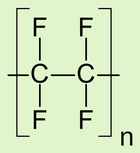
PFAS in Fluoropolymer-coated Cookware – Analysis by TD-GC-MS

Nancy Wolf, Lina Müller, Sarah Enge, Tina Ungethüm, Thomas Simat*

Technische Universität Dresden, Chair of Food Science and Food Contact Materials, Bergstr. 66, D-01062 Dresden; *Contact: thomas.simat@tu-dresden.de

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 **polytetrafluoroethylene (PTFE)**.
- **Per- and polyfluoralkyl substances (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 emissions of **PFAS from PTFE-based non-stick coatings** for food contact, including baking trays and mats as well as frying pans, by **thermal desorption – gas chromatography – mass spectrometry (TD-GC-MS)** after thermal extraction at **250 °C for 30 min.**

Conclusion

- 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 (PFECAs)** as well as their **thermolysis products, perfluoro ethers (PFEs),** which are formed by decarboxylation, can be analyzed by GC.
- A **screening** for PFAS 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.
- **No PFAS were detectable (LOD: 1-10 ng/dm²)** in 12 of 20 samples. In one baking tray several long chain **PFCAs (C_{13} - C_{23})** were quantified in the range of **0.5 to 34.4 ng/dm²**. A baking mat contained residues of **PFOA in 6 ng/dm²**. In a coating for frying pans, a **PFECA and its PFE** were detected in amounts up to **0.5 µg/dm²**. In five baking trays, the **PFECA mix Krytox™** were detected. The PFECAs were almost completely degraded to PFEs by decarboxylation due to thermal exposure.
- After a second and third thermal extraction of the coatings, no PFAS were detectable in all samples. Thus, a **removal** and **no heat induced formation of the analyzed PFAS** from the investigated fluoropolymer coatings at **250 °C** was observed.

TD-GC-MS instrument

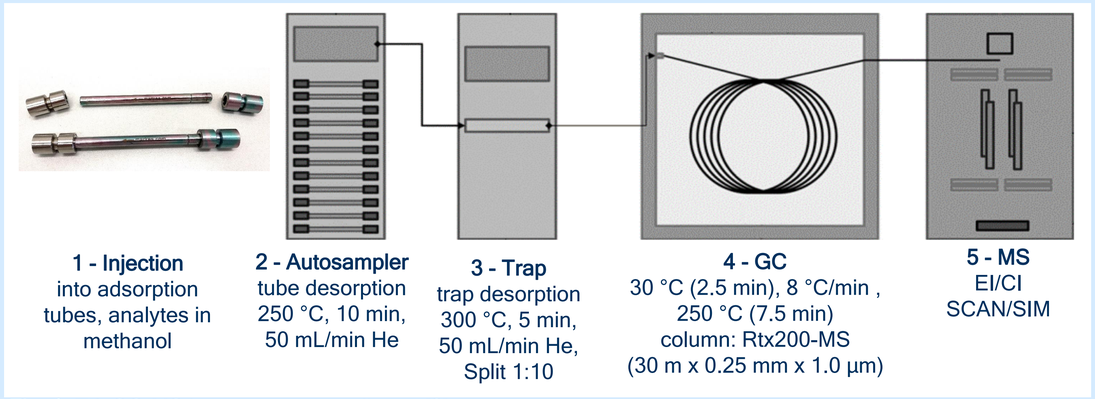
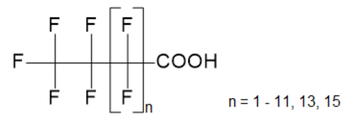


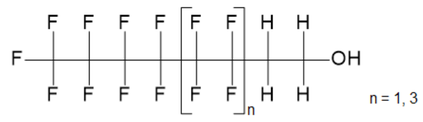
Fig. 1. TD-GC-MS instrument, according to [3] [figure (modified): Materic et al. Appl. Plant Sci.2015, 3, 1500044]

Selected analytes based on their use in production of fluoropolymer-based coatings for cookware, grease proof paper products and reports from literature, which investigated PFAS from these materials.

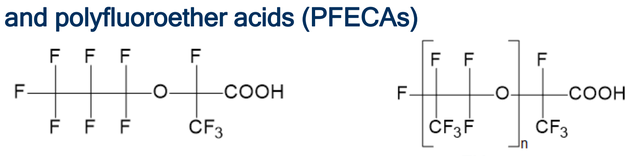
Perfluorocarboxylic acids (PFCAs)



Fluorotelomer alcohols (FTOHs)



Per- and polyfluoroether acids (PFECAs)

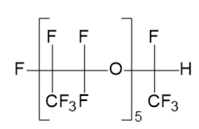


e.g. HFPO-DA (GenX) (CAS 13252-13-6), *Krytox™ (CAS 51798-33-5)*

Polyfluoroethers (PFEs)

degradation products of PFECAs

e.g. TFEE5
(CAS 37486-69-4)



Thermal extraction of coatings [4]

Thermal extraction was performed in the apparatus shown in Fig. 2. **Baking trays and mats** (Fig. 3) **were cut into stripes** (~ 0.6 dm²). **Coatings of pans** (Fig. 4) **were scraped off** (~ 0.4 dm²). Samples were placed in a glass tube. The glass tube was incubated in the preheated oven **at 250 °C for 30 min**. An **air flow of 50 ml/min** flushed the analytes desorbed from the sample into the adsorption tube.

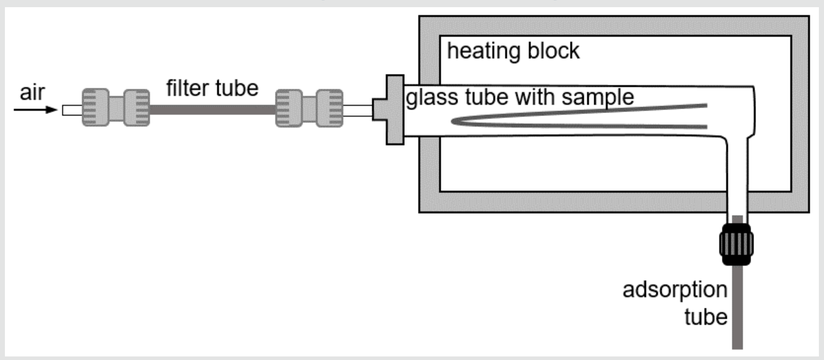


Fig. 2. Thermal desorption (TD) oven for thermal extraction of coatings

Fig. 4. Frying pans and coatings for frying pans

Fig. 3. Baking trays

Thermal degradation of PFECAs and PFCAs [5]

PFECAs are decarboxylated due to thermal exposure in the TD-GC-MS instrument. Thus, there are two peaks in their chromatogram (Fig. 5). This thermal degradation was also observed for the PFCAs (Fig. 6). If a further degradation to perfluoro-1-decene (PFD-1-en) takes place cannot be said, as this coelutes with the first peak of PFUnDA or its already degraded.

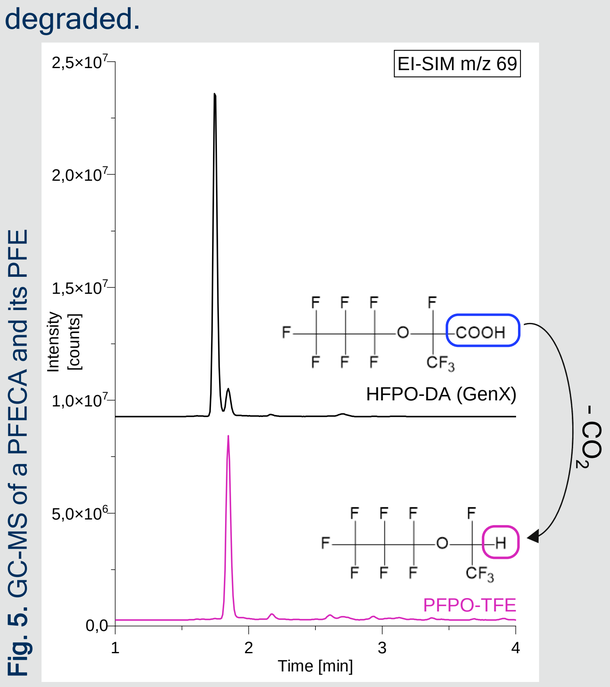


Fig. 5. GC-MS of a PFECA and its PFE

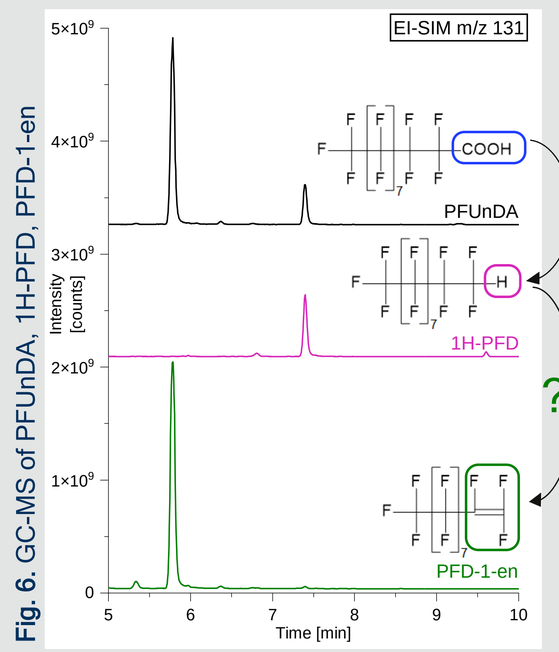


Fig. 6. GC-MS of PFUnDA, 1H-PFD, PFD-1-en

PFECA mix Krytox™ in baking trays [4]

In five baking trays, the PFECA mix Krytox™ was detected (Fig. 7). The PFECAs were almost completely degraded to hydrides by decarboxylation due to thermal exposure. Krytox™ is listed in the Plastic regulation 10/2011 and has been regarded during the evaluation by EFSA as ´non-genotoxic´ [6].

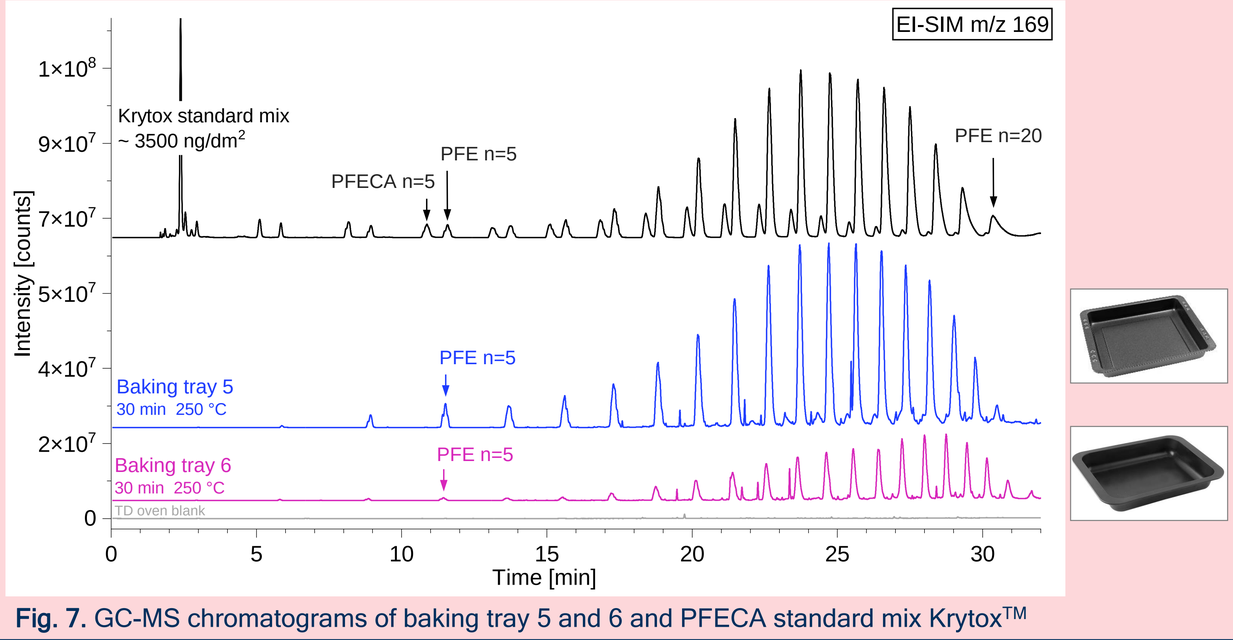


Fig. 7. GC-MS chromatograms of baking tray 5 and 6 and PFECA standard mix Krytox™

PFCAs in a baking tray [4]

In one baking tray, several long chain PFCAs (C_{13} - C_{23}) were quantified in the range of 0.5 to 34.4 ng/dm² (Fig. 8). After a second and third thermal extraction of the coating, no PFCAs were detectable (LOD: 1 ng/dm²).

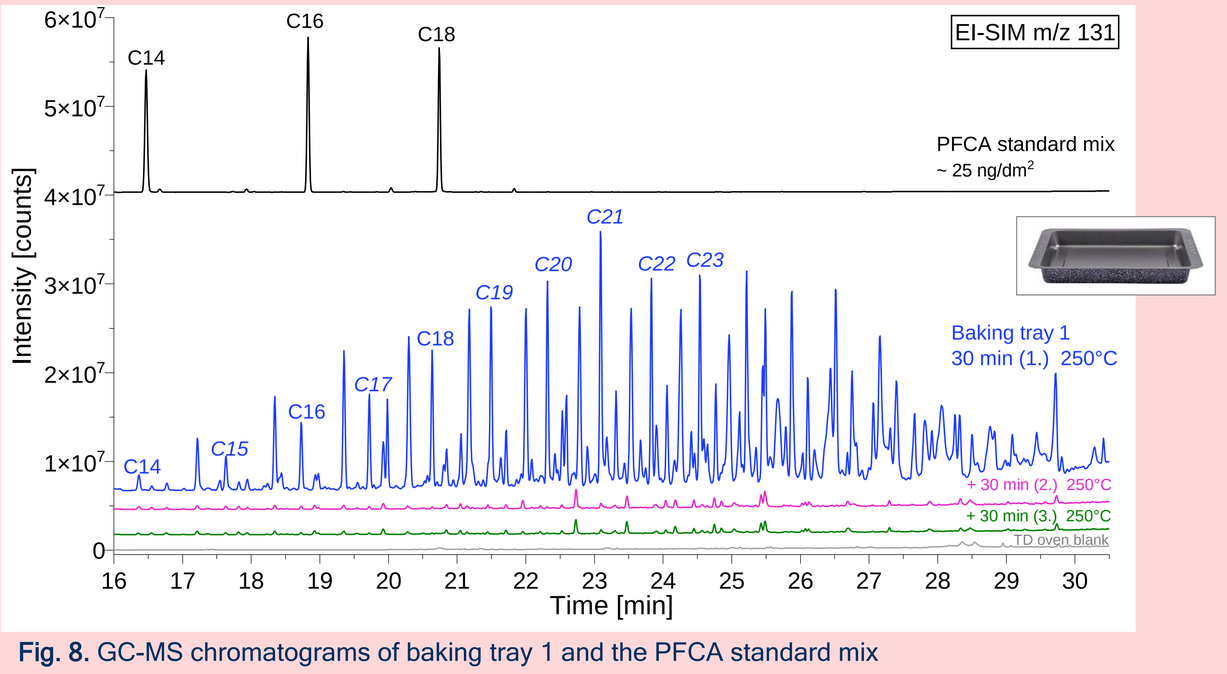


Fig. 8. GC-MS chromatograms of baking tray 1 and the PFCA standard mix

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
[4] Wolf, N. et al. Food Addit Contam – Part A 2024a 41, 1663-1678
[5] Wolf, N. et al. Food Addit Contam – Part A 2024b 41, 1099-1117
[6] EFSA, Scientific Opinion on 24th list of substances for food contact materials, The EFSA Journal (2009) 1157-1163, 1-27.

Acknowledgement
Thanks to the *Federation of European manufacturers of Cookware and cutlery* (FEC) for funding of a subproject.

8th International Symposium on Food Packaging
01/04/2025 – 04/04/2025 Dubrovnik, Croatia