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Analytical Report

Fluorochemical Characterization of POTW Effluent

Cleveland, Tennessee (W1973)

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

Revision Date 3/26/01

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 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 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 uL 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 C_{18} 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 6/9/00 and analyzed by MS/MS on 6/13/00. Additional dilutions were performed and analyzed on 6/29/00. 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 +/-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 100 ng/L using all compounds of interest. Matrix spike recoveries are given in Attachment B. High matrix spike recoveries were observed for PFOS and POAA; however, the indigenous amount of material in these samples was greater than four times the spiking amount.

Field spikes were also prepared at concentrations of 1000 ng/L. 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 — Date: 3/27/01

Kevin J Lloyd, Vice President — Date: 27 MARCH 2001

Other Lab Members Contributing to Data

Enaksha Wickremesinhe
Karen Smith

ANALYTICAL REPORT

Centre Analytical Laboratories, Inc.
3048 Research Drive, State College PA 16801 814-231-8032 FAX 814-231-1253

Analytical Results W1973 Cleveland, Tennesse

3M Sample Identification	Sample Description	PFOS (ng/L)	PFOSA (ng/L)	POAA (ng/L)
MC-139H POTW Effluent	P/N Ion Pair	417	NQ	655
NA Duplicate POTW Effluent	P/N Ion Pair Duplicate	454	NQ	674
MC-143H	Field Blank P/N Empty	ND	ND	ND

Limit of Detection (LOD) for the procedure is appoximately 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-142H

Spiked Amount (ng/L): 100

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	417	562	145.0	FAIL
PFOSA	3.8	116	112.2	PASS
POAA	655	829	174.0	FAIL

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.

Also note that PFOS and POAA sample concentrations are greater than 4X the spiking level

Attachment B: LC/MS/MS Field Spike Recovery

Sample ID: MC-141H

Spiked Amount (ng/L): 1000

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	417	1424	100.7	PASS
PFOSA	3.8	814	81.0	PASS
POAA	655	1670	101.5	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.

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 14670

Project ID/Project Name	GEN013 Water Samples taken at Cleveland, TN sent from Bottle
Template #	
Project Lead	KJH
Dept. # (main)	4291
Final Report Due Date	
Internal Due Date	
Class/Job/Project #	00105350 09

3M Env. Lab Project # For Internal Use Only: W1973

Report Results to:

Contact Name	Kris Hansen
Company	3M
Mailing Address	Building 2-3E-09 PO Box 33331
City, State, Zip	St. Paul, MN 55133
Telephone #	(651) 778-6018
FAX #	(651) 778-6176

Date Available	06/03/00
Date Due	
Contract Lab	CENTRE

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

Preservatives: (Enter the number of containers of each)

Item #	Client Sample Identification	3M LIMS#	Date Sampled	Time Sampled	Matrix/ Media	HNO_3	H_2SO_4	VOCs	None	Other	Total Number of Containers
1.	MC-139H-PIN Fan Pair	W1973	N/A	N/A	Water				1		1
2.	MC-141H-FieldSpike-PIN Fan Pair	↓	↓	↓	↓				1		1
3.	MC-142H-Lab Spike-PIN Fan Pair								1		1
4.	MC-143H-Field Blank-PIN-Empty Fan Pair								1		1
5.											N/A
6.											
7.											
8.											
9.											
10.											

KJD 6/2/00 KJD 6/2/00

Analysis Requested: Complete below. Attach any associated information.

(Enter an 'X' in the box below to indicate request)

Item #	KJD 6/2/00	KJH Special	KJH 6/2/00
1.	N/A	X	
2.		X	
3.		X	
4.		X	
5.			
6.			
7.			
8.			
9.			
10.			

KJD 6/2/00

Chain of Custody

Collected by (print): N/A

Collector's signature: N/A

Item #	Relinquished by/Affiliation	Time	Date	Shipped Via:	Received by/Affiliation	Time	Date
1-4	Kelly Dowviler / 3M	N/A	6/2/00	FedEx	LNo 6/6/00	1130	6/3/00

Sample Condition Upon Receipt: ✓ Acceptable O Other:

Temperature: °C O Received on Ice

Other Associated CoCs:
14671, 14672, 14673, 14674, 14675

Copies to:
LAC, DMA

Comments:

BACK TO MAIN