AR226-1934

Final Report

Analysis of PFOS and PFOA in Aqueous Samples
3M Dyneon, Oakdale Minnesota

Laboratory Request Number: E05-0007

Method Requirement: 3M Method ETS-8-154.1 (modified)

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Analytical Report E05-0007

Oakdale Dyneon FC Grab Samples
January 20, 2005

1 Introduction/Summary

Water samples were collected on January 4, 2005, from various locations at the Dyneon Oakdale facility and analyzed for perfluorooctanoate (PFOA, $C_7F_{15}COO^-$) and perfluorooctane sulfonate (PFOS, $C_8F_{17}SO_3^-$). George Millet at Dyneon escorted the Pace Analytical Services field analyst at the site. Millet provided a map of the facility and determined that four locations should be sampled that are representative of the drinking water sites at the facility.

Professional services personnel at the 3M Environmental laboratory prepared sample containers under the direction of Kent Lindstrom. Sample containers for each sampling location included a field sample, field sample duplicate, low field spike (0.05 ng/mL, ppb) and high field spike (1.0 ng/mL). Each empty container was marked with a "fill to here" line at 200 mL and was fortified with a surrogate spike or an appropriate matrix spike solution containing the surrogate, PFOA, and PFOS prior to being sent to the field for sample collection.

Table 1. Sample Results Summary.

Sample Identification	**PFOA Concentration PPB (ng/mL)*	**PFOS Concentration PPB (ng/mL)*
E05-0007-77781 Reception area rest room	0.75	0.86
E05-0007-77782 Reception area rest room Dup	0.66	0.86
E05-0007-77785 Ctr office rest rm ftn	0.18	0.14
E05-0007-77786 Ctr office rest rm ftn Dup	0.19	0.16
E05-0007-77789 Break room sink	0.14	0.18
E05-0007-77790 Break room sink Dup	0.14	0.15
E05-0007-77793 Utility room janitor sink	0.67	0.84
E05-0007-77794 Utility room janitor sink Dup	0.71	0.88

* Based on the analytical results of the surrogate, field matrix spikes, field duplicates, trip blank spikes, and laboratory control spikes, the analytical accuracy of the reported results is ±30%. The lower limit of quantitation (LOQ) for the samples is 0.025 ng/mL.

2 Methods - Analytical and Preparatory

2.1 Sample Collection

Samples were collected in pre-rinsed Nalgene™ (low-density polyethylene) bottles prepared at the 3M Environmental Laboratory. Prior to sample collection, all bottles were spiked in the laboratory with a known volume of either a surrogate solution or an appropriate matrix spiking solution containing the analytes of interest (PFOA and PFOS) and the surrogate. Table 2 below details the samples collected and spikes added to each bottle.

Table 2. Sample Collection and Spike Information.

Sample ID	Sample Description	Nominal Final Volume Collected (mL)	Volume of Spike Solution (mL)	Spike Solution Description	Final Nominal Spike Concentration (ng/mL)		
					PFOA [1,2 ^{13}C]	PFOA	PFOS
E05-0007-77781	Reception area rest room	200	1	Solution A	0.1	NA	NA
E05-0007-77782	Reception area rest room Dup	200	1	Solution A	0.1	NA	NA
E05-0007-77783	Reception area rest room Low Spike	200	1	Solution B	0.05	0.05	0.05
E05-0007-77784	Reception area rest room High Spike	200	1	Solution C	1.0	1.0	1.0
E05-0007-77785	Ctr office rest rm ftn	200	1	Solution A	0.1	NA	NA
E05-0007-77786	Ctr office rest rm ftn Dup	200	1	Solution A	0.1	NA	NA
E05-0007-77787	Ctr office rest rm ftn Low Spike	200	1	Solution B	0.05	0.05	0.05
E05-0007-77788	Ctr office rest rm ftn High Spike	200	1	Solution C	1.0	1.0	1.0
E05-0007-77789	Break room sink	200	1	Solution A	0.1	NA	NA
E05-0007-77790	Break room sink Dup	200	1	Solution A	0.1	NA	NA
E05-0007-77791	Break room sink Low Spike	200	1	Solution B	0.05	0.05	0.05
E05-0007-77792	Break room sink High Spike	200	1	Solution C	1.0	1.0	1.0
E05-0007-77793	Utility room janitor sink	200	1	Solution A	0.1	NA	NA
E05-0007-77794	Utility room janitor sink Dup	200	1	Solution A	0.1	NA	NA
E05-0007-77795	Utility room janitor sink Low spike	200	1	Solution B	0.05	0.05	0.05
E05-0007-77796	Utility room janitor sink High Spike	200	1	Solution C	1.0	1.0	1.0
E05-0007-77797	Field blank	200	1	Solution A	0.1	NA	NA
E05-0007-77798	Field blank Low Spike	200	1	Solution B	0.05	0.05	0.05
E05-0007-77799	Field blank High Spike	200	1	Solution C	1.0	1.0	1.0

Solution A = 20 ng/mL (nominal) PFOA [1,2 ^{13}C] Surrogate
Solution B = 10 ng/mL (nominal) PFOS, PFOA, and) PFOA [1,2 ^{13}C] Surrogate
Solution C = 200 ng/mL (nominal) PFOS, PFOA, and) PFOA [1,2 ^{13}C] Surrogate

2.2 Extraction

All samples, calibration standards, and associated quality control samples were extracted using a modified procedure of ETS-8-154.1 "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates in Water by Solid Phase Extractions and High Performance Liquid Chromatography/Mass Spectrometry". Briefly, approximately eighty mL of sample were loaded onto a pre-conditioned Waters C18 solid phase extraction (SPE) cartridge (Sep-Pak, 0.5g, 3cc) using a vacuum manifold. The loaded SPE cartridges were then transferred to a Zymark Rapid Trace Automated SPE System where they were then eluted with 2 mL of methanol using positive pressure. This extraction procedure concentrates the samples by a factor of forty. (Initial volume = 80 mL, final volume = 2 mL).

2.3 Analysis

All extracts were analyzed for PFOA, PFOS, and PFOA [1,2 ^{13}C] using high performance liquid chromatography/ tandem mass spectrometry (HPLC/MS/MS). Pertinent instrument parameters, the liquid chromatography gradient program, and the specific mass transitions analyzed are described in the tables below.

The analytical guard column is utilized to chromatographically separate instrument-associated background from the analytes of interest present in the injected sample. The combined use of the guard column, analytical column and liquid chromatography gradient program elute background analytes as one peak approximately 0.4 minutes after the analyte present in the injected sample. Isomers of compounds in samples elute in two or more peaks for which areas are summed for quantification.

Table 3. Instrument Parameters

Liquid Chromatograph	Agilent 1100
Guard column	Betasil C18 2X50, 5 µm
Analytical column	Betasil C18 (2.1 mm X 100 mm), 5 µm
Injection Volume	10 µL
Mass Spectrometer	Applied Biosystems API 4000
Electrode	Z-spray
Ion Source	Turbo Spray
Polarity	Negative

Table 4. Liquid Chromatography Gradient Program

Step Number	*Total Time (min)*	*Flow Rate (µL/min)*	*Percent A (2 mM ammonium acetate)*	*Percent B (Methanol)*
0	0	300	80.0	20.0
1	1.0	300	80.0	20.0
2	14.5	300	10.0	90.0
3	15.5	300	10.0	90.0
4	16.5	300	80.0	20.0
5	20.0	300	80.0	20.0

Table 5. Mass Transitions

Analyte	*Mass Transition Q1/Q3*	*Dwell Time (msec)*
*PFOA	413/369	150
	413/219	150
	413/169	150
*PFOS	499/99	150
	499/130	150
	499/80	150
PFOA [1,2 ^{13}C]	415/370	150

*Only the 413/369 and 499/99 transitions were used to quantify PFOA and PFOS, respectively. Other transitions were collected for confirmatory purposes only.

3 Data Analysis

3.1 Calibration

Calibration standards were prepared by spiking known amounts of stock solutions containing PFOA, PFOS, and PFOA [1,2 ^{13}C] into 80 mL of ASTM type I water. Each spiked water standard was then extracted in the same manner as the collected samples. A total of eight spiked standards ranging from 0.025 ng/mL to 5 ng/mL (nominal) were prepared. The 5 ng/mL curve point was deactivated for PFOA and the PFOA [1,2 ^{13}C] surrogate in order to meet accuracy criteria. The calibrated range bracketing all sample results was 0.025 ng/mL to 2.5 ng/L for PFOA and the PFOA [1,2 ^{13}C] surrogate and 0.025 to 5 ng/L for PFOS. A quadratic, 1/x weighted, calibration curve was used to fit the data for each analyte. The data was not forced through zero during the fitting process. Calculating the standard concentration using the peak area counts and the resultant calibration curve confirmed accuracy of each curve point. Each extracted calibration standard used to generate the final calibration curve met the method calibration accuracy requirement of ±25%. Coefficients of determination (r^2) were greater than 0.997 for all analytes.

3.2 Limit of Quantitation (LOQ)

The LOQ for this analysis, as defined in ETS-8-154.1, is the lowest non-zero active calibration standard in the curve. Here, the LOQ is 0.025 ng/mL for all analytes.

3.3 System Suitability

The 1 ng/mL extracted-calibration standard was analyzed in triplicate at the beginning and end of the analytical sequence to demonstrate overall system suitability. For all analytes, the relative standard deviation (RSD) of the analyte peak area counts and the RSD of the peak retention times was less than 5% and 2%, respectively, which met method criteria.

3.4 Continuing Calibration

During the course of the analytical sequence, several continuing calibration verification samples (CCVs) were analyzed to confirm that the instrument response and the initial calibration curve was still in control. All CCVs, for all three analytes, produced recoveries within ±25%, which met method criteria.

3.5 Blanks

Three types of blanks were prepared and analyzed with the samples: method blanks, solvent blanks, and field/trip blanks. Each blank type is described below. Analyte peak area counts in all blank samples were less than half the area counts of the lowest calibration standard, which met method criteria for establishing the LOQ of 0.025 ng/mL.

3.5.1 Method Blanks

Several method blanks were prepared by loading 80 mL of ASTM Type I water onto a C18 SPE cartridge and eluting with 2 mL of methanol using the same extraction procedure as the samples. Method blanks were prepared to evaluate the levels of background contamination in the overall extraction process (glassware, SPE cartridges, etc.)

3.5.2 Solvent Blanks

Several methanol solvent blanks were analyzed to assess system contamination and/or instrument carryover.

3.5.3 Field/Trip Blanks

Prior to sample collection, one sample container was filled with 200 mL of ASTM Type I water, sealed, and shipped to the sample collection site along with the empty containers. This sample was analyzed as field/trip blank.

3.6 Lab Control Spikes (LCSs)

Low (0.1 ng/mL nominal concentration) and high (1.0 ng/mL nominal concentration) lab control spikes were prepared and analyzed in triplicate. LCSs were prepared by spiking known amounts of the analytes into 80 mL of ASTM Type I water to produce the desired concentration. The spiked water samples were extracted and analyzed in the same manner as the samples. All LCSs produced recoveries within the method acceptance criteria of ±25% for accuracy and ±15% RSD for precision. Table 6 summarizes the LCS recovery results.

Table 6. Lab Control Spike Results.

Description	*Spike Level*	*Percent Recovery*		
		PFOA	*PFOS*	*PFOA [1,2 ^{13}C]*
LCS 1	low (0.1 ng/mL)	103	106	103
LCS 2	low (0.1 ng/mL)	97.3	99.2	97.6
LCS 3	low (0.1 ng/mL)	99.0	99.3	98.8
Average ± %RSD		**99.8 ± 2.9%**	**102 ± 4.1%**	**99.9 ± 3.0%**
LCS 4	high (1.0 ng/mL)	94.0	101	90.7
LCS 5	high (1.0 ng/mL)	77.2	90.6	80.9
LCS 6	high (1.0 ng/mL)	91.8	100	94.6
Average ± %RSD		**87.7 ± 10%**	**97.5 ± 6.1 %**	**88.8 ± 8.0%**

$$\text{LCS Percent Recovery} = \frac{\text{Calculated Concentration}}{\text{Spike Concentration}} * 100\%$$

$$\text{LCS\% RSD} = \frac{\text{standard deviation LCS replicates}}{\text{average LCS recovery}} * 100\%$$

3.7 Surrogates

PFOA [1,2 ^{13}C] was added to all samples and sample spikes to evaluate overall method performance. PFOA [1,2 ^{13}C] recoveries in collected samples and sample spikes ranged from 69.0% to 95.6% with an average recovery of 79.0%. Analytical results are not corrected for these recoveries. Table 7 lists the surrogate recoveries.

3.8 Sample Spikes

A low (nominal concentration of 0.05 ng/mL) and a high (nominal concentration 1.0 ng/mL) field spike were collected at each sampling point. Endogenous levels of PFOA and PFOS were in some cases much higher than the low spike amount of 0.05 ng/mL and therefore not all low spike recoveries were reported. The PFOA [1,2 ^{13}C] surrogate meets criteria and therefore data quality is not impacted. Reported spike recoveries ranged from 73.8 to 116%. Actual spike concentrations may vary slightly depending of the accuracy of marking and adhering to the "fill to here" line on the bottle. It is estimated that this variability is less than 5% and therefore data are not corrected for actual collection volumes. Table 7 below lists the sample spike data and recoveries.

Table 7. Summary of Sample Spike Recoveries

Sample ID	PFOA		PFOS		PFOA [1,2 ^{13}C]
	Concentration PPB (ng/mL)	%Spike Recovery	Concentration PPB (ng/mL)	%Spike Recovery	%Surrogate Recovery
E05-0007-77781 Reception area rest room	0.75	NA	0.86	NA	77.4
E05-0007-77782 Reception area rest room Dup	0.66	NA	0.86	NA	78.0
E05-0007-77783 Reception area rest room Low Spike	0.72	*	0.83	*	76.7
E05-0007-77784 Reception area rest room High Spike	1.6	93.5	1.7	86.0	81.4
E05-0007-77785 Ctr office rest rm ftn	0.18	NA	0.14	NA	69.0***
E05-0007-77786 Ctr office rest rm ftn Dup	0.19	NA	0.16	NA	79.4
E05-0007-77787 Ctr office rest rm ftn Low Spike	0.22	81.0	0.21	116	82.0
E05-0007-77788 Ctr office rest rm ftn High Spike	**	**	**	**	**
E05-0007-77789 Break room sink	0.14	NA	0.18	NA	81.0
E05-0007-77790 Break room sink Dup	0.14	NA	0.15	NA	86.2
E05-0007-77791 Break room sink Low Spike	0.16	*	0.18	*	81.1
E05-0007-77792 Break room sink High Spike	0.86	73.8	1.1	94.3	77.6
E05-0007-77793 Utility room janitor sink	0.67	NA	0.84	NA	81.6
E05-0007-77794 Utility room janitor sink Dup	0.71	NA	0.88	NA	72.7
E05-0007-77795 Utility room janitor sink Low spike	0.74	*	0.85	*	72.6
E05-0007-77796 Utility room janitor sink High Spike	1.6	93.7	1.9	106	80.0
E05-0007-77797 Field blank	<0.025	NA	<0.025	NA	95.6
E05-0007-77798 Field blank Low Spike	0.042	85.4	0.042	83.8	79.0
E05-0007-77799 Field blank High Spike	0.77	79.0	0.83	83.5	71.4

*Spike recoveries not calculated. The spiked amounts relative to the sample levels were too low to consistently evaluate the spike recoveries. The surrogate recoveries and the High Spike recoveries document analytical accuracy.
**Sample spilled during extraction. No results available.
***This field sample container was inadvertently filled past the 200 mL "fill to here" line by approximately 10-15%, resulting in a more dilute surrogate concentration. Results for PFOA and PFOS are not impacted since a known volume is removed for analysis.

$$\text{Sample Spike Recovery} = \frac{(\text{Spiked Sample Concentration} - \text{Average Endogenous Concentration})}{\text{Spike Concentraton}} * 100\%$$

4 Conclusion

The analytical results reported here for the aqueous samples collected on January 4, 2005, at the Dyneon Oakdale facility meet the analytical precision and accuracy requirements of EHS Opns Laboratory method ETS-8-154.1. Results are deemed to be accurate to ±30%.

5 Data / Sample Retention

All hardcopy and electronic data will be archived according to 3M Environmental Laboratory standard operating procedures. In most cases, the entire volume of each sample was consumed during the course of sample preparation procedures. Where residual amounts remain, an insufficient volume exists for further sample preparation. The sample bottles will not retained.

6 Signatures

Kent Lindstrom, Technical Lead — Date: 01/21/05

Casey A. Howell, QAU Supervisor — Date: 1-21-05

William K. Reagen Ph.D., Environmental Laboratory Management — Date: 01/21/05