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Analytical Report

3M Company

Analysis of PFOA and PFOS in Water Samples from Cottage Grove Municipality E04-0910

Exygen Report No. L0004153 Revised

Testing Laboratory

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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 L0004153. 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

Forty-three 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 12/30/04. 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%. All surrogate spike recoveries and all PFOS field matrix spike recoveries were within this range. All PFOA field matrix spike recoveries were within this range with 4 exceptions.

- The PFOA recovery for sample CG-W5-208806 High Spike was 65%.
- The PFOA recovery for sample CG-W3-208807 Low Spike was 298%
- The PFOA recovery for sample CG-W7-201127 High Spike was 58%
- The PFOA recovery for sample CG-W10-191904 High Spike was 65%

In each of these cases the second field matrix spike showed recovery between 70 and 130%. Specific sample recoveries are given in Attachment B.

7 Data/Sample Retention

Samples will be returned to 3M Corporation 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 Colby 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 E04-0910

		Analyte Found (ng/mL)	
		C8 Acid PFOA	C8 Sulfonate PFOS
Exygen ID	Sample ID	Perfluorooctanoic Acid	Perfluorooctanesulfonate
L4153-1	CG-W6-201238	ND	ND
L4153-2	CG-W6-201238 Dup	ND	ND
L4153-5	CG-W9-165602	ND	ND
L4153-6	CG-W9-165602 Dup	ND	ND
L4153-9	CG-W5-208806	ND	ND
L4153-10	CG-W5-208806 Dup	ND	ND
L4153-13	CG-W3-208807	ND	ND
L4153-14	CG-W3-208807 Dup	ND	ND
L4153-17	CG-W7-201227	ND	ND
L4153-18	CG-W7-201227 Dup	ND	ND
L4153-21	CG-W8-110464	ND	ND
L4153-22	CG-W8-110464 Dup	ND	ND
L4153-25	CG-W11-655944	ND	ND
L4153-26	CG-W11-655944 Dup	ND	ND
L4153-29	CG-W10-191904	ND	ND
L4153-30	CG-W10-191904 Dup	ND	ND
L4153-33	CG-W2-208809	ND	ND
L4153-34	CG-W2-208809 Dup	ND	ND
L4153-37	CG-W1-208808	ND	ND
L4153-38	CG-W1-208808 Dup	ND	ND
L4153-41	Trip Blank-CG	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.

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Section B

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Field Matrix Spike Recovery Summary for PFOA and PFOS in Water E04-0910

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 (%)
CG-W6-201238 Low Spike (L4153-3, 0.1 ppb Spike)	0.1	ND	0.106	106	ND	0.119	119
CG-W6-201238 High Spike (L4153-4, 5 ppb Spike)	5	ND	5.77	115	ND	5.71	114
CG-W9-165602 Low Spike (L4153-7, 0.1 ppb Spike)	0.1	ND	0.109	109	ND	0.122	122
CG-W9-165602 High Spike (L4153-8, 5 ppb Spike)	5	ND	5.84	117	ND	5.68	114
CG-W5-208806 Low Spike (L4153-11, 0.1 ppb Spike)	0.1	ND	0.118	118	ND	0.127	127
CG-W5-208806 High Spike (L4153-12, 5 ppb Spike)	5	ND	3.27	65	ND	4.79	96
CG-W3-208807 Low Spike (L4153-15, 0.1 ppb Spike)	0.1	ND	0.298	298	ND	0.123	123
CG-W3-208807 High Spike (L4153-16, 5 ppb Spike)	5	ND	3.69	74	ND	5.19	104
CG-W7-201227 Low Spike (L4153-19, 0.1 ppb Spike)	0.1	ND	0.126	126	ND	0.116	116
CG-W7-201227 High Spike (L4153-20, 5 ppb Spike)	5	ND	2.89	58	ND	5.39	108
CG-W8-110464 Low Spike (L4153-23, 0.1 ppb Spike)	0.1	ND	0.0985	99	ND	0.0973	97
CG-W8-110464 High Spike (L4153-24, 5 ppb Spike)	5	ND	3.56	71	ND	5.43	109
CG-W11-655944 Low Spike (L4153-27, 0.1 ppb Spike)	0.1	ND	0.105	105	ND	0.131	131
CG-W11-655944 High Spike (L4153-28, 5 ppb Spike)	5	ND	3.75	75	ND	6.31	126
CG-W10-191904 Low Spike (L4153-31, 0.1 ppb Spike)	0.1	ND	0.110	110	ND	0.125	125
CG-W10-191904 High Spike (L4153-32, 5 ppb Spike)	5	ND	3.26	65	ND	5.40	108
CG-W2-208809 Low Spike (L4153-35, 0.1 ppb Spike)	0.1	ND	0.113	113	ND	0.121	121
CG-W2-208809 High Spike (L4153-36, 5 ppb Spike)	5	ND	3.51	70	ND	5.67	113
CG-W1-208808 Low Spike (L4153-39, 0.1 ppb Spike)	0.1	ND	0.0894	89	ND	0.114	114
CG-W1-208808 High Spike (L4153-40, 5 ppb Spike)	5	ND	3.59	72	ND	5.73	115
Trip Blank-CG Low Spk (L4153-42, 0.1 ppb Spike)	0.1	ND	0.0879	88	ND	0.105	105
Trip Blank-CG High Spk (L4153-43, 5 ppb Spike)	5	ND	4.82	96	ND	5.16	103

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 E04-0910

		^{13}C-PFOA		
Exygen ID	Sample Description	Amount Spiked (ng/mL)	Amount Recovered (ng/mL)	Recovery (%)
L4153-1	CG-W6-201238	0.5	0.543	109
L4153-2	CG-W6-201238 Dup	0.5	0.500	100
L4153-3	CG-W6-201238 Low Spk	0.5	0.560	112
L4153-4	CG-W6-201238 High Spk	0.5	0.541	108
L4153-5	CG-W9-165602	0.5	0.489	98
L4153-6	CG-W9-165602 Dup	0.5	0.513	103
L4153-7	CG-W9-165602 Low Spk	0.5	0.575	115
L4153-8	CG-W9-165602 High Spk	0.5	0.593	119
L4153-9	CG-W5-208806	0.5	0.547	109
L4153-10	CG-W5-208806 Dup	0.5	0.507	101
L4153-11	CG-W5-208806 Low Spk	0.5	0.553	111
L4153-12	CG-W5-208806 High Spk	0.5	0.424	85
L4153-13	CG-W3-208807	0.5	0.490	98
L4153-14	CG-W3-208807 Dup	0.5	0.518	104
L4153-15	CG-W3-208807 Low Spk	0.5	0.535	107
L4153-16	CG-W3-208807 High Spk	0.5	0.486	97
L4153-17	CG-W7-201227	0.5	0.514	103
L4153-18	CG-W7-201227 Dup	0.5	0.583	117
L4153-19	CG-W7-201227 Low Spk	0.5	0.598	120
L4153-20	CG-W7-201227 High Spk	0.5	0.469	94
L4153-21	CG-W8-110464	0.5	0.478	96
L4153-22	CG-W8-110464 Dup	0.5	0.568	114
L4153-23	CG-W8-110464 Low Spk	0.5	0.459	92
L4153-24	CG-W8-110464 High Spk	0.5	0.547	109
L4153-25	CG-W11-655944	0.5	0.575	115
L4153-26	CG-W11-655944 Dup	0.5	0.548	110
L4153-27	CG-W11-655944 Low Spk	0.5	0.615	123
L4153-28	CG-W11-655944 High Spk	0.5	0.587	117
L4153-29	CG-W10-191904	0.5	0.578	116
L4153-30	CG-W10-191904 Dup	0.5	0.577	115
L4153-31	CG-W10-191904 Low Spk	0.5	0.567	113
L4153-32	CG-W10-191904 High Spk	0.5	0.537	107
L4153-33	CG-W2-208809	0.5	0.579	116
L4153-34	CG-W2-208809 Dup	0.5	0.526	105
L4153-35	CG-W2-208809 Low Spk	0.5	0.545	109
L4153-36	CG-W2-208809 High Spk	0.5	0.541	108
L4153-37	CG-W1-208808	0.5	0.551	110
L4153-38	CG-W1-208808 Dup	0.5	0.527	105
L4153-39	CG-W1-208808 Low Spk	0.5	0.548	110
L4153-40	CG-W1-208808 High Spk	0.5	0.528	106
L4153-41	Trip Blank-CG	0.5	0.532	106
L4153-42	Trip Blank-CG Low Spk	0.5	0.482	96
L4153-43	Trip Blank-CG High Spk	0.5	0.525	105

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