

Application of Total Oxidizable Precursor (TOP) assay for screening of per and polyfluoroalkyl substances (PFAS) from textile finishing agents available on Chinese market

Mumtaz M¹, Bao YX¹, Li WC², Huang J¹

¹School of Environment, POPs Research Center, Tsinghua University, Beijing, China, 100084 (mmw15@mails.tsinghua.edu.cn)

²CSD IDEA (Beijing) Environment Test & Analysis Co., Ltd. Beijing, China, 100192

Introduction

Long list of per- and polyfluoroalkyl substances (PFAS) (>3000) are available in the market including both long short and long carbon chain. Oleophobic and hydrophobic nature of PFAS make them to be used in wide range of commercial and industrial applications. Side chain fluorinated polymers are being used in numerous consumer products since 1950's such as in textiles to impart effective water, dirt and oil repellence to fabric. Several concerns aroused regarding toxicity of these compounds. And currently available methodologies are limited to analyze discrete list of 20 to 30 compounds for instance EPA 537 method. This method is also applicable to complex matrices with some modifications but the target list of available methodologies is far from commercially available PFAS. Total Oxidizable Precursor (TOP) assay developed in 2012 is a powerful tool to detect the concentration of known perfluoroalkyl acids (PFAAs) and difficult to measure PFAS. Chemically oxidative conditions are developed to convert precursors in the sample to perfluorocarboxylic acids (PFCAs). The difference in concentration of PFCAs in pre and post oxidized samples give the estimates of unidentified precursors. Though TOP assay give conservative estimate of PFASs but still it is widely used and adopted to understand the content of precursors. Recently in 2016, TOP assay has been adopted by Australia (Queensland) for the certification of aqueous firefighting foams and affected environmental media. And TOP assay is making progress from lab established method to well accepted analytical method. Previously this approach has been used for water, soil and the complex matrices such as firefighting foams^{1,2,3}. An attempt has also been made to apply this method for fabric and paper^[4]. China is among the largest apparel and textile exporter in world, textile industry is expanding and finishes used in this sector are contaminating the environment. Companies are using these PFASs as repellent in their products. Usually, textile finishing agents (TFA) are copolymers having side chain fluoropolymers (e.g methyl acrylate or perfluoroalkyl acrylate). But exact chemicals identification and trade percentages are secrete. It is also challenging to get such facts from the labels on products and also from the vendors. Anyhow the secret information about product and related health concerns is driving the attention of scientist. In the current scenario TOP assay is applied for the first time on TFA available in Chinese market.

Material and Method

Sampling strategy

Total 12 TFA samples were collected by following two approaches; 1) collected from the Chinese manufacturer (industries) particularly these samples were electrochemical fluorination based (ECF); 2) and telomerization based samples purchased from the online trading platform (www.alibaba.com).

Materials

The mass labeled internal standard obtained from Wellington Laboratories (Guelph, ON, Canada) and contained M4-PFBA, M5-PFPeA, M2-PFHxA, M4-PFHpA, M2-PFOA, M4-PFOA, M5-PFNA, M2-PFDA, M2-PFUnA, M2-PFDoA, M3-PFBS, M4-PFHxS and M4-PFOS. M2-PFOA was used as injection standard. HPLC grade methanol, acetone and n-hexane were purchased from Duksan (Kyoungkido, Korea). The other material includes: Sampling bottles (1L, PP), ultrapure water (18 MΩ·cm, Millipore, MA, USA), acetic acid reagent (HPLC grade), ammonia

solution (25% in H₂O), Oasis HLB cartridges (200 mg/6ml, Waters, MA), adjustable micropipettes (100-1000 μ L, 20-200 μ l) and microfiber filter (47mm, Whatman, Kent, UK).

Methodology

TOP assay

Application of TOP assay to complex matrices is challenging. When dealing with complex mixture the exhaustion of hydroxyl radical may happen (due to competition by other oxidizing substances). To ensure the complete oxidation of precursors the dilution was adjusted and best results were obtained at 1000 times dilution. The TFA was diluted 1000 times in water and oxidation was achieved by adding standard dose of potassium persulfate (60mM; 0.81g) and 10N NaOH (0.5ml)¹⁻⁵. The PH was maintained above 12. The samples were oxidized in the 50ml centrifuge tube at 85°C for 6h. To avoid the volatilization of FTOH at high temp the centrifuge tube was tightened and headspace was less than 1ml. Before final analysis samples were brought to room temperature. The sample was than neutralized and further PH was adjusted to 5-7 before SPE.

Pretreatment

For the screening of fluortelomer alcohols (FTOH) 0.5 ml of sample was diluted in methanol. The sample was ultrasonically extracted for 20min and then centrifuges at 3500rpm to get clear supernatant. This supernatant was filtered through 0.22 μ m column and analyzed on gas chromatography mass spectrometry (GCMS) for FTOH determination. For the analysis of PFCAs and perfluorosulphonic acids (PFSAs) sample was dissolved in water followed by solid phase extraction (SPE). The SPE cartridges were preconditioned with 4ml of ammonium methanol (25% ammonium hydroxide in methanol), methanol and ultrapure water respectively. The sample was loaded and passed through the column at rate of 1 drop /second. After loading the sample the cartridges were washed with sodium acetate buffer (25mM, PH=4) and dried for 30 minutes. The target PFASs were eluted with 4ml of methanol and 2ml of ammonium hydroxide in methanol (0.5%) respectively. The extract was concentrated by nitrogen steam evaporation and final volume of extract was 0.5ml after injection of selling spike. Finally sample was filtered through 0.22 μ m filter and stored in polypropylene vial (0.5ml volume). The prepared samples were stored at -18°C until final analysis.

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

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 \times 150 mm, 3.5 μ m from waters). 10 μ L of sample was injected by using mobile phase (A: 10 mM ammonium acetate solution, B: methanol) at 0.3ml/min flow rate. Following gradient program was followed: Initially 40 % B stayed for 1min, increased continuously at 26min to 90% B and stayed for 7min finally at 33.1 min decreased to 40 % B and maintained for 5min. Quantification of FTOH in negative chemical ionization mode was conducted on GCMS (QP-2010, Shimazu, Japan). J & W Scientific, DB-Wax column (0.5 μ m thickness, 30m \times 0.25mm id) was used. GC system inlet, MS interface and ion source temperature was maintained at 200°C, 230°C and 210°C respectively. The following temperature program was followed for the GC column: for 1 min temperature was maintained at 60°C, increased to 75°C at 5°C min⁻¹, and raised to 220 °C at 20°C min⁻¹ and detained for 6min. Helium was used as a carrier gas at maintained flow rate (0.8ml min⁻¹).

Quality assurance and quality control procedures were strictly followed. Throughout the experimental procedure glass ware was completely avoided and all the plastic ware was rinsed with acetone, n-hexane and methanol respectively. The relative standard deviation of replicate samples was below 20%. To calculate the recovery the real samples were spiked with the native standards. For ionic compounds and volatile compounds selected samples were spiked at 200 ppb and recovery was determined. The calculated recoveries of spiked samples were between 70-130%. To ensure the quality internal standard was also used and the recovery of mass labeled

internal standards in pre and post oxidized samples is between 30-150%. Blanks were below the limit of quantification.

Results and Discussion

Observed increase in PFASs upon TOP assay

In the twelve samples collected from Chinese market the PFCAs (C4-C6) were detected in all of the samples with 100% detection frequency. The mean detected concentration of PFCAs in pre TOP samples was ranged between 0.0036 mg/L perfluoroundecanoic acid (PFUndA) mg/L to 1.5 mg/L perfluorohexanoic acid (PFHxA). Regarding PFASs the perfluorohexane sulfonic acid (PHHxS) is the dominant compound with the mean detected concentration of 631 mg/L. The change in the concentration has been observed in post oxidized TFA. The total concentration ranged from 2.74-117.05mg/L. PFHxA was the predominant PFCAs with mean concentration of 6319.6mg/L followed by perfluoropentanoic acid (PFPeA; 2018.6 mg/L) and perfluorooctanoic acid (PFOA; 1630mg/L). The obvious increase is observed in pre and post TOP experiment. The mean increase of Δ PFHxA was 6301.2 mg/L followed Δ PFPeA (2016.12 mg/L) and Δ PFOA (1627.91 mg/L).

The results are in line with the information provided by vendors that most of formulations are C6 based. Detected high concentration of PFHxA may be related to presence of fluortelomer precursors. Upon oxidation fluortelomer precursors produce mixture of PFCAs (C4-C9). On the other hand detected high concentration of PFOA in post oxidized samples still cannot be avoided. This increase in concentration of PFOA could be related to presence of C8 or higher than C8 fluorocarbons precursors¹. The increase in concentration of pre and post TOP assay is presented in (Fig 1).

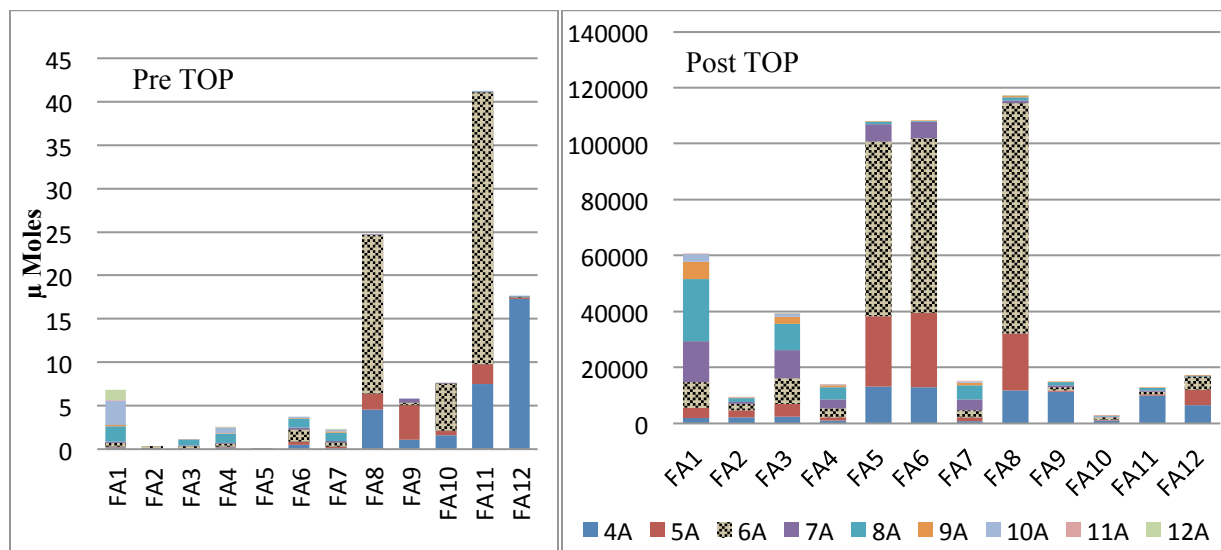


Fig 1. The observed increase in concentration of PFCAs in pre and post TOP analysis on molar basis

Estimation of total PFAS and unidentified precursors upon TOP assay

The formation of C_n acids upon TOP assay corresponds to the total concentration of precursors¹. Among the tested samples FTOH were the predominant precursors in telomerization based samples. The concentration was ranged from 77.8 mg/L to 13081mg/L for 6:2FTOH and 8:2FTOH respectively. As the FTOH is the dominant detected

precursor in the current situation and to ensure the complete oxidation of FTOH precursors 25ppb of 4:2FTOH, 6:2FTOH, 8:2FTOH and 10:2FTOH was spiked in the water. The sample was oxidized under same conditions and all of the FTOH were converted into equimolar quantities of PFCAs (C4-C9).

In current scenario detected molar concentration of PFCAs in post TOP assay cannot be attributed to only measured FTOH precursors. TOP assay revealed the presence of several unidentified precursors (unidentified precursors means concentration of PFCAs generated upon oxidative treatment step). The increase might be due to presence of fluortelomer sulphonates in telomere based samples or sulphonamide containing precursors in ECF based samples. Fig 2 shows that 70% oxidation products correspond to precursors that were not included in the current detection list. The result are similar to the some previously published reports particularly for firefighting foam showing that concentration of unidentified compounds cannot be ignored⁵. So using TOP method would be a wise choice for complex formulations.

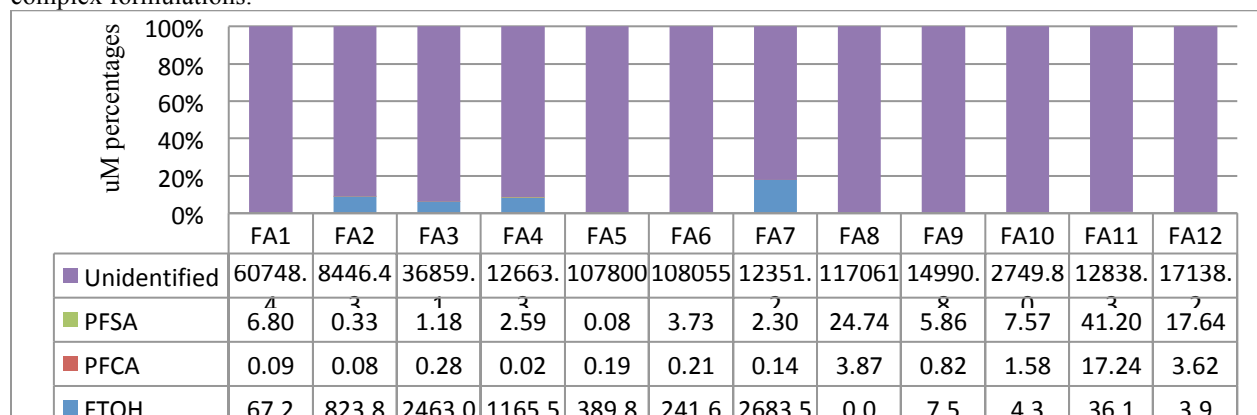


Fig 2. Molar fraction of total PFASs in textile finishing agent

Conclusion

The predominant detected compound in selected formulations is PFHxA.

Using extensive analytical techniques (LCMS/MS, GCMS) can determine only small percentage of PFAS present in complex textile formulations.

TOP assay can give the picture of unidentified PFAS. Though, it is conservative estimate but still a wise choice for TFA.

Acknowledgement

This research is financially supported by Major Science and Technology Program for Water Pollution Control and Treatment in China (No. 2017ZX07202004) and National Natural Science Fund of China (No.21477060).

References

1. Houtz EF, Sedlak DL. (2012); *Environ. Sci.Technol*, 46; 9342-9349
2. Houtz EF, Higgins CP, Field JA, etal. (2013); *Environ. Sci.Technol*, 47; 8187-819
3. Houtz EF, Sutton R, Park JS , etal. (2016); *Water Research*, 95; 142-149
4. Robel AE, Marshall K, Dickinson M, etal. (2017); *Environ. Sci.Technol*, 51(16);9022-9032.
5. EnviroMail™ 117 - PFAS Testing in Brisbane and TOP Assay Challenges and Developments <https://www.alsglobal.com/us/myals/news/2017/11/enviromail-117-pfas-testing-in-brisbane-and-top-assay-challenges-and-developments>