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Emission of perfluoroalkyl carboxylic acids (PFCA) from heated surfaces made of polytetrafluoroethylene (PTFE) applied in food contact materials and consumer products

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HIGHLIGHTS

- Perfluorinated carboxylic acids are emitted from heated PTFE surfaces.
- Emission decreases with increasing chain length.
- Emission increases with temperature.
- Basing on current TDIs there is no risk to human health at normal application temperatures.

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ABSTRACT

Polytetrafluoroethylene (PTFE) has been widely discussed as a source of perfluorooctanoic acid (PFOA), which has been used in the production of fluoropolymers. PTFE may also contain unintended perfluoroalkyl carboxylic acids (PFCAs) caused by thermolysis of PTFE, which has been observed at temperatures above 300 °C. Common PTFE coated food contact materials and consumer goods are operated at temperatures above 200 °C. However, knowledge on possible emissions of PFCAs is limited. Therefore, it was the aim of this study to investigate and evaluate the emission of PFCAs from PTFE coated products with both, normal use and overheating scenarios.

Four pans, claimed to be PFOA free, and nine consumer products were investigated. At normal use conditions (<230 °C), emissions from PTFE surfaces were trapped for 1 h. Overheating scenarios (>260 °C) recorded emissions during a 30 min heating of empty pans on a stove. Emissions were analyzed by LC–ESI-MS.

Results indicate the emission of PFCAs, whereas no perfluorinated sulfonic acids were traced. At normal use conditions total emissions of PFCAs accounted for 4.75 ng per hour. Overheated pans, however, released far higher amounts with up to 12 190 ng PFCAs per hour at 370 °C. Dominating contributors where PFBA and PFOA at normal use and PFBA and PFPeA during overheating. Temperature seems to be the main factor controlling the emission of PFCAs.

A worst case estimation of human exposure revealed that emissions of PFCAs from heated PTFE surfaces would be far below the TDI of 1500 ng PFOA per kg body weight.

1. Introduction

Polytetrafluororethylene (PTFE) is a material with outstanding properties. With a prolonged application temperature of 260 °C it possesses a fairly high heat resistance (Imbalzano, 1991) and is highly non-reactive due to the strength of carbon–fluorine bonds. Furthermore, PTFE is highly hydrophobic and oleophobic and has extremely good non-stick properties due to its resistance to van der Waals forces. Main industrial applications are coaxial cables as well as containers and pipework for reactive and corrosive chemicals (Smith et al., 2014). However, due to its non-stick properties PTFE has entered a variety of consumer applications, including heat exposed food contact materials (FCM) and consumer products (Begley et al., 2005).

PTFE is widely known as a potential source of perfluorooctanoic acid (PFOA), since this compound has been applied as an emulsifier in the production of PTFE (Prevedouros et al., 2006; Lindstrom

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et al., 2011). However, due to persistence as well as bioaccumulative and toxicological properties PFOA has been listed as candidate for being identified as a Substance of Very High Concern under REACH (Vierke et al., 2012; ECHA, 2013). Therefore, in more recent PTFE products PFOA has been partly replaced by other compounds, such as ammonium 4,8-dioxa-3H-perfluorononanoate, ADONA, (Gordon, 2011), which gave rise to the market of PFOA free PTFE products in the last years.

By GC–MS methods Ellis et al. (2001, 2003) determined the gaseous emission of poly- and perfluorinated carboxylic acids from PTFE at temperatures above 300 °C, with trifluoroacetate being the most dominant compound. These emissions were explained by a degradation mechanism of PTFE and were shown to release per- and polyfluorinated C_2–C_{14} acids. Thus it was hypothesized that thermolysis of PTFE may serve as an additional source of emission of perfluorinated carboxylic acids (PFCAs) from PTFE. However, Powley et al. (2005) did not detect PFOA in PTFE extracts obtained by water and ethanol/water mixtures at 100 and 125 °C and detection and quantification limits of 100 pg/cm^2. Washburn et al. (2005) could not identify PFOA in over 40 extraction tests on nonstick cookware, applying test conditions simulating cooking and prolonged food or consumer contact. The absence of PFOA in these PTFE extracts was rationalized by the manufacturing process of nonstick cookware which includes a high-temperature step (sintering) that would degrade residual PFO prior to article use by consumers (Krusic and Roe, 2004).

In conclusion, PTFE is used in a wide range of FCM and consumer products and it is unclear if and which PFCA may be emitted from these products at elevated temperatures. Therefore, this study investigated to which extent PFAA are released from PTFE products exposed to 180–370 °C. The experimental set-up included FCM and other consumer products not intended for food contact. Firstly, gaseous emissions were determined at conditions simulating an unintended overheating. Thereafter, tests were performed at normal use temperatures.

2. Experimentals

2.1. Materials

2.1.1. Samples

Samples and their abbreviations are listed in Table 1.

Food contact materials (FCM): In 2012 three PTFE coated pans were bought from German stores, one low price product and two pans from the medium and upper quality range. A fourth pan with a ceramic surface was also subjected to the test system and it was used for the determination of a method blank. Producers of all four pans claimed their products to be free of PFOA. Further, four electrically heated non-stick FCM were tested: three waffle irons and a sandwich maker. Three types of PTFE coated consumer goods were tested: electric irons, an iron sole plate and an electric hair straightener. Samples were acquired from households of members of our institute. As there was no knowledge on the exact dates of purchase we assessed the year of purchase as good as possible as (Table 1).

2.1.2. Chemicals

Per analysis grades of formic acid, methanol (MeOH), acetonitrile (ACN), tetrahydrofurane (THF), ammonium (NH_3) and hexane as well as HPLC-grade water were purchased from Fluka (Germany) and Merck (Germany).

A mix of 9 isotope labeled congeners of perfluoroalkyl acids (PFAAs), namely perfluorobutanoic, perfluorohexanoic, perfluorooctanoic, perfluorononanoic, perfluorodecanoic, perfluoroundecanoic and perfluorododecanoic acid as well as perfluorohexane and perfluorooctane sulfonate, was purchased from Wellington Laboratories Inc. and used as internal PFAA standard solution. Certified solutions of individual native perfluoroalkyl acids (chain lengths C_4–C_{15} and C_{18}), as well as K-perfluorobutane, K-perfluorohexane, K-perfluorooctane and K-perfluorodecane sulfonate were also purchased from Wellington Laboratories Inc. and used to produce native standard solutions concentrated from 0.1 to 200 ng/ml. Calibration standards were produced from these native and internal standard solutions.

2.2. Emission sampling

Two scenarios were tested. An "overheating scenario" of PTFE coated pans and a "normal use" scenario for all other FCM and consumer products. Sampling strategy was different since pans were heated on an electric stove and all but one of the other samples were heated by integrated electric heaters. An iron sole plate was heated in an oven.

Overheating scenario: Pans were pre-cleaned as recommended by their producers and put onto a stove. The pans were then heated with a 3000 W stove for 30 min without placing any food, fat or water inside. Temperatures at the PTFE surface were monitored by an IR thermometer. Gaseous emissions were trapped by a pre-cleaned glass lid connected by stainless steel tubes to three impinger glass vials (2 filled with methanol, the third one empty), followed by an SPE cartridge (Oasis® Wax, Waters), a pump and an online gas meter (details are given in Supplementary Information S1).

Normal use scenario: 30 L steel hobbocks and adequate lids were used to sample emissions from electrically heated consumer

Table 1
Samples and test conditions.

Abbreviation	Description	Bought in	Application tested	Maximum temperature
Food contact materials				
Pan A	PTFE coated pan, low priced, PFOA free	2012	Overheating scenario	300
Pan B	PTFE coated pan, upper priced, PFOA free	2012	Overheating scenario	250
Pan C	PTFE coated pan, medium priced, PFOA free	2012	Overheating scenario	370
Pan D	Ceramic coated pan, PFOA free	2012	Overheating scenario	300
T1	Sandwich maker (PTFE)	Before 2000	Normal application 1 h	185
W1	Waffle iron 1	Before 2006	Normal application 1 h	187
W2	Waffle irons 2	Before 2006	Normal application 1 h	216
W3	Waffle irons 3	Before 2006	Normal application 1 h	221
Consumer goods				
B1	Electric iron 1	2013	Normal application 1 h	213
B2	Electric iron 2	Before 2009	Normal application 1 h	189
B3	Electric iron 3	Before 2008	Normal application 1 h	190
S1	Iron sole plate	2013	Normal application 1 h	230
H1	Hair straightener	Before 2009	Normal application 1 h	180