Development of fast and efficient pretreatment method for improving detection efficiency of perfluoroalkyl acid precursors

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Introduction

Per- and polyfluoroalkyl substances (PFASs) are widely used compounds in the industrial and commercial applications. Among them, perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) are two typical perfluorinated compounds that have been produced to date and are the most widely used and detected at high frequency in environmental samples. Due to the gradual recognition of various toxicities, a global phase out initiative was taken and PFOS was included in Appendix B of the Stockholm Convention. PFOA has also been proposed for inclusion in the convention and will be phased out. With the ban of PFOS and PFOA, alternatives were developed. According to reports in the literature, at least 4,000 PFAS are currently produced and used in the world.[1] Partially-fluorinated compounds are also commercially available and reported, so far little is known about these precursors. Moreover, the list of available standards is far less than commercially available PFASs. Furthermore, due to the complexity of the structure and properties of PFASs, detection in samples is challenging. The most common method currently used is EPA-537 method (includes only 20-30 known PFASs). However, such test results do not provide a complete and accurate reflection of PFAS contamination. The target list of available methodologies is far from commercially available PFAS.[2] Precursors can be converted into perfluoroalkyl sulfonates (PFSAs) and perfluoroalkyl carboxylates (PFCAs) with different chain lengths in biological or physicochemical conditions. Therefore, besides legacy PFASs evaluation of precursors is also necessary. In previous literature, to fully evaluate the concentration levels of perfluoroalkyl acids (PFAAs) precursors, the total oxidizable precursor (TOP) assay method was developed and widely accepted.[3] TOP assay developed in 2012 is a powerful tool to detect the concentration of known PFAAs and difficult to measure PFASs. The principle of the method is addition of excess potassium persulfate to the sample to be tested and pretreatment under strong alkaline conditions and heating environment. Precursors were converted into different PFCAs in the presence of hydroxyl radical.[4] Finally, ultra-performance liquid chromatography mass spectrometry (UPLC-MS/MS) was used to detect PFCAs in samples before and after oxidation. Experiments have shown that the content of PFCAs is significantly increased after oxidation that represents unidentified precursors.[4] TOP assay is a commonly accepted method however; the pretreatment time of the sample to be tested is as long as 6 hours or more. Thus, in the present situation, this widely accepted method is simplified and the pretreatment time is significantly reduced by replacing heat activated persulfate oxidation with ultraviolet (UV)-activated persulfate oxidation. Furthermore, the updated method was successfully applied to the commercial products (the ultimate source of different PFASs to the environment).

Material and Method

Materials

The materials and chemicals used to perform UV/persulfate treatment include potassium persulfate ($K_2S_2O_8$, 97%; Sinopharm Chemical Reagents), methanol (MeOH), acetone, n-hexan (HPLC grade by Avantor performance materials) and NaOH. The laboratory grade ultrapure water (UPW, 18 MΩ·cm, Milipore, MA, USA) was used for dilution and rinsing purpose. The stock solutions of the 6:2 fluorotelomer sulfonate (FTS) was prepared in UPW. The 8:2 FTS and sulfonamides were purchased from the wellington laboratories (Guelph, ON, Canada). The other material includes: quartz tubes, acetic acid reagent (HPLC grade), ammonia solution (25% in H_2O), P-WAX cartridges (200 mg/6ml, Waters, MA), adjustable micropipettes (100-1000 uL, 20-200ul) and microfiber filter (47mm, Whatman, Kent, UK).

Method development

For UV-activated persulfate treatment, the photochemical reaction was performed for continuous five hours in the photoreactor (RPR200, Southern New England Ultraviolet) equipped with 16 lamps (253.7 nm). The measured (UV-B irradiometer) emission intensity of each lamp was 8.0 mW cm^{-2} to ensure uniform photo intensity (3.8 µE $L^{-1}s^{-1}$) in the chamber. The reactor was operated 5 min in advance and then the sample was placed in the center of the reactor, and rotated by using turn plate (10 rpm) and uniform photoflux was ensured throughout the photolytic reaction. The tubes having a maximum capacity of upto 50 mL were made up of quartz. All the tubes were capped throughout process except during sampling. The sample was taken both before and after oxidation to observe the increase in concentration.

For the method development, the representative fluorotelomer precursors (C8 and C6) and sulfonamide (FOSA) were selected. The conditions adopted were similar to the previous developed method (60mM of $K_2S_2O_8$ and pH above 12).[4] The selected concentration range (50 ng mL^{-1}-100 ng mL^{-1}) was representative over the range of

environmental samples and also comparable to the previous method.[4] The 6:2 FTS stock solution (100 ng mL^{-1}) was prepared in UPW. The 8:2 FTS and FOSA stock solutions were purchased from the wellington laboratories. Therefore, an aliquot was separated and MeOH was evaporated (by gentle nitrogen stream). The prepared solutions (60 ng mL^{-1}) were amended with the 60 mM of $K_2S_2O_8$. The pH was maintained at 12 with the 10N NaOH solution (150mM). Before UV/persulfate treatment the aliquot of the sample was separated in the vial to get the initial concentration of spiked precursor. The quartz tubes were placed in the reactor and the reaction was followed for continuous two hours; an aliquot of sample was separated in a vial after each half an hour. To make sure the repeatability, all the samples were tested in duplicates. After oxidation the pretreatment procedure was followed prior to final analysis on UPLC-MS/MS. Samples were purified by cartridges, which were activated and preconditioned with 4 mL of 0.5% ammonia methanol (NH_4OH in methanol, 4 mL), MeOH and UPW respectively. The sample was loaded and drawn through the cartridge at 1 mL min^{-1}. Columns were washed with 4 mL of sodium acetate aqueous solution (25 mM) followed by drying step for 1 h. The sample was eluted in 15 mL centrifuge tube with 4 mL of methanol followed by 4 mL of 0.5% NH_4OH in MeOH. The volume of the eluted sample was approximately 7-8 mL. The extract was concentrated by nitrogen stream and final volume of extract was 0.5ml. The sample was filtered by 0.22 µm filter and stored at -18ºC prior to final analysis. In order to ensure the stability of PFCAs and PFSAs, the PFOA and PFOS was spiked in the UPW (100 ng mL^{-1}), and amended with 60 mM of $K_2S_2O_8$. Further, the UV/treatment was followed and the concentration was observed.

Method validation

To validate the method and make sure the applicability in real scenarios, the Vatten fluorocarbon surfactant (VF-368) sample was selected and the wastewater was simulated in the laboratory. The selected sample was tested at different dilutions and also at different pH. The final PFCAs concentration was quantifies by UPLC-MS/MS. The selected samples were also tested by heat-activated persulfate and the results were compared to evaluate the efficiency of updated method.

Instrumental analysis, Quality assurance and quality control (QA/QC) and corresponding detection limits

Target PFASs were quantified on LC-MS (UltiMate™ 3000 ultra-performance liquid chromatography (Dionex, USA) coupled to AB Sciex triple quadrupole mass spectrometry API 3200) using XBridge C18, waters column (3×150 mm, 3.5 µm from waters). The corresponding mobile phase (A: 10 mM ammonium acetate solution, B: methanol) at 0.3mL min^{-1} flow rate. Following gradient program was followed: Initially 40% B stayed for 1min, increased continuously at 26 min to 90% B and stayed for 7 min finally at 33.1 min decreased to 40% B and maintained for 5 min. The corresponding limit of detection (LODs) and limit of quantification (LOQs) were also calculated. The LOD was three times of signal-to-noise ratio and the LOQ (0.03-1.79 ng mL^{-1}) was 10 times of signal-to-noise ratio. All the samples were prepared in duplicates and the relative standard deviation was also calculated. Calculated RSD of duplicates was >10%. The blanks were also below the LOQ. To ensure the efficiency of the pretreatment method the UPW was spiked with native standards and surrogate recovery was calculated. The calculated surrogate standard recoveries were between 70-130%.

Results and Discussion

Molar yield of PFCAs from precursors

Quantitative conversion of representative precursors was observed in aqueous solution. The control sample was consisting of PFOA and PFOS, depicted that throughout the reaction the molar concentration is stable.[5] In other words, the original PFCAs were conserved. The observed results can be supported by TOP assay that the oxidation conditions have no effect on PFOS and PFOA.[4] Oxidation of the aqueous solution of precursors (6:2 FTS, 8:2 FTS and FOSA), each generated a suit of carboxylates of different chain length. The total PFCAs observed after complete oxidation of corresponding precursor accounted for 105% ± 6.3% (*n*=2) of the initial concentration of 8:2 FTS. The observed oxidation products for the 6:2 FTS were 100.9% ± 5.3% (*n*=2). Whereas the PFCAs generated by the oxidation of sulfonamide-containing precursors were 103% ± 6.2%. (*n*=2). The molar yield of PFCAs from the precursors is presented in Table 1.

Table 1. Molar yield of carboxylates from precursors oxidized in UV-activated persulfate system

Selected precursor	ΔPFBA/ [precursor]$_o$	ΔPFPeA/ [precursor]$_o$	ΔPFHxA/ [precursor]$_o$	ΔPFHpA/ [precursor]$_o$	ΔPFOA/ [precursor]$_o$	ΔPFNA/ [precursor]$_o$	Total observed PFCAs
Fluorotelomer-containing precursors							
6:2 FTS	39.9%	40.2% ± 5.4%	15.7%	5.1% ± 0.3%			100.9% ± 5.3%
8:2 FTS	31.7% ± 1.9%	40.5% ± 0.5%	3.6% ± 0.6%	6.0% ± 1.3%	21.5% ± 2.3%	1.75%	105.1% ± 6.4%
Sulfonamide-containing precursors							
FOSA	12.6% ± 0.5%	11.0% ± 2.8%	0.9%	2.8%	76.5% ± 2.9 %		103.7% ± 6.2 %

Behavior of fluorotelomer and sulfonamide containing precursors

At the 60 mM concentration of persulfate, the 8:2 FTS showed the molar yield of 21.5% ± 2.2% for PFOA. The results were comparable to the TOP assay (PFOA: 21% ± 2%). However in the UV-activated persulfate treatment the observed oxidation product for perfluorbutanoic acid (PFBA: 31.7 % ± 1.89%) and perfluoropentanoic acid (PFPeA: 40% ± 0.45%) were comparatively greater than the TOP assay (11% and 12% respectively).[4] The initial spiked 8:2 FTS was completely disappeared in the first 30 min of the reaction and within one hour of the treatment the equimolar quantities of PFCAs were observed (Table 1). Concerning 6:2 FTS, the observed concentration was relatively higher for short-chain PFCAs (PFBA: 39.9% and PFPeA: 40.1%). The 6:2 FTS was transformed to perfluorohexanoic acid (PFHxA: 15.7%) whereas observed increase in the perfluoroheptanoic acid (PFHpA) was negligible (5.1%). The results were also comparable to the TOP assay, however, the UV-activated persulfate treatment is fast and reaction was finished in the one hour. Also the observed PFCAs profile showed that most of the 6:2 FTS (100.9% ± 5.3) was recovered as compared to TOP assay (72%).[4] Both, 6:2 FTS and 8:2 FTS yielded the identical distribution of PFCAs products. Extrapolating the depicted molar yield to remaining fluorotelomer precursors, it is predictable that mixture of PFCAs can be generated with chain length of C4 to C (n+1) by oxidation of n: 2 flurortelomer-containing precursors.

The observed PFCAs profile for FOSA was irrespective of the TOP assy. In UV-activated persulfate system one-to-one conversion was not followed. The dominant observed PFCAs was PFOA (76.55 ± 2.9%). However other PFCAs (26.7%) were also observed (Table 1). The initial spiked concentration of FOSA was completely vanished in the first 30 minutes of reaction and maximum by-products were recovered in 1 h of the treatment. The molar yield of PFCAs (103.2% ± 6.2%) was comparable to TOP assay (97.3% ± 3%), however, the observed homologue profile of PFCAs was irrespective of TOP assay. The quantified concentration of each PFCAs by-product from precursors is shown in Figure 1 a, b and c.

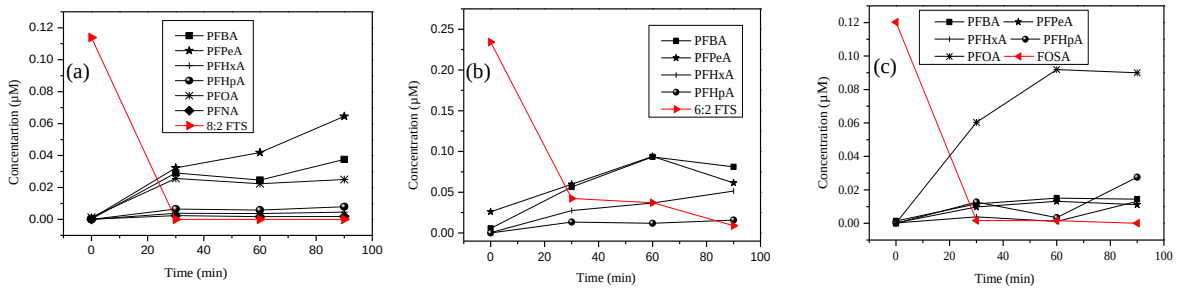

Figure 1. The molar concentration of generated PFCAs from 8:2 FTS (a); 6:2 FTS (b); and FOSA (c)

Method Validation

The selected sample was diluted in UPW at three different dilutions and increase in PFCAs (C4-C10) was noticed. First the FS sample was diluted 10,000 times with UPW and amended with 60 mM of $K_2S_2O_8$. The molar ratio of persulfate to the precursor was 400:1 and the initial pH of the solution was 10. The same surfactant (VF-368) was diluted 40,000 times with UPW, same amount of persulfate was added however, the pH of the solution was similar to the TOP assay (i.e. 12). The molar ratio of persulfate to perfluoroalkyl precursor was 16000:1. In another quartz tube, the VF-368 was diluted 200,000 times with UPW amended with 60 mM $K_2S_2O_8$. The molar ratio of persulfate to precursors was 80,000:1, and the initial pH of the solution was 2. After preparation of the simulated wastewater the quartz tube was placed in UV system with a wavelength of 254 nm for 1 h. The aliquot of sample was separated and the initial concentration of the sample was noted. Then the simulated wastewater was kept for

1 h in the UV system. The samples were pretreated and analyzed on the UPLC/MS-MS for PFCAs (C4-C10). The 6:2 FTS, 8:2 FTS were not detected in the sample collected at 30 mins. However, the FOSA was quantified that was significantly reduced in one hour of the treatment. The observed increase in the PFCAs concentration in VF-368 at different dilutions is presented in Figure 2. Furthermore, FS was tested at different pH and the observed PFCAs profile showed that the UV-activated persulfate treatment is not pH dependent. The basic conditions are favorable, however the reaction is not pH dependent. A significant increase in PFCAs was observed within 1 hour, the initial quantified PFCAs was 950 mg L^{-1}, which is increased to 26000 mg L^{-1} after oxidation. These results are comparable to TOP assay generated PFCAs (20970 mg L^{-1}) in the same FS.[6] However, the sample processing method requires less time, consumes less chemicals and detection efficiency is precise.

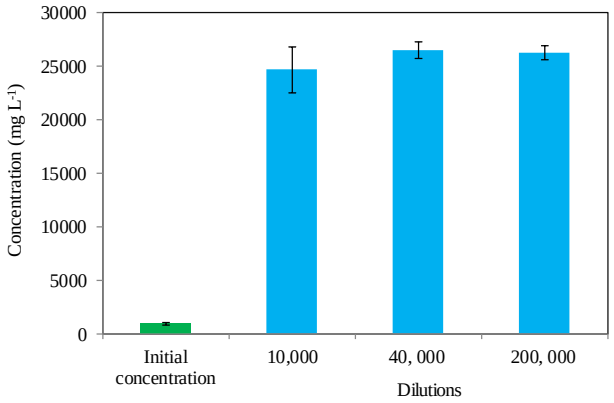

Figure 2. The quantified concentration in VF-368 at different dilutions

Conclusion

Simple targeted screening approach is insufficient to quantify the long list of PFASs and its precursors. The present method simplifies the quantification of precursors in UV-activated persulfate system.
The present method has several advantages; the whole pretreatment process does not exceed 1 h thus less pretreatment time, simple operation and no need to maintain the strong alkaline conditions. The method can obtain a more accurate precursor concentration; compared with the commercial TOP assay.
This method simplifies the pretreatment and can help the research to quantify the precursors from the commercial products.

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