APPENDIX TO ATTACHMENT 2
GROUNDWATER SAMPLING
TECHNICAL PROGRESS REPORT

INTERIM REPORT 4 – ANALYSIS OF PFOA FROM 3M DECATUR OFF-SITE 600 SERIES WELLS

Analytical Report

Analysis of PFOA from 3M Decatur Offsite 600 Series Wells

Interim Report #4
MPI Protocol P0003267

Data Requirement

40 CFR Part 792

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Phase Completion Date

Date of signing

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Project Identification

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GLP Compliance Statement

Project Title: Analysis of PFOA from 3M Decatur Offsite 600 Series Wells

Project Identification Number: GLP07-01-02

MPI GLP Protocol Number P0003267 Interim Report #4

This analytical phase was conducted in compliance with Toxic Substances Control Act (TSCA) Good Laboratory Practice (GLP) Standards, 40 CFR 792, with the exceptions listed below:

Exceptions to GLP compliance:

None.

Kesari 2/22/08

Jaisimha Kesari, P.E., DEE, Study Director Date

Michael A Santoro 02/12/08

Michael A. Santoro, Sponsor Representative Date

Quality Assurance Statement

Study Title: Analysis of PFOA from 3M Decatur Offsite 600 Series Wells

Study Identification Number: GLP07-01-02; 3M Protocol Number GLP07-01 (MPI Protocol Number P0003267 Interim Report #4)

This analytical phase was audited by the 3M Environmental Laboratory Quality Assurance Unit (QAU), as indicated in the following table. The findings were reported to the study director and laboratory management.

Inspection Dates	Phase	Date Reported To		
		Principal Analytical Investigator	Study Director's Management	Study Director
10/09/2007	In-Phase	11/1/2007	2/11/2007	2/10/2007
1/07/2008 – 1/14/2008	Data & Report Audit	1/14/2008	2/11/2007	2/10/2007

QAU Representative

02/11/08
Date

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Study Dates

Interim Experimental Initiation: October 1, 2007

Interim Completion: Date of interim report signing

Location of Archives

All original raw data, protocol, and analytical report have been archived at the 3M Environmental Laboratory according to 40 CFR Part 792. The test substance and analytical reference standard reserve samples are archived at the 3M Environmental Laboratory according to 40 CFR Part 792. All samples (specimens) will be retained and archived according to current 3M Environmental Laboratory standard operating procedures.

Summary and Introduction

The 3M Environmental Laboratory analyzed groundwater samples collected offsite from the 3M Decatur, AL facility by Weston Solutions personnel on September 20, 2007. Samples were submitted for analysis under 3M Environmental Laboratory Project Number GLP07-01-02. The GLP protocol number is P0003267: "Analysis of Perfluorooctanoic Acid (PFOA) in Water, Soil, Sediment, Fish, and Clams Using LC/MS/MS for the 3M Decatur Monitoring Program".

The groundwater samples were analyzed for PFOA using method ETS 8-44.0 "Method of Analysis for the Determination of Perfluorinated Compounds in Water by LC/MS/MS; Direct Injection Analysis". The experimental start date was October 1, 2007, the day samples were first prepared for analysis by 3M Environmental Laboratory personnel. The experimental completion date was October 13, 2007.

Sample collection containers were prepared at the 3M Environmental Laboratory. Sample containers for each sampling location included a field sample, field sample duplicate, low field spike, and a high field spike. Additionally, two equipment rinse blanks and two trip blanks with field spikes were submitted with the samples. Historical PFOA values for these locations were provided by Weston Solutions and the concentrations of the low and high field spike varied by sample location accordingly. Each empty 500 mL container was marked with a "fill to here" line to produce a final sample volume of 450 mL. Containers designated for field matrix samples were fortified with an appropriate matrix spike solution containing PFOA prior to being sent to the field for sample collection. Table 1 below summarizes the sample results. The average between the sample and the sample duplicate is provided along with the relative percent difference (%RPD), if applicable. The limit of quantitation (LOQ) of PFOA for the sample set was 0.0244 ng/mL. All results for quality control samples prepared and analyzed with the samples will be provided and discussed elsewhere in this report.

Table 1. Sample Results Summary.

Table 1. Sample Results Summary.

Sample Comment	*Sample Description*	*(1)PFOA Conc. (ng/mL)*
GLP07-01-02-001	DAL GW TRIP1 0 070920	<0.0244
GLP07-01-02-005	DAL GW 601R 0 070920	0.182
GLP07-01-02-006	DAL GW 601R DB 070920	0.176
Average		***0.179***
%RPD		***3.1***
GLP07-01-02-009	DAL GW 601S 0 070920	0.220
GLP07-01-02-010	DAL GW 601S DB 070920	0.223
Average		***0.221***
%RPD		***1.4***
GLP07-01-02-013	DAL GW 601L 0 070920	11.0
GLP07-01-02-014	DAL GW 601L DB 070920	11.0
Average		***11.0***
%RPD		***0.00***
GLP07-01-02-017	DAL GW 602S 0 070920	0.341
GLP07-01-02-018	DAL GW 602S DB 070920	0.386
Average		***0.363***
%RPD		***12***
GLP07-01-02-021	DAL GW 602L RB 070920	<0.0244
GLP07-01-02-022	DAL GW 602L 0 070920	2.74
GLP07-01-02-023	DAL GW 602L DB 070920	2.77
Average		***2.76***
%RPD		***1.3***
GLP07-01-02-026	DAL GW 603S 0 070920	1.22
GLP07-01-02-027	DAL GW 603S DB 070920	1.36
Average		***1.29***
%RPD		***11***
GLP07-01-02-030	DAL GW 603L 0 070920	0.343
GLP07-01-02-031	DAL GW 603L DB 070920	0.348
Average		***0.346***
%RPD		***1.5***

Table 1. Sample Results Summary. (Continued)

Sample Comment	*Sample Description*	*(1)PFOA Conc. (ng/mL)*
GLP07-01-02-034	DAL GW 604S 0 070920	1.16
GLP07-01-02-035	DAL GW 604S DB 070920	1.07
Average		***1.11***
%RPD		***8.4***
GLP07-01-02-038	DAL GW 604L 0 070920	1.29
GLP07-01-02-039	DAL GW 604L DB 070920	1.31
Average		***1.30***
%RPD		***1.5***
GLP07-01-02-042	DAL GW 605R 0 070920	0.0522
GLP07-01-02-043	DAL GW 605R DB 070920	0.0541
Average		***0.0532***
%RPD		***3.6***
GLP07-01-02-046	DAL GW 605L RB 070920	<0.0244
GLP07-01-02-047	DAL GW 605L 0 070920	(2)31.7
GLP07-01-02-048	DAL GW 605L DB 070920	31.4
Average		***(2)31.6***
%RPD		***0.95***
GLP07-01-02-051	DAL GW TRIP2 0 070920	<0.0244

(1) Recoveries of associated field matrix spikes were within 100±30%. Sample results considered accurate to within 100±25%, the overall analytical method uncertainty. See *Determination of Analytical Method Uncertainty* section for more information.

(2) A laboratory matrix spike of GLP07-01-02-047 was used to determine the accuracy of the sample results as the field matrix spikes were too low for the given endogenous concentration. The sample results for this location are considered accurate to within 100±25%, the overall analytical method uncertainty.

Test Samples

Fifty-four sample bottles collected by Weston Solutions, Inc personnel were received at the 3M Environmental Laboratory on September 21, 2007. The samples were logged in by 3M Environmental Laboratory personnel and placed in refrigerated storage on September 21, 2007 until they were removed for analysis. Samples were prepared for analysis on October 1, 2007 and October 11, 2007.

The test system for this study is "real world" groundwater samples, not dosed with a specific lot of test substance. The table below provides the key code for sample descriptions.

Table 2. Sample Description Key Code.

String Number	*String Descriptor*	*Example*
1	General Sampling Location	DAL= Decatur, Alabama
2	Sample Type	GW= Ground Water
3	Well Number	Example: 601
4	Geologic Unit/Well Type	S = Epikarst Well
		L = Limestone (bedrock) well
		R = Residuum well
5	Sample Type	0=primary sample volume
		DB=duplicate sample
		RB=equipment rinseate blank
		TRIP=trip blank
6	Sampling Date	070920 = September 20, 2007

Reference Substances

Table 3 lists the pertinent information regarding the reference substance used for this study.

Table 3. Study Reference Substances.

Reference Substance	*PFOA*
Chemical Name	Perfluorooctanoate
Chemical Formula	$C_7F_{15}COO^-NH_4^+$
Identifier	CAS # 335-67-1
Source	3M
Expiration Date	2/27/2017
Storage Conditions	Frozen
Chemical Lot Number	332
TCR Number	TCR-123
Physical Description	White Powder
Purity	95.0%

Method Summaries

Preparatory and Analytical Methods

Preparation

All samples, calibration standards, and associated quality control samples were prepared using the procedure outlined in ETS-8-44.0. Briefly, a 0.7 mL (approximate) aliquot of the water sample, calibration standard, etc. was transferred to a plastic autovial for analysis.

Samples were prepared for analysis on October 1, 2007 and were analyzed on October 4, 2007. Additional preparation was conducted on October 11, 2007 followed by analysis on October 13, 2007.

A laboratory matrix spike was prepared for GLP07-01-02-047 by spiking a separate 10 mL aliquot with a known amount of the target analyte prior to analysis. All samples and spikes associated with location DAL GW 605L (GLP07-01-02-047 through GLP07-01-02-050) required dilution as the concentrations exceeded the upper calibration range. Sample dilution was achieved by using a 25 µL or 10 µL injection volume against a calibration curve established with a 100 µL injection volume. The samples requiring dilution were analyzed on instrument ETSOllie.

Analysis

All sample and quality control extracts were analyzed for PFOA using high performance liquid chromatography/ tandem mass spectrometry (HPLC/MS/MS). Pertinent instrument parameters, the liquid chromatography program, and the specific mass transitions analyzed are described in the tables below.

Table 4. Instrument Parameters.

Analysis Date	10/4/2007	10/13/2007
Instrument Name	ETSMaryAnn	ETSOllie
Liquid Chromatograph	Agilent 1200	Agilent 1100
Guard column	Betasil C8 (4.6 mm X 150 mm), 5 µm	Betasil C8 (4.6 mm X 150 mm), 5 µm
Analytical column	Betasil C18 (4.6 mm X100 mm), 5 µm	Betasil C18 (4.6 mm X100 mm), 5 µm
Injection Volume	50 µL	100 µL
Mass Spectrometer	Applied Biosystem API 5000	Applied Biosystem API 4000
Ion Source	Z-spray	Z-spray
Polarity	Negative	Negative
Software	Analyst 1.4.2	Analyst 1.4.2

Table 5. Liquid Chromatography Program.

Step Number	Total Time (min)	Flow Rate (μL/min)	Percent A 2 mM Ammonium Acetate (aq)	Percent B Methanol
0	0.00	1000	97.0	3.0
1	0.5	1000	97.0	3.0
2	11.0	1000	5.0	95.0
3	13.5	1000	5.0	95.0
4	13.6	1000	97.0	3.0
5	17.0	1000	97.0	3.0

Table 6. Mass Transitions.

Analyte	Mass Transition Q1/Q3	Dwell Time (msec)
PFOA	413/369	200
	413/219	200
	413/169	200

Analytical Results

Calibration

Calibration standards were prepared by spiking known amounts of stock solutions containing the target analyte into 100 mL of reverse-osmosis purified water. A total of thirteen standards were prepared ranging from 0.025 ng/mL to 50 ng/mL (nominal concentrations). A quadratic, 1/x weighted, calibration curve was used to fit the data. The correlation coefficients (r) were greater than 0.999. The data were not forced through zero during the fitting process. Calculating the standard concentration using the peak area counts and the resultant calibration curve confirmed accuracy of each curve point. ETS 8-44.0 requires that each standard used to generate the final calibration should back calculate to within 100±25% of the theoretical value (100±30% for the LOQ standard). All calibration points used to generate the final calibration curve met this criterion.

Limit of Quantitation (LOQ)

The LOQ for this analysis, as defined in ETS-8-44.0, is the lowest non-zero calibration standard in the curve in which the area counts are at least twice the average of the method blank area counts and meets the calibration accuracy requirement described above (100±30%).

Blanks

Three types of blanks were prepared and analyzed with the samples: method (solvent) blanks, equipment rinseate blanks, and trip blanks. Each blank type is described below.

Solvent Blank

Several blanks of reverse-osmosis purified water were analyzed to assess system contamination and/or instrument carryover. In general, analyte peak area counts in solvent blank samples were less than half the area counts of the calibration standard used to establish the LOQ except during the initial instrument warm-up period prior to analyzing the calibration curve.

Equipment Blanks

Two aqueous equipment rinseate blanks were submitted as samples: GLP07-01-02-021 and GLP07-01-02-046. The 3M Environmental Laboratory provided two one-liter bottles of ASTM type I water for rinsing. The resultant PFOA concentration of these samples was <0.0244 ng/mL.

Trip Blanks

Prior to sample collection, two separate sample containers were filled with 450 mL of ASTM Type I water, sealed, and shipped to the sample collection site along with the empty containers. These two samples were analyzed as the field/trip blanks. The trip blank serves as an additional method blank that account for any storage conditions and/or holding time issues that the samples may experience. The resultant PFOA concentration for the two field/trip blanks was <0.0244 ng/mL.

Continuing Calibration

During the course of the analytical sequence, several continuing calibration verification samples (CCVs) were analyzed to confirm that the instrument response and the initial calibration curve were still in control. All CCVs met the ETS 8-44.0 method acceptance criteria for accuracy of 100±25% recovery.

Lab Control Spikes (LCSs)

Triplicate low (0.2 ng/mL nominal concentration) and high (4 ng/mL nominal concentration) lab control spikes (LCSs) were prepared each day samples were prepared. LCSs were prepared by spiking known amounts of the target analyte into separate 25 mL aliquots of reverse-osmosis purified water. The spiked water aliquots were then analyzed in the same manner as the samples. Individual LCS results, along with the average and percent RSD for each spike level are presented in the data table below. ETS 8-44.0 requires that each level of LCSs be evaluated independently and meet the following criteria: 100±20% (accuracy) and RSD<20%(precision). For the LCSs prepared on 10/1/2007, the average low level LCS recovery did not meet the accuracy requirement (159%). A spiking solution later suspected to be contaminated with PFOA was used to prepare the low level LCSs on this day. The same spiking solution was used to prepare the four lowest calibration standards which also did not meet method calibration criteria. During the course of the analysis on 10/4/2007, a new spiking solution was prepared and the four lowest calibration points were re-prepared which met method calibration criteria upon analysis; however, the low-level LCSs were not re-prepared. Low-level LCSs prepared on 10/11/2007 used a different spiking solution and met method criteria supporting the hypothesis that the LCS failures on 10/1/2007 were due to a suspect spiking solution and not the overall laboratory process. A method deviation has been issued as the accuracy requirement of 100±20% was not met for the low level LCSs. Samples analyzed on 10/4/2007 were not reanalyzed unless a dilution was required.

Table 7. Lab Control Spike Results.

Preparation Day: 10/1/2007 *Analysis Day: 10/4/2007*		*(1)PFOA*		
Sample Comment	***Sample ID***	***Spiked Conc. (ng/mL)***	***Calc. Conc. (ng/mL)***	***%Rec.***
LCS-071001-001	(2)0.2 ng/mL in RO water	0.195	0.339	(2)173
LCS-071001-002	(2)0.2 ng/mL in RO water	0.195	0.307	(2)157
LCS-071001-003	(2)0.2 ng/mL in RO water	0.195	0.285	(2)146
LCS-071001-004	4 ng/mL in RO water	3.91	3.57	91.3
LCS-071001-005	4 ng/mL in RO water	3.91	3.77	96.4
LCS-071001-006	4 ng/mL in RO water	3.91	3.93	100
Low Level Average				***(3)159***
Low Level %RSD				***8.7***
High Level Average				***96.1***
High Level %RSD				***4.8***

Preparation Day: 10/11/2007 *Analysis Day: 10/13/2007*		*(1)PFOA*		
Sample Comment	***Sample ID***	***Spiked Conc. (ng/mL)***	***Calc. Conc. (ng/mL)***	***%Rec.***
LCS-071011-001	0.2 ng/mL in RO water	0.195	0.199	102
LCS-071011-002	0.2 ng/mL in RO water	0.195	0.192	98.5
LCS-071011-003	0.2 ng/mL in RO water	0.195	0.222	114
LCS-071011-004	4 ng/mL in RO water	3.91	3.84	98.2
LCS-071011-005	4 ng/mL in RO water	3.91	3.99	102
LCS-071011-006	4 ng/mL in RO water	3.91	4.14	106
Overall Average				***103***
Overall %RSD				***7.1***
Low Level Average				***105***
Low Level %RSD				***7.7***
High Level Average				***102***
High Level %RSD				***3.8***

(1) Table displays rounded values for all concentration and percent recovery values (3 significant figures) and %RSD (2 significant figures). Reported values may vary slightly from the raw data.

(2) The low level LCSs prepared on 10/1/2007 were prepared with a spiking solution later suspected to be contaminated with PFOA. The same spiking solution was used to prepare the four lowest calibration standards which also did not meet method calibration criteria. During the course of the analysis on 10/4/2007, a new spiking solution was prepared and the four lowest calibration points were re-prepared and met method calibration criteria upon analysis; however, the low-level LCSs were not re-prepared. Low-level LCSs prepared on 10/11/2007 used a different spiking solution and met method criteria supporting the hypothesis that the LCS failures on 10/1/2007 were due to a suspect spiking solution and not the overall laboratory process. Samples analyzed on 10/4/2007 were not reanalyzed unless a dilution was required.

(3) The low level LCSs did not meet method acceptance criteria for accuracy (100±20%). A method deviation has been issued.

Sample Duplicates

All sample locations (except rinseate blanks and trip blanks) were collected in duplicate; therefore, laboratory duplicates were not prepared. The relative percent difference (%RPD) for each sample and sample duplicate is provided in Table 1. The %RPD for each location was less than 20%.

Field Matrix Spikes (FMSs)

Low level and high level field matrix spikes were collected at each sampling location to verify that the analytical method is applicable to the sample matrix. (Additional mid-level spikes were prepared for the Trip Blank spikes to account for all spike levels prepared for the sample locations.) Field matrix spike recoveries within 100±30% confirm that "unknown" components in the sample matrix do not interfere with the analysis of the analyte of interest. The low and high level spike concentrations varied depending on the historical concentration of the sample location. ETS-8-44.0 states that targeted fortification levels of field matrix spike levels should be between 0.5 and 10 times the endogenous level to be used to determine the statement of accuracy for the sample results without further justification. The table below lists the final concentrations of the low and high spikes for each location. Field matrix spike recoveries are reported in the *Data Summary and Discussion* section below.

Table 8. Field Matrix Spike Concentrations.

3M LIMS Sample ID	*Sample Location*	*Low Spike Concentration (ng/mL)*	*Mid Spike Concentration (ng/mL)*	*High Spike Concentration (ng/mL)*
GLP07-01-02-001 thru -004	DAL GW TRIP1	0.262	0.523	1.05
GLP07-01-02-005 thru -008	DAL GW 601R	0.262	NA	1.05
GLP07-01-02-009 thru -012	DAL GW 601S	0.262	NA	1.05
GLP07-01-02-013 thru -016	DAL GW 601L	0.262	NA	26.2
GLP07-01-017 thru -020	DAL GW 602S	0.523	NA	5.23
GLP07-01-021	DAL GW 602L RB	(1)NA	(1)NA	(1)NA
GLP07-01-022 thru -025	DAL GW 602L	0.523	NA	5.23
GLP07-01-026 thru -029	DAL GW 603S	0.262	NA	2.62
GLP07-01-030 thru -033	DAL GW 603L	0.262	NA	2.62
GLP07-01-034 thru -037	DAL GW 604S	0.262	NA	1.05
GLP07-01-038 thru -041	DAL GW 604L	0.262	NA	5.23
GLP07-01-042 thru -045	DAL GW 605R	0.262	NA	1.05
GLP07-01-046	DAL GW 605L RB	(1)NA	(1)NA	(1)NA
GLP07-01-047 thru -050	DAL GW 605L	0.523	NA	5.23
GLP07-01-051 thru -054	DAL GW TRIP2	0.262	5.23	26.2

(1) Field matrix spikes were not prepared for the equipment rinseate sample.

$$\text{FMS Spike Recovery} = \frac{[\text{Conc. FMS sample}(\frac{\text{ng}}{\text{mL}}) - (\text{Average Conc. of Sample/Sample Dup}(\frac{\text{ng}}{\text{mL}})]}{\text{Spike Amount (ng/mL)}} * 100\%$$

Laboratory Matrix Spikes (LMSs)

A separate laboratory matrix spike was prepared for GLP07-01-02-047 as the two field matrix spikes prepared for this location were less than half the resultant endogenous concentration. A 100 ng/mL (nominal) spike was prepared by spiking a known amount of

PFOA into a separate 10 mL aliquot of the sample. The LMS was used to assess the sample accuracy for this sample location. The LMS recovery is presented in the *Data Summary and Discussion* section below.

$$\text{LMS Spike Recovery} = \frac{[\text{Conc. LMS sample}(\frac{ng}{mL}) - (\text{Conc. GLP07-01-02-047}(\frac{ng}{mL})]}{\text{Spike Amount}\,(\frac{ng}{mL})} * 100\%$$

Data Summary and Discussion

Table 9 below summarizes the PFOA sample results and field matrix spike (FMS) recoveries for each sample submitted. The table provides the average concentration and the relative percent difference (%RPD) of the sample and sample duplicate. Results and average values are rounded to three significant figures. Percent relative difference (%RPD) values are rounded to two significant figures. Because of rounding, values may vary slightly from those listed in the raw data. Field matrix spikes meeting the method acceptance criteria of 100±30% demonstrate that the analytical method is appropriate for the given matrix. If the low level spike amount was less than half the resultant endogenous concentration, the low FMS recovery was not reported as the spike level was not appropriate for the given sample concentration.

All reportable field matrix spike recoveries were within 100±30%; therefore, the results were considered accurate to within the overall analytical method uncertainty of 100±25% (see *Determination of Analytical Method Uncertainty* for more information.) The lab matrix spike prepared for GLP07-01-02-047 produced a recovery of 89.3%. The accuracy of this location is considered to be within 100±25% as well.

Table 9. PFOA Sample Results with Field Matrix Spike Recoveries.

Table 9. PFOA Sample Results with Field Matrix Spike Recoveries.			*(1)PFOA*	
Sample Comment	***Sample Description***	***Dilution Factor***	***Calculated Conc. (ng/mL)***	***%Recovery***
GLP07-01-02-001	DAL GW TRIP1 0 070920	1	<0.0244	NA
GLP07-01-02-002	DAL GW TRIP1 LS 070920	1	0.260	99.4
GLP07-01-02-003	DAL GW TRIP1 MS 070920	1	0.582	111
GLP07-01-02-004	DAL GW TRIP1 HS 070920	1	1.23	118
GLP07-01-02-005	DAL GW 601R 0 070920	1	0.182	NA
GLP07-01-02-006	DAL GW 601R DB 070920	1	0.176	NA
GLP07-01-02-007	DAL GW 601R LS 070920	1	0.459	107
GLP07-01-02-008	DAL GW 601R HS 070920	1	1.37	114
Average			***0.179***	
%RPD			***3.1***	
GLP07-01-02-009	DAL GW 601S 0 070920	1	0.220	NA
GLP07-01-02-010	DAL GW 601S DB 070920	1	0.223	NA
GLP07-01-02-011	DAL GW 601S LS 070920	1	0.509	110
GLP07-01-02-012	DAL GW 601S HS 070920	1	1.42	114
Average			***0.221***	
%RPD			***1.4***	
GLP07-01-02-013	DAL GW 601L 0 070920	1	11.0	NA
GLP07-01-02-014	DAL GW 601L DB 070920	1	11.0	NA
GLP07-01-02-015	DAL GW 601L LS 070920	1	11.1	NR
GLP07-01-02-016	DAL GW 601L HS 070920	1	33.1	84.1
Average			***11.0***	
%RPD			***0.00***	
GLP07-01-02-017	DAL GW 602S 0 070920	1	0.341	NA
GLP07-01-02-018	DAL GW 602S DB 070920	1	0.386	NA
GLP07-01-02-019	DAL GW 602S LS 070920	1	0.798	83.0
GLP07-01-02-020	DAL GW 602S HS 070920	1	5.91	106
Average			***0.363***	
%RPD			***12***	
GLP07-01-02-021	DAL GW 602L RB 070920	1	<0.0244	NA
GLP07-01-02-022	DAL GW 602L 0 070920	1	2.74	NA
GLP07-01-02-023	DAL GW 602L DB 070920	1	2.77	NA
GLP07-01-02-024	DAL GW 602L LS 070920	1	3.22	NR
GLP07-01-02-025	DAL GW 602L HS 070920	1	8.24	105
Average			***2.75***	
%RPD			***1.3***	

Table 9. PFOA Sample Results with Field Matrix Spike Recoveries. (Continued)

			(1)PFOA	
Sample Comment	*Sample Description*	*Dilution Factor*	*Calculated Conc. (ng/mL)*	*%Recovery*
GLP07-01-02-026	DAL GW 603S 0 070920	1	1.22	NA
GLP07-01-02-027	DAL GW 603S DB 070920	1	1.36	NA
GLP07-01-02-028	DAL GW 603S LS 070920	1	1.52	NR
GLP07-01-02-029	DAL GW 603S HS 070920	1	3.79	95.5
Average			***1.29***	
%RPD			***11***	
GLP07-01-02-030	DAL GW 603L 0 070920	1	0.343	NA
GLP07-01-02-031	DAL GW 603L DB 070920	1	0.348	NA
GLP07-01-02-032	DAL GW 603L LS 070920	1	0.645	114
GLP07-01-02-033	DAL GW 603L HS 070920	1	3.10	105
Average			***0.346***	
%RPD			***1.5***	
GLP07-01-02-034	DAL GW 604S 0 070920	1	1.16	NA
GLP07-01-02-035	DAL GW 604S DB 070920	1	1.07	NA
GLP07-01-02-036	DAL GW 604S LS 070920	1	1.34	NR
GLP07-01-02-037	DAL GW 604S HS 070920	1	2.17	101
Average			***1.11***	
%RPD			***8.4***	
GLP07-01-02-038	DAL GW 604L 0 070920	1	1.29	NA
GLP07-01-02-039	DAL GW 604L DB 070920	1	1.31	NA
GLP07-01-02-040	DAL GW 604L LS 070920	1	1.45	NR
GLP07-01-02-041	DAL GW 604L HS 070920	1	5.68	83.8
Average			***1.30***	
%RPD			***1.5***	
GLP07-01-02-042	DAL GW 605R 0 070920	1	0.0522	NA
GLP07-01-02-043	DAL GW 605R DB 070920	1	0.0541	NA
GLP07-01-02-044	DAL GW 605R LS 070920	1	0.265	81.0
GLP07-01-02-045	DAL GW 605R HS 070920	1	1.05	95.5
Average			***0.0532***	
%RPD			***3.6***	

Table 9. PFOA Sample Results with Field Matrix Spike Recoveries. (Continued)			(1)*PFOA*	
Sample Comment	***Sample Description***	***Dilution Factor***	***Calculated Conc. (ng/mL)***	***%Recovery***
GLP07-01-02-046	DAL GW 605L RB 070920	1	<0.0244	NA
GLP07-01-02-047	DAL GW 605L 0 070920	4	31.7	NA
GLP07-01-02-048	DAL GW 605L DB 070920	4	31.4	NA
GLP07-01-02-049	DAL GW 605L LS 070920	4	31.3	NR
GLP07-01-02-050	DAL GW 605L HS 070920	4	31.2	NR
GLP07-01-02-047 LMS	DAL GW 605L 0 070920 LMS	10	119	(2)89.3
Average			***31.6***	
%RPD			***0.32***	
GLP07-01-02-051	DAL GW TRIP2 0 070920	1	<0.0244	NA
GLP07-01-02-052	DAL GW TRIP2 LS 070920	1	2.36	90.1
GLP07-01-02-053	DAL GW TRIP2 MS 070920	1	(3)19.6	75.0
GLP07-01-02-054	DAL GW TRIP2 HS 070920	1	(3)4.76	91.0

(1) Recoveries of associated field matrix spikes were within 100±30%. Sample results considered accurate to within 100±25%, the overall analytical method uncertainty. See *Determination of Analytical Method Uncertainty* section for more information.

(2) A laboratory matrix spike of GLP07-01-02-047 was used to determine the accuracy of the sample results as the field matrix spikes were too low for the given endogenous concentration. The sample results for this location are considered accurate to within 100±25%, the overall analytical method uncertainty.

(3) Sample descriptions for GLP07-01-02-053 and -054 were mislabeled when entered into the LIMS system. The sample bottle assigned to GLP07-01-02-053 contained the high level spike and the bottle assigned to GLP07-01-02-054 contained the mid level spike according to the 3M Environmental Lab label affixed to the bottle during bottle preparation.

NR=Not reportable. Spike level was less than half the endogenous concentration and not considered appropriate for the given sample.

Statistical Methods and Calculations

Statistical methods used to interpret sample results include averages and standard deviations. The Analyst software programs calculated sample concentrations using resultant analyte peak areas and the established quadratic, 1/x weighted, calibration curve. Sample calculations and equations used to report method accuracy and precision are described below.

Accuracy and Precision Equations

$$\text{LCS Percent Recovery} = \frac{\text{Calculated Concentration}}{\text{Spike Concentration}} * 100\%$$

$$\%\,\text{RSD (Relative Standard Deviation)} = \frac{\text{standard deviation of replicates}}{\text{replicate average}} * 100\%$$

$$\%\,\text{RPD (Relative Percent Difference)} = \frac{\text{Absolute difference between sample duplicates}}{\text{average sample concentration}} * 100\%$$

Determination of Analytical Method Uncertainty

The analytical method uncertainty for PFOA was determined using historical data that was control charted to evaluate the method accuracy and precision. (Analytical method uncertainty and control chart procedures are outlined in ETS 12-12.2 "Estimation of Uncertainty of Measurements" and ETS 4-026.2 "Control Charts for Laboratory Analyses". The control chart for ETS-8-044.0 consists of all reported laboratory control spike recoveries (in %) for data generated and reported using this method. The last fifty historical data points (including the points generated in this study) were extracted from the control chart and the overall average (103%) and standard deviation (12.5%) were determined. (Low level LCSs prepared on 10/01/2007 were excluded from the control chart as they were found to be prepared with a contaminated spiking solution.) The expanded uncertainty was then determined by multiplying the standard deviation by a factor of 2, which corresponds to the 95% confidence level. This produced an expanded analytical method uncertainty of 25%. This expanded analytical method uncertainty (95% confidence level) was used to assign the overall analytical method uncertainty to the final results presented in Table 1 and Table 9.

STATEMENT OF CONCLUSION

Sample results were summarized in Table 1. Historical values of lab control spikes for this method recorded in the laboratory's control chart were used to determine the overall analytical method uncertainty (100±25%). Sample results with field matrix spike recoveries within 100±30% were considered to be accurate within the stated method uncertainty.

References

ETS 8-44.0 "Method of Analysis for the Determination of Perfluorinated Compounds in Water by LC/MS/MS; Direct Injection Analysis".

ETS 4-026.2 "Control Charts for Laboratory Analyses".

ETS 12-012.2 "Estimation of Uncertainty of Measurements".

List of Attachments

- **Attachment A: Selected Chromatograms and Calibration Curves**
- **Attachment B: Extraction and Analytical Methods**
- **Attachment C: Protocol and Protocol Amendments**
- **Attachment D: Protocol and/or Method Deviations**

Signatures

Michelle D. Malinsky 2/8/2008
Michelle D. Malinsky, Ph.D. Principal Analytical Investigator Date

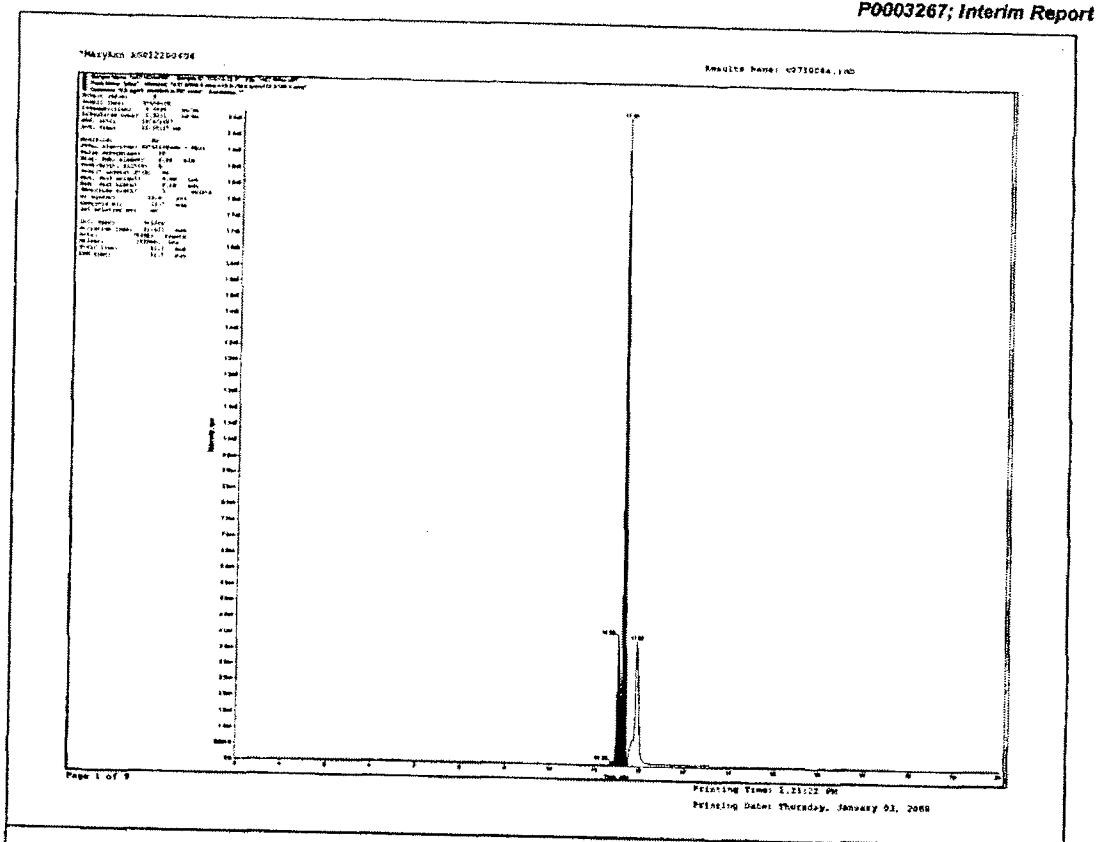
Jacoby 8 Feb. 2008
Clifftion B. Jacoby, Ph.D. 3M Technical Reviewer Date

11 FEB 2008
William K. Reagen, Ph.D. 3M Environmental Laboratory Manager Date

Michael A. Santoro 02/15/08
Michael A. Santoro Sponsor Representative Date

Kesari 2/22/08
Jaisimha Kesari, P.E., DEE, Study Director Date

ATTACHMENT A: SAMPLE CHROMATOGRAMS AND CALIBRATION CURVES



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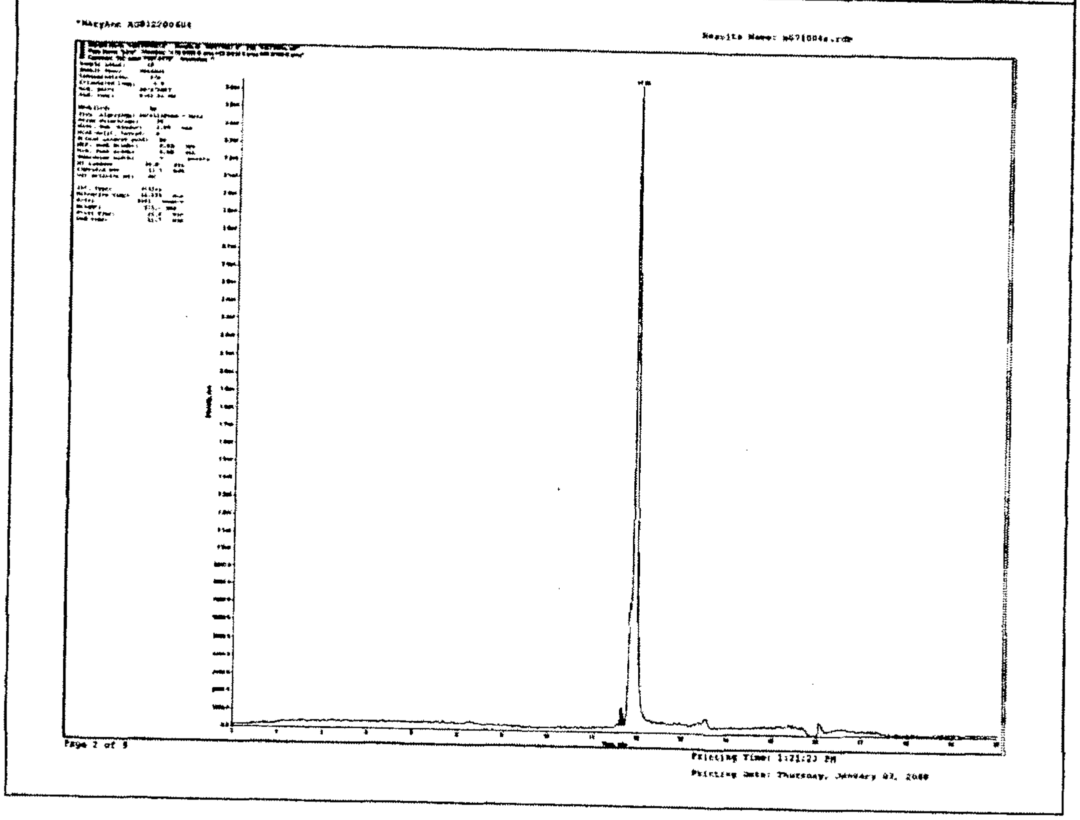

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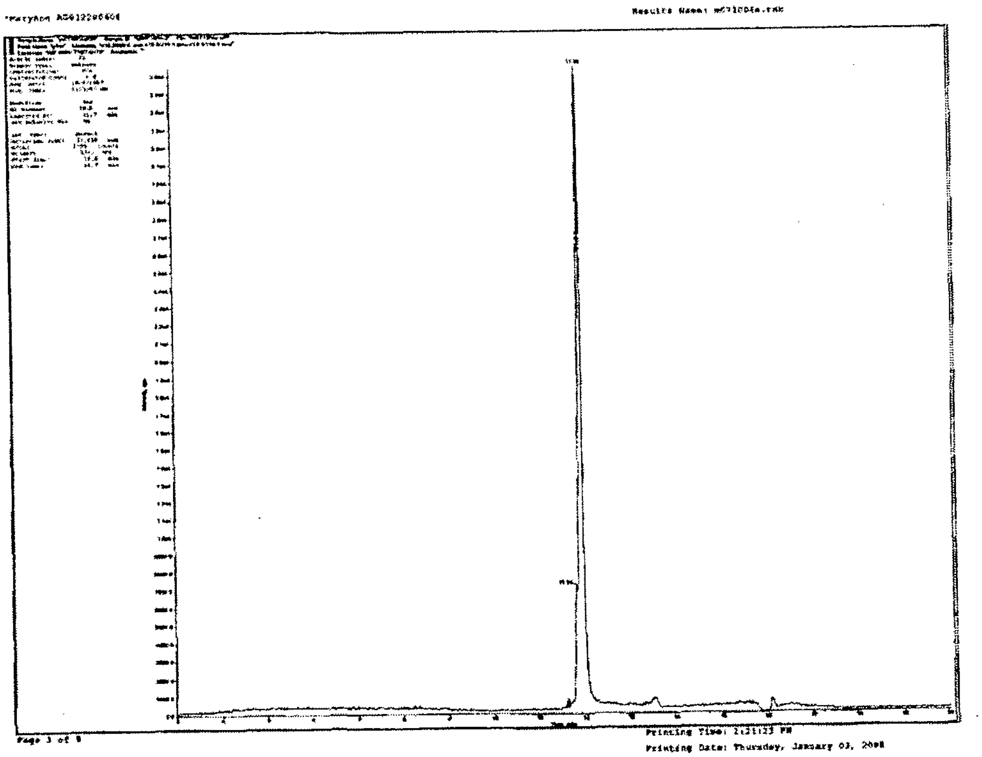

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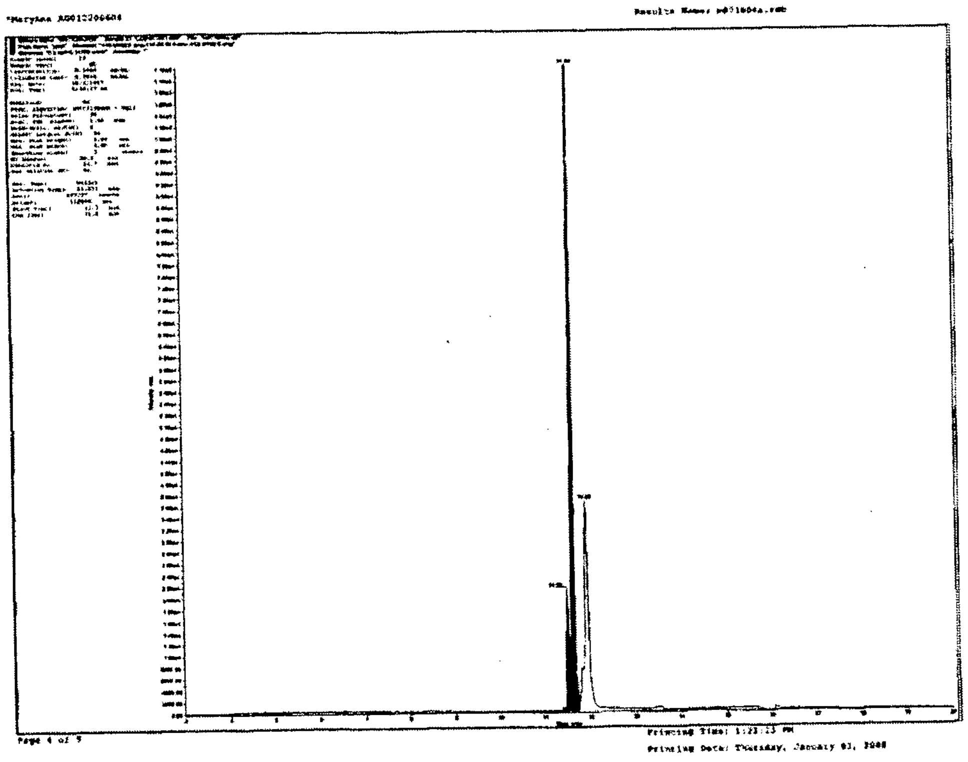

*MaryAnn A0012206604

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*MaryAnn ADD12280604

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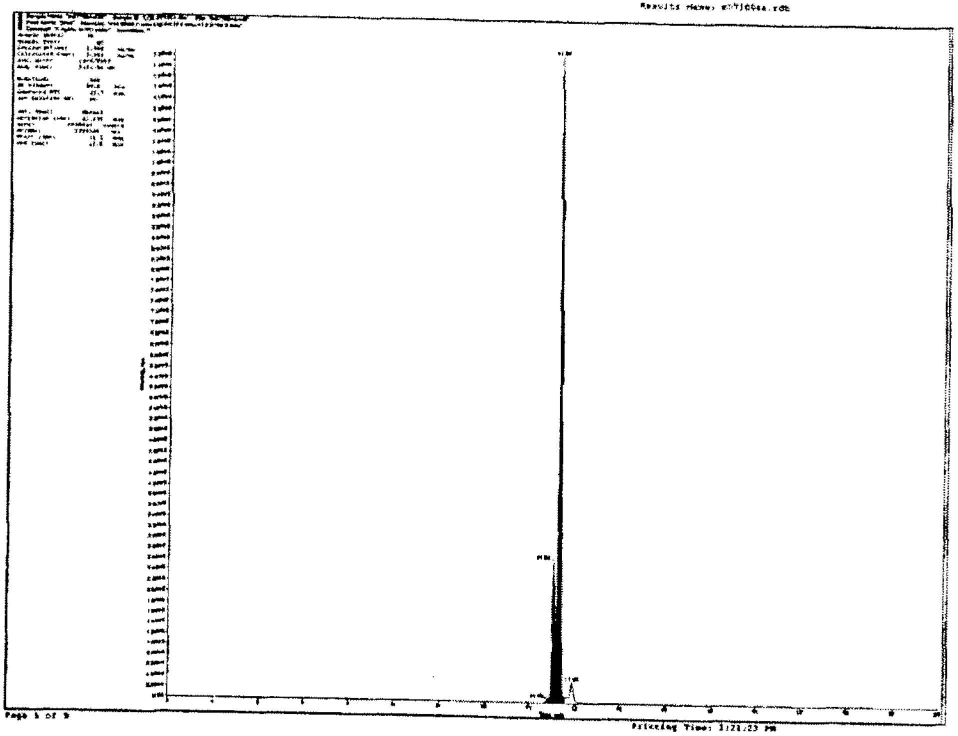

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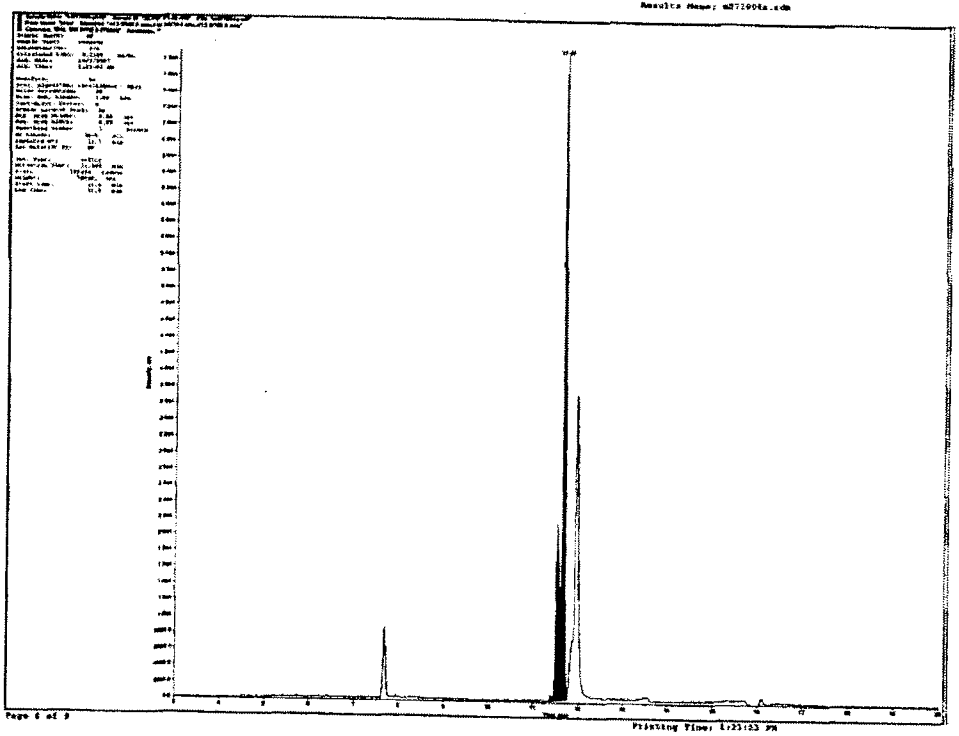

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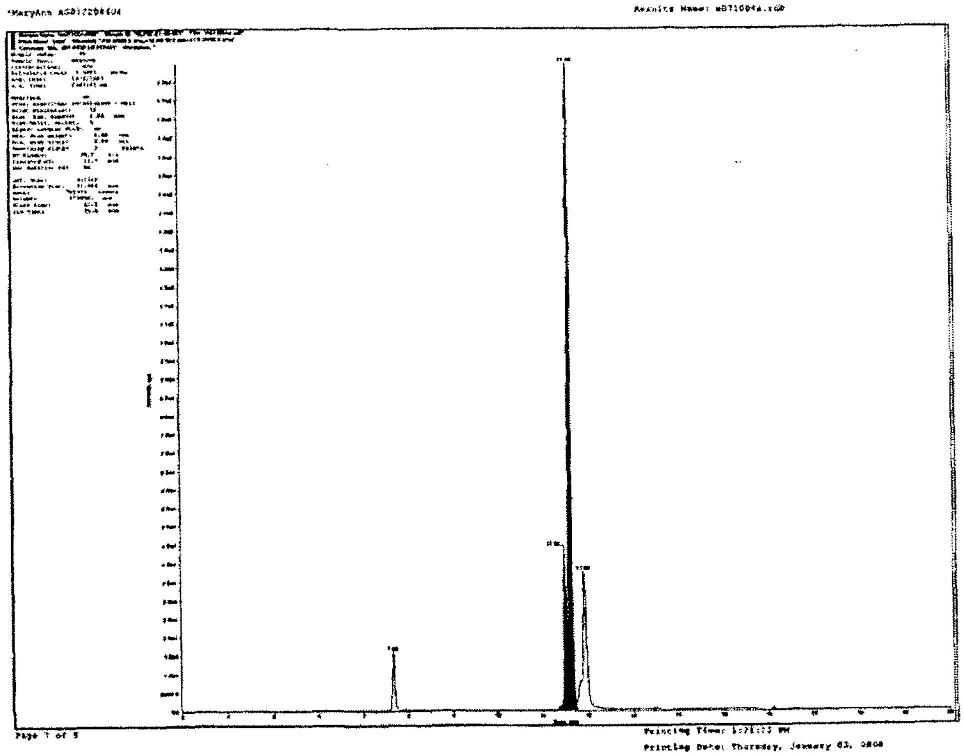

*MaryAnn AG01220904

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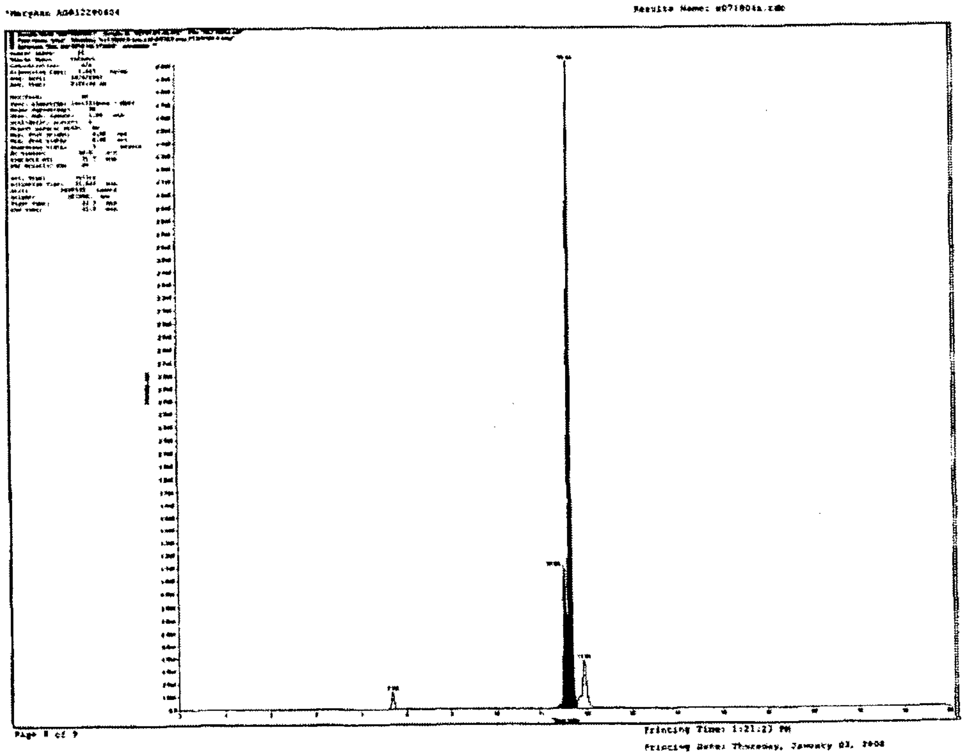

*MaryAnn AG01220904

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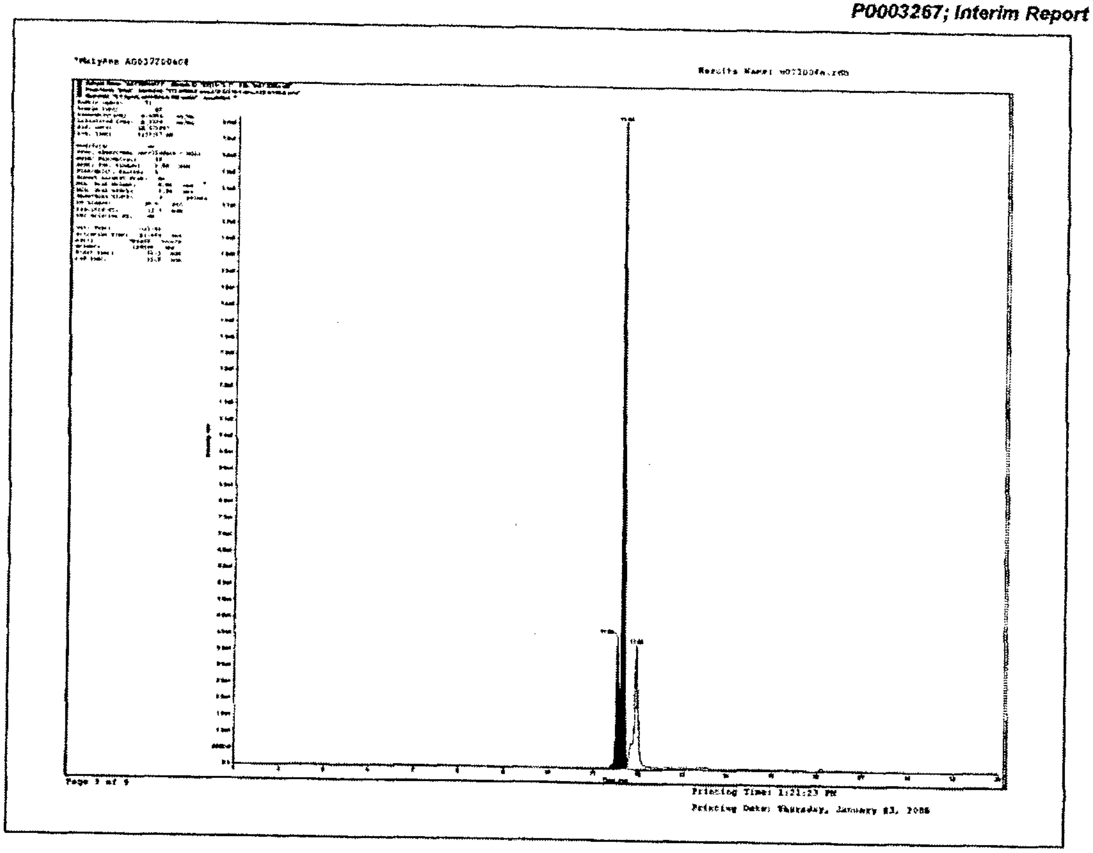

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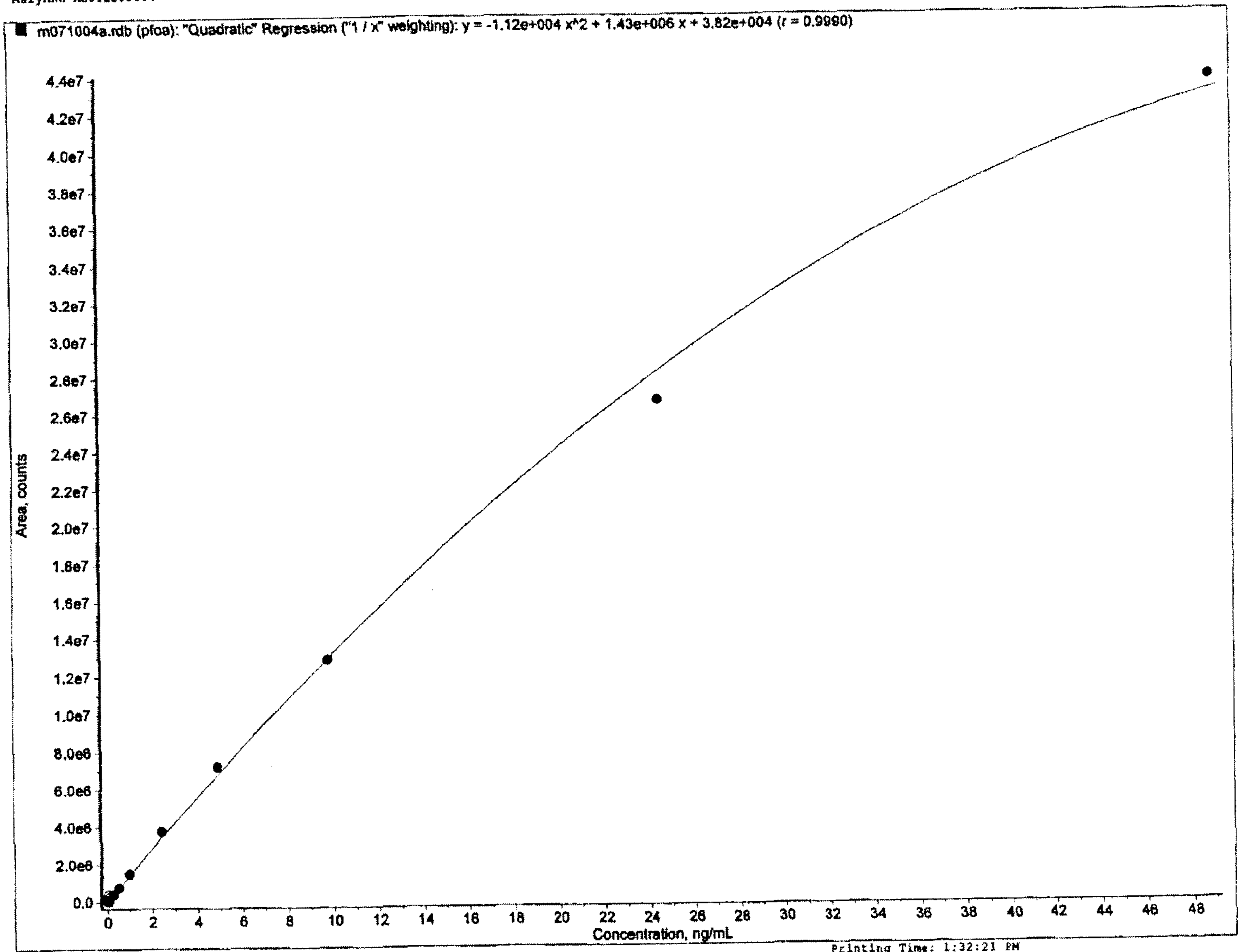
*MaryAnn AG012200604

Results Name: m071004a.rdb

m071004a.rdb (pfoa): "Quadratic" Regression ("1 / x" weighting): y = -1.12e+004 x^2 + 1.43e+006 x + 3.82e+004 (r = 0.9980)



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INTERIM REPORT 5–ANALYSIS OF PFOA FROM 3M DECATUR OFF-SITE 605 SERIES WELLS

Interim Report #5-Analysis of PFOA from 3M Decatur Offsite 605 Series Wells – April 2008

Study Title

Analysis of Perfluorooctanoic Acid (PFOA) in Water, Soil, Sediment, Fish, and Clams Using LC/MS/MS for the 3M Decatur Monitoring Program

MPI Protocol Number: P00003267

Data Requirement

EPA TSCA Good Laboratory Practice Standards 40 CFR Part 792

Study Director

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Date of signing

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Project Identification

GLP07-01-03

Total Number of Pages

121

This page has been reserved for specific country requirements.

GLP COMPLIANCE STATEMENT

Report Title: Interim Report #5-Analysis of PFOA from 3M Decatur Offsite 605 Series Wells–April 2008

Project Identification Number: GLP07-01-03

Study Title: Analysis of Perfluorooctanoic Acid (PFOA) in Water, Soil, Sediment, Fish, and Clams Using LC/MS/MS for the 3M Decatur Monitoring Program

MPI GLP Protocol Number P0003267

This analytical phase was conducted in compliance with Toxic Substances Control Act (TSCA) Good Laboratory Practice (GLP) Standards, 40 CFR 792, with the exceptions listed below:

Exceptions to GLP compliance:

Some of the reference substances used to prepare the calibration standard mix have expired. The expired neat materials have been sent out for recertification and are not expected to have any impact on the results contained in this report.

Michael A Santoro 04/29/08
Michael A. Santoro, Sponsor Representative Date

5/2/08
Jaisimha Kesari, P.E., DEE, Study Director Date

QUALITY ASSURANCE STATEMENT

Report Title: Interim Report #5-Analysis of PFOA from 3M Decatur Offsite 605 Series Wells–April 2008

Project Identification Number: GLP07-01-03

Study Title: Analysis of Perfluorooctanoic Acid (PFOA) in Water, Soil, Sediment, Fish, and Clams Using LC/MS/MS for the 3M Decatur Monitoring Program

MPI GLP Protocol Number P0003267

This analytical phase was audited by the 3M Environmental Laboratory Quality Assurance Unit (QAU), as indicated in the following table. The findings were reported to the principal investigator (P.I.), laboratory management and study director.

Inspection Dates	Phase	Date Reported to		
		Principal Analytical Investigator	**Study Director's Management**	**Study Director**
4/14/08	Data and Report	4/16/08	4/21/08	4/21/08

Carey Howell
QAU Representative

5-1-08
Date

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STUDY INFORMATION

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Michelle Malinsky, Principal Analytical Investigator
Susan Wolf, Report Author
Clifton B. Jacoby, Ph.D., 3M Technical Review
Zhuojing Liu; Analyst

Study Dates

Interim Analytical Initiation: April 3, 2008
Interim Analytical Completion: April 6, 2008
Interim Report Completion: Date of Interim Report Signing

Location of Archives

All original raw data, protocol, and the analytical report have been archived at the 3M Environmental Laboratory according to 40 CFR Part 792. The test substance and analytical reference standard reserve samples are archived at the 3M Environmental Laboratory according to 40 CFR Part 792. All samples (specimens) will be retained and archived according to current 3M Environmental Laboratory standard operating procedures.

SUMMARY AND INTRODUCTION

The 3M Environmental Laboratory analyzed groundwater samples collected offsite from the 3M Decatur, AL facility by Weston Solutions personnel on April 1, 2008. Samples were submitted for analysis under 3M Environmental Laboratory Project Number GLP07-01-03. The GLP protocol number is P0003267: "Analysis of Perfluorooctanoic Acid (PFOA) in Water, Soil, Sediment, Fish, and Clams Using LC/MS/MS for the 3M Decatur Monitoring Program".

The groundwater samples were analyzed for PFOA using method ETS-8-154.3 "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates in Water by Solid Phase Extractions and High Performance Liquid Chromatography/Mass Spectrometry". The experimental start date was April 3, 2008, the day samples were first prepared for analysis by 3M Environmental Laboratory personnel. The experimental completion date was April 6, 2008.

Sample collection containers were prepared at the 3M Environmental Laboratory. Sample containers for each sampling location included a field sample, field sample duplicate, low field spike, mid field matrix spike, and a high field spike. Additionally, one equipment rinse blank and one trip blank with field spikes were submitted with the samples. Each empty 500 mL container was marked with a "fill to here" line to produce a final sample volume of 450 mL. Containers designated for field matrix samples were fortified with an appropriate matrix spike solution containing PFOA prior to being sent to the field for sample collection. Table 1 below summarizes the sample results. The average between the sample and the sample duplicate is provided along with the relative percent difference (%RPD), if applicable. All results for quality control samples prepared and analyzed with the samples will be provided and discussed elsewhere in this report.

Table 1. Sample Results Summary(1).

3M LIMS ID	**Sample Description**	**PFOA Concentration (ng/mL)**
GLP07-01-03-001	DAL GW 605L 0 080401	4.74
GLP07-01-03-002	DAL GW 605L DB 080401	4.55
	Average	**4.65**
	%RPD Sample/Sample Duplicate	**4.1**
GLP07-01-03-006	DAL GW 605R 0 080401	0.101
GLP07-01-03-007	DAL GW 605R DB 080401	0.108
	Average	**0.105**
	%RPD Sample/Sample Duplicate	**6.7**

(1) Samples were extracted by solid-phase extraction using method ETS-8-154.3 on April 3, 2008 and analyzed on April 5-6, 2008. The analytical method uncertainties associated with the reported results is PFOA 100% ± 16%.

TEST & CONTROL SUBSTANCES

There was no test substance or control substances for this analytical phase in the classic sense. The study was purely analytical in nature. All materials used for this study are listed below and were reference materials as described herein.

REFERENCE SUBSTANCES

Table 2 lists the pertinent information regarding the reference substance used for this study.

Table 2. Study Reference Substances.

Reference Substance	**PFOA**
Chemical Name	Perfluorooctanoate
Chemical Formula	$C_7F_{15}COO^-$
Identifier	Ammonium Salt, CAS # 335-67-1
Source	3M
Expiration Date	02/27/2017
Storage Conditions	Frozen
Chemical Lot Number	332
TCR Number	TCR-123
Physical Description	White powder
Purity	95%

TEST SYSTEM

The test system for this study is water samples from 3M Decatur offsite wells collected April 1, 2008 by Weston Solutions, Inc. personnel. Samples for this study are "real world" samples, not dosed with a specific lot of test substance.

Table 3. Sample Description Key Code.

String Number	String Descriptor	Example
1	*General Sampling Location*	*DAL= Decatur, Alabama*
2	*Sample Type*	*GW= Ground Water*
3	*Well Number*	*605R = 605 residuum well*
		605L = 605 limestone bedrock well
4	*Sample Type*	*0=primary sample*
		DB=duplicate sample
		LS=low spike
		MS = mid spike
		HS = high spike
		RB=equipment rinse blank
5	*Sampling Date*	*080401 = April 1, 2008*

METHOD SUMMARY

Preparatory and Analytical Methods

Sample Collection

Samples were collected in 500 mL Nalgene™ (high-density polyethylene) bottles prepared at the 3M Environmental Laboratory. Sample bottles were returned to the laboratory at ambient conditions on April 3, 2008. Samples were stored refrigerated at the laboratory after receipt. A set of laboratory prepared Trip Blank and Trip Blank field matrix spikes were sent with the collection bottles.

Sample Preparation

All samples, calibration standards, and associated quality control samples were extracted using ETS-8-154.3 "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates in Water by Solid Phase Extractions and High Performance Liquid Chromatography/Mass Spectrometry". Briefly, 40 mL of sample were loaded onto a pre-conditioned Waters Sep-Pak tC18 solid-phase extraction (SPE) cartridge (1 g, 6 cc) using a vacuum manifold. The loaded SPE cartridges were then eluted with 5 mL of methanol. This extraction procedure concentrates the samples by a factor of eight. (Initial volume = 40 mL, final volume = 5 mL).

Samples were prepared for analysis on April 3, 2008 and were analyzed on April 5-6, 2008.

Analysis

All samples and quality control samples were analyzed for PFOA using high performance liquid chromatography/ tandem mass spectrometry (HPLC/MS/MS). Pertinent instrument parameters, the liquid chromatography gradient program, and the specific mass transitions analyzed are described in the tables below.

Table 4. Instrument Parameters.

Instrument Name	ETS Stan
Liquid Chromatograph	Agilent 1100
Guard column	Betasil C18 (100 mm X 2.1 mm), 5 μ
Analytical column	Betasil C18 (100 mm X 2.1 mm), 5 μ
Injection Volume	5 μL
Mass Spectrometer	Applied Biosystems API 4000
Ion Source	Turbo Spray
Electrode	Z-spray
Polarity	Negative
Software	Analyst 1.4.2

Table 5. Liquid Chromatography Conditions.

Step Number	*Total Time (min)*	*Flow Rate (µL/min)*	*Percent A (2 mM ammonium acetate)*	*Percent B (Methanol)*
0	0	300	90	10
1	2.0	300	90	10
2	14.5	300	10	90
3	15.5	300	10	90
4	16.5	300	90	10
5	20.0	300	90	10

Table 6. Mass Transitions.

Analyte	*Mass Transition Q1/Q3*	*Dwell Time (msec)*
PFOA	413/369	200
	413/219	200
	413/169	200

ANALYTICAL RESULTS

Calibration

Calibration standards were prepared by spiking known amounts of stock solutions containing the target analyte into 40 mL of laboratory water. Each spiked water standard was then extracted in the same manner as the collected samples. A total of twelve spiked standards ranging from 0.025 ng/mL to 25 ng/mL (nominal) were prepared. A quadratic, 1/x weighted, calibration curve was used to fit the data for each analyte. The data were not forced through zero during the fitting process. Calculating the standard concentration using the peak area counts and the resultant calibration curve confirmed accuracy of each curve point.

Each curve point was quantitated using the overall calibration curve and reviewed for accuracy. Method calibration accuracy requirements of 100±25% (100±30% for the lowest curve point) were met for all analytes in each analytical batch. The correlation coefficients (r) were greater than 0.995 for all analytes in each analysis.

System Suitability

The 1.0 ng/mL extracted-calibration standard was analyzed at least three times at the beginning of the analytical sequence to demonstrate overall system suitability. PFOA met the acceptance criteria of less than or equal to 5% relative standard deviation (RSD) for peak area and less than or equal to 2% RSD for retention time for the opening system suitability injections.

Limit of Quantitation (LOQ)

The LOQ for this analysis is the lowest non-zero calibration standard in the curve that meets linearity and accuracy requirements and for which the area counts are at least twice those of the appropriate blanks. The LOQ for PFOA for this analysis was 0.0262 ng/mL.

Continuing Calibration

During the course of each analytical sequence, continuing calibration verification samples (CCVs) were analyzed to confirm that the instrument response and the initial calibration curve were still in control. All CCVs met method criteria of 100% ± 25%.

Blanks

Four types of blanks were prepared and analyzed with the samples: solvent blanks, method blanks, equipment blanks, and field/trip blanks. Each blank type is described below.

Solvent Blanks

Several blanks of methanol were analyzed to assess system contamination and/or instrument carryover. Analyte peak area counts in solvent blank samples were less than half the area counts of the calibration standard used to establish the LOQ.

Method Blanks

Five method blanks were prepared and analyzed with the samples. The average analyte peak area counts in the method blank samples were less than half the area counts of the calibration standard used to establish the LOQ.

Equipment Blank

One aqueous equipment rinseate blank was submitted as a sample: GLP07-01-03-015. The 3M Environmental Laboratory provided two one-liter bottles of ASTM type I water for rinsing. The resultant PFOA concentration of this sample was <0.0262 ng/mL.

Trip Blank

Prior to sample collection, one separate sample container was filled with 450 mL of reverse-osmosis purified water, sealed, and shipped to the sample collection site along with the empty containers. This sample was analyzed as the field/trip blank. The trip blank serves as an additional method blank that account for any storage conditions and/or holding time issues that the samples may experience. The resultant PFOA concentration for the field/trip blank was <0.0262 ng/mL.

Lab Control Spikes (LCSs)

Low and mid-level lab control spikes were prepared and analyzed in triplicate with each preparation set. LCSs were prepared by spiking known amounts of the analytes into laboratory water to produce the desired concentration. The spiked water samples were then prepared and analyzed in the same manner as the samples. Analysis of triplicate LCSs at the two specified levels cross-validates the analytical method as used here for any modifications/deviations from method and ETS-8-154.3. All LCSs were used in the determination of analytical uncertainty.

Table 7. Laboratory Control Spike Recovery

	PFOA		
Lab ID	*Spiked Concentration (ng/mL)*	*Calculated Concentration (ng/mL)*	*%Recovery*
LCS-080403-1	0.210	0.209	99.6
LCS-080403-2	0.210	0.224	107
LCS-080403-3	0.210	0.202	96.2
LCS-080403-4	5.25	4.88	93.0
LCS-080403-5	5.25	4.89	93.2
LCS-080403-6	5.25	4.57	87.1
Average ± %RSD	*96.0% ± 7.1 %*		

Determination of Analytical Method Uncertainty

The analytical uncertainty was determined based on historical QC data that is used to evaluate method accuracy and precision. The method uncertainty is calculated following ETS-12-012.2. The analytical uncertainty was determined by the statistical evaluation of the recoveries for the individual analyte recovery as determined for laboratory matrix spiked samples. The standard deviation was calculated for the set of recovery results (in %). The expanded uncertainty is calculated by multiplying the standard deviation by a factor of 2, which correspond with a confidence level of 95%. A minimum of twenty data points is needed to determine method uncertainty by this method.

Table 8. Analytical Method Uncertainty

Analyte	Number of data points (n) used for determining uncertainty values	Mean Recovery (%)	Standard Deviation (%)	Method Uncertainty (%)
PFOA	50	97.3	± 7.83	± 16

Field Matrix Spikes (FMS)

Low, mid, and high field matrix spikes were collected at each sampling point (with the exception of the rinse blank) to verify that the analytical method is applicable to the collected matrix. Field matrix spikes are generated by adding a measured volume of field sample to a container spiked by the laboratory with the target analytes prior to shipping sample containers for sample collection. Field matrix spike recoveries within method acceptance criteria of 100±30% confirm that "unknown" components in the sample matrix do not significantly interfere with the extraction and analysis of the analytes of interest.

Sampling location DAL GW605R purged less than three volumes with a total quantity of 1.5 gallons. As a result, the well could not provide adequate water to meet the volume requirements for all sample bottles provided for this location. The sample, duplicate, and low spike bottles were filled to the line, while the mid and high field matrix spike bottles were filled approximately 50%. The volume collected for the mid and high field matrix spikes was determined and the field matrix spike concentrations were adjusted appropriately.

$$\text{FMS Spike Recovery} = \frac{[\text{Conc. FMS sample}(\frac{ng}{mL}) - (\text{Average Conc. of Sample/Sample Dup}(\frac{ng}{mL})]}{\text{Spike Amount (ng/mL)}} * 100\%$$

Table 9. Field Matrix Spike Concentrations.

		Final Concentration (ng/mL)
Location	Description	PFOA
DAL GW 605L	Low Field Matrix Spike	0.233
	Mid Field Matrix Spike	4.67
	High Field Matrix Spike	93.3
DAL GW 605R	Low Field Matrix Spike	0.233
	Mid Field Matrix Spike(1)	6.93
	High Field Matrix Spike(1)	188
Trip Blank	Low Field Matrix Spike	0.233
	Mid Field Matrix Spike	4.67
	High Field Matrix Spike	93.3

(1) Bottle was filled below the fill line. The sample volume was determined and the field matrix spike true values were adjusted appropriately.

DATA SUMMARY AND DISCUSSION

The tables below summarize the sample results and field matrix spike recoveries for the sampling locations as well as the Trip Blanks. The table provides the average concentration and the relative percent difference (%RPD) of the sample and sample duplicate. Results and average values are rounded to three significant figures according to EPA rounding rules. Relative percent difference values are rounded to two significant figures. Because of rounding, values may vary slightly from those listed in the raw data. Field matrix spikes meeting the method acceptance criteria of 100±30% demonstrate that the analytical method is appropriate for the given matrix. If the low level spike amount was less than half the resultant endogenous concentration, the low FMS recovery was not reported as the spike level was not appropriate for the given sample concentration.

All reportable field matrix spike recoveries were within 100±30%; therefore, the results were considered accurate to within the overall analytical method uncertainty of 100±16% (see *Determination of Analytical Method Uncertainty* for more information.)

Table 10. DAL GW 605L 080401.

		PFOA	
3M LIMS ID	*Description*	*Concentration (ng/mL)*	*%Recovery*
GLP07-01-03-001	DAL GW 605L 0 080401	4.74	NA
GLP07-01-03-002	DAL GW 605L DB 080401	4.55	NA
GLP07-01-03-003	DAL GW 605L LS 080401	4.64	NC
GLP07-01-03-004	DAL GW 605L MS 080401	9.34	101
GLP07-01-03-005	DAL GW 605L HS 08 0401 (1:20 dilution)	90.3	91.8
Average Concentration (ng/mL) ± %RPD		*4.65 ng/mL ± 4.1%*	

NA = Not Applicable
NC = Not Calculated; Endogenous sample concentration is greater than 2x spike level.

Table 11. DAL GW 605R 080401.

		PFOA	
3M LIMS ID	*Description*	*Concentration (ng/mL)*	*%Recovery*
GLP07-01-03-006	DAL GW 605R 0 080401	0.101	NA
GLP07-01-03-007	DAL GW 605R DB 080401	0.108	NA
GLP07-01-03-008	DAL GW 605R LS 080401	0.329	96.2
GLP07-01-03-009	DAL GW 605R MS 080401	6.16	87.4
GLP07-01-03-010	DAL GW 605R HS 080401 (1:20 dilution)	183	97.1
Average Concentration (ng/mL) ± %RPD		*0.105 ng/mL± 6.7%*	

NA = Not Applicable

Table 12. Field Blank Samples.

		PFOA	
3M LIMS ID	*Description*	*Concentration (ng/mL)*	*%Recovery*
GLP07-01-03-011	DAL GW TRIP 0 080401	<0.0262	NA
GLP07-01-03-012	DAL GW TRIP LS 080401	0.209	89.6
GLP07-01-03-013	DAL GW TRIP MS 080401	4.39	94.1
GLP07-01-03-014	DAL GW TRIP HS -080401 (1:20 dilution)	88.6	94.9
GLP07-01-03-015	DAL GW 605L RB	<0.0262	NA

NA = Not Applicable

STATISTICAL METHODS AND CALCULATIONS

Statistical methods used to interpret sample results include averages and standard deviations. The Analyst software programs calculated sample concentrations using resultant analyte peak areas and the established quadratic, 1/x weighted, calibration curve. Sample calculations and equations used to report method accuracy and precision are described below.

Accuracy and Precision Equations

$$\text{LCS Percent Recovery} = \frac{\text{Calculated Concentration}}{\text{Spike Concentration}} * 100\%$$

$$\%\,\text{RSD (Relative Standard Deviation)} = \frac{\text{standard deviation of replicates}}{\text{replicate average}} * 100\%$$

$$\%\,\text{RPD (Relative Percent Difference)} = \frac{\text{Absolute difference between sample duplicates}}{\text{average sample concentration}} * 100\%$$

STATEMENT OF CONCLUSION

Sample results were summarized in Table 1. Historical values of lab control spikes for this method recorded in the laboratory's control chart were used to determine the overall analytical method uncertainty (100±16%). Sample results with field matrix spike recoveries within 100±30% were considered to be accurate within the stated method uncertainty. All remaining samples and associated project data (hardcopy and electronic) will be archived according to 3M Environmental Laboratory standard operating procedures.

REFERENCES

ETS 8-154.3; "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates in Water by Solid Phase Extractions and High Performance Liquid Chromatography/Mass Spectrometry".

ETS 4-026.2; "Control Charts for Laboratory Analyses".

ETS 12-012.2; "Estimation of Uncertainty of Measurements".

LIST OF ATTACHMENTS

- **Attachment A: Selected Chromatograms and Calibration Curves**
- **Attachment B: Extraction and Analytical Method**
- **Attachment C: Protocol and Protocol Amendments**

SIGNATURES

25 APRIL 08
William K. Reagen, Ph.D. 3M Environmental Laboratory Manager Date

Jacoby 24 Apr 12008
Cliffton B. Jacoby, Ph.D. 3M Technical Review Date

Michael a Santo 04/29/08
Michael A. Santoro Sponsor Representative Date

Kesari 5/2/08
Jaisimha Kesari, P.E., DEE Study Director Date

ATTACHMENT A: SELECTED CHROMATOGRAMS AND CALIBRATION CURVE

***Stan API4000 V1660305

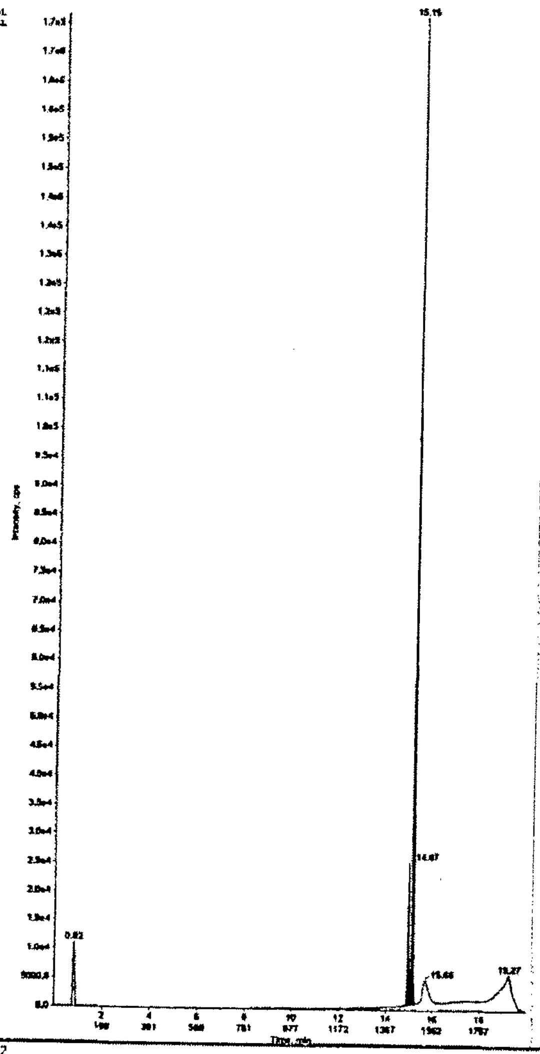
Results Name: s080405a.rdb

Sample Name: "s080405a030" Sample ID: "[illegible]" File: "s080405a.wiff"
Peak Name: "PFOA TIC" Mass(es): "413.0/368.9 amu,413.0/219.0 amu,413.0/169.0 amu"
Comment: "1.0 ppb extracted curve point" Annotation: ""

```
Sample Index:        20
Sample Type:         Standard
Concentration:       1.05      ng/mL
Calculated Conc:     1.10      ng/mL
Acq. Date:           4/5/2008
Acq. Time:           13:03:21

Modified:            Yes
RT Window:           30.0      sec
Expected RT:         15.2      min
Use Relative RT:     No

Int. Type:           Manual
Retention Time:      15.1      min
Area:              615036      counts
Height:            172000.     cps
Start Time:          14.7      min
End Time:            15.5      min
```

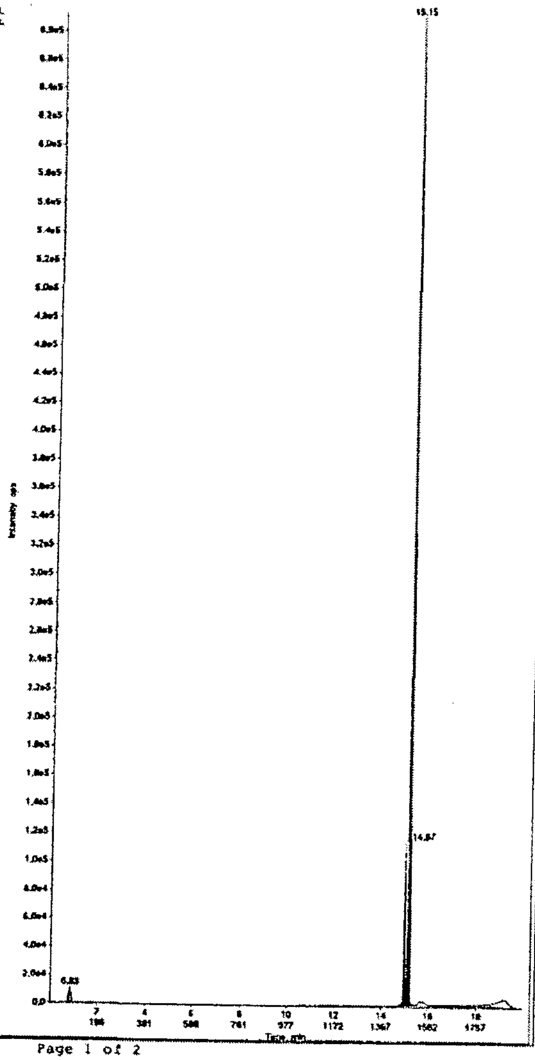


Sample Name: "s080405a031" Sample ID: "LCS-080405-4" File: "s080405a.wiff"
Peak Name: "PFOA TIC" Mass(es): "413.0/368.9 amu,413.0/218.0 amu,413.0/169.0 amu"
Comment: "5.0 ppb extracted LCS" Annotation: ""

```
Sample Index:        21
Sample Type:         QC
Concentration:       5.25      ng/mL
Calculated Conc:     4.88      ng/mL
Acq. Date:           4/5/2008
Acq. Time:           14:54:14

Modified:            Yes
RT Window:           30.0      sec
Expected RT:         15.2      min
Use Relative RT:     No

Int. Type:           Manual
Retention Time:      15.2      min
Area:             1423304      counts
Height:            692000.     cps
Start Time:          14.7      min
End Time:            15.4      min
```



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Printing Date: Monday, April 07, 2008

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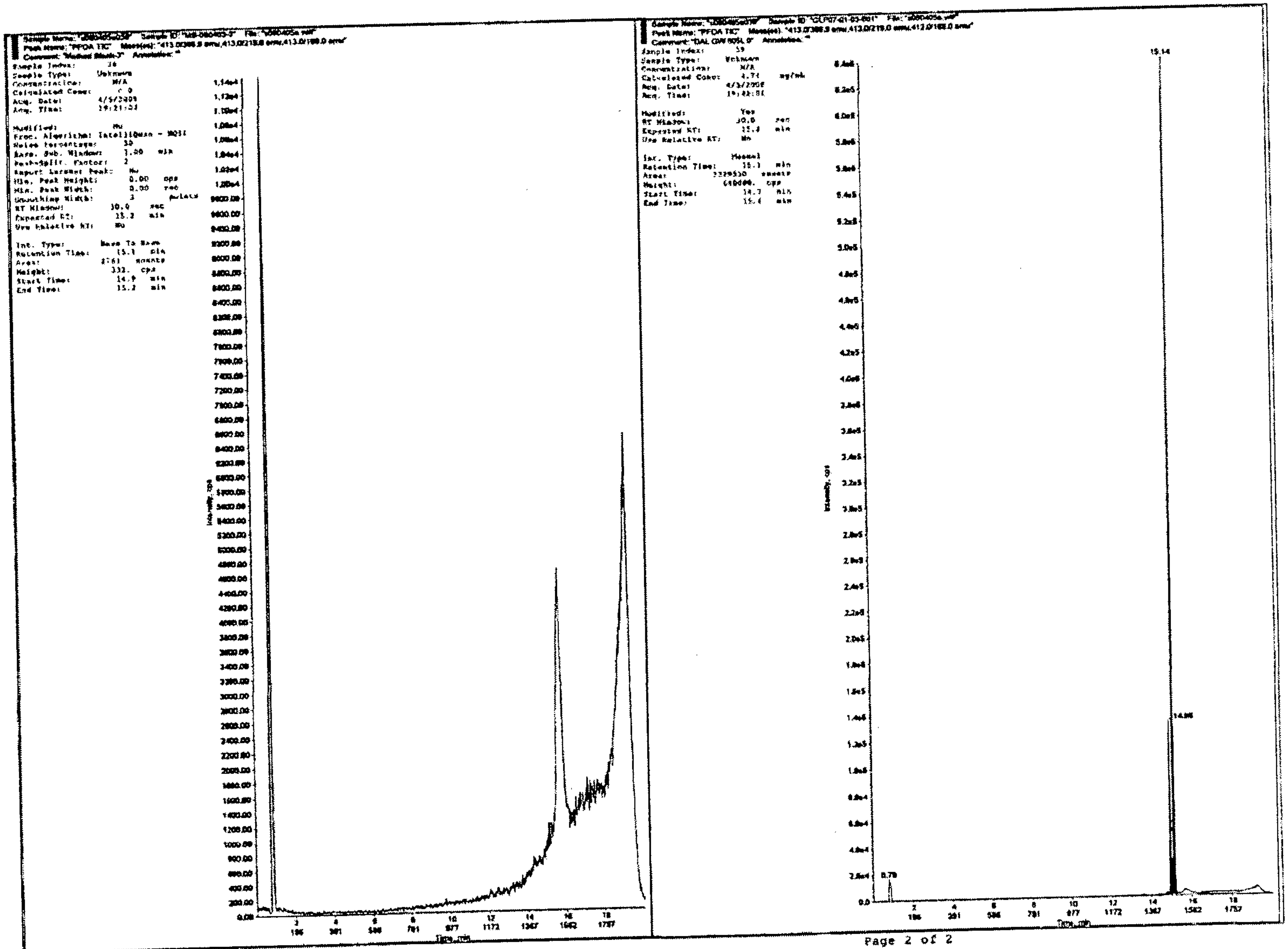
***Stan API4000 V1660305

Results Name: s080405a.rdb


Sample Name: "s080405a026" Sample ID: "MB-080405-3" File: "s080405a.wiff"
Peak Name: "PFOA TIC" Mass(es): "413.0/369.0 amu,413.0/219.0 amu,413.0/169.0 amu"
Comment: "Method Blank-3" Annotation: ""

```
Sample Index:          36
Sample Type:           Unknown
Concentration:         N/A
Calculated Conc:       < 0
Acq. Date:             4/5/2008
Acq. Time:             19:21:33

Modified:              No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage:        30
Base. Sub. Window:       1.00   min
Peak-Split. Factor:      2
Report Largest Peak:     No
Min. Peak Height:        0.00   cps
Min. Peak Width:         0.00   sec
Smoothing Width:         3          points
RT Window:             30.0    sec
Expected RT:            15.2   min
Use Relative RT:       No

Int. Type:             Base To Base
Retention Time:         15.1   min
Area:                  2761   counts
Height:                 332.  cps
Start Time:             14.9   min
End Time:               15.2   min
```

Sample Name: "s080405a039" Sample ID: "GLP07-01-03-601" File: "s080405a.wiff"
Peak Name: "PFOA TIC" Mass(es): "413.0/369.0 amu,413.0/219.0 amu,413.0/169.0 amu"
Comment: "DAL GW 605L 0" Annotation: ""

```
Sample Index:          39
Sample Type:           Unknown
Concentration:         N/A
Calculated Conc:       4.74    ng/mL
Acq. Date:             4/5/2008
Acq. Time:             19:42:51

Modified:              Yes
RT Window:             30.0    sec
Expected RT:            15.4   min
Use Relative RT:       No

Int. Type:             Manual
Retention Time:         15.1   min
Area:             2229510   counts
Height:            640000.  cps
Start Time:             14.7   min
End Time:               15.4   min
```

Printing Time: 13:30:13
Printing Date: Monday, April 07, 2008

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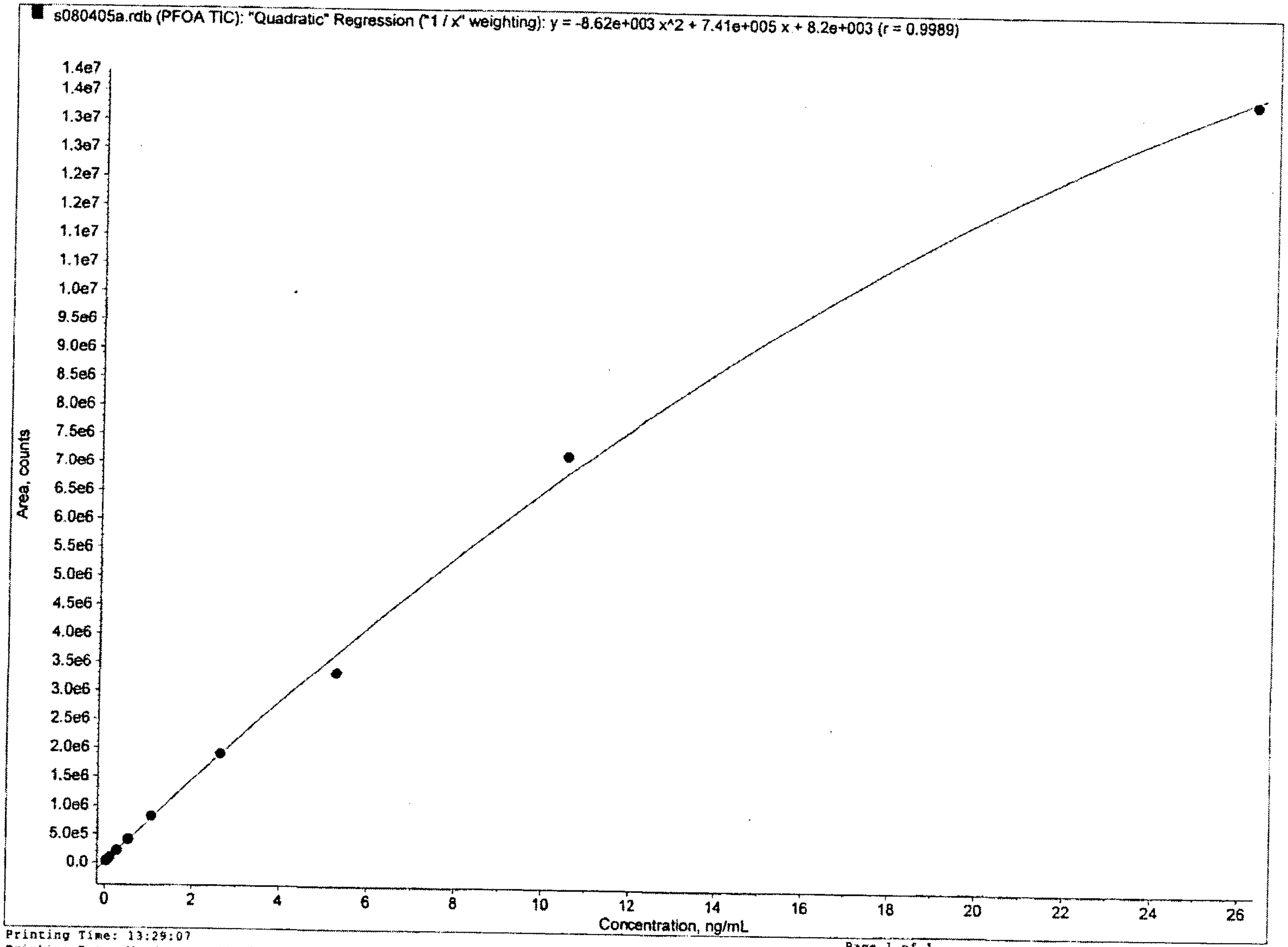
***Stan API4000 V1660305

Results Name: s080405a.rdb



s080405a.rdb (PFOA TIC): "Quadratic" Regression ("1 / x" weighting): y = -8.62e+003 x^2 + 7.41e+005 x + 8.2e+003 (r = 0.9989)

Printing Time: 13:29:07
Printing Date: Monday, April 07, 2008

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