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Determination of perfluorocarboxylic acids in aqueous matrices by ion-pair solid-phase microextraction–in-port derivatization–gas chromatography–negative ion chemical ionization mass spectrometry

Roberto Alzaga, Josep María Bayona*

[a] *IIQAB-CSIC Environmental Chemistry Department, Jordi Girona 18-26, E-08034 Barcelona, Spain*

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Abstract

A rapid, selective and simple analytical procedure using tetrabutylammonium as ion pair in conjunction with solid-phase microextraction followed by in-port derivatization–GC–negative ion chemical ionization mass spectrometry was developed. The procedure allows an accurate determination of perfluoroalkylcarboxylic acids in aqueous samples at ng L^{-1} levels (i.e. method detection limit 20 ng L^{-1} for perfluorodecanoic acid) improving previous GC methods in terms of analysis time and sensitivity. Ammonia as reagent gas in the negative ion chemical ionization mass spectrometry increased the sensitivity at least 3-fold compared to methane for perfluorocarboxylic acid butyl esters. The developed procedure was successfully applied to effluents from wastewater treatment plants (i.e. 0.05–8.2 μg L^{-1}) and harbor seawaters.

Keywords: Extraction methods; Derivatization, GC; Water analysis; Environmental analysis; Perfluorocarboxylic acids; Carboxylic acids; Organofluorine compounds

1. Introduction

Polyfluorinated organic compounds (PFCs) have unique physical, chemical, and biological properties, closely related on their high-energy carbon fluorine bond [1]. Perfluorinated surfactants belong to the PFC class which have recently arisen awareness because they are globally distributed, environmentally persistent, bioaccumulative and potentially harmful [1–3]. Perfluorinated surfactants have been used in different commercial and industrial applications [2,4] as paints, lubricants, polishers, food packaging and fire-fighting foams including aqueous film forming foams (AFFFs), which are widely used to extinguish hydrocarbon fuel fires [5]. Among the anionic perfluorinated surfactants, perfluorocarboxylic acids (PFCAs) have been determined in different matrices such as surface [6] and groundwater [9] and biota [6–8]. PFCAs have been determined in water samples by gas chromatography–mass spectrometry (GC–MS) with a prior methyl ester derivatization step [9] or direct introduction by liquid chromatography–tandem mass spectrometry (LC–MS–MS) [6,10]. PFCA determination in water matrices involves a preconcentration step using solid-phase extraction (SPE) with C_{18} and/or ion-exchange materials prior to LC or post-derivatization GC determination.

Although solid-phase microextraction (SPME) has been successfully applied for a wide range of organic compounds [11], few papers related to SPME of anionic compound determination have been published [12–14]. The use of ion-pair (tetramethylammonium) SPME to convert long-chain fatty acids into their volatile methyl esters via in-injector derivatization was proposed by Pan and Pawliszyn [15]. Ion-pair extraction is a method for partitioning of ionic compounds with the aid of counter-ions of opposite charge [16]. A simple reaction of the tetrabutylammonium salt of linear alkylbenzensulfonates in the GC hot injection port to form the butyl esters has been used for their quantitative determination [17–19] or employing SPME as preconcentration/derivatization step for their determination in water matrices [14].

The need for new analytical methods to determine perfluorinated surfactants is highlighted as a requirement for addressing questions about the occurrence, behavior,

* Corresponding author. Tel.: +34-93-4006119; fax: +34-93-2045904.
E-mail address: jbtqam@iiqab.csic.es (J.M. Bayona).

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and impact of this specialty chemical class in the environment [5]. Analytical methodologies available for PFCA determination show important constraints; they are time-consuming and either involve sensitive (low ng L^{-1}) but sophisticated and expensive equipment [10] or present high limits of detection (LODs) in the μg L^{-1} range [9]. Therefore, there is a gap between both methodologies demanding analytical developments. The conjunction of SPME (pre-concentration/derivatization step) with a highly selective detection method such as negative ion chemical ionization mass spectrometry (NCI-MS) employing ammonia as reagent gas can overcome the former drawbacks.

The aim of this work was to develop a rapid, selective, sensitive and solvent-free method for the determination of PFCAs in environmental aqueous samples by SPME–GC–NCI-MS. Direct SPME sampling has been used to pre-concentrate PFCAs as ion pairs. It allows the extraction of ionic analytes as hydrophobic species, thus increasing their fiber coating/water distribution coefficient, improving the SPME efficiency that can be followed by post-derivatization GC for their quantitation.

2. Experimental

2.1. Standards and reagents

The following reagents were obtained from Sigma–Aldrich (Steinheim, Germany) and used as received: heptafluorobutyric acid (PFC_4A, 99%), nonafluoropentanoic acid (PFC_5A, 97%), tridecafluoroheptanoic acid (PFC_7A, 99%), pentadecafluorooctanoic acid (PFC_8A, 96%), nonadecafluorodecanoic acid ($PFC_{10}A$, 98%), perfluorododecanoic acid ($PFC_{12}A$, 95%), and tetrabutylammonium hydrogensulfate (TBA, 97%). Thionyl chloride (for synthesis), water, hexane, butanol and methanol (LiChrosolv HPLC grade) were from Merck (Darmstadt, Germany). Polydimethylsiloxane (PDMS, 100 μm) fiber and the SPME holding device was from Supelco (Bellefonte, PA, USA).

PFCA standard solution ($PFC_{4,5,7,8,10}A$) and $PFC_{12}A$ (surrogate) were diluted in methanol to prepare a working standard solution of 2000 mg L^{-1}. Tetrabutylammonium hydrogensulfate was diluted in water to a final concentration of 0.5 M. Stock and working solutions were stored at 4 °C.

$PFC_{4,5,7,8,10,12}A$ butyl esters (PFCs-Bu) were synthetized as follow, 150 mg of PFCAs were dissolved in 1.0 mL of anhydrous butanol. The reaction was carried out in a fume hood with safety equipment. A drop of thionyl chloride ($SOCl_2$) was added (**caution**: $SOCl_2$ reacts violently with water, causes burns irritating to respiratory system). The solution was heated at 60 °C for 30 min. The butanol excess was evaporated under a nitrogen stream until dryness, and butyl esters derivatives were diluted in hexane. $PFC_{4,5,7,8,10,12}A$-Bu compounds were used for the NCI-MS optimization process and analyte identification. Although $PFC_{6,9,11}As$ have not been tested, low traces of those PFCAs were found when high concentration of PFCAs-Bu were synthesized, allowing establishment of their corresponding retention times and spectra.

2.2. Aqueous matrices

Two sampling campaigns collecting 5 grab wastewater samples in the tertiary effluent from urban/industrial waste water treatment plant (WWTP-1) serving to 45×10^4 equivalent habitants (EHs) were carried out. Furthermore, a urban WWTP-2 serving to 22×10^4 EHs (Catalonia, Spain) was also sampled. In addition, five underlying seawater samples (2 m from surface) from different zones of Barcelona harbor (Catalonia, Spain) were collected using a home made device that allows to sample the underlying water. Samples were stored under refrigerated conditions (4 °C) in Pyrex borosilicate amber glass bottles prior to analysis and analysed without any previous treatment.

2.3. Gas chromatography–mass spectrometry

GC–NCI-MS analysis was performed using an Agilent-6890 Plus GC system coupled to an Agilent 5973N MS system (Palo Alto, CA, USA). The GC system was equipped with a 60 m × 0.25 mm i.d. (cyanopropylphenyl-methylpolysiloxane, 1.4 μm film thickness) ZB-624 column (Phenomenex, Torrence, CA, USA). Injection at 300 °C was in the splitless mode keeping the split valve closed either 3 or 0.8 min for SPME analysis or solvent injection (1.0 μL), respectively. Helium was used as carrier gas (1.0 mL min^{-1}). High-purity (99.995%) ammonia (Air Liquide, Spain) was used as reagent gas in the NCI mode. Oven temperature was programmed from 50 °C (2 min) to 250 °C (3 min) at 8 °C min^{-1}. The transfer line temperature was held at 240 °C. The ion source temperature and reagent gas pressure in the ion source were optimized from 120 to 200 °C and $(1.3–1.8) \times 10^{-4}$ Torr (1 Torr = 133.322 Pa). Experimental results were fitted by a multiple linear regression (SPSS 8.0, Chicago, USA) taking into account the single variables, quadratic and cubic terms and their first order interactions. A surface of response from the equation was plotted by MATLAB (6.0, Natick, MA, USA). Enhanced Chemstation G1701CA software was used for data acquisition and analysis. The ion repeller voltage was 1.0 V. Scans were acquired from 175 to 750 m/z at 1.32 scan s^{-1} or alternatively in the selected-ion monitoring (SIM) mode with a dwell time of 100 ms with a solvent delay of 11 min. The ion windows used in this second case are listed in Table 1. PFCA quantification was carried out in the SIM mode. Quantitation of PFCAs was based on the sum of the ion currents corresponding to $m/z^- = [M]^-$, $[M\text{-}HF]^-$, $[M\text{-}OC_4H_9F]^-$, $[M\text{-}O_2C_5H_9F]^-$ and $[M\text{-}O_2C_5H_9F_3]^-$. PFCA calibration curves were computed as a ratio between the PFCA standard area to $PFC_{12}A$ surrogate. The correlation between PFC concentration was determined by linear regression with typical r^2 values of 0.992–0.997.

Table 1
Physicochemical properties, retention time (t_R) and selected ions (SIM mode) for PFCAs

Analyte (PFCA)	Acronym	pK_a	Molecular formula	t_R (min)	Time window (min)	Diagnostic ions (m/z^-)
Heptafluorobutyric acid	PFC_4A	0.18	C_3F_7COOH	12.35	10.0–12.9	270, 250, 213, 178
Nonafluoropentanoic acid	PFC_5A	0.20	C_4F_9COOH	13.41	12.9–13.8	320, 300, 263, 228
Undecafluoropentanoic acid	PFC_6A	0.23	$C_5F_{11}COOH$	14.46	13.8–15.0	370, 350, 313, 278
Tridecafluoroheptanoic acid	PFC_7A	0.31	$C_6F_{13}COOH$	15.51	15.0–16.0	420, 400, 328, 300, 262
Pentadecafluorooctanoic acid	PFC_8A	0.35	$C_7F_{15}COOH$	16.59	16.0–17.0	470, 450, 378, 350, 312
Heptadecafluorononanoic acid	PFC_9A	0.36	$C_8F_{17}COOH$	17.58	17.0–18.0	520, 500, 428, 400, 362
Nonadecafluorodecanoic acid	$PFC_{10}A$	0.37	$C_9F_{19}COOH$	18.56	18.0–19.0	570, 550, 478, 450, 412
Perfluoroundecanoic acid	$PFC_{11}A$	0.37	$C_{10}F_{21}COOH$	19.46	19.0–20.0	620, 600, 528, 500, 462
Perfluorododecanoic acid	$PFC_{12}A$	0.37	$C_{11}F_{23}COOH$	20.35	20.0–21.0	670, 650, 578, 550, 512

2.4. Solid-phase microextraction procedure

The main parameters that affect the SPME process (i.e. extraction time profile, desorption time and temperature) were optimized by using GC–NCI-MS. Before the initial analysis, fiber was conditioned for 60 min at 250 °C. Samples for method development were prepared by adding 5 mL of HPLC water or artificial seawater into a 7 mL vial, sealed with a PTFE-lined septum, stirred with a 10 mm × 3 mm PTFE stir bar at 1100 rpm keeping the temperature constant at 25 °C. Microliter amount of the analyte working standard solution were spiked into the extraction vial to obtain the following respective concentrations; $PFC_{4,5,7,8,10}As$ 0.035–150 μg L^{-1} and $PFC_{12}A$ as surrogate, 1 or 5 μg L^{-1}. A total of 100 μL of tetrabutylammonium hydrogensulfate (0.5 M) was added. The absorption time profile was obtained by exposing the fiber into the water solution for 10, 20, 30, 40 and 60 min. Desorption times were evaluated at 1, 2, 3 and 5 min. The stirring rate was 1100 rpm for all the experiments. The linearity was evaluated from 0.01 to 200 mg L^{-1} for total PFCAs. Detection (LOD) and quantitation (LOQ) limits were calculated from low concentration value calibration curves by considering the peak area corresponding from 3 (LOD = 3*s*) to 10 (LOQ = 10*s*) times the signal-to-noise ratio of a procedural blank.

3. Results and discussion

3.1. Gas chromatography–mass spectrometry

PFCAs need a derivatization step prior to GC determination, the methyl esters being the ones mostly used. However, among the columns evaluated, a non-polar thick-film column (4.0 μm) was mandatory for obtaining acceptable capacity factor (*k*) values in order to separate methyl esters of PFCA derivatives (PFCAs-Me) [9,20]. This approach has several drawbacks, PFCAs-Me lower than six carbon membered chains ($PFC_{<6}As$-Me) cannot be determined because they are almost not retained. Moreover, low efficiency is achieved and column bleeding is apparent in temperature programming. Moreover, PFC_4A-Me is too volatile for GC analysis in the conventional GC conditions (≥40 °C) and subambient GC oven temperature become unavoidable. Butyl ester derivatives (PFCAs-Bu) can overcome these drawbacks because *k* values are higher. Then, the PFCAs-Bu separation can be performed in a thinner (i.e. 1.4 μm) film capillary column at an attainable initial GC oven temperature (50 °C). High selectivity and efficiency are achieved, allowing $PFC_{<6}As$-Bu determination (Fig. 1a). Moreover, this column exhibits low bleeding, which benefits the MS determination.

Different approaches have been developed involving GC–MS for the determination of PFCAs in environmental samples. Electron impact (EI) in the SIM mode has been used for PFCA quantitative and NCI (full scan mode) for qualitative determination [9]. Also NCI and positive chemical ionization (PCI) modes have been evaluated for airborne PFCA determination, obtaining similar LODs in both modes. However, PCI at the SIM mode was selected because low fragmentation mass spectra is produced with a major molecular ion $[M + H]^+$ [21]. In both chemical ionization modes, methane was used as reagent gas. According to our experience, the selection of a reactive gas such as ammonia is crucial for improving the sensitivity in the halogenated organic compound determination when chemical ionization mode is selected [22]. Ammonia improves the sensitivity of organochlorine determination 5–10-fold compared to methane. Mass spectra of halogenated compounds obtained with ammonia show higher fragmentation than methane, increasing their ionic abundance. Despite these differences in the ionic abundance, the fragmentation pattern obtained with the two different reagent gases is similar [22]. The difference in sensitivity between methane and ammonia is probably due to the buffer capacity of the two gases to decrease the energy of the emitted electrons by the mass spectral filament to near-thermal values (ammonia serves to “thermalize” the electrons by inelastic scattering and dissociative ionization processes) [23]. Likewise, the rate constant for electron thermalization (K_e) of ammonia, was about fourteen times higher than the methane one [23]. Moreover, the use of ammonia as reactive gas can avoid the MS source damage. Indeed neutral fragment losses of hydrofluoric acid (HF, *m/z* = M-20) are produced in the PFCA of alkyl esters when chemical ionization is performed (Fig. 2b). Obviously, HF is a highly reactive and corrosive

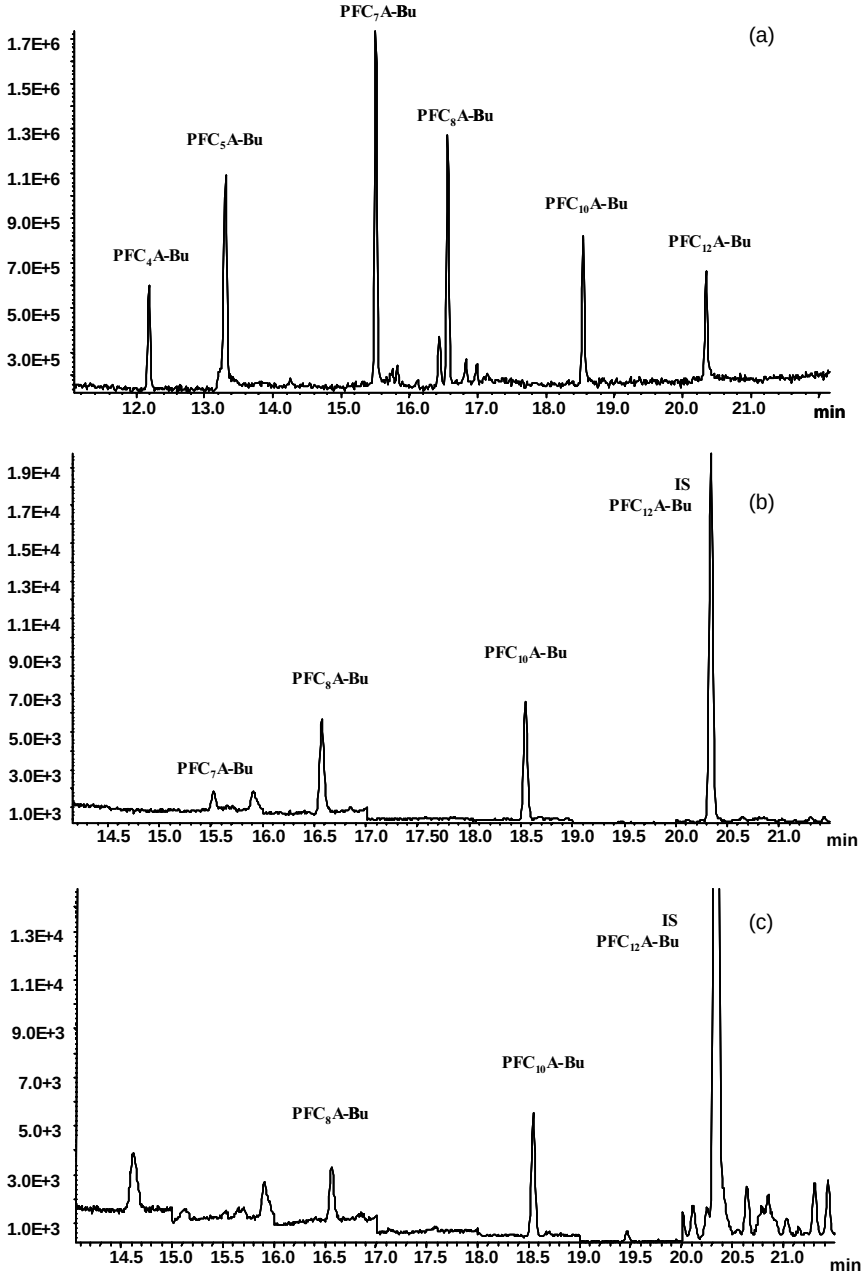

Fig. 1. GC–NCI-MS total ion current of a PFCA butyl ester standard solution (a) (full scan mode) and PFCA ion-pair SPME–in-port derivatization–GC–NCI-MS reconstructed selected ion chromatograms of (b) urban waste water and (c) Barcelona sea harbor surface samples ($PFC_{12}A$ was used as surrogate). Note that time scales of the reconstructed ion chromatograms (b and c) are different that (a).

agent, which can affect the filament. However, the basic properties of ammonia can neutralize the HF produced in chemical ionization, increasing the filament lifetime. Although electron capture is the mechanism proposed for the ionization of PFCAs-Bu by the NCI process, ammonia can generate a Brønsted base (NH_2^-), which can react with esters generating carboxylate anions [24].

EI and NCI mass spectra of $PFC_{10}A$-Bu are shown in Fig. 2. EI mass spectrum (Fig. 2a) shows a predominant base peak $m/z^+ = 57$ $[C_4H_9]^+$ and different fragment ions with varying carbon–fluorine proportion (i.e. $m/z^+ = 69$ $[CF_3]^+$, 100 $[C_2F_4]^+$, 131 $[C_3F_5]^+$, 169 $[C_3F_7]^+$, etc.), following a similar pattern reported for PFCAs-Me [9]. The rest of PFCAs-Bu evaluated has shown the same mass spectra in the EI mode. In fact, molecular ions were not detected showing the excess of energy produced in EI for PFCA alkyl ester derivative ionization. The main ions produced by EI (i.e. $m/z^+ = 57$ and 69) are not useful for qualitative/quantitative determination because they are not specific and those specific containing fluorine are minor (10–15% of the total ion abundance) worsening their LODs. PCI with ammonia or methane shows lower sensitivity than NCI (at least 5-fold).

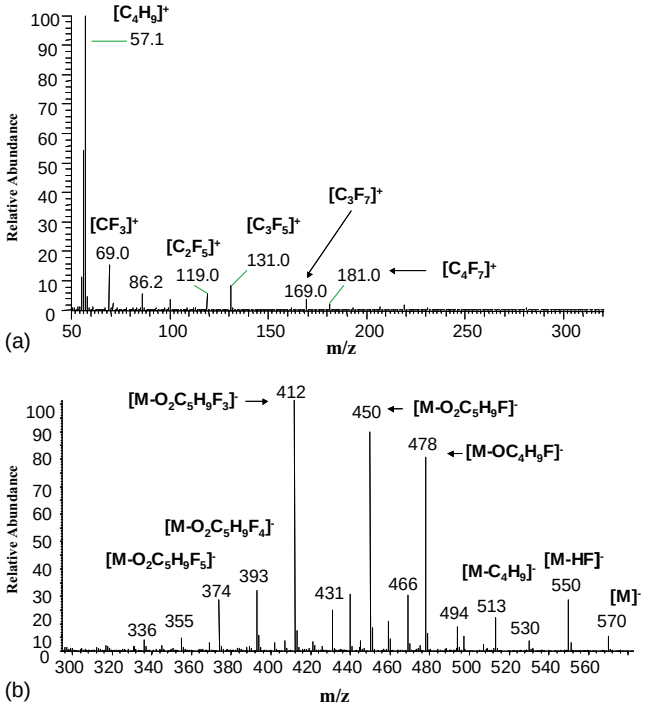

Fig. 2. EI (a) and NCI (b) mass spectra of $PFC_{10}A$-Bu. Ammonia was used as reagent gas.

NCI mass spectrum with ammonia (Fig. 2b) shows a selectivity and sensitivity allowing the molecular ion detection (10% versus 30% relative abundance for PFCAs-Me). All PFCAs-Bu spectra follow the same NCI fragmentation pattern, and they are similar to the spectra obtained when methane is employed for PFCAs-Me [9]. The main ions obtained in NCI (i.e. $[M]^-$, $[M\text{-}HF]^-$, $[M\text{-}C_4H_9OF]^-$, $[M\text{-}C_5H_9O_2F]^-$ and $[M\text{-}C_5H_9O_2F_3]^-$) are useful for qualitative/quantitative determination because they are specific for PFCAs-Bu and can be used in the SIM mode, improving their LODs. Moreover, preliminary studies with NCI and methane shows lower sensitivity compared to ammonia (at least 3-fold) corroborating the advantage of the ammonia as reagent gas use.

Following the reagent gas selection, ion source temperature and reagent gas pressure at the ion source, respectively were optimized. The response surface of the PFC_8A-Bu obtained by fractional factorial experimental design is shown in Fig. 3 obtaining optimum conditions at 175 °C in the ion source and 1.5×10^{-4} Torr for the reagent gas pressure. The highest molecular ion abundance (Fig. 3a) is obtained at low ion source temperature and decreases when temperature is raised. However, fragment ions (i.e. $[M\text{-}HF]^-$, $[M\text{-}C_5H_9O_2F]^-$ and $[M\text{-}O_2C_5H_9F_3]$) response is favored when temperature is increased (Fig. 3b and c). On the other hand, when reagent gas pressure is increased, the PFCA signal to noise ratio also increased until reaching a plateau. The sum of the evaluated ion abundance corresponds to 24.6% of the total ions present in the mass spectrum (Fig. 3d). The correlation coefficient of for the contour surface for the different ions ranged from $r^2 = 0.91$ to 0.99. Similar results were obtained for the rest of PFCAs evaluated. Optimum conditions obtained for PFCAs-Bu are in concordance with those reported for organochlorine compound determination by GC–NCI-MS [22].

3.2. Solid-phase microextraction

Beyond the analytical problems related to PFCA determination, the isolation and derivatization of perfluorinated surfactants from water is difficult due to the high water solubility [5]. PFCAs have very low pK_a values (see Table 1) compared to their carboxylic acid counterparts (i.e. CH_3COOH $pK_a = 4.74$ versus CF_3COOH $pK_a = 0.3$). Obviously, PFCAs occur in environmental water samples as anionic species, even if pH is reduced. Different approaches have been developed in order to preconcentrate PFCA in environmental samples using SPE with C_{18} or ion-exchange materials [6,9]. However, a time-consuming procedure is required in order to eliminate PFCA traces in the SPE sorbents to improve the procedural blanks [9]. Moreover, the PFCA pre-concentration process is strongly matrix-dependent yielding random recoveries. When the alkyl perfluorinated chain length is increased, different recoveries are obtained in spiked groundwater samples (i.e. PFC_8A 73–90%, $PFC_{12}A$ 35–88%) [9]. This fact limited the employment of $PFC_{12}A$ as internal standard when a SPE procedure was developed. However, SPME does not present this drawback because it is a non-exhaustive extraction.

Preliminary studies with PFCAs direct SPME and in-fiber derivatization (using diazomethane)–GC–MS, showed that free PFCAs can be pre-concentrated in the PDMS fiber but low extraction efficiencies are achived. On the other hand, due to the low PFCA pK_a values (Table 1), a decrease in the pH does not improve the extraction efficiency. It is clear that the TBA employment in order to form ion-pair can improve the SPME extraction efficiency. The ion-pairing reagent served two purposes. First, it allowed the extraction of PFCAs with the PDMS fiber by counterion association and second, the derivatization of the formed PFCA ion pairs in the GC injection port at 300 °C to form the corresponding PFCAs-Bu. Preliminary studies evaluating different tetraalkyl (i.e. methyl and ethyl) ammonium salts showed that the length of the ion pair is crucial for increasing PFCAs recoveries. TBA shows the best ion-pair reagent behaviour among the tetraalkyl amonium salts evaluated (butyl $\gg$ ethyl > methyl). However, the use of a surrogate is mandatory when this approach is developed [14], and $PFC_{12}A$ is suitable because it can control the extraction/derivatization process. The employment of TBA as ion pair for increasing PFCAs recoveries in biological matrices was evaluated before liquid–liquid extraction developed [7].

Due to the PFCA ion-pair properties and derivatization conditions, the PDMS (100 μm) fiber is the most suitable fiber for the analytical methodology developed [15]. Although the maximum recommended temperature for the

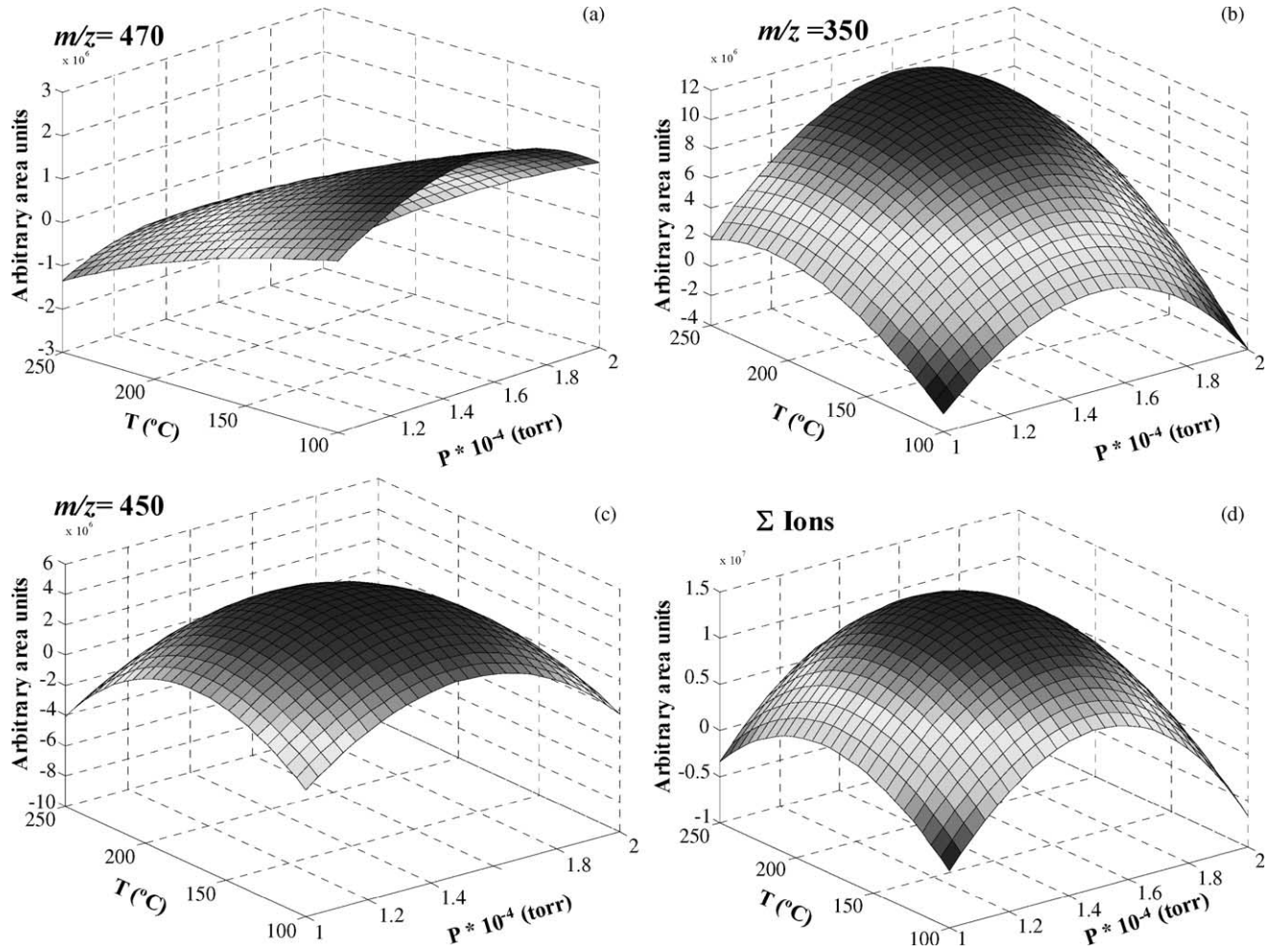

Fig. 3. Response surface obtained by experimental design optimisation (see Section 2) of the ion source temperature and reagent gas pressure (ammonia as reagent gas) effect in the PFC_8A-Bu NCI for (a) $[M]^-$ ($m/z = 470$), (b) $[M\text{-}O_2C_5H_9F]^-$ ($m/z = 350$) ($m/z = 450$), (c) $[M\text{-}HF]^-$ and (d) sum of the ions.

PDMS (100 μm) fiber is 280 °C, derivatization process can be performed at 300 °C, for a short time without any damage [14]. Different desorption times (2.0, 3.0 and 5.0 min in splitless mode) were evaluated. Fiber re-injection was carried out to check the carryover confirming that 3 min was sufficient for quantitative desorption of analytes from the extraction fiber. The PDMS fiber does not present drawbacks of PFCA contamination as in SPE. PFCA extraction efficiency decreased dramatically at elevated temperatures. Therefore, room temperature (25 °C) was selected.

The extraction time profile for different PFCA ion-pairs for PDMS (100 μm) fiber is shown in Fig. 4. As illustrated, PFCA extraction does not reached the equilibrium conditions. The extraction time selected (30 min) is adequate for GC analysis allowing: (a) new extraction meanwhile the GC run is carried out, and (b) allows trace level determination.

3.3. Accuracy, precision and detection limits

Although separation of PFCAs-Bu by GC–MS is possible (Fig. 1a), low-molecular-mass PFCAs-Bu (i.e. PFC_4A and PFC_5A) could not be determined following the analytical approach developed in this work. It is clear that two factors can affect their determination when the alkylperfluorinated chain in PFCA decreases: (1) the polarity of the ion pair increases, leading to a drop in the recovery, and (2) the number of fluorinated atoms in the molecule is closely related to the response factor in NCI. Consequently, these two factors affect to the LOD of PFCAs as shown in Table 2.

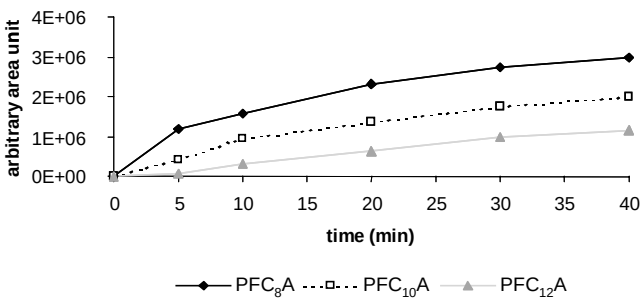

Fig. 4. Extraction time profile of $PFC_{8,10,12}A$s using PDMS (100 μm) fiber.

Table 2
Accuracy, precision and detection limits of the PFCA evaluated

PFCA	Spiked level ($\mu g\,L^{-1}$)	Measured ($\mu g\,L^{-1}$)	R.S.D.[a] (%)	LOD ($\mu g\,L^{-1}$)	LOQ ($\mu g\,L^{-1}$)
PFC_7A	3.0	2.85	8.3	0.75	2.5
	30.2	31.6	3.1		
PFC_8A	0.5	0.47	6.8	0.1	0.34
	15.3	16.2	2.5		
$PFC_{10}A$	0.1	0.12	5.5	0.02	0.05
	3.2	3.3	2.3		

[a] $n = 5$.

Table 3
Concentration ($\mu g\,L^{-1}$) of PFCAs in effluent wastewater plants and harbour seawater

Water samples	*N*	Sampling date	Mean value ($\mu g\,L^{-1}$)		Range ($\mu g\,L^{-1}$)	
			PFC_8A	$PFC_{10}A$	PFC_8A	$PFC_{10}A$
WWTP1	5	10 March 2003	1.4	2.38	0.1–4.3	0.05–8.17
	5	21 July 2003	0.8	1.68	<0.1–2.3	<0.02–4.23
WWTP2	5	16 July 2003	<0.1	<0.02	<0.1	<0.02
Barcelona harbour	6	5 March 2003	0.15	0.18	<0.1–0.34	<0.02–0.65

Similar drawback occurs when SPE is developed (i.e. PFC_5A recovery 15–35%) [10]. Matrix spike experiments (groundwater, without PFCAs detected) were performed to determine the precision and the accurancy of the method developed at two different final concentrations. Results are shown in Table 2. In general, the R.S.D. values for replicate analysis ($n = 5$) indicate an acceptable precision within the methodology. The previously reported LOQ for PFC_8A was $36\,\mu g\,L^{-1}$ when SPE off-line GC–MS (IE) was carried out [9]. The analytical methodology developed improves this LOQ in two orders of magnitude ($0.34\,\mu g\,L^{-1}$).

3.4. Application to aqueous matrices

The developed methodology was applied to aqueous matrices and results are shown in Table 3. Ion-pair SPME injector port derivatization (IPD) folllowed by GC–NCI-MS allowed the identification of $PFC_{8,10}As$ in effluent samples from an urban-industrial wastewater treatment plant. Despite the complexity of the sample, the total ion current (TIC) shown in Fig. 1b exhibited a high detection selectivity where only PFCAs are present. The combination of a highly selective detector such as NCI-MS and high reproduciblity in the GC retention time (R.S.D. <0.5%) ensures a PFCA positive identification. When PFCA concentration level exceeded to the $1.0\,mg\,L^{-1}$, full scan mode was performed in order to confirm the analyte presence. PFC_7A was detected only in one sample, however its quantification was not possible because the concentration was near the LOQ (see Table 2). $PFC_{8,10}A$ was detected in all effluent waste water samples from urban-industrial WWTP and their concentrations were in the range <0.34–4.32 and <0.5–8.2 $\mu g\,L^{-1}$, respectively. PFCA concentration in waste water samples were at the same level reported in contaminated river water following an AFFF spill (0.011–11.3 $\mu g\,L^{-1}$ for PFC_8A) measured by off-line SPE–LC–MS–MS [10] but they are at least 2-fold lower compared to highly contaminated groundwater (<36–6570 $\mu g\,L^{-1}$ for PFC_8A) measured by off-line SPE–GC–MS (EI) [9]. Although LC–MS–MS allows to quantify lower PFCA concentrations than the methodology developed, most PFCA determinations can be carried out following the methodology proposed in this study for medium-high PFCA-contaminated water samples, improving analysis time and cost. PFC_8A is one of the major components for AFFF commercial products, however PFC_8A and $PFC_{10}A$ are PFCs of industrial significance [25]. Effluent waste water analysis showed higher concentration of $PFC_{10}A$ than PFC_8A, and can be associated with industrial activities. Barcelona harbor seawater analysis showed low PFCAs concentration. Five samples covering different zones of Barcelona harbor were analysed and only one gave positive detection. However, this sample was located close to the liquid fuel stock dock where industrial activities are developed and potentially fire-fighting foams are employed. Although PFC_8A was detected, its concentration was close to LOD but $PFC_{10}A$ was able to be quantified.

4. Conclusions

The developedion-pair SPME–IPD–GC–NCI-MS demonstrated to be a reliable, sensitive and selective technique for the determination of PFCAs in aqueous environmental samples at low concentration levels (i.e. $50\,ng\,L^{-1}$ for $PFC_{10}A$). Ammonia as reagent gas increases the sensitivity at least 3-fold compared to methane for PFCAs-Bu in

NCI-MS. Moreover, the developed SPME procedure for PFCAs determination offered improved performance in comparison to conventional techniques in terms of procedural blank, analysis time, sample volume, recoveries and solvent elimination during the analytical procedure. Furthermore, it can be used as a rapid screening analytical methology to obtain information about sources, behavior and fate of PFCAs in environmental samples.

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