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Extraction of perfluorinated compounds from food matrices using fluorous solvent partitioning

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ABSTRACT

Perfluorinated compounds (PFCs) such as perfluorooctane sulfonic acid (PFOS) have emerged as a new class of global environmental pollutant; they bioaccumulate and are persistent in the environment and in wildlife. Fluorine–fluorine interactions have been investigated as a means to isolate PFCs for mass spectrometric quantification. A novel sample extraction and cleanup procedure has been developed for fat-containing samples based on fluorous liquid–liquid extraction (F-LLE) in a triphasic solvent system consisting of hybrid:fluorous:organic solvent (trifluoroethanol:perfluorohexane/dichloromethane-saturated with water). This system partially separates fluorous from non-fluorous compounds, allowing removal of co-extractants, which had previously resulted in liquid chromatography mass spectrometry (LC–MS/MS) peak suppression preventing low-level detection of PFCs. The developed F-LLE was coupled with an existing extraction protocol allowing the limits of detection of PFCs to be lowered an order of magnitude for high fat samples. The developed workflow was used to show the absence of a range of eleven PFCs in nine UK and one Irish cheese samples. This representative application demonstrates a new application of fluorous–organic extraction in sample cleanup for measurement of fluorinated analytes in food, environment and broader analytical chemistry.

1. Introduction

Perfluorinated compounds have recently emerged as a new class of global environmental pollutant. In the wider context of organo-halogen persistent organic pollutants (POPs), the acronym PFC is used to refer to toxic perfluorinated compounds and not to non-toxic perfluorocarbon solvents. The most studied PFC to date is perfluorooctane sulfonic acid (PFOS), which refers to the individual chemical ($C_8F_{17}SO_3H$) (Fig. 1) and any closely related derivatives. The PFOS acronym also includes larger structures, which may degrade in the environment to release perfluorooctane sulfonic acid. European legislation (Directive 2006/122/EC) [1] restricts the use of PFCs, and defines PFOS as the sulfonic acid, halide, amide, polymers of and all derivatives with structural parts that contain a perfluorooctane sulfonate. PFCs are persistent, toxic and bioaccumulate in the environment and wildlife, fulfilling the definition of a persistent organic pollutant. PFOS has therefore now been added to Stockholm Convention list of banned or restricted substances [2].

Whilst robust methods exist for measurement of PFOS in many environmental samples, especially those with high levels of contamination [3–7], it is technically challenging to achieve limits of detection in many types of samples, especially those with high fat content, such as liver and cheese. The accepted standard workflow for analysing PFOS in food samples involves solvent extraction and solid phase extraction (SPE), followed by liquid chromatography mass spectrometry (LC–MS/MS). Difficulties with samples that contain solid fats currently limits method performance in the above workflow. SPE extraction is problematic with fat samples and, during MS analysis, fatty matrices can cause peak suppression, preventing low levels of detection. In addition, when using LC–MS/MS to analyse for PFOS in avian and mammalian samples, isobaric interferents with a mass transition of $499 > 80$ can prevent accurate PFOS quantification. The most significant interferent has been identified as a bile salt taurodeoxycholic acid (TDCA) [7]. PFOS and TDCA are both sulfonic acids with masses $[M-H]^-$ 498.929 and 498.289 respectively (Fig. 1). We have previously noted that the interferent is the natural abundance $^{13}C_1$-labelled form of a larger set of species dependent bile salt isomers at $[M+1-H]^-$ 499.297 [8].

To date there are no published methods for the separation and removal of these isobaric compounds during the extraction step of the workflow. Separation is currently performed at the analysis stage, either by physical separation on a specific LC stationary

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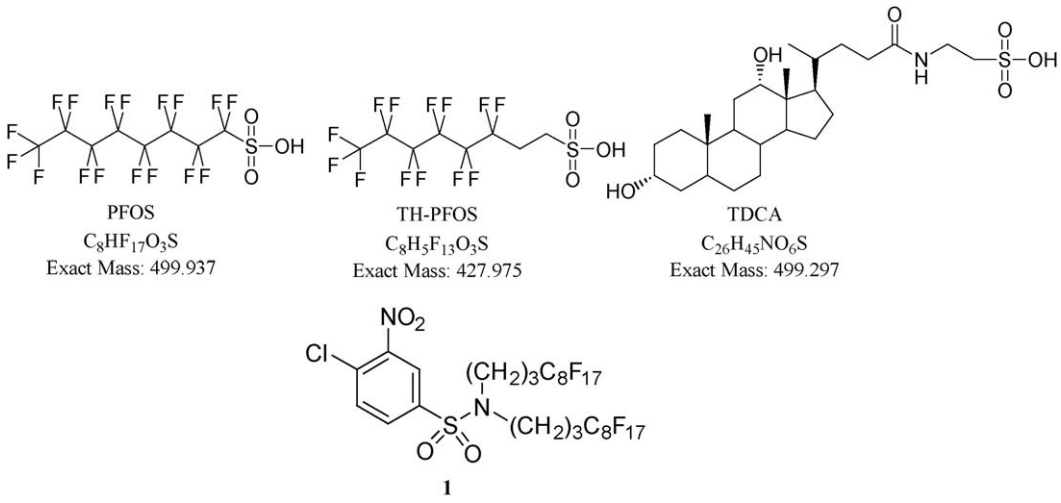


Fig. 1. Perfluorooctanesulfonic acid (PFOS) its internal standard tetrahydroperfluorooctanesulfonic acid (1H,1H,2H,2H-PFOS) and the isobaric interference taurodeoxycholic acid (TDCA).

phase [5], or using a high-resolution Time of Flight Mass Spectrometer [7].

Fluorine–fluorine interactions and fluorous partitioning is an unexploited orthogonal separation process that has the potential to be utilised for fluorinated compounds in food, environmental and analytical chemistry. Although fluorous partitioning is used extensively to separate organic reaction mixtures where organic molecules are rendered soluble in fluorocarbon solvents by chemical attachment of suitable groups in the form of fluorous tags ('ponytails'). Fluorous partitioning has not, to the best of our knowledge, been used to extract a fluoronated analyte of fixed fluorine content from a food or environmental sample.

The general phenomenon of fluorous partitioning exploits the low electronic polarizability of the C–F bond. The resultant weak interaction and immiscibility between alkanes and perfluoroalkanes provides a driver for fluorous analytes to interact in preference with fluorous solvents allowing, in theory, selective separation [9]. At room temperature the organic and fluorous phases are immiscible, but when heated, the solvents mix and a monophasic system is produced [10]. On cooling, the monophasic system returns to a biphasic system, leaving the fluorous analyte in the fluorous phase and the unwanted non-fluorinated materials in the organic phase. This separation method thereby selectively isolates fluorous from non-fluorous compounds. As a 'rule of thumb' to be effective, this procedure generally requires fluorinated compounds containing 60% or more fluorine by mass (the spatial arrangement of the fluorines is also a factor in efficient partitioning [11]). In addition, the absence of hydrogen bonding or polar groups is desirable as these can interact with the organic phase, hindering transfer [11,12]. Until recently the use of fluorous biphasic separations (F-LLE) was restricted to the field of synthetic chemistry, where a fluorophobic organic solvent in combination with a perfluorinated solvent, usually a perfluoroalkane, would be used to extract a fluorous tagged catalyst or substrate/reagent from a reaction mixture [13]. In these systems poor partitioning coefficients were often observed between the fluorous and organic phases, this was addressed by increasing the fluorine content of the compound of interest by chemically attaching longer, more heavily fluorinated tags; *a substrate tuning approach* [14].

In 2005, Yu demonstrated that partition coefficients could also be significantly improved using a *solvent tuning approach*, based on solvent polarity and fluorophilicity/fluorophobicity considerations, without the need to increase the fluorine content of the molecule to be partitioned. Fluorophilicity and the polarity of fluorous and organic solvents can be represented on a two dimensional scale, where one axis is the solvents polarity index and the other the fluorophilicity. Solvents that are close together on this graph are likely to be miscible. Solvent pairings that are miscible at room temperature can be rendered immiscible by an appropriate increase or decrease of the fluorophilicity or polarity, by blending with a co-solvent at one of the two extremes. The partition coefficient of a compound of interest can be roughly correlated to the distance between the analytes and the two solvents of the biphasic system. For example, it has been shown that perfluorobutyl methyl ether (HFE-7100) in combination with DMF (with 5% added water) could effectively partition a fluorous sulfonamide **1** by making the fluorous phase more polar and the organic phase less fluorophilic [15,16].

As the PFC analytes of interest in this study have a fixed fluorine content, our aim was to optimise extraction efficiency using *solvent tuning* in the extraction step of the workflow. Herein we report a sample cleanup method for the analysis of fat-containing samples based on fluorous partitioning. We examine the effectiveness of partitioning fluorous compounds from a range of organic/fluorous solvent mixtures. An additional cleanup stage using anion exchange SPE was also investigated in order to find an appropriate workflow to extract fluorous compounds from fatty food (cheese).

2. Results and discussion

2.1. Selection of fluorous solvent systems with high selectivity and recovery

Solvent polarity is not a uniquely defined physical property; the polarity index ranking (P') is a function of many parameters including dipole moment, proton acceptor and donor properties and dispersion forces. The advantage of this system is that a numerical value for solvent polarity is obtained. Although solvent polarity for mixed solvents is not a linear function of composition, a simplistic linear proportionation is sufficiently accurate to use in estimating the polarity of mixtures.

Fluorophilicity of a molecule has been defined as ln P where P is the partition coefficient between fluorous methylcyclohexane $CF_3C_6F_{11}$ and methylbenzene $CH_3C_6H_5$ [12]. It has also been predicted by 3D QSAR molecular descriptors and artificial neural networks [11] and by QSPR analysis [17]. For a bulk solvent the term is less well defined and it is not clear what numerical process has been used to calculate fluorophilicity of bulk solvents in the

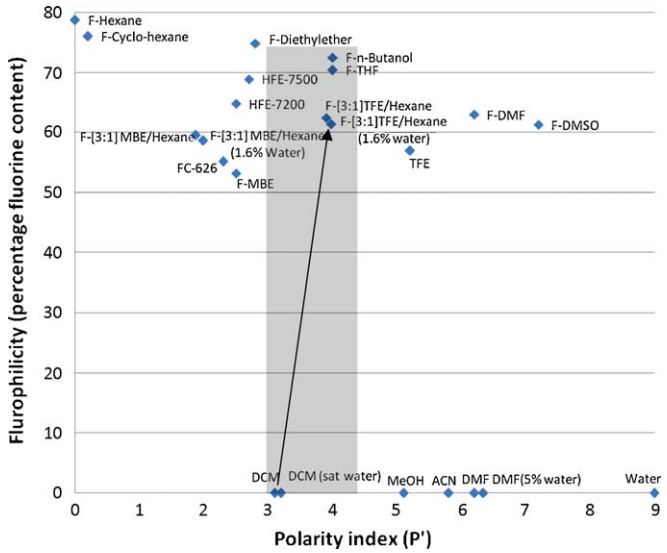


Fig. 2. Representation of polarity and fluorophilicity of various solvents and mixtures. TFE = trifluorethanol, HFE-7500 = hydrofluoroether $C_3F_7CF(OC_2H_5)CF(CF_3)_2$, HFE-7200 = $C_4F_9OC_2H_5$, F-626 = $CF_3(CF_2)_5(CH_2)_2OCH(CH_3)CH_2CH(CH_3)_2$ and MBE = methyl butyl ether (HFE-7100, $C_4F_9OCH_3$).

solvent tuning approach [15,16]. In the absence of published solvent fluorophilicity tables we have used simple percentage by mass fluorine content, as one graphical axes and polarity *P′* as the second axis (Fig. 2). On this representation it can be seen that most solvents have similar fluorine content (50–80%), with the hydrofluoroether candidates being plotted in similar positions. We did not consider it appropriate to use perfluorodimethylformamide or perfluorodimethylsulfoxide in this work as these are at the extreme of the polarity range and would be not be selective in partitioning the compounds of interest. Mixtures of fluorous solvents, such as 3:1 trifluoroethanol:perfluorohexane are plotted by direct proportional weighting, shifting one-quarter of the distance towards perfluorohexane. The preferred solvent for dissolution of PFCs is methanol (*P′* = 5.1). Partitioning will be facilitated by a constant or slightly increasing polarity gradient within the shaded portion of the plot (Fig. 2).

Fat removal from food extracts is commonly achieved by partitioning into a non-polar solvent such as hexane or dichloromethane. Given that the PFC analytes can be considered to resemble fluorinated fatty acids, it was unsurprising that standard non-polar solvent based de-fatting protocols also removed PFCs, especially the less polar sulfonamide.

A selection of fluorous solvents with increasing polarity; perfluorohexane, perfluorobutylmethyl ether, trifluoroethanol, and organic solvents similarly with increasing polarity; dichloromethane, methanol, dimethylformamide, water, were selected (Table 1). Using the *solvent tuning approach* [15,16], the fluorous solvents were used on their own or in 1:1 combinations and the organic solvents on their own or with added water. For each system the organic solvent was spiked at 5 μg/L (100 μL of 0.5 μg/mL) with a standard mix containing eleven PFCs. Fluorous solvent, or solvents were added to the solution, which was shaken for 30 min then left at room temperature to separate. Most mixtures that were miscible at room temperature separated after cooling to −20 °C, or −67 °C. Those that did not separate were excluded from further consideration. For the separated solutions the fluorous extract was removed, dried down and reconstituted in methanol (MeOH) for analysis by Time of Flight Mass Spectrometry (oaTOF-MS).

Table 2
Composition of fluorous and organic (1:1) partitioning solvent mixtures.

Mixture	Fluorous solvent	Organic solvent	Phases[a]
1	HFE-7100	DMF (+5% H_2O)	2
2	(1:1) HFE-7100:FC-72	DCM (H_2O saturated)	2
3	TFE	DCM (H_2O saturated)	2
4	(3:1) HFE-7100:FC-72	DCM (H_2O saturated)	2
5	(3:1) TFE:FC-72	DCM (H_2O saturated)	3

[a] Number of phases at 20 °C, mixtures became miscible at 80 °C.

From the 42 combinations of various polarities, those systems yielding less than 50% transfer of the various PFC analytes were not subjected to any further investigation. The three remaining solvent systems were investigated further. It was observed that the addition of water to the organic phase and perfluorohexane (FC-72) to the fluorous phase sharpened the transition between phases, making separation easier. Two additional mixtures with further solvent tunning (3:1 fluorous solvent and perflurohexane) and the remaining three mixtures were spiked as above (Table 2). In a previous experiment the five mixtures were heated to 50 °C however, all mixtures remained immiscible. When the temperature was increased to 80 °C all the mixtures became miscible therefore this temperature was chosen as the optimum miscibility temperature. The solutions were allowed to cool to their optimum immiscibility temperature at which they separated. The fluorous extract was removed from the separated solutions, dried down and reconstituted in methanol (MeOH) for analysis by Time of Flight Mass Spectrometry (oaTOF-MS). These five solvent mixtures were selected for more detailed investigations of the partitioning of PFC's and the non-fluorous interferent TDCA.

From the five organic/fluorous F-LLE systems (see Table 2, Fig. 3), two were selected for further investigation because of either their selectivity for fluorous over organic compounds, or for their overall high percentage transfer. The first system was (3:1) trifluoroethanol:perfluorohexane/DCM (saturated with water ~1.6%). This was not selective, but gave high percentage transfer from the organic to fluorous phase for both PFOS (96%) and TDCA (98%). The second system, perfluorobutylmethyl ether with DMF (with 5% water), was an order of magnitude more selective in

Table 1
Temperature of observed immiscibility of organic and fluorous (1:1) solvent mixtures.

Solvent		Organic solvent						
Mixture	Fluorous solvent(s)	H_2O	MeOH	aqMeOH	DCM	aqDCM	DMF	aqDMF
1	FC-72	20	20	20	20	20	20	20
2	HFE-7100	20	No[a]	20	−20	20	−20	20
3	TFE	No	No	No	20	−20	No	No
4	(1:1) HFE-7100:FC-72	20	20	20	20	20	20	20
5	(1:1) TFE:FC-72	20	20	20	20	20	20	20
6	(1:1) TFE:HFE-7100	20	No	−20	−67	−67	No	−20

[a] No = still miscible at −67 °C.
HFE-7100 = perfluorobutyl methyl ether, FC-72 = perflorohexane, TFE = trifluoroethanol.

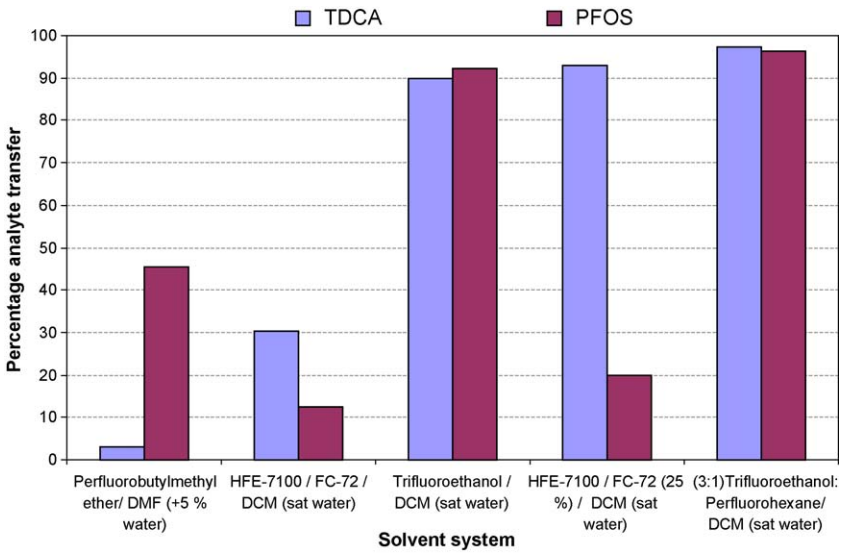


Fig. 3. Partitioning of TDCA and PFOS from the organic into the fluorous phases of 4 biphasic and one triphasic mixtures.

transferring fluorinated compounds, for example PFOS (45%), TDCA (3%).

2.2. Recovery of a range of PFCs

With two suitable solvent systems identified, optimised for either recovery or selectivity, the partitioning of a wider range of fluorinated compounds and TDCA were explored. The results showed that (3:1) trifluoroethanol:perfluorohexane/DCM (saturated with water) gave consistently high recovery of all the analytes tested, both fluorinated and non-fluorinated (TDCA). In contrast, perfluorobutyl methyl ether/DMF (with 5% water) gave varying recoveries. In general, the best recoveries (>50%) were observed with fluorinated compounds which have a higher fluorine content. This outcome is consistent with solvent tuning predictions [15,16] and previous work on homologous series [13] (Fig. 4). Having a polar terminal functionality on all of the PFC analytes increases their polarity relative to many of the other compounds previously assessed in the literature. Also the degree of fluorine content required for partitioning was observed to increase from 60 to 70% F.

2.3. Transfer of PFCs from cheese matrix

The next method development step was to simulate extraction from a fat-containing sample and add in the fatty matrix in order to observe both mass transfer – how much of the sample is removed in the cleanup process and the resulting mass spectrometer peak suppression effects of the matrix. The two systems were re-analysed with an additional cleanup stage, using weak anion exchange solid phase extraction (WAX-SPE) after fluorous extraction [8]. In order to quantify the matrix effects, the systems were each investigated in two experiments. Firstly, as simple solvent standards, and secondly, by inclusion of the problematic fatty

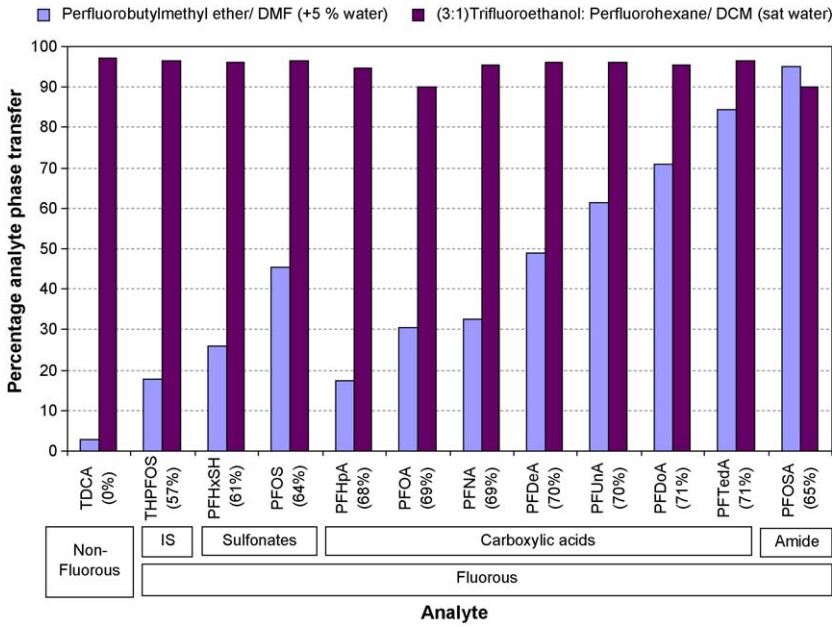


Fig. 4. Selectivity and percentage transfer efficiency of a 5 μg/L PFCs spike for fluorous and non-fluorous compounds in two systems. The percentage fluorine content of each analyte is shown after the analyte abbreviation.

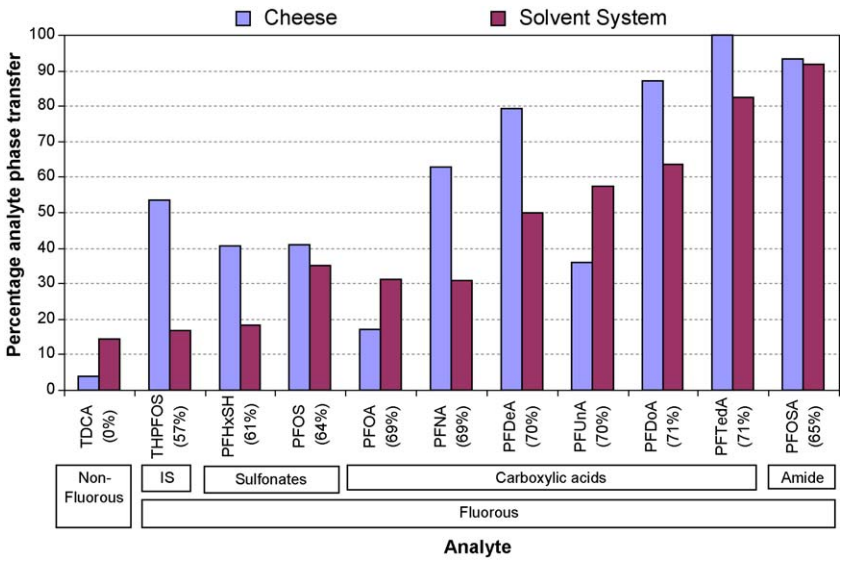


Fig. 5. Percentage transfer of 10 μg/kg of PFCs from cheese and solvent standards (10 μg/L) by F-LLE/WAX-SPE using perfluorobutylmethyl ether/DMF (5% water) system.

cheese (matrix matched). Therefore any suppression/enhancement effects that cause differences in peak sizes are directly attributable to the addition of the cheese matrix. With perfluorobutylmethyl ether/DMF (5% water) the cheese matrix affected the percentage of PFCs partitioned into the fluorous solvent (Fig. 5). While broadly in line with the solvent based experiment, the recoveries of PFCs from cheese were consistently higher, indicating the increased fat mass fraction in the organic phase was also assisting in driving the fluorinated analytes into the fluorous phase.

The (3:1) trifluoroethanol:perfluorohexane/DCM (saturated with water) showed minimal effect due to addition of the cheese matrix. All analytes gave consistently high (>80%) percentage transfer in both solvent only and cheese matrix systems, with the matrix system producing marginally lower recoveries (Fig. 6). Although not selective in separating PFCs from TDCA the latter workflow (F-LLE/WAX-SPE) was selected as the most effective at partitioning PFCs from cheese. At a practical level, it left behind the matrix components which had initially blocked the WAX-SPE cartridge, presumed to be fats which while soluble in methanol, were colloidal in the basic aqueous loading solvent. As a mass balance the combined F-LLE and WAX-SPE procedure removed 99.5% of the cheese mass, allowing identification and quantification of PFOS and other PFCs at lower levels than were achievable without the fluorous partitioning cleanup.

2.4. Cleanup and chromatography of cheese samples

Employing the F-LLE step immediately prior to the WAX-SPE step and compared to the same cheese extracted without the F-LLE step, gave a marked improvement in both overall analytical robustness and sensitivity. After standard anion exchange SPE cleanup PFOS is not detectable in either mass channel (A and C, Fig. 7). With a fluorous partitioning liquid–liquid extraction (F-LLE)

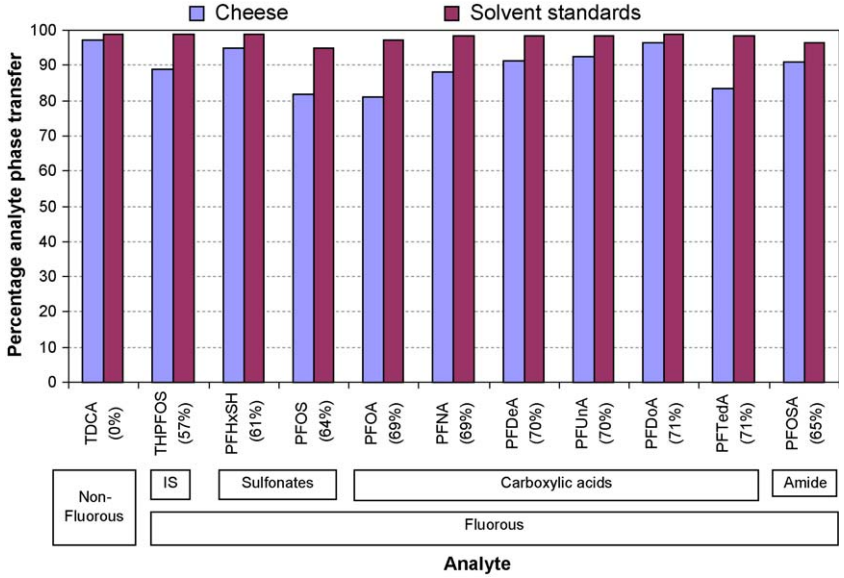
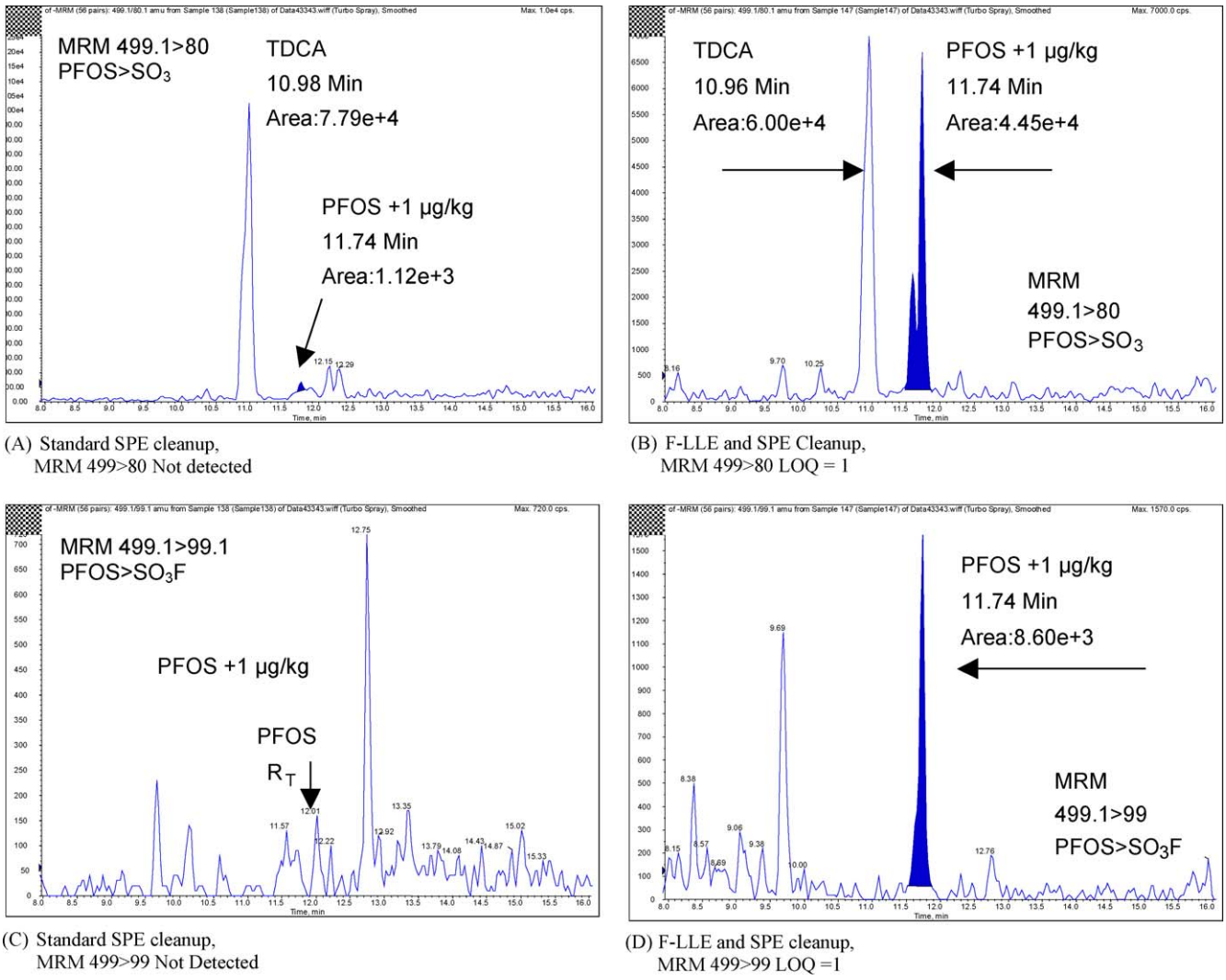


Fig. 6. Percentage transfer of 10 μg/kg PFCs from cheese and solvent standards (10 μg/L) by F-LLE/anion exchange SPE using (3:1) trifluoroethanol:perfluorohexane/DCM (saturated with H_2O).



(A) Standard SPE cleanup, MRM 499>80 Not detected

(B) F-LLE and SPE Cleanup, MRM 499>80 LOQ = 1

(C) Standard SPE cleanup, MRM 499>99 Not Detected

(D) F-LLE and SPE cleanup, MRM 499>99 LOQ =1

Fig. 7. Chromatographic separation and detection of PFOS added to half-fat cheese slices at a concentration of 1 µg/kg of PFOS.

cleanup step, before the SPE step, the response area of TDCA remains constant (A and B, Fig. 7), while the area response of PFOS increases demonstrating removal of a peak suppression effect. There is adequate signal-to-noise ratio (>3 S/N) in both mass channels (B and D) for a 1 µg/kg reporting limit. While the size of the TDCA interference peak [M > SO_3] remained constant due to the non-selectivity of the F-LLE step, the increased response for PFOS in both mass channels is proof of an improved ionisation environment due to removal of a matrix induced suppression effect.

With a validated F-LLE cleanup method, a survey of 10 UK and Irish retail cheese samples was conducted. It was now possible to prove that these cheeses were all free from PFOS and the other PFCs down to a reporting limit of 1 µg/kg (1 ppb).

3. Conclusions

This study has demonstrated that fluorous solvents can be used as a novel extraction/cleanup procedure for PFCs in fat-containing samples. The fluorophilicity and the polarity of the solvent influences selectivity for fluorous compounds. Partitioning is dependent on the polarity, chain length and the percentage of fluorine in the compound. Utilizing the solvent tuning approach, the most effective solvent system for partitioning PFCs was found to be (3:1) trifluoroethanol:perfluorohexane/DCM (saturated with water). Although this does not remove TDCA, using F-LLE prefixed to anion exchange SPE, eliminated the ion suppression caused by the bulk of the cheese matrix and allowed quantification of PFOS and the other analytes to the required reporting level. All 10 cheeses analysed using this procedure were found to be free of any PFC contamination.

4. Experimental

4.1. Chemicals

All chemicals were of analytical grade. Fluorous solvents, perfluorobutyl methyl ether (HFE-7100) and trifluoroethanol were obtained from Fluka (Poole, UK). perfluorohexane (FC-72) was obtained from Aldrich (Poole, UK). The PFC standards, PFOS (perfluorooctanesulfonic acid), PFHxSK (potassium perfluorohexanesulfonate) and PFHxA (perfluorohexanoic acid) were supplied by Fluka (Gillingham, UK), PFHpA (perfluoroheptanoic acid), PFOA (perfluorooctanoic acid), PFNA (perfluorononanoic acid), PFDeA (perfluorodecanoic acid), PFUnA (perfluoroundecanoic acid), PFDoA (perfluorododecanoic acid) and PFBS (perfluorobutanesulfonic acid), 3α,12α-dihydroxy-5β-cholicacid-*N*-(2-sulfoethyl)-amide (taurodeoxy cholic acid-sodium salt, TDCA) were supplied by Sigma (Poole, UK), PFOSA (perfluorooctanesulfonamide) and TH-PFOS (tetrahydro-PFOS) were supplied by ABCR GmbH (Karlsruhe, Germany).

4.2. Mass spectrometry

The determination of PFCs was performed on either a Waters LCT LC–TOF-MS for the preliminary solvent based experiments, or by using an API 4000 triple quadrupole mass spectrometer (Applied Biosystems, Warrington, UK) for analysis of cheese extracts. The sample extraction, solid phase extraction (SPE) cleanup and LC–MS/MS procedures have been described in full previously [8].

4.3. Fluorous liquid–liquid extraction (F-LLE) of cheese

Analytes of both the analytical standards and internal standard (IS) were spiked into 4 mL silanized glass vials (100 μL of 0.5 μg/mL) containing cheese (10 g) and a specified volume of organic solvent (2 mL). After the contents of the vial were sonicated (5 min), the fluorous solvent (2 mL) was added to the solution. Samples were placed on a heat block at 80 °C for 90 min, during which time the two solvents generated a homogeneous monophasic solution. The vials were removed from the heat block and allowed to cool to room temperature. After centrifuging (5 min at 3600 rpm) extracts were stored at −70 °C overnight to reform the triphasic system. On removal from −70 °C freezer, the unfrozen upper organic solvent was pipetted off into a separate glass vial (4 mL). The frozen fluorous solvents were warmed until re-liquefied into one or two layers and these were pipetted out together into a separate vial (4 mL). The two separated fractions were each dried down at 80 °C under a nitrogen stream, reconstituted by sonication (5 min) in MeOH (400 μL). Extracts (400 μL) were transferred into glass vials (450 μL) for analysis by Time of Flight Mass Spectrometry (oaTOF-MS). Partitioning coefficients were calculated from the relative proportions of the combined peak areas from the organic and fluorous fractions.

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References

[1] Directive 2006/122/EC.
[2] United Nations Environment Programme, Geneva, 4–8 May 2009, UNEP/POPS/COP.4/38.
[3] K.J. Hansen, L.A. Clemen, M.E. Ellefson, H.O. Johnson, Environ. Sci. Technol. 35 (2001) 766–770.
[4] P. de Voogt, M. Sáez., TrAC 25 (2006) 326–342.
[5] L.W.Y. Yeung, S. Taniyasu, K. Kannan, D.Z.Y. Xu, K.S. Guruge, P.K.S. Lam, N. Yamahita, J. Chromatogr. A 1216 (2009) 4950–4956.
[6] S.P.J. van Leeuwen, J. de Boer, J. Chromatogr. A 1153 (2007) 172–185.
[7] J.P. Benskin, M. Bataineh, J.W. Martin, Anal. Chem. 79 (2007) 6455–6464.
[8] A.S. Lloyd, V.A. Bailey, S.J. Hird, A. Routledge, D.B. Clarke, Rapid Commun. Mass Spectrom. 23 (2009) 2923–2938.
[9] E. Neil, G. Marsh, Chem. Biol. 7 (2000) R153–R157.
[10] L.P. Barthel-Rosa, J.A. Gladysz, Coord. Chem. Rev. 190–192 (1999) 587–605.
[11] L.E. Kiss, I. Kovesdi, J. Rábai, J. Fluorine Chem. 108 (2001) 95–109.
[12] F.T.T. Huque, K. Jones, R.A. Saunders, J.A. Platts, J. Fluorine Chem. 115 (2002) 119–128.
[13] D.P. Curran, Aldrichim. Acta 39 (2006) 3–9.
[14] E. de Wolf, G. van Koten, B. Deelman, Chem. Soc. Rev. 28 (1999) 37–41.
[15] M.S. Yu, D.P. Curran, T. Nagashima, Org. Lett. 7 (2005) 3677–3680.
[16] Q. Chu, M.S. Yu, D. Curran, Tetrahedron 63 (2007) 9890–9895.
[17] A.G. Mercader, P.R. Duchowicz, M.A. Sanservino, F.M. Fernández, E.A. Castro, J. Fluorine Chem. 128 (2007) 484–492.