Determination of perfluorinated compounds (PFCs) in various foodstuff packaging materials used in the Greek market

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HIGHLIGHTS

- A PLE combined with LC–MS/MS method for PFCs analysis was developed.
- It was applied in paper, paperboard or aluminum foil made foodstuff-packaging materials from the Greek market.
- No sample contained PFOA or PFOS. Some PFCs were detected in fast food wrappers.
- The highest levels of PFCs were found in a microwave popcorn bag.
- Compared to other countries very low PFC concentrations were found in the Greek samples.

ARTICLE INFO

ABSTRACT

Perfluorinated compounds (PFCs) are used in food packaging materials as coatings/additives for oil and moisture resistance. In the current study, foodstuff-packaging materials collected from the Greek market, made of paper, paperboard or aluminum foil were analyzed for the determination of PFCs. For the analysis of the samples, pressurized liquid extraction (PLE), liquid chromatography–tandem mass spectrometry (LC–MS/MS) and isotope dilution method were applied to develop a specific and sensitive method of analysis for the quantification of 12 PFCs: perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS) and perfluorooctane sulfonate (PFOS) and the qualitative detection of 5 more: perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), perflyohexadecanoic acid (PFHxDA), perfluorooctadecanoic acid (PFODA) and perfluorodecane sulfonate (PFDS). No PFCs were quantified in aluminum foil wrappers, baking paper materials or beverage cups. PFTrDA, PFTeDA and PFHxDA were detected in fast food boxes. In the ice cream cup sample only PFHxA was found. On the other hand, several PFCs were quantified and detected in fast food wrappers, while the highest levels of PFCs were found in the microwave popcorn bag. PFOA and PFOS were not detected in any of the samples. Compared to other studies from different countries, very low concentrations of PFCs were detected in the packaging materials analyzed. Our results suggest that probably no serious danger for consumers' health can be associated with PFCs contamination of packaging materials used in Greece.

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1. Introduction

Modern food packaging materials are designed to fulfill multiple purposes including the protection of food products from external sources of contamination and damage, and the information of consumers about ingredients and nutritional data (Coles, 2003). Furthermore, food packaging provides preservation, ease of transportation and storage of the food products (Lau and Wong, 2000; Koutsimanis et al., 2012). Thus, the production and use of packaging materials has increased during the last decades, comprising an indispensable part of food manufacturing. Packaging manufacturing industry is making an effort to combine low cost manufacturing, improvement of appearance and consumer appeal, maintenance of food safety and minimum environmental impacts. Concerning food safety, one of the major factors that manufacturers have to pay attention to is the migration of harmful chemical compounds from packaging materials to food, and the health effects that they could cause to consumers (Gallart-Ayala et al., 2013). In this context, strict national and EC regulations, applicable

to all materials which come in direct contact with food, have been established (EC Recommendation 1935/2004; Arvanitoyannis and Bosnea, 2004).

Nowadays, the most widely applicable packaging materials are made of paper and aluminum. In particular, paper and paperboard are commonly used in corrugated boxes, wrapping paper, milk cartons, folding cartons, bags and sacks, paper plates and beverage cups, fast-food containers, microwave popcorn bags, ice cream cups, dessert containers, baking paper, etc. More specifically, paperboard, due to its thickness, is commonly used for packages appropriate for shipping, such as boxes and cartons, but also as packaging material for fast food such as pizza. Plain paper does not possess good heat sealing and barrier properties, so it is almost always treated, coated, or impregnated with additives in order to improve its functional and protective properties, before its use as packaging material (Marsh and Bugusu, 2007).

As far as aluminum is concerned, it acts as a complete barrier to light and oxygen (which cause fats to oxidize or become rancid), protects from odors and flavors and resists to most forms of corrosion such as moisture, chemicals, air, temperature and microorganisms. It also has the advantage of flexibility, resilience, malleability and formability. Aluminum is usually used in long-life containers for beverages and dairy products enabling their storage without refrigeration. Moreover, aluminum is commonly used to make cans, laminated paper or plastic packaging and foil. Regarding foil, pure aluminum metal is rolled into very thin sheets and subsequently annealed, producing aluminum foil. Aluminum foil possesses the same properties as pure aluminum metal, and depending on its thickness it is used as wrapping material in food or in trays (Marsh and Bugusu, 2007).

An important group of compounds that have been used extensively since 1980s in the production of foodstuff packaging materials is the group of perfluorinated compounds (PFCs). These organic chemicals, due to their structure and the strength of the bond between carbon and fluorine possess thermal, chemical and biological stability, non-flammability and surface-activity properties (Schultz et al., 2003; Lau et al., 2007). Their unique physical and chemical characteristics render them useful for various industrial and consumer applications, including foodstuff packaging materials (Kissa, 2001).

In particular, the surface of the paper used as packaging material is usually treated before its use in order to achieve characteristics such as water and grease/oil resistance (Harada and Koizumi, 2009). In this context, paper is often treated with perfluorinated coatings/additives that make the package appropriate for fat-containing food products (Begley et al., 2005).

As far as aluminum packaging materials are concerned, PFCs are not known to be applied in their production, however it is worth mentioning that during the production of aluminum, PFCs (CF4 and C2F6) are produced and emitted (Rhoderick et al., 2001). Although the total amount of PFCs emitted is low compared to other products, they are very unreactive and because of this there is no method available to remove them, though an effort to minimize their emission is made (U.S. EPA Voluntary Aluminum Industrial Partnership Program).

Since food packaging materials come directly in contact with food, PFCs can migrate from package to food, and cause hazardous effects to human health (Tittlemier et al., 2007). Moreover, due to their amphiphilicity PFCs are able to persist in the environment and bioaccumulate in living organisms, therefore they biomagnify in the food chain (Quinete et al., 2009). Their high applicability combined with chemical stability has led to inevitable accumulation of PFCs in the environment and recently they have been detected in several environmental matrices i.e. air, sewage, drinking water, rivers, oceans (Gonzalez-Barreiro et al., 2006; Skutlarek et al., 2006; Jahnke et al., 2007; Esparza et al., 2011; Haug et al.,

2011; Llorca et al., 2011; Shoeib et al., 2011; Goosey and Harrad, 2012; Jogsten et al., 2012; Wang et al., 2012), food products (Ericson-Jogsten et al., 2009; van Leeuwen et al., 2009; Schuetze et al., 2010; Noorlander et al., 2011; Picó et al., 2011; Domingo et al., 2012; Vestergren et al., 2012; Wu et al., 2012) and in human tissues, breast milk and blood (Calafat et al., 2006; Costopoulou et al., 2008; Haug et al., 2009a,b; Vassiliadou et al., 2010; Kim et al., 2011; Ji et al., 2012).

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are the two most stable PFCs in the environment and the most studied among PFCs compounds. They have been produced in highest amounts for several decades in the past and have been recognized by the European Food Safety Authority (EFSA) as emerging contaminants in the food chain. Despite the fact that the main production company of PFOS, 3M Company, phased out the production of PFOS products around 2000 (Olsen et al., 1999, 2003), PFOS is still detected in various matrices. EFSA has established tolerable daily intakes (TDI) of 150 ng kg^{-1} b.w. day^{-1} for PFOS and 1500 ng kg^{-1} b.w. day^{-1} for PFOA (EFSA, 2008). As has been shown in many studies, they have moderate acute toxicity and have been classified as "harmful if swallowed" (US EPA, 2000; Kennedy et al., 2004). PFOS has been determined as a persistent, bioaccumulative and toxic (PBT) substance (OECD, 2002). Moreover, PFOS, its salts and PFOS-F (perfluorooctane sulfonyl fluoride) have been added to the list of persistent organic pollutants (POPs) of the Stockholm Convention on Persistent Organic Pollutants, in an amendment of May 2009 that included nine new chemicals as persistent organic pollutants. According to this amendment, PFOS "has a capacity to undergo long-range transport and also fulfills the toxicity criteria of the Stockholm Convention" (http://chm.pops.int/Programmes/NewPOPs/The9newPOPs/tabid/672/language/en-US/Default.aspx).

Although there are concerns about the toxicological effect of PFCs on humans, the information available is limited and sometimes contradictory. Studies in rodents have shown that PFOS and PFOA exhibit moderate toxicity (Lau et al., 2004, 2006, 2007; Olsen et al., 2009). The half-life of PFOS and PFOA in human serum is considered long (about 5 and 3.5 years respectively) (Olsen et al., 2007), and in the organs is probably longer (Jensen and Leffers, 2008). Developmental toxicity studies in rodents, as well as epidemiological studies in general and occupational populations, reported effects of lower birth weight, increased postnatal mortality, and decreased postnatal growth (Lin et al., 2009; Olsen et al., 2009; Stahl et al., 2011). A recent study shows that fluorochemicals used in food packaging and their metabolites can affect steroidogenesis and inhibit male sex hormone synthesis (Rosenmai et al., 2013).

Being both lipophobic and hydrophobic, PFCs accumulate mainly in blood, liver and kidneys of living organisms, through binding to proteins, in contrast with other POPs that accumulate exclusively in adipose tissue (Luebker et al., 2002). The main routes through which humans are exposed to PFCs are inhalation and consumption of food products, drinking water and household dust. It also has been proven that there is a placental transfer of PFCs during gestation, and exposure of newborns through lactation. Although the exact mechanism of human exposure to PFCs remains to be elucidated, up to now dietary intake is considered the main transfer route of PFCs especially PFOS and PFOA, and several studies have reported a correlation between dietary intake of PFCs and blood levels (Karrman et al., 2009; Harada et al., 2010; Domingo 2012).

Despite the wide-spread use of PFCs in food packaging materials, a very limited number of studies have been published concerning PFCs' concentrations in foodstuff packaging materials. More specifically, the samples that have been examined include polytetrafluoroethylene (PTFE) packaging materials and textiles (Lv et al., 2009) and/or the migration of PFCs from packaging materials and

cookware to food (Bradley et al., 2007; Tittlemier et al., 2007). Studies focusing on the detection of PFCs in paper packaging have demonstrated some amount of PFC contamination and PFC migration from the packaging materials to food (Begley et al., 2005, 2008; Trier et al., 2011; Martinez-Moral and Tena, 2012; Poothong et al., 2012).

Taking under consideration all the above, in the present study we developed an analytical method suitable for the determination of trace level concentrations of PFCs in food packaging materials and we analyzed various packaging materials used in the Greek market. The method developed combines pressurized liquid extraction (PLE), liquid chromatography–tandem mass spectrometry (LC–MS/MS) and isotope dilution method. In particular, the analytical protocol developed is suitable for quantitative determination of 12 perfluorinated compounds (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoA, PFBS, PFHxS and PFOS) and detection of 5 more (PFTrDA, PFTeDA, PFHxDA, PFODA and PFDS). The analyzed packaging materials from the Greek market were paper, paperboard and aluminum foil, and were used as wrapping materials of fast food items, chocolate, pharmaceutical products, and as yoghurt and marmalade lids. Beverage cups, ice cream cup, microwave bags for popcorn and rice, boxes of fast food and baking paper were also analyzed.

2. Materials and methods

2.1. Materials

The perfluorinated compounds analyzed in the present study are shown in Table 1. Standard solutions of $^{13}C_4$-labelled PFBA, PFOA and PFOS, $^{13}C_2$-labelled PFHxA, PFDA, PFUnDA and PFDoA, $^{13}C_5$-labelled PFNA and $^{18}O_2$-PFHxS were purchased from Wellington Laboratories (Guelph, Ontario, Canada). Methanol, petroleum ether, sea sand, ammonium acetate and sodium sulphate were purchased from Merck (Darmstadt, Germany). Florisil 60–100 mesh was purchased from Promochem (Germany) and Basic Alumina activity Super 1 from MP Biochemicals (Germany). Ultrapure water was provided by a Nanopure apparatus, (Barnstead/Thermolyne, USA). Basic alumina was activated in an oven at 200 °C overnight. Florisil sorbent was dried at 200 °C overnight and deactivated with 0.5% (w/w) ultrapure water prior to use.

2.2. Food packaging samples

42 samples of food packaging made of paper and/or aluminum were analyzed (beverage and ice cream cups, fast food wrappers for sandwiches, burgers etc., paper box for pop-corn, french fries, pizza and sandwiches, non-stick baking paper, muffin cup, microwave bags for pop-corn and rice and aluminum foil bags and wrappers for chocolate, coffee, croissant, cereals, potato chips). All samples were obtained randomly from retail sellers, their exact composition was not stated and there were no information about perfluorochemicals used in their manufacturing process or not. More specifically, beverage and ice cream cups, wrappers and paper boxes were collected in Athens from October to December 2012 from the most popular in Greece fast food chain restaurants, coffee shops and multiplex cinemas with venues in many locations all over the country. Prevailing brands of muffin cups, baking papers and microwave pop-corn and rice bags were purchased from big super markets. All samples collected with the exception of microwave pop-corn and rice bags were manufactured in Greece. Most packaging materials were unused while some already contained food products.

2.3. Sample preparation

2.3.1. Initial treatment

Before analysis, in the cases when the samples had a printed outside layer, this was removed when possible. Any food content

Table 1
Mass transitions (parent ion/product ion) for target compounds.

Compound	RT	Primary ion transition (m/z)	Collision cell energy (eV)	Secondary ion transition (m/z)	Collision cell energy (eV)	Tube lens offset voltage (V)
PFBA	4.56	213 → 169	20		40	90
PFPeA[a]	6.11	263 → 219	20	263 → 69	40	90
PFHxA	7.18	312.9 → 268.9	20	312.9 → 118.9	40	90
PFHpA[b]	8.26	363.2 → 319	20	363.2 → 168.8	40	90
PFOA	9.27	412.9 → 368.8	20	412.9 → 218.9	40	90
PFNA	10.22	462.7 → 418.9	20	462.7 → 219	40	90
PFDA	11.10	512.9 → 468.9	20	512.9 → 268.9	40	90
PFUnDA	11.84	562.9 → 518.9	20	562.9 → 168.9	40	90
PFDoDA	12.52	612.9 → 568.8	20	612.9 → 168.9	40	90
PFTrDA[c]	13.13	662.8 → 619	20	662.8 → 268.9	40	90
PFTeDA[c]	13.67	712.9 → 668.9	20	712.9 → 168.9	40	90
PFHxDA[c]	14.47	813 → 769	20	813 → 269	40	90
PFODA[c]	15.21	913 → 869	20	913 → 169	40	90
PFBS[d]	6.31	298.9 → 99	50	298.9 → 80	50	146
PFHxS	8.33	398.9 → 99	50	398.9 → 79.9	50	146
PFOS	10.22	498.9 → 99.1	50	498.9 → 80	50	146
PFDS[e]	11.78	598.9 → 99	50	598.9 → 79.9	50	146
$^{13}C_4$-PFBA	4.56	217 → 172	20		40	90
$^{13}C_2$-PFHxA	7.25	315 → 270	20	315 → 118.9	40	90
$^{13}C_4$-PFOA	9.28	416.9 → 371.8	20	416.9 → 168.9	40	90
$^{13}C_5$-PFNA	10.22	467.9 → 422.9	20	467.9 → 168.9	40	90
$^{13}C_2$-PFDA	11.10	515 → 470	20	515 → 219	40	90
$^{13}C_2$-PFUnDA	11.84	565 → 520	20	565 → 168.9	40	90
$^{13}C_2$-PFDoDA	12.59	615 → 570	20	615 → 169.1	40	90
$^{18}O_2$-PFHxS	8.33	402.7 → 103	50	402.7 → 84.1	50	146
$^{13}C_4$-PFOS	10.23	502.9 → 99.1	50	502.9 → 80	50	146

[a] $^{13}C_4$-PFBA is used as internal standard.
[b] $^{13}C_2$-PFHxA is used as internal standard.
[c] $^{13}C_2$-PFDoDA is used as internal standard.
[d] $^{18}O_2$-PFHxS is used as internal standard.
[e] $^{13}C_4$-PFOS is used as internal standard.

was removed from the packaging, which was then rinsed with ultrapure water to remove salt and dried. Subsequently samples were cut into pieces of approximately 1 cm² with scissors.

2.3.2. Extraction

Food packaging samples were extracted by pressurized liquid extraction (PLE), using an ASE Dionex 300 apparatus. Stainless steel ASE extraction cells (34 or 66 mL) were used. Two g of each sample were weighed and 200 μL of internal standard solution were added (200 ng mL^{-1} $^{13}C_4$-labelled PFBA, PFOA and PFOS, $^{13}C_2$-labelled PFHxA, PFDA, PFUnDA and PFDoA, $^{13}C_5$-labelled PFNA and $^{18}O_2$-PFHxS in methanol). Each sample was mixed with 35 g or 65 g of sea sand, depending on the extraction cell volume, and placed in the extraction cells with a cellulose fiber filter at the bottom. The cells were filled up with sea sand to reduce dead volume and minimize solvent quantity, capped and loaded on the ASE Dionex 300 apparatus. The extraction program included heating to 80 °C, 7 min static period, 3 cycles of extraction with MeOH, 100% flush volume, pressure at 1500 psi and purge to 1 min. The final extract was further cleaned up by solid phase extraction on florisil and basic alumina column as described below.

2.3.3. Clean-up

After completion of the ASE extraction, the methanol extract was centrifuged for 5 min at 5000 rpm (3857 × g), for precipitation and removal of insoluble particles. The extract was evaporated to dryness, re-dissolved in 3 mL of petroleum ether and brought onto the top of a glass column (30 cm length, 8 mm ID) plugged with precleaned glass wool and filled with 1.5 g florisil, 1 g basic alumina and 1 g of sodium sulphate. Prior to sample addition, the column was conditioned with 5 mL of methanol and 5 mL of petroleum ether. After sample addition the column was washed with 10 mL of petroleum ether and 8 mL of a MeOH/petroleum ether mixture (10:90 v/v). Target compounds were finally eluted with 8 mL of MeOH. The fraction collected was evaporated till dryness in a flash evaporator and the dry residue was dissolved in 200 μL of LC mobile phase (5 mM ammonium acetate – MeOH (80:20, v/v)). An aliquot of 100 μL of the re-dissolved residue was transferred to an auto-injector vial. A schematic presentation of the analytical protocol developed is shown in Fig. 1.

2.4. Instrumental analysis

All sample extracts were analyzed by liquid chromatography combined with tandem mass spectrometry (LC–MS/MS) with electrospray ionization (ESI) operating in negative mode. 35 μL were injected in a Hypersil GOLD C8 (150 mm × 2.1 mm i.d, 3 μm, Thermo) using a Surveyor MS Pump Plus (Thermo). The chromatographic gradient operated at a flow rate of 0.25 mL min^{-1} started with an initial condition of 80% 5 mM ammonium acetate – MeOH (80:20, v/v) (A) and 20% MeOH (B) and MeOH (B) increased to 50% (B) in 3 min. 100% (B) is reached in the next 12 min and held for 3 min.

The oven temperature of the analytical column was set at 26 °C. The HPLC was connected to a triple quadrupole mass spectrometer (TSQ QUANTUM ULTRA, Thermo) equipped with an Ion MAX-S thermoelectrospray source. The source temperature was maintained at 350 °C and the spray voltage at 3500 V. Analysis was performed by a multiple reaction monitoring (MRM) method that monitored two mass transitions (parent ion/product ion) for each analyte except for PFBA for which only one ion product was detected probably due to its small molecular weight. Ion transitions for target analytes and labeled standards are listed in Table 1. The values of the voltages applied to the tube lens offset and the collision cell were optimized for each ion transition.
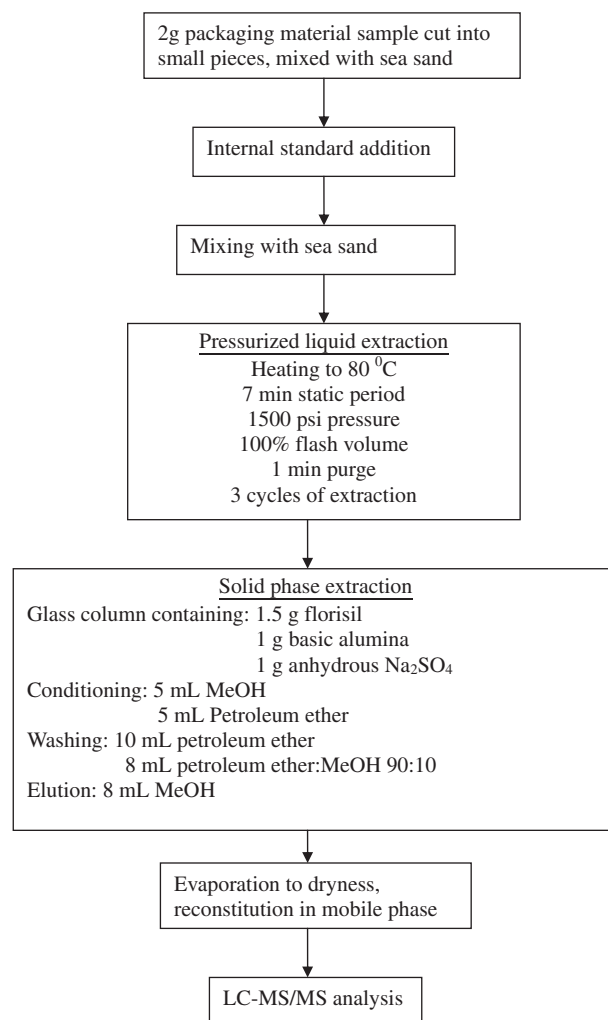

Fig. 1. Schematic presentation of the analytical protocol for PFC analysis in food packaging materials.

Confirmation of analyte identity was based on retention time, in addition to relative response of the secondary mass transition to the primary mass transition. Quantification of the target compounds was performed by the sum of areas of the two product ions using a response factor calibration curve vs the ^{13}C or ^{18}O-labelled standard.

2.5. Method validation

The method was validated for specificity, repeatability, reproducibility, recovery and sensitivity according to EURACHEM guide "The fitness for purpose of analytical methods – a laboratory guide to method validation and related topics". For analyte identity (specificity) confirmation, retention time (RT) of the analyte should correspond to that of the labeled standard ±0.2 s. Repeatability and reproducibility of the method developed were tested by multiple analyses of spiked samples at concentrations of 5 ng g^{-1}, 10 ng g^{-1} and 30 ng g^{-1}. Recovery was estimated by the use of internal isotopically labeled standards and found to vary between 60% and 90%.

Due to the very low noise in the LC–MS/MS system, the calculation of LOD and LOQ from a signal-to-noise ratio was not possible. Therefore, the LOD was calculated from the lowest concentration with acceptable signal-to-noise ratio, and LOQ from the lowest concentration with ion abundance ratio within ±15% of the

theoretical value and deviation of the relative response factor from the mean value $\leqslant 20\%$. The calculated LOD of the compounds analyzed ranged from 0.20 to 0.94 ng g^{-1}. Especially LOD for PFOS and PFOA were 0.49 and 0.60 ng g^{-1} respectively. Calculated LODs and LOQs are presented in Table 3.

The laboratory participates successfully in international interlaboratory studies and is accredited for PFOS and PFOA analysis according to ISO/IEC 17025/2005.

3. Results and discussion

Up to now, a lot of studies have been carried out for the determination of PFCs in a wide range of matrices, including sewage treatment samples, air, sediment, soil, biological fluids, food and extending to consumer products (floor-polish waxes and impregnating agents, carpets and textiles). Initial studies focused on the determination of the two most abundant PFCs, PFOS and PFOA,

Table 2
Overview of the reported methods for analysis of PFCs in food packaging materials.

Country	Analytes	Matrix	Origin of samples	Method of analysis	Results of analysis	Reference
USA	PFOA	Popcorn bags, hamburger wrapper, French fry box, paper plates, perfluoro paper coatings, etc.	US retail market	Sonication with 50/50 ethanol/water LC–MS/MS LC column: Zobrax SB-C8, 100 × 2.0 mm × 3.5 µm	PFOA was present in many samples, with highest amounts in popcorn bags (up to 290 µg kg^{-1}). The migration of PFCs from cookware and popcorn bags was studied	Begley et al., 2005, 2008
USA	PFOA PFPeA PFHpA PFNA PFDA PFUnDA PFDoDA 6:2 FTOH 8:2 FTOH	3 samples of popcorn packaging material	Not specified	Shaking with methanol and ethylacetate LC–MS/MS LC column: Keystone Betasil C18 50 × 2.0 mm × 5 µm	PFOA and FTOHs were detected in vapors released by microwave popcorn. All analytes were found in one popcorn container at ng cm^{-2} concentrations. Only PFOA was detected in another.	Sinclair et al., 2007
China	PFOS PFOA	PTFE packaging material	Manufactured and purchased in China	PLE with acetonitrile GC–MS, derivatization by silylation	PFOA 17.5–45.9 ng g^{-1} PFOS 33.7–81.3 ng g^{-1}	Lv et al., 2009
Australia	PFHxA PFHpA PFOA PFNA PFDA PFUnDA PFOS	Microwave popcorn bags, popped popcorn after microwaving, non-stick backing paper, french fry box, sandwich wrapper, hamburger box	Retail stores and a major fast food company in Australia	Sonication with water LC–MS LC column: Luna Phenyl-Hexyl, 50 mm × 2 × 3 µm	PFOA was detected in one microwave popcorn bag (9 µg kg^{-1})	Dolman and Pelzing, 2011
Denmark	Large number of PFCs	14 papers and board materials intended for contact with food at high temperatures	Retailers in Denmark	Sonication with ethanol LC–QTOF-MS LC column: Waters Acquity C18 150 × 2.1 mm × 1.7 µm	More than 115 polyfluorinated surfactants were detected	Trier et al., 2011
Thailand	PFOS PFOA	34 samples of food packaging material made of paper	Domestic and international restaurants in Bangkok, Thailand	PLE with methanol or saliva stimulant LC–MS/MS LC column: Agilent Eclipse XBD-C18 4.6 mm × 50 mm × 1.8 µm	PFOS and PFOA were detected in almost all paper packages. The highest concentration for PFOS (92.48 ng dm^{-2}) and PFOA (17.74 ng dm^{-2}) was found in a fried chicken box	Poothong et al., 2012
Spain	PFHpA PFOA PFNA PFOS PFDA PFUnDA PFDoA	Microwave popcorn bags of three different brands	Supermarkets in Spain	PLE with methanol LC–QTOF–MS/MS LC column: Waters Acquity C18 50 × 2.1 mm × 1.7 µm	Significant levels of PFOA (53–198 ng g^{-1}). Detectable levels of PFHpA, PFNA and PFDoA in some samples. All 7 PFCs were detected in two of the samples	Martinez-Moral and Tena, 2012
Greece	PFBA PFPeA PFHxA PFHpA PFOA PFNA PFDA PFUnDA PFDoA PFBS PHHxS PFOS PFTrDA PFTeDA PFHxDA PFODA PFDS	42 samples including beverage and ice cream cups, fast food wrappers, paper boxes, baking paper, aluminum foil bags and wrappers, microwave bags	Retail sellers, fast food chain restaurants, coffee shops and multiplex cinemas in Athens, Greece	PLE with methanol Clean-up with Florisil-Basic Alumina column LC–MS/MS LC column: Thermo Hypersil GOLD C8 150 mm × 2.1 mm i.d × 3 µm	Neither PFOA nor PFOS was detected in any sample. PFTrDA, PFTeDA and PFHxDA were detected in fast food boxes. PFHxA was found in ice cream cup. Several PFCs were detected in fast food wrappers and microwave popcorn bag	Present study, 2013

however later studies gradually included several other volatile and non-volatile perfluorinated compounds of varying chain lengths. The diversity of analytes and matrices created the need to develop several methods of sample extraction and clean-up combined to instrumental techniques of quantification. The methods developed until 2007 have been reviewed extensively. Several limitations that render the analysis of PFCs especially challenging have been specified, including the impurity of the standards available, matrix effects and contamination through clean-up (de Voogt and Saez, 2006; Villagrasa et al., 2006; van Leeuwen and de Boer, 2007).

Several studies report the determination of PFCs in food packaging materials and other food-related items, such as cookware and vapors produced during cooking processes. Most of these studies are based on LC–MS/MS methodology. Their overview is presented in Table 2.

In this paper we present a method using PLE combined to LC–MS/MS for the determination of PFCs in foodstuff packaging materials. Methanol as solvent has been shown efficient for the extraction of PFCs in several matrices, and an extensive study for the optimization of PFC extraction from polytetrafluoroethylene fluoropolymer has proven as optimal conditions the use of methanol in temperatures not exceeding 150 °C and at 12 min residence time (Larsen et al., 2006). In contrast to previous studies reporting methods of analysis of PFCs in packaging materials, we also deemed it necessary to include a clean-up step, especially since no pre-column clean-up was included in our LC system, as is the case in some of the other previous methods (Larsen et al., 2006; Martinez-Moral and Tena, 2012; Poothong et al., 2012). The fact that this step adds to analysis time is counter-balanced by the short time needed for the PLE step. In-house florisil and alumina columns were used instead of pre-packed C18 cartridges, reducing analysis cost. Although the use of florisil has not been reported in any of the other studies concerning the clean-up step in PFCs in food packaging materials, its use has been reported in clean-up method for the determination of PFCs in food samples (Vestergren et al., 2012) and in atmospheric air (Boulanger et al., 2005).

Instrumental analysis was carried out by LC–MS/MS using ESI ionization in the negative ion mode, a technique widely used for the analysis of anionic perfluorinated surfactants (Villagrasa et al., 2006). Crucial instrumental ionization parameters for detecting each one of the compounds of interest were optimized. These parameters included mainly voltages applied to the tube lens offset and the collision cell that are applied for the generation of the precursor and product ions of each ion transition. The developed method was applied for the quantification of 12 compounds: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoA, PFBS, PFHxS and PFOS, and detection of 5 compounds: PFTrDA, PFTeDA, PFHxDA, PFODA and PFDS. The transitions used for multiple reaction monitoring analysis of these analytes are presented in Table 1.

The results for 42 samples of food packaging items are presented in Table 3. The two PFCs (PFOS and PFOA) most commonly found in many biological and environmental matrices analyzed (food samples, biological fluids, water and air samples) were not detected in any of our samples, unlike previous studies of food packaging materials where PFOA (Begley et al., 2005; Sinclair et al., 2007; Dolman and Pelzing, 2011; Trier et al., 2011; Martinez-Moral and Tena, 2012; Poothong et al., 2012) and PFOS (Poothong et al., 2012) i.e. the two most common PFCs, were detected in significant quantities.

No PFCs were quantified in aluminum foil wrappers, baking paper materials or beverage cups. PFTrDA, PFTeDA and PFHxDA were detected in fast food boxes. Only PFHxA was found in the ice cream cup sample. On the other hand, several PFCs were quantified and detected in fast food wrappers while the highest levels of PFCs were found in the microwave popcorn bag sample (275.84 ng g^{-1} of PFBA, 341.21 ng g^{-1} of PFHxA and 5.19 ng g^{-1} of PFHpA).

The high concentration of PFCs in microwave popcorn bags is also reported in others studies. This food packaging item has been studied extensively, since it represents an extreme case of food in contact with its packaging during conditions of irradiation and high temperature in the presence of melted fatty acids, and is therefore considered a model for the migration of PFCs from foodstuff packages to food. Indeed, all previous studies of microwave popcorn bags report the presence of PFCs. In 2005, Begley et al., determined PFOA and fluorotelomers in popcorn bags. PFOA concentration was between 6 and 290 µg kg^{-1}. Migration studies showed that 1.4 mg kg^{-1} of fluorotelomers migrated to oil before microwaving, with an additional 2.1 mg kg^{-1} migrating after the microwaving procedure. Significant PFOA levels were also found in all three popcorn bags analyzed in the study of Martinez-Moral and Tena, 2012 (53–198 ng g^{-1}) and PFOS and PFOA were found in one of the two popcorn bags analyzed by Poothong et al. (2012).

Table 3
Concentrations (ng g^{-1}) of PFCs in packaging materials.

Compound	LOD	LOQ	Beverage cups ($n = 8$)	Ice cream cup ($n = 1$)	Fast food paper boxes[a] ($n = 8$)	Fast food wrappers ($n = 6$)	Paper materials for baking[b] ($n = 2$)	Microwave bags[c] ($n = 3$)	Aluminum foil bags/wrappers[d] ($n = 14$)
PFBA	0.51	1.54	<LOD	<LOD	<LOD	<LOD-3.19	<LOD	<LOD-275.84	<LOD
PFPeA	0.39	1.17	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxA	0.94	2.83	<LOD	25.56	<LOD	<LOD-19.17	<LOD	<LOD-341.21	<LOD
PFHpA	0.40	1.21	<LOD	<LOD	<LOD	<LOD-10.02	<LOD	<LOD-5.19	<LOD
PFOA	0.60	1.82	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFNA	0.42	1.25	<LOD	<LOD	<LOD	<LOD-4.97	<LOD	<LOD	<LOD
PFDA	0.69	2.08	<LOD	<LOD	<LOD	<LOD-28.25	<LOD	<LOD	<LOD
PFUnDA	0.70	2.11	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDoA	0.20	0.59	<LOD	<LOD	<LOD	<LOD-19.12	<LOD	<LOD	<LOD
PFTrDA	1.40		<LOD	<LOD	<LOD-detect.	<LOD-detect.	<LOD	<LOD	<LOD
PFTeDA	2.42		<LOD	<LOD	<LOD-detect.	<LOD	<LOD	<LOD	<LOD
PFHxDA	1.36		<LOD	<LOD	<LOD-detect.	<LOD-detect.	<LOD	<LOD	<LOD
PFODA	1.15		<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFBS	0.57	1.70	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxS	0.18	0.54	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFOS	0.49	1.48	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDS	2.65		<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

[a] Pop-corn box, French fries box, pizza box, burger box.
[b] Baking paper, muffin cup.
[c] Pop-corn bag, rice bag.
[d] Chocolate wrapper, coffee bag, croissant wrapper, cereal bag, potato chips bag, aluminum foil.

Table 4
Concentrations (ng/g^{-1}) of PFCs in microwave popcorn bag before and after cooking.

Compound	Popcorn bag before cooking	Popcorn bag after cooking
PFBA	275.84	155.55
PFPeA	<LOD	60.76
PFHxA	341.21	681.35
PFHpA	5.19	11.07
PFOA	<LOD	<LOD
PFNA	<LOD	<LOD
PFDA	<LOD	<LOD
PFUnDA	<LOD	<LOD
PFDoA	<LOD	<LOD
PFTrDA	<LOD	<LOD
PFTeDA	<LOD	<LOD
PFHxDA	<LOD	<LOD
PFODA	<LOD	<LOD
PFBS	<LOD	<LOD
PFHxS	<LOD	<LOD
PFOS	<LOD	<LOD
PFDS	<LOD	<LOD

Dolman and Pelzing (2011) also detected 9.1 μg kg^{-1} of PFOA in one of the two microwave popcorn bags analyzed, while no PFCs could be detected in the popped popcorn after microwaving, suggesting that either the PFCs did not migrate to the popcorn or that they could not be extracted from it. None of the above studies investigated further PFCs besides PFOS and PFOA.

We analyzed 17 PFCs in a microwave popcorn bag before and after the microwave cooking of the popcorn it contained. The results are presented in Table 4. PFOS and PFOA were not detected in the analyzed sample, but other PFCs were detected and showed different levels after cooking: PFBA (275.84 and 155.55 ng g^{-1}), PFPeA (<LOD and 60.76 ng g^{-1}), PFHxA (341.21 and 681.35 ng g^{-1}) and PFHpA (5.19 and 11.07 ng g^{-1}) before and after microwaving respectively. The concentrations of PFCs, except PFBA, on the surface of the bag are increased by microwave cooking conditions required for preparing popcorn. This could be explained by the release of these compounds from the matrix due to the temperature raise. The lowering of PFBA concentration after microwaving could be attributed to its higher volatility. In the study of Sinclair et al. (2007), where several PFCs, including PFOA were detected in one of the 3 microwave popcorn bags studied, only FTOHs were found at greater concentrations following cooking than before cooking.

4. Conclusion

A method based on PLE and LC–MS/MS was developed and applied in the determination of 17 PFCs in 42 samples of food packaging material from the Greek market. No PFCs were quantified in aluminum foil wrappers, baking paper materials or beverage cups. PFTrDA, PFTeDA and PFHxDA were detected in fast food boxes. In the ice cream cup sample only PFHxA was found. On the other hand, several PFCs were quantified and detected in fast food wrappers, while the highest levels of PFCs were found in the microwave popcorn bag. PFOA and PFOS were not detected in any of the samples. Compared to other studies from different countries, very low concentrations of PFCs were detected in the packaging materials analyzed. Most of the packaging materials studied were manufactured in Greece where perhaps PFC alternatives as fluorophosphates and fluorinated polyethers are used in the manufacturing process. As the items analyzed were selected from the most popular chain restaurants, coffee shops and multiplex cinemas, we can assume that they are representative of the Greek market. Our results suggest that probably no serious danger for consumers' health can be associated with PFCs contamination of packaging material used in Greece.

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