the fluorotelomer alcohols were not emitted at 20°C or 30°C.

sample weight. When comparing samples at 20°C and 30°C, little difference in the emission is seen (Figure 3). The sample with the highest emission rates for a number of compounds was found to be the BBQ grill mat when analysed at 200°C. It shows a clear jump in emissions from ambient temperatures to the use temperature (Figure 4).

The MRM chromatogram for this sample is shown in Figure 5. The chromatogram shows that the fluorotelomer alcohol species are emitted in the highest concentration. There are also species eluting where we would expect to find the derivatised PFCAs which indicates that the sample should be assessed using a complementary technique.

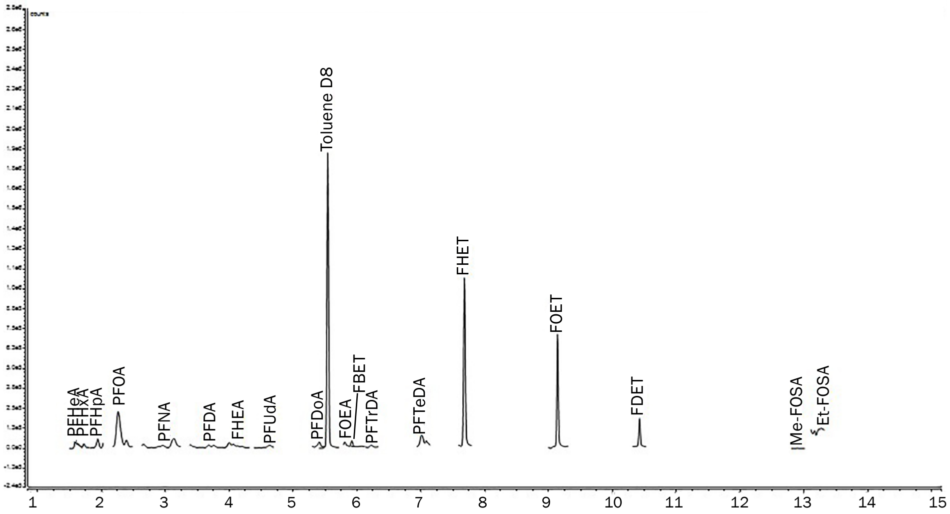

Figure 5: Chromatogram showing the MRM trace for the BBQ grill mat when tested at 200°C.

The Micro-Chamber/Thermal Extractor can be easily adapted to fit samplers other than sorbent tubes, and can be utilised to generate a sample compatible with liquid chromatography (LC).

Emission of PFAS from all the samples highlights two concerns about the use of PFAS in food contact materials and cookware: the contamination of food, and emissions into the air which can then be inhaled. The calculated emission rate from these products gives an understanding of exposure/migration over time. The highest emission rate of 112.9 pg/g/minute was for FHET (6:2 FTOH) when the BBQ grill mat was tested at 200°C. The fluorotelomer alcohol species are of special interest because they have been shown to transform into the perfluorinated carboxylic acids.

PFCA derivatisation

Since this study, new evidence has shown that the perfluorinated carboxylic acids undergo derivatisation to form both $C_{(n-1)}$ alkane and alkene products. Reference to them has been retained throughout this article as compounds were detected in real samples at their respective retention times. PFCA identification should be thoroughly investigated with an alternative technique if quantitative results are required.

Conclusions

The findings of this study underscore the significance of monitoring PFAS emissions from food contact materials, and the suitability of TD–GC–MS for the analysis. It was found that using a dynamic headspace technique enabled relatively large sample sizes (around 1g) to be analysed, which offers added versatility for analysing non-uniform samples, and importantly facilitates the low-level detection of PFAS at concentrations as low as 1 pg/g. The use of dynamic headspace sampling, coupled with preconcentration through the thermal desorption analysis, means detection limits can be pushed to incredibly low levels which may prove vital as more information is gained about PFAS toxicology.

Selectivity for the target PFAS was achieved through use of a triple quadrupole mass spectrometer. This enabled low concentrations for the target compounds to be detected without interference from the background which would have been in the region of 10^3 times higher. The data provides valuable insights into the presence and concentration of these harmful substances, as well as demonstrating the effectiveness of the analytical methods employed. This study offers a valuable perspective on the need for stringent testing and regulation of PFAS in food contact materials.

References

1. PFAS overview page, Stockholm convention website, accessed 27/04/2023, http://chm.pops.int/Implementation/IndustrialPOPs/PFAS/Overview/tabid/5221/Default.aspx
2. US EPA PFAS master list, CompTox Chemicals Dashboard, accessed 27/04/2023, https://comptox.epa.gov/dashboard/chemical-lists/pfasmaster
3. European parliament, accessed 27/04/2023, https://www.europarl.europa.eu/doceo/document/E-9-2021-002977_EN.html
4. Determination of organic compounds (VVOC, VOC, SVOC) in indoor and test chamber air by active sampling on sorbent tubes, thermal desorption and gas chromatography using MS or MS FID. (ISO Standard No. 16000-6:2021) https://www.iso.org/standard/73522.html
5. Standard Practice for Choosing Sorbents, Sampling Parameters and Thermal Desorption Analytical Conditions for Monitoring Volatile Organic Chemicals in Air (ASTM Standard D6196-15e1 Updated March 03, 2023) https://www.astm.org/d6196-15e01.html
6. Application Note 166, https://markes.com/content-hub/application-notes/application-note-166

Appendix

Compound name	Abbreviation	RT	R^2	Quantitation MRM transition	% RSD	MDL (pg)
Perfluoroalkyl carboxylic acids (PFCAs)						
Perfluoro-n-butanoic acid	PFBA	1.593	0.9985	131/69	4.52	5
Perfluoro-n-pentanoic acid	PFPeA	1.638	0.9966	131/69	3.80	2
Perfluoro-n-hexanoic acid	PFHxA	1.728	0.9970	131/69	3.25	23
Perfluoro-n-heptanoic acid	PFHpA	1.933	0.9981	131/69	2.42	3
Perfluoro-n-octanoic acid	PFOA	2.311	0.9986	131/69	2.00	2
Perfluoro-n-nonanoic acid	PFNA	2.9	0.9983	131/69	1.48	46
Perfluoro-n-decanoic acid	PFDA	3.665	0.9978	131/69	2.48	27
Perfluoro-n-undecanoic acid	PFUdA	4.522	0.9974	131/69	3.67	4
Perfluoro-n-dodecanoic acid	PFDoA	5.392	0.9975	131/69	2.71	21
Perfluoro-n-tridecanoic acid	PFTrDA	6.216	0.9974	131/69	3.00	3
Perfluoro-n-tetradecanoic acid	PFTeDA	6.981	0.9975	131/69	3.01	2
Fluorotelomer carboxylic acids (FTCAs)						
2-Perfluorohexyl ethanoic acid (6:2)	FHEA	3.973	0.9953	131/69	5.75	64
2-Perfluorooctyl ethanoic acid (8:2)	FOEA	5.904	0.9983	131/69	2.65	52
Fluorotelomer alcohols (FTOHs)						
2-Perfluorobutyl ethanol (4:2)	FBET	6.01	0.9951	95/69	4.10	13
2-Perfluorohexyl ethanol (6:2)	FHET	7.669	0.9971	95/69	2.61	18
2-Perfluorooctyl ethanol (8:2)	FOET	9.122	0.9963	95/69	3.99	4
2-Perfluorodecyl ethanol (10:2)	FDET	10.41	0.9937	95/69	4.08	6
Perfluorooctanesulfonamides (FOSAs)						
N-Methylperfluoro-1-octanesulfonamide	Me-FOSA	12.87	0.9953	94/30	0.83	1
N-Ethylperfluoro-1-octanesulfonamide	Et-FOSA	13.18	0.9953	108/80	5.29	1

Table 1A: Full data table for individual PFAS species analysed during this study.

Emission (pg/g)										
Sample	**Food storage bags**		**Grease proof paper**		**BBQ grill mat**			**Cupcake mould**		
Compound	**20°C**	**30°C**	**20°C**	**30°C**	**20°C**	**30°C**	**200°C**	**20°C**	**30°C**	**200°C**
PFBA*	30	30	33	27	-	6	95	-	-	66
PFPeA*	-	-	-	-	-	-	44	-	-	16
PFHxA*	-	-	-	-	-	-	35	-	-	73
PFHpA*	-	-	-	-	-	-	77	-	-	377
PFOA*	27	25	24	23	18	22	531	20	25	45
PFNA*	-	-	-	-	-	-	-	-	-	-
PFDA*	-	-	-	-	-	-	16	-	-	140
FHEA	-	-	-	-	-	322	467	-	461	2139
PFUdA*	-	-	-	-	-	2	-	-	-	-
PFDoA*	4	3	5	1	4	16	36	9	14	35
FOEA	-	-	-	-	-	-	-	76	286	752
FBET	-	-	-	-	-	-	-	-	-	357
PFTrDA*	-	-	3	-	-	15	16	-	12	53
PFTeDA*	-	-	-	-	-	4	-	-	1	-
FHET	-	-	-	-	-	-	6772	36	-	1246
FOET	-	-	-	-	-	-	3457	-	-	-
FDET	-	-	-	-	-	-	1014	-	-	-
Me-FOSA	38	38	-	-	35	-	38	40	40	36
Et-FOSA	38	33	-	-	-	-	-	239	255	359

Emission rate (pg/g/min)										
Sample	**Food storage bags**		**Grease proof paper**		**BBQ grill mat**			**Cupcake mould**		
Compound	**20°C**	**30°C**	**20°C**	**30°C**	**20°C**	**30°C**	**200°C**	**20°C**	**30°C**	**200°C**
PFBA*	0.5	0.5	0.6	0.4	-	0.1	1.6	-	-	1.1
PFPeA*	-	-	-	-	-	-	0.7	-	-	0.3
PFHxA*	-	-	-	-	-	-	0.6	-	-	1.2
PFHpA*	-	-	-	-	-	-	1.3	-	-	6.3
PFOA*	0.4	0.4	0.4	0.4	0.3	0.4	8.9	0.3	0.4	0.7
PFNA*	-	-	-	-	-	-	-	-	-	-
PFDA*	-	-	-	-	-	-	0.3	-	-	2.3
FHEA	-	-	-	-	-	5.4	7.8	-	7.7	35.7
PFUdA*	-	-	-	-	-	-	-	-	-	-
PFDoA*	0.1	-	0.1	-	0.1	0.3	0.6	0.1	0.2	0.6
FOEA	-	-	-	-	-	-	-	1.3	4.8	12.5
FBET	-	-	-	-	-	-	-	-	-	5.9
PFTrDA*	-	-	-	-	-	0.2	0.3	-	0.2	0.9
PFTeDA*	-	-	-	-	-	0.1	-	-	-	-
FHET	-	-	-	-	-	-	112.9	0.6	-	20.8
FOET	-	-	-	-	-	-	57.6	-	-	-
FDET	-	-	-	-	-	-	16.9	-	-	-
Me-FOSA	0.6	0.6	-	-	0.6	-	0.6	0.7	0.7	0.6
Et-FOSA	0.6	0.5	-	-	-	-	-	4.0	4.2	6.0

Table 2A: Emission of the target species detected from each material tested in pg/g.
Emissions are shown at each of the temperatures the material was tested at which varied depending on use case.