Date	Report No.	Prepared By	
03/14/2017	SSI-LCMS-085	J. Edwardsen	

LCMS-8060 Evaluation Report

Analysis of Perfluorinated Compounds (PFC's) in Water Samples Following DOD/DOE Requirements Using the Shimadzu LCMS-8060

Liquid Chromatograph Mass Spectrometer

LCMS-8060

PFC Analysis in Water

Summary:

Quantitative analysis of Perfluorinated Compounds (PFC's) by US DOD/DOE QSM v5.1 with and without the use of solid phase extraction for sample preparation was conducted using the LCMS-8060 triple quadrupole mass spectrometer.

Background:

Environmental contamination has been regulated since the US EPA was established in 1970. Recently, the US DOD and DOE have developed and published requirements for the analysis of different environmental pollutants using triple quadrupole liquid chromatography mass spectrometry (LCMS) instrumentation. Because of a renewed interest in the analysis of Perfluorinated Compounds (PFC's) in water, the DOD/DOE QSM 5.1 has a section specifically used for the analysis of PFC's in drinking water or groundwater.

US DOD/DOE QSM v5.1 requires the use of solid phase extraction (SPE) for sample preparation in order to meet the detection limits stated in the method but by using the Shimadzu LCMS-8060 the analysis of PFC's is possible by direct injection or with the use of SPE.

Method:

This study was conducted following the guidelines established in US DOD/DOE QSM v5.1 using the Shimadzu LCMS-8060 located at Empirical Laboratories in Tennessee. Direct injection along with SPE sample preparation/cleanup were investigated during this study.

Utilizing the heated ESI probe in negative mode, quantifier and qualifier MRM transitions were fully optimized by Flow Injection Analysis (FIA) to enhance sensitivity for all PFC analytes, surrogate standards, and internal standards as defined in US DOD/DOE QSM v5.1. Following MRM optimization, a 10 minute chromatographic method with near baseline resolution was developed using a Restek Raptor ARC-C18 2.7µ analytical column as seen in in the chromatogram in Figure 1.

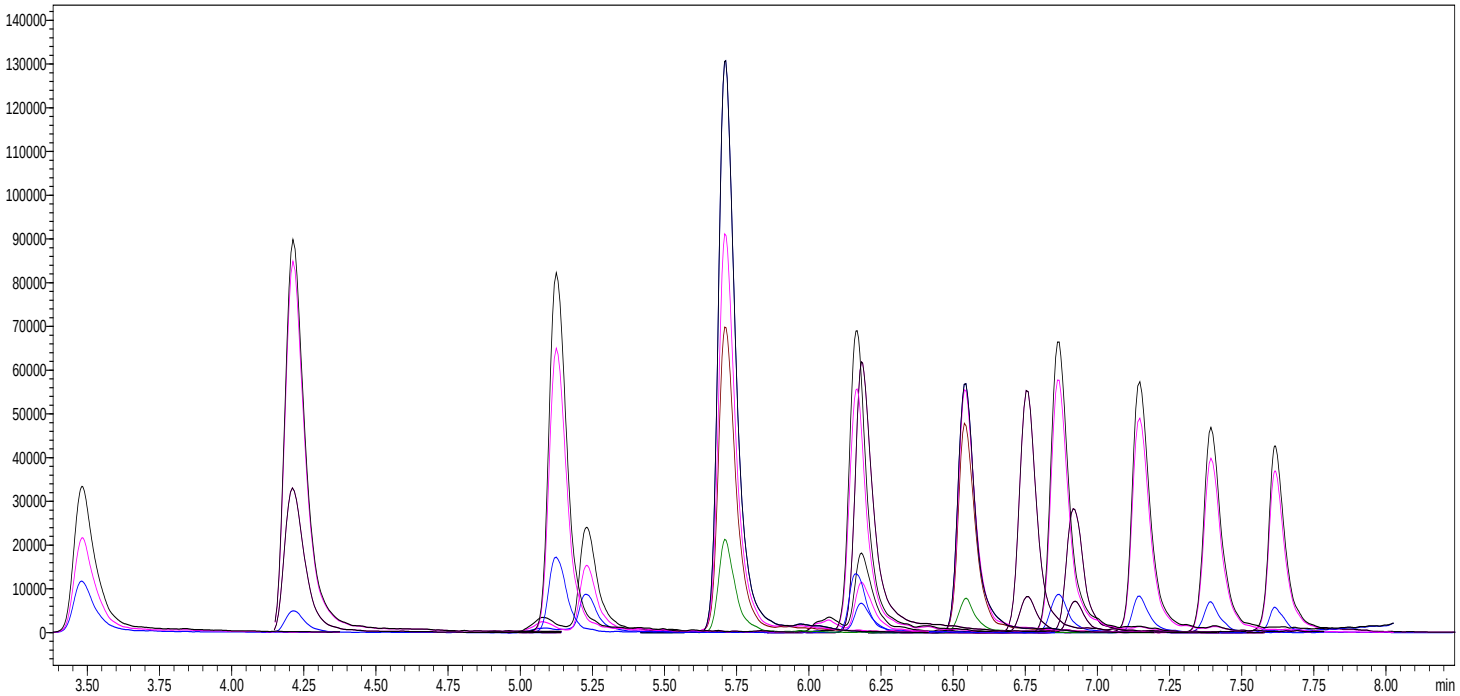

Figure 1: A representative chromatogram of a middle calibration point (200 ng/L) showing separation of all PFC's found in US DOD/DOE QSM v5.1.

Results and Discussion: *All data was obtained at Empirical Laboratories, TN.*

ICV & CCV

A series of ten initial calibration standards across the range of 20 to 2000 ng/L (parts-per-trillion, ppt) were prepared. The two internal standards (IS) were held constant at 500 ng/L, one internal standard was held at 2000 ng/L while the three surrogate standards (SUR) were varied in concentration in all samples analyzed.

The calibration curve was evaluated using both correlation coefficient (R^2) from a linear regression, and using the percent relative standard deviation (% RSD) for each data point in the curve. The calibration curve was evaluated and passed the US DOD/DOE QSM v5.1 criteria (% RSD < 20%, $R^2 \geq 0.9900$) for all compounds being analyzed. Figure 2 shows the calibration curves for all compounds.

Target Analytes

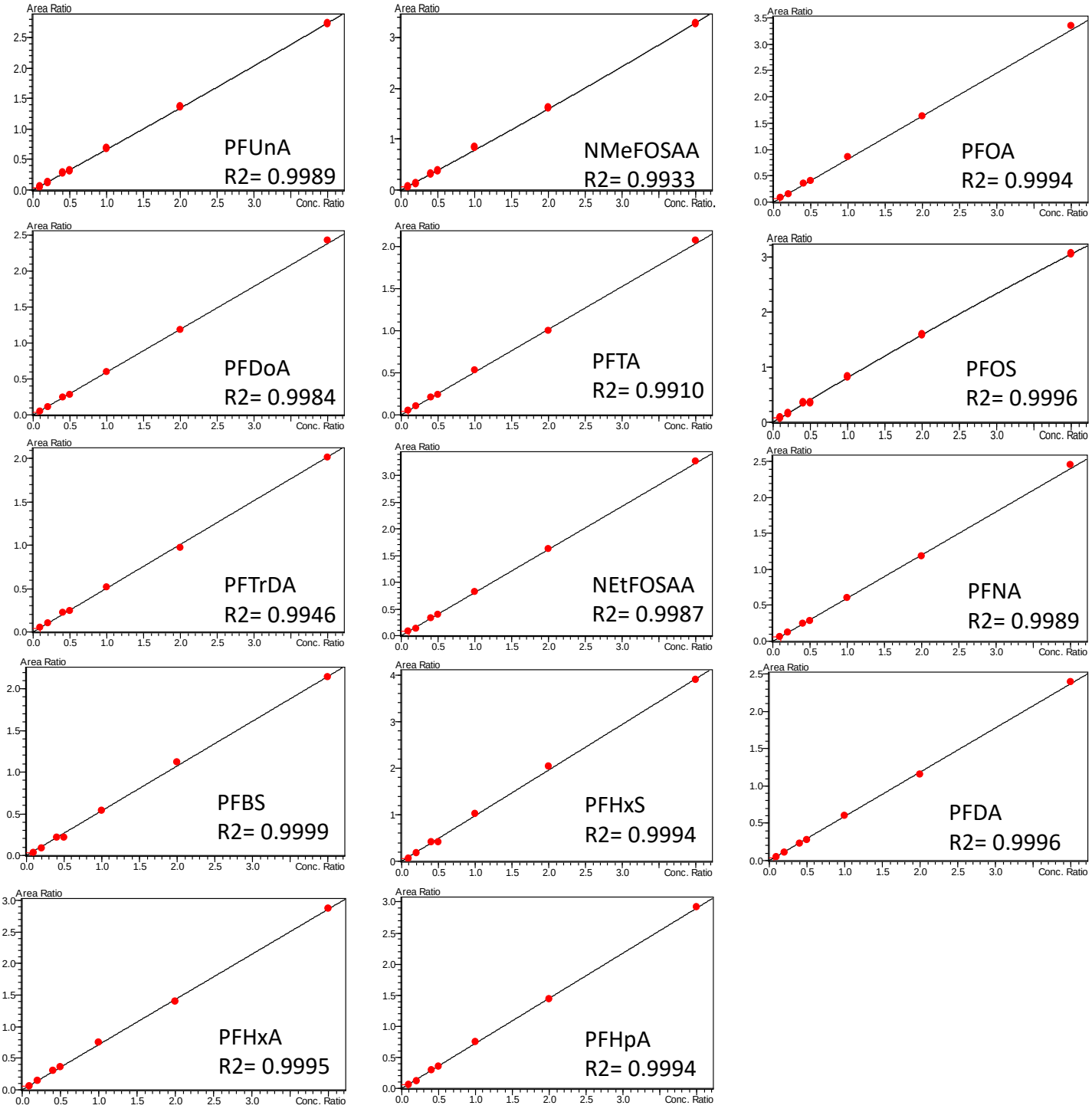

Figure 2: Calibration curves for all target compounds contained in US DOD/DOE QSM v5.1

Surrogate Internal Standards

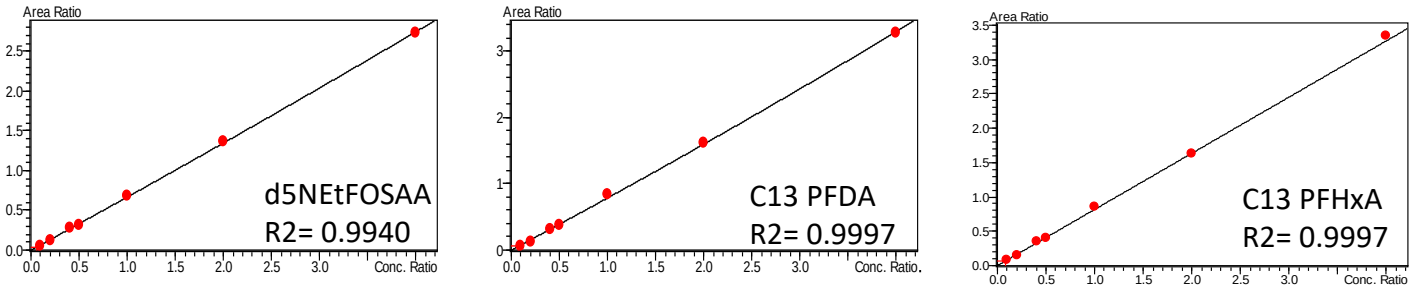

Figure 3: Calibration curves for all surrogate compounds in US DOD/DOE QSM v5.1

Continuing calibration verification (CCV) standards with a concentration of 5 ng/L for all compounds except PFOS and PFHpA (which contained a concentration of 10 ng/L) were analyzed periodically throughout the project as specified in US EPA Method 537. The CCV concentrations were calculated based on one of the calibration curves, and recoveries were between the allowable ranges of 70 to 130%). Complete statistical results for the initial calibration curve and three representative CCVs analyzed during the project are shown in Table 1.

10 Point Calibration Curve0.99									
20 - 2000 ng/L				Low CCV 20ng/L (n=10)		Mid CCV 250 ng/L (n=10)		High CCV 750 ng/L (n=10)	
Compound	RT	R^2	%RSD	Conc	%RSD	Conc	%RSD	Conc	%RSD
PFBS	3.470	0.9999	2.98	19.912	6.24	235.659	4.21	761.868	4.34
PFHxA	4.224	0.9995	3.15	19.072	6.27	212.897	8.70	677.559	6.07
PFHpA	5.135	0.9994	3.44	21.750	5.86	250.011	7.74	752.27	3.89
PFHxS	5.238	0.9994	3.65	21.982	8.61	259.166	6.06	798.456	4.62
PFOA	5.719	0.9994	5.64	23.490	2.89	265.206	1.52	802.025	1.18
PFOS	6.191	0.9996	6.45	25.882	11.21	295.406	2.98	888.054	1.72
PFNA	6.172	0.9989	7.07	22.151	10.60	286.489	7.46	851.293	2.63
PFDA	6.547	0.9996	3.78	21.017	10.02	260.657	8.08	776.626	2.28
NMeFOSAA	6.765	0.9933	12.22	16.531	10.76	272.492	1.85	862.353	3.53
PFUnA	6.871	0.9989	6.20	23.066	8.51	307.695	6.18	938.296	3.23
NEtFOSAA	6.925	0.9987	14.51	14.322	10.60	235.708	4.09	720.423	3.63
PFDoA	7.150	0.9984	12.68	18.773	12.09	258.837	8.42	808.966	5.22
PFTrDA	7.397	0.9946	6.99	14.527	12.34	245.979	8.38	823.504	4.70
PFTA	7.617	0.9910	9.69	17.873	10.85	214.582	7.17	752.596	5.12

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 replicate aliquots each at a 20 ng/L concentration for all compounds. The MDLs were calculated using the procedure outlined in the EPA Document #815-R-05-006, and all MDLs met the criteria established in US DOD/DOE QSM v5.1. Table 2 lists the details of the MDL study results.

Minimum Reporting Level (ng/L) n=10						
Compound	**Ret. Time**	**MRL (ng/L)**	**MDL (ng/L)**	**Conc.**	**Accuracy[%]**	**%RSD**
PFBS	3.470	20	5.39	23.788	118.9	4.63
PFHxA	4.224	20	2.03	20.905	104.5	7.47
PFHpA	5.135	20	2.77	21.547	107.7	4.33
PFHxS	5.238	20	6.23	22.109	110.5	5.20
PFOA	5.719	20	3.30	22.248	111.2	6.06
PFOS	6.191	20	13.49	23.170	115.9	5.43
PFNA	6.172	20	5.00	21.549	107.7	10.31
PFDA	6.547	20	3.57	18.736	93.7	8.31
NMeFOSAA	6.765	20	4.44	16.622	83.1	8.35
PFUnA	6.871	20	4.58	21.438	107.2	6.58
NEtFOSAA	6.925	20	4.08	13.645	70.0	16.88
PFDoA	7.150	20	4.46	15.500	77.5	6.73
PFTrDA	7.397	20	3.49	14.140	70.7	9.00
PFTA	7.617	20	2.45	11.795	70.1	8.14

Table 2: Method Detection Limit (MDL) study results.

Precision and Accuracy Study

A Precision and Accuracy (P&A) study was conducted to gauge the expected performance of the method. Ten replicate aliquots each of the 250 ng/L standard was analyzed using the operating conditions described in US DOD/DOE QSM v5.1. Table 3 lists the detailed results of the P&A study, reporting the average concentration for each compound (n = 10), the percent recovery, and the %RSD for all compounds.

Internal standard response remained stable during the entire study and Surrogate recoveries fell within the 70 – 130 % method criteria for all analyses.

Precision & Accuracy at 250ng/L (n=10)			
Compound	**Mean Concentration (ng/L)**	**% Recovery**	**% RSD**
PFBS	277.982	111.2	3.00
PFHxA	254.284	91.7	5.53
PFHpA	229.297	101.7	2.50
PFHxS	275.786	110.3	1.54
PFOA	264.984	106.0	1.54
PFOS	289.224	115.7	4.61
PFNA	281.009	112.4	1.54
PFDA	252.370	100.9	3.03
NMeFOSAA	280.211	112.1	2.50
PFUnA	295.719	118.3	2.20
NEtFOSAA	235.695	94.3	4.40
PFDoA	248.117	99.2	2.60
PFTrDA	236.412	94.6	2.09
PFTA	217.949	87.2	2.90

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

Summary and Conclusions

The Shimadzu LCMS-8060 and analytical conditions shown in this application note have demonstrated to provide outstanding results for US DOD/DOE QSM v5.1, meeting or exceeding all existing method criteria. Because of the high sensitivity performance of the LCMS-8060, it has been demonstrated that the analysis of water samples for PFCs is possible without SPE cleanup step. Calibration curves with varying ranges can be established to meet analytical needs. MDL's are below the required MRL's as cited in the method, some compounds MRL's are even lower than established in US DOD/DOE QSM v5.1. A high level of precision and accuracy was demonstrated.

Shimadzu Scientific Instruments would like to thank its collaborator, Empirical Laboratories, who worked to develop the analytical conditions that made this application note possible.

Founded in 1875, Shimadzu Corporation, a leader in the development of advanced technologies, has a distinguished history of innovation built on the foundation of contributing to society through science and technology. We maintain a global network of sales, service, technical support and applications centers on six continents, and have established long-term relationships with a host of highly trained distributors located in over 100 countries. For information about Shimadzu, and to contact your local office, please visit our Web site at www.shimadzu.com

SHIMADZU

SHIMADZU SCIENTIFIC INSTRUMENTS, INC. Applications Laboratory
7102 Riverwood Drive, Columbia, MD 21045
Phone: 800-477-1227 Fax: 410-381-1222
URL http://www.ssi.shimadzu.com

Empirical Laboratories, LLC

Empirical Laboratories, LLC
621 Mainstream Drive, Suite 270
Nashville, TN 37228
http://empirlabs.com