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Analytical Report

Fluorochemical Characterization of Surface Water Samples

Cleveland, Tennessee (W1973)

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

Revision Date 3/21/01

Testing Laboratory

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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 surface water samples received by Centre Analytical Laboratories, Inc. (Centre) from the 3M Environmental Laboratory. The samples were collected from Cleveland, Tennessee. 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 8 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 here 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. Eight individual sample containers were received. Samples were received on 05/03/00. The sample collection dates were not supplied. Chain-of-custody information is presented in Attachment C.

Sample MC-102H was not analyzed as per client request. (E-mail communication from Kris Hansen on 5/16/00). Please note that no "quiet water" samples were collected for this site.

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 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 extracted on 5/16/00 and analyzed by MS/MS on 5/18/00. Sample MC-108H was extracted on 5/22/00 and analyzed on 5/23/00. 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 field sample (excluding blanks) at a concentration of 100 ng/L using all compounds of interest. Matrix spike recoveries are given in Attachment B. All laboratory matrix spikes showed recoveries of all compounds between 70-130%.

Field spikes were prepared on sample MC-101H at a concentration of 100 ng/L using all compounds of interest. The field spike sample is identified as MC-104H. Field spike recoveries are also given in Attachment B. PFOSA showed low recovery in the field spike. All other compounds showed recoveries between 70-130%.

5.5 Duplicates

All field samples (excluding blanks) 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. Recoveries are given with the raw data in Attachment D.

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.

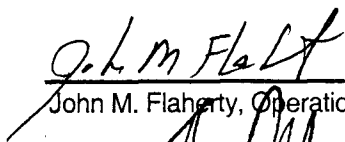
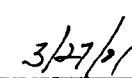
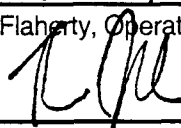
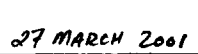
7 Data/Sample Retention

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	Date
	
Kevin J Lloyd, Vice President	Date

Other Lab Members Contributing to Data

Enaksha Wickremesinhe
Karen Smith
David Bell



Centre Analytical Laboratories, Inc.

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

Analytical Results W1973 Cleveland, Tennessee

3M Sample Identification	Sample Description	PFOS (ng/L)	PFOSA (ng/L)	POAA (ng/L)
MC-101H	Site 1 P/N Surface Water	NQ	NQ	NQ
MC-103H	Site 1 P/N Surface Water Duplicate	ND	ND	ND
MC-106H	Site 2 P/N Surface Water	ND	ND	ND
NA	Site 2 P/N Surface Water Duplicate	ND	ND	ND
MC-107H	Site 3 P/N Surface Water	ND	ND	ND
NA	Site 3 P/N Surface Water Duplicate	ND	ND	ND
MC-108H	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:

Spiked Amount (ng/L):

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	14.7	93.3	78.6	PASS
PFOSA	5.6	102	96.4	PASS
POAA	16.7	113	96.3	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.

Also note that sample MC-105H is a laboratory spike of sample MC-101H

Attachment B: LC/MS/MS Laboratory 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	0	115	115.0	PASS
PFOSA	0	108	108.0	PASS
POAA	0	113	113.0	PASS

Lower Recovery Limit:

Upper Recovery Limit:

Attachment B: LC/MS/MS Laboratory 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	0	107	107.0	PASS
PFOSA	0	106	106.0	PASS
POAA	0	106	106.0	PASS

Lower Recovery Limit:

Upper Recovery Limit:

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	14.7	101	86.3	PASS
PFOSA	5.6	34.5	28.9	FAIL
POAA	16.7	95.4	78.7	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.

Also note that sample MC104-H is a field spike of sample MC-101H

3M Environmental Laboratory

Form 38778 - PWO

Chain of Custody /Request for Laboratory Analytical

14265

3M Env. Lab Project #
For Internal Use Only

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

Telephone:
Sample Receiving: (651) 778-4948
Alternate: (651) 778-6763
FAX: (651) 778-6178

Project ID/Project Name 6EN013/Water Samples taken at Cleveland TN sent from Battelle
Template #
Project Lead KJH
Dept. # (main) 4291
Final Report Due Date
Internal Due Date
Class/Job/Project # 0010535009

W1973

Report Results to:	Contact Name <u>Kris Hansen</u>	Date Available	<u>0</u>	<u>5</u>	<u>0</u>	<u>3</u>	<u>0</u>	<u>0</u>									
	Company <u>3M</u>	Date Due															
	Mailing Address <u>Building 2-3E-09 PO Box 33331</u>	Contract Lab	<u>C</u>	<u>E</u>	<u>N</u>	<u>T</u>	<u>R</u>	<u>E</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:

HNO ₃	H ₂ SO ₄	VOCs	None	Other

Total Number of Containers

Analysis Requested:

Complete below. Attach any associated information.

<u>KID 512100</u>	
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Item #	Client Sample Identification	3M LIMS#	Date Sampled	Time Sampled	Matrix/Media	Enter the number of containers of each	(Enter an 'X' in the box below to indicate request)
1.	MC-101H-Sib 1-PIN Don Air HALL-ESMS Surface Water - Cleveland, TN	<u>W1973</u>	<u>NA</u>	<u>NA</u>	<u>Water</u>		
2.	MC-102H-Sib 1-TOTAL PROS Don Air HALL-ESMS Surface Water - Cleveland, TN						
3.	MC-103H-Sib 1-Field Lab Dup-P Don Air HALL-ESMS Surface Water - Cleveland, TN						
4.	MC-104H-Sib 1-Field Spike-PIN Don Air HALL-ESMS Surface Water - Cleveland, TN						
5.	MC-105H-Sib 1-Field Spike-PIN Don Air HALL-ESMS Surface Water - Cleveland, TN						
6.	MC-106H-Sib 2-PIN Don Air HALL-ESMS Surface Water - Cleveland, TN						
7.	MC-107H-Sib 3-PIN Don Air HALL-ESMS Surface Water - Cleveland, TN						
8.	MC-108H-Field Blank-PIN Empty Don Air HALL-ESMS Surface Water - Cleveland, TN						
9.							
10.	<u>KID 512100</u>						

Chain of Custody	Collected by (print): <u>Battelle</u>	Collector's signature: <u>N/A</u>						
	Item #	Relinquished by/Affiliation	Time	Date	Shipped Via:	Received by/Affiliation	Time	Date
	<u>1-8</u>	<u>Kelly Donwiler / 3M</u>	<u>14:00</u>	<u>5/3/00</u>	<u>FedEx</u>	<u>R. Keller</u>	<u>10:30</u>	<u>5-3-00</u>

Sample Condition Upon Receipt: ☒ Acceptable ☐ Other:

Temperature: 1°C ☒ Received on Ice

Other Associated CoCs: 14266, 14267, 14268, 14269, 14270

Copies to: KJH, LAC, DMA

Comments: