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## Fast and sensitive determination of per- and polyfluoroalkyl substances in seawater

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### ABSTRACT

In this work, a novel, fast, and sensitive method was developed for perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS) and PFOS precursor's determination in seawater. The proposed method consists in a vortex-assisted liquid-liquid microextraction (VALLME) combined with liquid chromatography (LC) and LTQ-Orbitrap high resolution mass spectrometry (LTQ-Orbitrap HRMS) determination. Several parameters affecting both the HPLC-LTQ Orbitrap HRMS determination and the VALLME were studied, with special attention to blank contamination problem. The use of LTQ-Orbitrap-HRMS in full mode, quantifying the target analytes using the exact mass, provides a very powerful detection in terms of sensitivity and specificity maintaining all the information provided by the full mass spectra, allowing, also, the identification of non-target substances. The use of matrix-matched calibration, together with labelled surrogate standards, minimize matrix effects and compensate potential recovery losses, resulting in recoveries between 95 and 105%, with excellent sensitivity (quantitation limit between 0.7 and 6 ng L<sup>-1</sup>) and precision (4–10%). The proposed method requires only 35 mL of sample and 100 μL of extracting solvent, is fast and avoids the use of other solvents to obtain the dispersive cloudy solution, simplifying the procedure and improving the existing procedures for the determination of per- and polyfluoroalkyl substances (PFASs) in seawater in terms of green analytical chemistry. The method was successfully validated by participating in a proficiency test assay provided by the National Measurement Institute of the Australian Government for the determination of PFOA, total PFOS and linear PFOS in waters. A revision of the state of the art in the last twelve years of methods for the analysis of PFASs in seawater and other types of water was performed, and a critical comparison between the developed method and the previously published was included. Finally, the method was applied to the analysis of samples from Ría de Vigo, a sensitive and semiconfined coastal area located in the northwest of Spain. PFOS, N-methyl perfluorooctanesulfonamide (*n*-MeFOSA) and N-ethyl perfluorooctanesulfonamide (*n*-EtFOSA) were detected in samples at levels lower than the maximum allowable concentration (MAC) established by Directive 2013/39/EU, but above the annual average (AA) levels.

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### 1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are a group of anthropogenic chemicals, consisting of an alkylated hydrophobic chain fully or partially fluorinated, hydrophilic group terminated. This configuration provides to PFASs simultaneous hydrophobic-

ity and lipophobicity. Moreover, these substances present a great chemical and thermal stability. Due to their properties, as water and lipid repellents and stability, PFASs have been widely used as surfactants in industry for surface treatment, paper coatings, performance chemicals etc [1,2]. The “long chain” perfluoroalkyl sulfonic acids (C<sub>n</sub>F<sub>2n+1</sub>SO<sub>3</sub>H, n ≥ 6) and perfluoroalkyl carboxylic acids (C<sub>n</sub>F<sub>2n+1</sub>COOH, n ≥ 7) and their corresponding anions, have demonstrated to be more bioaccumulative than the short-chain analogues [3]. According to the OCDE 2002 report [4] perfluorooctane sulfonic

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acid (PFOS) is persistent, bioaccumulative and toxic to mammalian specie. Repeated exposures result in hepatotoxicity and mortality.

The wide usages, resistance to degradation, bioaccumulation, toxicity, and persistence of PFASs have resulted in their consideration as global environmental contaminants [5]. As consequence, PFOS and its salts have been listed under Annex B (restricted use) of the Stockholm Convention in 2009 [6,7] and included in water Directive 2013/39/EU as priority substances in the field of water policy. The maximum allowable concentration (MAC) for PFOS and its derivatives in surface waters (not inland) established by the water Directive is  $7.2 \mu\text{g L}^{-1}$ .

Presence of PFASs in seawater is caused by discharges of treated or untreated wastewater effluents or river flows [8], urban runoff following rain episodes, atmospheric deposition of volatile precursors and subsequent transformation, or direct application of fire-fighting foams containing PFASs, among others [9]. Although PFASs are diluted in the open seawaters, the continuous input, and their persistence cause that some PFASs have been detected in open seas and coastal areas [8,10–12]. In the last years few papers have focussed its aim on the study of PFASs in seawater samples. PFOS and perfluorooctanoic acid (PFOA) are the most frequently measured PFASs in waters (Table 1). In this work, FOSA (perfluorooctanesulfonamide), N-EtFOSA (N-ethyl perfluorooctanesulfonamide) and N-MeFOSA (N-methyl perfluorooctanesulfonamide) were included, in addition to the most frequently measured PFOS and PFOA, because of their importance. FOSA, used as protective coatings, is a precursor of PFOS that is frequently detected in water monitoring programs (20% of samples) [13]. N-EtFOSA is a termiticide (Sulfluramid) still in use in some countries in insecticide formulations [14]. It is a precursor of FOSA, and its major degradate is PFOS. N-MeFOSA is also a precursor of FOSA (and PFOS), and both (N-EtFOSA and N-MeFOSA) are scarcely determined in water samples [15]. For these reason, we found the determination of these compounds very interesting.

The low concentrations (few  $\text{ng L}^{-1}$ ) reported in the literature for these compounds in water samples makes necessary the use of a pre-concentration step for their analysis. The pre-concentration method most frequently used for the determination of PFASs in water samples is the solid phase extraction (SPE) of a high volume of sample (between 250–1000 mL), being the Oasis HLB cartridges the most popular device [11,12,16–19] (Table 1). Other sorbents used for the SPE are Oasis Wax [20,21],  $\text{C}_{18}$  [22], styrene divinylbenzene (SDVB) [23], Strat X-AW cartridges [13] or mixed hemimicelles [24]. This procedure (SPE) requires high volumes of sample, involves several steps, increasing the risk of PFASs contamination (mainly PFOA) by the contact of the sample and extracts with many laboratory materials [17,23], and frequently is time consuming. The use of microextraction techniques like in-tube SPME [25], dispersive liquid–liquid microextraction (DLLME) [27] or vortex-assisted liquid–liquid microextraction (VALLME) [26,27] for the determination of PFASs in water samples is still scarcely extended, possibly due to the low limit value established in the environmental regulations. These techniques allow a considerable reduction of the volume of sample (0.8–40 mL), are fast, involve few steps, reducing the sample handling and also the risks of contamination [28]. Dispersive liquid–liquid microextraction, was introduced by Rezaee et al. in 2006 [29] and is based on the extraction of analytes in aqueous samples by an appropriated mixture of extraction solvent and dispersant agent producing a cloudy solution. In order to avoid the use of two different solvents, one for the extraction and the other to obtain the dispersion, some authors suggest replacing the dispersant by an agitation step to achieve the formation of the cloudy (VALLME) [30,31]. By this way the DLLME is simplified and only the most appropriate extraction solvent needs to be selected. That was the approach used for this work.

The chromatographic determination is often performed by HPLC tandem mass spectrometry with electrospray ionization in negative mode, with few exceptions using LC–ToF–MS [19], LC–Orbitrap Tribrid HRMS [20] or even GC–MS with derivatization [32]. The LTQ–Orbitrap used in this work is a hybrid mass spectrometer that combines the linear ion trap and the Orbitrap. HRMS on LTQ–Orbitrap system in full-scan mode has demonstrated to be the most powerful determination approach in terms of sensitivity and specificity [33].

One of the main problems in the determination of PFASs at trace levels is the difficulty to keep blank levels at minimum, due to the potential presence of these compounds in the plastic equipment and materials used in the laboratory such as tubing, fitting, filters, septa, etc. All the steps (sampling, storage, extraction, and determination) must be carefully controlled trying to avoid Teflon<sup>®</sup> and other components that could introduce blank signal, hampering the achievement of the low detection limits required for the determination. In this work a careful selection of materials and analytical conditions was performed in order to maintain the procedural blanks at minimum. In addition, a reduction of the instrumental contamination was achieved by changing the mobile phase Teflon filters by glass filters.

The aim of this work is to develop a fast and sensitive method especially suitable for the determination of PFOS, PFOA, and PFOS precursors in seawater in order to evaluate their presence in marine environment.

As far as we know, this is the first work that combines a miniaturized extraction technique with the LTQ–Orbitrap determination of PFASs in seawater, allowing the reliable quantitation of the linear and branched isomers of PFOS and PFOA and the identification of non-target analytes. The proposed VALLME–LC–LTQ–Orbitrap HRMS method has been validated by an in-house procedure, and also by participating in a proficiency test report organized by the National Measurement Institute of the Australian Government.

The optimized method was applied to the analysis of samples from Ría de Vigo (Galicia, Spain). This estuary is affected by an intense outflow of nutrients which produces a consequent high primary productivity. It is surrounded by small and dispersed villages and also affected by Vigo city (>300,000 inhabitants) with medium industrial development and significant port operation. All this, added to geographic and oceanographic characteristics that do not permit a good level of water exchange with the ocean, could lead to an accumulation of certain contaminants within the estuary.

## 2. Experimental

### 2.1. Reagents and standards

Individual standards of sodium perfluoro-1-octanesulfonate (L-PFOS), perfluoro-n-octanoic acid (PFOA), N-methyl perfluorooctanesulfonamide (N-MeFOSA), N-ethyl perfluorooctanesulfonamide (N-EtFOSA), N-ethyl-d<sub>5</sub>perfluorooctanesulfonamide (d-N-EtFOSA-M), sodium perfluoro-1-[1,2,3,4-<sup>13</sup>C<sub>4</sub>]-octanesulfonate (MPFOS) and perfluoro-n-[1,2,3,4-<sup>13</sup>C<sub>4</sub>]-octanoic acid (MPFOA) 50  $\mu\text{g/ml}$  in methanol from Wellington Laboratories (Canada). Perfluoro-1-octanesulfonamide (FOSA) and perfluoro-1-[<sup>13</sup>C<sub>8</sub>]octanesulfonamide 50  $\mu\text{g mL}^{-1}$  in isopropanol were also supplied by Wellington Laboratories. Stock standards were stored at  $-18^\circ\text{C}$  in polypropylene screw vials with ethylene-propylene o-ring (Deltalab, Spain). Cap vials were also tested for the storage, with polypropylene septa, but this system is not useful for the long term storage because solvent losses by evaporation were detected. The labelled standards were used as surrogates.

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