Migration of Perfluorochemicals From Food Contact Materials

Tim Begley
Office of Regulatory Science
Center for Food Safety and Applied Nutrition
Food and Drug Administration

Why are we interested in perfluoro chemical migration?

- Perfluoro chemicals found in human serum (Olsen et al. 1999) . Occupational exposure.
- May 2000, 3M Company announce phase out of perfluorooctyl chemistry.
- August 2002, marine mammals, fishes and birds (Kannan et al. Environ. Sci. Technol.)
- Elderly in Seatle WA are found to have perfluoro chemicals in their serum (Olsen et al. 2003) .

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Why are we interested in perfluoro chemical migration?

- PFOA is biopersistent / bioaccumulative
- Half-life in human serum may be 4.4 years (Butenhoff et al. 2004).
- Potential concerns for carcinogenesis; developmental/reproductive and immunotoxic.
- Many fluorochemicals regulated for food-contact contain PFOA as an impurity and/or have chemical moieties similar to PFOA.

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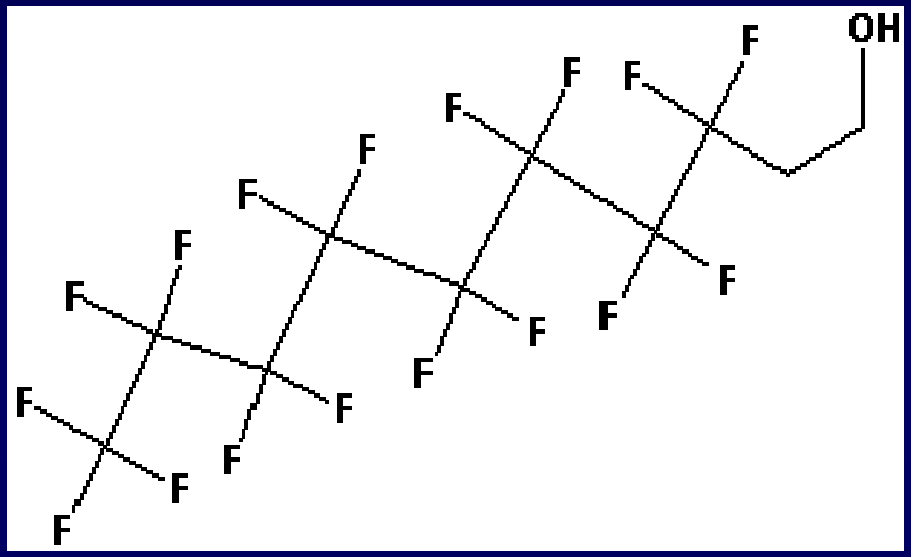
2-perfluorooctylethanol or (8:2 telomer alcohol) has been shown to biodegrade to PFOA



Perfluorooctanoic acid = PFOA

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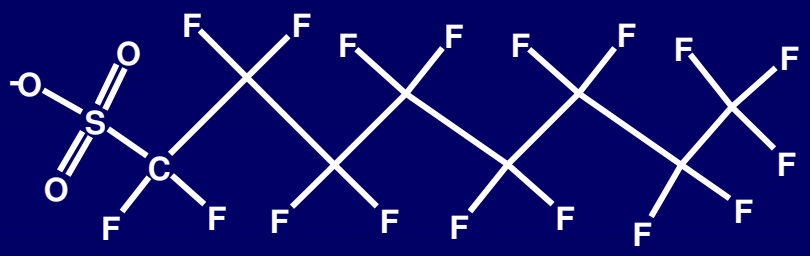
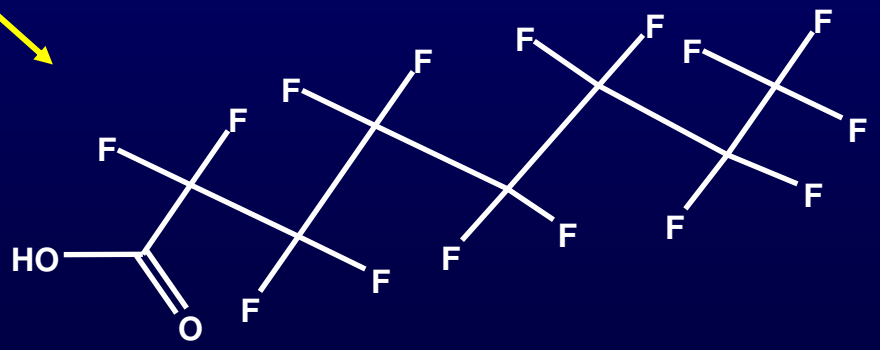
Dinglasan, M.J.A., et al., 2004, Environmental Science and Technology, 38, 2857-2864.

Structures of perfluorochemicals found in human serum

- Perfluoroocatanesulfonate = PFOS



- Perfluorooctanoic acid = PFOA



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Typical Commercial Products Potentially Made with Fluorochemicals

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Food package types that contain fluorochemicals

Polymers

cookware
tubing
gaskets

Paper

microwave popcorn
muffin bags
french fry bags
pizza liners
sandwich wrappers
burger/pizza boxes

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Historical Regulation in the USA

- 1962 PTFE for cookware
- 1984 perfluorochemical elastomers

- 1958 paper coatings (prior-sanctioned)
- 1962 1st paper coatings (petition)

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Where are perfluorochemicals for paper regulated?

- In US approximately 15 materials are regulated
- BfR also has a number of perfluoro chemicals regulated

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Types of perfluorochemicals added to food contact paper

- **Perfluoro telomer type**

  C_6 C_8 C_{10} C_{12} C_{14} based

- **Polymeric type**

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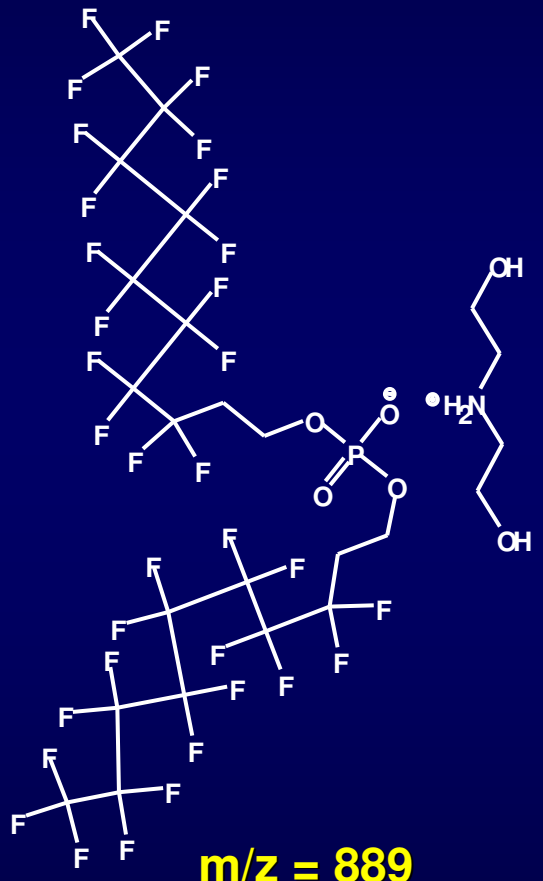
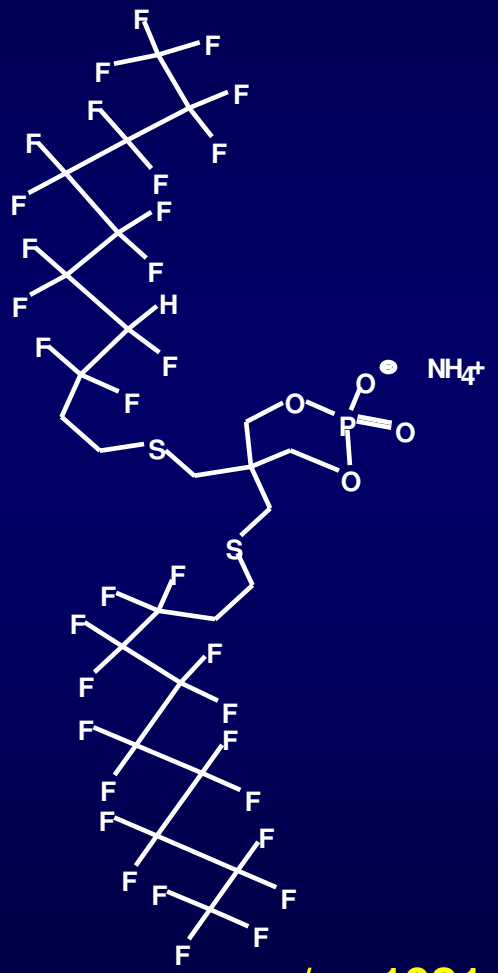
Typical structures of perfluoro telomer based paper coatings



m/z = 889



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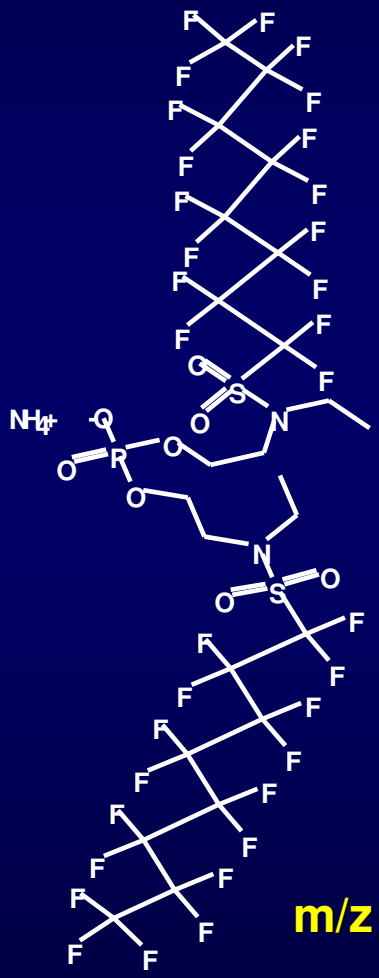

m/z 1202

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Analysis of PTFE Cookware for PFOA

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Summary of PFOA analysis of some polymers

Material	Conc. PFOA µg/kg
PTFE Cookware	4-75
Dental Floss	3
Dental Tape	4
PTFE Sealant Tape	1800
FEP Tubing	ND

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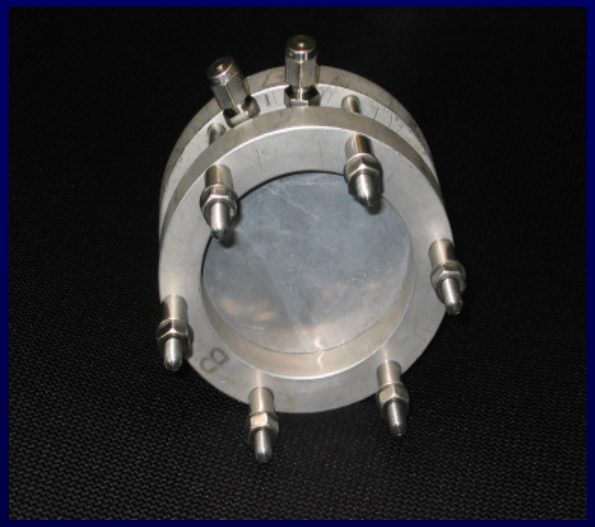
Does PFOA migrate from PTFE during cooking?

- Use PTFE sealant film for migration test.
- PTFE film has C_{p0} = 1.8 mg/kg
- Test for migration at 100°C and 175°C into water and oil.



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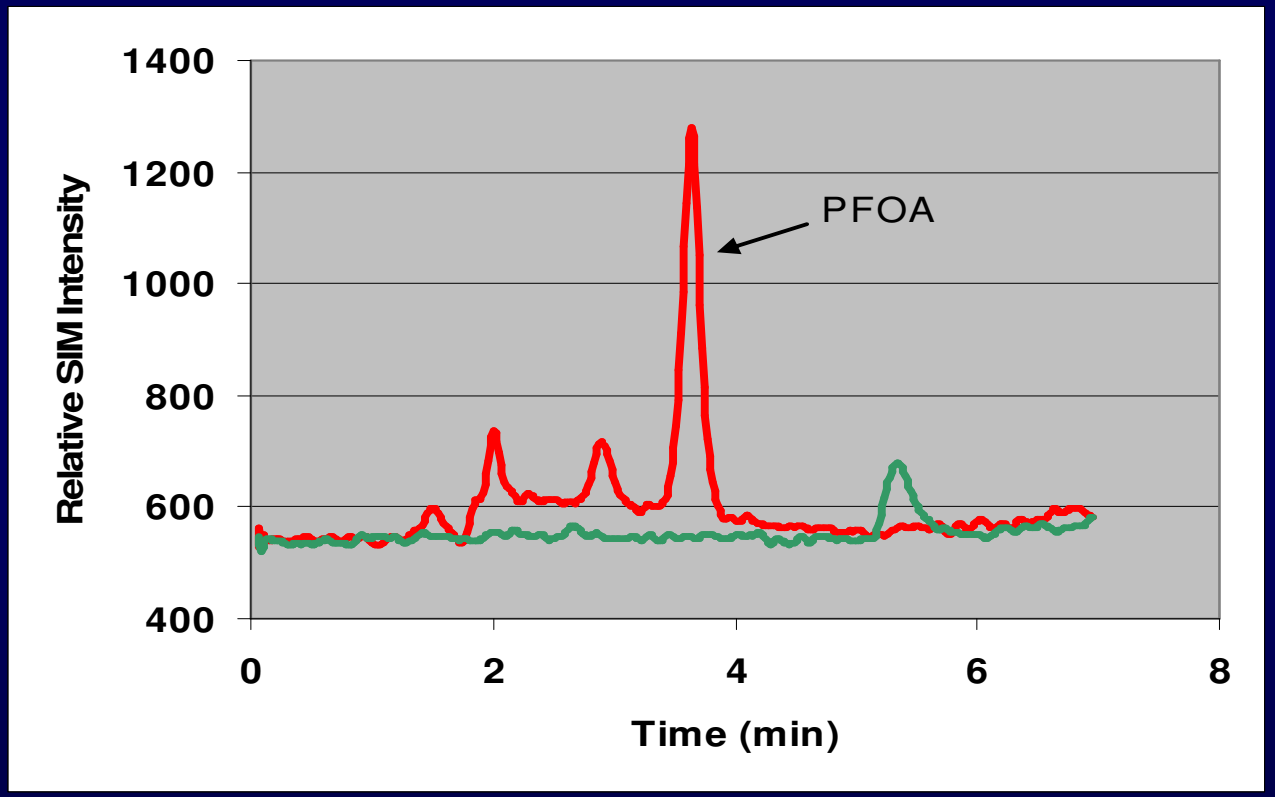
Typical LCMS analysis for PFOA migrating from PTFE into Miglyol at 100°C



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Migration of PFOA from PTFE sealant film after 2hrs at cooking temperatures

		M_t (PFOA)
100℃	Water	150 ng/dm^2 (1.6 ± 0.4µg/kg)
	Miglyol	120 ng/dm^2 (1.3 ±.07 µg/kg)
175℃	Miglyol	710 ng/dm^2 (7.7± 0.1 µg/kg)

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Fractional PFOA Migration from PTFE

- Fractional Migration oil at 175°C M_t/M_∞= 17%
- Fractional Migration water at 100°C M_t/M_∞= 4%

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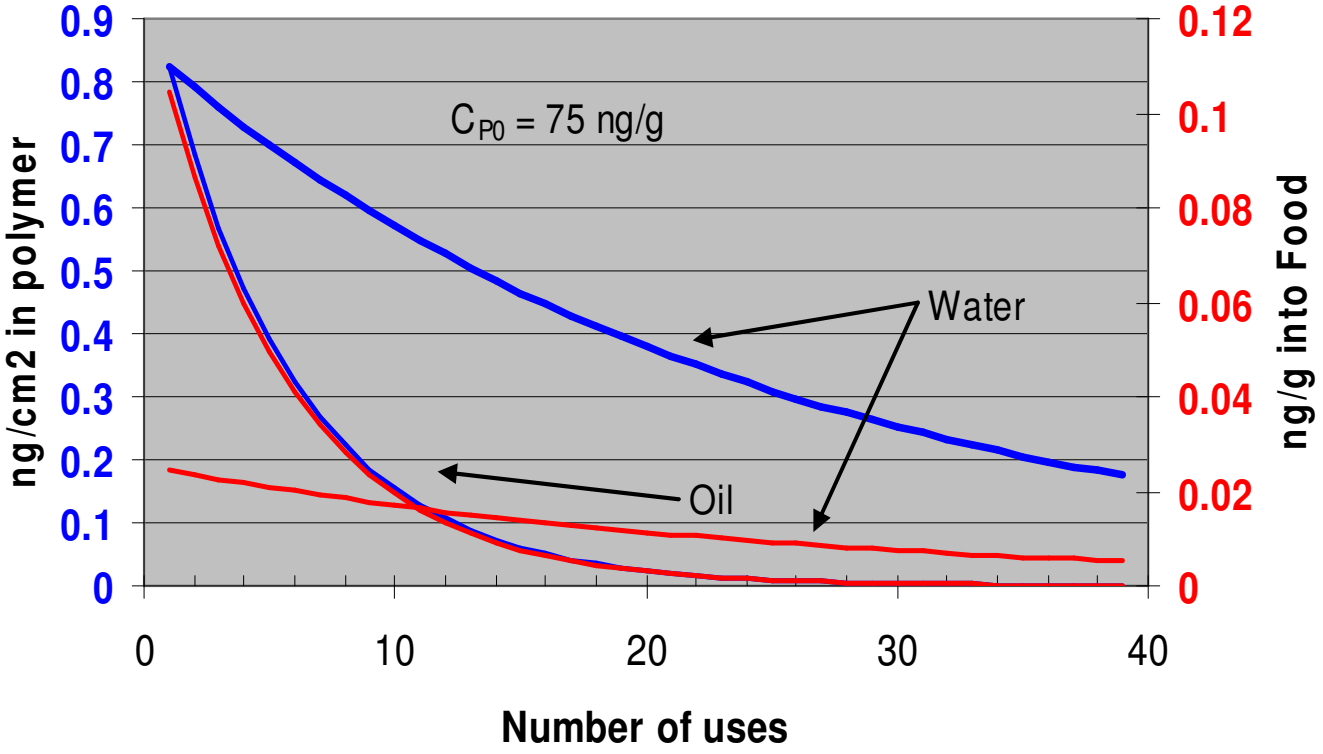
Simulated Loss of PFOA from Cookware based on Fractional Migration, Potential Values



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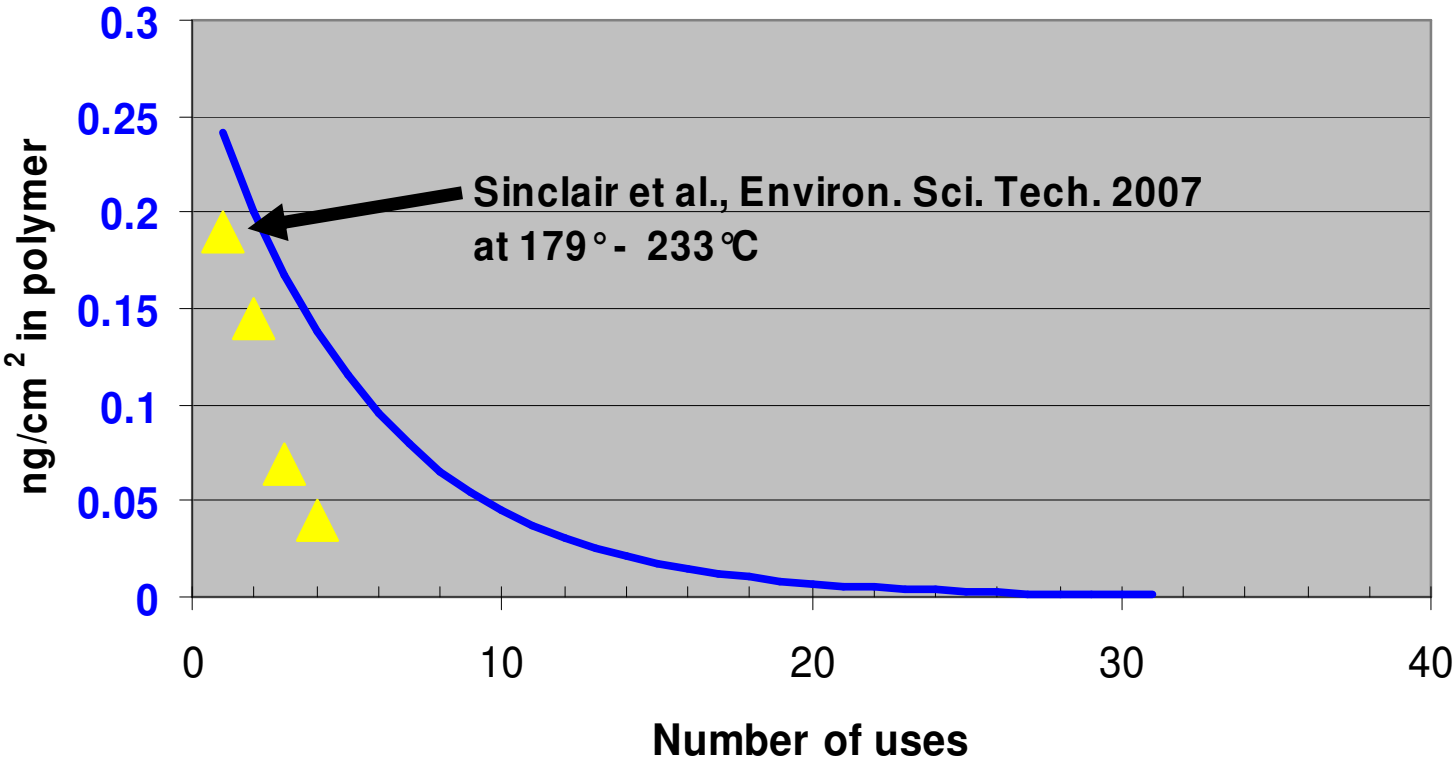
Simulated Loss of PFOA from Cookware based on Fractional Migration, Potential Values



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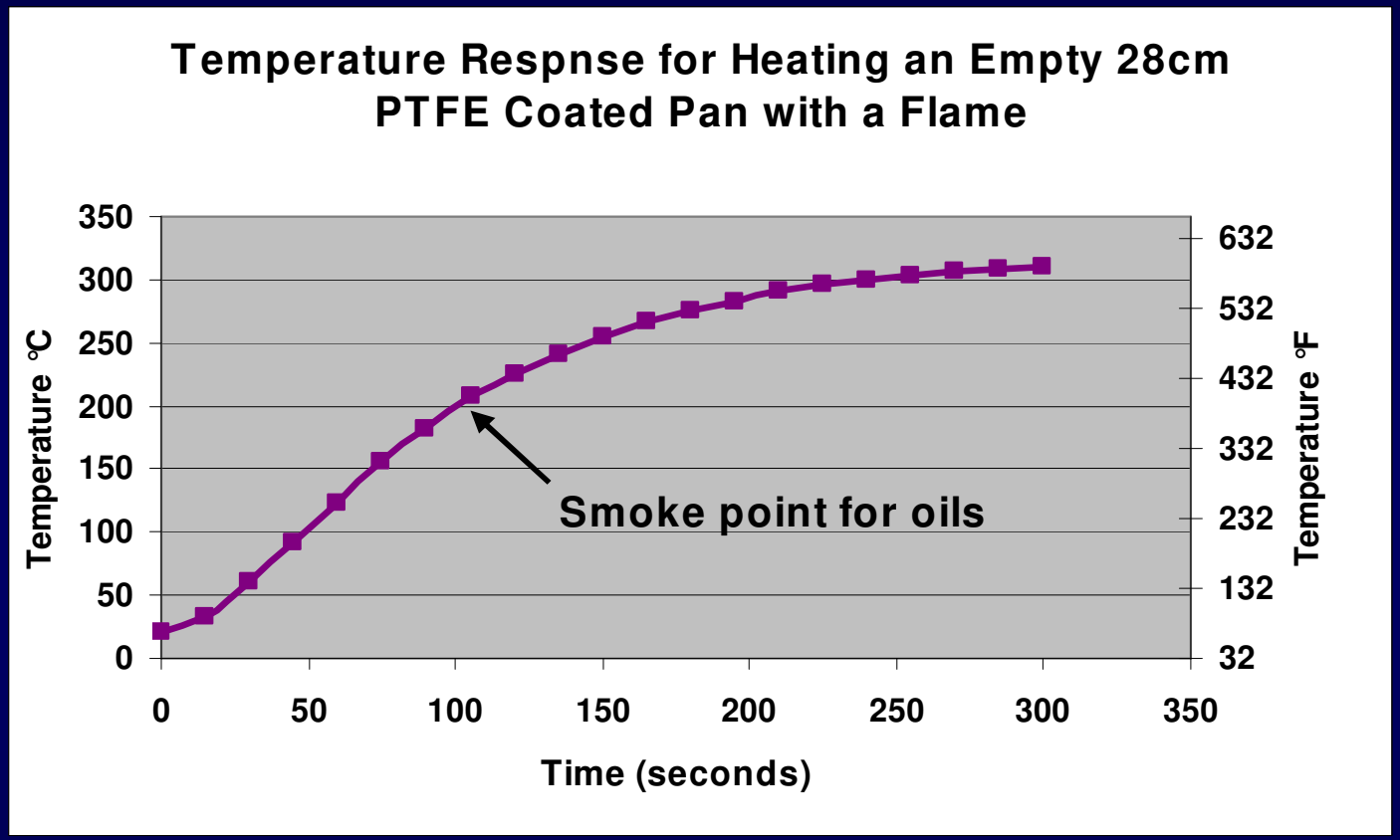
Does PTFE Degrade to PFOA at High Temperature?



- FDA, No detectable increase in PFOA in PTFE
- Sinclair et al., Environ. Sci. Tech. 2007, No PFOA

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Fluorochemicals for Food Contact Paper

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Fluorochemical Paper coatings

- Fluorochemical paper concentrations can be up to 0.5% or 5000 mg/kg.
- Temperature range for paper applications -5℃ – 200+℃.
- Most perfluoro telomer based paper treatments have molecular weights >1000 but the molecular size is similar to much smaller molecules.

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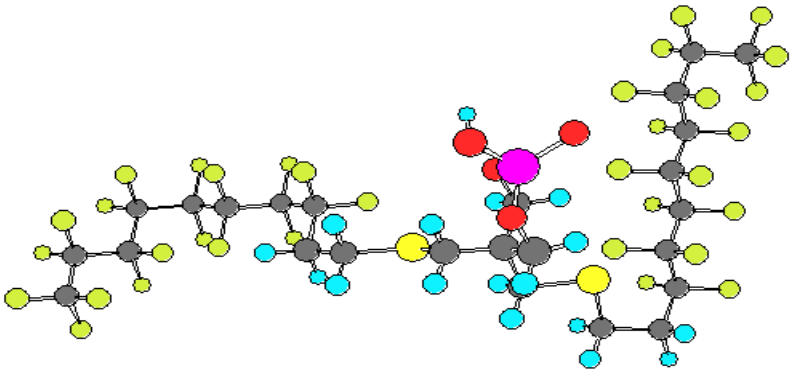
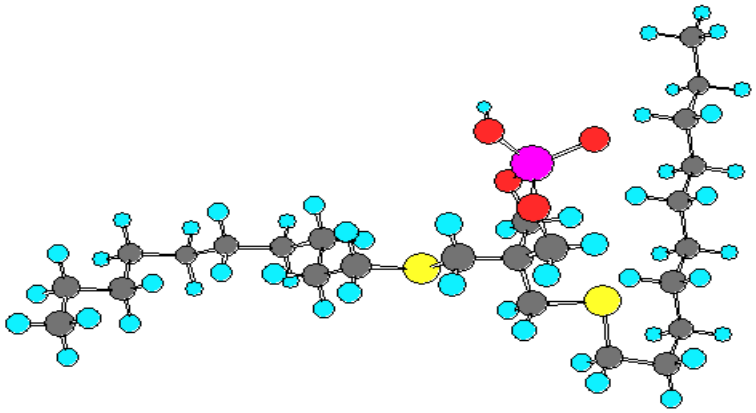
Migration of chemicals with MW > 1000 ?

F versus H



MW = 1121



MW = 510

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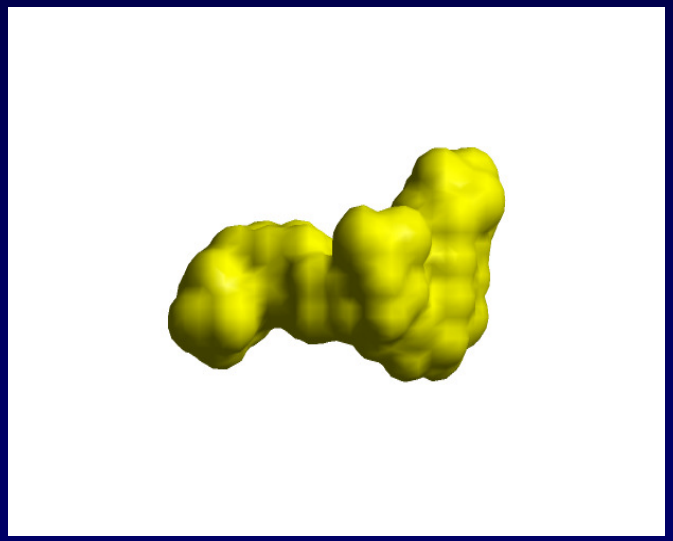
F

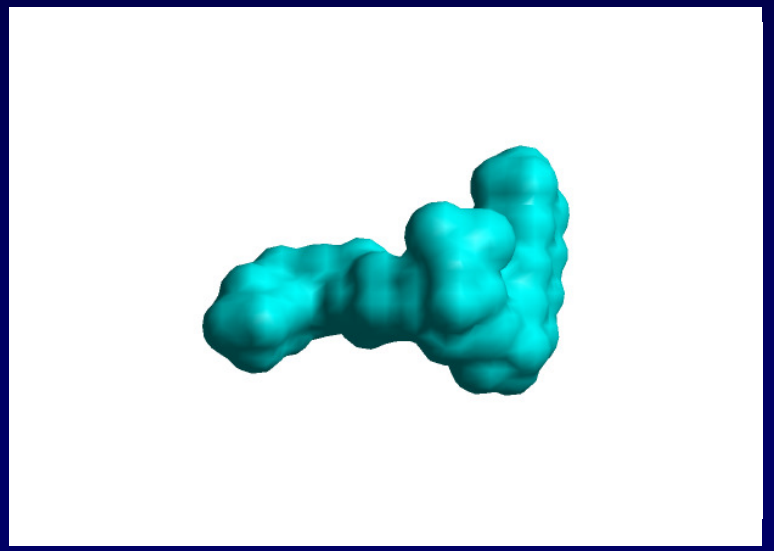


MW = 1121

Molecular Area = 558Å^2

Molecular Volume = 609Å^3

H



MW = 510

Molecular Area = 541Å^2

Molecular Volume = 530Å^3

$C_{71}H_{141}$ MW = 997 Molecular Volume = 1225Å^3

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Is PFOA in Perfluorochemical Paper Coatings and treated Paper Products?

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Concentration of PFOA in Perfluoro Paper Coatings and Paper Products

Material	C_{p0} PFOA (mg/kg)
Perfluoro paper coating (not applied)	88 - 160
Popcorn bags	0.3
Muffin bag	0.5
Sub Sandwich wrapper	0.5 – 1.2
Hash brown potato bag	0.9

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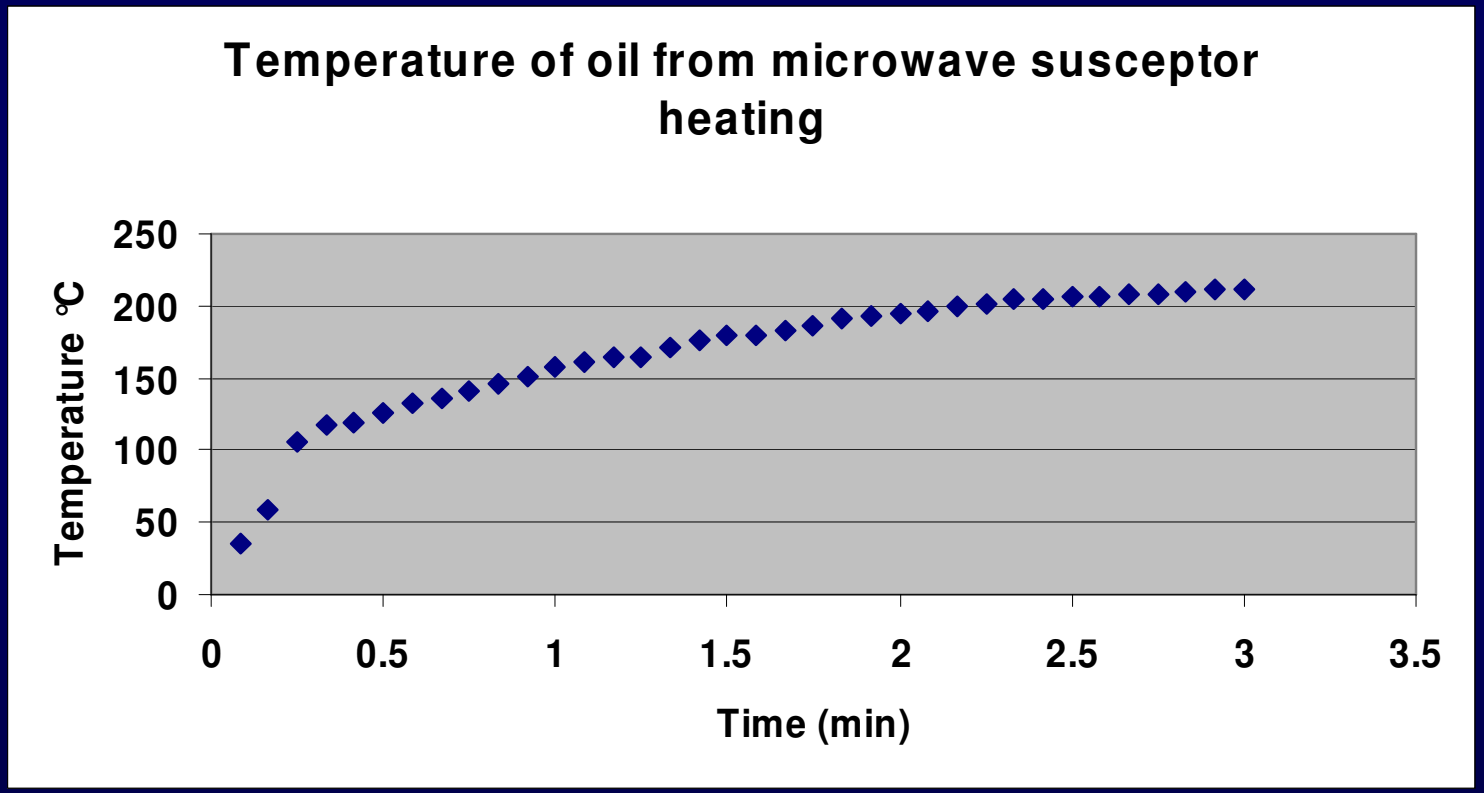
Migration of PFOA from microwave popcorn bags?



Migration of PFOA from microwave popcorn bags?

None detected into oil

T. H. Begley, et al., 2005, Perfluorochemicals: Potential sources of and migration from food packaging. *Food Additives and Contaminats*, 22 (10) 1023-1031.

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Test for perfluorochemical migration from commercially produced paper

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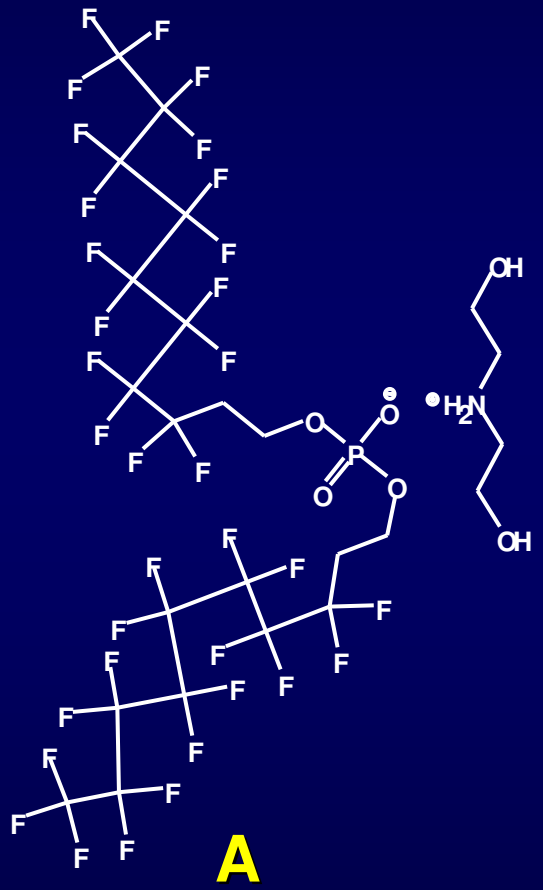
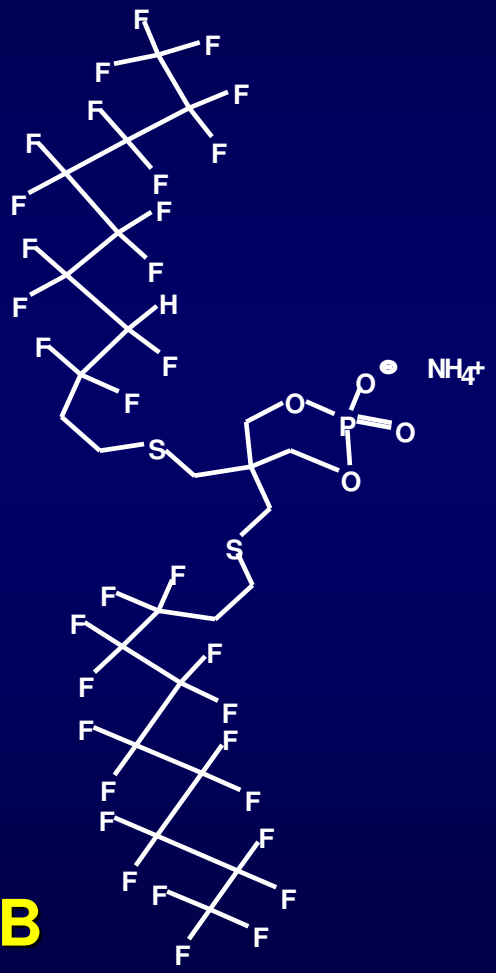
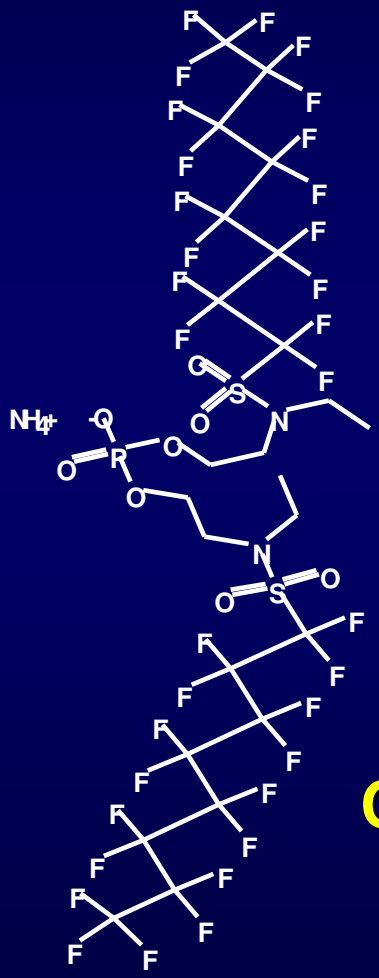
Typical structures of Perfluoro telomer based paper coatings



A



B



C

Test conditions for perfluorochemical migration

- Food simulating liquids/foods at 100°C
- Single-sided contact with paper
- Contact time 15 minutes
- LCMS analysis for perfluorochemical

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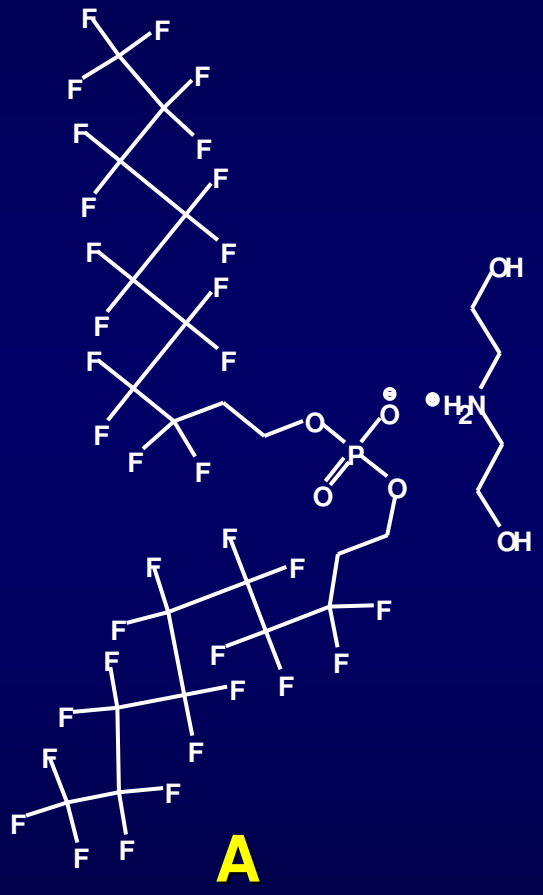
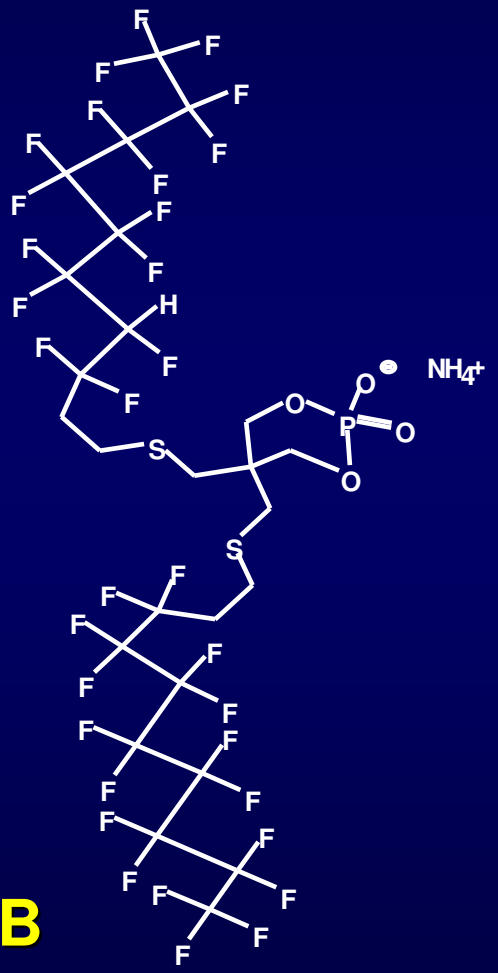
Typical structures of Perfluoro telomer based paper coatings



A



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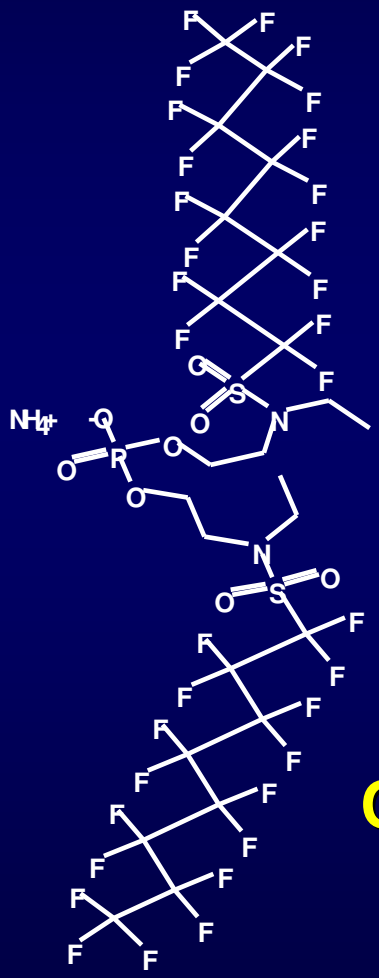

C

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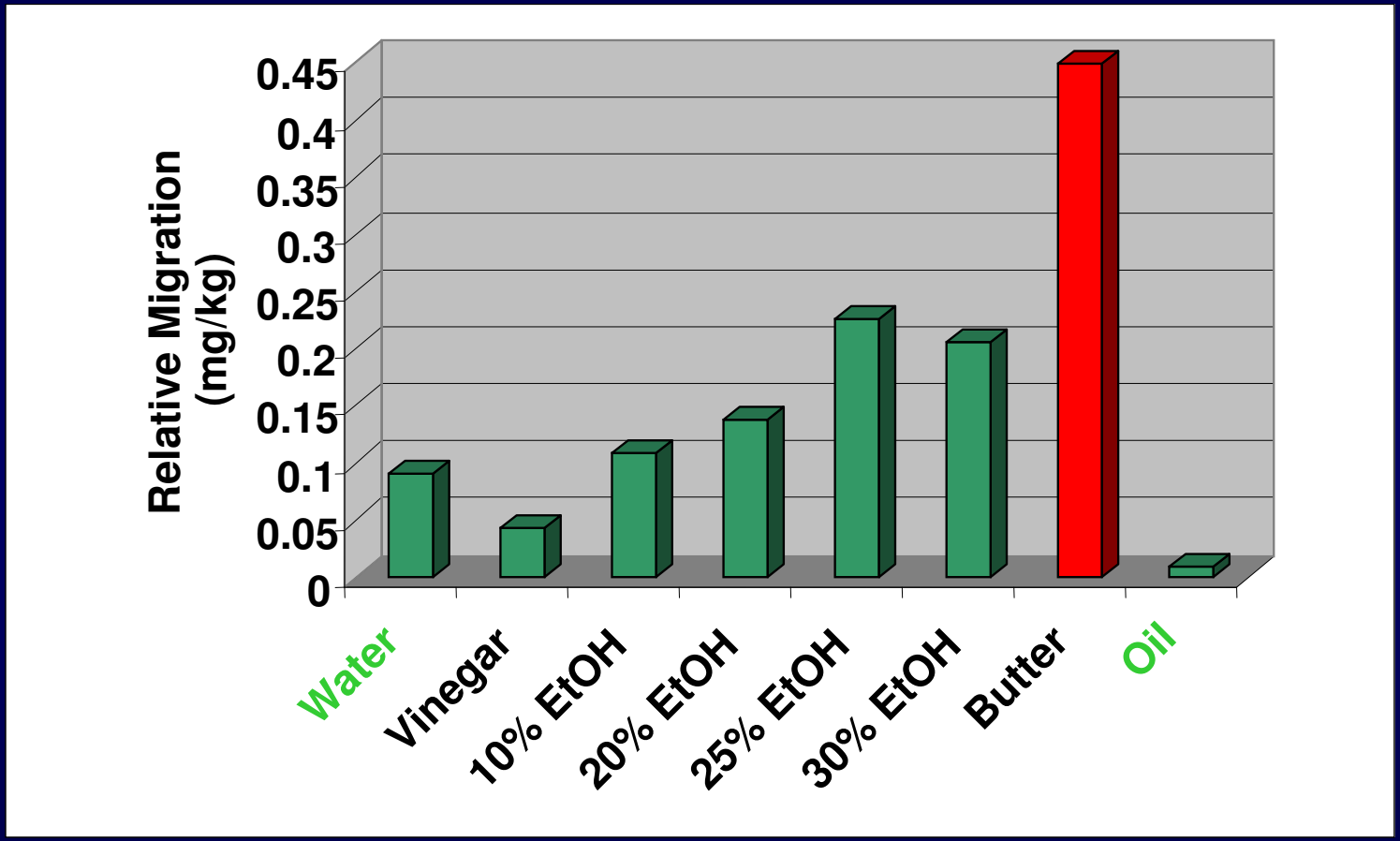
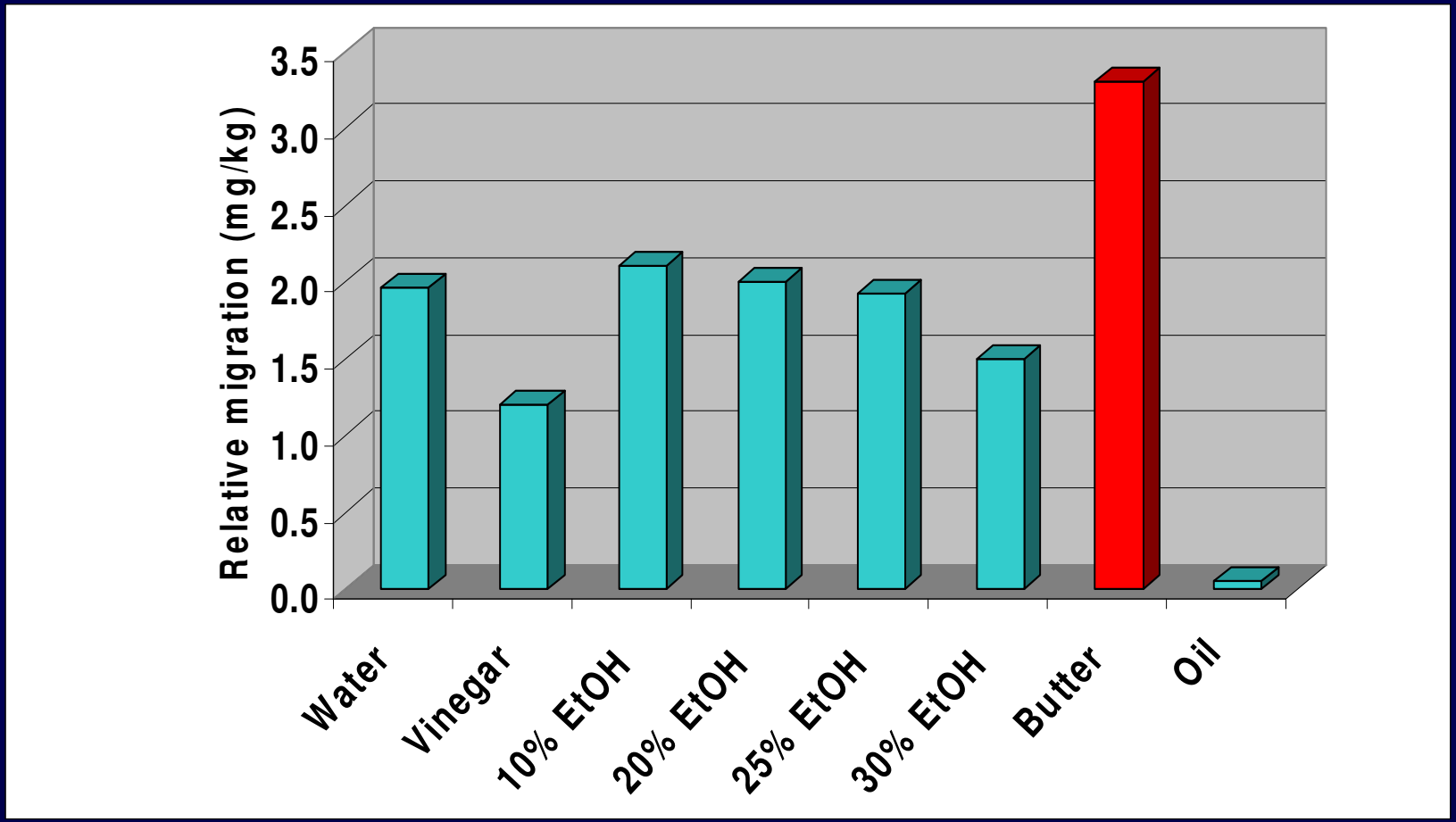
Migration results for incidental contact, Coating A



Migration results for incidental contact, Coating B



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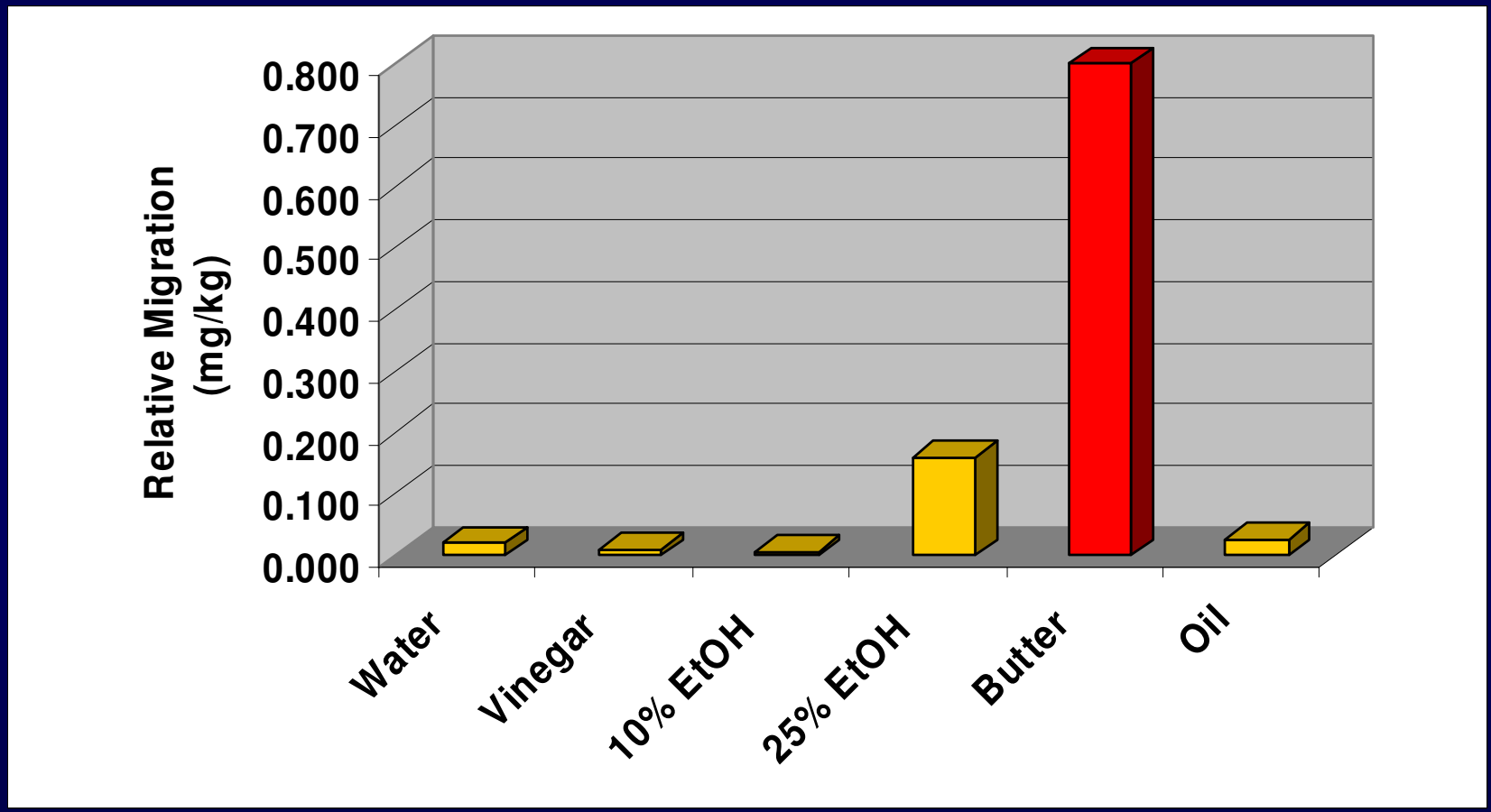
Migration results for incidental contact, Coating C, paper produce in 1987



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Potential Problem for Exposure Estimates?

Water and oil are not the extremes!

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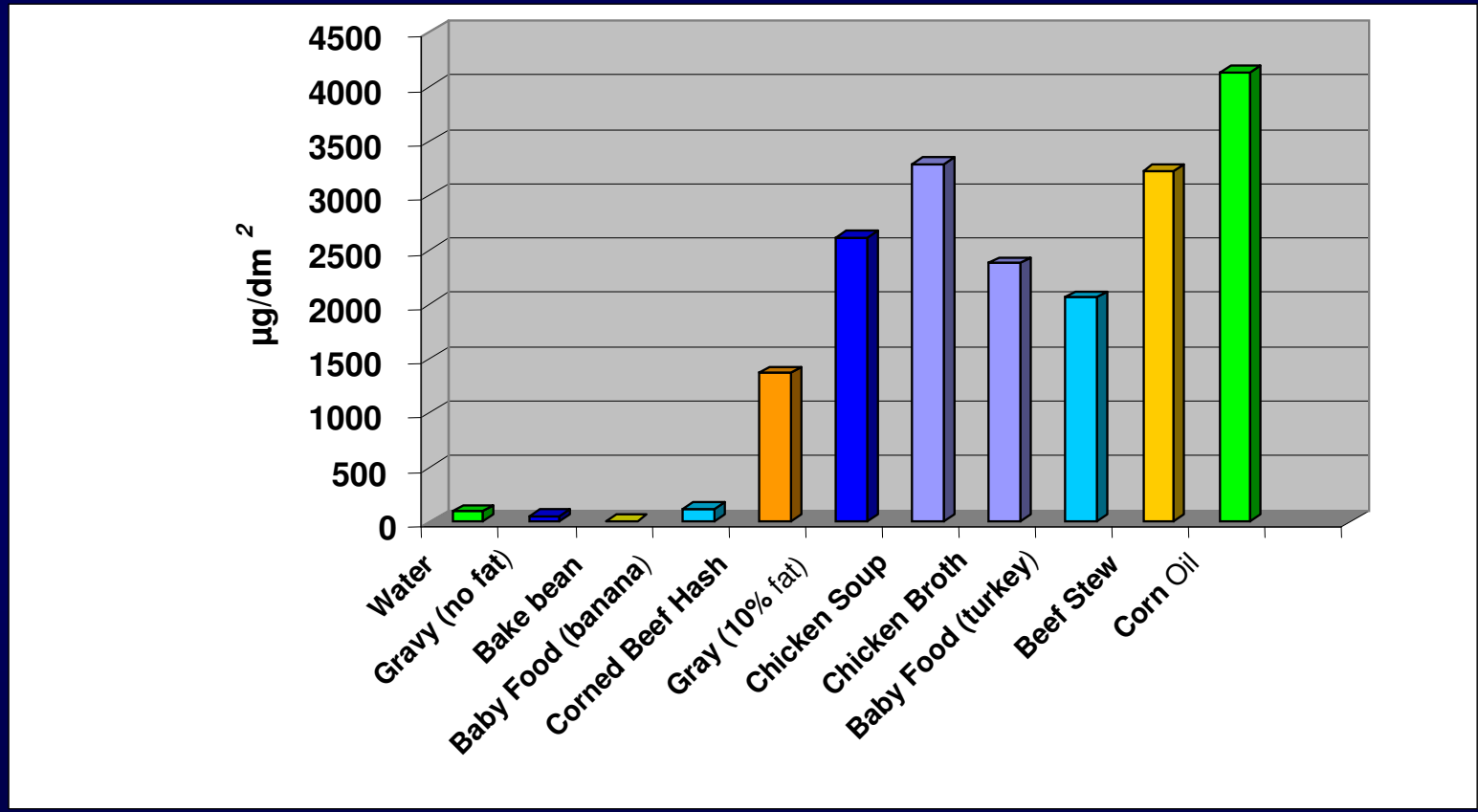
Typical Migration Results From a Polymer

Migration of Irganox 1076 from PP at 135°C



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Migration into Emulsions

- Butter = water-in-oil Emulsion (20% / 80%)
- Non-ionic surfactant (polyoxyethylene sorbitan / oil / water)
- Ionic surfactant (lecithin / oil / water)

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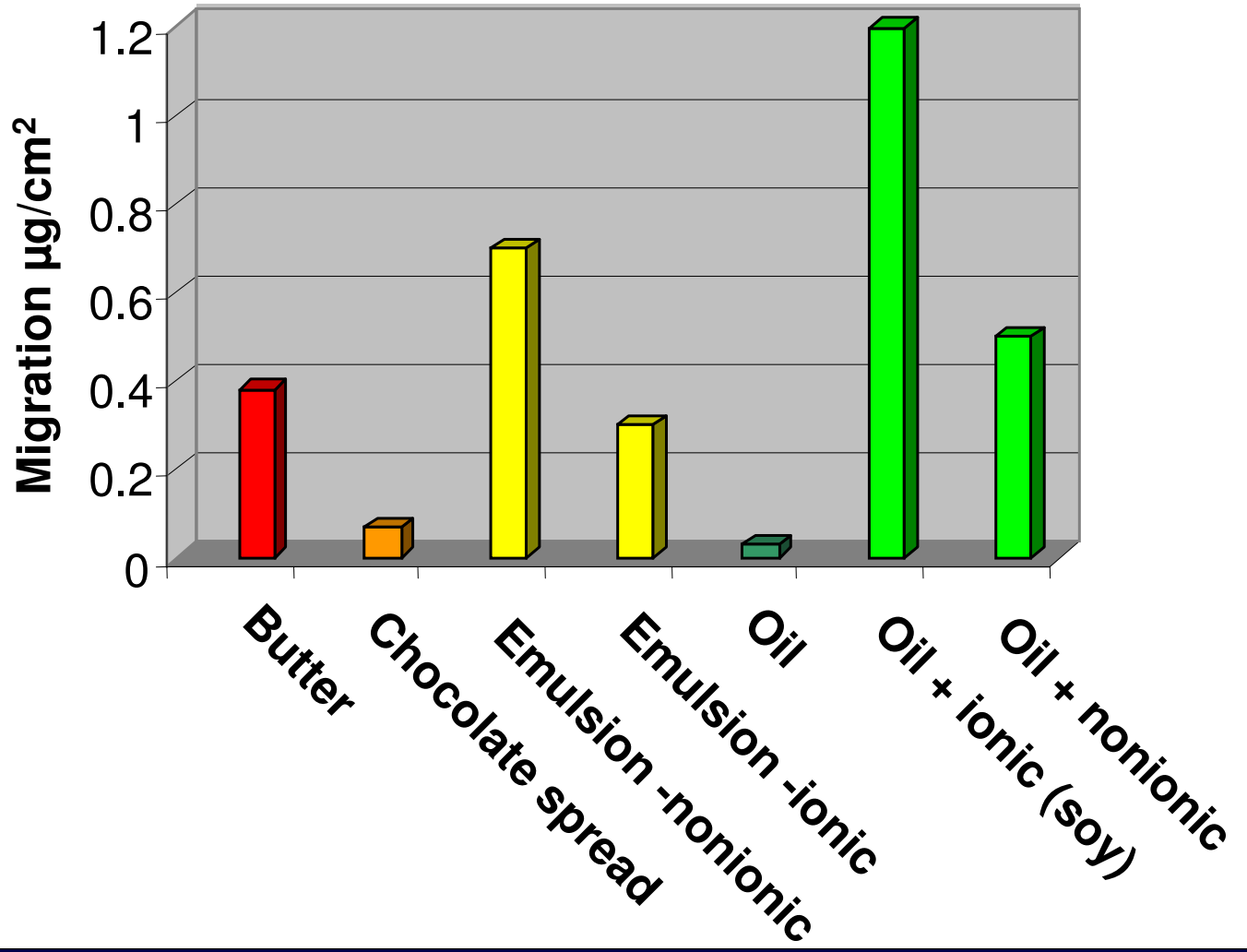
Migration from paper, 40°C 1 day



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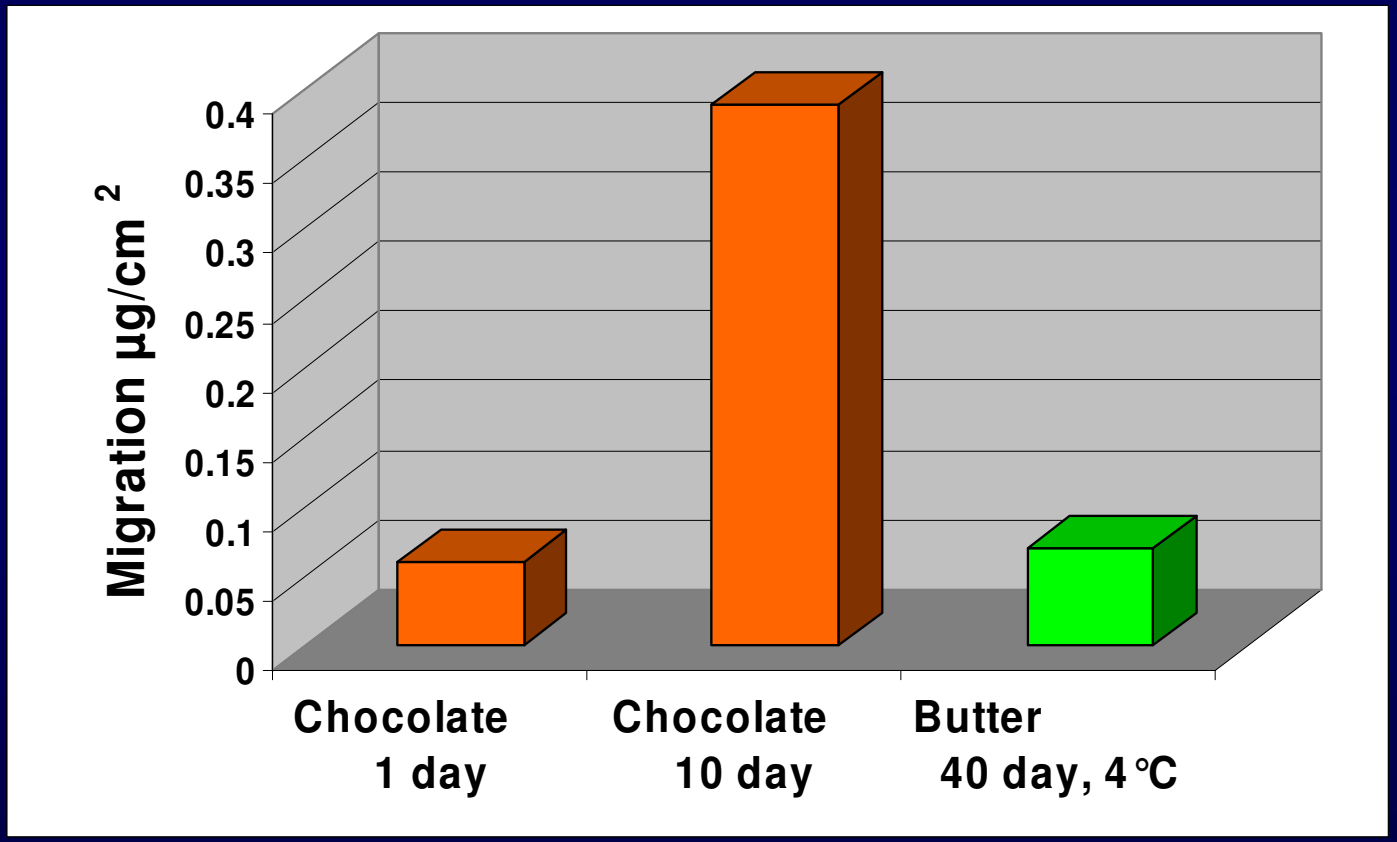
Migration of Fluorochemical is Kinetic to food at 40°C



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Do Perfluoro telomer Paper Coatings Migrate Under Actual Conditions of Use?

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Migration from microwave susceptor into oil

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Results for migration of fluorotelomer from popcorn bags

Concentration in Popcorn Oil before Heating	1.4 mg/kg 4 µg/ dm^2
Concentration in Miglyol after 2 min. microwave heating	2.1 mg/kg 7µg/ dm^2

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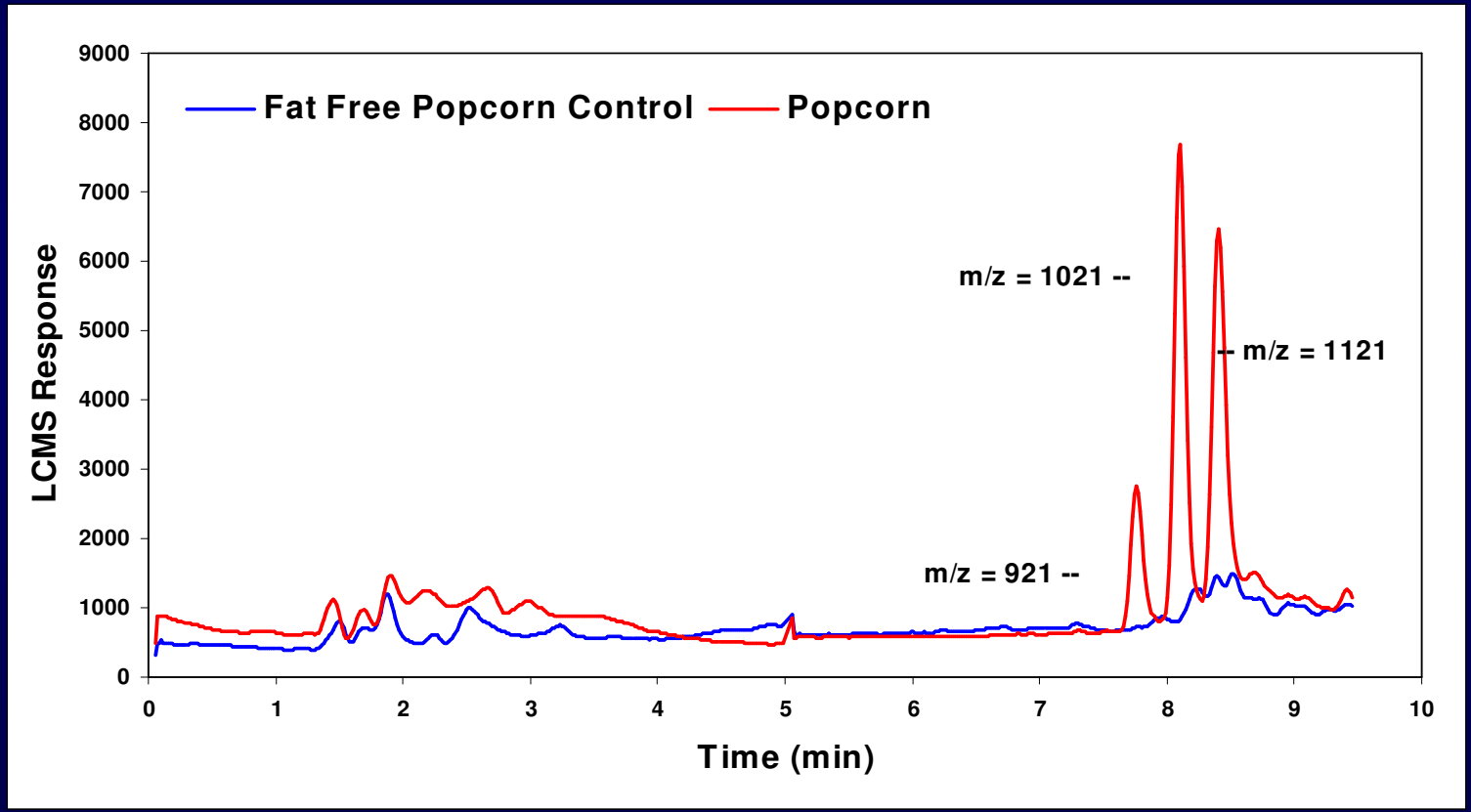
LCMS analysis of Popcorn for the Migration of Fluorotelomer from Popcorn bag



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Migration of perfluorotelomer into microwave popcorn

Brand	mg/kg
A	1.2
B	0.8
C	3.8
D	1.2
E	2.1

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Conclusions of Migration Tests

- The food simulants water and oil are not the extremes for these fluorochemicals.
- The soy emulsifier (lecithin, 0.05%) can change oil into a potent solvent for migration.
- Fluorotelomers do migrate to food in the mg/kg (ppm) range.

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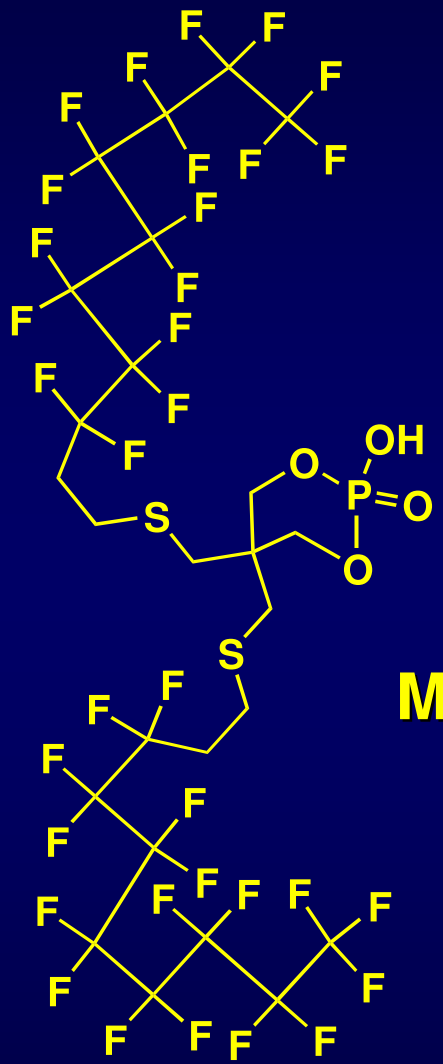

Migration to oil = none

Migration to oil + emulsifier = huge