Emissions of PFAS from Fluoropolymer-coated Cookware – Analysis by TD-GC-MS

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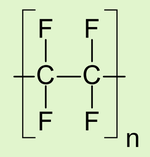
Introduction

- **Non-stick coated cookware** is often heated to high temperatures during use. Temperatures up to 250 °C are possible, for example when roasting nuts on the stove or baking in the oven.
- Non-stick coatings of commercially available cookware are mostly based on **polytetra-fluoroethylene (PTFE)**. PTFE is a polymer of the substance group of **per- and polyfluoroalkyl substances (PFAS)**.



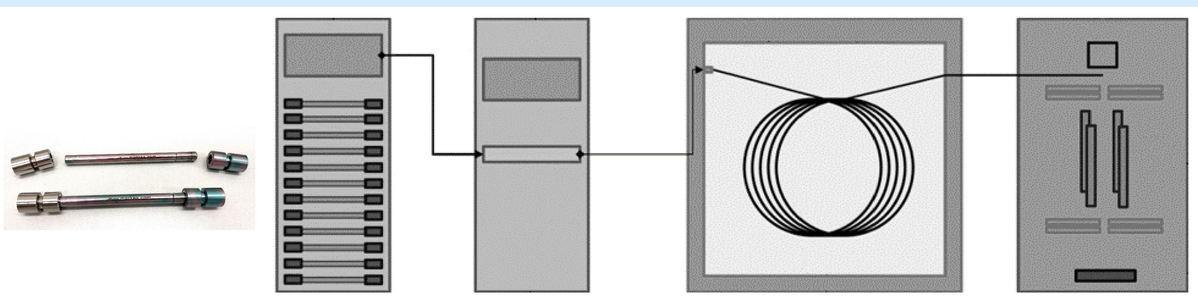
- **Non-polymeric PFAS** are used as **production aids** in the fabrication of PTFE-coatings. Some of these surfactants are **persistent, accumulative and immune system suppressing** [1]. They should be eliminated during sintering at > 380 °C, which is the last step in the production of coatings. However, in studies investigating PTFE-coatings, PFAS could be detected. Moreover, thermal degradation of PTFE to perfluorocarboxylic acids has been reported [2].
- The aim of this work was to investigate the emission of PFAS from cookware by **thermal desorption – gas chromatography – mass spectrometry (TD-GC-MS)**. Target analysis of specific PFAS as well as possibilities for a screening approach should be tested for this purpose.

Conclusion

- **PTFE-based non-stick coatings** for food contact were heated at **250 °C for 30 min** and the emissions were analyzed by **TD-GC-MS**.
- It was proven that besides fluorotelomer alcohols (FTOHs), which are the only PFAS commonly analyzed by GC-MS, also **perfluorocarboxylic acids (PFCAs)** and **perfluoroether acids (PFEAs)** as well as their **thermolysis products, perfluoro ethers (PFEs)**, can be analyzed by GC. However, perfluorosulfonic acids (PFSAs) were not detectable.
- A **screening** for PFCAs and FTOHs is possible by **electron impact ionization (EI)** using group specific SIM fragments. Confirmation of **identity** has been done by EI SCAN as well as **chemical ionization (CI)** SIM measurements.
- Four commercially purchased baking trays were analyzed. In **three samples** there were **no PFAS detectable (LOD: 1 ng/dm²)**. In **one sample** several long chain **PFCAs (C_{13} – C_{23})** were quantified in the range of **0.5 to 34.4 ng/dm²**. After a second and third thermal extraction of the coatings, no PFAS were detectable (LOD: 1 ng/dm²) in all samples. Thus, there is no detectable heat induced formation of PFAS from the investigated PTFE coatings up to 250 °C.

TD-GC-MS instrument setup

For calibration, analytes were injected directly into adsorption tubes (**1**, Fig. 1), filled with Tenax® and activated carbon, using a microlitre syringe followed by purging with nitrogen. In the thermal desorption system, analytes were desorbed from the tubes in an autosampler oven (**2**), collected on a trap (**3**) and desorbed again to be transferred to the GC column (**4**). A trifluoropropylmethyl polysiloxane column (Rtx200-MS) was used for separation. The MS detection (**5**) was performed using electron impact as well as chemical ionization in SIM and SCAN mode. [3]



1 - Injection	2 - Autosampler	3 - Trap	4 - GC	5 - MS
Into tubes, analytes in methanol	tube desorption 250 °C, 10 min, 50 mL/min He	trap desorption 300 °C, 5 min, 50 mL/min He, Split 1:10	30 °C (10 min), 10 °C/min , 250 °C (12 min) column: Rtx200-MS (30 m x 0.25 mm x 1.0 µm)	EI/CI SCAN/SIM

Fig. 1. TD-GC-MS instrument [figure (modified): Materic et al. Appl. Plant Sci.2015, 3, 1500044]

Identification and Quantification

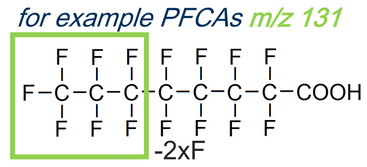
Identification of each analyte was verified by three characteristics:

1 Retetion time

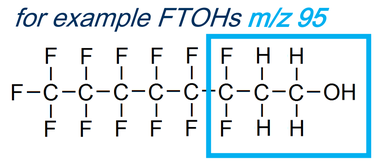
2 Electron impact ionization (EI)

- SIM mode: specific fragments allow screening for PFAS groups

for example PFCAs m/z 131



for example FTOHs m/z 95

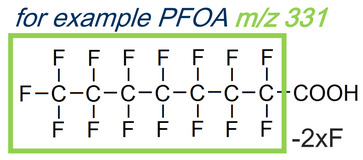


- SCAN mode: specific fragmentation pattern for confirmation

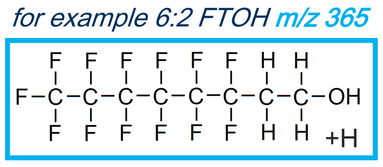
3 Chemical ionization (CI)

- SIM mode: substance-specific fragments for confirmation

for example PFOA m/z 331



for example 6:2 FTOH m/z 365



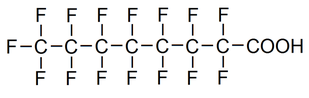
Quantification was performed by EI-SIM measurements. Instrumental detection limits of 0.001 – 0.04 ng were achieved (signal-to-noise ratio S/N = 3).

Selected analytes

In this study, 27 analytes were considered. The selection was based on their use in the production of fluoropolymer-based coatings for cookware and on reports from the literature, which investigated PFAS from these materials.

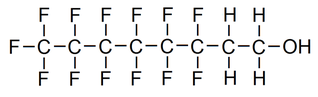
13 Perfluorocarboxylic acids (PFCAs)

for example perfluorooctanoic acid (PFOA)



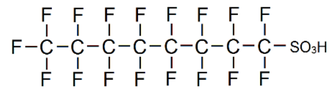
3 Fluorotelomers (alcohols (FTOHs), acid (FTCA))

for example 6:2 fluorotelomer alcohol (6:2 FTOH)



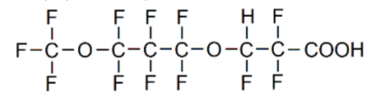
6 Perfluorosulfonic acids (PFSAs)

for example perfluorooctanesulfonic acid (PFOS)



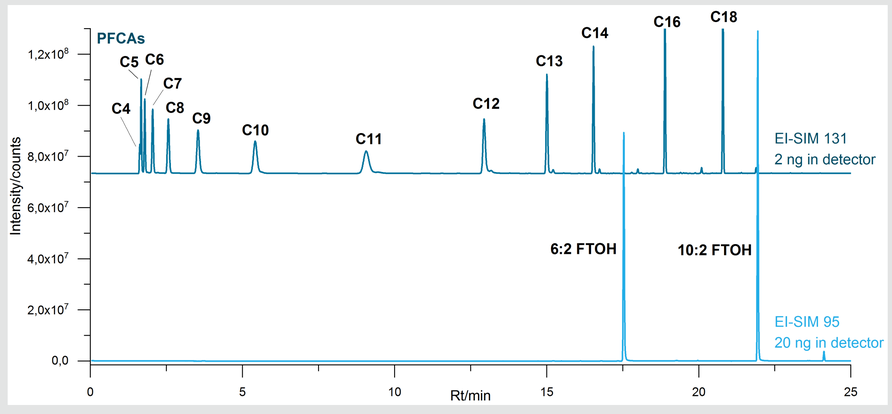
5 Perfluoroether acids (PFEAs)

for example 3H-perfluoro-3-((3-methoxypropoxy)-propanoic acid) (DONA)



GC-detectable analytes

21 of the 27 analytes were detectable via GC-MS (some of them shown in Fig. 2). Sulfonic acids were not detectable due to their low volatility.



- ✓ PFCAs
- ✓ FTOHs + FTCA
- ✓ PFEAs
- ✗ PFSAs

Fig. 2. GC-MS-SIM chomatograms of PFCAs and FTOHs

Thermal extraction of coatings

Thermal extraction of the coatings was performed in the apparatus shown in Fig. 3. A coating (on a metal stripe, 30 cm x 2 cm) was placed in a glass tube (**1**) and ^{13}C-PFNA was added as internal standard. The glass tube was incubated in the preheated oven (**2**) at 250 °C for 30 min. A nitrogen flow of 50 ml/min (**3**) flushed the analytes desorbed from the sample into the adsorption tube (**4**), which was previously spiked with the injection standard ^{13}C-PFOA. Satisfactory recoveries were proven for C_6 to C_{18} PFCAs (Fig. 4).

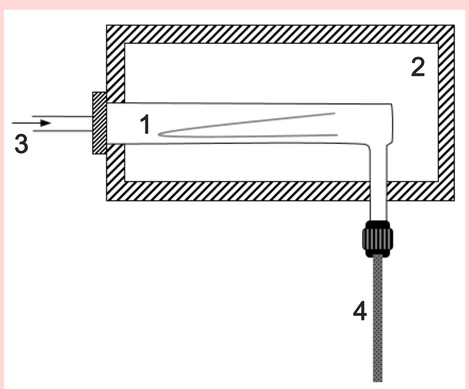


Fig. 3. Oven for thermal extraction

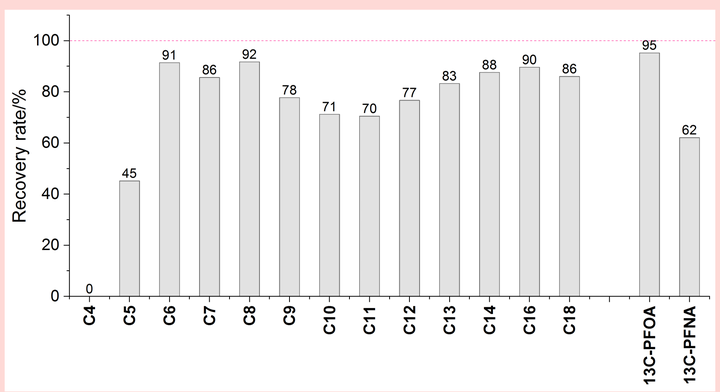


Fig. 4. Recovery rates of PFCAs; absolute amounts: 2 ng of each PFCA (in methanol) injected into the glass tube

PFAS from commercial samples

Four commercial baking trays were examined for their emission of PFAS. There were no PFAS detectable in three of the samples (LOD: 1 ng/dm²). In one sample (Fig. 5) several long chain PFCAs (C_{13} – C_{23}) were quantified in the range of 0.5 to 34.4 ng/dm² (Fig. 6). After a second and third thermal extraction of the coatings, no PFAS were detectable (LOD: 1 ng/dm²) in all samples.

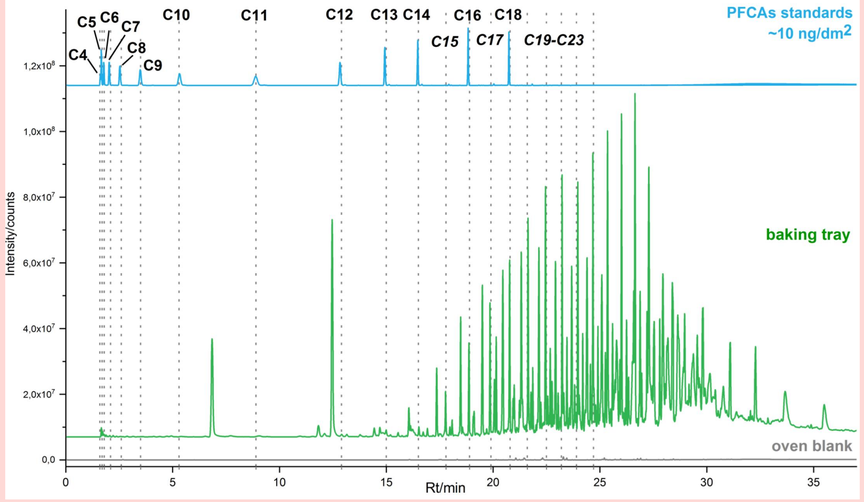


Fig. 6. GC-MS chromatograms (EI-SIM 131)

Fig. 5. Commercial baking tray

Literature

[1] Bundesinstitut für Risikobewertung: PFAS in Lebensmitteln. Stellungnahme Nr. 020/2021
[2] Schlummer, M. et al. Chemosphere 2015 129, 46-53
[3] Markes international 2021, Application Note 158

Acknowledgement

Thanks to the Federation of European manufacturers of Cookware and cutlery (FEC) for their support.

50. Deutscher Lebensmittelchemikertag 19.-21.09.2022, Hamburg