



# Enrichment of perfluorinated alkyl substances on polyethersulfone using 1-methylpyperidine as ion-pair reagent for the clean-up of carrot and amended soil extracts



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## ABSTRACT

The development of a simple, cheap and environment friendly analytical method for the simultaneous determination of different perfluoroalkyl substances (PFASs) including seven perfluoroalkyl carboxylic acids, three perfluoroalkane sulfonic acids and perfluorooctanesulfonamide in carrot and amended soil was carried out in the present work. The method was based on focused ultrasound solid-liquid extraction followed by extract clean-up through enrichment of the target compounds on a polymeric material using an ion-pair reagent and detection by liquid chromatography-tandem mass spectrometry. The following variables affecting the clean-up step were evaluated: the nature of the polymeric material (polyethersulfone, PES, versus silicone rod), the amount of the polymeric material (from 1 to 9 mg), the ion-pair reagent (1-methylpyperidine, 1-MP, versus tetrabutylammonium salts), the concentration of the ion-pair reagent (from 5 to 50 mM) and the extraction time (from 15 min to 24 h). Optimum clean-up conditions were obtained using preconcentration on 9 mg of PES polymeric material combined with 5 mM 1-MP as ion-pair reagent for 3 h. The method was validated in terms of apparent recoveries in the range of 77–140% and 95–137% at the low concentration (50 ng g<sup>-1</sup>) and in the range of 70–136% and 79–132% at the high concentration (290 ng g<sup>-1</sup>) for amended soil and carrot, respectively, after correction with the corresponding labeled standards. Precision, as relative standard deviation, was within 2–23%, while method detection limits were 0.31–2.85 ng g<sup>-1</sup> for amended soil and 0.11–1.83 ng g<sup>-1</sup> for carrot. In the absence of a certified reference material for the target analytes in the matrices studied, inter-method comparison was carried out and the same samples were processed using two independent clean-up procedures, the one developed in the present work and a classical based on solid-phase extraction. Statistically comparable results were obtained according to the one-way analysis of variance for peel, core, leaves as well as amended soil ( $F_{\text{Calc}}=2.59, 5.06, 5.82$  and  $2.34 < F_{\text{Crit}}=7.71$ ). Finally, the method was applied for the determination of PFASs in uptake experiments where carrots were cultivated in an amended soil polluted with perfluorooctane sulfonic acid (PFOS) at 500 ng g<sup>-1</sup> level. The highest concentration was measured in the carrot leaves (669 ng g<sup>-1</sup>), while the concentrations in peel and core were at the same level (72 ng g<sup>-1</sup> and 62 ng g<sup>-1</sup> respectively), concluding that translocation of PFOS from the soil to the leaves had occurred.

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## 1. Introduction

Per- and polyfluoroalkyl substances (PFASs) include a broad range of ionic and neutral compounds. Among them, perfluoroalkyl acids (PFAAs), which take a prominent place in the literature, are a family of about 30 chemicals consisting on an

aliphatic carbon chain (typically from C4 to C16) attached to one hydrophilic end group, such as carboxylic, sulfonic, sulfinic, phosphonic or phosphinic acids. PFAAs are resistant against hydrolysis, photolysis, microbial degradation and metabolization [1]. Moreover, long chain PFAAs have been found to be highly persistent, toxic and bio-accumulative in wildlife and humans [2,3]. Due to the carbon-fluorine (C–F) covalent bond stability, one of the strongest found in organic chemistry, numerous PFASs, including PFAAs, have some unique chemical properties such as extremely high thermal and chemical stability [4,5]. Besides, due

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to their surface tension lowering properties, PFASs have been and are still widely used in many industrial applications and consumer products, including stain repellents, metal plating foams, paints, alkaline cleaners, polishes, non-stick cookware, semiconductors, photographic films, pesticide formulations, denture cleaners, electronics adhesives, food packaging, etc.

Once they enter the human body, PFASs are poorly eliminated. Longer carbon chain PFASs ( $C > 8$ ) have been reported to bioaccumulate more than the short chain ones [6–8]. The slow elimination rates of PFASs [9,10] suggest that “continued exposure could increase body burdens to levels that would result in adverse outcomes” (USEPA 2009, [http://www.epa.gov/oppt/existingchemicals/pubs/pfcs\\_action\\_plan1230\\_09.pdf](http://www.epa.gov/oppt/existingchemicals/pubs/pfcs_action_plan1230_09.pdf)), which has led the European Union, North America and the major world manufacturers, such as 3M and DuPont, to impose restrictions on the production and use of long chain PFAAs (such as perfluorooctane sulfonic acid, PFOS, and perfluorooctanoic acid, PFOA). In the year 2000 the largest global producer of PFASs, the 3M company, announced the phase out of the production of PFOS and related chemicals. Since then, new shorter-chain PFAAs (C4–C7) and their precursors are being introduced as replacements considering that the latter are less bio-accumulative or toxic in living beings [11,12].

The US Environmental Protection Agency (USEPA) recently included PFOA and linear L-PFOS in its pared-down third drinking water contaminant candidate list 3 of 32 compounds for further regulatory studies (USEPA 2011, [http://www.epa.gov/safewater/ccl/pdfs/cc13\\_docs/pre-fr\\_cc13.pdf](http://www.epa.gov/safewater/ccl/pdfs/cc13_docs/pre-fr_cc13.pdf)). The agency also included six PFAAs (perfluoro-1-butanefluorobutylsulfonate, L-PFBS, perfluoro-1-hexanesulfonate, L-PFHxS, L-PFOS, perfluoro-*n*-heptanoic acid, PFHpA, PFOA and perfluoro-*n*-nonanoic acid, PFNA) in its final list of 32 contaminants for the unregulated contaminants monitoring rule 3 (USEPA 2011, [http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/ucmr3/upload/UCMR3\\_FinalRule.pdf](http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/ucmr3/upload/UCMR3_FinalRule.pdf)). Besides, directive 2013/39/EU of the European Parliament lays down the environmental quality standards (EQSs) for a group of priority substances, where PFOS has been included.

Because of their widespread use, analytical approaches for PFAS determination in different matrices such as air [13,14], water [4,15], sediments [16,17], biota [18], food [19,20], sludge [21,22], crops [23,24] and humans [25] are continuously being developed. Alkaline digestion [26], acid digestion [27], ion-pair extraction [28], solvent extraction [19], pressurized liquid extraction (PLE) [17], focused ultrasound solid–liquid extraction (FUSLE) [29,30] and matrix solid–phase dispersion (MSPD) [18] are the most commonly used extraction techniques for the PFAS analysis in solid matrices.

Due to the lack of selectivity of the above mentioned extraction techniques, matrix effects are a challenge in the analysis of PFASs in solid samples. As reported previously in the literature, ion suppression or enhancement can occur during the analysis of PFASs by liquid chromatography tandem mass spectrometry (LC–MS/MS) [16]. Therefore, extracts require further clean-up to remove co-extracted lipids and other potential matrix components that interfere with the ionization of the target compounds. According to the literature, individual or serial weak anion exchange (WAX) SPE and Envi-Carb (dispersive graphitized carbon) are the most widely used clean-up strategies for quantification of PFASs in food [17,22,31,32]. Other sorbent mixtures such as Florisil and Envi-Carb mixture [33] and CUQAX256 SPE cartridge (mixed mode C8+quaternary amine) [34] have also been used.

For the analysis of PFASs, LC coupled to triple–quadrupole (QqQ) MS is the most common instrument [35,36] and gas chromatography (GC) is less frequently used because a derivatization step is necessary for carboxylic and sulfonic acid analysis [37,38].

Within this context, the aim of the present work was to develop an alternative cheap and easily achievable clean-up

approach for the enrichment of perfluoroalkyl carboxylic acids (PFCA), perfluoroalkane sulfonic acids (PFSA) and perfluorooctane sulfonamide (FOSA) using a polymeric material and an ion-pair reagent after the extraction by means of FUSLE from carrot and amended soil samples. For the polymeric material, silicone rod (SR) and polyethersulfone (PES) were tested and 1-methylpyrrolidine (1-MP) and tetrabutylammonium (TBA) salts were studied as ion-pair reagents. Finally, the method was applied for the determination of PFASs in uptake experiments where carrots were cultivated in a compost amended soil polluted with PFOS. To the best of our knowledge, neither sorptive extraction nor polymeric materials such as SR and/or PES have been previously applied to the clean-up extracts of PFASs from solid samples.

## 2. Experimental section

### 2.1. Chemicals and materials

A mixture of native perfluorinated standards and isotopically mass-labeled compounds at  $5 \mu\text{g mL}^{-1}$  and  $2 \mu\text{g mL}^{-1}$  in MeOH (see Table 1), respectively, were obtained from Wellington Laboratories (Guelph, Ontario, Canada). FOSA was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The abbreviation, the structure, the purity of the standards and the acidity constant (as  $pK_a$ ) values, as well as their corresponding surrogates, are included in Table 1.

MeOH (HPLC grade, 99.9%) was supplied by LabScan (Dublin, Ireland) and acetonitrile (ACN, HPLC grade, 99.9%) from Sigma Aldrich (Steinheim, Germany). Ultra-pure water was obtained using a Milli-Q water purification system ( $< 0.05 \mu\text{S/cm}$ , Milli-Q model 185, Millipore, Bedford, MA, USA).

Ion-pair reagent tetra-*n*-butylammonium bromide (TBABr,  $> 98\%$ ) was obtained from Sigma-Aldrich, whereas tetra-*n*-butylammonium hydrogen sulfate (TABHSO<sub>4</sub>,  $> 98\%$ ) and 1-MP (purity  $> 98\%$ ) were provided by Merck (Schuchardt OHG, Germany). Formic acid (HCOOH, 98–100%) was purchased from Scharlau (Barcelona, Spain).

For the mobile phase composition MeOH from Fisher Scientific (Loughborough, UK) was used. Ammonium acetate (NH<sub>4</sub>OAc,  $\geq 99\%$ ) was purchased from Sigma-Aldrich. For chromatographic separation of PFASs, Zorbax Eclipse XDB-C18 guard column (2.1 mm  $\times$  5 mm, 1.8  $\mu\text{m}$ ) followed by Zorbax Extend-C18 Rapid Resolution HT (2.1 mm  $\times$  50 mm, 1.8  $\mu\text{m}$ ) column were provided by Agilent Technologies (Palo Alto, CA, USA). Sure-Guard in-line filter (24.4 mm, 10 mm, 0.5  $\mu\text{m}$ ) obtained from VICI Jour (Schenkon, Switzerland) followed by ACE UltraCore 2.5 SuperC18 core-shell (2.1 mm  $\times$  50 mm, 2.5  $\mu\text{m}$ ) column purchased by Advanced Chromatography Technologies (Aberdeen, Scotland) were also tested for target analyte separation.

For extraction, 50-mL polypropylene conical tubes (PP, internal diameter 27.2 mm  $\times$  117.5 mm length) obtained from Deltalab (Barcelona, Spain) and a Bandelin sonifier ultrasonic cell disruptor/homogenizer (20 kHz; Bandelin Electronic, Berlin, Germany) equipped with a 3 mm titanium microtip were used. Desorption was made using a Digital Ultrasonic Cleaner (2500 mL, Axtor by Lovango, Barcelona). Fractions were evaporated in a Turbovap LV Evaporator (Zymark, Hopkinton, MA, USA) using a gentle stream of nitrogen ( $> 99.999\%$  of purity) supplied by Messer (Tarragona, Spain). After the extraction step, the supernatant was filtered through polyamide filters (0.45  $\mu\text{m}$ , 25 mm, Macherey–Nagel, Germany). GHP (hydrophilic polypropylene) microfilters (0.2  $\mu\text{m}$ , 13 mm, Pall, USA) were used to filter extracts to polypropylene plastic vials (Waters Corporation, Milford, MA, USA) before LC–MS/MS analysis.

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