MIGRATION OF FLUORINATED TELOMER ALCOHOLS (FTOH) FROM FOOD CONTACT MATERIALS INTO FOOD AT ELEVATED TEMPERATURES

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Introduction

Perfluorinated alkylated substances (PFAS), persistent and partly bioaccumulative compounds, have been identified in our daily diet, including perfluorinated carboxylic acids (PFCA) and perfluorinated sulphonic acids (PFSA) [1]. As several authors found PFOS and PFOA levels to 3500 ppb in paper-based food packaging with oleophobic coatings, it was discussed that a transfer of these compounds from packing into packed food items may contribute to overall PFAS levels in diet[2, 3]. In addition to PFCA and PFSA, fluorinated telomer alcohols (FTOHs) have been identified in paper-based packaging[4], with 10- to 100-fold higher levels than PFCA and PFSA. Since FTOH are well-known precursor substances for PFCA, these precursors may add to PFCA levels in our diet or end up in human tissues, if degradation does not start before ingestion.

According the German Bundesinstitut für Risikobewertung (BfR) there are about ten fluorine-based materials for grease-proof papers and cardboards, used for food contact materials. Their molecular masses range from around 1000 to over 100000 Daltons. These coating materials contain side groups based on FTOHs, which can potentially split off and furthermore degrade into PFCAs. The probability of such reactions increases with increasing temperatures, and, thus, paper-based baking aids with oleophobic surface treatment may be critical food contact materials.

Therefore, the aim of the present work was to investigate the migration of FTOH from paper-based baking aids into real food samples at defined parameters (temperature, time). Besides dough, butter and Tenax (a food stimulant for dry and fatty foods) were studied. Butter was chosen in order to compare the migration behaviour with similar studies carried out with fluorine containing packaging materials at ambient temperatures and at 4°C.

Materials and methods

At first, fluorine-positive muffin papers were identified by using sliding spark spectroscopy and Headspace GC/EI-MS as described elsewhere[4]. Then, methanol extracts of the muffin papers were subjected to FTOH specific analysis based on GC/CI-MS[4, 5] and quantified with isotope-labeled standards of 4:2-, 6:2-, 8:2- and 10:2-FTOHs.

13 migration tests with muffin paper were accomplished at oven temperatures as specified in Table 1. So self-made muffin doughs, differentiating in composition, two types of butter from the German market and Tenax were used for migration tests from 120 to 220 °C for 5 to 60 minutes. Butter 1 was packed in fluorine free butter wraps, whereas butter 2 had been exposed to FTOH containing butter wraps after production. While butter and muffin doughs are real food samples normally used at temperatures up to 150 °C (butter) and up to 220 °C (muffin), Tenax is an accepted simulant for high temperatures in general (Plastics Implementation Measure, (EG) Nr. 10/2011).

Petri dishes were applied for migration tests with butter and glass vials, closed by safety caps, for Tenax experiments. Muffins were prepared as usual by filling up the whole muffin mould with dough.

After migration contact, muffins were homogenized and sub samples of about 3g were fortified with isotope-labelled standards mentioned above and extracted with n-hexane by pressurized liquid extraction (ASE 200, Dionex, Germany), prepared with Teflon®-free equipment. In contrast, butter and Tenax samples were extracted with n-hexane by vortexing and ultrasonic bath after fortification with labeled standards. Afterwards, the n-hexane extracts were cleaned by solid phase extraction using silica as adsorbent (Phenomenex Strata Si-1). Reduced extracts were subjected to GC/CI-MS (TSQ 7000, Thermo) analysis using methane for chemical

ionisation. The quantification of the analytical apparatus was carried out by an isotope dilution method. Using the same analytical approach Tenax, both types of muffin dough and butter were analysed for FTOH blanks.

Tab. 1: Migration parameters and food item/simulants chosen for migration trials at elevated temperatures

temperature [°C]	time [min]	food item/ simulant	temperature [°C]	time [min]	food item/ simulant
120	15	butter	200	10	muffin dough 2
150	5	butter	200	20	muffin dough 1
150	10	butter	200	20	muffin dough 2
150	15	butter	200	30	muffin dough 2
180	30	muffin dough 2	220	20	muffin dough 2
180	40	muffin dough 1	220	60	TENAX®
180	40	muffin dough 2			

In order to understand the FTOH transfer in more detail, a further set of experiments was carried out: Muffin paper, and both butter types were separately analyzed for FTOH, in each case before and after exposure to 150° C for 15min. In addition, butter previously exposed to muffin paper at 120 °C for 15 min in the first set of trials was heated up a second time to 150 °C for 15 min and analyzed as described above.

Results and discussion:
Results of migration tests with two types of muffin dough are presented in Figure 1. With exception of muffin dough 2 exposed to 200° C for 20 min, FTOH concentrations in muffin dough 2 were lower than levels in muffin dough 1 and lower than the initial value of the specific FTOH in the muffin paper, indicating at a transfer of less than 20% of FTOH initially present in the baking aid. However, dough 1 and in one case dough 2 (200° C, 20 min) exhibited levels significantly higher than the initial values in he paper. Since blank levels in muffin doughs were low, these data point to a production of FTOH from precursor compounds. Migration levels for dough 1 are independent on the exposure time. In contrast, the values for all FTOHs for muffin dough 2 arise with higher temperature and longer time with highest levels at 200 °C for 20 min. Further increase of time or temperature resulted in a rapid decline.

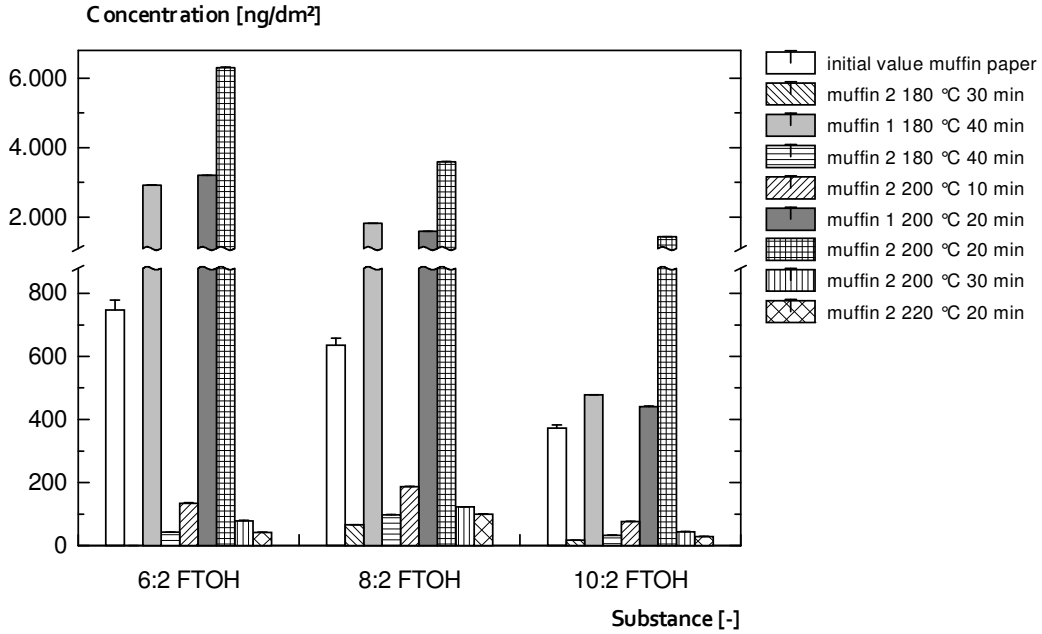

Fig. 1: Migration of FTOHs from muffin paper into several muffin doughs at given temperatures and times

A reason for this behavior may be the difference in humidity. Muffin dough 1 is a dry and low-fat version of dough 2. Caused by the quicker evaporation, temperatures in the muffin crust rise fast to more than 100 °C. So FTOHs are initiated to quickly migrate into the muffin (boundary surface paper-muffin). As the conditions for dough 1 don't seem to be so various, there is no obvious modification of values.

As dough 2 has higher humidity, values firstly raise and with continuous evaporation FTOHs quickly volatilize into the gaseous phase and the amounts in the muffin dough decrease.

Figure 2 shows the results of the migration tests with butter and Tenax. As seen in the results of the muffin migration experiments, values for butter raise unto 150 °C 5 min and decrease with higher conditions, excepting for 10:2 FTOH, which increases only slightly with exposure time. The most significant result is, that all values of every FTOH overtop the initial values of the muffin paper, again indicating at a reproduction of FTOHs from precursor compounds.

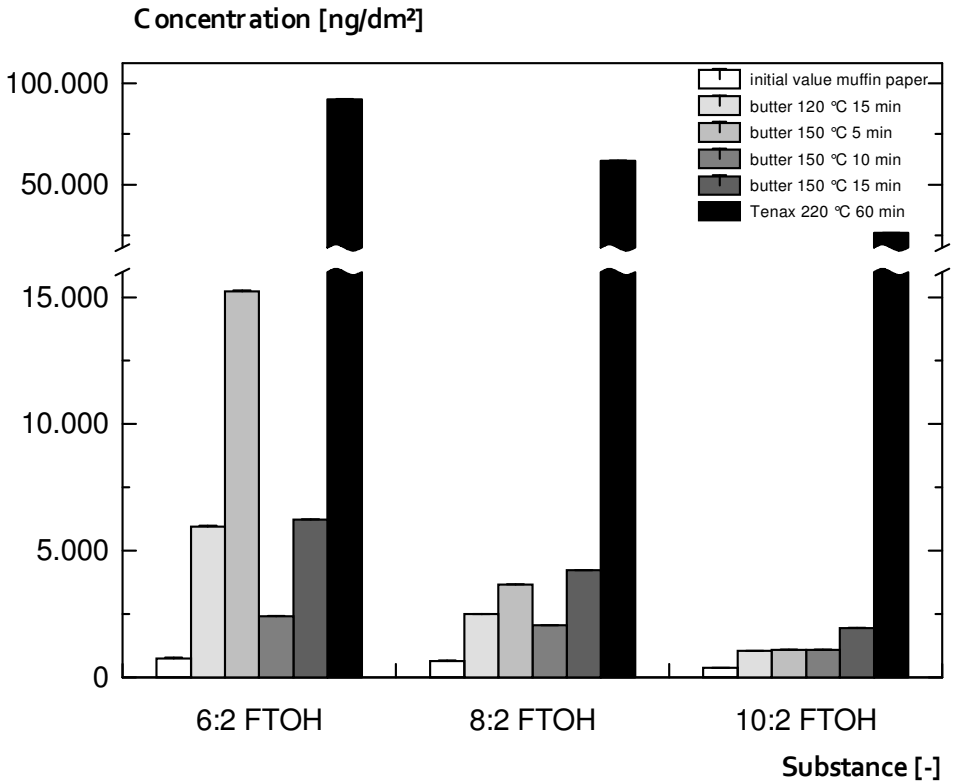

Fig. 2: Migration of FTOHs from muffin paper into butter and Tenax at defined temperatures and times

Figure 3 displays the investigated samples for a better understanding of FTOH levels, increasing the initial amounts in the applied food contact materials. Whereas there is almost no change in FTOH levels for butter and paper alone at temperatures of 150°C, butter previously exposed to muffin papers exhibits significantly higher levels following another heat exposure. Thus, it is concluded, that precursor compounds have migrated into the butter during the first heat exposure and delivers further FTOH by degaradtion during the second heating phase.

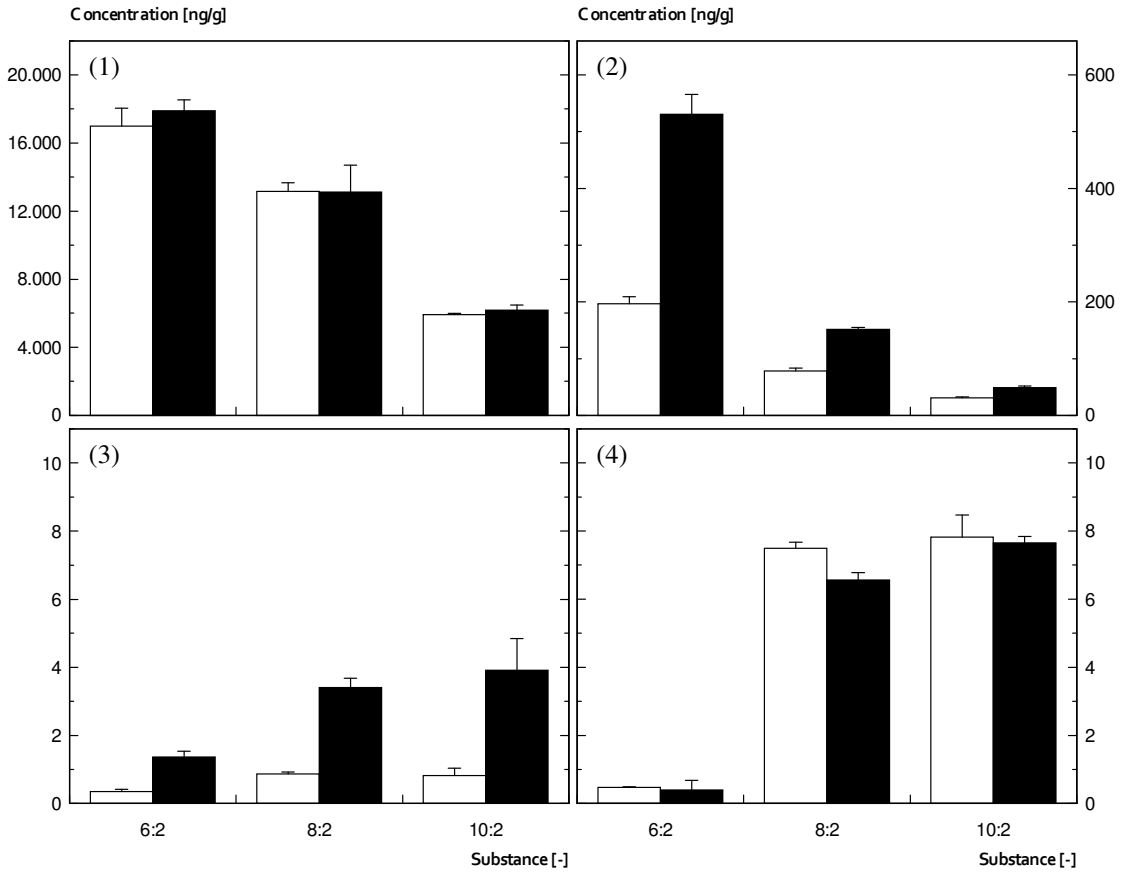

Fig. 3: Investigation of reproduction in pure muffin paper (1), butter from migration with muffin paper at 120 °C for 15 min (2), pure *Bergbauer* butter (3), pure *Kerrygold* butter (4); White bar: not heated; black bar: heated

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