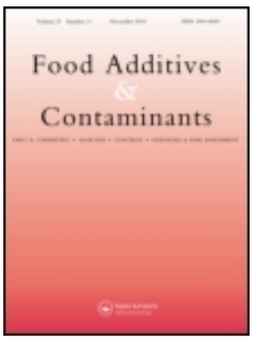

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Perfluorochemicals: Potential sources of and migration from food packaging

T. H. BEGLEY[1], K. WHITE[1], P. HONIGFORT[1], M. L. TWAROSKI[1], R. NECHES[2], & R. A. WALKER[2]

[1]*US Food and Drug Administration, Center for Food Safety and Applied Nutrition, College Park, MD 20740, USA and* [2]*Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA*

Abstract
Perfluorochemicals are widely used in the manufacturing and processing of a vast array of consumer goods, including electrical wiring, clothing, household and automotive products. Furthermore, relatively small quantities of perfluorochemicals are also used in the manufacturing of food-contact substances that represent potential sources of oral exposure to these chemicals. The most recognizable products to consumers are the uses of perfluorochemicals in non-stick coatings (polytetrafluoroethylene (PTFE)) for cookware and also their use in paper coatings for oil and moisture resistance. Recent epidemiology studies have demonstrated the presence of two particular perfluorochemicals, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in human serum at very low part per billion levels. These perfluorochemicals are biopersistent and are the subject of numerous studies investigating the many possible sources of human exposure. Among the various uses of these two chemicals, PFOS is a residual impurity in some paper coatings used for food contact and PFOA is a processing aid in the manufacture of PTFE used for many purposes including non-stick cookware. Little information is available on the types of perfluorochemicals that have the potential to migrate from perfluoro coatings into food. One obstacle to studying migration is the difficulty in measuring perfluorochemicals by routine conventional analytical techniques such as GC/MS or LC-UV. Many perfluorochemicals used in food-contact substances are not detectable by these conventional methods. As liquid chromatography-mass spectrometry (LC/MS) develops into a routine analytical technique, potential migrants from perfluoro coatings can be more easily characterized. In this paper, data will be presented on the types of perfluoro chemicals that are used in food packaging and cookware. Additionally, research will be presented on the migration or potential for migration of these chemicals into foods or food simulating liquids. Results from migration tests show $mg\,kg^{-1}$ amounts of perfluoro paper additives/coatings transfer to food oil. Analysis of PTFE cookware shows residual amounts of PFOA in the low $\mu g\,kg^{-1}$ range. PFOA is present in microwave popcorn bag paper at amounts as high as $300\,\mu g\,kg^{-1}$.

Keywords: *Perfluorochemicals, perfluorooctanoic acid, perfluoro telomers, food packaging, migration*

Introduction

Perfluoro materials/chemicals represent a specialized group of materials known for their unique properties including stability and resistance to degradation. In particular, PTFE is known to have a high melting point (327°C) relative to other food-packaging polymers, and is known to be extremely chemically resistant to a large variety of chemicals (Wall 1972; Drobny 2001). This chemical resistance and thermal stability have led to PTFE's use in some unique applications for food contact. For example, it is used to coat some cookware intended for stovetop cooking. Other perfluorochemicals are used to treat paper to improve its moisture and oil barrier properties. In particular, papers used in contact with high-fat content foods tend to be treated with fluorotelomer or fluorotelomer-based paper additives/coatings to prevent oil stains or oil soak through on the paper. Typically, these fluorotelomer paper coatings/additives are either very low molecular weight fluorotelomers, which are mixtures of C_6, C_8, C_{10} and C_{12} perfluoro chemicals (with the predominant molecules in the mixture having two

Correspondence: T. H. Begley. E-mail: tbegley@cfsan.fda.gov

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C_8 or C_{10} perfluoro groups), or high molecular weight polymers with fluorotelomer-based side chains. The results presented in this paper deal solely with low molecular weight fluorotelomer coatings.

Fluorochemicals are permitted for food-contact use in many countries throughout the world. In the USA, these regulations are listed in the Code of Federal Regulations Title 21, sections 177.1380, 177.1550, 177.1615, 177.2400 and 177.2510 for use in polymers and in sections 176.160 and 176.170 for use in paper coatings. In addition, several fluorochemicals are permitted for food-contact use as a result of effective food-contact notifications (FCNs). For a listing of these chemicals, see the US FDA's website for Food Contact Notifications (www.cfsan.fda.gov/~dms/opa-fcn.html). In Europe, a number of fluorochemical paper coatings are approved by the Bundesinstitut für Risicobewertung (2005) in Germany.

Recent epidemiology studies have demonstrated measurable levels of perfluorochemicals in the serum of fluorochemical production workers (Olsen et al. 1999, 2003) and in the general US population and other developed countries (Kannan et al. 2004; Kennedy et al. 2004; Kubwabo et al. 2004). Specifically, perfluorooctanesulfonate (PFOS), an impurity in some grease-proofing paper coatings/additives and perfluorooctanoic acid (PFOA), a processing aid in the manufacture of PTFE, have been detected in the serum of elderly Americans as high as 175 and 16.7 ng ml^{-1}, respectively, with higher amounts being measured in production workers (Olsen et al. 2004). Toxicologically, PFOA is a peroxisome proliferator (PP), a term used to describe a diverse group of non-genotoxic chemicals that target the liver, inducing peroxisomal β-oxidation and activation of the peroxisome proliferator activated receptor (PPAR) (Intrasuksri et al. 1998; Maloney and Waxman 1999). In rodents, PPs induce hepatomegly, causing hypertrophy and hyperplasia of the liver, ultimately resulting in the formation of hepatic tumours (Riker 1987, Biegel et al. 2001). In addition, rodent studies indicate that some PPs, including PFOA, induce tumours in Leydig and pancreatic acinar cells (Biegel et al. 2001). PFOA has also been characterized as a developmental toxicant, causing increased mortality, reduced body weights and delayed sexual maturation in pups (US Environmental Protection Agency 2003) and as having a long human half-life of 4.4 years ($\pm$3.5) (Butenhoff et al. 2004). Conversely, PFOA's half-life in rodents appears to be in the order of days with a clear sexual differentiation: females have rapid clearance rates relative to males (Vanden Heuvel et al. 1991; Ohmori et al. 2003; US Environmental Protection Agency 2003). This divergence in half-lives between animals/sexes complicates the risk assessment of PFOA using animal models. Using a half-life of 4.4 years and the one compartment pharmacokinetic model by Harada et al. (2003) for estimating serum concentrations, the time for PFOA serum concentrations to approach equilibrium is 15–20 years. Therefore, continued ingestion of very small amounts of these perfluorochemicals may only become apparent many years later.

Other potential sources of PFOA in human serum are the biodegradation of other fluorochemical products, some of which are used on paper. In particular, perfluorooctylethanol, a monomer industrially known as the 8:2 telomer alcohol ($CF_3(CF_2)_7CH_2CH_2OH$), which is used to make fluorotelomer coatings/additives for food-contact paper, biodegrades aerobically into PFOA (Dinglasan 2004) using enriched sediment and ground water cultures. Furthermore, Hagen et al. (1981) demonstrated the biotransformation of a perfluorodecanol to perfluorooctanoate in male rats, suggesting that fluorocarbons of $>C_8$ could lead to the formation of C_8 *in vivo*. Based on these data, the potential may exist for components of the fluorotelomer products themselves to metabolize into PFOA after ingestion. Importantly, many fluorotelomer paper coatings/additives are mixtures of C_6, C_8, C_{10} and C_{12} fluorochemicals, where the C_8 and higher fluorochemicals are potential candidates for biodegradation. Figure 1 shows the molecular structures of PFOA (A), the telomer alcohol (D) and some primary components of fluorotelomer coatings/additives (B, phosphoric acid, *bis*[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanylmethyl)]-2-hydroxy-2-oxo-1,3,2-dioxaphosphorinane, ammonium salt; C, phosphoric acid, *bis*[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decyl)] ester 2-(2-hydroxyethyl amino); and E, phosphoric acid, *bis*[(N-ethyl-2-1,1,2,2,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-octyl sulfonamido ethyl)]) for food-contact paper. Figure 1 shows that many fluorochemical paper coatings/additives may be potential sources of the $C_8F_{17}^-$ moiety, the structural basis for PFOA. Consequently, our accurate understanding of the migration characteristics of these fluorochemicals from food-contact materials may be important to the risk characterization for PFOA.

This paper describes the determination of the amounts of PFOA and other fluorochemicals in different commercial product (mostly food-contact materials) as well as the migration characteristics of representative fluorochemical species from actual food-contact materials. In particular, the PFOA content in PTFE and paper coating products is measured as well as the mass transfer of PFOA

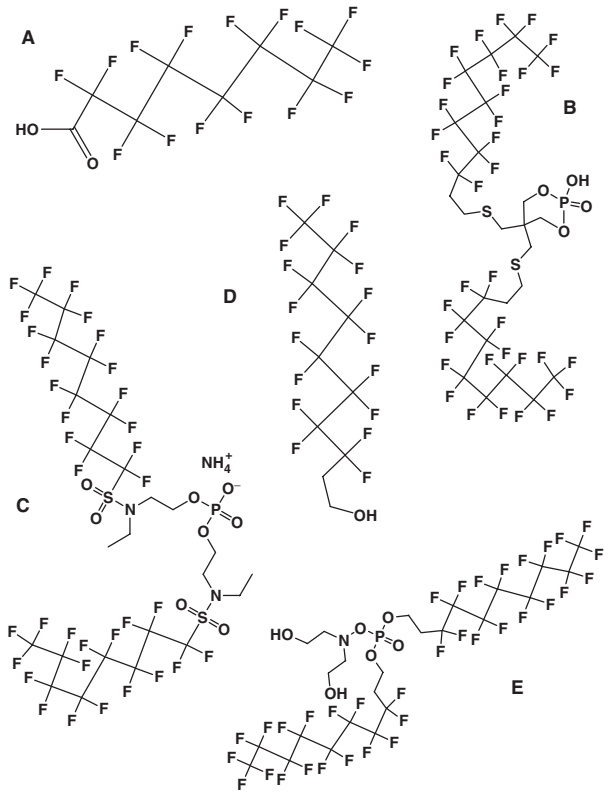

Figure 1. Molecular structures of components of paper coatings: (A) PFOA, (B, C) primary structures of regulated paper coatings/additives, (D) fluoroalcohol, 8:2 telomer alcohol, which has been shown to biodegrade into PFOA, (E) primary structure of a paper coating/additives.

and some fluorotelomers from these materials into a food oil simulant (Miglyol®) and water. Many fluorochemicals used in food-contact substances are not detectable by conventional methods, i.e. GC/MS or LC-UV because they are non-volatile or lack a sensitive chromophore. Liquid chromatography-mass spectrometry (LC/MS) with electrospray ionization is essential to overcome these detection problems and is used to determine the presence of these chemicals in the materials or as migrants.

Materials and methods

Materials

All materials, fluoropolymers (fluoro-ethylene-propylene copolymer (FEP) tubing), PTFE products (sealant tape, dental floss) and paper products were purchased at retail establishments. PFOA was purchased from Aldrich Chemical Co. (Milwaukee, WI, USA). Di-labelled ^{13}C-PFOA was supplied by DuPont (Wilmington, DE, USA). All solvents used were ultra-residual analysed or HPLC grade. All materials were used as received.

Instruments

Concentrations of PFOA and fluorotelomers in paper coatings were measured using an Agilent 1100 series LC assembly (degasser G1322A, pump G1312A, autosampler G1313A, column compartment G1316A, diode array detector G1315B) connected to an Agilent 1100 Series LC/MSD mass selective detector (G1946D) via the electrospray ionization (ES)-interface (G1947A) (Agilent Technologies, Palo Alto, CA, USA).

Experiments used a Zorbax SB-C_8, reverse-phase column with a 3.5-μm particle size, and dimensions of 100 × 2.0 mm (Agilent).

Sample volumes of 5 μl were injected into a column thermostated at 45°C and a flow rate of 0.3 ml min^{-1}. The initial mobile phase consisted of a 45% H_2O/55% MeOH/2 mM ammonium acetate mixture. Over a 10-min interval, the mobile phase changed linearly to a 95% MeOH solution. Analysis of fluorotelomers from paper used slightly different LC conditions: solvent A = water containing 2 mM ammonium acetate buffered to pH 4 with acetic acid and solvent B = 90% acetonitrile with 10% methanol. The gradient: initial mobile phase: 65% solvent B followed by a 5-min linear gradient to 99% B, hold at 99% B for 5 min.

ES-interface parameters

A drying gas flow of 10 l min^{-1}, resulted from a nebulizer pressure of 60 psi and temperature of 350°C. The capillary voltage was kept constant at 4000 V (negative ion mode), and the fragmentor voltage was kept constant at 100 V.

Electrospray MS/MS for confirmation of PFOA was performed on a Waters (Milford, MA, USA) Micromass Quattro Premier triple quadrupole mass spectrometer. An Agilent 1100 series HPLC configured with a vacuum degasser, binary pump, autosampler and column oven provided the chromatographic separation using a Phenomenex (Torrance, CA, USA) LUNA 3μ C8(2) reversed phase column (3 μ, 150 × 2.0 mm i.d.) and a gradient mobile phase of water, methanol and ammonium acetate. The flow rate was 0.2 ml min^{-1}, and the column oven temperature was 35°C. Mobile phase: solvent A = 45% H_2O/55% MeOH/2 mM ammonium acetate; solvent B = MeOH. Gradient: initial mobile phase: 0% solvent B followed by a 10-min linear gradient to 95% B. The mass spectrometer was operated in the negative-ion mode. Instrument parameters were: 1 kV spray voltage, cone 20 V, extractor 4 V, RF lens 0 V, source temperature 120°C, desolvation temperature 250°C, cone gas flow 51 h^{-1}, desolvation gas flow 550 l h^{-1}, quad-1 low mass resolution and high mass resolution = 14,

quad-1 ion energy 1, collision gas pressure 4.1e − 3 mbar, collision energy 15 V, quad-3 low mass resolution and high mass resolution 15, quad-3 ion energy 1, and multiplier 650 V. Multiple reaction monitoring (MRM) experiments observed the collisionally induced decomposition (CID) of ions 413, 369, 415 and 370 to the structurally significant fragment at *m/z* 169. Ions at *m/z* 413 and 369 correspond to the native (PFOA) compound, while ions at *m/z* 415 and 370 correspond to the C13 labelled internal standard.

The power of the microwave oven used in cooking experiments was determined by measuring the temperature change of approximately 1 kg distilled water held in a foamed polystyrene container and heated for 2 min. The average power of the microwave oven was measured as 702 W.

Heating PTFE-coated cookware

Cooking pans (frying or omelette style) consisting of PTFE-coated aluminium (588 g and 28 cm diameter) were heated on a three-point stand above a Meker type high-temperature burner. A stainless steel K-type thermocouple probe (ISO 9001 compliant) was placed off centre in contact with the heating surface to record the surface temperature of the cookware during heating. The pans were heated empty. Following heating, the PTFE pan coatings were analysed for PFOA.

Determination of PFOA in PTFE

Preferably, the analysis of additives and residual by-products in polymers is by polymer dissolution techniques. Unfortunately, PTFE does not dissolve, therefore analysis must be by extraction of a ground or powdered material. PTFE was cryogenically ground to a powder by placing the pieces of polymer in liquid nitrogen then pouring the polymer and the liquid nitrogen into the grinder. The grinder (Wiley mill design) was equipped with a 20 mesh screen (840 μm hole size). A controlled amount of PTFE (1.0 g) was placed into a 20 ml headspace vial, 5 ml methanol were added, a di-labelled ^{13}C-PFOA internal standard was added and the vial was sealed and placed on an end-over-end rotator (turning at 16 rpm) in an oven set at 50°C. Vials were kept at 50°C for 24 h. Methanol was much more effective than chloroform at extracting PFOA from PTFE, which is consistent with results of others (Larsen et al. 2005). The fluorinated solvent hexafluoro-2-propanol was also effective at extracting PFOA from PTFE, but this solvent is difficult to work with (affected septa) and is extremely expensive for routine work. After heating, the methanol was withdrawn, the polymer washed with 5 ml methanol, and the washing combined with the original 5 ml extract. The methanol was concentrated to dryness under nitrogen, and the sample was re-dissolved in 2.0 ml 50/50 (v/v) methanol/water for analysis by LC/MS or LC/MS/MS. Direct injection of PFOA in methanol leads to very poor chromatographic peak shape vs. using methanol/water solutions. For PTFE-coated cookware, the coatings were gently brushed off using a wire brush connected to a power drill. This procedure produced a fine powder that was extracted in methanol as described above. Quantitation was performed by comparison to the labelled ^{13}C-PFOA internal standard. This procedure yields recovery corrected values. The recovery rate of the internal standard from the powdered PTFE was greater than 90%. The repeatability (relative standard deviation) of the PFOA measurement in the powdered PTFE was 7%. Spiking experiments on powdered PTFE showed linear response to spike amount.

Determination of PFOA in paper

Paper (about 5–6 g) was extracted in an Erlenmeyer flask using sonication for 60 min in 25 ml 50/50 (v/v) ethanol water. Following sonication, the solution was filtered using a 0.2-μm nylon syringe filter followed by direct LC/MS analysis for PFOA. Spike and recovery studies on paper plates that were spiked at 30 μg kg^{-1} PFOA and dried at room temperature show a 60–75% recovery rate without using an internal standard. All quantitative PFOA measurements from paper samples were determined by comparison to a di-labelled ^{13}C-PFOA internal standard that was added to the extraction mixture before extraction, which corrects for recovery losses.

Determination of PFOA in Miglyol

To determine the concentration of PFOA in Miglyol (a food oil simulant) as a result of migration from PTFE, 2.0 g Miglyol were measured into a 50-ml polypropylene centrifuge tube. The sample was then dissolved in 45 ml hexane and 2.0 ml water were added. The internal standard (^{13}C-PFOA) was added and the tube was sealed and mixed on an end-over-end mixer for 1 h. The water phase was removed and directly injected into the LC/MS. The calibration curve from 0.5 to 9.0 ng g^{-1} PFOA in oil (Miglyol) had a linear regression coefficient, $R^2 = 0.99$. Quantitation was based on the relative response to the internal standard.

Determination of fluorotelomer migrating from microwave popcorn bags into Miglyol

The microwave popcorn bags used were purchased at local retail stores. The bags were frozen then opened to remove the oily contents from the inside of the bags. The insides of the bags were wiped clean of oil residue with paper towels. The paper towels were not tested for potential removal of fluorotelomer due to mechanical cleaning. Not all brands of popcorn bags appeared to have a fluorotelomer coating on the food-contact side. Bags selected for migration tests showed C_6, C_8, C_{10} and C_{12} fluorochemicals on the food-contact side as evidenced by a quick single-sided extraction test using a 50/50 water/ethanol wash. The cleaned bags (11.7 dm^2 food-contact surface area) were filled with 40 g Miglyol, folded, held closed with plastic clamps and microwaved for 2 min. Following microwave heating, the bag was rotated end-over-end. The extremely hot oil was transferred first to a beaker and then to a polypropylene centrifuge tube for storage. An aliquot of about 1 g microwaved oil was diluted with 4 ml 99% ethanol, shaken and directly injected into the LC/MS. Quantitation was performed using an external calibration curve constructed by fortifying Miglyol with different concentrations (0.4–7 $\mu g\,g^{-1}$) of the fluorotelomer. The instrument response for the fluorotelomer was defined as the sum of three SIM responses (*m/z* 1021, 1121 and 1221), which are characteristic parent ions of some of the individual fluorotelomer components of the particular fluorotelomer oil resistant paper coating/additive. Fluorotelomer coatings/additives have unique SIM signatures depending on the manufacturer of the coating. The calibration curve from 0.4 to 7.0 $\mu g\,g^{-1}$ fluorotelomer in Miglyol had a linear regression correlation coefficient, $R^2 = 0.99$. Analysis of actual popcorn oil was similar to Miglyol, but because this oil does not dissolve in ethanol, the popcorn oil was dispersed in the ethanol by shaking and then filtered through a 0.2-μm nylon filter, followed by direct injection into LC/MS.

Discussion

The amounts of PFOA detected in a limited sampling of food-contact materials or coatings applied to food-contact materials are listed in Table I. These data show low levels of PFOA ($\mu g\,kg^{-1}$) are present in the products, but with a very large range in the materials. PTFE sealant films and some paper products have the highest amounts of PFOA. The paper products tested are all retail samples and not necessarily coated with fluorochemicals, which may explain the absence of detectable PFOA levels in some samples. Fluorotelomer-based paper coating/additive formulations before application onto paper have the highest PFOA content, but during normal application rates this amount of PFOA will be diluted by about 300 times on the final paper product. Therefore, the PFOA content on finished paper should be in the few hundred $\mu g\,kg^{-1}$ range, which is consistent with the data in Table I. The amount of PFOA in PTFE products appears to be related directly to the processing temperatures used to make the products. Cookware and dental products use a high heat sintering process that should volatilize PFOA, while production of PTFE film used as sealant tape does not use a sintering process (Drobny 2001). Therefore, one might expect the highest concentrations of PFOA to be found in PTFE sealant film rather than in other PTFE products. This is consistent with the data in Table I.

Table I. Summary of PFOA analysis in products.

	Concentration of PFOA ($\mu g\,kg^{-1}$)
PTFE cookware	4–75
Dental floss (PTFE based)	3
Dental tape (PTFE based)	4
PTFE film/sealant tape	1800
FEP (fluoro-ethylene-propene copolymer) tubing	n.d.
Popcorn bags[1]	6–290
Hamburger wrapper	n.d.[1]
Sandwich wrapper[1]	n.d.
French fry box[1]	n.d.
Paper plates (soak-proof shield)[1]	n.d.
Perfluoro paper coatings (not applied)	88 000–160 000

[1]Paper products were not necessarily treated with perfluoro paper coatings.

Migration of PFOA from PTFE

The residual amount of extractable PFOA found in PTFE-coated cookware is not high enough to determine whether mass transfer of PFOA occurs from PTFE-coated cookware into water or oil at cooking temperatures. This conclusion is based on the following calculations that use several worst-case assumptions. A common frying style pan with a 28-cm diameter has a total surface area of about 893 cm^2. The mass of food/simulant in this half-filled pan is about 1200 g. If a pan had a uniform thickness of 75 μm (a very thick coating), then the total amount of PTFE coating on the pan is, at most, 15 g, assuming a polymer density of 2.2 $g\,cm^{-3}$. This coating estimate is limited because the film thickness on cookware is not uniformly thick and the film thicknesses in many pans appear to be much less than 75 μm. Under these conditions

using the highest concentration of PFOA measured in cookware (75 ng g^{-1}) and assuming 100% PFOA migration from the pan to the food, the concentration of PFOA in the food/food simulant would be 0.9 µg kg^{-1} (0.9 ppb) in a single-use scenario. Typically though, only 1% not 100% migration is observed for additives migrating from polyolefin packaging materials at cooking temperatures of 100°C (Goydan et al. 1990). Therefore, characterization of actual PFOA migration from PTFE-coated cookware is not likely.

If one wishes to simulate actual PFOA migration from PTFE to food/food simulants, the low residual PFOA content in PTFE-coated cookware and the fact that cookware has a geometry that is not conducive for accurate migration tests leads to the need for a representative surrogate PTFE test material that can be easily manipulated and has a higher residual PFOA concentration. Surrogate test materials are commonly used in the evaluation of migration from food-contact materials (Till et al. 1987). This representative test material could potentially be used as a surrogate model for determining the percentage of residual PFOA that may actually migrate from PTFE-coated cookware to food. Due to the higher residual PFOA content in PTFE film (used for sealant applications) vs. cookware (Table I), PTFE film (sealant) meets this requirement. In addition, since morphology of PTFE film is different than cookware, migration is more likely from the film than from cookware and therefore it represents a conservative approach to estimating migration from PTFE. Using this surrogate approach, characterization of PFOA migration from PTFE during cooking conditions as measured using a representative PTFE film typically used in sealant applications rather than migration testing using actual PTFE-coated cookware.

In these surrogate experiments, single-sided migration tests were performed on 75-µm thick PTFE film (sealant film) that contained enough residual PFOA (1.8 mg kg^{-1}) to make reliable mass transfer measurements. Experiments were conducted into water and oil (Miglyol) at 100°C and into oil (Miglyol) at 175°C. These experiments used 45 g simulant placed in contact with 49 cm^2 PTFE in sealed stainless steel migration cells. The migration cells were heated for 2 h at the specified temperature. Thermocouple measurements determined that the simulant took 50 min to reach the desired temperature. A typical LC/MS analysis demonstrating migration of PFOA from PTFE into a food oil (Miglyol) is illustrated in Figure 2 and the results of these tests are listed in Table II. All reported values in Table II represent the average of triplicate tests using three migration cells plus one control (no PTFE). No PFOA response was detected in controls. The data in Table II demonstrate that PFOA migrates from PTFE to both water and oil at 100°C. Additionally, as expected, more PFOA migration is measured at the higher temperatures. At 175°C approximately seven times more PFOA migration is observed from PTFE than is measured at 100°C. However, the amount of PFOA migration at 175°C represents only 17% of the total PFOA content of the film or a fractional migration of 0.17 $[(7.7\,ng_{PFOA}\,g^{-1}{}_{Miglyol} \times 45\,g_{Miglyol})/(1.1\,g_{PTFEincell} \times 1800\,ng_{PFOA}\,g^{-1}{}_{PTFE}) = 0.17]$. At 100°C the fractional PFOA migration from PTFE is about 0.04 or 4%.

Potential for continued formation of PFOA during use of PTFE products

The above analysis accounts only for the initial residual PFOA concentration in coated cookware after manufacturing and does not address the possibility that more PFOA may form in the product during use or misuse. To determine if significant amounts of PFOA could be generated during

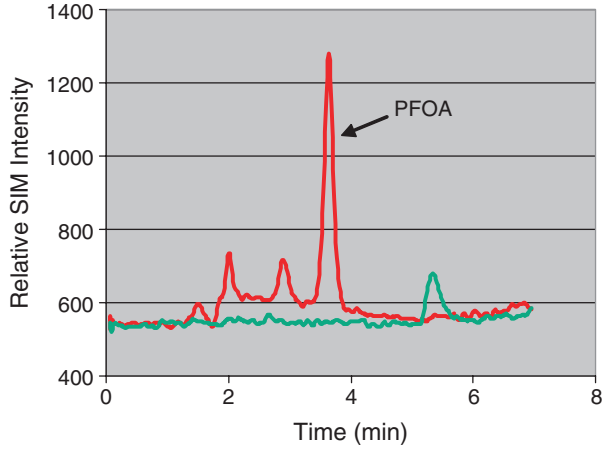

Figure 2. Typical LC/MS chromatogram (*m/z* 413) for the analysis of PFOA, which has migrated from PTFE into oil at 100°C. The green represents the control (see online version for colour figure).

Table II. Migration (M_t) of PFOA from PTFE film at 100 and 175°C after 2 h heating.

Temperature (°C)	Simulant	M_t (PFOA)	Simulant	M_t (PFOA)
100	Water	150 ng dm^{-2} (1.6 ± 0.4 µg kg^{-1})	Miglyol	120 ng dm^{-2} (1.3 ± 0.07 µg kg^{-1})
175			Miglyol	710 ng dm^{-2} (7.7 ± 0.1 µg kg^{-1})

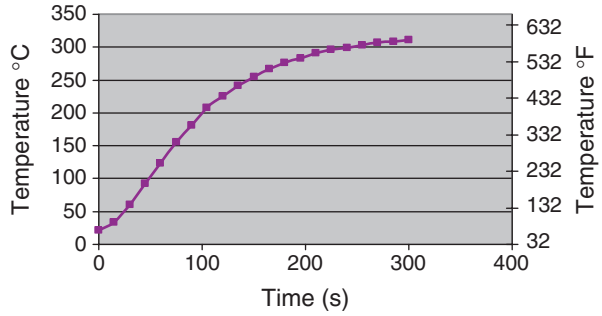

Figure 3. Heating response for a PTFE-coated aluminium frying or omelette style pan (588 g and 28 cm diameter) heated with a flame by a Meker-type high-temperature burner.

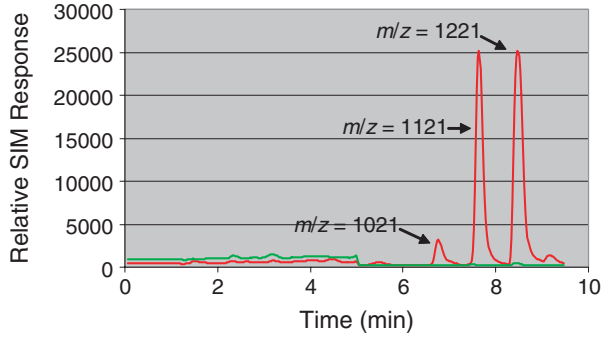

Figure 4. Typical LC/MS chromatogram for the analysis of fluorotelomer coating migrating from a microwave popcorn bag into oil. The *m/z* shown are characteristic ions of individual fluorotelomers unique to this paper coating.

misusing cookware, a heating test without food was conducted. Three pans (frying or omelette style) were heated empty over a flame burner to 320°C and allowed to cool. Figure 3 illustrates the average heating curve of the pans. This heating profile resulted in pan coatings that looked (visually) similar to the original coating on the pan. It should be noted that food oils begin to generate smoke around 190°C, which would be an indication that the cooking pan is overheating. Therefore, the testing used is a worst-case scenario that covers use and misuse of the product. After the pan cooled, the PTFE coating was removed from the pan, and the resultant fine powder was extracted with methanol to determine if additional PFOA had formed. No detectable increase in PFOA was measured. In fact, all heated pans had less PFOA than non heated pans of the same style and manufacturer. This experiment did not attempt to measure the volatilized PFOA, but results suggest that significant amounts of PFOA are not generated and remain in the cookware after an extreme heating event.

Migration of PFOA and fluorotelomers from microwave popcorn bags

Microwave susceptor popcorn bags represent an extreme use of paper as a food-contact surface. Specifically, susceptor heating elements in microwave popcorn bags heat to over 200°C in about 1–2 min. These temperatures significantly increase the potential for migration of the packaging components to foods.

To determine if any fluorotelomers migrate into popcorn oil during the bag filling process, the popcorn oil was removed from the bags before heating and was tested for the presence of fluorotelomer before heating the bag. This analysis shows 1.4 mg kg^{-1} (4 μg dm$^{-2}_{paper}$) fluorotelomer has migrated to the oil before microwaving. New simulating oil was then added to these bags and migration experiments under microwave conditions (2 min heating) show an additional 2.1 ± 0.9 mg kg^{-1} (or 7 μg dm$^{-2}_{paper}$) of fluorotelomer migrating to Miglyol, a food oil, as a result of heating. A typical LC/MS analysis detecting this migration of fluorotelomer is illustrated in Figure 4. It illustrates the instrumental response to individual fluorotelomers unique to the paper additive/coating. The primary structure to the *m/z* 1121 ion is illustrated in Figure 1B.

Migration of PFOA during microwaving from microwave popcorn bags, which initially contained about 0.3 mg kg^{-1} PFOA in/on the bag, show the average concentration of PFOA in Miglyol after microwaving to be less than 1 μg kg^{-1} or 3 ng dm$^{-2}_{paper}$ or less than the lowest standard used for quantitation. Subsequent analysis of these bags for fluorotelomer additives suggests these particular test bags had the fluorotelomer coating/additive containing PFOA primarily on the outside of the bags.

Conclusion

Data presented in this paper suggest that fluoropolymer food-contact materials do not appear to be a significant source of perfluorochemicals (e.g. PFOA) relative to paper that will migrate to food and be consumed. This conclusion is based on the residual analysis of PFOA in fluorinated ethylene-propene copolymer (FEP) tubing, PTFE film used for sealant applications and PTFE-coated cookware and migration experiments on PTFE film. In particular, the coated cookware tested here do not appear to be a significant source of PFOA which will migrate due to cookware's low μg kg^{-1} initial residual level of PFOA. Furthermore, an extreme heating test (abusive) of the cookware did not appear to increase the residual amount of PFOA in the cookware. That is, additional PFOA does not appear to form during the normal use or misuse of these products.

Because the amount of residual PFOA in cookware is rather low ($\mu g\,kg^{-1}$) accurate migration experiments are not practical or informative. Model experiments using PTFE film heated to a cooking temperature of 175°C for 2 h showed that only 17% of the total PFOA in the film migrated from the film into the food simulant. In other words, the fractional migration from PTFE at this use condition is 0.17. At 100°C the fractional PFOA migration from PTFE into water and oil is only 0.04. Consequently, the percentage of total residual PFOA migrating from PTFE-coated cookware into food should be similar to our model surrogate migration tests. Taking into account the difference in initial residual PFOA concentrations between the cookware and the PTFE film, and knowing that migration is directly proportional to the initial concentration (assuming mass transfer obeys Fick's Law for diffusion), we calculate a maximum migration of $30\,ng\,dm^{-2}_{polymer}$ in the first use and decreasing amounts thereafter. This conclusion also assumes that all cookware has the same highest initial concentration of PFOA. In fact, a number of cookware items had at least ten times less PFOA. Additionally, we assume a uniform maximum thickness throughout the cookware, an assumption that likely represents an overestimated upper limit in many cases. Eventually because the cookware is a repeat use item, the amount of PFOA in cookware should approach zero provided that no PFOA is generated over time.

From the data presented here, the largest potential source of migratable fluorochemicals from food-contact materials appears to be paper with fluorochemical coatings/additives. In general, fluorochemical treated paper contain a relatively large quantities of fluorotelomers. Some of these coatings/additives can be applied to paper in the concentration range of 0.4% ($4000\,mg\,kg^{-1}$ or $25\,mg\,dm^{-2}$). Therefore, migration of fluorotelomer to food (popcorn bag experiments) in the 3–4 $mg\,kg^{-1}$ ($11\,000\,ng\,dm^{-2}_{paper}$) range, as found here, could be expected. This amount of fluorotelomer migration ($11\,000\,ng\,dm^{-2}_{paper}$) from popcorn bags is hundreds of times more than the amount of fluorochemical (e.g. PFOA) that can calculated to migrate at 175°C from cookware during its first use ($30\,ng\,dm^{-2}_{polymber}$). One should recognize that the data presented represent only a snapshot of the fluorochemical migration picture from paper. In particular, not all popcorn bags have C_6, C_8, C_{10} and C_{12} fluorotelomers on the food-contact surface. FDA is continuing to conduct post-market analysis on additional products where these same coatings/additives are present to have a more complete assessment of the exposure to fluorochemicals from paper.

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