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Determination of perfluorinated alkyl acids in corn, popcorn and popcorn bags before and after cooking by focused ultrasound solid–liquid extraction, liquid chromatography and quadrupole-time of flight mass spectrometry

Cristina Moreta, María Teresa Tena *

Department of Chemistry, University of La Rioja, C/ Madre de Dios 51, E-26006 Logroño, La Rioja, Spain

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ABSTRACT

An analytical method is proposed to determine ten perfluorinated alkyl acids (PFAAs) [nine perfluorocarboxylic acids (PFCAs) and perfluorooctane sulfonate (PFOS)] in corn, popcorn and microwave popcorn packaging by focused ultrasound solid–liquid extraction (FUSLE) and ultra high performance liquid chromatography (UHPLC) coupled to quadrupole-time of flight mass spectrometry (QTOF-MS/MS). Selected PFAAs were extracted efficiently in only one 10-s cycle by FUSLE, a simple, safe and inexpensive technique. The developed method was validated for microwave popcorn bags matrix as well as corn and popcorn matrices in terms of linearity, matrix effect error, detection and quantification limits, repeatability and recovery values. The method showed good accuracy with recovery values around 100% except for the lowest chain length PFAAs, satisfactory reproducibility with RSDs under 16%, and sensitivity with limits of detection in the order of hundreds picograms per gram of sample (between 0.2 and 0.7 ng/g). This method was also applied to the analysis of six microwave popcorn bags and the popcorn inside before and after cooking. PFCAs contents between 3.50 ng/g and 750 ng/g were found in bags, being PFHxA (perfluorohexanoic acid) the most abundant of them. However, no PFAAs were detected either corn or popcorn, therefore no migration was assumed.

1. Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) have been broadly used since the late 1940s in different industrial and commercial applications due to their effect of the reduction of the surface tension and their hydrophobic and oleophobic properties [1,2]. Hence, they have been extensively distributed in the environment.

However, perfluorinated compounds show high thermal, biological and chemical inertness owing to carbon–fluorine is the strongest existing covalent bond (450 kJ/mol) [3]. Moreover, it has been also proved that perfluoroalkyl acids (PFAAs) exhibit toxicity in laboratory animals causing developmental diseases, liver cancer, affect the lipid metabolism and disturb the immune system [4]. Additionally, these compounds may come from the degradation of other PFASs, such as polyfluoroalkyl phosphate surfactants (PAPs) and fluorotelomers (FTOHs), which may be atmospherically or metabolically degraded to them, increasing the PFAAs concentration, such as perfluorocarboxylic acids (PFCAs) and perfluorooctane sulfonate (PFOS), in the environment and the human exposure [5–7].

Due to their hazardous, PFASs have been determined over the last few years in a wide variety of matrices, such as human and wildlife biological ones (urine, milk, plasma, serum, blood, liver, brain and kidney), environmental liquid (river water, seawater and wastewater) and solid matrices (dust, sewage sludge, sediments and soil), consumer products (textile, carpet, cookware and food packaging), food and even in indoor and outdoor air [1,8].

One of the main applications of the PFASs has been as additives in food-contact packaging due to their ability to make the covering oil, stain and water resistant [9]. In previous studies, PFOA (perfluorooctanoic acid) has been found at levels up to 198 ng/g and 290 ng/g in microwave popcorn packaging [10,11], but fortunately, the concentration of long chain PFASs in packaging have decreased in recent years [12,13] because the manufacture of PFOS and other PFASs have been banned in the U.S. and in Europe. However, these compounds can still be present in food contact packaging due to

* Corresponding author. Tel.: +34 941299627; fax: +34 941299621.
E-mail addresses: cristina.moreta@unirioja.es (C. Moreta), maria-teresa.tena@unirioja.es (M.T. Tena).

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the acquisition of products that can still contain PFASs from other countries outside the U.S. or Europe.

PFASs have been typically extracted quantitatively by classical solid–liquid extraction (SLE) [12,14], by ultrasound assisted extraction (USE) [10,15–17] and by pressurized liquid extraction (PLE) [11,13,18,19] from different kinds of food-contact packaging samples. However, the focused ultrasound solid–liquid extraction (FUSLE) has offered an efficient extraction in only several seconds [20]. FUSLE is a low-cost, fast, simple and safe extraction technique based on the cavitation phenomenon. It is more reproducible and more efficient than traditional ultrasonic bath extraction (USE) due to its 100 times higher ultrasonic power and the immersion of the ultrasound microtip directly in the extracting solution [21,22].

FUSLE has also been used for the fast extraction (seconds or few minutes) of organic analytes, such as UV filters [23] and bisphenols [24] from packaging, as well as, polychlorinated biphenyls [25], phthalate esters [25], nonylphenols [25], polycyclic aromatic hydrocarbons [21,22,25,26] and brominated diphenyl ethers [27] from environmental matrices. However, longer extraction times were needed for the extraction of metals from sediments [28] using FUSLE.

Regarding to extract PFASs from food, this matrix has been more widely studied than packaging. The most commonly used extraction methods have been based on SLE using an orbital shaker [29–32] and USE [12,33,34]. Ion pair extraction (IPE) [35,36], alkaline digestion [36,37], PLE [38] and QuEChERS methods [40] have also been employed. However, any of these techniques are more time-consuming or difficult to implement than FUSLE technique, and this is the first time that this extraction has been used to preparation of food samples.

In this study, a fast and simple method based on FUSLE and UHPLC–(QTOF)MS/MS has been developed, validated and applied for the detection and quantification of ten PFAAs in six different microwave popcorn bags and the popcorn inside them, before and after microwave cooking. Thereby, the absence of migration from packaging to food has been shown and the effect of the microwaving process on PFAAs has also been studied.

2. Experimental

2.1. Materials and reagents

Individual standards of perfluorooctanesulfonic acid tetraethylammonium salt (PFOS) 98%, perfluorobutanoic acid (PFBA) 98%, perfluoropentanoic acid (PFPeA) 97%, perfluorohexanoic acid (PFHxA) >97%, perfluoroheptanoic acid (PFHpA) 99%, perfluorooctanoic acid (PFOA) 98%, perfluorononanoic acid (PFNA) 97%, perfluorodecanoic acid (PFDA) 98%, perfluoroundecanoic acid (PFUnA) 95% and perfluorododecanoic acid (PFDoA) 95%, were provided by Sigma–Aldrich (Madrid, Spain).

Isotopically labelled internal standards of sodium perfluoro-1-[$^{13}C_8$]-octanesulfonate (M8PFOS) isotopic purity >99%, perfluoro-n-[3,4,5-$^{13}C_3$]-pentanoic acid (M3PFPeA) isotopic purity >99%, perfluoro-n-[$^{13}C_8$]-octanoic acid (M8PFOA) isotopic purity >97.9% and perfluoro-n-[1,2-$^{13}C_2$]-dodecanoic acid (MPFDoA) isotopic purity >99%, were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada) as 50 μg/ml solutions in methanol. M8PFOS was used as internal standard for PFOS; M3PFPeA was used for PFBA and PFPeA; MPFDoA was used for PFDoA; and M8PFOA was used for the rest of PFCAs.

LC–MS grade acetonitrile (ACN), methanol (MeOH) and formic acid, and HPLC grade ethanol (EtOH) were obtained from Scharlau (Barcelona, Spain).

Sodium formate 99.998% and ammonium formate ≥99.0% were obtained from Scharlau (Barcelona, Spain).

Aqueous solutions were prepared in Milli-Q deionised water (Bedford, MA, USA).

2.2. Samples

Microwave popcorn bags of six different types were obtained from local supermarkets in mid-2013. There were three different brands (A–C) among which were four types of flavours (salty (ST), butter (B), sweet (SW) and with no added fats (NF)). A and C were generic brands and B was a name brand.

Before analysis, fat, salt and/or sugar were thoroughly removed from packaging and corn samples with the aid of paper towel. All samples were ground using an IKA A10 Analytical Mill purchased from IKA-Werke GmbH & Co. KG (Staufen, Germany) and then corn and popcorn were sieved through a 0.5 mm mesh sieve. The ground samples were stored protected from light at 4 °C in polyethylene plastic containers purchased from Lin Lab Rioja (La Rioja, Spain).

Three pulls of samples (one for each kind of sample): uncooked microwave popcorn bags, corn and popcorn samples were prepared to be used during method validation. The three pulls were spiked at a concentration level of 20 ng/g of each analyte. The microwave popcorn bag pull was also spiked at a concentration level of 2.5 times the limit of quantification of each analyte.

These spiked samples were prepared by adding a methanolic PFAAs standard solution to the grounded matrix (packaging or food) dispersed in ethyl acetate. The mixture was thoroughly homogenized and maintained at 45 °C water bath until the solvent was completely evaporated, and then it was triturated again to ensure proper homogenization of the sample. Then the samples were aged in polyethylene plastic containers protected from light at 4 °C for at least two weeks before use.

2.3. FUSLE procedure

A SONOPLUS 2070 focused ultrasound system, with a power of 70 W and a 20 kHz frequency, equipped with a 3 mm titanium microtip and a sound proof box (Bandelin Sonoplus, GmbH & Co. KG, Berlin, Germany) was used.

The optimal extraction conditions were as follows: 1.5 g of ground sample was placed into a 34 mm × 100 mm centrifuge glass tube, and then 24 ml of EtOH were added. Before each extraction, 100 μl of the 300 ng/ml internal standards solution was also added. Then, the probe was immersed in the mixture. The extractions were performed in an ice-water bath and the sample was exposed once to a 30% ultrasonic irradiation power for 10 s at 50% of pulsed cycle.

Extracts were filtered through a 50 ml capacity and 35 mm disc diameter filter funnel porosity 3 (16–40 μm nominal max. pore size) (DURAN Produktions GmbH & Co. KG, Mainz, Germany) using a vacuum pump. The glassware and the extracted sample were washed twice with 2 ml of extraction solvent. The three liquid portions were transferred to a 50 ml vessel in order to be evaporated to dryness under a nitrogen stream using a Calliper Turbo Vap II concentrator (Zymark, Hopkinton. MA, USA). However, for corn and popcorn samples an oily residue remained. Therefore, a micro-scale liquid-liquid extraction (LLE) of the highly viscous yellow liquid was performed for these matrices. LLE was carried out twice with 1.0 ml MeOH. It is worth mentioning that salt had to be added as an additive in order to keep immiscible the two phases in the case of sweet popcorn extract. The two methanolic layers were transferred to a 50 ml vessel in order to be evaporated to dryness under a nitrogen stream using a Calliper Turbo Vap II concentrator.

Extracts were reconstituted with 1 ml of LC–MS grade MeOH and filtered through a 0.22 μm nylon filter (Scharlau, Barcelona, Spain) before UHPLC injection.