

Trace analysis of perfluorinated alkyl substances in textile goods by LC-MS/MS

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Abstract

A simultaneous trace analysis method was established to determine ten kinds of perfluorinated alkyl substances (PFAS) in textile goods by High-Performance Liquid Chromatography-tandem Mass Spectrometry (HPLC-MS/MS). Samples were extracted by ultrasonication with methanol, and the extract was separated on C₁₈ reversed phase column with methanol-5mmol/Lammonium acetate as the mobile phase. ¹³C-PFOA and ¹³C-PFOS was used as internal standards for quantification. The extraction efficiency were compared among three different extraction methods--ion-pair extraction, soxhlet extraction and ultrasonication. The limit of detection, linear range, and recovery range of the method were 0.5ng/g, 0.5ng/g -10ng/g, and 84.6%-111.8%, respectively. Some PFAS, specially PFOS and PFOA, could be found in waterproof, oil proof, and dust proof coating textiles in China.

Introduction

Perfluorinated alkyl substances (PFAS) are used extensively in numerous industry and consumer products, including textile coatings, paper, food packaging, and others since the 1950s, because of their unique and useful properties (they are stable, chemically inert and generally unreactive). Perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), two widely used PFAS, are persistent, bioaccumulative, and have been found around the world¹⁻³. Nevertheless, animal studies have suggested potential developmental, reproductive, and systemic toxicity of PFOS⁴. In May 2000, 3M announced it was discontinuing its perfluorooctanyl chemistries, including PFOS. Furthermore, Europe Union published a Directive (2006/122/ECOF) that it may not be placed on the market for textiles or other coated materials which contained the amount of PFOS is equal to or higher than 1 μ g/m². Although, it was reported that PFAS have been found in many environmental matrix, human and biological samples³, there are few researches reported the levels of PFAS in commercial productes⁵. Textiles are treated with a wide range of chemical substances that provide functional attributes such as wrinkle resistance, softness, and UV light protection⁶. Some PFAS, especially PFOA and its salts, could be used to provide waterproof, oil-proof and dust proof attributes in textiles.

In the present study, a trace analysis method was established to determine 10 kinds of PFAS, including PFOS, PFOA, perfluorohexanoate (PFHxA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFuDA), perfluorododecanoate (PFDoA), perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS) and perfluorodecanesulfonate (PFDS). This is the first investigation of PFAS levels in Chinese textiles.

Materials and Methods

Sample collection

Twenty textile samples were purchased from market, including four kinds of textiles, silk, terylene, hemp, and coated textile. All samples were packed into polyethylene bags and kept at room temperature.

Analytical procedures

For the analysis, 20 cm×20cm textile samples were cut into approximately 1cm×1cm pieces and put these pieces into a 50 mL pp centrifuged tube.

Analysis of PFAS was performed using a high performance liquid chromatograph-tandem mass spectrometer (HPLC-MS/MS), coupled to a modular Spectra LC system interfaced with a LC Quan version 2.0. Quantam Ultra AM mass spectrometer operated in the electrospray negative ionization mode. A 10 μ L aliquot of the sample extract was injected into a Hypersil C18 column (2.1mm i.d.×50mm length, 5 μ m) with 5mM ammonium acetate aqueous solution (solvent A) and methanol (solvent B) as mobile phases, starting at 30% methanol and increasing linearly. At a flow rate of 250 μ L/min, the gradient was increased to 100% methanol at 4 min, and was kept at that level until 9 min before reversion to original conditions, at the 13 min time point. The details are shown in Table 1⁷.

Table 1 List of target compounds analyzed and parameters of MS/MS used

Acronym	Formula	MS/MS mass transition (<i>m/z</i>)	Collision energy (eV)
PFBS	C ₄ F ₉ SO ₃ NA	298.8→79.9	27
PFH _x S	C ₆ F ₁₃ SO ₃ NA	399.2→79.7	38
PFOS	C ₈ F ₁₇ SO ₃ NA	498.9→79.7	41
PFDS	C ₁₀ F ₂₁ SO ₃ NA	598.9→79.7	40
PFH _x A	C ₅ F ₁₁ COOH	313.1→268.9	10
PFOA	C ₇ F ₁₅ COOH	412.9→368.9	11
PFNA	C ₈ F ₁₇ COOH	462.9→418.9	12
PFDA	C ₉ F ₁₉ COOH	512.7→468.9	11
PFUdA	C ₁₀ F ₂₁ COOH	562.7→519	12
PFDoA	C ₁₁ F ₂₃ COOH	612.8→568.8	22

Quality assurance and quality control (QA/QC)

QA/QC protocols included the analysis of matrix spikes and procedural blanks. Peaks were identified by comparison of the retention times of samples to standards if the signal-to-noise (S/N) ratio was >3, and were quantified if target/qualifier ion ratios were within 20% of the theoretical values. ¹³C-labeled PFOA and ¹³C-labeled PFOS standards (Wellington Lab., CA) were spiked into all samples before extraction.

Results and Discussion

Method develop

Early studies have reported the application of different extraction method for PFAS analysis⁸. In the present study, the ultrasonic extraction using methanol, soxhlet extraction using methanol and ion-pairing extraction followed the method reported elsewhere⁹ were compared (Fig. 1). Recoveries of PFAS between soxhlet extraction and ultrasonic extraction were comparable, which were both better than the recoveries of ion-pairing extraction. The ultrasonic extraction was a relatively easy and timesaving operation compared to soxhlet extraction; therefore, it was chose as extract method in following study.

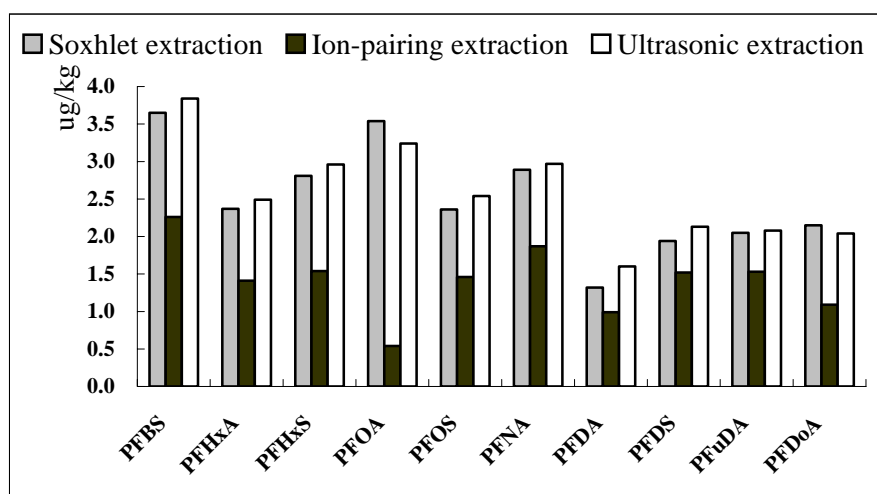


Fig. 1 Extraction efficiency of PFAS with three kinds of different extraction methods

The recoveries of PFAS by ultrasonication with different extraction solvents were compared in Fig.2. The highest concentration of total PFAS in a positive textile was thought as the one hundred-percentage, while the other recoveries were compared to the highest one. Obviously, methanol had the highest extract effective compared to water (0.1%), acetonitrile (52%), acetone (97%), methanol: water/2:1 (40%), methanol: water/1:1(6.6%) and methanol: water/1:2(4.6%), respectively. Therefore, methanol was chose as extract method in real sample analyze.

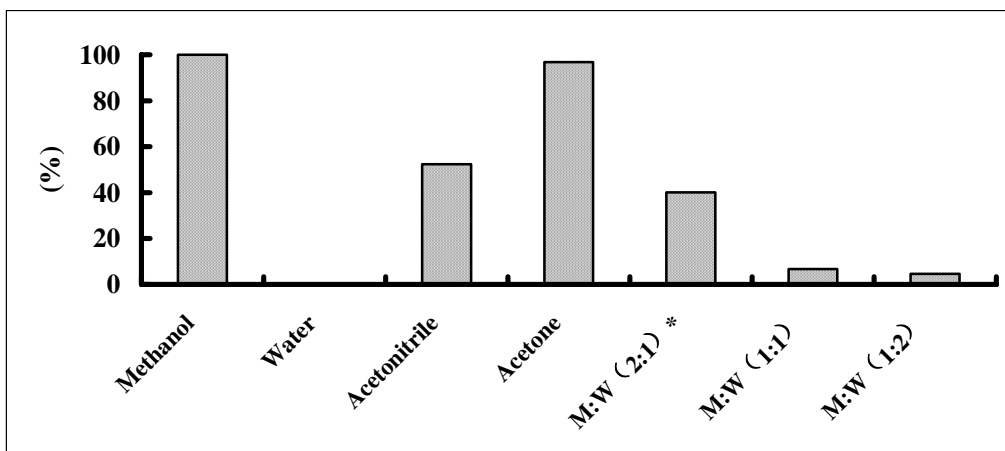


Fig. 2 Recoveries of total PFAS with different extraction solvent

Procedural recoveries

The recovery rates of PFHXA, PFOA, PFNA, PFDA, PFUDA, PFDOA, PFBS, PHXS, PFOS and PFDS through the whole analytical procedure were $94.8 \pm 7.88\%$, $93.3 \pm 14.3\%$, $97.3 \pm 10.9\%$, $84.6 \pm 4.07\%$, $99.1 \pm 7.96\%$, $96.0 \pm 11.6\%$, $98.9 \pm 9.45\%$, $99.9 \pm 40.9\%$, $97.8 \pm 9.68\%$ and $95.7 \pm 10.2\%$, respectively.

Levels of PFAS

Textile samples were extracted by ultrasonication with 30 mL methanol for 40 minutes and then centrifuged (4000 r.p.m.) for 3 min. The extract was passed through a $0.22 \mu\text{m}$ nylon filter and put into pp HPLC vial for instrument determination. The levels of 10 PFAS in different textile goods are shown in Table 2. Only one hemp sample was found PFOA at $0.92 \mu\text{g}/\text{m}^2$ level, while all silk and terylene samples were not contained PFAS at LOQ of $0.5 \mu\text{g}/\text{m}^2$. Most of PFAS, such as PFOA, PFBS, PFHxS, PFOS and PFDA, were found in all five coated textile samples. The concentrations of PFOS in those samples were $1.63 \mu\text{g}/\text{m}^2$, $0.99 \mu\text{g}/\text{m}^2$ and $0.97 \mu\text{g}/\text{m}^2$, respectively. These levels were higher than or close to the limitation from Europe Union. The highest concentration of PFOA was $1.37 \mu\text{g}/\text{m}^2$. Similar to Stadalius's study that low levels of PFOA and PFOS were found in all untreated textiles⁵.

Table 2 The levels of PFAS in textiles goods ($\mu\text{g}/\text{m}^2$)

	PFHxA	PFOA	PFNA	PFDA	PFuDA	PFDoA	PFBS	PFHxS	PFOS	PFDS
Hemp										
Sample1										
Sample2		0.92								
Sample3										
Sample4										
Sample5										
Coated textile										
Sample1		0.75					0.68	1.08	1.63	
Sample2		1.11		0.82				0.89		
Sample3		0.52								
Sample4		1.37							0.99	
Sample5		0.89					0.52	0.51	0.97	

It was concluded that there are some PFAS, specially PFOS and PFOA, could be found in the waterproof, oil proof, and dust proof coating textiles, which were called “three-proof” materials, in China. PFOS and PFOA were both highest PFAS in textile samples. It was similar to the previous reports that some PFAS were detected in human blood samples⁹ and seafood in China¹⁰, which suggested that textile industry might be one of the sources of PFAS in environment.

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