Migration of poly- and perfluorinated compounds from food contact materials into food – Part I

Ludwig Gruber, Martin Schlummer, Romy Fengler

Fraunhofer Institute for Process Engineering and Packaging IVV, Freising, Germany
Part I
Ludwig Gruber (Fraunhofer IVV):
Migration of poly- and perfluorinated compounds from food contact materials into food
* Screening for fluorinated compounds
* Migration at ambient temperature
* Migration at elevated temperature
* Formation of FTOH from precursors

Part II
Jutta Tentschert (BfR):
Actual situation: Poly- and perfluorinated compounds for food contact materials
F-Screening methods for FCM

Surface spectrometry
• Sliding spark spectrometry
• WDXRF (new)
• neg: EDXRF and FTIR

Volatile fluorinated Compounds
• HS-GC-(EI)-MS
• P&T-GC-EPED

Screening samples (n=123)
Results of F-Screening

See: Fiedler et al.: Poster A05

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Per- and polyfluorinated compounds in food contact material

See:
PFAS levels in food contact material

Fluorine containing coatings
- e.g. PAPS
- 0,2 % F (surface)
- ~100 µg/dm²

Precursors
- FTOH dominate
- up to 10 µg/dm²
- 8:2 dominating congener

PFCA
- nn - 900ng/g
- broad spectrum
- No fixed ratio of ΣFTOH/ΣPFCA
What is migration?

Migration: \( C_{p,t=0} \)

Packaging

Diffusion

Partition

Food

Diffusion

\( C_{food,t} \)
Development of migration methods

Refrigerator (16 tests)
- Long-term storage 1 – 30 days
- Low temperature (5°C)
- 3 food items, 4 simulants

Ambient conditions (8 tests)
- Medium-term storage 1 – 10 d
- Ambient temperature (20-40°C)
- 3 food items, 1 simulant

Fast-Food Restaurant (8 tests)
- Short-term storage up to 30 min
- Elevated temperature (60-80°C)
- 1 food items, 1 simulant

Oven (11 tests)
- Short-term heating 10 – 120 min
- High temperatures (180-250°C)
- 3 food items, 1 simulant

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Muffins were homogenized and sub samples of about 3g were fortified with isotope-labelled standards and extracted with n-hexane by pressurized liquid extraction (ASE 200, Dionex, Germany), applying Teflon®-free equipment.

Butter and Tenax samples were extracted with n-hexane by vortexing and ultrasonic bath after fortification with labeled standards. Afterwards, the extracts were cleaned by solid phase extraction using silica as adsorbent (Phenomenex Strata Si 1). Reduced extracts were subjected to GC/CI-MS analysis (TSQ 7000, Thermo) using methane for chemical ionisation.

Quantification 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.
FTOH-Migration at ambient temperature

Ambient T

FTOH_{Butter} > FTOH_{Tenax}
PFCA-Analysis of migration samples

**Muffins, Butter** and **Tenax** samples were extracted with methanol by using an ultrasonic bath after fortification with labeled standards.

Extracts were cleaned by solid phase extraction using a weak ion exchanger as adsorbent (Phenomenex Strata XAW) and analyzed with HPLC-ESI-MS (Waters Quattro LC).

Quantification was carried out by an isotope dilution method. Using the same analytical approach Tenax, both types of muffin dough and butter were analysed for blanks.
PFOA-Migration at ambient temperature

- PFOA migrates into Tenax
- Migration depends on time and temperature
- Blank levels are an issue to be solved

Migration of PFOA from butter wrap into food simulant Tenax

Mid term meeting PERFOOD, June 7, 2011
**Migration conditions at elevated T**

<table>
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<tr>
<th>T [°C]</th>
<th>time [min]</th>
<th>food item/ simulant</th>
<th>T [°C]</th>
<th>time [min]</th>
<th>food item/ simulant</th>
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<tr>
<td>120</td>
<td>15</td>
<td>butter</td>
<td>200</td>
<td>10</td>
<td>muffin dough 2</td>
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<td>200</td>
<td>20</td>
<td>muffin dough 1</td>
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<td>10</td>
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<td>180</td>
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<td>muffin dough 2</td>
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</tr>
</tbody>
</table>
FTOH-Migration at elevated T

![Graph showing concentration of FTOH migration at different temperatures and times for 6:2, 8:2, and 10:2 FTOH substances.

- **Initial Value Muffin Paper**
- **Muffin 2 180 °C 30 min**
- **Muffin 1 180 °C 40 min**
- **Muffin 2 180 °C 40 min**
- **Muffin 2 200 °C 10 min**
- **Muffin 1 200 °C 20 min**
- **Muffin 2 200 °C 20 min**
- **Muffin 2 200 °C 30 min**
- **Muffin 2 220 °C 20 min**

The graph shows the concentration [ng/dm²] of FTOH migration for different substances and conditions.
FTOH-Migration at elevated T

Concentration [ng/dm²]

ng/dm²

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Substance [-]
Daily Intake?

Simplified calculation example:

A migration/formation of

\[ 10,000 \text{ ng/dm}^2 \sum \text{FTOH} \]

equates to a daily Intake of

\[ 1,000 \text{ ng } \sum \text{FTOH} / \text{kg b.w.} \]

Assumptions (Conventional approach):
- EU cube (6 dm², 1 kg food)
- Consumption of 1 kg food
- 60 kg bodyweight
Formation of FTOH from precursors

Migration at elevated T

- Precursor transfer upon baking
- FTOH-Formation from precursors in the food
  - ppm levels
  - most likely hydrolysis
- Found Precursors now identified as diPAPs. Work is ongoing.

Results after another heating

White before, black after another 15 min @ 150°C

- Pure muffin paper (1)
- Butter previously in contact with muffin paper at 120 °C for 15 min (2)
- Pure butter 1, contaminated from butter wrapper (3)
- Pure butter 2, from diPAP-free butter wrapper (4)
Precursor migration into food

• No change in FTOH levels for butter and paper, treated separately with temperatures of 150°C
• Butter previously exposed to muffin papers exhibits significantly higher levels following a second heat exposure.

→Precursor compounds have migrated into the butter during the first heating process and delivers further FTOH by degradation during the second heating phase.
Summary

• Butter and Tenax are appropriate food simulants at ambient temperatures.
• Butter, Tenax and also some doughs are appropriate food simulants for elevated temperature.
• Migration experiments at elevated temperatures show formation of FTOH from precursors (diPAPs) orders of magnitude higher then initial FTOH values.
Acknowledgements:

This study was part of the EU project PERFOOD (KBBE 227525) and the financial support of the European Union is gratefully acknowledged.

Thank You for your attention!