Application Note

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Analysis of Perfluoroalkyl Substances in Textile and Leather Using the Agilent 6470 Triple Quadrupole LC/MS

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Abstract

Many technical textiles that are used to make apparel and equipment contain per- and polyfluoroalkyl substances (PFAS). However, PFAS may have a negative impact on health and the environment so are under increased scrutiny and monitoring by regulatory bodies.[1] To detect and quantify the levels of PFAS in textiles and leather substrates, an Agilent 6470 triple quadrupole LC/MS system was coupled with an Agilent Infinity II HPLC. To reduce the background noise during the analysis, the HPLC was fitted with an Agilent PFC-Free-Kit. The method was used to characterize 33 PFAS in textile and leather samples, satisfying the performance requirements specified in the ISO 23702-1 method for the measurement of PFAS in leather by LC/MS/MS.[2]

Introduction

PFAS represent a wide range of chemicals, such as perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA), and perfluorohexane sulfonic acid (PFHxS). These compounds are widely used in the textile, leather, and consumer product sectors due to properties such as high chemical (stain) resistance and water-resistance. However, PFAS are of increasing interest to regulatory bodies because of their negative impact on health and the environment.[1] LC/MS/MS is the most popular technique for analyzing PFAS because of its high sensitivity and selectivity. But analyzing complex matrices such as leather samples using a conventional electrospray ionization (ESI) source can be problematic, as matrix components may coelute with the analyte and suppress ionization. Other challenges include the adsorption/carryover of PFAS in samples onto the instrument. Also, contamination from PFAS in equipment used during sample processing/preparation or analysis can affect trace analysis at the parts-per-billion (ppb) or parts-per-trillion (ppt) concentration level.

To resolve the difficulties in analyzing PFAS in textiles and leather substrates, an Agilent 1290 Infinity II HPLC system was fitted with the Agilent PFC-Free HPLC Conversion Kit and a 6470 triple quadrupole LC/MS system (6470 LC/TQ). To overcome matrix effects of leather, the standard addition method was used to quantify 33 PFAS in leather samples, while external 'solvent' calibration was used to measure the PFAS in textiles.

Experimental

Regents and standards

All reagents were of analytical grade. HPLC-grade acetonitrile and glacial acetic acid were supplied by Merck (Darmstadt, Germany). Methanol was obtained from Baker (Xalostoc, México). Anhydrous sodium acetate and ammonium acetate (purity ≥98%) were bought from Vetec (Rio de Janeiro, Brazil). Formic acid was bought from Tedia (Ohio, USA). Ultrapure water was generated by a Millipore Milli-Q system (Milford, MA, USA).

Thirty-three PFAS standards and one internal standard (IS, >99% purity) were used in this study. All the standards were of high purity grade (>98.0%) and were bought from Wellington Laboratories (Canada). Individual stock solutions and the IS were prepared at 1,000 µg/L in methanol and stored at −20 ±2 °C in a freezer. The working solutions were prepared from appropriate dilutions of the PFAS stock solutions.

Sample preparation

The sample preparation outlined in the ISO 23702-1 standard method for the determination of the nonvolatile PFAS content of leather was used.[2] The PFAS were extracted with methanol and the extract was analyzed by LC/MS/MS. Figure 1 shows a detailed description of the optimized sample preparation protocol used in this study.

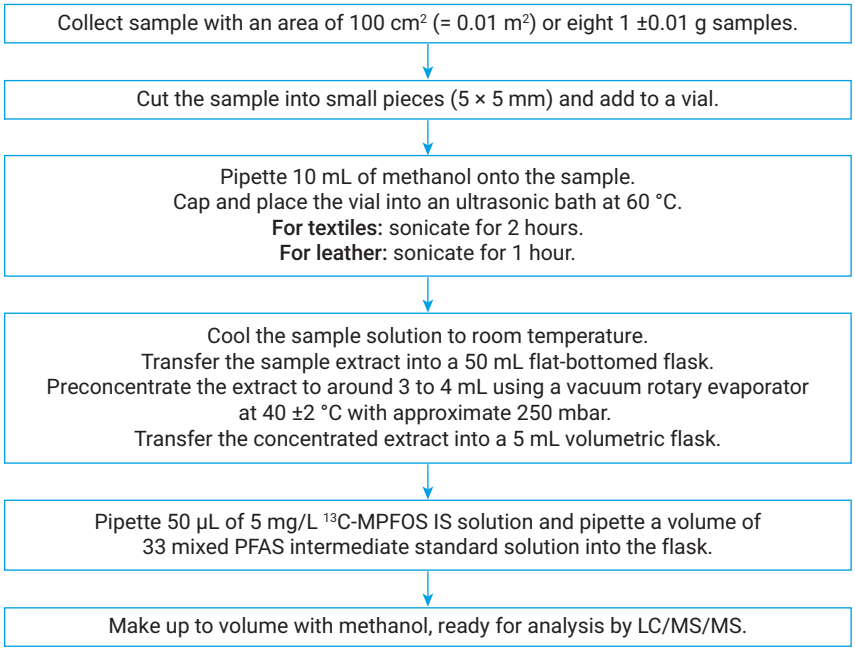

Figure 1. Sample preparation procedure for the extraction of PFAS from textiles and leather.

Instrumentation

A 1290 Infinity II HPLC equipped with the PFC-Free HPLC Conversion Kit and a 6470 triple quadrupole LC/MS (G6470A) was used. The PFC-free kit is designed for a 1290 Infinity II LC fitted with a high-speed pump (G7120A) and an Agilent 1290 Infinity II Multisampler (G7167B) with multiwash option. The parameters of LC and MS were obtained using Agilent MassHunter Optimizer and Ion Source Optimizer software.

Dynamic-multiple reaction monitoring (dMRM) mode was used for data acquisition. The acquisition windows and dwell times were adjusted to optimize acquisition frequency of 10 data points for each peak. Most of the MRM transitions were referenced from the Agilent PFAS MRM database for LC/TQ. Table 3 gives a complete list of the analyte retention times and MRM transitions for the PFAS that were analyzed in this study.

Table 1. LC configuration and operating parameters.

Parameter	Value
Instruments	1290 Infinity II High Speed Pump (G7120A), 1290 Infinity II Multisampler with multiwash option (G7167B), 1290 Infinity II Multicolumn Thermostat (G7116B)
Needle Wash	Multiwash
Solvent 1	15/85 methanol/water
Solvent 2	1:1 acetonitrile:2-propanol
Thermostat Temperature	5 °C
Injection Volume	5 µL
Analytical Column	C18, 2.0 × 150 mm, 5 µm column Guard column for C18 HPLC columns with internal diameters of 2.0 to 3.0 mm
Column Temperature	40 °C
Delay Column	InfinityLab PFC delay column, 4.6 × 30 mm
Mobile Phase A	5 mM ammonium acetate in water
Mobile Phase B	Acetonitrile
Flow Rate Gradient	0.3 mL/min
Gradient	**Time (min) / A (%) / B (%) / Flow (mL/min)** 0.5 / 70 / 30 / 0.3 20 / 0 / 100 / 0.3 22 / 0 / 100 / 0.3 22.1 / 70 / 30 / 0.45 26 / 70 / 30 / 0.45
Stop Time	26 minutes

Table 2. Ion source parameters used for the Agilent 6470 LC/TQ.

Ion Source Parameter	Value
MS Acquisition	Agilent Jet Stream Electrospray Ionization (AJS ESI)
Gas Temperature	250 °C
Gas Flow	9 L/min
Nebulizer	45 psi
Sheath Gas Heater	380 °C
Sheath Gas Flow	11 L/min
Capillary	3,500 (–V)
Nozzle Voltage	0

Table 3. MRM parameters.

Compound Name	Precursor Ion	Product Ion	Fragmentor Voltage (V)	Cell Accelerate Voltage (V)	Collision Energy (V)	Retention Time (min)
10-2 FTS	626.9	607	70	2	36	12.14
10-2 FTS	626.9	80.9	70	2	44	12.14
^{13}C-MPFOS*	503	99	125	2	48	11.20
^{13}C-MPFOS*	503	80	125	7	52	11.20
4-2 FTS	327	307	85	2	20	4.35
4-2 FTS	327	286.9	85	2	28	4.35
6-2 FTS	427	407	155	3	24	7.31
6-2 FTS	427	80	155	7	44	7.31
8-2 FTS	527	507	145	6	28	9.79
8-2 FTS	527	81	145	6	44	9.79
FOSAA	556	497.9	180	2	28	9.69
FOSAA	556	169	180	2	36	9.69
H2PFDA*	457	393	75	1	16	8.48
H2PFDA*	457	343	75	1	48	8.48
H4PFUnA*	491	387	55	1	12	9.59
H4PFUnA*	491	367	55	1	28	9.59
HFPO-DA	329	185	85	3	28	5.68
HFPO-DA	329	119	85	3	44	5.68
HPFHpA*	345	281	70	2	8	5.21
HPFHpA*	345	131	70	3	28	5.21
N-EtFOSA	526	219	25	1	28	16.71
N-EtFOSA	526	169	25	1	32	16.71
N-EtFOSAA	584	526	85	2	24	10.79
N-EtFOSAA	584	419	85	2	20	10.79
N-EtFOSE	630	59	77	1	56	16.37
N-MeFOSA	512	219	35	1	28	15.88
N-MeFOSA	512	169	35	1	32	15.88
N-MeFOSAA	570	512	80	2	24	10.28
N-MeFOSAA	570	482.9	80	2	16	10.28
N-MeFOSE	616	59	77	1	56	15.53
PF-3,7-DMOA*	469	269	35	1	24	9.74
PF-3,7-DMOA*	469	219	35	1	28	9.74
PFBA	213	169	65	1	8	2.08
PFBS	298.9	99	144	3	32	5.49
PFBS	298.9	80	144	7	44	5.49
PFDA	513	469	81	2	8	10.43
PFDA	513	219	81	5	16	10.43
PFDoA	613	569	102	4	8	12.79
PFDoA	613	169	102	1	28	12.79
PFDS	598.9	99	120	1	56	13.55
PFDS	598.9	80	120	2	120	13.55
PFHpA	363	319	70	1	8	6.58
PFHpA	363	169	70	1	16	6.58
PFHpS	448.9	99	192	5	40	9.95

Compound Name	Precursor Ion	Product Ion	Fragmentor Voltage (V)	Cell Accelerate Voltage (V)	Collision Energy (V)	Retention Time (min)
PFHpS	448.9	80	192	7	48	9.95
PFHxA	313	269	47	2	8	5.04
PFHxA	313	119	47	2	24	5.04
PFHxS	398.9	99	174	5	40	8.61
PFHxS	398.9	80	174	7	48	8.61
PFNA	463	419	35	3	8	9.22
PFNA	463	169	35	1	20	9.22
PFOA	413	369	35	1	8	7.94
PFOA	413	169	35	1	20	7.94
PFOS	498.9	99	192	1	48	10.75
PFOS	498.9	80	192	7	92	10.75
PFOSA	497.9	78	156	7	40	12.82
PFOSA	497.9	64	156	2	168	12.82
PFPA*	263	219	47	1	8	3.24
PFTeA	712.9	669	35	3	12	15.02
PFTeA	712.9	169	35	1	32	15.02
PFTrA*	663	619	35	3	12	13.92
PFTrA	663	169	35	1	32	13.92
PFUnA	563	519	94	1	8	11.63
PFUnA	563	269	94	3	20	11.63

*Compounds not in the Agilent PFAS MRM database.

Method validation

The practical usefulness of the method was evaluated based on the analysis of leather (1 g and 100 cm^2) and textile (1 g and 100 cm^2) samples. Quantitative results were calculated using a linear least-squares regression weighted with the IS. Samples with complex matrix compositions such as leather can be affected by coeluting components from the sample's matrix during ionization. Therefore, a matrix-matched (standard addition) method was used to overcome any matrix-based interferences from the leather matrix.

Linearity and range: A linear least-squares regression weighted by the inverse concentration (1/x) was applied to all target compounds using external calibration. The solvent and matrix-matched calibration curves were prepared from 1 to 20 µg/L (five points). According to ISO 23702-1:2018, acceptance criteria for the calibration should be determined by the regression model's predictability. For the lowest concentration standard, the calculated concentration must be within 50 to 150% of the actual concentration. For all other standards, the calculated concentration must be within 70 to 130% of the actual concentration.

Instrument detection limit (IDL): The IDL was estimated based on the standard deviation (SD) of the seven replicate injections of the 1 µg/L PFAS mixed standard.

Method detection limit (MDL): The MDL was estimated based on the SD of the analysis results of nine spiked samples on three different days at 0.01 mg/kg (for 1 g sample) and 1 $µg/m^2$ (for 100 cm^2).

Recovery, repeatability, and reproducibility: The recovery, repeatability, and reproducibility were evaluated based on the results of the analysis of nine spiked samples on three different days. The samples were spiked at concentrations of 0.01 mg/kg (for 1 g sample), 1 $µg/m^2$ (for 100 cm^2), 0.075 mg/kg (with 1 g of sample), and 7.5 g/m^2 (for 100 cm^2).

Results and discussion

Chromatographic performance

US EPA Method 537 describes a 37-minute LC method for the determination of selected per- and polyfluorinated alkyl substances in drinking water by LC-MS/MS.[3] The LC conditions specified in the EPA method were optimized in this study. The MRM chromatogram of the 20 µg/L standard solution containing the PFAS is shown in Figure 2. Good chromatographic peak shapes and signal-to-noise ratio (S/N) were obtained for 34 PFAS (including the IS) in 17 minutes. This time is much faster than the 37-minute method suggested in EPA Method 537.

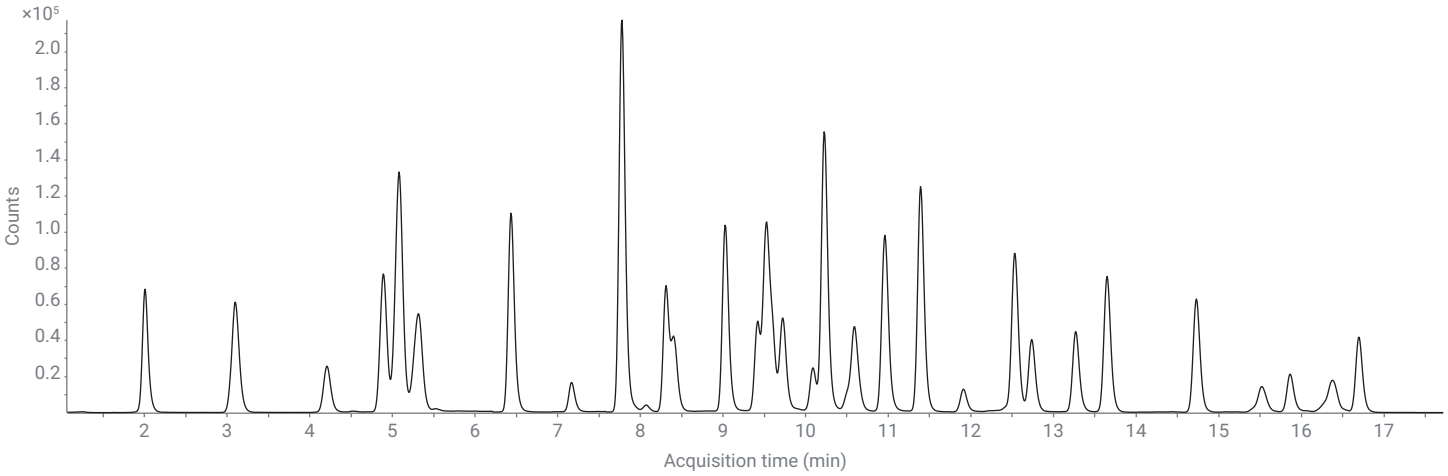

Figure 2. LC/MS/MS chromatogram of 34 PFAS analyzed at 20.0 µg/L.

Linearity and range: Solvent and standard addition calibration curves were linear for all PFAS from 0.5 to 20 µg/L, as indicated by R^2 values greater than 0.996. Figure 3 shows representative calibration plots for four PFAS. The bias % of all PFAS was in the acceptable range of 50 to 150% of the actual concentration for the lowest concentration standard (STD 1). The response at the lowest concentration (1 µg/L) was stable across the seven IDL samples analyzed over 24 hours, as indicated by the percent relative standard deviation (%RSD) below 7% (Table 4).

Table 4. Linear least-squares regression weighted calibration data for 33 PFAS.

Compounds	R^2	%RSD STD 1	%Bias STD1	IDL (µg/L)	Compounds	R^2	%RSD STD 1	%Bias STD 1	IDL (µg/L)
PFBA	0.9999	2.91	−2.15	0.047	PFHpS	0.9998	3.22	−4.01	0.051
PFPA	0.9995	0.58	3.16	0.010	FOSAA	0.9990	3.01	−11.19	0.044
4:2 FTS	1.0000	2.06	−5.28	0.032	PFDA	0.9998	0.90	−6.67	0.014
HFPO-DA	0.9964	4.41	18.79	0.091	N-MeFOSAA	0.9997	4.15	−9.49	0.062
PFHxA	0.9997	1.30	−1.17	0.021	PFOS	0.9997	3.15	−2.15	0.051
HPFHpA	0.9992	0.68	0.54	0.011	N-EtFOSAA	0.9993	2.47	0.59	0.041
PFBS	0.9995	2.01	4.86	0.035	PFUnA	0.9998	1.27	−5.95	0.020
PFHpA	0.9998	0.78	−0.67	0.013	10:2 FTS	0.9997	3.95	−12.28	0.057
6:2 FTS	0.9999	2.87	−5.26	0.045	PFDoA	1.0000	1.30	−6.10	0.020
PFOA	0.9998	0.59	−0.16	0.010	PFDS	0.9999	1.27	−6.07	0.020
H2PFDA	0.9997	1.60	6.22	0.028	PFTrA	1.0000	1.34	−5.99	0.021
PFHxS	0.9995	2.71	−0.50	0.044	N-MeFOSE	0.9996	1.84	0.25	0.030
PFNA	0.9999	1.49	−0.83	0.024	PFOSA	0.9993	2.96	4.96	0.051
H4PFUnA	0.9991	1.93	10.89	0.035	PFTeA	0.9997	1.53	−3.94	0.024
PF-3,7-DMOA	0.9998	6.28	−17.05	0.086	N-MeFOSA	0.9996	1.47	2.32	0.025
8:2 FTS	0.9993	1.42	−17.22	0.019	N-EtFOSE	0.9997	1.67	0.52	0.028
					N-EtFOSA	0.9999	0.83	1.66	0.014

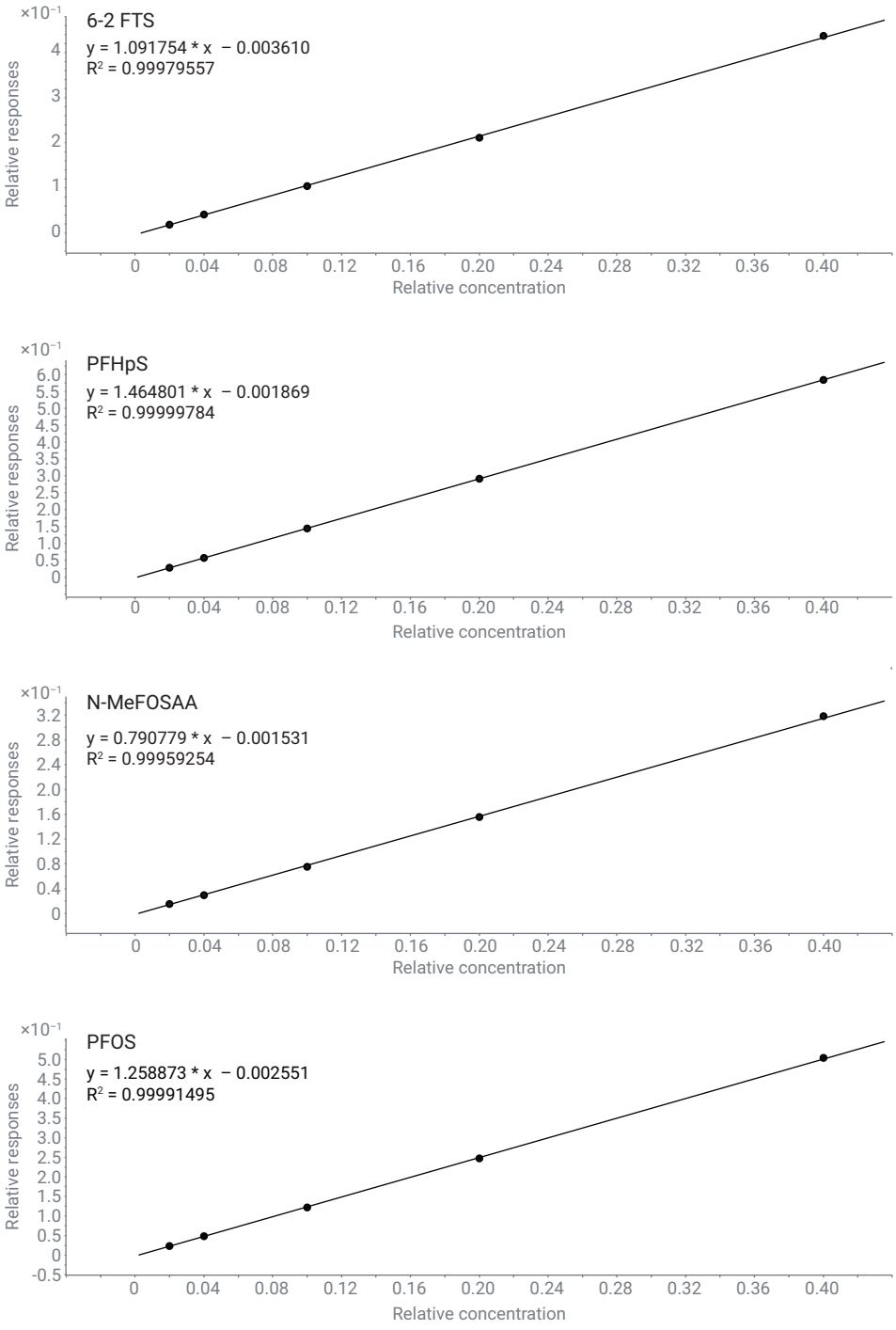

Figure 3. Calibration curves for four representative PFAS: 6-2 FTS, PFHpS, N- MeFOSAA, and PFOS.

Instrument Detection Limit (IDL): the IDLs were determined by analyzing seven replicates of the PFAS at 1 µg/L. Chromatograms of three representative PFAS at 1 µg/L (Figure 4) show that the instrument is suitable for the low-level analysis of PFAS in textile and leather samples. The IDLs of PFBA, PFPA and 4:2 FTS were 0.05, 0.01, and 0.03 µg/L, respectively, and the %RSD of the measurements was less than 3%. The IDLs and %RSDs for all PFAS are shown in Figure 5.

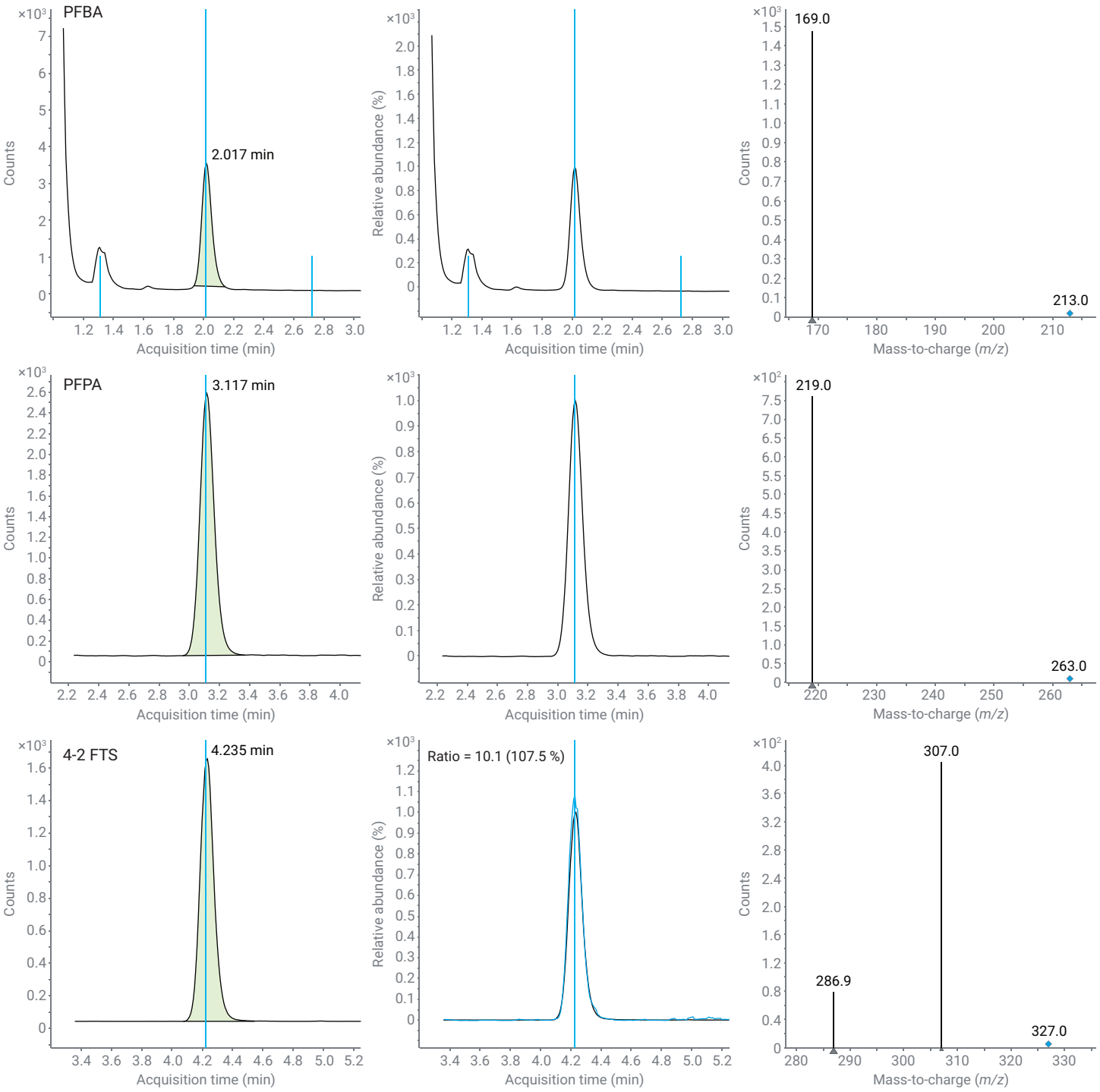

Figure 4. Chromatograms of PFAS (PFBA, PFPA, and 4:2 FTS) at 1 µg/L used for IDL calculations.

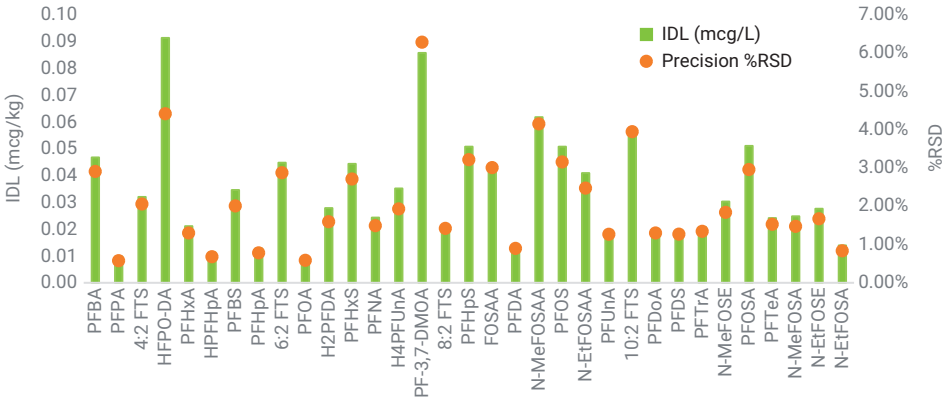

Figure 5. Instrument detection limits (IDLs).

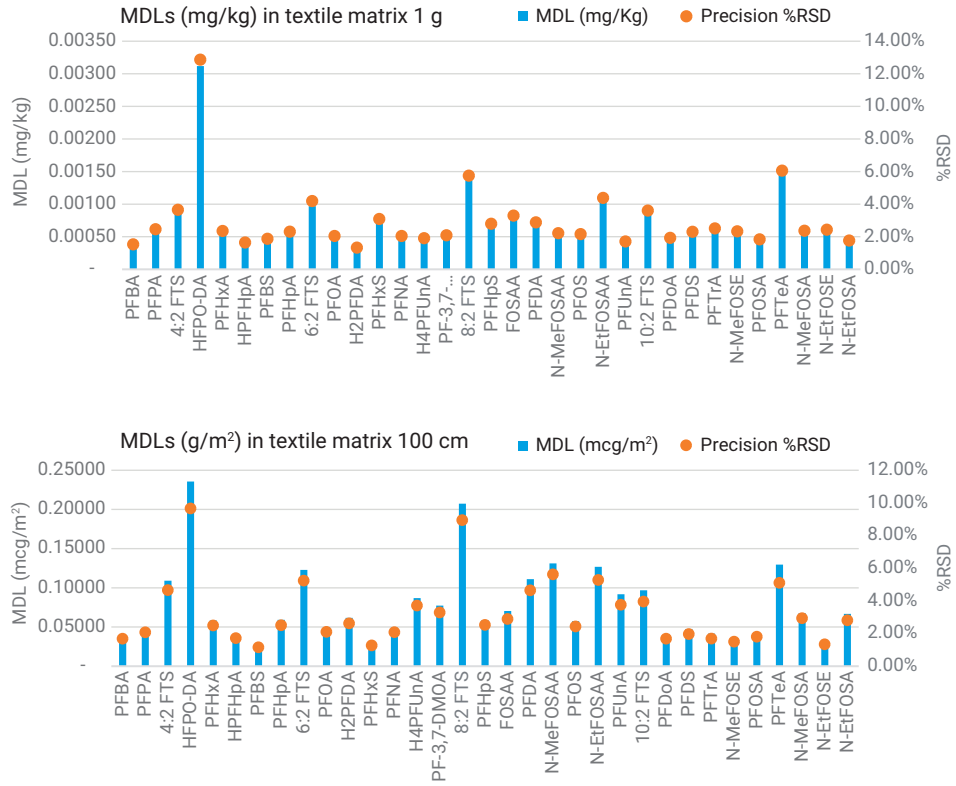

Figure 6. MDLs of PFAS in textile matrices.

Method detection limits (MDLs): The MDLs obtained for PFAS in the textile matrices (1 g and 100 cm^2) were in the range of 0.00031 to 0.00312 mg/kg and 0.027 to 0.23 µg/m^2, respectively, as shown in Figure 6. For the leather sample-matrices (1 g and 100 cm^2), the PFAS-MDLs were in the range of 0.00034 to 0.0017 mg/kg and 0.023 to 0.26 µg/m^2, respectively, as shown in Figure 7. The calculated RSDs for all 33 PFAS were below 20% for both textile and leather samples. The MDLs are low for most compounds, as required for the PFAS-residue analysis of both textile and leather samples.

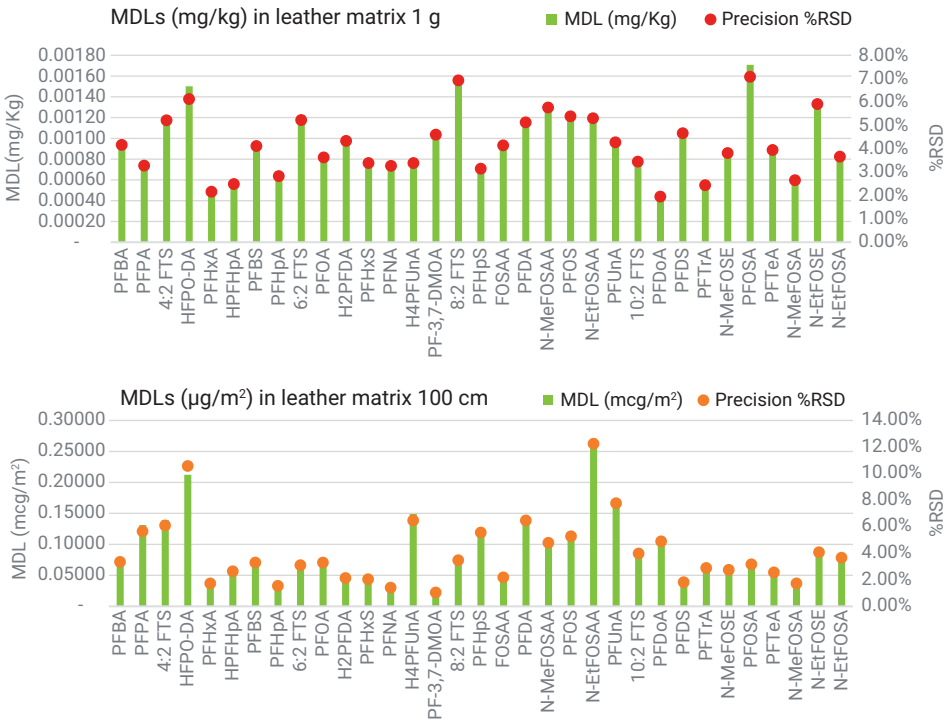

Figure 7. MDLs of PFAS in leather matrices.

Table 5. Recovery of 10 PFAS postspiked into a leather extract at 5 ng/mL quantified using solvent (non-matrix-matched) calibration curves.

Spiked Compound	Spike Recovery (%)
HFPO-DA	134
PFHpA	138
H2PFDA	142
PFNA	125
H4PFUnA	135
8-2 FTS	202
N-MeFOSAA	45
N-EtFOSAA	122
10-2 FTS	365
N-EtFOSE	14

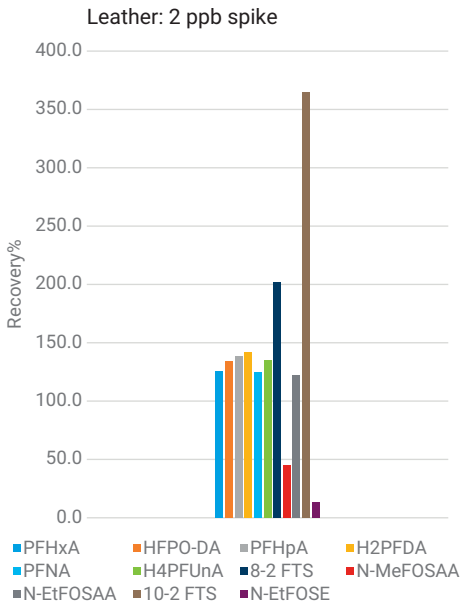

Figure 8. Recovery for the PFAS spiked at 2 µg/L into a leather extract. The PFAS were quantified using external solvent calibration curves.

Recovery: To understand the impact of matrix effects from the leather-matrix, a spike recovery test was carried out by spiking a leather extract at 2 µg/L with 10 PFAS. The PFAS in the spiked sample were quantified using external solvent calibration curves. Chromogenic compounds and lipids in leather can coelute with the analyte causing ionic suppression or enhancement. As shown in Table 5, the high recoveries of 10-2 FTS and 8-2 FTS (365 and 202%, respectively) indicated an interference, leading to a significant enhancement of the signal. In contrast, the ionization of two compounds, N-EtFOSE and N-MeFOSAA, was suppressed, as indicated by the low recoveries of 14 and 45%, respectively. The results in Figure 8 show that matrix-matched (standard addition) curves are needed for the measurement of PFAS in leather to compensate for matrix-based interferences.

When matrix-matched (standard addition) calibration was used for the analysis of the leather samples, the mean recoveries of 33 PFAS were greatly improved, as shown in Figure 9. In the 1 g leather matrix, the mean recoveries from samples with spiked 33 analytes at 0.01 and 0.075 mg/kg were 95.7 to 106% and 98.4 to 109%, respectively. For the 1 µg/m^2 leather sample, recoveries ranged from 99.0 to 110.3%, and for the 7.5 µg/m^2 sample, recoveries ranged from 107.4 to 100.5%.

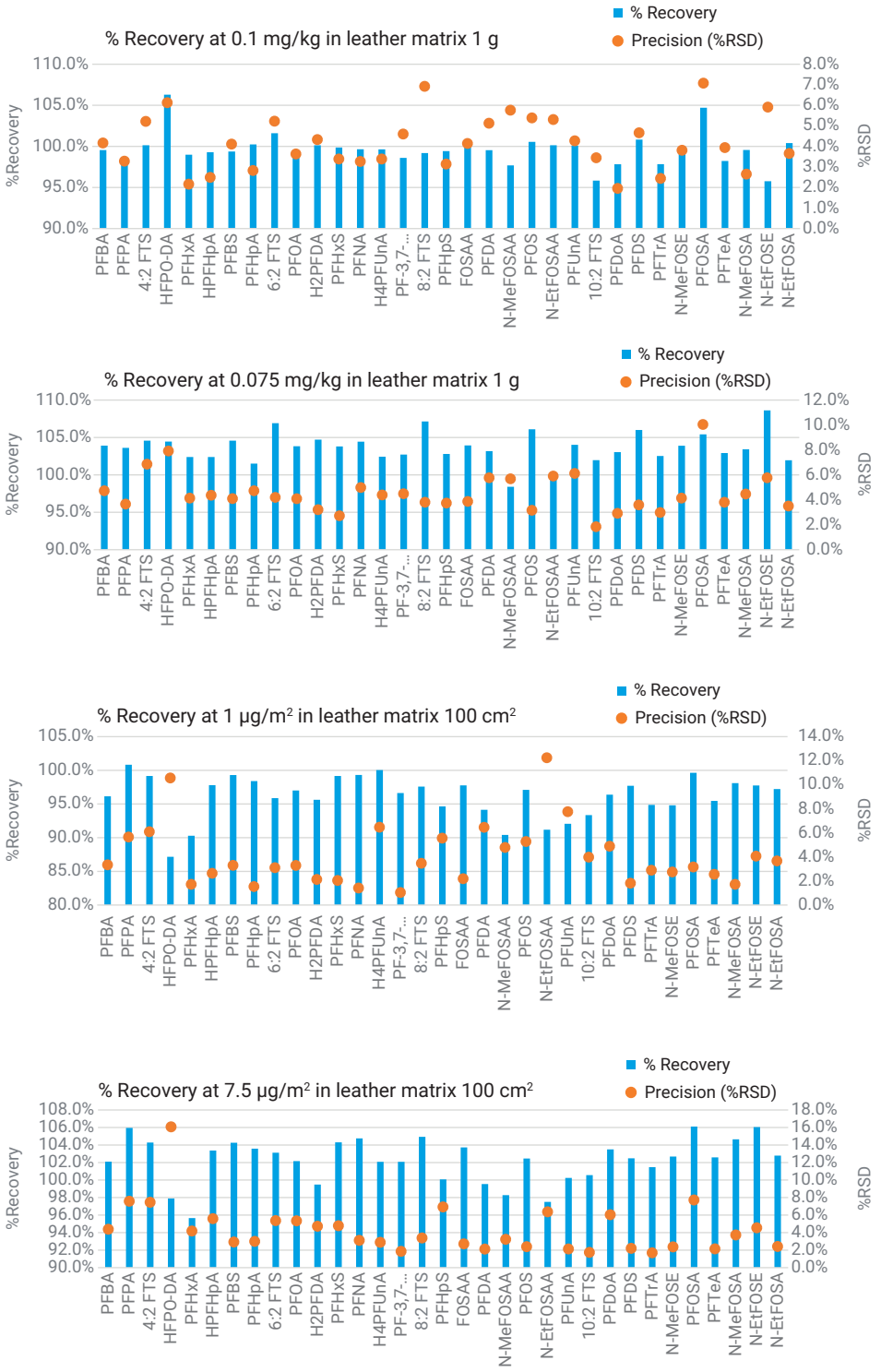

Figure 9. Recovery (%) of PFAS in leather matrix samples.

Matrix effects are less problematic for the analysis of textile samples, so solvent calibration was used for quantification of PFAS in textiles. The average values of recovery obtained for the textile samples (1 g and 100 cm^2) at different concentrations ranged from 92.9 to 110%, as shown in Figure 10. Recovery between 70 and 120% is considered satisfactory based on the limits specified in ISO 23702-1:2018. In addition, the %RSD of the recovery values calculated from nine spiked samples on three days for each concentration was less than 20%, which satisfies the requirements of ISO method.

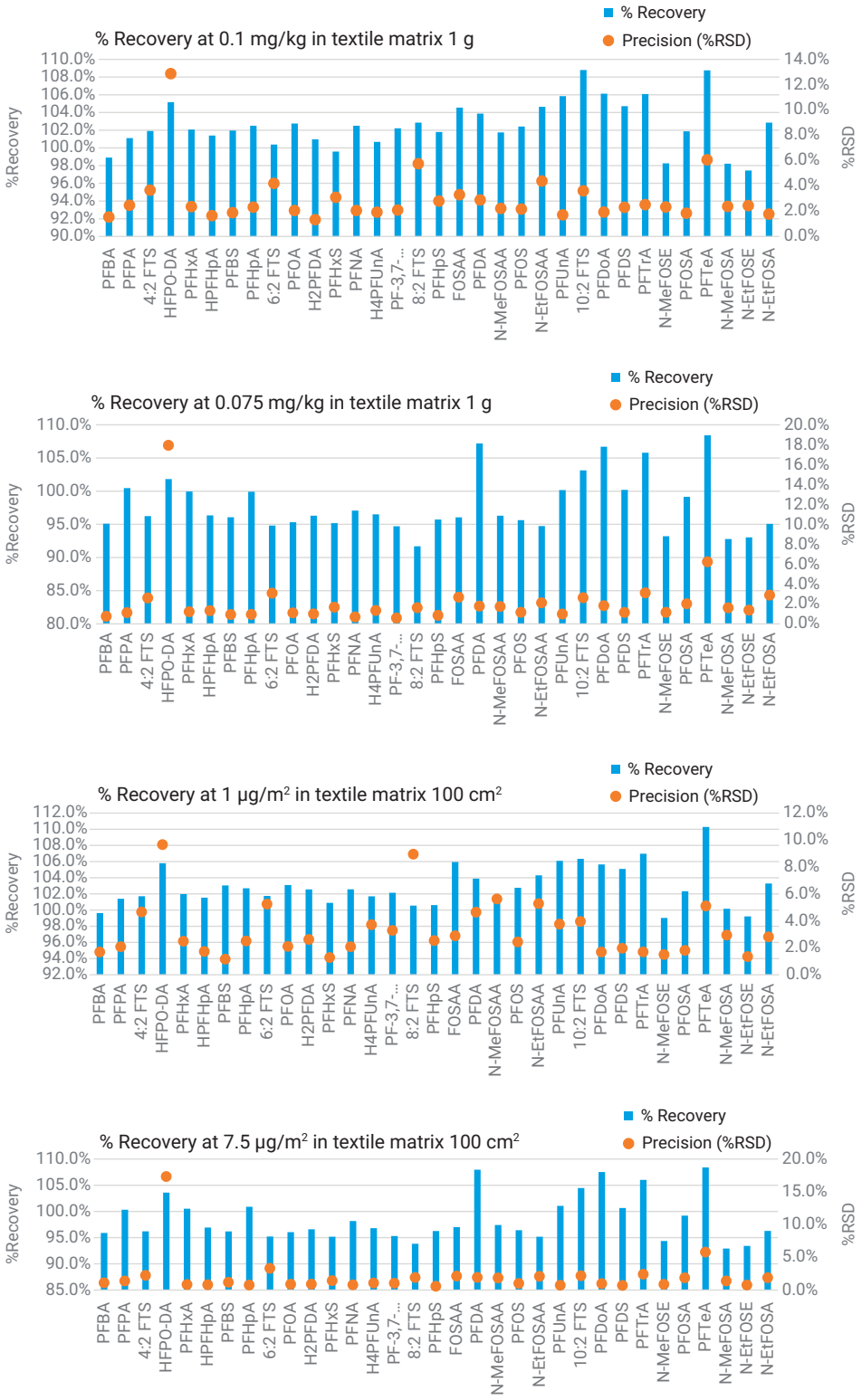

Figure 10. Recovery (%) of PFAS in textile matrix samples.

Conclusion

A rapid, sensitive, and accurate LC/MS/MS method was presented for the identification and quantification of 33 PFAS in complex sample matrices.

To reduce carryover between samples from the instrumentation, the Agilent Infinity II HPLC method was fitted with a PFC-Free HPLC Conversion Kit. All 33 PFAS and the internal standard were separated within 17 minutes. The compounds were then detected simultaneously in one run using an Agilent 6470 triple quadrupole LC/MS. To compensate for matrix-based interferences, the method of standard addition was used for the analysis of the leather samples only. Good recoveries, repeatability, and reproducibility were obtained for PFAS measured in all samples.

The method was shown to achieve the specificity, linearity, recovery, and accuracy required for the analysis of PFAS in fabrics. The application is useful as PFAS are persistent in the environment so are increasingly subject to restrictions and regulation.

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DE03071434

Printed in the USA, March 3, 2022
5994-4588EN

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