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Analytical Report

3M Company

Analysis of PFOA and PFOS in Water Samples from Hastings Municipality

E04-0909

Exygen Report No. L0004146 Revised

Testing Laboratory

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Requester

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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 L0004146. 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-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 12/28/04. 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 exception:

- The PFOS recovery for sample H-W6-207643 High Spike was 132%.

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 Conley 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 E04-0909

Exygen ID	Sample ID	Analyte Found (ng/mL) C8 Acid PFOA Perfluorooctanoic Acid	C8 Sulfonate PFOS Perfluorooctanesulfonate
L4146-1	H-W6-207643	NQ	ND
L4146-2	H-W6-207643 Dup	NQ	ND
L4146-5	H-W4-207993	ND	ND
L4146-6	H-W4-207993 Dup	ND	ND
L4146-9	H-W5-207639	ND	ND
L4146-10	H-W5-207639 Dup	ND	ND
L4146-13	H-W3-206333	ND	ND
L4146-14	H-W3-206333 Dup	ND	ND
L4146-17	H-W7-509053	ND	ND
L4146-18	H-W7-509053 Dup	ND	ND
L4146-21	E04-0909 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.

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Section B

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Field Matrix Spike Recovery Summary for PFOA and PFOS in Water E04-0909

Sample Description	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 (%)
H-W6-207643 Low Spike (L4146-3, 0.1 ppb Spike)	0.1	NQ	0.115	115	ND	0.119	119
H-W6-207643 High Spike (L4146-4, 5 ppb Spike)	5	NQ	4.95	99	ND	6.58	132
H-W4-207993 Low Spike (L4146-7, 0.1 ppb Spike)	0.1	ND	0.0903	90	ND	0.126	126
H-W4-207993 High Spike (L4146-8, 5 ppb Spike)	5	ND	4.97	99	ND	5.94	119
H-W5-207639 Low Spike (L4146-11, 0.1 ppb Spike)	0.1	ND	0.0978	98	ND	0.118	118
H-W5-207639 High Spike (L4146-12, 5 ppb Spike)	5	ND	4.38	88	ND	4.66	93
H-W3-206333 Low Spike (L4146-15, 0.1 ppb Spike)	0.1	ND	0.0937	94	ND	0.119	119
H-W3-206333 High Spike (L4146-16, 5 ppb Spike)	5	ND	5.96	119	ND	6.36	127
H-W7-509053 Low Spike (L4146-19, 0.1 ppb Spike)	0.1	ND	0.0844	84	ND	0.0952	95
H-W7-509053 High Spike (L4146-20, 5 ppb Spike)	5	ND	6.21	124	ND	6.47	129
E04-0909 Trip Blank Low Spk (L4146-22, 0.1 ppb Spike)	0.1	ND	0.100	100	ND	0.110	110
E04-0909 Trip Blank High Spk (L4146-23, 5 ppb Spike)	5	ND	5.58	112	ND	4.61	92

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 E04-0909

		^{13}C-PFOA		
Exygen ID	Sample Description	Amount Spiked (ng/mL)	Amount Recovered (ng/mL)	Recovery (%)
L4146-1	H-W6-207643	0.5	0.494	99
L4146-2	H-W6-207643 Dup	0.5	0.594	119
L4146-3	H-W6-207643 Low Spk	0.5	0.557	111
L4146-4	H-W6-207643 High Spk	0.5	0.582	116
L4146-5	H-W4-207993	0.5	0.570	114
L4146-6	H-W4-207993 Dup	0.5	0.512	102
L4146-7	H-W4-207993 Low Spk	0.5	0.547	109
L4146-8	H-W4-207993 High Spk	0.5	0.513	103
L4146-9	H-W5-207639	0.5	0.547	109
L4146-10	H-W5-207639 Dup	0.5	0.535	107
L4146-11	H-W5-207639 Low Spk	0.5	0.551	110
L4146-12	H-W5-207639 High Spk	0.5	0.487	97
L4146-13	H-W3-206333	0.5	0.550	110
L4146-14	H-W3-206333 Dup	0.5	0.621	124
L4146-15	H-W3-206333 Low Spk	0.5	0.576	115
L4146-16	H-W3-206333 High Spk	0.5	0.574	115
L4146-17	H-W7-509053	0.5	0.571	114
L4146-18	H-W7-509053 Dup	0.5	0.484	97
L4146-19	H-W7-509053 Low Spk	0.5	0.524	105
L4146-20	H-W7-509053 High Spk	0.5	0.575	115
L4146-21	E04-0909 Trip Blank	0.5	0.556	111
L4146-22	E04-0909 Trip Blank Low Spk	0.5	0.526	105
L4146-23	E04-0909 Trip Blank High Spk	0.5	0.482	96

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