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A fast and sensitive method for the simultaneous analysis of a wide range of per- and polyfluoroalkyl substances in indoor dust using on-line solid phase extraction-ultrahigh performance liquid chromatography-time-of-flight-mass spectrometry

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ABSTRACT

A fast and sensitive method for simultaneous determination of 18 traditional and 6 alternative per- and polyfluoroalkyl substances (PFASs) using solid-liquid extraction (SLE), off-line clean-up using activated carbon and on-line solid phase extraction-ultrahigh performance liquid chromatography-time-of-flight-mass spectrometry (on-line SPE-UHPLC-TOF-MS) was developed. The extraction efficiency was studied and recoveries in range the 58–114% were obtained. Extraction and injection volumes were also optimized to 2 mL and 400 μL, respectively. The method was validated by spiking dust from a vacuum cleaner bag that had been found to contain low levels of the PFASs in focus. Low method detection limits (MDLs) and method quantification limits (MQLs) in the range 0.008–0.846 ng g^{-1} and 0.027–2.820 ng g^{-1} were obtained, respectively. For most of the PFASs, the accuracies were between 70 and 125% in the range from 2 to100 ng g^{-1} dust. Intra-day and inter-day precisions were in general well below 30%. Analysis of a Standard Reference Material (SRM 2585) showed high accordance with results obtained by other laboratories. Finally, the method was applied to seven indoor dust samples, and PFAS concentrations in the range 0.02–132 ng g^{-1} were found. The highest median concentrations were observed for some of the alternative PFASs, such as 6:2-diPAP (25 ng g^{-1}), 8:2-diPAP (49 ng g^{-1}), and PFOPA (23 ng g^{-1}), illustrating the importance of inclusion of new PFASs in the analytical methods.

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are highly versatile substances that have been frequently used in industry since the 1950-60s due to their unique physic-chemical properties, such as chemical resistance, surface tension lowering properties and ability to create stable foams. Their main applications have been in inks, varnishes, waxes, lubricants, leather, paper, textiles and fluoropolymers [1,2], which are used daily by the general population. The release of PFASs from consumer products have resulted in a human exposure concern since PFASs have been found in several matrices [3–5] and indoor dust is suspected to be a relevant exposure pathway since PFASs accumulate in dust [6–9].

In 2000, a phase-out of the production of "perfluorooctanyl" compounds was announced by the main US manufacturer, 3M [10] after perfluorooctanesulfonate (PFOS) was found to be widespread in human populations and wildlife [11–13]. PFOS and its salts were also found to fulfil the criteria of the Stockholm Convention on persistent organic pollutants (POPs), and were included in the list of restricted chemicals in 2009 (Annex B) [14]. Subsequently, the US Environmental Protection Agency (US EPA) requested eight manufacturers to voluntarily eliminate their production and use of perfluorooctanoate (PFOA), its precursors and related chemicals [15]. In 2014, PFOA was included in the list of substances of very high concern in the European REACH regulation as it was concluded to be toxic for reproduction and found to be persistent, bioaccumulative and toxic (PBT) according to the criteria defined by ECHA [16].

These measures were thought to lead to decreasing concentrations of several PFASs in human blood. However, the observed trends of e.g. PFOA concentrations in blood indicate additional sources of human exposure to PFASs. One of the sources could be indirect exposure via biotransformation of commercial fluorochemicals, such as polyfluoroalkyl phosphoric acid esters (PAPs), which have been shown to biotransform to PFOA in rats [17]. The PAPs can be divided in subgroups depending of the substitution

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degree of the phosphorus group by polyfluoroalkyl chains. In this sense, if one, two or three polyfluoroalkyl chains are linked to the phosphorous atom they are called monoPAPs, diPAPs and triPAPs, respectively. PAPs have been found in indoor dust in a few studies [18,19] and information on the human exposure to these compounds is urgently needed. Further, phase-out of some compounds might also lead to introduction of other compounds with similar properties e.g. perfluoroalkyl phosphonates (PFPAs), which finally might end up in our bodies. In this sense, the development of analytical methodologies for the determination of both traditional PFASs and their alternatives in indoor dust is important.

Analysis methods of traditional and alternative PFASs in dust are usually based on a solid-liquid extraction using ultrasonication (USE), clean-up by solid phase extraction using either C_{18}, weak anion exchange (WAX) or ENVI-Carb sorbents and, finally, an evaporation step before analysis by liquid chromatography coupled to a single or triple quadrupole mass spectrometer (LC-Q-MS or LC-QqQ-MS/MS, respectively) [18–23]. Those methods include time-consuming sample preparation steps that imply extensive sample manipulation, increasing analysis time and the risk of sample losses and contamination. Furthermore, the use of low resolution MS analyzers working in selected ion monitoring (SIM) or multiple recording monitoring (MRM) mode give restricted identification possibilities. High resolution MS offers the possibility of screening for a much larger number of compounds in full scan acquisition and facilitate retrospective analysis of PFASs that were not considered in the first place. In general, a drawback when using HRMS is the shorter dynamic range for quantification compared to triple quadrupoles (TQ) [24,25]. Although, modern HRMS overcome this issue and in terms of sensitivity they are comparable to triple quadrupole mass spectrometers [24]. Thus, faster methods that increase sample throughput and allow restropective analysis of non-targeted contaminats are needed for future PFASs analyses.

The aim of this work is to develop and validate a fast and sensitive analytical method for the simultaneous analysis of a large number of traditional PFASs representative to different compound groups, e.g. perfluoroalkyl carboxylates (PFCAs), perfluoroalkyl sulfonates (PFSAs), perfluoroalkyl sulfonamides (FOSAs) and perfluoroalkyl sulfonamido ethanols (FOSEs) as well as several alternative PFASs such as PAPs and PFPAs, in indoor dust. To accomplish this, a simple and fast SLE extraction was optimized avoiding time consuming evaporation steps. Extraction and injection volumes were optimized in order to increase method sensitivity. Extraction efficiency was also tested. To show the applicability of the method, PFASs were determined in selected indoor dust samples from Norway.

2. Material and methods

2.1. Chemicals and apparatus

Standard solutions of the individual compounds, perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS), prefluoroheptanesulfonate (PFHpS), PFOS, perfluorodecanesulfonate (PFDS), *N*-methylperfluorooctanesulfonamide (MeFOSA), *N*-ethylperfluorooctanesulfonamide (EtFOSA), *N*-methylperfluorooctanesulfonamido ethanol (MeFOSE), *N*-ethylperfluorooctanesulfonamido ethanol (EtFOSE), 1H, 1H, 2H, 2H-polyfluorooctylphosphate (6:2-monoPAP), 1H, 1H, 2H, 2H-polyfluorodecylphosphate (8:2-monoPAP), bis(1H, 1H, 2H, 2H-polyfluorooctyl)phosphate (6:2-diPAP), bis(1H, 1H, 2H, 2H-polyfluorodecyl)phosphate (8:2-diPAP), perfluorooctylphosphoric acid (PFOPA), perfluorodecylphosphoric acid (PFDPA), and surrogate internal standards (IS), perfluoro[1,2-$^{13}C_2$]hexanoic acid (MPFHxA), perfluoro[1,2,3,4-$^{13}C_4$]octanoic acid (MPFOA), perfluoro[1,2,3,4,5-$^{13}C_4$]nonanoic acid (MPFNA), perfluoro[1,2-$^{13}C_2$]decanoic acid (MPFDA), perfluoro[1,2-$^{13}C_2$]undecanoic acid (MPFUnDA), perfluoro[1,2-$^{13}C_2$]dodecanoic acid (MPFDoDA), perfluorohexane[$^{18}O_2$]sulfonate (MPFHxS), perfluorooctane[1,2,3,4-$^{13}C_4$]sulfonate (MPFOS), *N*-methyl-d_3-perfluorooctanelsulfonamide (D-MeFOSA), *N*-methyl-d_3-perfluorooctanesulfonamido ethan-d_4-ol (D-MeFOSE), *N*-ethyl-d_5-perfluorooctanesulfonamido ethan-d_4-ol (D-EtFOSE), 1H, 1H, 2H, 2H-[1,2-$^{13}C_2$]polyfluorooctylphosphate (M2-6:2-monoPAP), 1H, 1H, 2H, 2H-[1,2-$^{13}C_2$]polyfluorodecylphosphate (M2-8:2-monoPAP), bis(1H, 1H, 2H, 2H-[1,2-$^{13}C_2$]polyfluorooctyl)phosphate (M4-6:2-diPAP), bis(1H, 1H, 2H, 2H-[1,2-$^{13}C_2$]polyfluorodecyl)phosphate (M4-8:2-diPAP) were obtained from Wellington Laboratories (Ontario, Canada), all of them in concentrations of 50 μg mL^{-1} in methanol (MeOH). Stock solutions of the standards and IS were prepared separately, at concentrations of 25, 10 and 2,5 pg μL^{-1} and stored at −20 °C. MeOH, acetonitrile (AcN) and water (H_2O), all of them LC–MS grade, were purchased from J.T. Baker (Deventer, Netherlands). Activated carbon (AX-21) was obtained from Anderson Development Company (MI, USA). An indoor dust Standard Reference Material (SRM 2585) was purchased from the National Institute of Standards and Technology (Gaithersburg, MD, United States). Wide mouth polypropylene (PP) bottles, 30 and 500 mL, were obtained from Thermo-Scientific (Rochester, NY, United States), 25 mL PP syringe filters 0.45 μm pore size and a 510–2620 test sieve with beaded frame, stainless steel, reduced nominal height (diameter: 300 mm, nominal height: 30 mm, mesh diameter: 500 μm) were provided by VWR International (Radnor, PA, United States). Plastic syringes, 2 mL, were purchased from BD Plastipak (Madrid, Spain).

An AG204 analytical balance from Mettler-Toledo (Greifensee, Switzerland), was used for weighing purposes, while a 2510 Branson ultrasonic bath (Danbury, CT, United States) and a Heidolph Reax-top shaker (Schwabach, Germany) were used for ultrasonication and shaking purposes, respectively.

2.2. Collection of dust samples

Dust samples were collected from vacuum cleaners bags provided by colleagues from the Norwegian Institute of Public Health (NIPH). In each house, the vacuum cleaner bag was removed from the vacuum cleaner, wrapped in aluminum foil and placed in a plastic bag. Then, the sample was transported to the laboratory where the dust was sieved using a 500 μm mesh sieve and stored in 500 mL PP bottles at room temperature until analysis.

2.3. Dust extraction

Dust (0.10 g) was placed in a 30 mL wide mouth PP bottle and 40 μL of a 25 pg μL^{-1} internal standard (IS) working solution in MeOH was added. Bottles were kept open for 10 min, in order to allow the MeOH to evaporate. The bottles were then closed and shaken. After that, 2 mL of MeOH was added, the bottles were tightly closed and then vigorously shaken by hand for 1 min and by whirl mixer for another 1 min. The mixture was filtered to a 2 mL autosampler vial using a 2 mL plastic syringe coupled to a 0.45 μm PP filter. Then, 500 μL of the extract was transferred to a 2 mL Eppendorf tube containing 0.25 mg of activated carbon and mixed using a whirl mixer. Afterwards, the mixture was centrifuged for 5 min at 14,000 rpm (20,817*g*) and 200 μL of the extract was