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Analytical Report

3M Company

Analysis of PFOA and PFOS in Water Samples from Oakdale Municipality

E04-0911

Exygen Report No. L0004145 Revised

Testing Laboratory

Exygen Research
3058 Research Drive
State College, PA 16801

Requester

Gary A. Hohenstein
Manager, Environmental Operations
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

1 Introduction

In this revised report, 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 report was revised to update the requester information and to make minor changes to the text of the report. Analytical results were not changed in this revision.

The Exygen project number assigned to the samples is L0004145. 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	$C_8F_{17}SO_3H$

2 Sample Receipt

Twenty-seven 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 A.

The samples were received on 12/28/04. 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 C.

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 and high matrix spike was 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 B.

5 Data Summary

Please see Attachment B 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%. 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 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-W7-463534 Low Spike was 48%.
- The PFOA recovery for sample O-W2-208463 Low Spike was 61%.

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

Paul Crosby for Karen Risha 1/17/05

Karen Risha, Principal Investigator Date

John M Flaherty 1/17/05

John M. Flaherty, Vice President Date

Section A

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Analytical Report

Summary of PFOA and PFOS in Water Samples E04-0911

Exygen ID	Sample ID	Analyte Found (ng/mL) C8 Acid PFOA Perfluorooctanoic Acid	C8 Sulfonate PFOS Perfluorooctanesulfonate
L4145-3	O-W1-208462	0.0891	0.0561
L4145-4	O-W1-208462 Dup	0.0965	0.0566
L4145-7	O-W2-208463	0.0764	NQ
L4145-8	O-W2-208463 Dup	0.0999	NQ
L4145-11	O-W5-127287	0.815	0.861
L4145-12	O-W5-127287 Dup	0.900	1.07
L4145-15	O-W7-463534	0.322	0.250
L4145-16	O-W7-463534 Dup	0.317	0.262
L4145-17	O-W8-572608	0.676	0.895
L4145-18	O-W8-572608 Dup	0.677	0.869
L4145-21	O-W3-208454	ND	ND
L4145-22	O-W3-208454 Dup	ND	ND
L4145-25	E04-0911 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

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Field Matrix Spike Recovery Summary for PFOA and PFOS in Water E04-0911

Sample Description	C8 Acid PFOA				C8 Sulfonate PFOS		
	Amount Spiked (ng/mL)	Amt Found in Sample (ng/mL)	Amount Recovered (ng/mL)	Recovery (%)	Amt Found in Sample (ng/mL)	Amount Recovered (ng/mL)	Recovery (%)
O-W1-208462 Low Spike (L4145-5, 0.1 ppb Spike)	0.1	0.0891	0.195	106	0.0561	0.182	126
O-W1-208462 High Spike (L4145-6, 5 ppb Spike)	5	0.0891	6.42	127	0.0561	6.30	125
O-W2-208463 Low Spike (L4145-9, 0.1 ppb Spike)	0.1	0.0764	0.137	61	NQ	0.119	119
O-W2-208463 High Spike (L4145-10, 5 ppb Spike)	5	0.0764	5.78	114	NQ	6.20	124
O-W5-127287 Low Spike (L4145-13, 0.1 ppb Spike)	0.1	0.815	0.976	*	0.861	1.23	*
O-W5-127287 High Spike (L4145-14, 5 ppb Spike)	5	0.815	6.37	111	0.861	7.35	130
O-W7-463534 Low Spike (L4145-1, 0.1 ppb Spike)	0.1	0.322	0.402	80	0.250	0.298	48
O-W7-463534 High Spike (L4145-2, 5 ppb Spike)	5	0.322	5.54	104	0.250	5.53	106
O-W8-572608 Low Spike (L4145-19, 0.1 ppb Spike)	0.1	0.676	0.768	*	0.895	0.885	*
O-W8-572608 High Spike (L4145-20, 5 ppb Spike)	5	0.676	6.30	112	0.895	5.79	98
O-W3-208454 Low Spike (L4145-23, 0.1 ppb Spike)	0.1	ND	0.092	92	ND	0.126	126
O-W3-208454 High Spike (L4145-24, 5 ppb Spike)	5	ND	5.13	103	ND	5.88	118
E04-0911 Trip Blank Low Spk (L4145-26, 0.1 ppb Spike)	0.1	ND	0.088	88	ND	0.103	103
E04-0911 Trip Blank High Spk (L4145-27, 5 ppb Spike)	5	ND	5.59	112	ND	5.61	112

*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.

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Surrogate Spike Recovery Summary for ^{13}C-PFOA in Water E04-0911

		^{13}C-PFOA		
Exygen ID	Sample Description	Amount Spiked (ng/mL)	Amount Recovered (ng/mL)	Recovery (%)
L4145-3	O-W1-208462	0.5	0.570	114
L4145-4	O-W1-208462 Dup	0.5	0.557	111
L4145-5	O-W1-208462 Low Spk	0.5	0.579	116
L4145-6	O-W1-208462 High Spk	0.5	0.583	117
L4145-7	O-W2-208463	0.5	0.548	110
L4145-8	O-W2-208463 Dup	0.5	0.602	120
L4145-9	O-W2-208463 Low Spk	0.5	0.379	76
L4145-10	O-W2-208463 High Spk	0.5	0.573	115
L4145-11	O-W5-127287	0.5	0.466	93
L4145-12	O-W5-127287 Dup	0.5	0.569	114
L4145-13	O-W5-127287 Low Spk	0.5	0.578	116
L4145-14	O-W5-127287 High Spk	0.5	0.528	106
L4145-15	O-W7-463534	0.5	0.541	108
L4145-16	O-W7-463534 Dup	0.5	0.551	110
L4145-1	O-W7-463534 Low Spk	0.5	0.558	112
L4145-2	O-W7-463534 High Spk	0.5	0.541	108
L4145-17	O-W8-572608	0.5	0.516	103
L4145-18	O-W8-572608 Dup	0.5	0.536	107
L4145-19	O-W8-572608 Low Spk	0.5	0.575	115
L4145-20	O-W8-572608 High Spk	0.5	0.534	107
L4145-21	O-W3-208454	0.5	0.566	113
L4145-22	O-W3-208454 Dup	0.5	0.581	116
L4145-23	O-W3-208454 Low Spk	0.5	0.608	122
L4145-24	O-W3-208454 High Spk	0.5	0.541	108
L4145-25	E04-0911 Trip Blank	0.5	0.513	103
L4145-26	E04-0911 Trip Blank Low Spk	0.5	0.520	104
L4145-27	E04-0911 Trip Blank High Spk	0.5	0.514	103

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