

# Screening and Determination of PFASs in Textile Finishing Agents on Chinese Market

Kong LX<sup>1</sup>, Li WC<sup>1</sup>, Huang J<sup>2,\*</sup>

<sup>1</sup> CSD IDEA (Beijing) Environment Test & Analysis Co., Ltd. Beijing, China, 100192

<sup>2</sup> School of Environment, POPs Research Center, Tsinghua University, Beijing, China, 100084

## Introduction

Per- and polyfluoroalkyl substances (PFASs) have been applied in commercial textile finishing agents to impart water, oil and stain repellence. The potential risk caused by the PFASs has attracted great concerns in recent years, especially for those long chain PFASs. For example, U.S. EPA has organized the PFOA stewardship program to reduce use and emission of PFOA and precursor chemicals from emissions and products by 2015 [1]. There are some investigations about the occurrence of PFASs in outdoor apparel [2], aquatic life and human blood [3,4]. However, very few data about the characterization of PFASs in commercial textile finishing agents is now available. In the present study, the Kendrick Mass Defect (KMD) plot was employed for the screening of PFASs in 12 commercial textile finishing agents collected from Chinese market, followed by the quantitative determination by LC-MS/MS. Besides, the cluster analysis and principal component analysis (PCA) were utilized for data exploration

## Materials and methods

A total of 12 commercial textile finishing agents were collected from Chinese markets in 2016. For rapid screening and fluorotelomer alcohol (4:2 FTOH, 6:2 FTOH, 8:2 FTOH and 10:2 FTOH), 1 mL sample was ultrasonic extracted with 9 mL methanol. The supernatant obtained after centrifugation was pre-filtered (0.2 µm) before injection. The 24 target PFASs (see Table 1) were extracted by WAX cartridge (Agela, 150 mg, 6 ml) as described elsewhere [5] with some modifications. Briefly, 1 mL sample spiked with isotope-labeled internal standard was ultra-sonic extracted by 9 mL methanol (two times). After centrifugation, combine the supernatants and add 200 ml water. The SPE cartridge was preconditioned with 4 mL of 25% ammonium hydroxide in methanol, methanol and Millipore water, then loaded with extracts. The cartridge was washed by 4 mL of 25 mM sodium acetate buffer (pH = 4) and dried under vacuum. Elution was performed using 4 mL of methanol and 4 mL of 0.1% ammonium hydroxide in methanol, respectively.

## Instrumental analysis

UltiMate™ 3000 ultra-performance liquid chromatography (Dionex, USA) coupled to time-of-flight mass spectrometry (Bruker micrOTOF, Bremen, Germany) was used for screening analysis. UltiMate™ 3000 ultra-performance liquid chromatography (Dionex, USA) coupled to AB Sciex triple quadrupole mass spectrometry API 3200 was used for the quantitative determination of 24 target PFASs. An aliquot of 10 µL extract was injected into a Waters XBridge C18 column (3.5 µm, 3.0 × 150 mm), with 10 mM ammonium acetate aqueous solution (solvent A) and methanol (solvent B) as the mobile phases at a flow rate of 0.3 mL min<sup>-1</sup>. A gradient program was given as follows: 40% B at 0 min held for 1 min, continuously increased to 90% B at 26 min, held for 7 min, and then reverted to 40% B at 33.1 min held for 5 min. FTOHs were quantified on GC/MS(QP-2010, Shimadzu, Japan) in NCI mode by using DB-Wax column (30 m × 0.25 mm id, 0.25 µm film thickness, J&W Scientific). Temperatures of GC system inlet, ion source and MS interface were set at 200, 210 and 230 °C, respectively. The column temperature was programmed as follows: held at 60 °C for 1 min, and then ramped

up at 5 °C min<sup>-1</sup> to 75 °C, then at 20 °C min<sup>-1</sup> to 220 °C held for 6 min. The carrier gas was helium at a constant flow of 0.8 mL min<sup>-1</sup>. The lowest quantification limits for 28 targets were 0.75 – 5 ng ml<sup>-1</sup> and recovery ranged from 23% to 185%. For rapid screening of fluorochemicals, Kendrick mass (KM) and Kendrick mass defect (KMD) plots were applied to identify, and computed using the following equation:  $KM = \text{exact mass} \times 50 / 49.9968$ ;  $KMD = (\text{exact mass} - \text{nominal mass (rounded down)}) \times 50 / 49.9968$

## Results and discussion

### Screening analysis using UPLC/TOF-MS

The intensity of *m/z* obtained from total ion chromatogram of UPLC/TOF-MS over 500 was selected. The KM against KMD plot for sample s41 and AGE was showed in Fig. 1a and Fig. 2a, respectively. The KMD over 0.8 were related to perfluorinated sulfates and carboxylic acids (Fig. 1b and Fig. 2b). The results clearly simplified the identification of fluorochemicals in complex matrices. Total 11 PFASs including PFPrA, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFHxPA, PFHxS, N-EtFOSA and 6:2 FTUA were detected in 12 textile finishing agents tested.

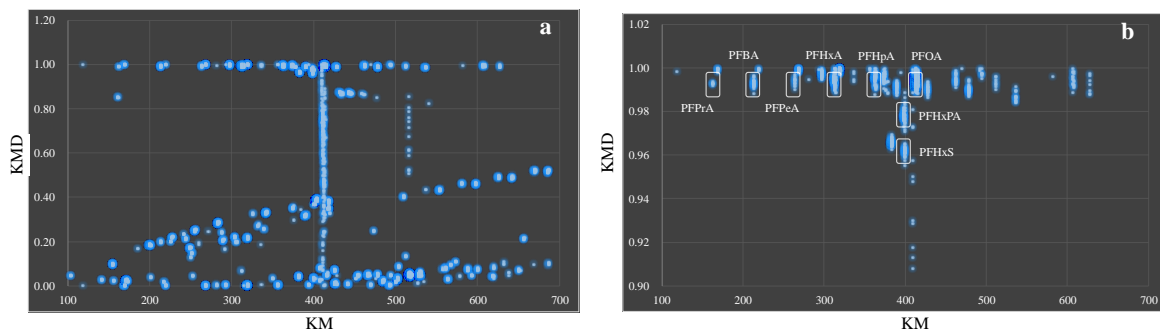


Fig. 1 KMD against KM plot for all the mass spectrum in sample s41

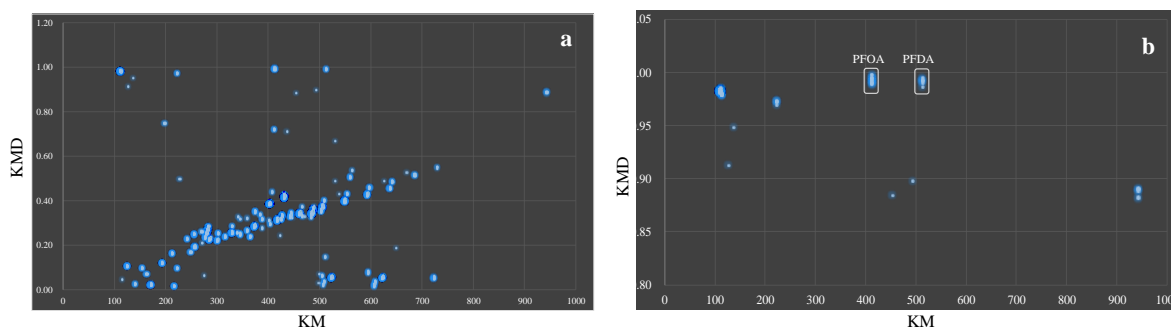


Fig. 2 KMD against KM plot for all the mass spectrum in sample AGE

### Quantitative analysis using UPLC/MS-MS and GC/MS

A total of 16 target PFASs were detected in 12 textile finishing agent samples, with the summary of analytical

results showed in Table 1. The ubiquitous compounds were mainly referred to the short chain perfluorinated carboxylic acids, including PFBA, PFPeA, PFHxA and PFHpA which were found in all samples. The highest median concentration was measured for PFBS ( $1.1 \mu\text{g ml}^{-1}$ ), followed by PFOA ( $0.54 \mu\text{g ml}^{-1}$ ), PFHxS ( $0.33 \mu\text{g ml}^{-1}$ ) and PFHxA ( $0.24 \mu\text{g ml}^{-1}$ ).

**Table 1 Concentration of target compounds in 12 textile finishing**

Compounds	Frequency (%)	Average (ng/ml)	Median (ng/ml)	Maximum (ng/ml)	Minimum (ng/ml)
PFHxA	100	6392	241	40100	49
PFBA	100	3838	164	17900	14
PFPeA	100	434	60	2430	6.7
PFHpA	100	64	54	169	1.7
PFOA	83	562	540	1208	70
PFHxS	75	1961	333	13800	0.46
PFDA	67	398	252	1448	24
8:2 FTOH	67	151	23	1044	0.16
10:2 FTOH	67	85	28	549	0.67
PFNA	67	62	62	158	2.2
PFUdA	67	34	39	53	3.8
6:2 FTOH	58	120	3.6	578	0.82
PFOS	50	757	48	2350	29
PFBS	42	2720	1100	6730	23
PFHpS	33	102	105	184	14
PFPeS	8.3	6.1	6.1	6.1	6.1

#### Cluster analysis and PCA

The hierarchical cluster analysis was applied to evaluate the variation of above 16 detected compounds. Squared Euclidean distance was calculated and the dendrogram was rendered in Fig. 3. The results significantly separated PFBA and PFHxA from other chemicals at  $D_{\text{link}}/D_{\text{max}} \times 25 < 5$ , which suggests these two compounds were predominant in 12 textile finishing agents. This result also reflect the formulation transition from long chain to alternative short chain. Similar results have been found in finished textile products reported by Greenpeace [6].

PCA on the same data rendered three principal components (PC) accounting for 80% of total variance and the loadings plot for the PCA analysis was given in Fig. 4. PC 1 explained 36% of total variance and was correlated with 6 parameters including PFOA, PFNA, PFDA, PFHpA, PFUdA, 6:2 FTOH, 8:2 FTOH and 10:2 FTOH associated with manufacturing process shift from electrochemical fluorination (ECF) to telomerization. PC 2 accounting for 25% of total variance showed correlations PFPeA, PFHxA, PFPeS and PFHxS, which mainly includes C5 and C6 perfluorinated sulfonic and carboxylic acid. Important contributors for PC 3 were PFBA, PFBS, PFHpS and PFOS, accounting for 19% of total variance. These chemicals were mainly short chain perfluorinated sulfonic acids.

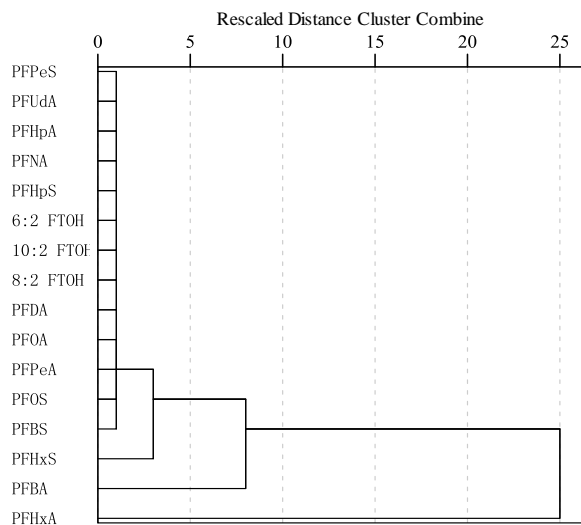


Fig. 3 Dendrogram of hierarchical cluster analysis

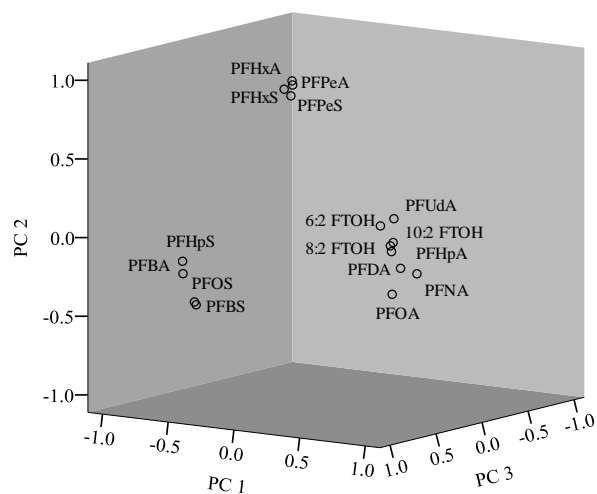


Fig. 4 Loadings plot from the PCA analysis

### Acknowledgements

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