SHIMADZU RJ Lee Group

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Development of an LCMS Methodology to Characterize and Quantitate Fluorinated Compounds in Consumer Products

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1. Introduction

Per-and Polyfluorinated alkyl substances (PFAS) are a broad class of thousands of chemicals with a varied global definition that include carbon-fluorine bonds. Since the carbon-fluorine bond is the strongest in organic chemistry, PFAS was manufactured for desirable water resistant, oil resistant, and heat resistant properties. Since the 1940's, industries have integrated PFAS in products such as food packaging, textiles, and household products due to their unique properties. However, a characteristic of PFAS of concern is their slow breakdown rate, leading to potential accumulation in people, animals, and the environment. Studies have shown widespread exposure to PFAS among the United States population[1]. In response to growing concerns regarding consumer exposure to PFAS, many states have initiated bans of PFAS uses in various consumer products and food packaging materials. These bans have led to a need for analytical testing to determine the amount of PFAS in consumer products, however, the lack of standardized methods present challenges in ensuring reliability and reproducibility between labs. This work provides a foundation for the collaborative efforts between Shimadzu Scientific Instruments, Inc., and RJ Lee Group Inc., along with ASTM, towards establishing the first standardized method for the quantitation of extractable PFAS in various consumer product categories, using a Shimadzu LCMS-8060NX LCMS, **Figure 1.**

2. Methods

Stock standard solutions containing native analytes and labeled isotopes (surrogates) were diluted from commercially available mixed or single stock standards using a 95:5 methanol:water mixture. The stocks were prepared in high-density polyethylene (HDPE) bottles and stored at 4ºC. The stock solutions were not filtered, and a 7-9 point calibration curve was prepared in 50:50 (vol:vol) methanol:water with 0.1% acetic acid mixture at the levels shown in **Table 1.**

Table 1. In-vial Native and Surrogate Calibration Curve Concentrations (ng/L)

Analyte/ Surrogate	Cal 1	Cal 2	Cal 3	Cal 4	Cal 5	Cal 6	Cal 7	Cal 8	Cal 9
All Analytes not Specified Below	5	10	20	40	60	80	100	150	200
3:3 FTCA	--	--	20	40	60	80	100	150	200
8:2 FTS, 4:2 FTS	--	10	20	40	60	80	100	150	200
PFPeA, 6:2-diPAP, 8:2-diPAP	25	50	100	200	300	400	500	750	1000
PFPrA, PFBA	--	50	100	200	300	400	500	750	1000

Samples (0.5 grams +/- 0.01g) were weighed into 50-ml polypropylene centrifuge tube and spiked with 40µl of surrogate spiking solutions (SSS). A 50:50 (vol:vol) methanol:water solution was added to the sample and vortexed for approximately 1 minute. The sample's pH was then adjusted to approximately 9-10 using 20µL of ammonium hydroxide, and briefly vortexed again. The centrifuge tubes were then tumbled on a rotator for 2 hours. After tumbling, the entire sample was filtered through a 0.2 µm preconditioned polypropylene syringe filter. Post filtration, the sample's pH was adjusted to approximately 3-4 using 5µL acetic acid per 1mL recovered filtered sample volume. The samples were then briefly vortexed and centrifuged at 8ºC for 15 minutes at 3000 rpm. The sample preparation is outlined in **Figure 2**. Compound parameters including quantitation ion, confirmation ion, and collision energies, were optimized using Labsolutions LCMS software. Analytical conditions are shown in **Table 2**.

Figure 1. Shimadzu LCMS-8060NX

Figure 2. Sample preparation procedure for consumer products

Table 2. Analytical conditions for consumer product PFAS assay

[LC] Nexera	
Mobile Phase (LCMS Grades)	A: 2 mmol/L Ammonium Acetate in H_2O/ Acetonitrile = 95/5
	B: Acetonitrile
Delay Column	Shimadzu Nexcol PFAS Delay
	50 mm x 3.0 mm, 5 µm (P/N: 220-91394-09)
Analytical Column	Shim-pack Scepter C18-120
	2.1 mm x 100 mm, 3 µm (P/N: 227-31014-05)
Gradient (%B)	10% (0.5 min) ⇒22% (2.3-3.0 min) ⇒45% (6.0 min) ⇒ 75% (12.0 min) ⇒95% (12.1-14.0 min) ⇒10% (14.1-17.0 min)
Interface	IonFocus ESI (-)
Column Oven Temp.	45 ℃
Flow rate	0.45 mL/min
Injection volume	40 µL
Multiple draw injection program	Co-injection 20 µL Sample → 25 µL 0.1% Acetic acid in H_2O → Co-injection 20 µL Sample → 25 µL 0.1% Acetic acid in H_2O
Autosampler Rinsing	60/40 Acetonitrile/2-propanol, Before/After Aspiration 5 seconds
[MS] LCMS-8060NX	
Interface Temp.	170℃
Probe position	+3 mm
Nebulizer gas flow	3 L/min
Heating gas flow	15 L/min
Interface Voltage	-0.5 kV (same value for all compounds)
DL Temp.	200 ℃
Heatblock Temp.	300 ℃
Drying gas flow	8 L/min
Focus bias	-2 kV (same value for all compounds)
CID Cell Pressure	270 kPa; 350 kPa 6.6 - 7.6 min and 11.6 - 12.6 min

3. Results

Calibration curves for each analyte were found to have an % RSD RF of less than 20%. **Table 3** shows the quantitation and confirmation ions (if available) analyte retention time, curve % RSD RF, and measurement range.

Table 3. Summary of calibration data for native analytes

Compound	Quantitation Ion	Confirmation Ion	Retention Time (min)	% RSD RF	Range (ng/kg)
PFTreA	712.95>668.95	712.95>169.00	10.84	9.3	100-4000
PFTriA	662.95>618.95	662.95>169.00	10.19	8	100-4000
PFDoA	612.95>568.95	612.95>319.00	9.55	9.7	100-4000
PFUnA	562.95>518.95	562.95>269.00	8.91	6.2	100-4000
PFDA	512.95>468.95	512.95>219.00	8.29	14.5	100-4000
PFNA	462.95>418.95	462.95>219.00	7.72	12.7	100-4000
PFOA	412.95>369.00	412.95>169.00	7.16	4.8	100-4000
PFHpA	362.95>319.00	362.95>169.00	6.51	7.9	100-4000
PFHxA	312.95>269.00	312.95>119.00	5.64	2.9	100-4000
PFPeA	263.00>219.00	263.00>69.00	4.15	1.6	500-20000
PFBA	213.00>169.00	----	2.32	7.6	1000-20000
PFDS	598.90>79.95	598.90>98.95	9.91	4.3	100-4000
PFNS	548.95>79.95	548.95>98.95	9.24	2.8	100-4000
PFOS	498.95>79.95	498.95>98.95	8.59	7.9	100-4000
PFHpS	448.95>79.95	448.95>98.95	7.96	12.5	100-4000
PFHxS	398.95>79.95	398.95>98.95	7.35	7.9	100-4000
PFPeS	348.95>79.95	348.95>98.95	6.64	6.8	100-4000
PFBS	298.95>79.95	298.95>98.95	5.63	9.6	100-4000
PFOSA	497.95>77.95	497.95>477.95	10.45	3.7	100-4000
8:2FTS	526.95>506.95	526.95>80.90	8	19	200-4000
6:2FTS	426.95>406.95	426.95>80.90	6.9	12.9	100-4000
4:2FTS	326.95>306.95	326.95>80.90	5.23	19.8	200-4000
NEtFOSAA	584.00>418.95	584.00>526.00	8.55	9.4	100-4000
NMeFOSAA	569.95>418.95	569.95>482.95	8.28	4.7	100-4000
PFDoS	698.90>79.95	698.90>98.95	11.21	7.6	100-4000
NMeFOSA	511.95>219.00	511.95>169.00	12.75	4.8	100-4000
NEtFOSA	526.00>219.00	526.00>169.00	13.36	4.9	100-4000
NMeFOSE	616.00>59.00	----	12.45	4.9	100-4000
NEtFOSE	630.00>59.00	----	13.07	14.5	100-4000
HFPO-DA	285.00>169.00	285.00>185.00	6.01	3.7	100-4000
ADONA	376.95>251.00	376.95>85.00	6.77	6.2	100-4000
9Cl-PF3ONS	530.90>350.95	532.90>352.95	9.07	3.4	100-4000
11Cl-PF3OUdS	630.90>450.95	632.90>452.95	10.4	4.1	100-4000
PFPrA	163.00>119.00	----	1.16	6.8	1000-20000
NFDHA	294.95>201.00	294.95>85.00	5.51	5.5	100-4000
PFEESA	314.95>135.00	314.95>82.95	6.16	6.2	100-4000
PFMPA	228.95>85.00	----	3.21	8.1	100-4000
PFMBA	278.95>85.00	----	4.61	6.3	100-4000
3:3 FTCA	241.00>177.00	241.00>117.00	3.55	14.6	400-4000
5:3 FTCA	341.00>237.00	341.00>217.00	6.16	13.3	100-4000
7:3 FTCA	441.00>317.00	441.00>337.00	7.57	9.5	100-4000
FHUEA	357.00>293.00	----	6.23	2.4	100-4000
FOUEA	456.95>393.00	----	7.44	3.5	100-4000
HQ-115	279.90>146.95	279.90>210.90	6.57	3.6	100-4000
6:2-diPAP	789.00>442.90	789.00>97.00	9.99	8.3	500-20000
8:2-diPAP	989.00>543.00	989.00>97.00	12.07	9.8	500-20000

Recovery and repeatability were evaluated for the surrogates in PFAS free Ottawa sand, a plastic product, and nonstick aluminum foil. Each matrix was spiked with surrogate spiking solution at the concentration specified in **Table 4**, based on a 0.5g sample.

Table 4. Blank sand matrix, plastic product, and non-stick foil surrogate spiking recovery (n=3_

Compound	Spike Conc. ng/kg	Sand Matrix %Recovery	Sand %RSD	Plastic Product % Recovery	Plastic Product %RSD	Non-stick Foil % Recovery	Non-stick Foil %RSD
13C4-PFBA_Surr	8000	104.6	9.7	102.6	2.4	100.5	1.4
13C5-PFPeA_Surr	8000	99.8	6.3	103.4	0.5	101.5	0.6
13C5-PFHxA_Surr	1600	95.7	5.6	98.2	1.4	99.3	0.4
13C4-PFHpA_Surr	1600	96.2	2.1	100.4	2.9	105.3	2.5
13C8-PFOA_Surr	1600	96.4	1.9	96.7	0.8	102.9	3.3
13C9-PFNA_Surr	1600	95.9	2.1	98.1	3.6	95.3	7.1
13C6-PFDA_Surr	1600	95.9	1.6	102.1	2.4	101.4	4.3
13C7-PFUnA_Surr	1600	95.0	4.6	96.7	1.0	103.7	0.5
13C2-PFDoA_Surr	1600	97.0	3.8	119.2	1.6	118.4	2.9
13C2-PFTreA_Surr	1600	92.0	8.6	116.4	0.9	104.1	4.7
13C8-PFOSA_Surr	1600	96.0	7.0	90.8	3.1	93.2	2.0
D3-NMeFOSAA_Surr	1600	97.7	2.5	105.3	1.7	112.0	12.5
D5-NEtFOSAA_Surr	1600	102.2	4.1	98.5	4.1	88.2	12.7
D3-NMeFOSA_Surr	1600	91.2	13.2	97.3	2.5	93.5	4.1
D5-NEtFOSA_Surr	1600	93.4	5.4	88.1	3.5	90.8	3.5
D7-NMeFOSE_Surr	1600	91.5	0.8	99.0	1.5	93.9	1.7
D9-NEtFOSE_Surr	1600	85.1	5.0	91.0	0.5	90.1	3.3
13C3-HFPO-DA_Surr	1600	95.1	3.6	104.5	1.0	103.1	2.9
13C2-4:2FTS_Surr	1600	97.1	6.7	102.7	8.2	104.4	8.2
13C2-6:2FTS_Surr	1600	96.0	14.8	93.4	2.5	102.7	0.2
13C2-8:2FTS_Surr	1600	94.7	12.9	102.5	15.4	101.9	9.6
13C8-PFOS_Surr	1600	99.0	10.3	102.6	1.5	102.4	4.4
13C3-PFBS_Surr	1600	103.0	3.1	100.1	3.4	98.4	1.0
13C3-PFHxS_Surr	1600	95.3	2.1	97.7	8.4	102.1	4.5
M4-6:2-diPAP_Surr	8000	128.7	3.2	117.8	3.2	102.2	6.4

4. Conclusion

This work demonstrates the analysis of 46 PFAS and 25 surrogate compounds in solid matrices, such as plastic and foil consumer products, using a newly developed method employing a Shimadzu LCMS-8060NX LC-MS/MS system. PFAS free Ottawa sand was used to confirm surrogate recoveries within a blank solid sample matrix. The extraction procedure, chromatography, and mass spectrometry conditions were optimized to ensure optimal sensitivity for co-solvation sample preparation procedure. These conditions resulted in a method that eliminates the need for solid phase extraction, therefore significantly reducing cost and time associated with SPE sample preparation. Target analytes were quantitated using a 7-9-point calibration curve with a reporting range between 100-4,000 ng/kg (dependent on analyte, **Table 3**). Excellent surrogate recoveries were obtained on the plastic and non-stick foil samples, with recovery values within 70-130%. Triplicate extractions resulted in %RSD less than 15%. This method provides a foundation for ongoing efforts to develop a new standardized method with ASTM on PFAS analysis in consumer products.

Reference
1) https://www.atsdr.cdc.gov/pfas/

Conflict of Interest Statement:
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