Analysis of PFAS in food contact papers using thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS)

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Introduction

- **Paper and board in contact with liquids, fatty foods or in use at high temperatures** require an **additive or coating** to improve moisture and grease resistance. Frequently, this is achieved by certain resins containing per- and polyfluoroalkyl substances (PFAS) like polyacrylates that are partly esterified with fluorotelomer alcohols (FTOHs), predominantly 6:2 FTOH. [1]
- These papers are used as food contact materials (FCMs) in fast food restaurants, in high temperature contact applications such as **baking paper and muffin cups, and in microwave applications**.
- The aim of this project is to establish a **rapid method for the detection of PFAS in paper** products. Paper samples are tested for **grease resistance** according to DIN 53116 [2]. The paper products that perform grease resistance are then analyzed for the presence of PFAS by **thermal incubation in a 'micro chamber'** and subsequently by **TD-GC-MS**.
- In addition, **alkaline hydrolysis** is tested to release PFAS from hydrolysable grease proof coatings, like ester or urethane bound FTOHs.

Conclusion

- It was possible to **determine residual 6:2 FTOH** in 5 grease proof papers ranging from 5 ng/g to 350 ng/g.
- An **alkaline hydrolysis releases fluorotelomer alcohols**, like 6:2 FTOH, from fluorotelomer poly(met)acrylates and polymeric urethanes in paper coatings. The hydrolyzable **content of 6:2 FTOH was > 10,000 fold compared to the residual content.**
- The hydrolysis method of **Nikiforov (2021)** [3] had a much higher yield of bound FTOH than the fast 'in-situ method'.
- The **'in-situ method'** shall be further optimized gaining a fast detection of bound PFAS in paper products by TD-GC-MS without quantification of those.
- The **BfR XXXVI.** contains even more grease proof additives for paper and board apart from the investigated acrylate ester and urethane: It contains resins with amide and phosphate bound PFAS [1]. These substances will be tested for hydrolysis in the ongoing project.

TD-GC-MS instrument setup [4]

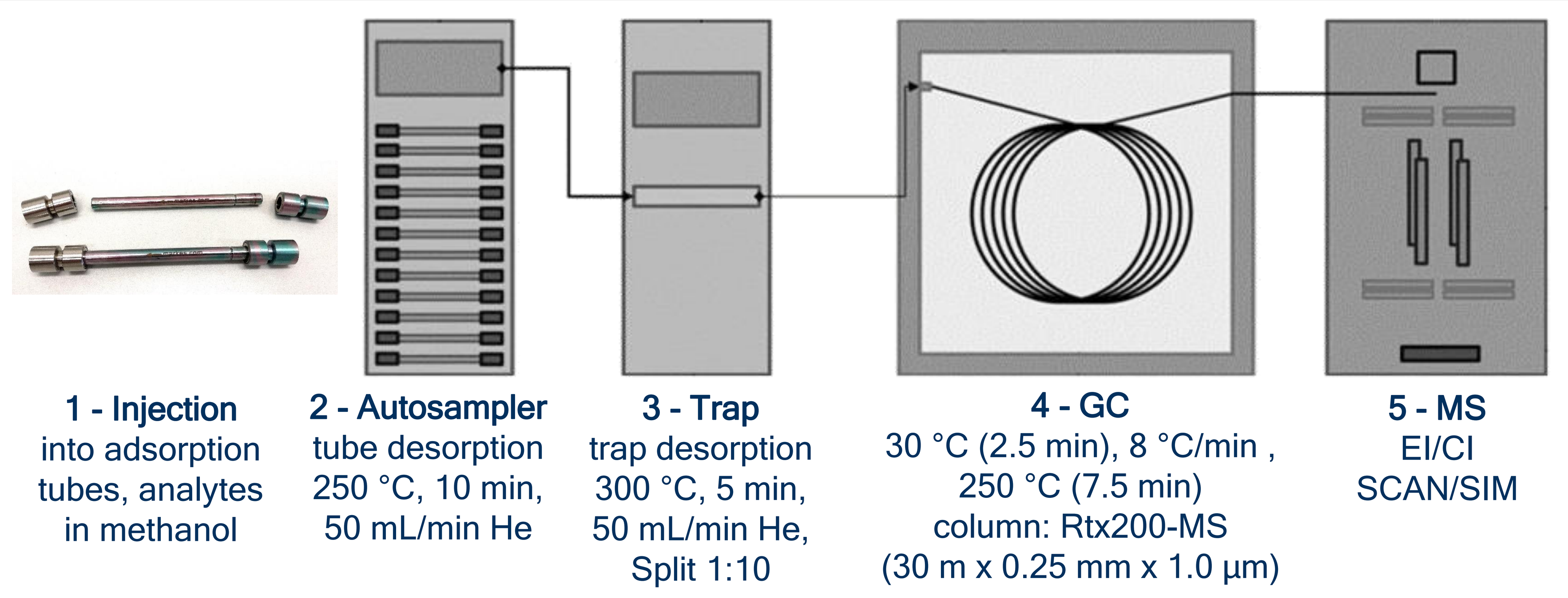
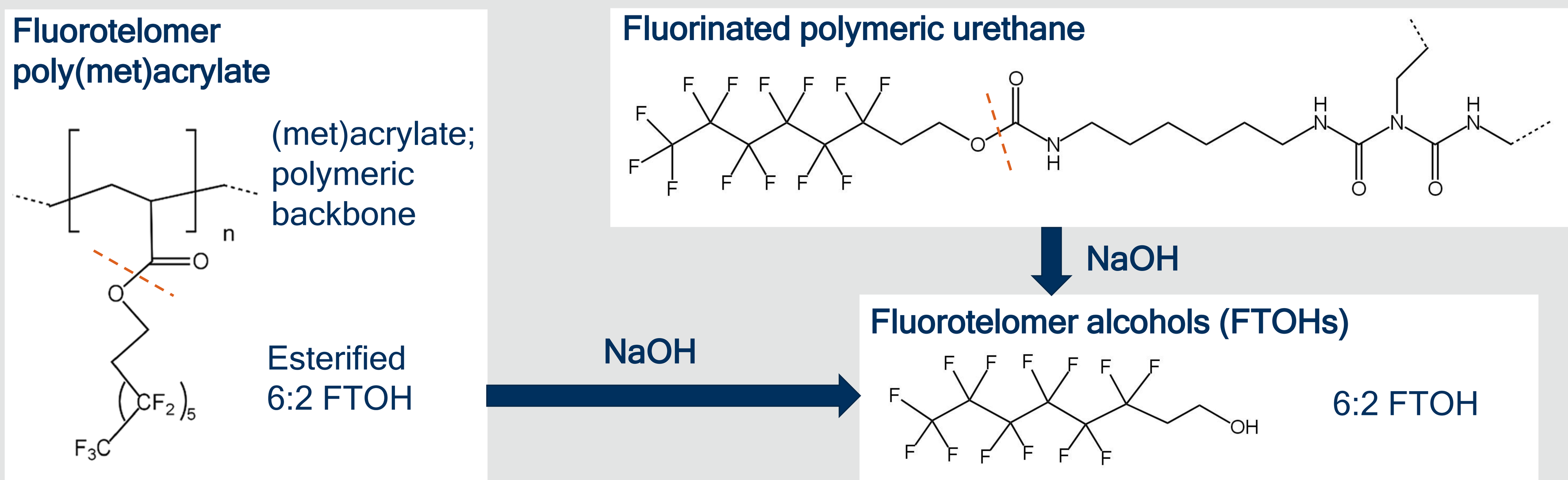


Fig. 1. TD-GC-MS instrument, according to [5] [figure (modified): Materic et al. Appl. Plant Sci.2015, 3, 1500044] **[4]**

Selected analytes

The selection of analytes was based on their use in fluoropolymer-based coatings for food contact papers according to the BfR recommendation XXXVI. [1]. An ester- and a urethane bound FTOH resin was selected for this investigation.



Test for grease resistance of coated papers

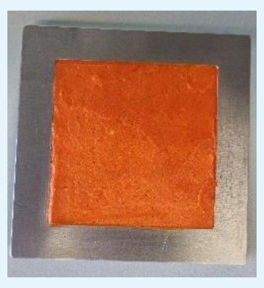
DIN 53116 [2]

This test was used to select food contact papers that reveal a grease resistance. After a positive test this paper is tested for the presence of PFAS.

The **test setup** was modified as shown in Fig. 2. The **six layers** are stacked in a frame with a cut-out (**0**) from bottom to top: glass plate (**1**), foil (**2**), display paper (**3**), paper sample (**4**), template (**5**) and glass plate (**6**).

For detection palm kernel fat coloured with sudan red III (0.1 %) is applied on the sample paper. The grease resistance is then assessed according to the various grease permeability levels:

- V: 10 min without weight
- IV: 10 min with weight (1 kg)
- III: 50 min with weight (1 kg)
- II: 23 h with weight (1 kg)
- I: 24 h with weight (2 kg)



applied palm kernel fat coloured with sudan red III (0.1 %) on the paper sample

The grease resistance is evaluated by judging the fat spots visible on the display paper (3).

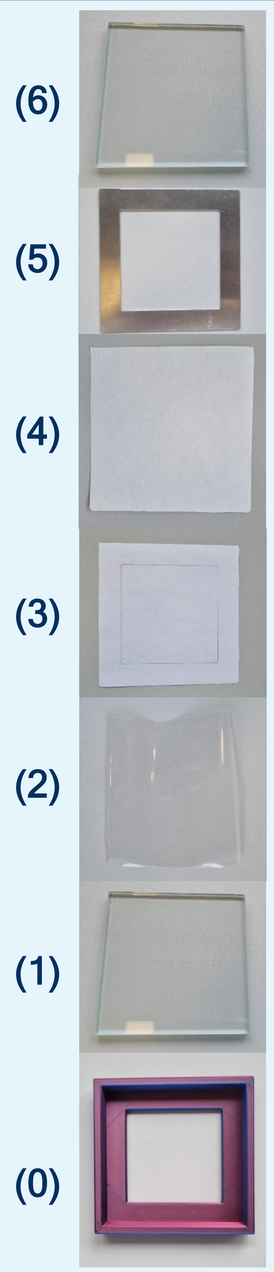


Fig. 2. Test for grease resistance setup (modified), according to [2]

Determination of residual PFAS in paper

Paper samples are thermally incubated in stainless steel bowls in the micro chamber at **90 °C** under a **nitrogen flow of 50 ml/min for 30 min**. The gas emission is collected on adsorption tubes which are subsequently analyzed by TD-GC-MS (Fig. 1). It was possible to detect residual 6:2 FTOH in five out of six paper samples with contents ranging from 5 ng/g to 350 ng/g.

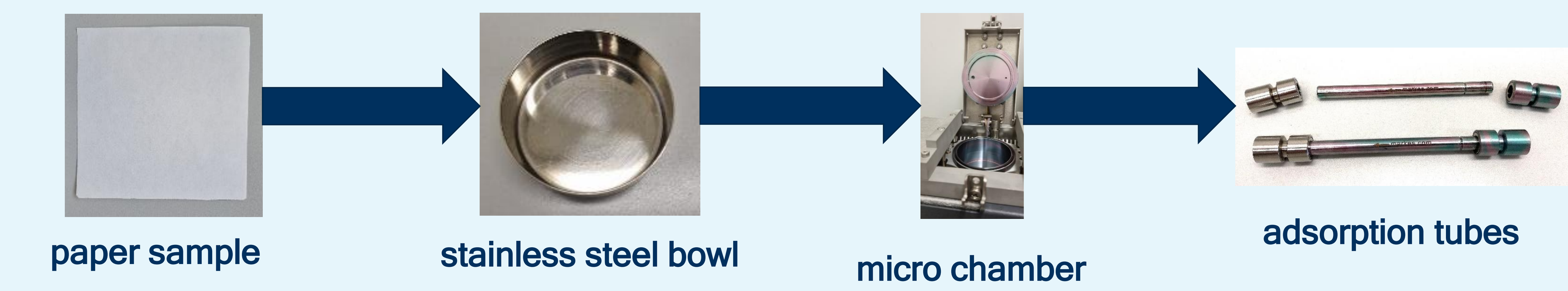


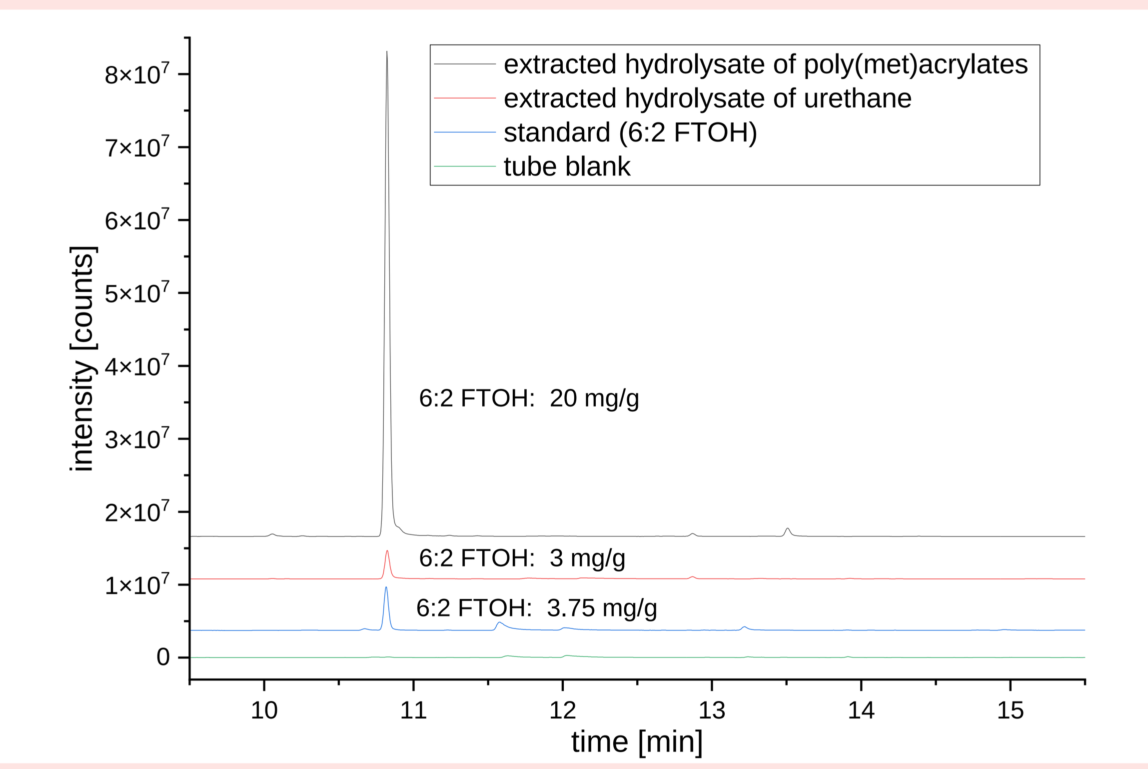
Fig. 3. Procedure of thermal incubation of a paper sample in a micro chamber

Detection of chemically bound PFAS in paper

An '**in-situ extraction**' is tested as a rapid method for the hydrolysis. A paper sample is moistened with methanolic sodium hydroxide solution (1 M) in a stainless steel bowl. The evaporation process takes place in a microchamber at 20 °C under a nitrogen flow of 50 ml/min for 30 min and is collected on an adsorption tube. The treated paper is additionally thermally incubated at 90 °C for 30 min under the same nitrogen flow. The resulting emissions are also collected on an adsorption tube and analyzed by TD-GC-MS (Fig. 1). The contents are calculated via external calibration. For comparison the paper samples are also hydrolyzed according to Nikoforov (2021) [3].

Alkaline hydrolysis of reference materials

The fluorotelomer poly(met)acrylate (BfR No. 25 [1]) and the polymeric urethane (BfR No. 33 [1]) were hydrolyzed with 1 M NaOH in methanol:water (9:1) for 16 hours at 60 °C according to Nikiforov (2021) [3]. The hydrolysate was then extracted with a n-hexane/tertbutyl methyl ether mixture (1:1) and was measured by the TD-GC-MS (Fig. 4).



It was possible to confirm the hydrolysis and therefore release of esterfied or bound 6:2 FTOH from fluorotelomer poly(met)acrylates and fluorinated polymeric urethanes.

Fig. 4. Chromatogram of the hydrolyzed standards according to Nikiforov (2021), EI-SIM 95

Alkaline hydrolysis of coated food contact paper

For a paper sample the '**in-situ extraction**'/TD-GC-MS determination (Fig. 5) was compared with the hydrolysis performed after **Nikiforov (2021)** (Fig. 6) [3]. In both cases 6:2 FTOH was detectable > 10,000-fold compared with the residual content. However, the Nikiforov hydrolysis had a much higher yield than the 'in-situ method' (1130 µg/g vs. 174 µg/g). Further hydrolysis and optimisation studies are underway.

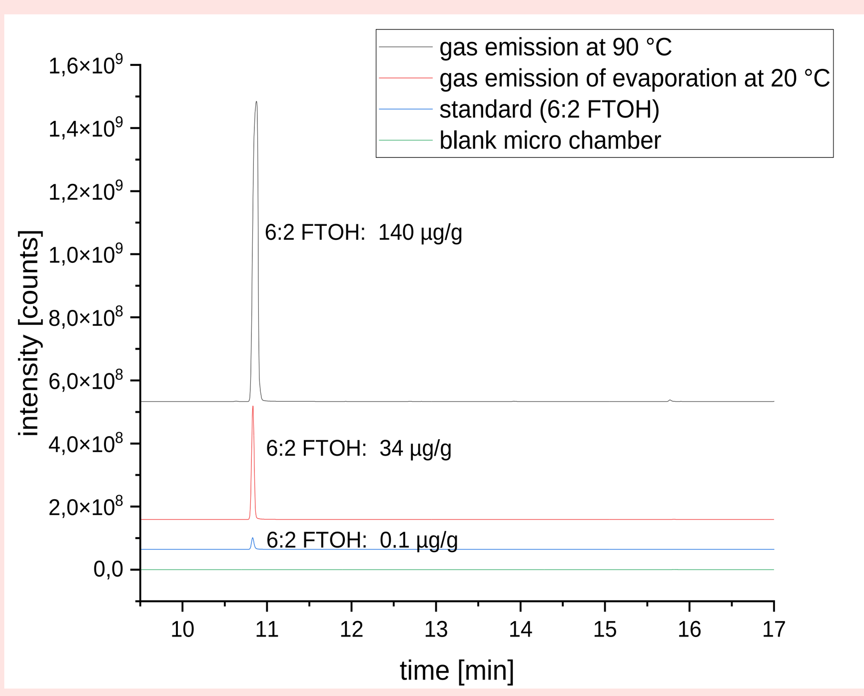


Fig. 5. Chromatogram of the emissions of the in-situ hydrolyzed paper at 20 °C and at 90 °C, EI-SIM 95

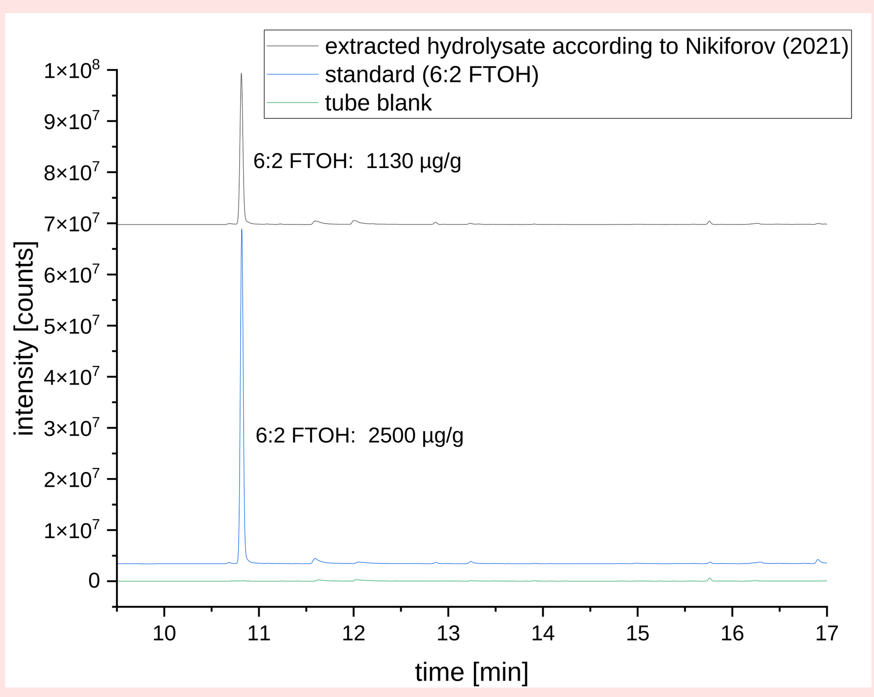


Fig. 6. Chromatogram of the extract of the hydrolyzed paper according to Nikiforov (2021), EI-SIM 95

Literature

[1] Bundesinstitut für Risikobewertung (BfR) (2023). XXXVI/1. Papiere, Kartons und Pappen für den Lebensmittelkontakt.
[2] DIN 53116, Prüfung von Papier - Bestimmung der Fettdurchlässigkeit, 2003.
[3] Nikiforov, V. A. (2021) Hydrolysis of FTOH precursors, a simple method to account for some of the unknown PFAS. Chemosphere, 276, S. 130044.
[4] Wolf, N. et al. Food Addit Contam - Part A 2024b 41, 1099-1117
[5] Markes international 2021, Application Note 158

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