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Development and validation of a pressurized liquid extraction liquid chromatography–tandem mass spectrometry method for perfluorinated compounds determination in fish

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ABSTRACT

This paper describes the development and validation of an analytical methodology to determine eight perfluorinated compounds (PFCs) in edible fish using pressurized liquid extraction (PLE) with water and solid-phase extraction (SPE) with an ion-exchanger as extraction and pre-concentration procedures, followed by liquid chromatography–quadrupole-linear ion trap mass spectrometry (LC–QqLIT–MS). The rapidity and effectiveness of the proposed extraction procedure were compared with those most commonly used to isolate PFCs from fish (ion-pairing and alkaline digestion). The average recoveries of the different fish samples, spiked with the eight PFCs at three levels (the LOQ, 10 and 100 $\mu g\,kg^{-1}$ of each PFC), were always higher than 85% with relative standard deviation (RSD) lower than 17%. A good linearity was established for the eight PFCs in the range from 0.003–0.05 to 100 $\mu g\,kg^{-1}$, with $r > 0.9994$. The limits of quantification (LOQs) were between 0.003 and 0.05 $\mu g\,kg^{-1}$, which are well below those previously reported for this type of samples. Compared with previous methods, sample preparation time and/or LOQs are reduced. The method demonstrated its successful application for the analysis of different parts of several fish species. Most of the samples tested positive, mainly for perfluoropentanoic acid (PFPA), perfluorobutane sulfonate (PFBS) and perfluorooctanoic acid (PFOA) but other of the eight studied PFCs were also present.

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1. Introduction

Perfluorinated compounds (PFCs) have been and are used in a wide variety of industrial applications, such as stain repellents, textile, paints, waxes, polishes, electronics, adhesives and food packaging [1,2]. They have been manufactured for more than 50 years, having been estimated that from 1951 to 2004 up to 7300 tons were released into the environment following production and use [1]. As a consequence, these compounds show a global distribution all over the world and have been detected not only in environmental samples but also in human blood and liver. PFCs show persistence in the environment and some of them are related to different carcinogenic actions, for example perfluorooctanoic acid (PFOA) has been identified as a potent hepatocarcinogen in rodents [3,4]. Meanwhile PFCs have been recognized as emerging contaminants in the food chain by the European Food Safety Authority (EFSA), which have recently finalized its opinion on perfluorooctane sulfonate (PFOS), PFOA and its salts establishing tolerable daily intakes (TDI) of 150 $ng\,kg^{-1}$ b.w. day^{-1} for PFOS and 1500 $ng\,kg^{-1}$ b.w. day^{-1} for PFOA [5]. The opinion of the EFSA on these compounds also highlights that concentration levels, contamination pathways, and toxicological potency should be assessed in the food chain and expresses its concern by the lack of available data [5].

A growing but still insufficient number of studies report on the occurrence of PFCs in food and drink [6–9]. In these papers, bioaccumulation in fish has been shown to be the main influence of PFCs in dietary exposure [10]. Some reports have also found a positive correlation between PFCs concentrations in plasma and consumption of fish, corroborating the importance of this exposure route [11]. Accordingly, these compounds have been widely analyzed in blood, bile and liver [12–16] but not so often in the edible part (muscle) of fish [17,18]. Levels of PFOS and PFOA have been reported in mussels, oysters, shrimp and fish from different countries [19–22]. However, it is often impossible to give details of the other PFCs homologues present in this matrix.

So far, most of the analysis methods to determine PFCs are based on liquid chromatography coupled to mass spectrometry

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or tandem mass spectrometry approaches (LC–MS or LC–MS/MS) [1,2]. Among them, triple quadrupole (QqQ) MS is the most widely employed analyzer because of their high dynamic range and good performance when working in selected reaction monitoring (SRM) mode [1]. In the recent LC–MS/MS methods, ion paired, potassium hydroxide or solvent extractions were applied, for which the reported limits of quantification (LOQ) for PFOA and PFOS were as low as 1 $\mu g\,kg^{-1}$ [2]. However, many challenges still remain for either LC–MS/MS or the sample preparation protocols. Hybrid MS instruments have proved to be powerful tools to achieve high sensitivity, specificity and selectivity, as they combine the main advantages of the two analyzers (i.e. quadrupole and time of flight in case of QqTOF or quadrupole and liner ion trap in case of QqLIT) [23,24]. The main advantage of the hybrid QqLIT over other LC–tandem MS equipments relies on that it achieves unequivocal identification and confirmation of target compounds at highly sensitive levels [23,25]. Its unique feature is that the second mass analyzer, Q3, can be run in two different modes, retaining the classical QqQ scan functions such as SRM, product ion, neutral loss, and precursor ion while providing access to sensitive ion trap scans. This allows very powerful scan combinations when performing information-dependent data acquisition (IDA), enhanced product ion (EPI) or MS^3 experiments obtaining concomitantly both quantitative and qualitative information. Simultaneously, modern extraction and clean-up techniques, such as pressurized liquid extraction (PLE), microwave assisted extraction (MAE) or solid-phase microextraction (SPME), have not been applied to the determination of PFCs yet. These techniques provide rapidly and accurately clean extracts for sensitive analysis [24].

Consequently, the aim of this study was the development and validation of a simple, sensitive and selective analytical methodology to determine eight PFCs, using PLE with water and SPE on ion-exchanger for the extraction and pre-concentration of target compounds from various fish samples including liver, muscle and roe. To our knowledge, this work is the first example of the application of PLE for the determination of PFCs from food. Target compounds were perfluorobutanesulfonate (PFBS), perfluoropentanoic acid (PFPA), PFOA, PFOS, perfluoro-7-methyloctanoic acid (i,p-PFNA), perfluorononaoic acid (PFNA), perfluorodecanoic acid (PFDA) and perfluoro-1-decanesulfonate (L-PFDS). Validation comprised the assessment of linearity, limit of quantification, recovery and precision. To prove the potential of this method, a comparison with ion-pairing and alkaline digestion extractions, – the two most widely employed procedures to extract PFCs from fish – was also included in this study. The ion-pairing forms neutral species of the anionic surface-active FFCs making them extractable from food samples by organic solvents. The use of alkaline digestion helps to extract bound PFC residues by removing lipids and proteins before extraction. Analyte identification and confirmation was performed using a LC–QqLIT–MS/MS in compliance with the EU regulations (EU Commission Decision 2002/657/EC). Finally, PFC residues were determined in different fishes taken in several markets of Valencia and Barcelona cities.

2. Experimental

2.1. Chemicals

The isotope-labelled internal standards (ISs) perfluoro-n-[1,2,3,4$^{13}C_4$]octanoic acid (MPFOA), perfluoro-1-[1,2,3,4$^{13}C_4$] octanesulfonate potassium salt (MPFOS), and perfluoro-n-[1,2$^{13}C_2$]decanoic acid (MPFDA) as well as sodium L-PFDS, PFNA and i,p-PFNA were purchased from Wellington Laboratories (Guelph, Ontario, Canada) as 50 $\mu g\,ml^{-1}$ methanolic solutions (1.2 ml). Tetrabutylammonium PFBS (purum ≥ 98%), PFOS sodium salt (98%), PFPA (97%) PFOA (96%), PFDA (97%), were purchased from Aldrich (Steinheim, Germany). Separate stock solutions of the analytes were prepared in methanol at a concentration of 1.0 $mg\,ml^{-1}$ of free compound or salt. A standard mixture containing the 8 analytes was made from the stock solutions (commercial or laboratory made) to provide different concentrations of the analytes depending on their expected concentrations in fish and on the sensitivity of the method. Concentrations of the analytes in the standard mixture were calculated as free compounds. Working mixtures were diluted from the standard mixture in methanol/water both 20 mM ammonium acetate (10/90, v/v). Solutions of ISs were diluted to a concentration of 2 $\mu g\,ml^{-1}$ with methanol/water both 20 mM ammonium acetate (10/90, v/v), and appropriate volumes of the ISs were added to fish samples so as to obtain concentrations of 1.5 $\mu g\,kg^{-1}$ in the sample material.

LC-grade 'suprasolv' water, methanol and acetonitrile were purchased from Merck (Darmstadt, Germany). Deionized water (<18 MΩ cm resistivity) was from a Milli-Q SP Reagent Water System (Millipore, Bedford, MA, USA). All the solvents were passed through a 0.45 μm cellulose filter from Scharlau (Barcelona, Spain) before use. Analytical grade reagent sodium sulfate anhydrous and glacial acetic acid were also from Scharlau. Ammonium acetate (99%, pa for HPLC) and sea sand were from (Sigma–Aldrich, Steinheim, Germany). Ammonium hydroxide (25% in water), sodium hydroxide (analytical grade), tetrabutyl ammonium hydrogen sulfate and methyl-ter-butyl ether were from Merck (Darmstadt, Germany).

Oasis Wax cartridges of 60 mg (3 cm^3), particle size 30 μg and pore size 80 Å used were from Waters (Milford, MA, USA). Oasis WAX is a polymeric reversed-phase, Weak Anion Exchange mixed-mode sorbent that allows for the retention and release of strong acidic compounds (e.g. such as sulfonates).

2.2. Sampling

The following fish species were purchased in retail fish markets and supermarkets as a whole fish: young hake (*Merluccius bilinearis*, $n = 5$), anchovy (*Engraulis encrasicolus*, $n = 5$) and striped mullet (*Mujil cephalus*, $n = 3$). Each sample of young hake and anchovy weighted around 2 kg (ca. 16 specimens/sample and 100 specimens/sample, respectively) and each sample of striped mullet consisted of only one specimen (weights between 180 and 520 g). Furthermore, hake roe ($n = 2$) and swordfish fillets (*Xiphias gladius*, $n = 3$) were also taken in these markets. All the samples were sent in fresh conditions (on ice) to the laboratory. Whole fishes were dissected, taken the liver and the entire right dorsal lateral fillet with the skin. The liver was completely and carefully separated. The livers corresponding to each sample were homogenized together. The right dorsal lateral fillets, swordfish fillets and hake roe were cut in small pieces. Subsamples of 200 g were homogenized using a bapitaurus food chopped (Taurus, Berlin, Germany), placed into polyethylene (PP) bags and stored at −80 °C prior to analysis.

2.3. Sample preparation

2.3.1. Pressurized liquid extraction

The muscle and liver samples (ca. 2 g, fresh weight) were weighted into a porcelain mortar, added with the ISs and homogenized with approximately 25 g of sea sand using a pestle. The advantages of homogenizing the tissue with sea sand were to disrupt the cell membranes (the great pore and particle sizes of this solid support in comparison with others helps to gridding the sample) and to disperse the sample over a large surface area to obtain better extraction. This mixture was put into a 22 ml extraction cell then, this cell was filled up with washed sea sand. Whatman glass fiber filters were placed at the bottom and top of the extraction cell

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