

Application News

No. LCMS-078

Liquid Chromatography Mass Spectrometry

Shimadzu's Guide to US EPA Method 537: Determination of Selected Perfluorinated Compounds in Drinking Water Using the Triple Quadrupole LCMS-8060



■ Summary

EPA Method 537 is a solid phase extraction (SPE), liquid chromatography/tandem mass spectrometry (LC-MS/MS) method for selected Perfluorinated Compounds (PFCs) in drinking water. This paper presents an evaluation of the instrumental portion of the method using the Shimadzu LCMS-8060 triple quadrupole mass spectrometer. The LCMS-8060 is Shimadzu's most sensitive LC-MS/MS. Calibration ranges and estimated detection limits were well below method requirements. In addition, the chromatography was shortened from the 25 minutes in EPA 537 to less than 10 minutes without loss of resolution.

■ Background

Environmental contamination has been regulated since the US EPA was established in 1970. Over the years the US EPA has developed and published methods for the analysis of different environmental pollutants using triple quadrupole liquid chromatography mass spectrometry (LCMS) instrumentation. Recently, there has been a renewed interest in the analysis of Perfluorinated Compounds (PFCs).

US EPA Method 537 was first published in 2009 and is specifically used for the analysis of PFCs in drinking water. ASTM methods D7579 and D7968 are used for the analysis of PFCs in wastewater or drinking water.

The EPA has issued a health advisory of 70 parts per trillion (ppt) for PFCs in drinking water. The Unregulated Contaminant Monitoring Rule 3 (UCMR3) program detected PFCs in a small percentage of the samples tested. EPA Method 537 was used for analysis of PFCs under UCMR3.

■ Method

In this study, the performance of Shimadzu's most sensitive LC-MS/MS, the LCMS-8060, was evaluated. Since extraction efficiency varies by laboratory, and by analyst, only the instrumental portion of the method was evaluated. In this study, direct injection of fortified reagent water samples diluted with methanol was performed.

Using heated ESI in negative mode, MRM transitions were adjusted using Flow Injection Analysis (FIA) to optimize sensitivity for all PFC analytes, surrogate standards, and internal standards as defined in US EPA Method 537 sections 10.2.1.2 and 10.2.1.3.

Following MRM optimization, standard solutions in 96:4 percentage (v/v) methanol and reagent water were prepared and chromatography adjusted for resolution and peak shape, meeting the criteria in section 10.2.2 and 10.2.3 with a 10-minute chromatogram. This near-baseline resolution was accomplished using a Restek Raptor ARC-C18 2.7 μ analytical column, an allowed modification, as seen in the chromatogram in Figure 1. A Shimadzu Nexera UHPLC system was used because operating pressures exceeded 10,000 psi.

■ Results and Discussion:

Initial Calibration and Continuing Calibration Verification

A series of seven initial calibration standards ranging from 5 to 200 ng/L (parts-per-trillion, ppt) were prepared. The three internal standards (IS) and the three surrogate standards (SUR) were held constant at 50 ng/L in all samples analyzed.

The calibration curves were evaluated by linear regression correlation coefficient (r^2). All calibration curves passed the US EPA Method 537 criteria ($r^2 \geq 0.9900$). Figure 2 shows the calibration curves for all compounds. The %RSD for replicate injections are shown in Table 1; all were <20%.

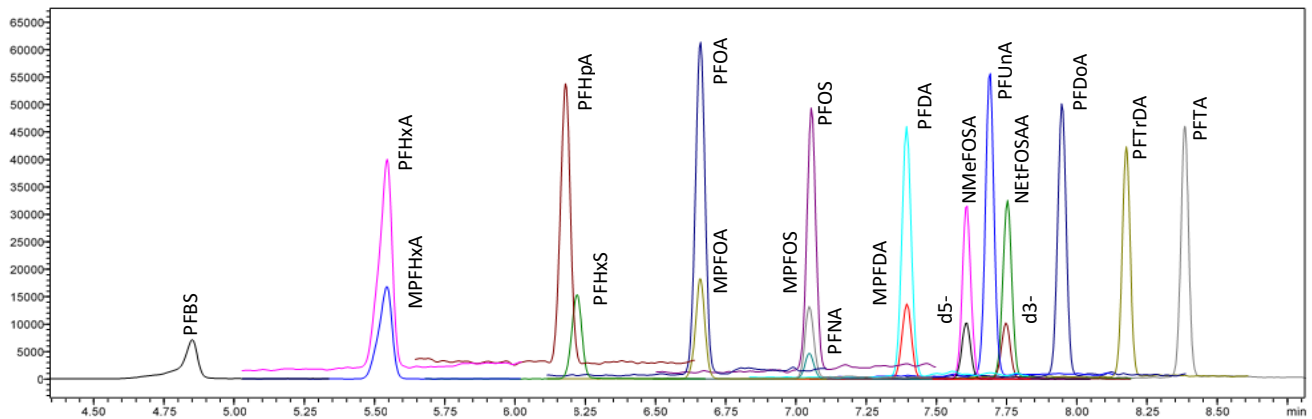


Figure 1: A representative chromatogram of the highest calibration point (200 ng/L) showing separation of all PFCs listed in US EPA Method 537

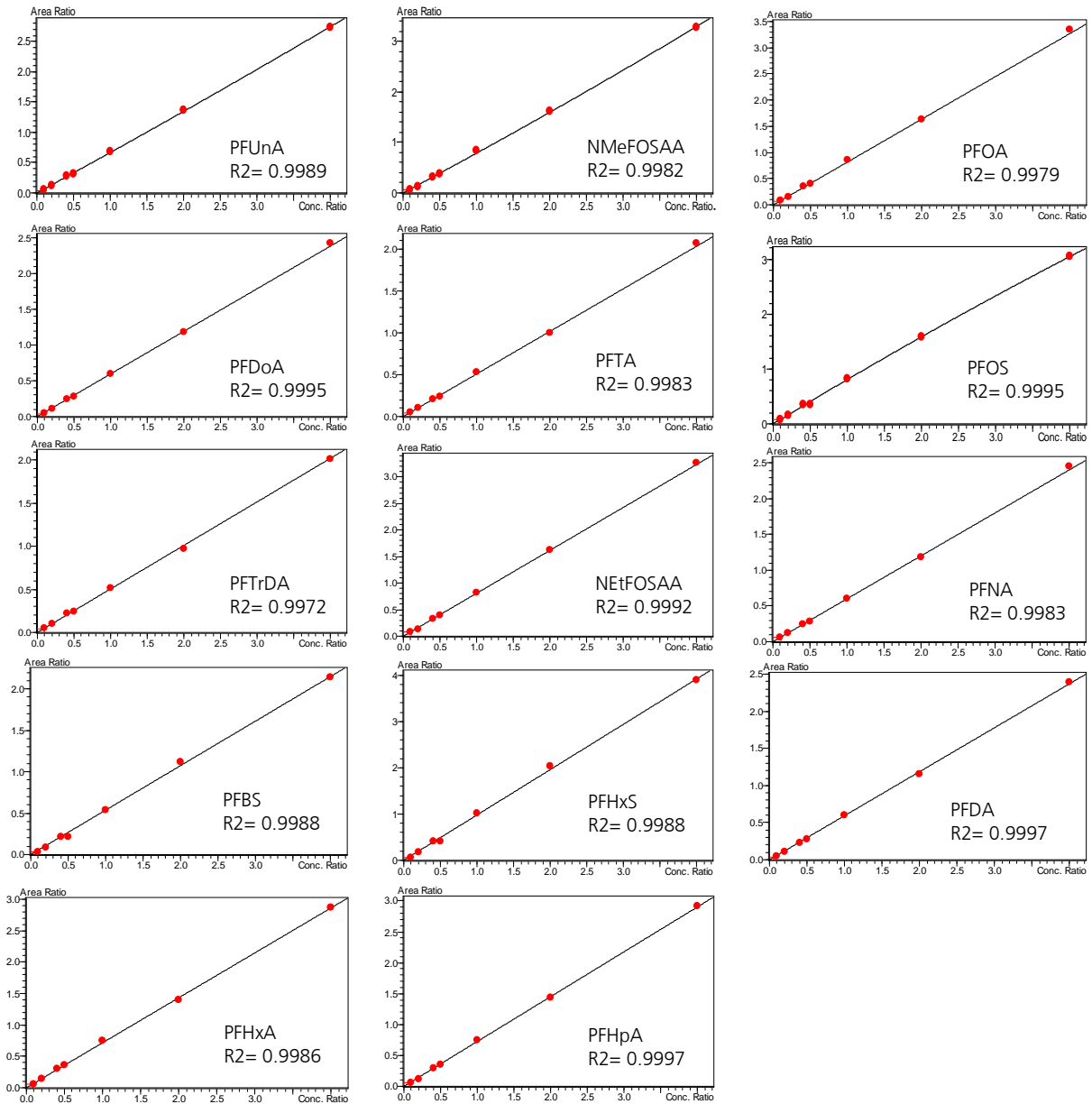


Figure 2: Calibration curves for all compounds listed in EPA Method 537

Continuing calibration verification (CCV) standards were analyzed periodically as specified in US EPA Method 537. The CCV concentrations were calculated based on the initial calibration, and

recoveries were between 70 to 130%, meeting section 10.2.7 calibration acceptance criteria. Table 1 shows the statistical results for the initial calibration curves and three representative CCVs.

7 Point Calibration Curve (n=7)									
5 - 200 ng/L				Low CCV 10ng/L		Mid CCV 50 ng/L		High CCV 100 ng/L	
Compound	RT	R ²	%RSD	Conc	%RSD	Conc	%RSD	Conc	%RSD
PFBS	4.846	0.9988	17.1	11.6	13.8	56.6	7.07	113	8.35
PFHxA	5.541	0.9986	10.0	11.8	7.31	58.9	1.54	116	0.505
PFHpA	6.178	0.9997	12.2	12.5	1.81	56.4	2.31	117	2.64
PFHxS	6.219	0.9988	15.5	11.8	2.61	60.3	6.40	114	4.98
PFOA	6.659	0.9979	8.27	12.3	2.16	58.8	4.19	119	2.49
PFOS	7.048	0.9995	13.5	10.6	10.8	60.0	4.10	114	6.35
PFNA	7.055	0.9998	12.0	11.3	11.3	57.9	6.29	115	3.71
PFDA	7.392	0.9997	10.7	11.5	1.32	58.3	5.32	114	2.29
NMeFOSAA	7.606	0.9982	13.8	12.3	4.70	58.8	2.46	119	6.42
PFUnA	7.687	0.9989	10.5	11.9	8.41	55.2	5.50	117	2.10
NEtFOSAA	7.751	0.9992	11.3	11.6	11.9	54.3	9.06	117	3.55
PFDoA	7.947	0.9995	12.5	11.9	1.44	58.6	8.52	115	4.49
PFTTrDA	8.177	0.9972	6.77	12.5	2.11	56.6	8.13	112	1.19
PFTA	8.385	0.9983	5.81	12.8	0.653	58.1	6.68	116	1.09

Table 1: Statistical results from the Initial Calibration and three representative CCVs

Method Detection Limit Study

A Method Detection Limit (MDL) study was conducted by analyzing 10 replicates at 5 ng/L for all compounds except PFOS and PFHpA, which were at 10 ng/L. The Method Detection Limits (MDL) were determined using 40 CFR Part 136 Appendix B. All MDLs significantly exceeded the criteria established

in the US EPA Method 537. Table 2 lists the MDL study results. It should be noted that these MDLs were calculated from direct injections at the concentrations listed without the benefit of sample preconcentration, nor did this study include the added variability of SPE.

Minimum Reporting Level (ng/L) n=10							
Compound	Ret. Time	MRL (ng/L)	MDL (ng/L)	Conc.	Accuracy[%]	%Dev	%RSD
PFBS	4.769	5	1.93	5.34	106.9	10.4	11.1
PFHxA	5.456	5	2.27	5.02	100.3	12.3	13.9
PFHpA	6.091	10	2.50	12.0	119.7	19.7	6.44
PFHxS	6.136	5	1.93	5.06	101.2	9.83	11.7
PFOA	6.574	5	1.52	5.16	103.3	8.41	9.04
PFOS	6.964	10	2.65	8.04	80.3	19.7	10.2
PFNA	6.971	5	1.59	5.68	113.6	15.3	8.59
PFDA	7.312	5	1.44	5.25	104.9	8.02	8.47
NMeFOSAA	7.525	5	1.79	4.85	96.9	8.61	11.4
PFUnA	7.611	5	1.90	4.71	94.2	10.9	12.4
NEtFOSAA	7.673	5	1.36	4.93	98.7	5.28	8.51
PFDoA	7.876	5	1.68	4.55	90.9	11.1	11.3
PFTTrDA	8.111	5	2.36	4.99	99.8	11.6	14.6
PFTA	8.323	5	1.69	5.45	109.0	12.8	9.52

Table 2: Method Detection Limit (MDL) study results

Precision and Accuracy Study

A Precision and Accuracy (P&A) study was conducted to assess the performance of the system. Eight replicates of the 50 ng/L standard were analyzed using the operating conditions developed for the LCMS-8060. Table 3 lists the results of the P&A study.

Internal standard response remained stable during the entire study at $\leq 7.3\%$. Surrogate recoveries fell within the 70 – 130 % method criteria for all analyses. IS and SUR results from a representative 12-hour sequence are shown in Figures 3 and 4, respectively. Since background contamination is of great concern when analyzing PFCs, blank injections were analyzed regularly. Figure 5 shows a representative bank sample overlaid with a 10 ppt PFOA sample.

Precision & Accuracy at 50ng/L (n=8)			
Compound	Mean Concentration (ng/L)	% Recovery	% RSD
PFBS	58.5	117.1	6.68
PFHxA	56.2	112.5	7.43
PFHpA	58.0	116.0	4.90
PFHxS	61.9	123.7	3.63
PFOA	54.5	109.1	7.67
PFOS	52.4	104.8	9.76
PFNA	55.0	110.1	7.71
PFDA	57.6	115.2	6.27
NMeFOSAA	55.6	111.1	4.31
PFUnA	53.2	106.4	7.72
NEtFOSAA	56.7	113.4	4.23
PFDoA	51.3	102.6	7.21
PFTTrDA	52.9	105.8	10.0
PFTA	57.5	115.0	7.41

Table 3: Precision and Accuracy (P&A) study results

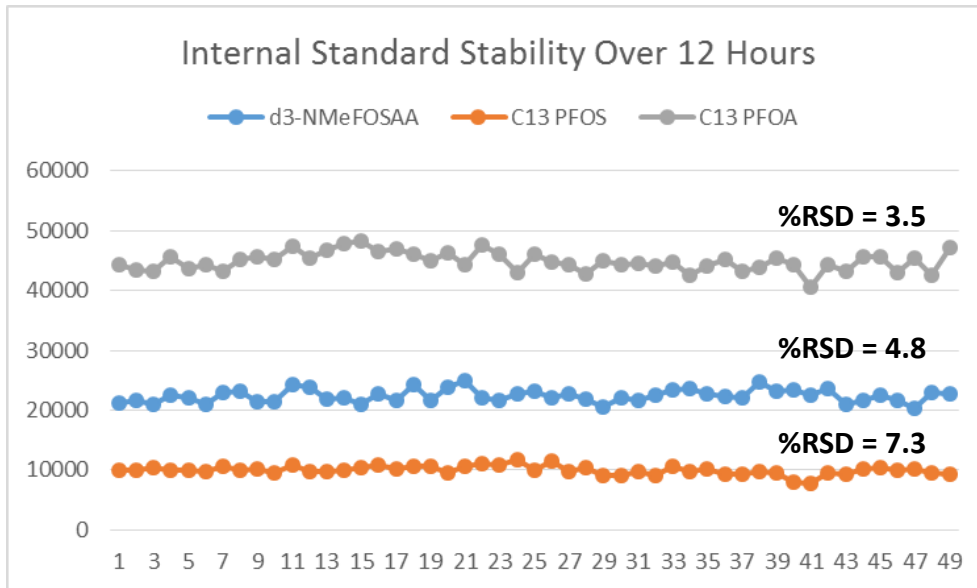


Figure 3: Internal Standard response over a representative 12-hour period

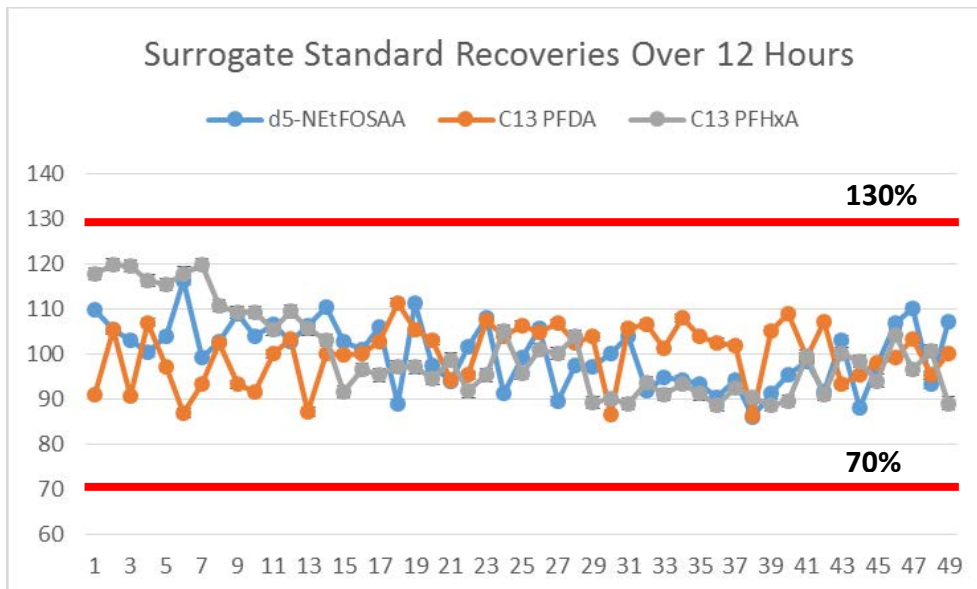


Figure 4: Surrogate Standard recoveries over a representative 12-hour period

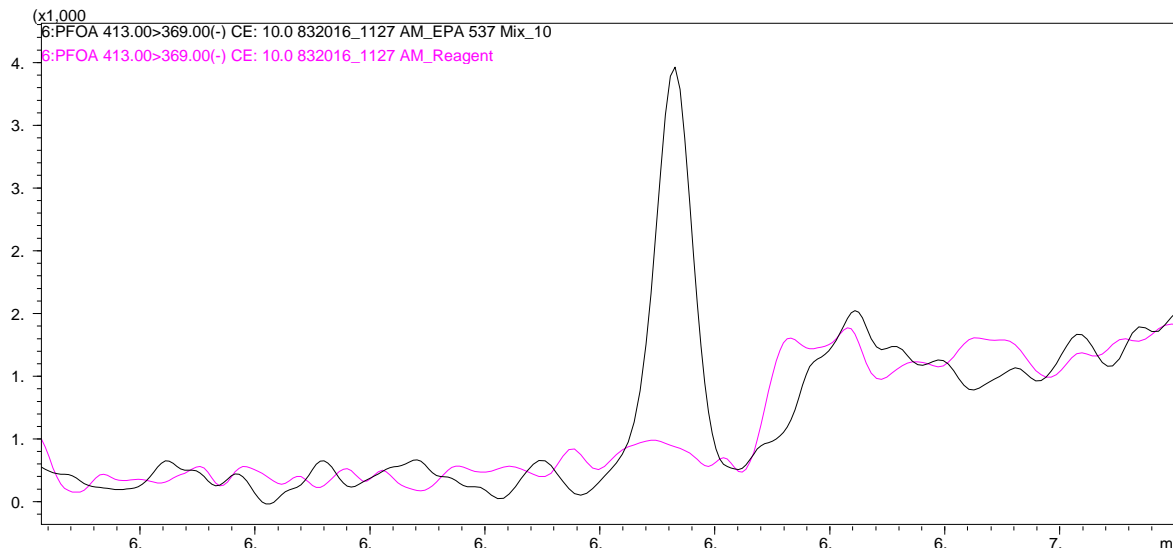


Figure 5: Representative chromatograms (A) 10ppt PFOA injection (black trace), and (B) Blank injection (pink trace)

■ Summary and Conclusions

The Shimadzu LCMS-8060 exceeds performance criteria specified for EPA Method 537. Because of the high-sensitivity performance of the LCMS-8060, it is recommended for use for methods allowing direct injection of PFCs.

■ References

1. <https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos>
2. <https://www.epa.gov/dwucmr/learn-about-unregulated-contaminant-monitoring-rule>
3. <https://www.epa.gov/dwucmr/data-summary-third-unregulated-contaminant-monitoring-rule>

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LCMS-8050



LCMS-8060



LCMS-2020



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