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Woodbury combined/ effluent
04/01/04

Analytical Report

Fluorochemical Characterization of Aqueous Samples

Woodbury Combined Main FC Monitoring (E04-0241)

Exygen Research Laboratory Report No. L0002234 Revision 1

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1 Introduction

Results are reported for the analysis of aqueous samples received by Exygen Research (Exygen) from 3M Corporation. The Exygen study number assigned to the project is L0002234.

Specific fluorochemical characterization by liquid chromatography / tandem mass spectrometry (LC/MS/MS) was requested for all samples. A total of 7 samples (including field duplicates, blanks, and spikes) 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
Perfluorobutanesulfonate	C4 Sulfonate (PFBS)
Perfluorohexanesulfonate	C6 Sulfonate (PFHS)
Perfluorooctanesulfonate	C8 Sulfonate (PFOS)
Perfluorooctanesulfonamide	C8 Primary Amide (FOSA)
Perfluorooctanoic Acid	C8 Acid (PFOA)

The analytical methods used were originally developed for groundwater samples and were validated by Exygen. The validation protocol and results are on file with Exygen. Only the C8 Sulfonate, C8 Primary Amide, and C8 Acid were included in the original method validation. It should be noted that the quality control elements included in this analysis demonstrate the applicability of the method to the additional analytes.

2 Sample Receipt

The water samples were submitted in plastic containers. Samples were received at ambient temperature. Samples were stored at 4°C from receipt until analysis. Seven individual containers were received. Field samples were collected on 4/1/04. Samples were received on 4/3/04. Chain-of-custody information is presented in Attachment C.

3 Holding Times

Field and laboratory spikes of these fluorochemicals have shown stability for periods greater than 90 days. Samples were analyzed within 30 days of collection.

4 Methods - Analytical and Preparatory

4.1 LC/MS/MS

4.1.1 Sample Preparation for LC/MS/MS Analysis

Water 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 40 mL sample volume, or a portion of sample diluted to 40 mL was used for analysis. The samples were transferred to a C_{18} SPE cartridge. The cartridge was eluted with 5 mL of 100% methanol. This treatment resulted in an eight-fold concentration of the diluted 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 4/7/04 and analyzed between 4/17/04 and 4/21/04. Raw analytical data is provided 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) for LC/MS/MS analysis. The instrument response 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.

All calibration criteria were met for this analysis.

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 methods.

5.4 Matrix Spikes

Field and laboratory spikes were prepared using all compounds of interest. Field spikes were prepared by adding a measured volume of field sample to a container spiked with the target analytes by the laboratory prior to shipping containers for sample collection. Laboratory spikes consisted of aliquots of un-spiked field samples that were fortified at the laboratory at the time of extraction. Field blank spikes consisted of laboratory water fortified at the laboratory and shipped with the sample containers to the field and back to the laboratory for analysis. Laboratory control spikes (see section 5.6) are samples of laboratory water spiked at the time of extraction. Each type of spike provides information needed to assess analyte stability, extraction efficiency, and matrix effects that may impact analytical results. Matrix spike recoveries are given in Attachment B. Please see Section 5.7 for additional discussion of matrix spike recoveries.

5.5 Duplicates

Field and laboratory duplicates were prepared for each field sample. Duplicate results are given along with the sample results in Attachment A.

5.6 Laboratory Control Samples

For LC/MS/MS analyses, Milliq water was spiked with all compounds of interest at 100 and 500 ng/mL during each extraction set. All recoveries for all compounds were between 70-130% in each LCS. Results are given along with the raw data in Attachment D.

5.7 Statement of Accuracy

Based on results of field spikes, laboratory fortified field samples, field blank spikes, and laboratory control spikes, the analytical accuracy of all compounds except PFOA is ± 30%. The accuracy for PFOA is ± 50%. All field blank spikes, laboratory control spikes and laboratory matrix spikes for all compounds showed recoveries within these ranges. All spike data are reported in the data tables.

6 Data Summary

Please see Attachment A for a detailed listing of the analytical results. Results are reported in parts per billion (ppb) (ng/mL).

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 Exygen.

8 Attachments

8.1 Attachment A: Results

8.2 Attachment B: Matrix Spike Recoveries

8.3 Attachment C: Chain of Custody

8.4 Attachment D: Raw Analytical Data

9 Signatures

Paul Connolly, Team Leader - LCMS — Date 5/5/04

John M. Flaherty, Vice President — Date 5/5/04

Other Lab Members Contributing to Data

Karen Smith