AR226-1935

Exygen™ RESEARCH
Precise Research.
Proven Results.

Analytical Report

3M Company

Analysis of PFOA and PFOS in Water Samples from Oakdale Municipality

E05-0074

Exygen Report No. L0004351

Testing Laboratory

Exygen Research
3058 Research Drive
State College, PA 16801

Requester

Gary A. Hohenstein
Environmental Manager, Special Projects
EHS Operations
3M Company
Building 42-2E-27
St. Paul, MN 55106

3058 Research Drive
State College, PA 16801, USA
T: 800.281.3219
F: 814.272.1019
exygen.com

42

1 Introduction

Results are reported for the analysis of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) in water samples received at Exygen as requested by Gary Hohenstein of 3M Company. The Exygen project number assigned to the samples is L0004351. Table I lists the target analytes quantitated for the samples.

Table I. Target Analytes for Quantitation

Parameter	Acronym	Formula
Perfluorooctanoic Acid	PFOA	$C_7F_{15}COOH$
Perfluorooctanesulfonate	PFOS	$C_8F_{17}SO_3^-$

2 Sample Receipt

Thirty-five samples were received at Exygen in 500 mL white plastic narrow-mouth bottles. At the request of 3M, all samples were analyzed. A copy of all sample log-in information is presented in Attachment C.

The samples were received on 01/26/05. The samples were shipped ambient via UPS. The samples were stored refrigerated from time of receipt until analysis.

3 Methods - Analytical and Preparatory

3.1 Water Sample Preparation

Solid phase extraction (SPE) was used to prepare the water samples for LC/MS/MS analysis. Forty milliliters of the water sample was transferred to a C_{18} SPE cartridge. The cartridge was washed with 5 mL of a 40% methanol: 60% water wash. The cartridge was eluted with 5 mL of 100% methanol. A portion of the extract was transferred to autosampler vials and analyzed using electrospray LC/MS/MS.

3.2 Sample Analysis by LC/MS/MS

In High Pressure Liquid Chromatography (HPLC), an aliquot of extract is injected and passed through a liquid-phase chromatographic column. Based on the affinity of the analyte for the stationary phase in the column relative to the liquid mobile phase, the analyte is retained for a characteristic amount of time. Following HPLC separation, mass spectrometry provides a rapid and accurate means for analyzing a wide range of organic compounds. Molecules are ionized, fragmented, and detected. The ions characteristic of the compounds are observed and quantitated against extracted standards.

An HP1100 system interfaced to an Applied Biosystems API 4000 was used to analyze the sample extracts for quantitation.

Isomer separation was obtained using a gradient elution through a Thermo Fluophase RP, 50 x 2.1 mm x 5µm column. The sum of the isomers is reported as a single value for each of the analytes.

The following gradient was performed:

Mobile Phase (A): 2mM Ammonium Acetate in Water
Mobile Phase (B): Methanol

Time	%A	%B
0.0	65	35
1.0	65	35
8.0	25	75
10.0	25	75
11.0	65	35
18.0	65	35

The following parameters were used for operation of the mass spectrometer:

Parameter	Setting
Ionization Mode	Electrospray
Polarity	Negative
Transitions Monitored	413->369 (PFOA), 499->80 (PFOS), 415->370 (^{13}C-PFOA)
Gas Temperature	350°C
Drying Gas (N2)	7.0 L/min

4 Analysis

4.1 Calibration

A 7-point calibration curve was analyzed initially and throughout the analytical sequence for PFOA, PFOS and ^{13}C PFOA. The calibration points were prepared at 0, 25, 50, 100, 250, 500, and 1000 ng/L (ppt) for LC/MS/MS analysis. Calibration standards are prepared using the same SPE procedure used for samples. The instrument response versus the concentration was plotted for each point. Using linear regression with 1/x weighting, the slope, y-intercept and coefficient of determination (r^2) were determined. A calibration curve is acceptable if $r^2 \geq 0.985$.

For the results reported here, calibration criteria were met. The calibration curves are included in the raw data in Attachment D.

4.2 Surrogates

^{13}C PFOA is used as a surrogate for the water samples. ^{13}C PFOA was added to the empty sample containers before the bottles were sent to the field for sampling. In the field, the bottles were filled to a volumetric fill line with the sample.

^{13}C PFOA recoveries can be found in Attachment B.

4.3 Laboratory Control Spikes

Laboratory control spikes in the analytical set were prepared by adding a known concentration of PFOA, ^{13}C-PFOA, and PFOS to laboratory reagents. Laboratory control spikes are used to assess method accuracy. The laboratory control spikes must show recoveries between 70-130% or the data is rejected. For the results reported here, the laboratory control spikes were within the acceptable range.

4.4 Field Matrix Spikes

A low (0.1 ng/mL) and high matrix spike (1.0 ng/mL) were prepared for every water sample in the field. Compounds were added to the empty sample containers before the bottles were sent to the field for sampling. Matrix spikes are used to assess method accuracy in the matrix. The matrix spikes should show recoveries between 70-130%. For the results reported here, the matrix spikes were within the acceptable range, except as noted in Section 6 of this report.

4.5 Sample Related Comments

All water samples were collected in duplicate. Duplicate sample results are reported along with the sample results in Attachment A.

5 Data Summary

Please see Attachment A for a detailed listing of the analytical results. The results are reported in parts per billion (ng/mL) for PFOA and PFOS.

6 Statement of Accuracy

Based on results of laboratory control spikes, field matrix spikes, and surrogate spikes, the analytical accuracy for PFOS and PFOA results is ± 30%, except for sample O-W2-208463 which is ± 50%. Laboratory control spikes, surrogate spikes and field matrix spikes showed recoveries within these ranges, with the following exceptions:

- The PFOA and PFOS recovery in O-W5-127287 Low Spike, O-W9-151575 Low Spike, and O-W8-572608 Low Spike could not be calculated because the inherent sample concentration in this sample was over 3 times greater than the spiking concentration.

- The PFOS recovery for sample O-W1-208462 Low Spike was 177%. The PFOS concentration in this sample is reported as NQ (Not Quantifiable), meaning that the measured concentration is between 0.025 ng/mL and the Limit of Quantitation (LOQ) that is 0.050 ng/mL.

- The PFOS recovery for sample O-W2-208463 Low Spike was 208%. The PFOS concentration for this sample is reported as NQ.

- The PFOS recoveries for samples O-W3-208454 Low Spike and Whispering Oaks Mobile Park High Spike were 134%. The PFOS concentrations for these samples are reported as ND, meaning that PFOS is not detected at or above 0.025 ng/mL.

- Samples O-W5-127287 Low Spike, O-W9-15175 Dup, O-W7-463534, O-W8-572608, and Whispering Oaks Mobile Home Park showed surrogate recoveries between 131% and 138%.

Specific sample recoveries are given in Attachment B.

7 *Data/Sample Retention*

Samples will be returned to 3M 60 days after final reporting. All electronic data is archived on retrievable media and hard copy reports are stored in data folders maintained by Exygen. Hardcopy data is stored for a minimum of five years. The client will be notified 30 days prior to the disposal of hardcopy data.

8 *Attachments*

7.1 Attachment A: Analytical Results

7.2 Attachment B: Spike Recovery Data

7.3 Attachment C: Chain of Custody Forms

7.4 Attachment D: Raw Analytical Data

9 *Signatures*

Karen Risha — 02/02/05

Karen Risha, Principal Investigator — Date

John M. Flaherty — 2/2/05

John M. Flaherty, Vice President — Date

SECTION A

Exygen™ RESEARCH
Precise Research.
Proven Results.

Analytical Report

Summary of PFOA and PFOS in Water Samples E05-0074

		Analyte Found (ng/mL)	
		C8 Acid PFOA	C8 Sulfonate PFOS
Exygen ID	Sample ID	Perfluorooctanoic Acid	Perfluorooctanesulfonate
L4351-1	O-W5-127287	0.821	1.12
L4351-2	O-W5-127287 Dup	0.736	1.01
L4351-5	O-W9-15175	0.825	0.583
L4351-6	O-W9-15175 Dup	0.892	0.653
L4351-9	O-W1-208462	0.0746	NQ
L4351-10	O-W1-208462 Dup	0.0790	0.0514
L4351-13	O-W2-208463	0.0773	NQ
L4351-14	O-W2-208463 Dup	0.0750	ND
L4351-17	O-W7-463534	0.285	0.276
L4351-18	O-W7-463534 Dup	0.274	0.269
L4351-21	O-W8-572608	0.668	1.02
L4351-22	O-W8-572608 Dup	0.647	0.977
L4351-25	O-W3-208454	ND	ND
L4351-26	O-W3-208454 Dup	ND	ND
L4351-29	Whispering OAKS Mobile Park	ND	ND
L4351-30	Whispering OAKS Mobile Park Dup	ND	ND
L4351-33	E05-0074 Trip Blank	ND	ND

ND = Not detected at or above 0.025 ng/mL.
NQ = Not quantifiable = Measured concentration between 0.025 ng/mL and the Limit of Quantitation (LOQ) which is 0.050 ng/mL.

3058 Research Drive
State College, PA 16801, USA
T: 814.272.1039
F: 814.231.1580
exygen.com

SECTION B

Exygen™ RESEARCH
Precise Research.
Proven Results.

Field Matrix Spike Recovery Summary for PFOA and PFOS in Water E05-0074

Sample Description	C8 Acid PFOA Amount Spiked (ng/mL)	C8 Acid PFOA Amt Found in Sample (ng/mL)	C8 Acid PFOA Amount Recovered (ng/mL)	C8 Acid PFOA Recovery (%)	C8 Sulfonate PFOS Amt Found in Sample (ng/mL)	C8 Sulfonate PFOS Amount Recovered (ng/mL)	C8 Sulfonate PFOS Recovery (%)
O-W5-127287 Low Spike (L4351-3, 0.1 ppb Spike)	0.1	0.821	0.971	*	1.12	1.34	*
O-W5-127287 High Spike (L4351-4, 1 ppb Spike)	1	0.821	1.86	104	1.12	1.98	86
O-W9-151575 Low Spike (L4351-7, 0.1 ppb Spike)	0.1	0.825	0.859	*	0.583	0.636	*
O-W9-151575 High Spike (L4351-8, 1 ppb Spike)	1	0.825	2.03	121	0.583	1.89	131
O-W1-208462 Low Spike (L4351-11, 0.1 ppb Spike)	0.1	0.0746	0.203	128	NQ	0.177	177
O-W1-208462 High Spike (L4351-12, 1 ppb Spike)	1	0.0746	1.22	115	NQ	1.29	129
O-W2-208463 Low Spike (L4351-15, 0.1 ppb Spike)	0.1	0.0773	0.225	148	NQ	0.208	208
O-W2-208463 High Spike (L4351-16, 1 ppb Spike)	1	0.0773	1.45	137	NQ	1.43	143
O-W7-463534 Low Spike (L4351-19, 0.1 ppb Spike)	0.1	0.285	0.403	118	0.276	0.398	122
O-W7-463534 High Spike (L4351-20, 1 ppb Spike)	1	0.285	1.48	120	0.276	1.57	129
O-W8-572608 Low Spike (L4351-23, 0.1 ppb Spike)	0.1	0.668	0.668	*	1.02	0.855	*
O-W8-572608 High Spike (L4351-24, 1 ppb Spike)	1	0.668	1.93	126	1.02	2.29	127
O-W3-208454 Low Spike (L4351-27, 0.1 ppb Spike)	0.1	ND	0.124	124	ND	0.134	134
O-W3-208454 High Spike (L4351-28, 1 ppb Spike)	1	ND	1.22	122	ND	1.28	128
Whispering OAKS Mobile Park Low Spike (L4351-31, 0.1 ppb Spike)	0.1	ND	0.0819	82	ND	0.0931	93
Whispering OAKS Mobile Park High Spike (L4351-32, 1 ppb Spike)	1	ND	1.23	123	ND	1.34	134
E05-0074 Trip Blank Low Spk (L4351-34, 0.1 ppb Spike)	0.1	ND	0.119	119	ND	0.130	130
E05-0074 Trip Blank High Spk (L4351-35, 1 ppb Spike)	1	ND	1.09	109	ND	1.30	130

*Sample residue exceeds the spiking level significantly; therefore, an accurate recovery value cannot be calculated
ND = Not detected at or above 0.025 ng/mL.
NQ = Not quantifiable = Measured concentration between 0.025 ng/mL and the Limit of Quantitation (LOQ) which is 0.050 ng/mL.

3058 Research Drive
State College, PA 16801, USA
T: 800.281.3219
F: 814.272.1019
exygen.com

Exygen™ RESEARCH
Precise Research.
Proven Results.

Surrogate Spike Recovery Summary for ^{13}C-PFOA in Water E05-0074

		^{13}C-PFOA		
Exygen ID	Sample Description	Amount Spiked (ng/mL)	Amount Recovered (ng/mL)	Recovery (%)
L4351-1	O-W5-127287	0.5	0.584	117
L4351-2	O-W5-127287 Dup	0.5	0.530	106
L4351-3	O-W5-127287 Low Spk	0.5	0.655	131
L4351-4	O-W5-127287 High Spk	0.5	0.537	107
L4351-5	O-W9-15175	0.5	0.608	122
L4351-6	O-W9-15175 Dup	0.5	0.674	135
L4351-7	O-W9-15175 Low Spk	0.5	0.512	102
L4351-8	O-W9-15175 High Spk	0.5	0.590	118
L4351-9	O-W1-208462	0.5	0.575	115
L4351-10	O-W1-208462 Dup	0.5	0.643	129
L4351-11	O-W1-208462 Low Spk	0.5	0.644	129
L4351-12	O-W1-208462 High Spk	0.5	0.587	117
L4351-13	O-W2-208463	0.5	0.559	112
L4351-14	O-W2-208463 Dup	0.5	0.519	104
L4351-15	O-W2-208463 Low Spk	0.5	0.735	147
L4351-16	O-W2-208463 High Spk	0.5	0.623	125
L4351-17	O-W7-463534	0.5	0.680	136
L4351-18	O-W7-463534 Dup	0.5	0.647	129
L4351-19	O-W7-463534 Low Spk	0.5	0.639	128
L4351-20	O-W7-463534 High Spk	0.5	0.591	118
L4351-21	O-W8-572608	0.5	0.692	138
L4351-22	O-W8-572608 Dup	0.5	0.567	113
L4351-23	O-W8-572608 Low Spk	0.5	0.515	103
L4351-24	O-W8-572608 High Spk	0.5	0.609	122
L4351-25	O-W3-208454	0.5	0.528	106
L4351-26	O-W3-208454 Dup	0.5	0.564	113
L4351-27	O-W3-208454 Low Spk	0.5	0.624	125
L4351-28	O-W3-208454 High Spk	0.5	0.592	118
L4351-29	Whispering OAKS Mobile Park	0.5	0.671	134
L4351-30	Whispering OAKS Mobile Park Dup	0.5	0.357	71
L4351-31	Whispering OAKS Mobile Park Low Spk	0.5	0.414	83
L4351-32	Whispering OAKS Mobile Park High Spk	0.5	0.617	123
L4351-33	E05-0074 Trip Blank	0.5	0.528	106
L4351-34	E05-0074 Trip Blank Low Spk	0.5	0.542	108
L4351-35	E05-0074 Trip Blank High Spk	0.5	0.531	106

3058 Research Drive
State College, PA 16801, USA
T: 800.281.3219
F: 814.272.1019
exygen.com