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Determination of perfluorocompounds in popcorn packaging by pressurised liquid extraction and ultra-performance liquid chromatography–tandem mass spectrometry

María Pilar Martínez-Moral, 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

The development and characterisation of a method based on reverse-phase ultra-performance liquid chromatography (UPLC) coupled to a quadrupole-time of flight mass spectrometer (Q-TOF-MS) with negative electrospray ionisation (ESI) to determine perfluorinated compounds (PFCs) in packaging is presented in this paper. Analytes were quantitatively recovered from packaging with methanol in only one PLE cycle of 6 min at 100 °C. The UPLC allowed the successful separation of the studied PFCs in less than 4 min. The whole method presented good precision, with RSDs below 8%, LODs from 0.6 to 16 ng g^{-1}; and excellent recovery values, around 100% in all cases, were achieved. The PLE–UPLC–MS method was applied to the analysis of popcorn packaging for microwave cooking. Besides the most commonly studied PFCs: PFOA and PFOS, the presence of other perfluorocarboxylic acids (PFCAs) in popcorn packaging is evidenced in this work.

1. Introduction

Perfluorocarboxylic acids, such as perfluoroheptanoic (PFHpA), perfluorooctanoic (PFOA), perfluorononanoic (PFNA), perfluorodecanoic (PFDA), perfluoroundecanoic (PFUnA), perfluorododecanoic (PFDoA) acids, and perfluorooctanosulphonate (PFOS) belong to the group of perfluorinated compounds (PFCs) that have been globally distributed due to extensive industrial application and consumer use.

PFCs are bioaccumulative and resistant to biological and chemical degradation; they are resistant to hydrolysis, photolysis, and metabolic processes in living organisms. As perfluoroalkyl chains are oleophobic and hydrophobic and exhibit surface tension lowering properties, PFCs have been widely used in different commercial and industrial applications such as paints, lubricants, PTFE synthesis, polishers and food packaging.

Some compounds, such as polyfluoroalkyl phosphate surfactants (PAPs) or fluorotelomers (FTOH), have been used as surface active agents in domestic products as carpet treatments, paints, cleaning agents and in surface protection products for food contact coatings such as those used in some brands of microwave popcorn bags. They may be atmospherically or metabolically degraded to PFCAs; and this fact means an increase of PFCA concentrations in the environment and an indirect source of human exposure [1–3].

Due to this, increasing PFCA and PFOS concentrations in environmental samples, wildlife and humans, as well as biomagnification through food chains, have been reported [4,5]. PFCs are environmentally persistent, bioaccumulative and potentially harmful. PFOS and PFCAs have long half-lives in humans and it has been proved that they exhibit toxicity in laboratory animals causing developmental toxicity, carcinogenicity, liver cancer, affect the lipid metabolism and disturb the immune system [6].

Therefore the concern about the environmental contamination and human exposure has increased in the last few years. Methods for the determination of PFCs in environmental and biological samples such as sewage sludge [7–11], water [12,13], sediments [14–16], molluscs [17], sunfish fillets [18] or biota [19] have been developed [20]. The accumulation in humans has been studied through the analysis of blood [20,21] or tissue [22]; furthermore the human exposure to sources such as articles of commerce [23], food and drinking water [24–26] and food packaging is also of interest. For instance, included among the latter is popcorn packaging for microwave cooking that is usually treated with PFCs to give water and oil repellent properties [27–29].

Pressurised liquid extraction followed by liquid chromatography-mass spectrometry has been demonstrated to be a fast and efficient method for the determination of PFCAs and PFOS in sewage sludge [11], articles of commerce [23] and polymers [30], however it has not yet been applied to the analysis of these compounds in popcorn packaging.

* Corresponding author. Tel.: +34 941 299 627; fax: +34 941 299 621.
E-mail address: maria-teresa.tena@unirioja.es (M.T. Tena).

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In this paper a PLE–UPLC–(QTOF)MS/MS method is presented. The use of PLE has advantages over conventional solvent extraction [31] or sonication [27,32] used for extracting PFCs from popcorn packaging such as automation and shorter analysis time. For instance, analytes were extracted in 6 min by PLE while conventional solvent extraction [32] and ultrasonication [27,29] times of 24 and 1–2 h, respectively, have been reported. In addition, UPLC is very fast and avoids the analyte derivatisation needed for GC [28]. Finally the PLE–UPLC–(QTOF)MS/MS method allows the fast, sensitive and quantitative determination of not only the most commonly determined PFCs: PFOA and PFOS; but also other PFCAs in popcorn packaging and its application to real samples.

2. Material and methods

2.1. Standards and materials

Individual standards of perfluoroheptanoic acid (PFHpA) perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA) and perfluorooctanesulphonic acid (PFOS) were provided by Sigma Aldrich (Madrid, Spain). The isotopically labelled perfluoro-n-[$^{13}C_8$]octanoic acid and sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulphonate standards (M8PFOA and MPFOS), at a concentration of 50 μg mL^{-1}, used as an internal standard for perfluorocarboxylic acids and perfluorooctanesulphonic acid respectively, were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada). LC–MS grade acetonitrile and methanol and formic acid for LC–MS were obtained from Scharlau (Barcelona, Spain). Cellulose filters (20 mm diameter) were purchased from Restek (Bellefonte, PA, USA).

2.2. Samples

Microwave popcorn bags from three different brands were obtained from local supermarkets. They were ground using an A10 mill (IKA Labortechnik Staufen, Janke & Kunkel GmbH & Co. KG) and stored at 4 °C in plastic containers protected from light. A pull of samples was used for the method of optimisation.

Spiked samples at a concentration level of 200 ng g^{-1} and 80 ng g^{-1} of each analyte were used to study the influence of PLE conditions and the features of the method respectively. These samples were prepared by adding an analyte standard solution in ethyl acetate and the mixture was thoroughly homogenised and maintained at room temperature until the solvent was completely evaporated. Then the samples were aged in plastic containers, protected from light at 4 °C, for at least 2 weeks before use.

2.3. Pressurised liquid extraction (PLE)

An ASE200 accelerated solvent extractor from Dionex, furnished with 11-mL stainless-steel extraction cells, was used to perform PLE. Samples (0.5 g) were mixed in a glass mortar with 1 g of anhydrous sodium sulphate before PLE. Extraction cells were filled inserting two cellulose filters at the bottom of the cell to ensure that any particles pass through and thus the extraction cell frit is protected and its lifetime is extended. Then, 1 g of anhydrous sodium sulphate and the mixture of sample and desiccant were added and the cell was completely filled with anhydrous sodium sulphate. Finally, a cellulose filter was placed on top.

The extraction optimised conditions were one extraction step with methanol as extraction solvent for 6 min at a temperature of 100 °C and a pressure of 1500 psi.

After the extraction step, internal standards (M8PFOA and MPFOS) were added to PLE extracts at 100 ng mL^{-1} concentration level and then PLE extracts (ca. 15 mL) were evaporated to dryness under a nitrogen stream using a Turbo Vap II concentrator (Zymark, Hopkinton, MA, USA). The residue was reconstituted in 2 mL of LC–MS grade methanol. Extracts were filtered through a 0.2 μm nylon filter before the UPLC–MS/MS analysis.

2.4. UPLC–MS/MS

A Waters Acquity UPLC chromatograph (Milford, MA, USA) equipped with a Waters Acquity BEH C18 50 × 2.1 (i.d.) mm, 1.7 μm particle size column and a Waters VanGuard precolumn of the same material, and coupled to a Microtof-Q (Q-TOF) mass spectrometer from Bruker Daltonik (GMBH, Germany) with an electrospray interface was employed for the separation and quantification of PFCs. The chromatographic and mass spectrometry data were acquired with the software Data Analysis Version 4.0 from Bruker Daltonik (GMBH, Germany). The sample tray was held at 5 °C, and the column was maintained at 35 °C.

The chromatographic separation conditions were similar to those reported by Yoo et al. [10] with some modifications. A 0.1% formic acid–acetonitrile mixture (solvent A) and a 0.1% formic acid aqueous solution (solvent B) were used as mobile phases. The mobile phase composition was varied according to a linear gradient that increased from 35% to 55.7% A in 1.84 min, then increased until 58% A in 0.43 min; increased again until 65.7% in 0.5 min and 100% A is reached in 0.23 min, at minute 3.00, and held for 1.5 min. Then mobile phase composition returned to the initial conditions. The flow rate was set at 0.45 mL min^{-1} and the injection volume was 5 μL (half-loop, 50% of the total loop volume). The chromatographic separation took place in only 4 min. A chromatogram of the mixture of the analytes is shown in Fig. 1. Although PFOS and PFDA at the fourth time segment overlapped, their quantification could be performed because a chromatogram was recorded for each compound at its corresponding m/z ratio.

Electrospray ionisation was carried out using a capillary voltage of 3500 V in negative mode. A coaxial nebuliser N_2 gas flow (9.0 L min^{-1}) at 200 °C and 3.0 bar of pressure around the ESI emitter was used to assist the generation of ions. The mass spectrometer was calibrated across the mass range of 50–1500m/z using internal references. The collision energy was set at 10 eV for PFHpA, 12 eV for PFOA, PFUnA and PFDoA and 14 eV for PFNA and PFDA. Quantification was performed by multiple reaction monitoring (MRM) and ion extraction. Retention time and quantification ions used for the analytes are listed in Table 1.

2.5. Software for statistical analysis

Experimental designs and statistical analysis were performed using Statgraphics Centurion XV (Statpoint, Herndon, VA, USA).

3. Results and discussion

3.1. QTOF-MS conditions

In order to obtain a sensitive and reproducible method, the summation ratio and the quantification modes (MS and MRM) were studied. Quantification ions for MS and MRM detection and the summation ratio values finally selected for each compound are shown in Table 1. The summation ratio was studied at three different levels (high, medium and low); corresponding to values of × 5000, × 3750 and × 2500 for PFHpA, PFNA, PFUnA and PFDoA; and × 3750, × 2500 and × 1666 for the coeluting

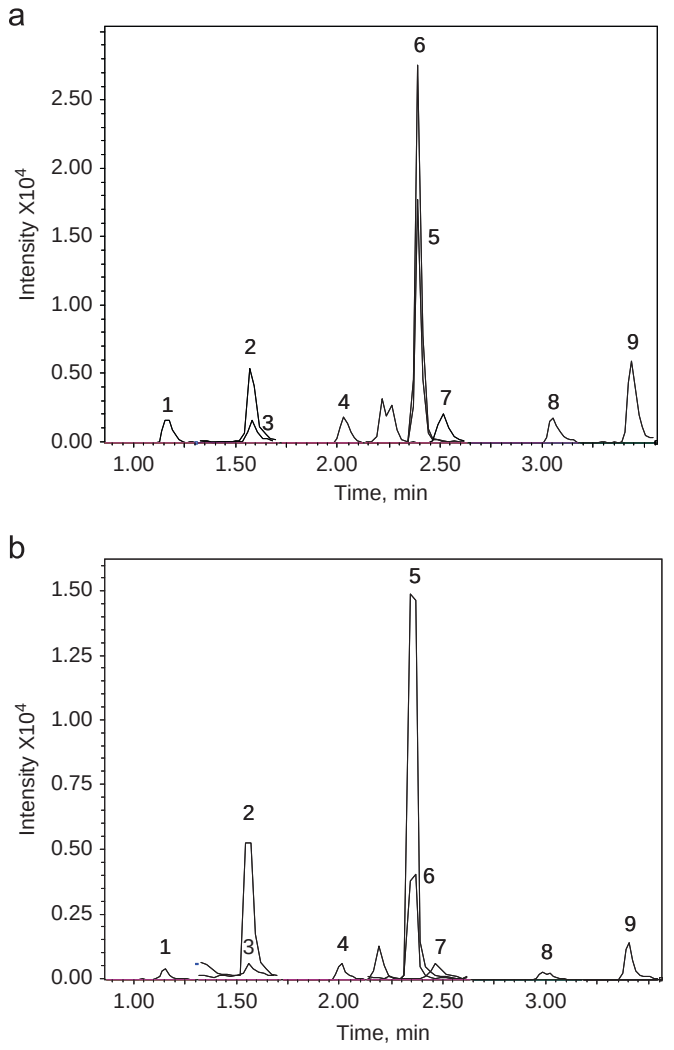

Fig. 1. UPLC–(QTOF)MS/MS chromatogram of (a) a methanolic standard solution of PFCs and (b) a sample extract. Peak identification: (1) PFHpA, (2) MPFOA; (3) PFOA; (4) PFNA; (5) MPFOS; (6) PFOS; (7) PFDA, (8) PFUnA and (9) PFDoA.

Table 1
Analyte retention times and quantification ions for MS and MRM detection and selected summation ratio values.

	Retention time, min	Quantification ions, *m/z*		Summation ratio
		MS	MRM	
PFHpA	1.18	363.00	318.97	5000
MPFOA[a]	1.59	420.96	376.97	3750
PFOA	1.59	412.96	368.97	3750
PFNA	2.04	462.96	418.96	5000
MPFOS[b]	2.40	502.92	502.92	2500
PFOS	2.40	498.92	498.92	2500
PFDA	2.52	512.96	468.92	2500
PFUnA	3.06	562.96	518.95	5000
PFDoA	3.45	612.95	568.95	5000

[a] Internal standard for all PFCAs.
[b] Internal standard for PFOS.

compounds (PFOA, MPFOA, PFOS, MPFOS and PFDA). The evaluated response was signal-to-noise ratio (S/N) in order to select the most sensitive conditions. The signal-to-noise ratio was calculated for each compound as the ratio between the peak area obtained for a standard solution and the peak area corresponding to a blank at the same time range. As shown in Fig. 2, the best signal to noise

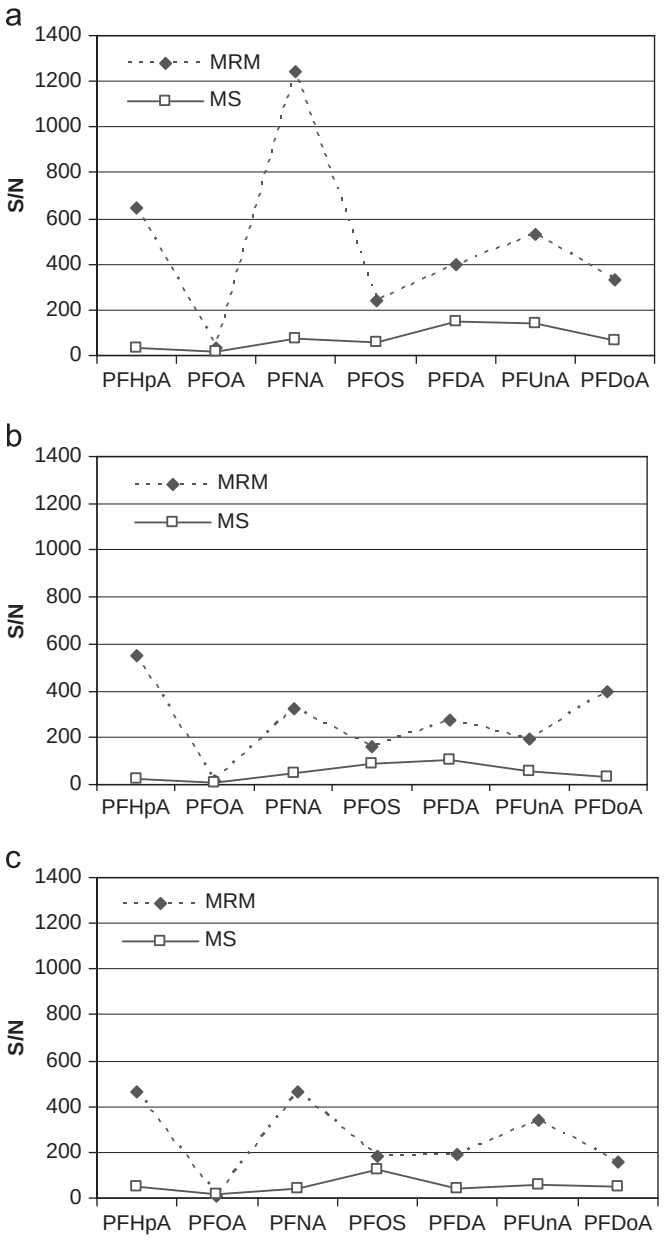

Fig. 2. Signal-to-noise ratio (S/N) obtained with MS and MRM detection modes at (a) high; (b) medium and (c) low summation ratio.

ratios were obtained with MRM mode for all the target analytes. Moreover, it was higher at high summation value. However at the high summation value fewer data are acquired per second and therefore chromatographic peaks are less defined. Therefore a repeatability study ($N=11$) was done in order to obtain a reliable method. Summation ratio values were selected as a compromise between maximal S/N ratio and acceptable repeatability (relative standard deviation (RSD) below 10%). Finally, selected conditions were the highest summation ratio for MPFOA and PFNA with RSDs from 4.8% to 8.3% respectively. Relative standard deviation values for MPFOS, PFOS and PFDA at a high summation ratio were 33.1%, 152.3% and 12.5% respectively. Therefore a medium summation ratio was selected for these compounds which provided RSD values of 2.6%, 8.8% and 6.0%. To sum up, summation ratio values $\times 5000$ for PFHpA, PFNA, PFUnA and PFDoA, $\times 3750$ for MPFOA and PFOA, and $\times 2500$ for MPFOS, PFOS and PFDA were selected with the MRM detection.

The features of the UPLC–(QTOF)MS/MS method are shown in Table 2. The analytical signal used for calibration and quantification was the analyte-to-internal standard peak area ratio.

Linearity was studied up to 150 ng mL^{-1}. Analytical signal showed a linear behaviour with concentration. R values were between 0.996 and 0.9994. Mandel's fitting test showed that differences between the residual variances of linear and quadratic regressions are not significant. F values obtained ranged from 0.002 to 4.00, far from the critical F-value 18.51, except for PFDoA with F=15.76 (see Table 2). For PFDoA, signal is better fitted to a quadratic model (R=0.9997) than a linear one (R=0.996).

Limits of detection and quantification were calculated in two different ways: (a) using the signal-to-noise ratio (S/N) of a diluted solution as a reference, and (b) using the standard deviation of the intercept. Thus, when LOD was defined as the concentration corresponding to a S/N=3.3 ($\alpha=\beta=5\%$), LOD values were around 0.01 ng mL^{-1}, and LOQ values (S/N=10) were between 0.02 and 0.03 ng mL^{-1}. These instrumental LOD and LOQ values are lower than those reported by Esparza et al. [16] (0.05 and 0.15 ng mL^{-1}, respectively) for PFOS in water, sludge and sediments by PLE followed by SPE and LC–(QqQ)MS/MS. Dolman and Pelzing [27] reported LOD and LOQ values of 0.025 and 0.05 ng mL^{-1} for PFOA and PFOS by LC–(IT)MS.

However, higher LOD and LOQ values were obtained when the regression parameters were used. LOD values, calculated as 3.3 times the standard deviation of the intercept divided by the slope (corresponding to α and β errors of 5%), were between 0.1 and 0.8 ng mL^{-1}. LOQ values, calculated as 10 times the standard deviation of the intercept divided by the slope, were between 0.3 and 2.3 ng mL^{-1}.

Repeatability was calculated as the relative standard deviation of eleven replicates. RSD values less than 9% were obtained in all cases. PFOS RSD was higher than that obtained by Esparza et al. [16].

3.2. Study of PLE variables

The aim of this study was to optimise the PLE variables (extraction temperature, time and extraction steps) in order to improve the efficiency and accuracy of the method. The pressurised liquid extractions were performed using methanol as extraction solvent. This solvent has already been selected to extract PFCs from articles of commerce [23] and polymers [30]. In order to study temperature and time, a central composite design (CCD) consisting of a 2^2 factorial design with four star points located at $\pm\alpha$ from the centre of the experimental domain was developed. The axial distance α for this design was 1.41 in order to establish the rotatability condition. The design was also

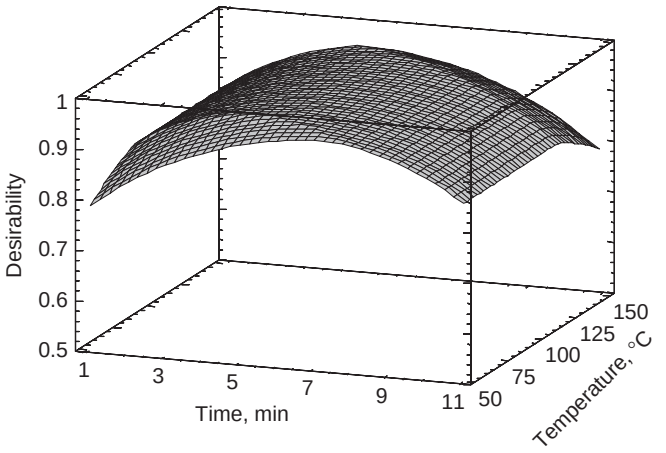

Fig. 3. Desirability function calculated for the compounds with significant effects on extraction efficiency.

Table 2
Features of the UPLC–(QTOF)MS/MS method.

	Slope[a] ± SD, mL ng^{-1}	R	Mandel' fitting test, ($F_{0.05;1;2}$=18.51)	Standard addition slope ± SC, mL ng^{-1}	LOD, ng mL^{-1}	LOQ, ng mL^{-1}	Repeatability[f] RSD, %
PFHpA	0.0023 ± 0.0001	0.998	2.30	0.0024 ± 0.0001	0.010[b] 0.8[c]	0.03[d] 2.3[e]	7.2
PFOA	0.0022 ± 0.0001	0.998	0.43	0.0021 ± 0.0001	0.011[b] 0.5[c]	0.03[d] 1.4[e]	6.3
PFNA	0.0052 ± 0.0001	0.998	4.00	0.0046 ± 0.0002	0.010[b] 0.10[c]	0.03[d] 0.3[e]	8.3
PFOS	0.012 ± 0.001	0.995	0.21	0.013 ± 0.001	0.009[b] 0.12[c]	0.03[d] 0.4[e]	8.8
PFDA	0.0033 ± 0.0001	0.9994	1.94	0.0033 ± 0.0001	0.008[b] 0.4[c]	0.024[d] 1.3[e]	6.0
PFUnA	0.0046 ± 0.0001	0.9990	0.0020	0.0048 ± 0.0003	0.010[b] 0.19[c]	0.03[d] 0.6[e]	6.1
PFDoA	0.0083 ± 0.0001	0.996	15.76	0.0087 ± 0.0003	0.007[b] 0.22[c]	0.020[d] 0.7[e]	5.4

[a] Linear range from LOQ to 150 ng mL^{-1}.
[b] LOD defined as the concentration corresponding to a signal-to-noise ratio (S/N) of 3.3 ($\alpha=\beta=5\%$).
[c] LOD calculated as 3.3 times the standard deviation of the intercept divided by the slope ($\alpha=\beta=5\%$).
[d] LOQ defined as the concentration corresponding to a S/N ratio of 10.
[e] LOQ calculated as 10 times the standard deviation of the intercept divided by the slope.
[f] N=11.

Table 3
ANOVA coefficients (p-value) obtained from the 2^2 central composite design results used for PLE optimisation. A: time, B: temperature, AB: time–temperature interaction, AA: time quadratic effect and BB: temperature quadratic effect.

Compound	Constant	A	B	AA	AB	BB
PFHpA	−0.071	8.33×10^{-2} (0.477)	1.83×10^{-2} (0.096)	-2.38×10^{-3} (0.248)	$\mathbf{-8.29\times10^{-4}}$ (0.0146)[a]	$\mathbf{-6.65\times10^{-5}}$ (0.0065)[a]
PFOA	0.827	6.98×10^{-2} (0.247)	6.69×10^{-2} (0.266)	-4.68×10^{-2} (0.429)	3.27×10^{-2} (0.524)	3.75×10^{-2} (0.693)
PFNA	1.191	5.56×10^{-2} (0.548)	5.56×10^{-2} (0.535)	-6.88×10^{-2} (0.451)	0.203 (0.367)	-8.30×10^{-2} (0.133)
PFOS	1.581	$\mathbf{1.22\times10^{-2}}$ (0.0468)[a]	-6.74×10^{-2} (0.0565)	2.46×10^{-2} (0.424)	7.59×10^{-2} (0.099)	6.98×10^{-2} (0.0740)
PFDA	0.428	2.86×10^{-2} (0.349)	-2.26×10^{-2} (0.456)	-2.67×10^{-2} (0.380)	4.12×10^{-2} (0.341)	2.49×10^{-2} (0.413)
PFUnA	1.082	4.71×10^{-2} (0.715)	$\mathbf{2.21\times10^{-3}}$ (0.039)[a]	-4.96×10^{-4} (0.117)	8.50×10^{-5} (0.837)	1.23×10^{-5} (0.671)
PFDoA	3.76	0.313 (0.146)	1.40×10^{-3} (0.183)	$\mathbf{-2.61\times10^{-2}}$ (0.011)[a]	-2.28×10^{-4} (0.854)	2.14×10^{-5} (0.805)

[a] Significant effect, for α=0.05.

completed with eight replicates of the central point. Therefore the complete design consisted of 16 randomly performed experiments. All the experiments were carried out using a spiked sample containing 200 ng g^{-1} of each analyte. Temperature values ranged from 50 to 150 °C, including the levels 50, 65, 100 (central value), 135 and 150 °C. Extraction time was studied between 1 and 11 min, and the levels were 1, 2.5, 6 (central value), 9.5 and 11 min.

The ANOVA of the data (Table 3) showed that the only factors with a significant effect (at a confidence level of 95%) on extraction efficiency were the temperature and time interaction and the temperature quadratic effect for PFHpA (-8.3×10^{-4} and -6.6×10^{-5} coefficients, and *p*-values of 0.0146 and 0.0065, respectively); time for PFOS (0.012 coefficient value, *p*-value 0.0468); temperature for PFUnA (*p*-value 0.0390, and 2.2×10^{-3} coefficient value) and the quadratic effect of time for PFDoA with a −0.026 as coefficient and 0.0109 *p*-value. A desirability function was constructed in order to select the optimal values for temperature and time. As can be seen in Fig. 3, the optimum was set at 100 °C and 6 min.

Once the temperature and time conditions were optimised, the last variable studied was the number of extraction steps (cycles) required for exhaustive extraction. One-, two- and three-cycle extractions of a spiked sample were performed in triplicate under optimal PLE conditions. Results are shown in Fig. 4 as mean area values with their ±95% confidence interval (CI). As can be seen, the peak area did not increase with the number of cycles since no significant differences were observed between 1, 2 or 3 cycles. Moreover the ANOVA of the results showed *p*-values between 0.06 and 0.81 for PFDoA and PFUnA, respectively. Therefore the extraction of PFCs was complete at 100 °C with only one 6 min extraction cycle.

3.3. Features of the PLE–UPLC–MS/MS method

The linearity of the UPLC–MS/MS method was studied in both methanol solution and packaging extract in order to check the absence of a matrix effect. No significant differences were found between the slopes obtained for the analytes in both matrices (data shown in Table 2). Therefore no matrix effects were observed for the quantification of the PFCs and external calibration in methanol is proposed.

The method was also characterised in terms of limit of detection (LOD) and limits of quantification by means of the signal-to-noise ratio (S/N=3.3 and S/N=10, respectively). In addition, the repeatability and intermediate precision (expressed as RSD, %) were calculated by an ANOVA of three replicate extractions of a spiked sample (80 ng g^{-1}) for 3 days. Finally a recovery study was carried out at 80 ng g^{-1} concentration to assess accuracy. Limit of detection, repeatability, intermediate precision and recovery values are shown in Table 4.

The LODs were between 0.6 and 16 ng g^{-1} for all compounds. Method LOD of 0.01 ng g^{-1} has been reported for PFOS in sediment [16] but the method included a pre-concentration step by SPE with a weak anion exchanger.

Repeatability was below 8% in all cases, similar to that reported by Dolman and Pelzing [27] and Esparza et al. [16].

Excellent recovery values, around 100%, were obtained for all the studied compounds improving previously reported method for determining PFOA and PFOS in popcorn packaging [27].

3.4. Sample analysis

The developed method was applied to determine PFCAs and PFOS in microwave popcorn bags of three different brands. Results are shown in Table 5. As can be seen, high PFOA levels were found in the three samples analysed, from 53 to 198 ng g^{-1}. This result is in agreement with those previously reported for

Table 4
Features of the PLE–UPLC–(QTOF)MS/MS method.

	LOD[a], ng g^{-1}	LOQ[b], ng g^{-1}	Repeatability[c] RSD, %	Intermediate precision[c], %	Recovery[d] ± 95% CI, %
PFHpA	6.6	20	5	8	96 ± 22
PFOA	18	53	6	16	108 ± 15
PFNA	9	28	2	8	95 ± 18
PFOS	2.2	5	5	3	108 ± 21
PFDA	9	28	8	11	100 ± 12
PFUnA	0.7	2	5	3	100 ± 17
PFDoA	0.7	2	5	4	114 ± 17

[a] LOD calculated as signal to noise ratio (S/N)=3.3.
[b] LOQ calculated as S/N=10.
[c] Calculated by ANOVA, 3 replicates × 3 days. Spiked sample at 80 ng g^{-1}.
[d] *N*=4, concentration level of 80 ng g^{-1}.

Table 5
Concentration of PFCs in microwave popcorn bags.

	Concentration ± 95% CI, ng g^{-1}		
	Sample 1	Sample 2	Sample 3
PFHpA	37 ± 2	99 ± 5	98 ± 5
PFOA	53 ± 8	88 ± 12	198 ± 30
PFNA	30 ± 2	61 ± 5	55 ± 6
PFOS	< LOQ	12 ± 2	23 ± 3
PFDA	< LOQ	43 ± 9	81 ± 11
PFUnA	6.1 ± 0.3	13 ± 1	3.7 ± 0.3
PFDoA	33 ± 4	39 ± 6	90 ± 12

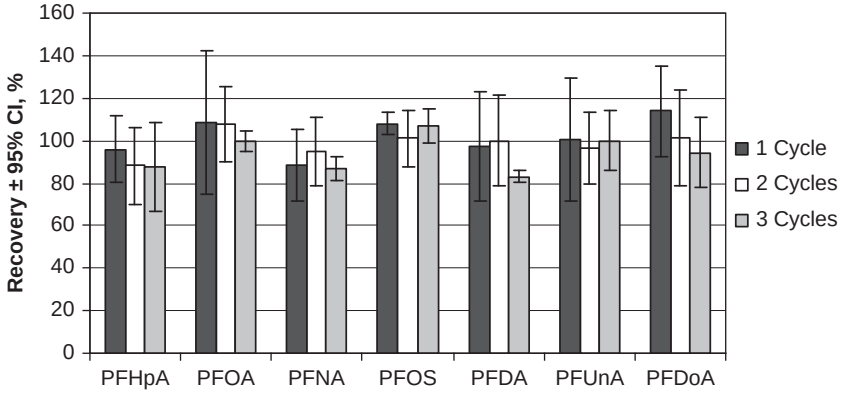

Fig. 4. Influence of the number of extraction cycles on recovery.

PFOA concentrations in popcorn packaging by Begley et al. [32]. In addition, levels of PFHpA, PFNA, PFDA and PFDoA were also significant for some of the samples. Total PFC concentration in the samples was different: 159, 355 and 549 ng g^{-1}, and the two samples with the highest PFCs content contained the seven PFCs studied.

4. Conclusion

A fast and simple PLE–UPLC–(QTOF)MS/MS method has been developed to determine PFCAs and PFOS in microwave popcorn packaging. Pressurised liquid extraction variables, temperature and time, were optimised and finally set at 100 °C and 6 min; and only one extraction step was shown to provide an exhaustive extraction of the studied compounds from the popcorn packaging. The whole method PLE–UPLC–MS/MS provided excellent repeatability and intermediate precision, with RSDs below 8% and good recovery values between 95% and 114%. The PLE–UPLC–(QTOF)MS/MS method has been applied to determine PFCAs and PFOS in microwave popcorn bags. High concentration levels of PFOA were found in all the samples and all the PFCs studied were found in two of the three samples analysed.

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