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Ion-pair sorptive extraction of perfluorinated compounds from water with low-cost polymeric materials: Polyethersulfone vs polydimethylsiloxane

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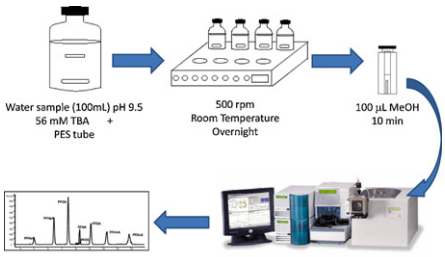
HIGHLIGHTS

- Ion-pair disposable sorptive extraction of PFCs in water.
- Polydimethylsiloxane (PDMS) vs Polyethersulfone (PES).
- Different extraction variables optimized.
- PES provided better extraction efficiency of polar analytes.
- LODs in the 0.2–20 ng L^{-1} range with PES.

GRAPHICAL ABSTRACT



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ABSTRACT

A method for the determination of seven perfluorinated carboxylic acids and perfluorooctane sulphonate (PFOS) in aqueous samples using low-cost polymeric sorptive extraction as sample preparation technique, followed by liquid chromatography–tandem mass spectrometry (LC–MS/MS) determination has been developed and validated. Simplicity of the analytical procedure, low volume of solvent and sample required, low global price and a good selectivity providing cleaner extracts are the main advantages of this extraction technique. Polydimethylsiloxane (PDMS) and polyethersulfone (PES) materials were evaluated and compared to achieve the best extraction efficiencies. Hence, different variables have been optimized, viz.: sample pH, concentration of an ion-pairing agent (tetrabutylammonium), ionic strength, sample volume, extraction time, desorption solvent volume, desorption time and the need for auxiliary desorption techniques (sonication). Overall, PES leaded to a better sensitivity than PDMS, particularly for the most polar compounds, reaching detection limits (LODs) in the 0.2–20 ng L^{-1} range. The precision of the method, expressed as relative standard deviation (RSD), was lower than 16%. Finally, the PES material was employed for the analysis of sea, sewage and fresh water samples. Perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA) and perfluorodecanoic acid (PFDA) were detected in all the analyzed influent samples reaching levels of up to 401 ng L^{-1}. In surface water, perfluorohexanoic acid (PFHxA) exhibited the highest concentrations, up to 137 ng L^{-1}.

1. Introduction

Perfluorinated compounds (PFCs) are a group of emerging contaminants, which have been manufactured for over 40 years as a direct product in electrochemical fluorination and telomerization processes [1,2]. These chemicals consist of a hydrophobic alkyl chain of varying length (typically C4–C18), which is normally fully fluorinated, and a hydrophilic functional end group [3]. Depending on this functional group, PFCs are divided into three main categories: perfluoroalkyl carboxylates (PFCAs), perfluoroalkyl sufonates (PFASs) and perfluoroalkyl sulfonamides (PFSAs) [4,5].

PFCs occur in many products, derived from a wide variety of commercial, consumer and industrial applications, mainly as

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surfactants and surface protectors. Thus, they can be found as ingredients in paper, carpets, lubricants, leather, food packaging, fire-fighting foams, flame retardants and fire-prevention agents [6–9]. Due to the high electronegativity of fluorine, covalent bonds between carbon and fluorine are very strong, conferring PFCs a high resistance towards acid and alkaline hydrolysis, photolysis, biodegradation and metabolism. These properties explain the persistence and bioaccumulation of PFCs in the environment [9–12] and the preference to accumulate in protein-rich tissues, such as liver and blood, rather than in fat tissues [13]. To date, PFCs have been detected in several environmental compartments, like different types of waters [3,8], sediments [3,14], soil [3], air [15] or biota [8,16]; normally at concentrations at the ng L^{-1} or ng g^{-1} level.

Among PFCs, perfluorooctane sulphonate (PFOS) and perfluorooctanoic acid (PFOA) are the two most commonly detected PFCs in the environment and human blood [17,18]. Both were considered biologically inactive during the decade of the 50 s, but subsequent studies have found toxic effects in liver, immune system and reproduction organs in animals. PFOA and PFOS affect homeostatic sexuality hormones and are associated with an increase in fetal resorptions and aborts in animals. They also affect the neuroendocrine system of rodents, causing hepatocellular hypertrophy and the increment of cholesterol and triglycerides in rats [19–22].

Since 2006, PFOS and PFOA began to be regarded as persistent organic pollutants (POPs) after the Stockholm Convention [23]. The European Food Safety Authority has recognized them as emerging contaminants in the food chain and estimated the human tolerable daily intake on 150 ng kg body $weight^{-1}$ for PFOS and 1500 ng kg body $weight^{-1}$ for PFOA [24]. Due to the current interest on PFCs, several sample preparation methods have been developed for their determination in the environment [25]. In the case of water samples, liquid–liquid extraction (LLE) [26,27] and solid phase extraction (SPE) [7,27–31] followed by solvent evaporation are the traditional methods used for enrichment and isolation of trace levels of PFCs. Furthermore, when very low detection limits (pg L^{-1}) are required, SPE procedures have been modified by increasing the sample volume up to 30 L [32,33]. However, over the years, some more recent and innovative techniques, which lower the consumption of organic solvents, have also been applied for PFCs extraction, as e.g. solid-phase microextraction (SPME) [34]. In that work, Alzaga et al. employed an ion-pairing agent, tetrabutylamonium (TBA) in order to improve the SPME extractability of PFCs and determination was then performed by gas chromatography–negative chemical ionization–mass spectrometry (GC–NCI–MS), after derivatization. However, detection limits (LODs) were still relatively high due to the low mass of polydimethylsiloxane (PDMS) of SPME fibers, that leads to low extraction efficiencies [34]. An alternative to SPME, in order to increase the amount of extractant sorbent, is the use of stir-bar sorptive extraction (SBSE) or better off, the use of disposable low cost polymeric materials, which do not need to be reused, avoiding cross-contamination problems. In this last case, PDMS has been the most frequently used sorbent [35]. Yet, in a recent work, we have shown that polyethersulfone (PES), may represent a more efficient alternative, particularly for polar analytes [36].

As regards separation and determination of PFCs, this is usually accomplished by liquid chromatography–mass spectrometry (LC–MS) and liquid chromatography coupled to tandem mass spectrometry (LC–MS/MS) [7,27–30,32,37]. GC is less frequently used because it needs a derivatization step prior to analysis and some of the analytes of interest cannot generate stable and volatile derivatives compounds, as e.g. PFOS [6,34,38].

In this work, a low-cost polymeric sorbent extraction method was optimized and evaluated for the preconcentration of PFCs (PFOS and seven PFCAs, from 6 to 12 carbons) from water samples. This technique was chosen based on the simplicity of the analytical procedure, low volume of solvent consumed and an important reduction of the overall cost of the process. Moreover, it allows the simple simultaneous extraction of a large number of samples. To the best of our knowledge, neither SBSE nor sorptive extraction have been previously applied to the determination of perfluorinated compounds in aqueous samples.

2. Experimental

2.1. Chemicals

Perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA) and PFOS were obtained from Sigma Aldrich (Steinheim, Germany). As internal standards (ISs), a mixture containing 2 μg mL^{-1} of $^{13}C_4$ PFOS, $^{13}C_2$ PFHxA, $^{13}C_4$ PFOA, $^{13}C_5$ PFNA, $^{13}C_2$ PFDA, $^{13}C_2$ PFUnA and $^{13}C_2$ PFDoA in methanol was obtained from Wellington Laboratories (Guelph, Canada).

Methanol (MeOH) of chromatographic analysis grade, hydrochloric acid (37%) and sodium hydroxide were provided by Merck (Darmstadt, Germany). Ammonium acetate was from Riedel-de Haën (Seelze, Germany). TBA bromide was purchased from Sigma Aldrich, sodium chloride from VWR (Llinars del Vallès, Spain) and sodium carbonate anhydrous from Scharlau (Barcelona, Spain). Ultrapure water was obtained in the laboratory from a Milli-Q (Millipore, Billerica, MA, USA) water purifier.

PDMS rod with 2 mm diameter was obtained from Goodfellow (Huntingdon, UK) and PES tube with 0.7 mm of external diameter from Membrane GmbH (Wuppertal, Germany).

2.2. Samples

Surface water samples were collected from Sar river in Santiago de Compostela on January 2011 and from Lérez river in Pontevedra on March 2011 (Spain). Sea water samples were collected from coastal areas on the northwestern coast of Spain (January 2011). Effluent and influent wastewater samples were collected from January to March in 2011 from a wastewater treatment plant (WWTP) located in the Northwest of Spain and receiving the discharges from a ca. 100,000 inhabitants city.

The samples were taken in amber glass bottles previously rinsed with methanol and ultrapure water and stored in the dark at 4 °C for a maximum of 48 h. Prior to their analysis, water samples were filtered using cellulose acetate membranes (0.45 μm pore size).

2.3. Equipment

The liquid chromatographic system used is equipped with two ProStar 210 high-pressure mixing pumps (Varian, Walnut Creek, CA, USA), a Metachem Technologies vacuum membrane degasser (Bath, UK), an autosampler and a thermostatted column compartment ProStar 410 module (Varian).

A sample volume of 10 μL was injected into a Luna C18 column (50 mm × 2.0 mm, 3.2 μm particle diameter; 100 Å pore size) (Phenomenex, USA) maintained at a constant temperature of 45 °C. The target compounds were separated at a flow rate of 0.4 mL min^{-1} using 5 mM of ammonium acetate in both, Milli-Q water (A) and MeOH (B). The following binary gradient was applied: 0–1 min, 40% B; 1–7 min, linear gradient to 75% B; 7–11 min, 75% B and finally 11–14 min, 40% B.

The LC was coupled to a triple quadrupole mass spectrometer (1200L-Varian) which incorporates an electrospray interface (ESI). Nitrogen, used as nebulizing and drying gas, was provided by a nitrogen generator (Domnick Hunter, Durham, UK). Argon (99.999%) was used as collision gas. Instrument control and data