Quantitation of per- and polyfluoroalkyl substances (PFAS) in textiles

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This technical note describes the analysis of per- and polyfluoroalkyl substances (PFAS) in textiles using the SCIEX 6500+ system. In-sample equivalent limits of quantitation (LOQs) ranged between 25 pg/g and 125 pg/g except for PFBA (5000 pg/g) and NFDHA (1250 pg/g). Matrix spikes were performed at 0.25, 5 and 25 ng/g using a cotton shirt that did not contain background PFAS levels, Overall, the matrix spikes showed excellent recovery (95.4–131%) and precision (%CV 3.1–28%) at the 0.25 ng/g spiking level. The method was applied to four locally purchased clothing pieces. PFPeA, PFHxA, 4:2 FTS, and 6:2 FTS were detected in the clothing at low ng/g levels.

Key benefits of the SCIEX 6500+ system for PFAS quantitation in textiles

- **Mid-range pg/g sensitivity using the SCIEX 6500+ system:** In-sample equivalent LOQs ranged from 25 to 125 pg/g for all target PFAS, except for PFBA (5000 pg/g) and NFDHA (1250 pg/g).
- **Good quantitative performance in matrix spikes:** Matrix spikes at 5 and 25 ng/g demonstrated recoveries of 100±10% and precision %CV <10%. The 0.25 ng/g spike showed accuracy from 95% to 131% and precision %CV <28%.
- **Method applicability in purchased clothing**: Low ng/g levels of PFPeA, PFHxA, 4:2 FTS, and 6:2 FTS were detected.

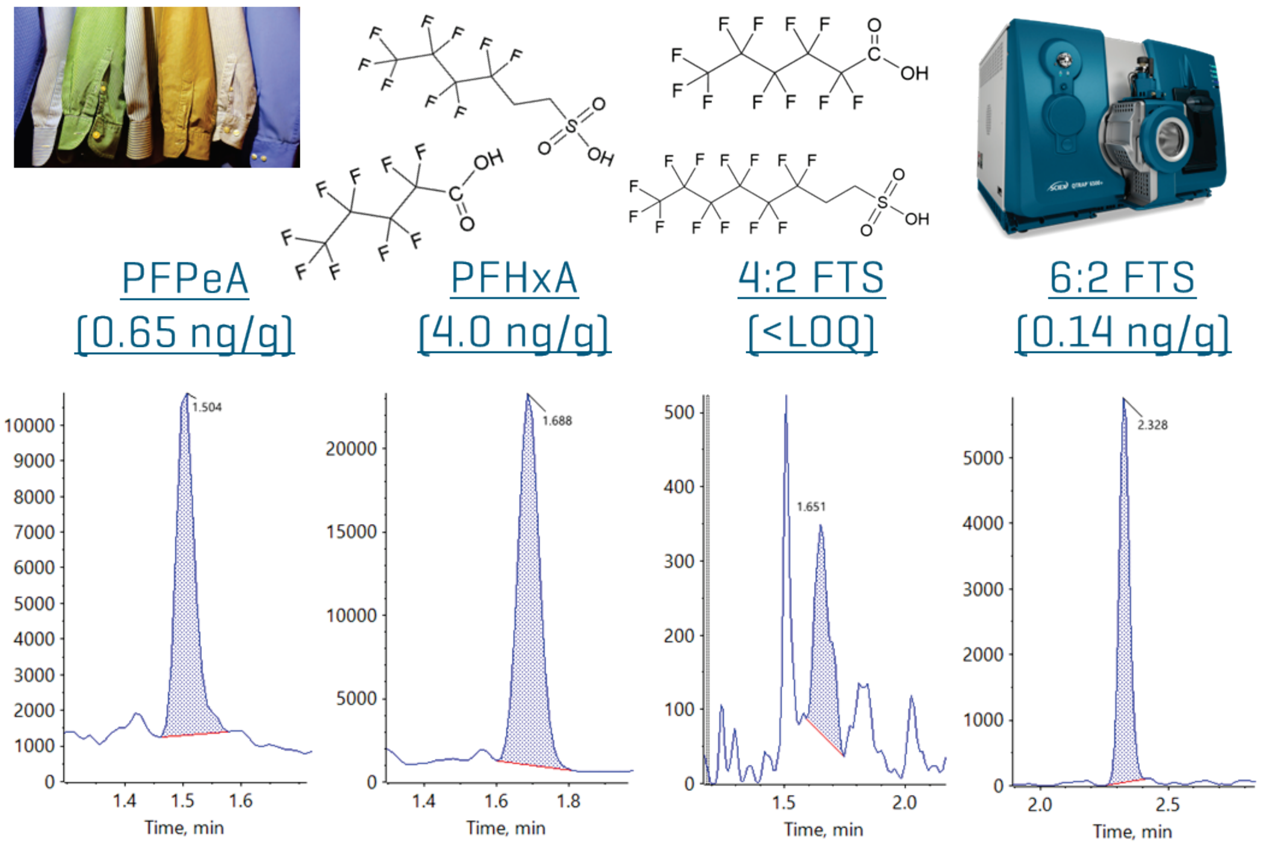

Figure 1. Extracted ion chromatograms (XICs) of PFPeA, PFHxA, 4:2 FTS and 6:2 FTS detected in clothing sample #1.

Introduction

PFAS are widely used on textiles due to their durability and unique ability to repel both oil- and water-based stains. It has been estimated that textile applications are responsible for ~35% of the total global PFAS demand.[1] A broad range of PFAS compounds have been detected in textiles, demonstrating their extensive use and persistence in commercial products.[2,3] PFAS may be released to the environment during all stages of the textile lifecycle, including during initial manufacture, product application, product wear such as leaching and abrasion, and final disposal or recycling. Therefore, the textile industry may represent a diverse and significant source of PFAS contamination to the soil, water and air. Further, textiles are predominately manufactured in Asia and exported worldwide, representing a potential mechanism of global PFAS contamination distribution.

Due to their high usage and potential human health effects, many governments have implemented PFAS textile bans. For example, California and New York have banned the sale of PFAS in various apparel and textiles, effective January 1, 2025.[4,5] In the European Union, Denmark and France announced their intention to ban PFAS in textiles.[6] Further, the EU PFAS Restriction Proposal aims to significantly reduce PFAS manufacture, use and import from all products, including textiles. Therefore, a sensitive, accurate and precise method is needed to analyze PFAS in textiles.

Methods

Samples and reagents: The calibration standard mixture was purchased from LGC Standards and the stable-isotope internal standard mixture was purchased from Cambridge Isotope Laboratories.

Sample preparation: A 5 x 5 cm (1 g) portion was cut from the textile sample and placed in a 50 mL polypropylene tube. The internal standard mixture was spiked (final concentration = 2.5 ng/g) and 20 mL of methanol with 0.5% (v/v) formic acid was added. The vial was vortexed thoroughly, sonicated for 30 min, vortexed again and centrifuged at 4500 rpm for 20 min. After centrifugation, an aliquot was transferred to a clean vial and diluted 5-fold with 0.5% (v/v) formic acid in water to yield a final solvent composition of 80:20 (v/v) water: methanol.

LC chromatography: Chromatographic separation was performed using an ExionAD LC system. A Phenomenex Luna Omega PS C18 column was used as the analytical (3 µm, 100 x 2.1 mm, P/N: 00D-4758-AN) and delay (5 µm, 50 x 3 mm, P/N: 00B-4753-Y0)) columns. Mobile phase A was water with 5mM ammonium acetate, and mobile phase B was methanol with 5 mM ammonium acetate. The gradient conditions used are presented in **Table 1**. The flow rate was 600 µL/min, the injection volume was 20 µL, and the column oven was 40°C.

Mass spectrometry: Samples were analyzed using the QTRAP 6500+ system with electrospray ionization operating in negative mode. Data was acquired using the scheduled multiple reaction monitoring (MRM) algorithm with optimized source and gas conditions (**Table 2**) and compound-specific parameters (**Table 6 in the Appendix**).

Data processing: Data acquisition and processing were performed using SCIEX OS software (version 3.1.6.44).

Table 1: Chromatographic gradient for the analysis of PFAS in textiles.

Time (min)	Mobile phase A (%)	Mobile phase B (%)
0.0	90	10
0.1	45	55
4.5	1	99
7.45	1	99
7.5	90	10
8.5	90	10

Table 2: Source and gas parameters for the analysis of PFAS in textiles using the QTRAP 6500+ system.

Parameter	Value
Polarity	Negative
Ion source gas 1	60 psi
Ion source gas 2	60 psi
Curtain gas	35 psi
Source temperature	450°C
Ion spray voltage	-4500 V
CAD gas	8

Sensitivity, precision, and linear dynamic range of the solvent-based calibration standards

The sensitivity, accuracy, precision and linear dynamic range of the QTRAP 6500+ system was evaluated through triplicate injections of the solvent-based calibration standards. Overall, the in-vial LOQs were at low pg/mL levels, ranging from 0.5 pg/mL to 50 pg/mL **(Table 3)**. The notable exception was PFBA, which showed a LOQ of 200 pg/mL due to blank contamination from the internal standard mix and potentially the solvents and consumables used and the general laboratory environment (air, dust). Good quantitative performance was observed at the LOQ level. At the LOQ level, the mean accuracy ranged from 96.2% to 106%, and the mean precision ranged from 4.4%CV to 22%CV. Considering the entire calibration range, the mean accuracy was generally within ±10% of the nominal value. Most PFAS compounds showed 4 orders of linear dynamic range with r^2 values >0.99. The LOQ was chosen based on the 2 MRM transitions achieving a signal-to-noise (S/N) ratio of ≥10, accuracy ±10%, precision <10% and ion ratio tolerance of ±30%.

Table 3. Sensitivity, accuracy, precision and linear dynamic range in solvent-based standards (n=3) for PFAS analysis using the QTRAP 6500+ system.

Compound	LOQ (in vial, pg/mL)	LOQ (in sample, pg/g)	Mean LOQ % accuracy (n=3)	Mean LOQ %CV (n=3)	Linear range (pg/mL)	Correlation coefficient (r^2)
PFBA	200	5000	98.9	20	200-10,000	0.984
PFPeA	2	50	96.3	22	2-10,000	0.989
PFHxA	5	125	97.8	4.4	5-10,000	0.992
PFHpA	5	125	101	16.5	5-10,000	0.990
PFOA	5	125	96.2	19	5-10,000	0.991
PFNA	5	125	102	5.2	5-10,000	0.990
PFDA	2	50	96.6	7.4	2-10,000	0.987
PFUdA	5	125	98.6	11	5-5,000	0.996
PFDoA	5	125	97.8	11	5-10,000	0.995
PFBS	2	50	99.4	13	2-10,000	0.997
PFPeS	1	25	99.7	9.6	1-10,000	0.996
PFHxS	1	25	99.4	21	1-10,000	0.994
PFHpS	1	25	98.6	16	1-5,000	0.994
PFOS	2	50	104	13	2-5,000	0.992
PFMPA	2	50	99.1	9.4	2-10,000	0.994
PFMBA	5	125	102	8.4	5-10,000	0.993
PFEESA	0.5	12.5	97.1	9.9	0.5-10,0000	0.995
HFPO-DA	2	50	102	13	2-10,000	0.994
NFDHA	50	1250	99.2	7.1	50-10,000	0.986
ADONA	2	50	106	6.3	2-5,000	0.988
9Cl-PF3ONS	0.5	12.5	99.8	8.8	0.5-5,000	0.996
4:2 FTS	1	25	98.6	21	1-10,000	0.992
6:2 FTS	2	50	101	7.0	2-10,000	0.996
8:2 FTS	2	50	101	18	2-10,000	0.992

Quantitative performance in textile matrix spikes

Several cotton shirts, one towel and one dhoti were purchased and screened to confirm negligible background PFAS levels for the matrix spike study. Ultimately, no target PFAS analytes were detected in the shirt chosen except for trace levels of 4:2 FTS. Matrix spikes were performed in triplicate at three spiking levels: 0.25 ng/g (low), 5 ng/g (medium) and 25 ng/g (high). **Table 4** shows the PFAS recovery and precision for the matrix spikes. **Figure 2** shows the PFAS recovery with red dashed lines indicating the 80% and 120% tolerances. Overall, all PFAS compounds showed very good recovery and precision at the 3 spiking levels, demonstrating excellent quantitative method performance. At the 0.25 ng/g spiking level, the mean accuracy was 95.4-131%, and the mean precision was 3.1-28 %CV. The exceptions were NFDHA, which was below the LOQ, and PFBA, which was below the blank level. At the 5 ng/g and 25 ng/g spiking levels, the PFAS recoveries were generally within 100±10% and precision <10%CV. PFBA showed lower recovery due to the relatively high blank levels.

Table 4. PFAS recovery from a cotton shirt spiked at 0.25 ng/g, 5 ng/g and 25 ng/g using the QTRAP 6500+ system. Recoveries were calculated from the quantifier MRM transition.

Compound	0.25 ng/g		5 ng/g		25 ng/g	
	Accuracy (%)	Precision (%)	Accuracy (%)	Precision (%)	Accuracy (%)	Precision (%)
PFBA	nd	nd	32.8	54.7	75.3	9.3
PFPeA	110	13	91.3	4.9	90	5.5
PFHxA	95.4	21	97.7	5.2	91.2	4.9
PFHpA	131	28	101	7.2	93.3	8.2
PFOA	115	7.8	101	7.5	96.7	5.8
PFNA	112	11	104	3.3	101	5.2
PFDA	101	8.9	98.8	7.8	92.5	3.2
PFUdA	116	9.0	106	7.3	96.9	3.0
PFDoA	108	19	100	3.5	92.1	4.6
PFBS	113	6.9	101	3.0	93.8	1.3
PFPeS	109	7.5	102	3.4	96.3	1.7
PFHxS	107	6.4	101	1.4	94.7	1.5
PFHpS	112	7.3	107	3.0	95.2	2.2
PFOS	111	5.4	105	3.5	95.1	2.8
PFMPA	112	6.9	95.3	5.5	94.2	5.7
PFMBA	107	8.5	93.1	5.0	88.3	4.5
PFEESA	108	3.1	101	2.8	94.1	1.1
HFPO-DA	110	7.8	104	3.7	95.8	3.2
NFDHA	nd	nd	100	6.7	87.6	2.4
ADONA	105	9.9	99.3	6.4	91.5	10
9Cl-PF3ONS	117	3.8	108	2.7	99.5	2.9
4:2 FTS	116	7.6	101	2.4	93.8	1.5
6:2 FTS	110	5.0	102	4.0	94.5	1.5
8:2 FTS	104	3.4	101	3.9	94.4	1.4

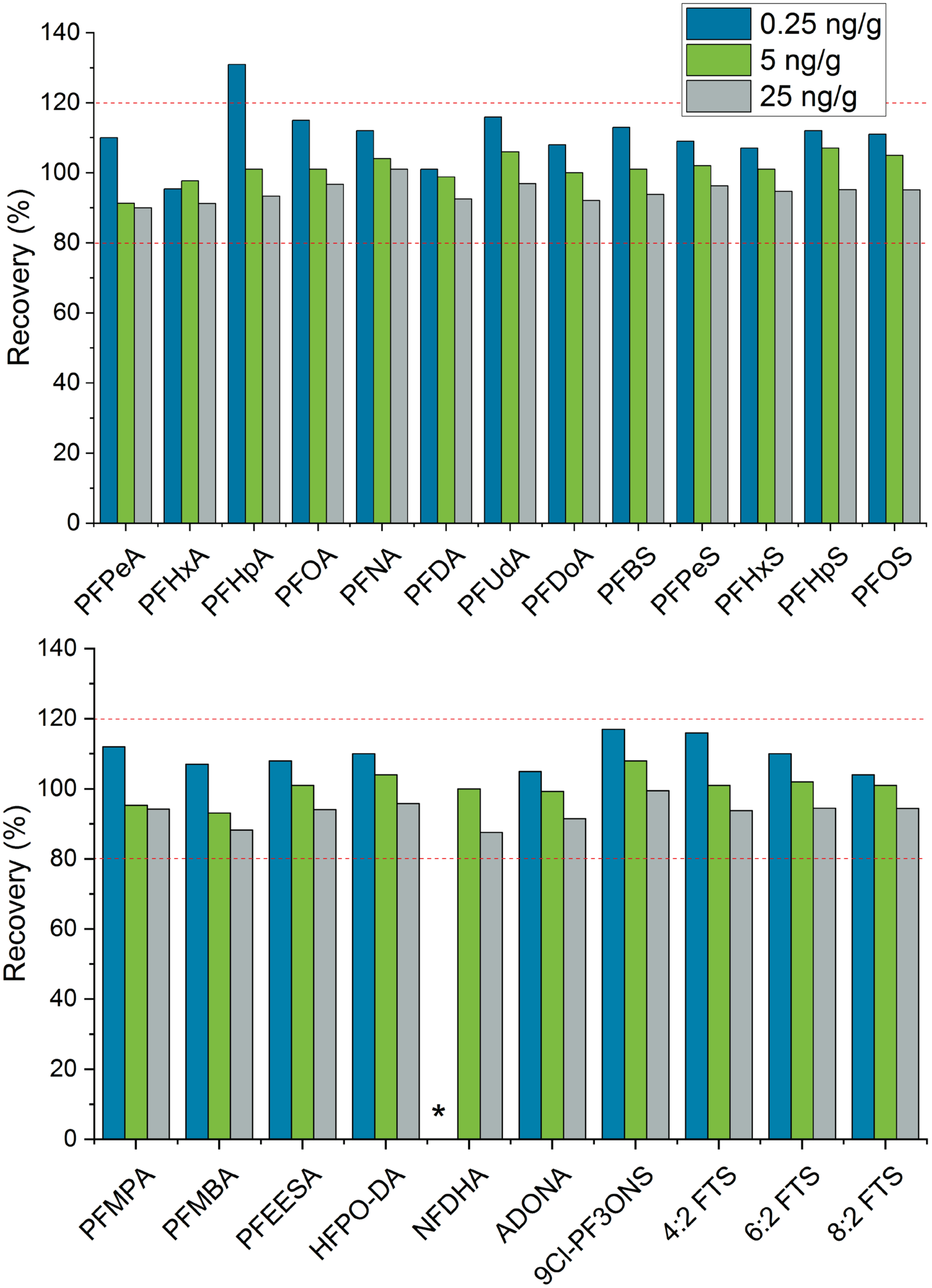

Figure 2. PFAS recovery from a cotton shirt spiked at 0.25 ng/g, 5 ng/g and 25 ng/g using the QTRAP 6500+ system. Recoveries were calculated from the quantifier MRM transition. The low spike for NFDHA not detected and has been marked with an "*". PFBA was omitted since high background levels prevented recovery calculation at the 0.25 ng/g and 5 ng/g levels.

PFAS analysis of purchased clothing

The sample preparation and analysis methods were applied to three shirts and one dhoti purchased from local stores. All garments were labeled as containing PFAS or having stain- and water-repellent properties. Overall, few PFAS were observed in the clothing samples and the detected PFAS included: PFPeA, PFHxA, 4:2 FTS, and 6:2 FTS **(Table 5 and Figure 1)**. Clothing sample #1 contained the highest number of PFAS analytes and the mean levels ranged from 0.14 ng/g for 6:2 FTS to 4.0 ng/g for PFHxA. The highest mean PFAS concentration detected was 12.3 ng/g for PFHxA in sample #2, and this sample also contained trace levels of 6:2 FTS (<LOQ). Clothing sample #4 contained 0.04 ng/g of 4:2 FTS and trace levels of 6:2 FTS (<LOQ). The PFAS concentrations measured in this technical note were consistent with those reported in the literature.[2]

Although a limited number of clothing samples were analyzed, only short-chain PFAS compounds were detected. This trend is consistent with global PFAS manufacturing practices, which have largely phased out the production of long-chain PFAS (>8 carbons). Previous studies[2,3] have shown that volatile PFAS, such as fluorotelomer alcohols (FTOHs) and fluorotelomer methacylates (FTMAcs), comprise the majority of the PFAS burden in textiles. However, these volatile PFAS compounds are either not amenable to electrospray ionization or show very low sensitivity and, therefore, were not included in the current method.

Table 5. PFAS concentration (ng/g) in purchased clothing (n=3).

	Sample 1	Sample 2	Sample 3	Sample 4
PFPeA	0.65	nd	nd	nd
PFHxA	4.0	12.3	nd	nd
4:2 FTS	<LOQ	nd	<LOQ	0.04
6:2 FTS	0.14	<LOQ	<LOQ	<LOQ

Conclusions

- A simple extraction method was developed to analyze PFAS in textiles using the 6500+ system
- In-sample equivalent LOQs ranged from 12.5 to 125 pg/g, except PFBA and NFDHA, demonstrating mid-range pg/g sensitivity
- Method quantitative performance was demonstrated in matrix spikes at 0.25, 5 and 25 ng/g. The 0.25 ng/g spike showed accuracy within ±31% and precision <28%, 5 and 25 ng/g spikes showed PFAS recoveries generally within 100±10% and precision <10%CV
- Method applicability was shown by analyzing four purchased clothing items. Low ng/g levels of PFPeA, PFHxA, 4:2 FTS, and 6:2 FTS were detected.

References

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Appendix

Table 6: Compound-specific MRM parameters and internal standard assignment for PFAS analysis in textiles using the 6500+ system.

ID	Precursor ion (m/z)	Fragment ion (m/z)	DP (V)	CE (V)	CXP (V)	Internal std
PFBA	213	168.9	-10	-10	-11	$^{13}C_4$-PFBA
PFMPA	229	84.9	-5	-15	-9	$^{13}C_4$-PFBA
PFPeA	263	219	-5	-10	-17	$^{13}C_5$-PFPeA
PFMBA_01	279	85	-45	-10	-19	$^{13}C_5$-PFPeA
PFBS_01	299	80	-80	-65	-11	$^{13}C_4$-PFBS
PFBS_02	299	99	-80	-35	-11	$^{13}C_4$-PFBS
PFEESA_01	315	135	-55	-30	-13	$^{13}C_4$-PFBS
HFPO-DA_01	285	169	-20	-11	-11	$^{13}C_3$-HFPO-DA_01
NFDHA_01	295	201	-30	-17	-15	$^{13}C_6$-PFHxA
PFHxA_01	313	269	-25	-12	-13	$^{13}C_6$-PFHxA
PFHxA_02	313	119	-25	-27	-11	$^{13}C_6$-PFHxA
4:2 FTS_01	327	307	-65	-27	-11	$^{13}C_2$, D_4-4:2 FTS
PFPeS_01	349	80	-60	-80	-11	$^{13}C_6$-PFHxS
PFPeS_02	349	99	-60	-40	-11	$^{13}C_6$-PFHxS
PFHxS_01	399	80	-100	-90	-11	$^{13}C_6$-PFHxS
PFHxS_02	399	99	-100	-75	-11	$^{13}C_6$-PFHxS
PFHpA_01	363	319	-30	-14	-13	$^{13}C_7$-PFHpA
PFHpA_02	363	169	-30	-24	-11	$^{13}C_7$-PFHpA
ADONA_01	377	251	-22	-17	-11	$^{13}C_7$-PFHpA
ADONA_02	377	85	-22	-35	-11	$^{13}C_7$-PFHpA
PFOA_01	413	369	-30	-15	-13	$^{13}C_8$-PFOA
PFOA_02	413	169	-30	-24	-11	$^{13}C_8$-PFOA
6:2 FTS_01	427	407	-80	-32	-11	$^{13}C_2$,D_4-6:2FTS
PFHpS_01	449	80	-120	-100	-11	$^{13}C_8$-PFOS
PFHpS_02	449	99	-120	-85	-11	$^{13}C_8$-PFOS
PFOS_01	499	80	-120	-110	-11	$^{13}C_8$-PFOS
PFOS_02	499	99	-120	-100	-11	$^{13}C_8$-PFOS
9Cl-PF3ONS_1	531	351	-80	-37	-11	$^{13}C_8$-PFOS
PFNA_1	463	419	-45	-15	-14	13C9-PFNA
PFNA_2	463	169	-45	-26	-11	13C9-PFNA
PFDA_1	513	469	-45	-15	-16	$^{13}C_9$-PFDA
PFDA_2	513	169	-45	-29	-11	$^{13}C_9$-PFDA
8:2 FTS_1	527	507	-130	-37	-11	$^{13}C_2$,D_4-8:2FTS
PFUdA_1	563	519	-50	-16	-18	$^{13}C_9$-PFUnA
PFUdA_2	563	169	-50	-31	-11	$^{13}C_9$-PFUnA

Table 6: Compound-specific MRM parameters and internal standard assignment for PFAS analysis in textiles using the 6500+ system.

ID	Precursor ion (m/z)	Fragment ion (m/z)	DP (V)	CE (V)	CXP (V)	Internal std
PFDoA_1	613	569	-50	-18	-20	$^{13}C_{12}$-PFDoA
PFDoA_2	613	169	-50	-36	-11	$^{13}C_{12}$-PFDoA
$^{13}C_4$-PFBA	217	171.9	-5	-15	-10	n/a
$^{13}C_5$-PFPeA	268	223	-5	-10	-17	n/a
$^{13}C_4$-PFBS	302.9	79.9	-65	-65	-9	n/a
$^{13}C_3$-HFPO-DA_1	288	171.9	-10	-10	-11	n/a
$^{13}C_3$-HFPO-DA_2	288	187.9	-10	-25	-15	n/a
$^{13}C_6$-PFHxA	319	273.9	-5	-15	-13	n/a
$^{13}C_2$, D_4-4:2 FTS	333	312	-75	-30	-10	n/a
$^{13}C_6$-PFHxS	405	79.9	-65	-85	-11	n/a
$^{13}C_7$-PFHpA	370	325	-10	-15	-10	n/a
$^{13}C_8$-PFOA	421	376	-30	-15	-13	n/a
$^{13}C_2$,D_4-6:2FTS	433	412	-85	-35	-10	n/a
$^{13}C_8$-PFOS	507	80	-120	-110	-11	n/a
13C_9-PFNA	472	427	-45	-15	-14	n/a
$^{13}C_9$-PFDA	522	476.9	-25	-15	-13	n/a
$^{13}C_2$,D_4-8:2FTS	532.9	512	-80	-40	-10	n/a
$^{13}C_9$-PFUnA	572	528	-20	-15	-15	n/a
$^{13}C_{12}$-PFDoA	625	580	-35	-20	-10	n/a

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