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Analytical Report

Fluorochemical Characterization of POTW Effluent

Port St. Lucie, FL

Centre Analytical Laboratory Report No. 023-014N (Revision 1)

Revision Date 3/27/01

Testing Laboratory

Centre Analytical Laboratory, Inc.
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3M Environmental Laboratory Contact

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Requester

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1 Introduction

Results are reported for the analysis of a series of POTW effluent samples received by Centre Analytical Laboratories, Inc. (Centre) from the 3M Environmental Laboratory. The samples were collected from Port St. Lucie, FL. The Centre study number assigned to the project is 023-014.

Specific fluorochemical characterization by liquid chromatography / tandem mass spectrometry (LC/MS/MS) was requested for all samples. A total of 4 samples were received for analysis.

The samples were prepared and analyzed by LC/MS/MS for the following list of fluorochemicals:

- Table 1: Target Analysis

Compound Name	Acronym
Perfluorooctane Sulfonate	PFOS
Perfluorooctane Sulfonylamide	PFOSA
Perfluorooctanoate	POAA

The analytical method used was validated by Centre. The validation protocol and results are on file with Centre. Data presented here is the highest quality data available at this time.

2 Sample Receipt

The samples were submitted in individual plastic containers and were not preserved. Four individual sample containers were received. Samples were received on 6/6/00. The sample collection dates were not supplied. Chain-of-custody information is presented in Attachment C.

3 Holding Times

The analytical method used was validated against a maximum holding time of 14 days. The stability of the analytes of interest for longer periods has not been determined. However, it should be noted that field fortifications in water and other matrices have shown acceptable recoveries at 100 and 1000 ng/L for periods longer than 14 days.

4 Methods - Analytical and Preparatory

4.1 LC/MS/MS

4.1.1 Sample Preparation for LC/MS/MS Analysis

Samples were initially treated with 200 μ L of 250 mg/L sodium thiosulfate solution to remove residual chlorine. Solid phase extraction (SPE) was used to prepare the samples for LC/MS/MS analysis. A forty-milliliter portion of sample was transferred to a C₁₈ SPE cartridge. The cartridge was first eluted with 5 mL of 40% methanol in water solution. The eluate was discarded and the SPE column was then eluted with 100% methanol. A 5 mL portion of

methanol was collected for analysis by LC/MS/MS. This treatment resulted in an eight-fold concentration of the samples prior to analysis.

4.1.2 Sample Analysis by LC/MS/MS

In 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, ES/MS provides a rapid and accurate means for analyzing a wide range of organic compounds, including fluorochemicals. Electrospray is generally operated at relatively mild temperatures; molecules are ionized, fragmented, and detected. Ions characteristic of known fluorochemicals are observed and quantitated against standards.

A Hewlett-Packard HP1100 HPLC system coupled to a Micromass Ultima MS/MS was used to analyze the sample extracts. Analysis was performed using selected reaction monitoring (SRM). Samples were initially extracted on 6/12/00 and analyzed by MS/MS on 6/15/00. The initial run was rejected because of control sample recoveries outside of acceptable ranges. The samples were re-extracted on 6/28/00 and re-analyzed by MS/MS between 6/28/00 and 6/29/00. Both sets of raw data are included for informational purposes. The HPLC and MS/MS methods used for analysis and instrument parameters can be found in Attachment D.

5 Analysis

5.1 Calibration

A 7-point calibration curve was analyzed at the beginning and end of the analytical sequence for the compounds of interest. The calibration points were prepared at 0, 25, 50, 100, 250, 500, and 1000 ng/L (ppt). The response of the quantitation ion versus the concentration was plotted for each point. Using linear regression with 1/x weighting, the slope, y-intercept and correlation coefficient (r) and coefficient of determination (r^2) were determined. A calibration curve is acceptable if $r \geq 0.985$ ($r^2 \geq 0.970$).

Calibration standards are prepared using the same SPE procedure used for samples.

Calibration check standards were analyzed periodically (every three to five sample injections) throughout the analysis sequence. Compliance is obtained if the standard analyte concentrations are within $\pm 20\%$ of the actual value.

For the results reported here, calibration criteria were met.

5.2 Blanks

Extraction blanks were prepared and analyzed with every extraction batch of samples. The extraction blanks should not have any target analytes present at or above the concentration of the low-level calibration standard. For these samples, the extraction blanks were compliant.

Instrument blanks in the form of clean methanol solvent were also analyzed after every high-level calibration standard, and after known high-level samples. Again, the blanks should not have any target analytes present at or above the low-level calibration standard. For the samples presented here the instrument blanks are compliant.

5.3 Surrogates

Surrogate spikes are not a component of the LC/MS/MS analytical method.

5.4 Matrix Spikes

Matrix spikes were prepared for every sample at a concentration of 1000 ng/L using all compounds of interest. Matrix spike recoveries are given in Attachment B. All recoveries were between 70-130%.

Field spikes were also prepared at a concentration of 1000 ng/L. All field spike recoveries were between 70 –130%. Field spike recoveries are also given in Attachment B.

5.5 Duplicates

All samples were analyzed in duplicate. Results are given along with the sample results in Attachment A.

5.6 Laboratory Control Samples

Milliq water was spiked with all compound of interest at 25 and 250 ng/L. All recoveries for all compounds were between 70-130% in each LCS.

5.7 Sample Related Comments

Field blank samples consisted of empty containers. Forty milliliters of type I water filtered through a hypercarb cartridge was added to the empty container and analyzed in the same manner as the other samples.

6 Data Summary

Please see Attachment A for a detailed listing of the analytical results.

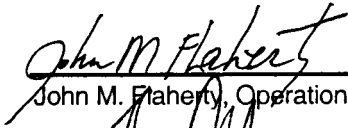
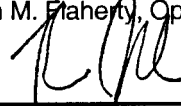
7 Data/Sample Retention

Samples are disposed of one month after the report is issued unless otherwise specified. All electronic data is archived on retrievable media and hard copy reports are stored in data folders maintained by Centre.

8 Attachments

- 8.1 Attachment A: Results
- 8.2 Attachment B: Matrix Spike Recoveries (Field and Laboratory Spikes)
- 8.3 Attachment C: Chain of Custody
- 8.4 Attachment D: LC/MS/MS Raw Analytical Data

9 **Signatures**

 John M. Flaherty, Operations Manager	<u>3/27/01</u> Date
 Kevin J Lloyd, Vice President	<u>27 MARCH 2001</u> Date

Other Lab Members Contributing to Data

Enaksha Wickremesinhe
Karen Smith



Centre Analytical Laboratories, Inc.

3048 Research Drive, State College PA 16801 814-231-8032 FAX 814-231-1253

Analytical Results W2363 Port St. Lucie, FL

3M Sample Identification	Sample Description	PFOS (ng/L)	PFOSA (ng/L)	POAA (ng/L)
MC-639H POTW Effluent	P/N Ion Pair	47.7	NQ	41.2
NA Duplicate POTW Effluent	P/N Ion Pair Duplicate	62.6	NQ	43.6
MC-643H	Field Blank P/N Empty	ND	ND	ND

Limit of Detection (LOD) for the procedure is approximately 2.5 ng/L for PFOS and PFOSA and 7.5 ng/L for POAA

Limit of Quantitation (LOQ) for the procedure is 25 ng/L for all compounds

ND - Compound not detected

NQ - Compound detected at a level between the LOD and LOQ. Result is not quantifiable.

ND < LOD < NQ < LOQ



Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-642H

Spiked Amount (ng/L): 1000

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	47.7	1017	96.9	PASS
PFOSA	3.7	970	96.6	PASS
POAA	41.2	907	86.6	PASS

Lower Recovery Limit: 70

Upper Recovery Limit: 130

Note: Sample results less than 25 ng/L are reported as NQ in the results section as they are below the limit of quantitation. Results are given in this table for recovery calculations only.

Attachment B: LC/MS/MS Field Spike Recovery

Sample ID:

Spiked Amount (ng/L):

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	47.7	1110	106.2	PASS
PFOSA	3.7	1206	120.2	PASS
POAA	41.2	1176	113.5	PASS

Lower Recovery Limit:

Upper Recovery Limit:

Note: Sample results less than 25 ng/L are reported as NQ in the results section as they are below the limit of quantitation. Results are given in this table for recovery calculations only.

3M Environmental Laboratory

Form 38778 - PWO

Shipping Address:
3M Bldg. 2-3E-09
935 Bush Avenue
St. Paul, MN 55106

Telephone:
Sample Receiving: (651) 778-4948
Alternate: (651) 778-6753
FAX: (651) 778-6176

Chain of Custody /Request for Laboratory Analytical

14675

3M Env. Lab Project #
For Internal Use Only

Project ID/Project Name GEVD19 Water Samples taken from Port St. Lucie, FL, sent from Battelle
Template #
Project Lead KTH
Dept. # (main) 4291
Final Report Due Date
Internal Due Date
Class/Job/Project # 0010535009

W2363

Report Results to:	Contact Name	<u>Krist Hansen</u>	Date Available	<u>060300</u>
	Company	<u>3M</u>	Date Due	
	Mailing Address	<u>Building 2-3E-09 PO Box 33331</u>	Contract Lab	<u>CENTRE</u>
	City, State, Zip	<u>St. Paul, mn 55133</u>		
	Telephone #	<u>(651) 778-6018</u>		
	FAX #	<u>(651) 778-6176</u>		

Special Instructions and/or Specific Regulatory Requirements:
(method, limit of detection, reporting units, etc.)

Preservatives:

HNO3	H2SO4	VOCs	None	Other

Total Number of Containers

Analysis Requested:

Complete below. Attach any associated information.

Item #	Client Sample Identification	3M LIMS#	Date Sampled	Time Sampled	Matrix/Media	Enter the number of containers of each	Total Number of Containers	Analysis Requested
1.	<u>ML-639H-PIN Ion Pair</u>	<u>W2363</u>	<u>N/A</u>	<u>N/A</u>	<u>Water</u>		<u>1</u>	<u>X</u>
2.	<u>ML-641H-Field Spike-PIN Ion Pair</u>	<u>↓</u>	<u>↓</u>	<u>↓</u>	<u>↓</u>		<u>1</u>	<u>X</u>
3.	<u>ML-642H-Lab Spike-PIN Ion Pair</u>	<u>↓</u>	<u>↓</u>	<u>↓</u>	<u>↓</u>		<u>1</u>	<u>X</u>
4.	<u>ML-643H-Field Blank-PIN-Empty Ion Pair</u>	<u>↓</u>	<u>↓</u>	<u>↓</u>	<u>↓</u>		<u>1</u>	<u>X</u>
5.							<u>N/A</u>	
6.								
7.								
8.								
9.								
10.								

Chain of Custody	Collected by (print):	<u>N/A</u>	Collector's signature:	<u>N/A</u>
	Item #	Relinquished by/Affiliation	Time	Date
	<u>1-4</u>	<u>Kelly Dowdler 3M</u>	<u>N/A</u>	<u>6/2/00</u>
	Shipped Via:	Received by/Affiliation	Time	Date
	<u>Fed Ex</u>	<u>Sumner, H. E. L no 6/6/00</u>	<u>1130</u>	<u>6/7/00</u>

Sample Condition Upon Receipt:	☒ Acceptable	☐ Other:	Comments:
Temperature:	<u>°C</u>	☐ Received on Ice	
Other Associated CoCs:	Copies to:		
<u>14670, 14671, 14672, 14673, 14674</u>	<u>LAC, DMA</u>		