Interim Report #13: Analysis of Tennessee River Water Samples

Study Title

ANALYSIS OF PERFLUOROBUTANESULFONATE (PFBS), PERFLUOROHEXANESULFONATE (PFHS), AND PERFLUOROOCTANESULFONATE (PFOS) IN WATER, SOIL, SEDIMENT, FISH, CLAMS, VEGETATION, SMALL MAMMAL LIVER AND SMALL MAMMAL SERUM USING LC/MS/MS FOR THE 3M DECATUR MONITORING PROGRAM

Data Requirement

EPA TSCA Good Laboratory Practice Standards 40 CFR 792

Author

Michelle D. Malinsky, Ph.D
3M Environmental Laboratory

Interim Report Completion Date

Date of signing

Performing Laboratory

3M Environmental Laboratory
Building 2-3E-09
935 Bush Ave.
St. Paul, MN 55106

Project Identification

E05-0210

160

Total Number of Pages

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GLP COMPLIANCE STATEMENT

Study Title: Analysis of Perfluorobutanesulfonate (PFBS), Perfluorohexanesulfonate (PFHS), and Perfluorooctanesulfonate (PFOS) in Water, Soil, Sediment, Fish, Clams,Vegetation, Small Mammal Liver and Small Mammal Serum Using LC/MS/MS for the 3M Decatur Monitoring Program

Interim Study: Analysis of Tennessee River Water Samples

Interim Study Identification Number: E05-210

This study 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:

Jaisimha Kesari P. E., DEE, Study Director — Date 3/21/06

Michael A. Santoro, 3M Company, Sponsor Representative — Date 3/23/06

QUALITY ASSURANCE STATEMENT

Study Title: Analysis of Perfluorobutanesulfonate (PFBS), Perfluorohexanesulfonate (PFHS), and Perfluorooctanesulfonate (PFOS) n Water, Soil, Sediment, Fish, Clams,Vegetation, Small Mammal Liver and Small Mammal Serum Using LC/MS/MS for the 3M Decatur Monitoring Program

Interim Study: Analysis of Tennessee River Water Samples

Interim Study Identification Number: E05-0210, Interim Report #13

This study 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	
		Management	Study Director
July 27, 2005	In-phase	11-07-2005	11-07-2005
October 5-7, 12, 13, 2005	Data/Final Report	11-17-2005	11-17-2005

Casey Howell 11-17-05

QAU Representative Date

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STUDY INFORMATION

Sponsor

3M Company

Sponsor Representative

Michael A. Santoro
3M Company
3M Building 0236-01-B-10
St. Paul, MN 55144

Study Director

Jaisimha Kesari, P.E., DEE
Weston Solutions, Inc.
1400 Weston Way
West Chester, PA 19380

Study Location

Testing Facilities

Exygen Research
3058 Research Drive
State College, PA 16801

3M Environmental Laboratory
3M Building 2-3E-09
935 Bush Avenue
St. Paul, MN 55144

Study Dates

Study Initiation: 11/5/2004

Interim Experimental Initiation: July 26, 2005

Interim Experimental Completion: August 1, 2005

Interim Study Completion: State of Study Director's Signature

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.

SUMMARY AND INTRODUCTION

The 3M Environmental Laboratory extracted and analyzed water samples collected from the Tennessee River by Weston Solutions personnel on July 18-22, 2005. Samples were collected from Tennessee River Mile (TRM) 307, located six miles upstream from the 3M Decatur Alabama facility to TRM 254, located 47 miles downstream from the 3M facility. Samples were submitted for analysis as part of 3M Environmental Laboratory project number E05-0210 (3M Decatur Fluorochemical GLP Monitoring Program, Interim Study #13: Analysis of Tennessee River Water Samples).

Water samples were analyzed for perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHS), and perfluorobutane sulfonate (PFBS) using 3M Environmental Laboratory Method ETS 8-154.1 "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates in Water by Solid Phase Extractions and High Performance Liquid Chromatography/Mass Spectrometry" in accordance with Exygen Research Protocol P0001131 (Attachment C). The analytical start date for this interim report was July 26, 2005 and the analytical termination date was August 1, 2005.

Sample containers were prepared at the 3M Environmental Laboratory. Sample containers for each sampling location included a field sample, field sample duplicate, low field spike (0.05 ng/mL) and high field spike (0.5 ng/mL). Each empty container was marked with a "fill to here" line and was fortified with a surrogate spike or an appropriate matrix spike solution containing the surrogate and the three target analytes 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) for all the analytes varied depending on the extraction and analysis dates. All results for quality control samples prepared and analyzed with the samples will be reported and discussed elsewhere in this report.

Table 1. Sample Results Summary

Sample Description	*3M LIMS ID Number*	*[1]PFBS (ng/mL)*	*[1]PFHS (ng/mL)*	*[1]PFOS (ng/mL)*
DLS-SW-TRM307-0-050718	E05-0210-86358	< 0.00221	< 0.00104	0.0067
DLS-SW-TRM307-0-050718 Dup	E05-0210-86359	< 0.00221	< 0.00104	< 0.00496
	Average	**[2]< 0.00221**	**[2]< 0.00104**	**[2]< 0.00496**
	%RPD	**NA**	**NA**	**NA**
DLS-SW-TRM301-0-050718	E05-0210-86362	< 0.00221	< 0.00104	< 0.00496
DLS-SW-TRM301-0-050718 Dup	E05-0210-86363	< 0.00221	0.00134	< 0.00496
	Average	**[2]< 0.00221**	**[3]0.00134**	**[2]< 0.00496**
	%RPD	**NA**	**NA**	**NA**
DLS-SW-TRM301-F-050718	E05-0210-86366	< 0.00221	< 0.00104	< 0.00496
DLS-SW-TRM301-F-050718 Dup	E05-0210-86367	< 0.00221	< 0.00104	< 0.00496
	Average	**[2]< 0.00221**	**[2]< 0.00104**	**[2]< 0.00496**
	%RPD	**NA**	**NA**	**NA**
DLS-SW-TRM295-0-050719	E05-0210-86372	[3]0.0143	0.0115	0.0736
DLS-SW-TRM295-0-050719 Dup	E05-0210-86373	[3]0.0150	0.0118	0.0747
	Average	**0.0146**	**0.0116**	**0.0742**
	%RPD	**4.79**	**2.59**	**1.48**
DLS-SW-TRM289-0-050719	E05-0210-86374	0.0225	0.0133	0.0763
DLS-SW-TRM289-0-050719 Dup	E05-0210-86375	0.0213	0.0123	0.0722
	Average	**0.0218**	**0.0127**	**0.0742**
	%RPD	**5.50**	**7.87**	**5.52**
DLS-SW-TRM289-F-050719	E05-0210-86378	0.0197	0.0129	0.0588
DLS-SW-TRM289-F-050719 Dup	E05-0210-86379	0.0201	0.0120	0.0462
	Average	**0.0199**	**0.0124**	**0.0524**
	%RPD	**2.01**	**7.26**	**24.0**
DLS-SW-TRM283-0-050719	E05-0210-86382	0.0203	0.00888	0.0528
DLS-SW-TRM283-0-050719 Dup	E05-0210-86383	0.0181	0.00883	0.0703
	Average	**0.0192**	**0.00886**	**0.0616**
	%RPD	**11.4**	**0.564**	**28.4**
DLS-SW-TRM277-0-050719	E05-0210-86386	0.0115	0.00579	0.0336
DLS-SW-TRM277-0-050719 Dup	E05-0210-86387	0.0123	0.00704	0.0530
	Average	**0.0119**	**0.00642**	**0.0432**
	%RPD	**6.72**	**19.5**	**44.9**
DLS-SW-TRM277-F-050719	E05-0210-86390	0.0111	0.00609	0.0304
DLS-SW-TRM277-F-050719 Dup	E05-0210-86391	0.0125	0.00672	0.0390
	Average	**0.0118**	**0.00640**	**0.0347**
	%RPD	**11.9**	**9.84**	**24.8**
DLS-SW-TRM271-0-050719	E05-0210-86394	0.0133	0.00512	0.0320
DLS-SW-TRM271-0-050719 Dup	E05-0210-86395	0.0142	0.00574	0.0332
	Average	**0.0138**	**0.00543**	**0.0326**
	%RPD	**6.52**	**11.4**	**3.68**

Table 1. Sample Results Summary Continued.

Sample Description	*3M LIMS ID Number*	*[1]PFBS (ng/mL)*	*[1]PFHS (ng/mL)*	*[1]PFOS (ng/mL)*
DLS-SW-TRM265-0-050719	E05-0210-86398	0.0103	0.00525	0.0377
DLS-SW-TRM265-0-050719 Dup	E05-0210-86399	0.0104	0.00542	0.0375
	Average	**0.0104**	**0.00534**	**0.0375**
	%RPD	**0.962**	**3.18**	**0.533**
DLS-SW-TRM261-2-050720	E05-0210-86402	< 0.00221	< 0.00104	< 0.00496
DLS-SW-TRM261-2-050720 Dup	E05-0210-86403	< 0.00221	< 0.00104	< 0.00496
	Average	**[2]< 0.00221**	**[2]< 0.00104**	**[2]< 0.00496**
	%RPD	**NA**	**NA**	**NA**
DLS-SW-TRM261-0-050720	E05-0210-86406	0.0118	0.0052	0.0324
DLS-SW-TRM261-0-050720 Dup	E05-0210-86407	0.0110	0.00481	0.0330
	Average	**0.0114**	**0.00500**	**0.0323**
	%RPD	**7.02**	**7.80**	**1.86**
DLS-SW-TRM261-F-050720	E05-0210-86410	0.0116	0.00542	0.0333
DLS-SW-TRM261-F-050720 Dup	E05-0210-86411	0.0107	0.00486	0.0232
	Average	**0.0112**	**0.00514**	**0.0282**
	%RPD	**8.04**	**10.9**	**35.8**
DLS-SW-TRM256-0-050720	E05-0210-86414	0.0111	0.00485	0.0326
DLS-SW-TRM256-0-050720 Dup	E05-0210-86415	0.0125	0.0047	0.0342
	Average	**0.0118**	**0.00478**	**0.0333**
	%RPD	**11.9**	**3.14**	**4.80**
DLS-SW-TRM254-0-050720	E05-0210-86418	0.0124	0.0055	0.0352
DLS-SW-TRM254-0-050720 Dup	E05-0210-86419	0.0120	0.00481	0.0341
	Average	**0.0121**	**0.00516**	**0.0346**
	%RPD	**3.30**	**13.4**	**3.18**
DLS-SW-TRM254-F-050720	E05-0210-86422	0.0128	0.00533	0.0300
DLS-SW-TRM254-F-050720 Dup	E05-0210-86423	0.0121	0.00525	0.0342
	Average	**0.0124**	**0.00528**	**0.0321**
	%RPD	**5.64**	**1.52**	**13.1**
DLS-SW-TRM254-2-050720	E05-0210-86426	< 0.00221	< 0.00104	< 0.00992
DLS-SW-TRM254-2-050720 Dup	E05-0210-86427	< 0.00221	< 0.00104	< 0.00992
	Average	**[2]<0.00221**	**[2]<0.00104**	**[2]<0.00992**
	%RPD	**NA**	**NA**	**NA**
DXS-SW-T01001-0-050721	E05-0210-86430	0.0215	0.0121	0.0739
DXS-SW-T01001-0-050721 Dup	E05-0210-86431	0.0201	0.0116	0.0680
	Average	**0.0208**	**0.0118**	**0.0710**
	%RPD	**6.73**	**4.24**	**8.31**
DXS-SW-T01002-0-050721	E05-0210-86434	0.0161	0.0101	0.0607
DXS-SW-T01002-0-050721 Dup	E05-0210-86435	0.0164	0.00959	0.0594
	Average	**0.0162**	**0.00984**	**0.0600**
	%RPD	**1.85**	**5.18**	**2.17**

Table 1. Sample Results Summary Continued.

Sample Description	*3M LIMS ID Number*	*[(1)]PFBS (ng/mL)*	*[(1)]PFHS (ng/mL)*	*[(1)]PFOS (ng/mL)*
DXS-SW-T01003-0-050721	E05-0210-86438	0.0165	0.00827	0.0542
DXS-SW-T01003-0-050721 Dup	E05-0210-86439	0.0166	0.00941	0.0555
	Average	**0.0166**	**0.00884**	**0.0548**
	%RPD	**0.602**	**12.9**	**2.37**
DXS-SW-T01004-0-050721	E05-0210-86442	0.0158	0.00967	0.056
DXS-SW-T01004-0-050721 Dup	E05-0210-86443	0.0165	0.0101	0.0636
	Average	**0.0162**	**0.00988**	**0.0598**
	%RPD	**4.32**	**4.35**	**12.7**
DXS-SW-T01005-0-050721	E05-0210-86446	0.00957	0.00633	0.0383
DXS-SW-T01005-0-050721 Dup	E05-0210-86447	0.00985	0.00667	0.039
	Average	**0.00971**	**0.00649**	**0.0386**
	%RPD	**2.88**	**5.24**	**1.81**
DXS-SW-T01006-0-050721	E05-0210-86450	0.00432	0.00346	0.0209
DXS-SW-T01006-0-050721 Dup	E05-0210-86451	0.00366	0.00333	0.0219
	Average	**0.00399**	**0.00340**	**0.0213**
	%RPD	**16.5**	**3.82**	**4.69**
DXS-SW-T01007-0-050721	E05-0210-86454	0.00566	0.00419	0.0273
DXS-SW-T01007-0-050721 Dup	E05-0210-86455	0.00564	0.00429	0.0268
	Average	**0.00565**	**0.00424**	**0.0270**
	%RPD	**0.354**	**2.36**	**1.85**
DXS-SW-T01008-0-050721	E05-0210-86458	0.00369	0.00316	0.0219
DXS-SW-T01008-0-050721 Dup	E05-0210-86459	0.00502	0.00328	0.0217
	Average	**0.00436**	**0.00321**	**0.0218**
	%RPD	**30.5**	**3.74**	**0.917**
DXS-SW-T01009-0-050721	E05-0210-86462	0.00491	0.00301	0.0202
DXS-SW-T01009-0-050721 Dup	E05-0210-86463	0.00444	0.0033	0.0203
	Average	**0.00468**	**0.00316**	**0.0202**
	%RPD	**10.0**	**9.18**	**0.495**
DXS-SW-T01010-0-050721	E05-0210-86466	0.00395	0.00332	0.0216
DXS-SW-T01010-0-050721 Dup	E05-0210-86467	0.00385	0.00277	0.0219
	Average	**0.00390**	**0.00304**	**0.0218**
	%RPD	**2.56**	**18.1**	**1.38**
DXS-SW-T02001-0-050721	E05-0210-86470	0.0414	0.0205	0.129
DXS-SW-T02001-0-050721 Dup	E05-0210-86471	0.0423	0.0187	0.117
	Average	**0.0418**	**0.0195**	**0.123**
	%RPD	**2.15**	**9.23**	**9.76**
DXS-SW-T02002-0-050721	E05-0210-86474	0.0306	0.0124	0.0707
DXS-SW-T02002-0-050721 Dup	E05-0210-86475	0.0316	0.0126	0.0762
	Average	**0.0311**	**0.0125**	**0.0734**
	%RPD	**3.22**	**1.60**	**7.49**

Table 1. Sample Results Summary Continued.

Sample Description	*3M LIMS ID Number*	*[1]PFBS (ng/mL)*	*[1]PFHS (ng/mL)*	*[1]PFOS (ng/mL)*
DXS-SW-T02003-0-050721	E05-0210-86478	< 0.00221	< 0.00104	< 0.00992
DXS-SW-T02003-0-050721 Dup	E05-0210-86479	< 0.00221	< 0.00104	< 0.00992
	Average	**[2]<0.00221**	**[2]<0.00104**	**[2]<0.00992**
	%RPD	**NA**	**NA**	**NA**
DXS-SW-T02004-0-050721	E05-0210-86482	< 0.00221	< 0.00104	< 0.00992
DXS-SW-T02004-0-050721 Dup	E05-0210-86483	< 0.00221	< 0.00104	< 0.00992
	Average	**[2]<0.00221**	**[2]<0.00104**	**[2]<0.00992**
	%RPD	**NA**	**NA**	**NA**
DXS-SW-T02005-0-050721	E05-0210-86486	< 0.000883	< 0.0026	< 0.00744
DXS-SW-T02005-0-050721 Dup	E05-0210-86487	< 0.00221	< 0.0026	< 0.0496
	Average	**[2]<0.00221**	**[2]<0.0026**	**[2]<0.0496**
	%RPD	**NA**	**NA**	**NA**
DXS-SW-T02006-0-050721	E05-0210-86490	< 0.000883	< 0.0026	< 0.00744
DXS-SW-T02006-0-050721 Dup	E05-0210-86491	0.00101	< 0.0026	0.00799
	Average	**[4]0.00101**	**[2]<0.0026**	**[4]0.00799**
	%RPD	**NA**	**NA**	**NA**
DXS-SW-T02007-0-050721	E05-0210-86494	< 0.000883	< 0.0026	< 0.00744
DXS-SW-T02007-0-050721 Dup	E05-0210-86495	< 0.000883	< 0.0026	< 0.00744
	Average	**[2]< 0.000883**	**[2]< 0.0026**	**[2]< 0.00744**
	%RPD	**NA**	**NA**	**NA**
DXS-SW-T02008-0-050721	E05-0210-86498	0.00109	< 0.0026	< 0.00744
DXS-SW-T02008-0-050721 Dup	E05-0210-86499	0.00115	< 0.0026	< 0.00744
	Average	**0.00111**	**[2]< 0.0026**	**[2]< 0.00744**
	%RPD	**5.40**	**NA**	**NA**
DXS-SW-T02009-0-050721	E05-0210-86502	0.00288	< 0.0026	0.00872
DXS-SW-T02009-0-050721 Dup	E05-0210-86503	0.00244	< 0.0026	0.00883
	Average	**0.00266**	**[2]< 0.0026**	**0.00878**
	%RPD	**16.5**	**NA**	**1.25**
DXS-SW-T02010-0-050721	E05-0210-86506	0.00628	0.00363	0.0426
DXS-SW-T02010-0-050721 Dup	E05-0210-86507	0.00553	0.00342	0.0285
	Average	**0.00590**	**0.00352**	**0.0356**
	%RPD	**12.7**	**5.96**	**39.6**
DXS-SW-T03001-0-050721	E05-0210-86510	0.818	0.176	0.782
DXS-SW-T03001-0-050721 Dup	E05-0210-86511	0.854	0.185	0.807
	Average	**0.836**	**0.180**	**0.794**
	%RPD	**4.31**	**5.00**	**3.15**
DXS-SW-T03002-0-050721	E05-0210-86514	0.00519	< 0.0026	0.0235
DXS-SW-T03002-0-050721 Dup	E05-0210-86515	0.00424	< 0.0026	0.0169
	Average	**0.00472**	**[2]< 0.0026**	**0.0201**
	%RPD	**20.1**	**NA**	**32.8**

Table 1. Sample Results Summary Continued.

Sample Description	*3M LIMS ID Number*	*(1)PFBS (ng/mL)*	*(1)PFHS (ng/mL)*	*(1)PFOS (ng/mL)*
DXS-SW-T03003-0-050721	E05-0210-86518	< 0.000883	< 0.0026	0.0111
DXS-SW-T03003-0-050721 Dup	E05-0210-86519	< 0.000883	< 0.0026	0.0118
	Average	**(2)< 0.000883**	**(2)< 0.0026**	**0.0114**
	%RPD	**NA**	**NA**	**6.14**
DXS-SW-T03004-0-050722	E05-0210-86522	0.0043	0.00756	0.0226
DXS-SW-T03004-0-050722 Dup	E05-0210-86523	0.00106	< 0.0026	0.0167
	Average	**0.00268**	**0.00756**	**0.0196**
	%RPD	**121**	**NA**	**30.1**
DXS-SW-T03005-0-050722	E05-0210-86526	< 0.000883	< 0.0026	< 0.00744
DXS-SW-T03005-0-050722 Dup	E05-0210-86527	0.00171	0.00331	0.0773
	Average	**(3)0.00171**	**(4)0.00331**	**(4)0.0773**
	%RPD	**NA**	**NA**	**NA**
DXS-SW-T03006-0-050722	E05-0210-86530	< 0.000883	< 0.0026	0.00763
DXS-SW-T03006-0-050722 Dup	E05-0210-86531	< 0.000883	< 0.0026	< 0.00744
	Average	**(2)< 0.000883**	**(2)< 0.0026**	**(4)0.00763**
	%RPD	**NA**	**NA**	**NA**
DXS-SW-T03007-0-050722	E05-0210-86534	< 0.000883	< 0.0026	< 0.00744
DXS-SW-T03007-0-050722 Dup	E05-0210-86535	0.00107	0.00366	< 0.0496
	Average	**(4)0.00107**	**(4)0.00366**	**(2)<0.0496**
	%RPD	**NA**	**NA**	**NA**
DXS-SW-T03008-0-050722	E05-0210-86538	< 0.000883	< 0.0026	< 0.00744
DXS-SW-T03008-0-050722 Dup	E05-0210-86539	< 0.000883	< 0.0026	< 0.00744
	Average	**(2)< 0.000883**	**(2)< 0.0026**	**(2)< 0.00744**
	%RPD	**NA**	**NA**	**NA**
DXS-SW-T03009-0-050722	E05-0210-86542	< 0.000883	< 0.0026	0.00809
DXS-SW-T03009-0-050722 Dup	E05-0210-86543	< 0.000883	< 0.0026	< 0.00744
	Average	**(2)< 0.000883**	**(2)< 0.0026**	**(4)0.00809**
	%RPD	**NA**	**NA**	**NA**
DXS-SW-T03010-0-050722	E05-0210-86546	0.000908	< 0.0026	0.00749
DXS-SW-T03010-0-050722 Dup	E05-0210-86547	< 0.000883	< 0.0026	< 0.00744
	Average	**(4)0.000908**	**(2)< 0.0026**	**(4)0.00749**
	%RPD	**NA**	**NA**	**NA**

(1) All results and calculations are presented with three significant figures. Sample concentrations, averages, and %RPD values may vary slightly from the raw data. The analytical uncertainty for the PFBS, PFHS, and PFOS results is 100±10.6%, 100±15.2%, and 100±13.8%, respectively.

(2) NA: Not applicable. %RPD values not determined when concentrations for the sample and/or sample duplicate are below the stated LOQ.

(3) Sample descriptions were misidentified when checked into LIMS. Samples with LIMS ID numbers 86370 and 86371 were in bottles labeled low and high spike, respectively. Bottles with LIMS ID numbers 86372 and 86373 were surrogate spiked only (sample and sample duplicate bottles).

(4) The average value listed is the concentration for the sample or sample duplicate that produced a value above the LOQ. A true average and %RPD between the sample and sample duplicate was not determined.

TEST SAMPLES

Water samples (3M LIMS ID #86358-86558) were received on July 23, 2005 from Charles Young of Weston Solutions, Inc. Two hundred one (201) containers representing 48 samples and an equipment rinse blank were submitted for analysis. The samples were logged in by 3M Environmental Laboratory professional services personnel and placed in refrigerated storage prior to extraction on July 26-28, 2005.

REFERENCE SUBSTANCES

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

Table 2. Study Reference Substance.

Reference Substance	*PFBS*	*PFHS*	*PFOS*
Chemical Name	Perfluorobutanesulfonate	Perfluorohexanesulfonate	Perfluorooctanesulfonate
Chemical Formula	$C_4F_9SO_3^-K^+$	$C_6F_{13}SO_3^-K^+$	$C_8F_{17}SO_3 \cdot K^+$
Identifier	CAS # 29420-49-3	CAS # 3871-99-6	CAS # 2795-39-3
(1)Source	3M	3M	3M
Expiration Date	10/17/2006	10/18/2006	8/31/2006
Storage Conditions	Frozen	Frozen	Frozen
Chemical Lot Number	101	NB# 120067-69	171
TCR Number	TCR-116 (99030-023)	TCR-83 (SE036)	TCR-696
Physical Description	White Powder	White Powder	White powder
Purity	96.7%	98.6%	86.4%
(2)Solubility	54,400 ppm	No Information available	680 ppm

(1) Documentation regarding synthesis of the test substances is located at the source.

(2) All test substances are believed to be soluble in water at the levels to be investigated. No visual precipitates observed.

CONTROL SUBSTANCE

PFOA [1,2 ^{13}C] was analyzed as a surrogate against a multi-level extracted calibration curve. A known amount of PFOA [1,2 ^{13}C] was spiked into each sample container in the laboratory prior to sample collection. Table 3 lists the pertinent information regarding the study control substance.

Table 3. Study Control Substance (Surrogate).

Reference Substance	PFOA [1,2 ^{13}C]
Chemical Name	Perfluorooctanoic Acid
Chemical Formula	$C_6F_{15}[^{13}C]F_2[^{13}C]OOH$
Identifier	N/A
Source	Perkin Elmer
Expiration Date	03/29/2009
Storage Conditions	Frozen
Chemical Lot Number	3507-195
TCR Number	TCR-744
Physical Description	White powder
Purity	>97%

METHOD SUMMARIES

Sample Collection

Samples were collected on July 18-23, 2005 in pre-rinsed Nalgene™ (low-density polyethylene) bottles prepared at the 3M Environmental Laboratory on July 14, 2005. Prior to sample collection, all bottles were spiked in the laboratory with a known volume of a surrogate solution or appropriate matrix spiking solution containing the surrogate and the analyte of interest. Four collection bottles were associated with each individual sampling location: sample, sample duplicate, low level field matrix spike (LS), and high level field matrix spike (HS). Additionally, three "Trip Blank" sample sets were prepared. A Trip Blank set consisted of three individual bottles: trip blank sample, trip blank low spike, and trip blank high spike. The surrogate and matrix spike levels for the trip blanks were the same as the samples. Table 4 below details the spike amounts for the four bottles comprising the sample location set.

Table 4. Sample Collection Information

(1)Bottle Description	*Nominal Final Volume Collected (mL)*	*Final Spike Concentration (ng/mL)*			
		PFBS	*PFHS*	*PFOS*	*PFOA [1,2 ^{13}C] (Surrogate)*
Sample	450	NA	NA	NA	0.274
Sample Dup	450	NA	NA	NA	0.274
Low Field Matrix Spike (LS)	450	0.0441	0.0521	0.0496	0.254
High Field Matrix Spike (HS)	450	0.441	0.521	0.496	0.254

(1) The sample description was assigned in the field by Weston Solutions personnel.

Preparatory and Analytical Methods

Extraction

All samples, calibration standards, and associated quality control samples were extracted using a modified procedure of ETS-8-154.1 "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates in Water by Solid Phase Extractions and High Performance Liquid Chromatography/Mass Spectrometry". Briefly, approximately 100 mL of sample were loaded onto a pre-conditioned Waters C18 solid phase extraction (SPE) cartridge (Sep-Pak, 6 cc) using a vacuum manifold. The loaded cartridges were then eluted with 2 mL of methanol This extraction procedure concentrates the samples by a factor of fifty. (Initial volume = 100 mL, final volume = 2 mL). As written, ETS-8-154.1 calls for a 40 mL and 5 mL extraction and elution volume, respectively.

Due to the large number of samples associated with this project, samples were extracted over the course of three days (July 26-July 28, 2005). The extracted calibration curve used to quantify the data was only prepared on the first extraction day; however, method blanks and lab control spikes were prepared each day samples were extracted. During the second day of extraction, six samples clogged the SPE cartridge preventing complete loading of the sample. On the third extraction day, these six samples were centrifuged at 6000 rcf (relative centrifugal force) for 20 minutes prior to loading the SPE cartridge. Method blanks and lab control spikes were also centrifuged and extracted in a similar manner.

Analysis

All sample and quality control extracts were analyzed for PFBS, PFHS, PFOS, and PFOA [1,2 ^{13}C] 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 5. Instrument Parameters

Instrument Name	ETStan
Liquid Chromatograph	Agilent 1100
Guard column	Betasil C18 2X50, 5 μm
Analytical column	Betasil C18 (2.1 mm X 100 mm), 5 μm
Injection Volume	5 μL
Mass Spectrometer	Applied Biosystems API 4000
Electrode	Z-spray
Ion Source	Turbo Spray
Polarity	Negative
Software	Analyst 1.4.1

Table 6. Liquid Chromatography Gradient Program

Step Number	*Total Time (min)*	*Flow Rate (μL/min)*	*Percent A (2 mM ammonium acetate)*	*Percent B (Methanol)*
0	0	300	80.0	20.0
1	1.0	300	80.0	20.0
2	14.5	300	10.0	90.0
3	15.5	300	10.0	90.0
4	16.5	300	80.0	20.0
5	20.0	300	80.0	20.0

Table 7. Mass Transitions

Analyte	*Mass Transition Q1/Q3*	*Dwell Time (msec)*
(1)PFBS	299/80	150
	299/99	150
(1)PFHS	399/80	150
	399/99	150
(1)PFOS	499/130	150
	499/99	150
	499/80	150
PFOA [1,2 ^{13}C]	415/370	150

(1) The individual transitions were summed to produce a "total ion chromatogram" (TIC). The TIC was used for quantitation.

ANALYTICAL RESULTS

Calibration

Calibration standards were prepared by spiking known amounts of stock solutions containing PFBS, PFHS, PFOS, and PFOA [1,2 ^{13}C] into 100 mL of ASTM type I water. Each spiked water standard was then extracted in the same manner as the collected samples. A total of twelve spiked standards ranging from 0.001 ng/mL to 2.5 ng/mL (nominal) were prepared. A quadratic, 1/x weighted, calibration curve was used to fit the data for each analyte. The data was 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 extracted calibration standard used to generate the final calibration curve met the method calibration accuracy requirement of 100±25%. Coefficients of determination (r^2) were greater than 0.995 for all analytes.

Limit of Quantitation (LOQ)

The LOQ for this analysis, as defined in ETS-8-154.1, is the lowest non-zero calibration standard in the curve in which the area counts are at least twice those of the method blank(s). The LOQ varied from day to day depending on instrument sensitivity and method blank area counts for the extraction set. This will be presented and discussed in more detail in the section below regarding method blanks. Table 8 below provides the individual LOQs for the three analytes of interest.

Table 8. LOQs by Extraction Set and Analysis Day

		LOQ		
Extraction Set	*Analysis Day*	*PFBS (ng/mL)*	*PFHS (ng/mL)*	*PFOS (ng/mL)*
07/26/2005	07/26/2005	0.00221	0.00104	0.00496
07/27/2005	07/28/2005	0.00221	0.00104	0.00992
	07/30/2005	0.000883	0.00260	0.00744
07/28/2005 (Centrifuged Samples)	08/01/2005	0.00221	0.00260	0.0496

Blanks

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

Solvent Blank

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

Method Blank

Over the three days in which samples, calibration standards, and quality control samples were extracted, several method blanks were prepared by loading 100 mL of ASTM Type I water onto a C18 SPE cartridge and eluting with 2 mL of methanol using the same extraction procedure as the samples. Method blanks were prepared to evaluate the levels of background contamination in the overall extraction process (glassware, SPE cartridges, etc.) Approximately half of the method blanks prepared each day were spiked with a known amount of PFOA [1,2 ^{13}C] surrogate prior to extraction. Table 9 and Table 10 list the analyte area counts for the method blanks and the corresponding LOQ standard for the given analysis day. Table 11 lists the analyte area counts of the method blanks associated with the centrifuged samples. The PFOS LOQ for these six samples was raised to 0.0496 ng/mL due to higher amounts of PFOS detected in the method blanks prepared on that day.

Surrogate recoveries for the spiked method blanks are presented in Table 12. Method blanks spiked with surrogate solution produced an average recovery of 176% with a RSD of 8.45%. An older spiking solution that had been used extensively since preparation is hypothesized to be the underlying cause of the high recovery. Solvent evaporation due to opening the storage container several times is plausible.

Table 9. Method Blank Area Counts for Extractions Performed on 07/26/2005; Samples Analyzed on 07/26/2005.

Sample Name	*Sample Comment*	*Sample ID*	*PFBS Area Counts*	*PFHS Area Counts*	*PFOS Area Counts*
s050726a028	Method Blank-1	MB-050726-1	2250	1301	3358
s050726a029	Method Blank-2	MB-050726-2	2770	1881	5306
s050726a030	Method Blank-3	MB-050726-3	4317	1793	5128
s050726a031	Method Blank-4	MB-050726-4	2314	1754	2802
s050726a032	Method Blank-5	MB-050726-5	8191	1642	4514
s050726a033	Method Blank-6	MB-050726-6	3771	1804	4259
s050726a034	Method Blank-7	MB-050726-7	3668	1546	4700
s050726a035	Method Blank-8	MB-050726-8	2600	949	3662
LOQ Standard Area Counts			**26255**	**8250**	**12939**
LOQ Standard Concentration			**0.00221**	**0.00104**	**0.00496**

Table 10. Method Blank Area Counts for Extractions Performed on 07/27/2005; Samples Analyzed on 07/28/2005 and 07/30/2005.

Sample Name	*Sample Comment*	*Sample ID*	*PFBS Area Counts*	*PFHS Area Counts*	*PFOS Area Counts*
s050728a025	Method Blank-1	MB-050727-1	3215	1001	3488
s050728a026	Method Blank-2	MB-050727-2	4573	1930	9299
s050728a027	Method Blank-5	MB-050727-5	3369	39	3045
s050728a028	Method Blank-6	MB-050727-6	3316	0	4497
LOQ Standard Area Counts			**27360**	**6707**	**21214**
LOQ Standard Concentration			**0.00221**	**0.00104**	**0.00992**
s050730a025	Method Blank-3	MB-050727-3	3414	28	4043
s050730a026	Method Blank-4	MB-050727-4	5089	213	9052
s050730a027	Method Blank-7	MB-050727-7	3632	48	5865
s050730a028	Method Blank-8	MB-050727-8	3941	1796	9632
LOQ Standard Area Counts			**14056**	**15862**	**20564**
LOQ Standard Concentration			**0.000880**	**0.00260**	**0.00744**

Table 11. Method Blank Area Counts for Extraction Performed on 07/28/2005 (Centrifuged Samples); Samples Analyzed on 08/01/2005.

Sample Name	*Sample Comment*	*Sample ID*	*PFBS Area Counts*	*PFHS Area Counts*	*PFOS Area Counts*	*Centrifuge*
s050801a025	Method Blank-1	MB-050728-1	7312	3369	27461	Yes
s050801a026	Method Blank-2	MB-050728-2	3505	2182	24740	Yes
s050801a027	Method Blank-3	MB-050728-3	7853	5636	42506	No
s050801a028	Method Blank-4	MB-050728-4	4363	2456	28031	No
s050801a029	Method Blank-5	MB-050728-5	2528	925	19878	Yes
s050801a030	Method Blank-6	MB-050728-6	2673	1104	18783	Yes
s050801a031	Method Blank-7	MB-050728-7	(1)73234	(1)105441	(1)1495463	No
s050801a032	Method Blank-8	MB-050728-8	(1)29997	(1)38166	(1)237882	No
LOQ Standard Area Counts			**26908**	**15530**	**107559**	
LOQ Standard Concentration			**0.00221**	**0.00260**	**0.0496**	

(1) The area counts for Method Blank-7 and Method Blank-8 were determined to be statistical outliers using Dixon's Q test. These data points were excluded when determining the LOQs for the centrifuged samples.

Table 12. Surrogate Spiked Method Blank Recoveries.

Sample Name	*Sample Comment*	*Sample ID*	*Analyte Concentration (ng/mL)*	*Calculated Concentration PFOA [1,2 ^{13}C] ng/mL*	*Percent Surrogate Recovery*
s050726a032	Method Blank-5	MB-050726-5	0.102	0.197	193
s050726a033	Method Blank-6	MB-050726-6	0.102	0.169	166
s050726a034	Method Blank-7	MB-050726-7	0.102	0.197	193
s050726a035	Method Blank-8	MB-050726-8	0.102	0.175	172
s050728a027	Method Blank-5	MB-050727-5	0.102	0.16	157
s050728a028	Method Blank-6	MB-050727-6	0.102	0.163	160
s050730a027	Method Blank-7	MB-050727-7	0.102	0.166	163
s050730a028	Method Blank-8	MB-050727-8	0.102	<0.00249	(1)NA
s050801a029	Method Blank-5	MB-050728-5	0.102	0.184	180
s050801a030	Method Blank-6	MB-050728-6	0.102	0.178	174
s050801a031	Method Blank-7	MB-050728-7	0.102	0.206	202
s050801a032	Method Blank-8	MB-050728-8	0.102	0.182	178

(1) NA: Not applicable. Surrogate not measured in final extract suggesting that the solution was inadvertently not spiked prior to extraction.

(2) The average surrogate recovery in spiked method blanks was 176% (RSD=8.45%).

Trip Blank

Prior to sample collection, three sample containers were filled with 450 mL of ASTM Type I water, spiked with surrogate, sealed, and shipped to the sample collection site along with the empty containers. These samples were analyzed as field/trip blanks. Trip blanks serve as additional method blanks that account for any storage conditions and/or holding time issues that the samples may experience. The resultant field/trip blank concentrations for PFBS, PFHS, and PFOS were <0.000883 ng/mL, <0.00260 ng/mL, and <0.00744 ng/mL, respectively.

System Suitability

A 1.0 ng/mL (nominal concentration) extracted calibration standard was analyzed in triplicate at the beginning and end of the analytical sequence to demonstrate overall system suitability. For all analytes, the relative standard deviation (RSD) of the analyte peak area counts and the RSD of the peak retention times was less than 5% and 2%, respectively, which met method criteria.

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 was still in control. All CCVs for all four analytes produced recoveries within ±25%, which met method criteria.

Lab Control Spikes (LCSs)

Replicate low (0.025 ng/mL nominal concentration) and high (1.25 ng/mL nominal concentration) lab control spikes were prepared and extracted each day samples or calibration standards were extracted. LCSs were prepared by spiking known amounts of the analytes into 100 mL of ASTM Type I water to produce the desired concentration. The spiked water samples were extracted and analyzed in the same manner as the samples. Individual LCS results, along with the average and percent RSD, for each extraction day are

presented in the data tables below. LCSs were used to evaluate method accuracy and precision which was then used to determine analytical uncertainty for each of the analytes reported with the results in Table 1. Information on how the analytical uncertainty was determined is provided at the end of this report in the "Statistical Methods and Calculations" section. For the third extraction day (07/28/2005 - centrifuged samples), a total of twelve LCSs were prepared. Six of the twelve replicates (three low, three high) were centrifuged before extraction in a manner similar to the samples. The remaining six replicates (three low, three high) were not centrifuged prior to extraction. These samples were prepared to verify that the added centrifugation step did not result in loss of target analytes. All LCS recoveries for the first two extraction days met method criteria for accuracy (percent recovery:100±25%) and precision (%RSD ≤ 15%) for all analytes (Table 13 and Table 14). However, for the third extraction day, three LCS measurements exceeded method criteria for accuracy (two high level replicates of PFOA[1,2 ^{13}C] both with 131% recovery and one high level PFBS with 129% recovery). Despite these three exceedences, the LCS recoveries demonstrate excellent accuracy and precision, at both individual levels, and when considered collectively for this extraction day. Therefore, the samples extracted on that day are considered to be accurate within the stated method uncertainty. The overall project accuracy (percent recovery) and precision (percent RSD) was determined for each analyte using the LCS data from the three separate extraction days. The overall project accuracy and precision for PFBS, PFHS, and PFOS was 107±3.49%, 110±4.72%, and 108±5.79%, respectively. These values were used to estimate the analytical uncertainty for each analyte which is described in detail in the Statistical Methods and Calculations section of this report.

Table 13. Lab Control Spike Results: Extraction Day 07/26/2005; Analysis Day 07/26/2005.

		[(1)]PFBS			[(1)]PFHS			[(1)]PFOS			[(1)]PFOA [1,2 ^{13}C]		
Sample Description	*Sample ID*	*Analyte Conc. (ng/mL)*	*Calc. Conc. (ng/mL)*	*Percent Recovery*	*Analyte Conc. (ng/mL)*	*Calc. Conc. (ng/mL)*	*Percent Recovery*	*Analyte Conc. (ng/mL)*	*Calc. Conc. (ng/mL)*	*Percent Recovery*	*Analyte Conc. (ng/mL)*	*Calc. Conc. (ng/mL)*	*Percent Recovery*
LCS Low-1	LCS-050726-1	0.0221	0.0243	110	0.026	0.0285	110	0.0248	0.0244	98.4	0.0249	0.0262	105
LCS Low-2	LCS-050726-2	0.0221	0.0233	105	0.026	0.0298	115	0.0248	0.0279	112	0.0249	0.0283	114
LCS Low-3	LCS-050726-3	0.0221	0.0246	111	0.026	0.0294	113	0.0248	0.03	121	0.0249	0.0275	110
Average Low Recovery ±%RSD (Extraction Day 7/26/2005)		***109% ± 2.83%***			***112% ± 2.28%***			***111% ± 10.3%***			***110% ± 4.26%***		
LCS High-1	LCS-050726-4	1.10	1.15	104	1.30	1.4	108	1.24	1.35	109	1.25	1.25	100
LCS High-2	LCS-050726-5	1.10	1.18	107	1.30	1.41	108	1.24	1.35	109	1.25	1.18	94.4
LCS High-3	LCS-050726-6	1.10	1.19	108	1.30	1.44	111	1.24	1.42	114	1.25	1.23	98.4
Average High Recovery ±%RSD (Extraction Day 7/26/2005)		***107%±1.77%***			***109%±1.47%***			***111%±2.94%***			***97.6%± 2.96%***		
Average All LCSs±%RSD (Extraction Day 7/26/2005)		***108%±2.40%***			***111%±2.43%***			***111%±6.78%***			***104%±7.15%***		

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

Table 14. Lab Control Spike Results: Extraction Day 07/27/2005; Analysis Days 07/28/2005 & 07/30/2005.

		(1)PFBS			(1)PFHS			(1)PFOS			(1)PFOA [1,2 ^{13}C]		
Sample Description	*Sample ID*	*Analyte Conc. (ng/mL)*	*Calc. Conc. (ng/mL)*	*Percent Recovery*	*Analyte Conc. (ng/mL)*	*Calc. Conc. (ng/mL)*	*Percent Recovery*	*Analyte Conc. (ng/mL)*	*Calc. Conc. (ng/mL)*	*Percent Recovery*	*Analyte Conc. (ng/mL)*	*Calc. Conc. (ng/mL)*	*Percent Recovery*
LCS Low-1	LCS-050727-1	0.0221	0.0238	108	0.026	0.029	112	0.0248	0.0243	98.0	0.0249	0.0255	102
LCS Low-2	LCS-050727-2	0.0221	0.0238	108	0.026	0.0286	110	0.0248	0.0241	97.2	0.0249	0.0275	110
LCS Low-3	LCS-050727-3	0.0221	0.0233	105	0.026	0.0278	107	0.0248	0.0257	104	0.0249	0.0241	96.8
Average Low Recovery ±%RSD (Extraction Day 7/27/2005)		***107%± 1.22%***			***109% ±2.15%***			***99.6%±3.53%***			***103%± 6.86%***		
LCS High-1	LCS-050727-4	1.1	1.11	101	1.3	1.37	105	1.24	1.31	106	1.25	1.08	86.4
LCS High-2	LCS-050727-5	1.1	1.14	104	1.3	1.41	108	1.24	1.32	106	1.25	1.02	81.6
LCS High-3	LCS-050727-6	1.1	1.12	102	1.3	1.37	105	1.24	1.28	103	1.25	1.05	84.0
Average High Recovery ±%RSD (Extraction Day 7/27/2005)		***102%±1.36%***			***106%±1.67%***			***105%±1.60%***			***84.0%±2.86%***		
Average All LCSs±%RSD (Extraction Day 7/27/2005)		***104%±2.78%***			***108%±2.33%***			***102%±3.81%***			***93.6%±12.3%***		

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

Table 15. Lab Control Spike Results: Extraction Day 07/28/2005 (Centrifuged Samples); Analysis Day: 08/01/2005.

		[1]PFBS			[1]PFHS			[1]PFOS			[1]PFOA [1,2 ^{13}C]		
Sample Description	*Sample ID*	*Analyte Conc. (ng/mL)*	*Calculated Conc. (ng/mL)*	*Percent Recovery*	*Analyte Conc. (ng/mL)*	*Calculated Conc. (ng/mL)*	*Percent Recovery*	*Analyte Conc. (ng/mL)*	*Calculated Conc. (ng/mL)*	*Percent Recovery*	*Analyte Conc. (ng/mL)*	*Calculated Conc. (ng/mL)*	*Percent Recovery*
LCS Low-1 Centrifuged	LCS-050728-1	0.0221	0.024	108	0.026	0.029	112	0.0248	[2]<0.0496	NA	0.0249	0.028	112
LCS Low-2 Centrifuged	LCS-050728-2	0.0221	0.0241	109	0.026	0.0284	109	0.0248	[2]<0.0496	NA	0.0249	0.0307	123
LCS Low-3 Centrifuged	LCS-050728-3	0.0221	0.0235	106	0.026	0.0288	111	0.0248	([2]<0.0496	NA	0.0249	0.0297	119
Average Low Centrifuged (Extraction Day 7/28/2005)		***108%±1.35%***			***110%±1.06%***			***NA***			***118%±5.48%***		
LCS High-1 Centrifuged	LCS-050728-4	1.1	1.2	109	1.3	1.43	110	1.24	1.42	114	1.25	1.45	116
LCS High-2 Centrifuged	LCS-050728-5	1.1	1.2	109	1.3	1.38	106	1.24	1.36	110	1.25	1.49	119
LCS High-3 Centrifuged	LCS-050728-6	1.1	1.16	105	1.3	1.37	105	1.24	1.35	109	1.25	1.45	116
Average High Centrifuged (Extraction Day 7/28/2005)		***108%±1.95%***			***107%±2.47%***			***111%±2.75%***			***117%±1.58%***		
Average All Centrifuged LCSs (Extraction Day 7/28/2005)		***108%±1.50%***			***109%±2.31%***			***[3]111%±2.75%***			***118%±3.16%***		
LCS Low-7	LCS-050728-7	0.0221	0.0236	107	0.026	0.0294	113	0.0248	[2]<0.0496	NA	0.0249	0.0295	118
LCS Low-8	LCS-050728-8	0.0221	0.0263	119	0.026	0.0335	129	0.0248	[2]<0.0496	NA	0.0249	0.0326	131
LCS Low-9	LCS-050728-9	0.0221	0.023	104	0.026	0.0304	117	0.0248	([2]<0.0496	NA	0.0249	0.0289	116
Average Low Non-Centrifugeed (Extraction Day 7/28/2005)		***110%±7.23***			***120%±6.87%***			***NA***			***121%±7.98%***		
LCS High-10	LCS-050728-10	1.1	1.12	102	1.3	1.36	105	1.24	1.29	104	1.25	1.43	114
LCS High-11	LCS-050728-11	1.1	1.17	106	1.3	1.36	105	1.24	1.36	110	1.25	1.45	116
LCS High-12	LCS-050728-12	1.1	1.15	104	1.3	1.38	106	1.24	1.37	110	1.25	1.64	131
Average High Non-Centrifuged (Extraction Day 7/28/2005)		***104%±2.19%***			***105%±0.888%***			***108%±3.25%***			***120%±7.69%***		
Average All Non-Centrifuged LCSs (Extraction Day 7/28/2005)		***107%±5.69%***			***112%±8.46%***			***[3]108%±3.25%***			***121%±6.41%***		

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

(2) The PFOS LOQ for this analysis set was raised to 0.0496 due to method blank contamination. LCS results and recoveries were not reported.

(3) The average value and %RSD were calculated using only the high level results.

Sample Duplicates

Because a field sample duplicate (separate container) was collected at each sampling location, duplicate/replicate extractions of a given sample were not performed. Overall method precision was determined using surrogate spikes and LCSs.

Surrogates

Although not specified in the ETS 8-154.1, PFOA [1,2 ^{13}C] was added to all samples and sample spikes as a surrogate to evaluate overall method performance. The final PFOA[1,2^{13}C] concentration was 0.274 ng/mL. Surrogate recoveries are reported in the next section with sample data and will be discussed in further detail in the Data Summary and Discussion section below.

Field Matrix Spikes

Low (nominal concentration of 0.05 ng/mL) and high (nominal concentration 0.5 ng/mL) field matrix spikes were collected at each sampling point to verify that the analytical method is applicable to the collected matrix. The PFOA [1,2 ^{13}C] surrogate was added to each field matrix spike at a final concentration of 0.254 ng/mL. Field matrix spike recoveries within 100±30% confirm that "unknown" components in the sample matrix do not interfere with the extraction and analysis of the analytes of interest. Field matrix spikes will be presented in the next section with the sample data.

DATA SUMMARY AND DISCUSSION

The data tables below individually summarize the sample results and field matrix spike recoveries for each of the three analytes and the surrogate for all of the sampling locations plus the three trip blanks.

PFBS

PFBS matrix spike recoveries were within method acceptance criteria of 100±30% for all sampling locations with the following exceptions: 3M LIMS sample numbers 86448 (low spike 174%), 86452 (low spike 137%), 86456 (low spike 223%), 86460 (low spike 134%), 86489 (high spike 136%), 86528 (low spike 133%), 86533 (high spike 134%) and 86558 (trip blank #3 high spike 18.0%). (See Table 16). For each of these instances, the corresponding high or low spike for the given location produced a spike recovery within method criteria of 100±30%. Therefore, the sample results for these locations are reported within the stated method analytical uncertainty and are considered accurate to within 100±30% for the given location.

PFHS

PFHS matrix spike recoveries were within method acceptance criteria of 100±30% for all sampling locations with the following exceptions: 3M LIMS sample numbers 86448 (low spike 170%), 86452 (low spike 134%), 86509 (high spike 67.8%), 86512 (low spike 133%), and 86532 (low spike 54.7%). Refer to Table 17 for more information. For each of these instances, the corresponding high or low spike for the given sampling location produced a spike recovery within method criteria of 100±30%. Therefore, the sample results for these locations are reported within the stated method analytical uncertainty and are considered accurate to within 100±30% for the given location.

PFOS

In general, PFOS matrix spike recoveries were within method acceptance criteria of 100±30% with a few exceptions. Six locations produced recoveries that exceeded method critera for the low-level spike but were acceptable for the high-level spike. The 3M LIMS sample numbers for these instances were 86380 (low spike 136%), 86448 (low spike 191%), 86452 (low spike 139%), 86460 (low spike 136%), 86489 (low spike 138%), and 86536 (low spike 134%). With the exception of sample number 86448, the low-level spike recovery was high, but less than 150%. Because the high-level spike recoveries for these samples met method criteria, the sample results for these locations are reported within the stated method analytical accuracy and are considered accurate to within 100±30%. Additionally, three sampling locations produced matrix spike recoveries outside the 100±30% criteria for both spike levels: DXS-SW-T02006-0-050721 (low spike 131%, high spike 133%), DXS-SW-T02010-0-050721 (low spike 47.4%, high spike 51.9%), and DXS-SW-T03006-0-050722 (low spike 2.91%, high spike 132%). For locations DXS-SW-T02006-0-050721 and DXS-SW-T02010-050721, the accuracy for the sample/sample duplicate results has been increased to 100±50% to account for the slightly high recoveries for DXS-SW-T02006-0-050721 (132% average) and the low recoveries for DXS-SW-T02010-050721 (approximately 50% average). Furthermore, the sample/sample duplicate %RPD for DXS-SW-T02010-050721 was greater than 30%. The accuracy for location DXS-SW-T03006-0-050722 has been increased to of 100±50% based solely on the high spike recovery (132%). All sample locations with adjusted accuracy statements for PFOS have been duly footnoted in Table 18.

PFOA[1,2 ^{13}C] Surrogate

Recoveries of the PFOA[1,2^{13}C] surrogate in the sample, sample duplicate, and field matrix spikes for each sampling location is provided in Table 19. When the results in Table 19 are considered collectively, one of the most noticeable observations was that the surrogate recovery was consistently low for all samples, sample duplicates, low matrix spikes and high matrix spikes. The overall average surrogate recovery was 56.1% with a RSD of 11.6%. The spiking solutions used to prepare the collection bottle spikes were evaluated prior to bottle preparation under non-GLP provisions. Surrogate recoveries from this study do not suggest that a solution preparation/calculation error is responsible for the recoveries observed here. At this time, the 3M Environmental Laboratory cannot explain the precise, but low surrogate recoveries. A separate investigation will be conducted to explore possible loss mechanisms/holding time issues.

The average surrogate recovery was used as a correction factor to normalize surrogate recoveries for a potential holding time effect. Both the corrected and uncorrected recoveries are listed in Table 19. It should be emphasized that sample results for PFBS, PFHS, and PFOS were **NOT** corrected for surrogate recoveries. Of the 201 bottles extracted, only three produced corrected surrogate less than 70% (sample numbers 86509, 86527, and 86532). Sample number 86509 was a high-level matrix spike and exhibited low recoveries for the three target analytes (PFBS 76.7%, PFHS 67.8%, and PFOS 51.9%). Thus, the low recovery may be attributable to an error during spiking of the collection bottle.

Table 16. PFBS Sample Results.

3M Sample Number	*Sample Description*	*[1]PFBS Conc. (ng/mL)*	*[2] Field Matrix Spike % Recovery*	*Average Result Sample/Sample Duplicate (ng/mL)*	*%RPD*	*Extraction Date*
E05-0210-86358	DLS-SW-TRM307-0-050718	< 0.00221	NA	**< 0.00221**	**[3]NA**	07/26/2005
E05-0210-86359	DLS-SW-TRM307-0-050718 Dup	< 0.00221	NA			07/26/2005
E05-0210-86360	DLS-SW-TRM307-0-050718 LS	0.0490	111			07/26/2005
E05-0210-86361	DLS-SW-TRM307-0-050718 HS	0.508	115			07/26/2005
E05-0210-86362	DLS-SW-TRM301-0-050718	< 0.00221	NA	**< 0.00221**	**[3]NA**	07/26/2005
E05-0210-86363	DLS-SW-TRM301-0-050718 Dup	< 0.00221	NA			07/26/2005
E05-0210-86364	DLS-SW-TRM301-0-050718 LS	0.0465	105			07/26/2005
E05-0210-86365	DLS-SW-TRM301-0-050718 HS	0.533	121			07/26/2005
E05-0210-86366	DLS-SW-TRM301-F-050718	< 0.00221	NA	**< 0.00221**	**[3]NA**	07/26/2005
E05-0210-86367	DLS-SW-TRM301-F-050718 Dup	< 0.00221	NA			07/26/2005
E05-0210-86368	DLS-SW-TRM301-F-050718 LS	0.0479	109			07/26/2005
E05-0210-86369	DLS-SW-TRM301-F-050718 HS	0.524	119			07/26/2005
E05-0210-86370	DLS-SW-TRM295-0-050719[4]	0.0679	121	**0.0147**	**4.78**	07/26/2005
E05-0210-86371	DLS-SW-TRM295-0-050719 Dup[4]	0.493	108			07/26/2005
E05-0210-86372	DLS-SW-TRM295-0-050719 LS[4]	0.0143	NA			07/26/2005
E05-0210-86373	DLS-SW-TRM295-0-050719 HS[4]	0.0150	NA			07/26/2005
E05-0210-86374	DLS-SW-TRM289-0-050719	0.0225	NA	**0.0219**	**5.48**	07/26/2005
E05-0210-86375	DLS-SW-TRM289-0-050719 Dup	0.0213	NA			07/26/2005
E05-0210-86376	DLS-SW-TRM289-0-050719 LS	0.0706	110			07/26/2005
E05-0210-86377	DLS-SW-TRM289-0-050719 HS	0.453	97.8			07/26/2005
E05-0210-86378	DLS-SW-TRM289-F-050719	0.0197	NA	**0.0199**	**2.01**	07/26/2005
E05-0210-86379	DLS-SW-TRM289-F-050719 Dup	0.0201	NA			07/26/2005
E05-0210-86380	DLS-SW-TRM289-F-050719 LS	0.0693	112			07/26/2005
E05-0210-86381	DLS-SW-TRM289-F-050719 HS	0.522	114			07/26/2005
E05-0210-86382	DLS-SW-TRM283-0-050719	0.0203	NA	**0.0192**	**11.4**	07/26/2005
E05-0210-86383	DLS-SW-TRM283-0-050719 Dup	0.0181	NA			07/26/2005
E05-0210-86384	DLS-SW-TRM283-0-050719 LS	0.0677	110			07/26/2005
E05-0210-86385	DLS-SW-TRM283-0-050719 HS	0.508	111			07/26/2005
E05-0210-86386	DLS-SW-TRM277-0-050719	0.0115	NA	**0.0119**	**6.72**	07/26/2005
E05-0210-86387	DLS-SW-TRM277-0-050719 Dup	0.0123	NA			07/26/2005
E05-0210-86388	DLS-SW-TRM277-0-050719 LS	0.0607	111			07/26/2005
E05-0210-86389	DLS-SW-TRM277-0-050719 HS	0.515	114			07/26/2005
E05-0210-86390	DLS-SW-TRM277-F-050719	0.0111	NA	**0.0118**	**11.9**	07/26/2005
E05-0210-86391	DLS-SW-TRM277-F-050719 Dup	0.0125	NA			07/26/2005
E05-0210-86392	DLS-SW-TRM277-F-050719 LS	0.0633	117			07/26/2005
E05-0210-86393	DLS-SW-TRM277-F-050719 HS	0.464	102			07/26/2005

Table 16. PFBS Sample Results Continued.

3M Sample Number	*Sample Description*	*(1)PFBS Conc. (ng/mL)*	*(2)Field Matrix Spike % Recovery*	*Average Result Sample/Sample Duplicate (ng/mL)*	*%RPD*	*Extraction Date*
E05-0210-86394	DLS-SW-TRM271-0-050719	0.0133	NA	**0.0138**	**6.54**	07/26/2005
E05-0210-86395	DLS-SW-TRM271-0-050719 Dup	0.0142	NA			07/26/2005
E05-0210-86396	DLS-SW-TRM271-0-050719 LS	0.0586	102			07/26/2005
E05-0210-86397	DLS-SW-TRM271-0-050719 HS	0.483	106			07/26/2005
E05-0210-86398	DLS-SW-TRM265-0-050719	0.0103	NA	**0.0104**	**0.966**	07/26/2005
E05-0210-86399	DLS-SW-TRM265-0-050719 Dup	0.0104	NA			07/26/2005
E05-0210-86400	DLS-SW-TRM265-0-050719 LS	0.0544	99.9			07/26/2005
E05-0210-86401	DLS-SW-TRM265-0-050719 HS	0.484	107			07/26/2005
E05-0210-86402	DLS-SW-TRM261-2-050720	< 0.00221	NA	**< 0.00221**	**NA**	07/26/2005
E05-0210-86403	DLS-SW-TRM261-2-050720 Dup	< 0.00221	NA			07/26/2005
E05-0210-86404	DLS-SW-TRM261-2-050720 LS	0.0497	113			07/26/2005
E05-0210-86405	DLS-SW-TRM261-2-050720 HS	0.485	110			07/26/2005
E05-0210-86406	DLS-SW-TRM261-0-050720	0.0118	NA	**0.0114**	**7.02**	07/26/2005
E05-0210-86407	DLS-SW-TRM261-0-050720 Dup	0.0110	NA			07/26/2005
E05-0210-86408	DLS-SW-TRM261-0-050720 LS	0.0556	100			07/26/2005
E05-0210-86409	DLS-SW-TRM261-0-050720 HS	0.456	101			07/26/2005
E05-0210-86410	DLS-SW-TRM261-F-050720	0.0116	NA	**0.0112**	**8.07**	07/26/2005
E05-0210-86411	DLS-SW-TRM261-F-050720 Dup	0.0107	NA			07/26/2005
E05-0210-86412	DLS-SW-TRM261-F-050720 LS	0.0621	130			07/26/2005
E05-0210-86413	DLS-SW-TRM261-F-050720 HS	0.460	103			07/26/2005
E05-0210-86414	DLS-SW-TRM256-0-050720	0.0111	NA	**0.0118**	**11.9**	07/26/2005
E05-0210-86415	DLS-SW-TRM256-0-050720 Dup	0.0125	NA			07/26/2005
E05-0210-86416	DLS-SW-TRM256-0-050720 LS	0.0607	111			07/26/2005
E05-0210-86417	DLS-SW-TRM256-0-050720 HS	0.498	110			07/26/2005
E05-0210-86418	DLS-SW-TRM254-0-050720	0.0124	NA	**0.0122**	**3.28**	07/26/2005
E05-0210-86419	DLS-SW-TRM254-0-050720 Dup	0.0120	NA			07/26/2005
E05-0210-86420	DLS-SW-TRM254-0-050720 LS	0.0648	119			07/27/2005
E05-0210-86421	DLS-SW-TRM254-0-050720 HS	0.493	109			07/27/2005
E05-0210-86422	DLS-SW-TRM254-F-050720	0.0128	NA	**0.0125**	**5.62**	07/27/2005
E05-0210-86423	DLS-SW-TRM254-F-050720 Dup	0.0121	NA			07/27/2005
E05-0210-86424	DLS-SW-TRM254-F-050720 LS	0.0598	107			07/27/2005
E05-0210-86425	DLS-SW-TRM254-F-050720 HS	0.530	112			07/27/2005
E05-0210-86426	DLS-SW-TRM254-2-050720	< 0.00221	NA	**< 0.00221**	**(3)NA**	07/27/2005
E05-0210-86427	DLS-SW-TRM254-2-050720 Dup	< 0.00221	NA			07/27/2005
E05-0210-86428	DLS-SW-TRM254-2-050720 LS	0.0502	114			07/27/2005
E05-0210-86429	DLS-SW-TRM254-2-050720 HS	0.485	110			07/27/2005
E05-0210-86430	DXS-SW-T01001-0-050721	0.0215	NA	**0.0208**	**6.73**	07/27/2005
E05-0210-86431	DXS-SW-T01001-0-050721 Dup	0.0201	NA			07/27/2005
E05-0210-86432	DXS-SW-T01001-0-050721 LS	0.0707	113			07/27/2005
E05-0210-86433	DXS-SW-T01001-0-050721 HS	0.519	113			07/27/2005

Table 16. PFBS Sample Results Continued.

3M Sample Number	*Sample Description*	*(1)PFBS Conc. (ng/mL)*	*(2)Field Matrix Spike % Recovery*	*Average Result Sample/Sample Duplicate (ng/mL)*	*%RPD*	*Extraction Date*
E05-0210-86434	DXS-SW-T01002-0-050721	0.0161	NA	**0.0163**	**1.85**	07/27/2005
E05-0210-86435	DXS-SW-T01002-0-050721 Dup	0.0164	NA			07/27/2005
E05-0210-86436	DXS-SW-T01002-0-050721 LS	0.0663	113			07/27/2005
E05-0210-86437	DXS-SW-T01002-0-050721 HS	0.521	114			07/27/2005
E05-0210-86438	DXS-SW-T01003-0-050721	0.0165	NA	**0.0166**	**0.604**	07/27/2005
E05-0210-86439	DXS-SW-T01003-0-050721 Dup	0.0166	NA			07/27/2005
E05-0210-86440	DXS-SW-T01003-0-050721 LS	0.0624	104			07/27/2005
E05-0210-86441	DXS-SW-T01003-0-050721 HS	0.460	104			07/28/2005 centrifuged
E05-0210-86442	DXS-SW-T01004-0-050721	0.0158	NA	**0.0162**	**4.33**	07/27/2005
E05-0210-86443	DXS-SW-T01004-0-050721 Dup	0.0165	NA			07/27/2005
E05-0210-86444	DXS-SW-T01004-0-050721 LS	0.0678	117			07/27/2005
E05-0210-86445	DXS-SW-T01004-0-050721 HS	0.470	103			07/27/2005
E05-0210-86446	DXS-SW-T01005-0-050721	0.00957	NA	**0.00971**	**2.88**	07/27/2005
E05-0210-86447	DXS-SW-T01005-0-050721 Dup	0.00985	NA			07/27/2005
E05-0210-86448	DXS-SW-T01005-0-050721 LS	0.0863	174			07/27/2005
E05-0210-86449	DXS-SW-T01005-0-050721 HS	0.482	107			07/27/2005
E05-0210-86450	DXS-SW-T01006-0-050721	0.00432	NA	**0.00399**	**16.5**	07/27/2005
E05-0210-86451	DXS-SW-T01006-0-050721 Dup	0.00366	NA			07/27/2005
E05-0210-86452	DXS-SW-T01006-0-050721 LS	0.0646	137			07/27/2005
E05-0210-86453	DXS-SW-T01006-0-050721 HS	0.546	123			07/27/2005
E05-0210-86454	DXS-SW-T01007-0-050721	0.00566	NA	**0.00565**	**0.354**	07/27/2005
E05-0210-86455	DXS-SW-T01007-0-050721 Dup	0.00564	NA			07/27/2005
E05-0210-86456	DXS-SW-T01007-0-050721 LS	0.1040	223			07/27/2005
E05-0210-86457	DXS-SW-T01007-0-050721 HS	0.485	109			07/27/2005
E05-0210-86458	DXS-SW-T01008-0-050721	0.00369	NA	**0.00436**	**30.5**	07/27/2005
E05-0210-86459	DXS-SW-T01008-0-050721 Dup	0.00502	NA			07/27/2005
E05-0210-86460	DXS-SW-T01008-0-050721 LS	0.0635	134			07/27/2005
E05-0210-86461	DXS-SW-T01008-0-050721 HS	0.452	102			07/27/2005
E05-0210-86462	DXS-SW-T01009-0-050721	0.00491	NA	**0.00468**	**10.0**	07/27/2005
E05-0210-86463	DXS-SW-T01009-0-050721 Dup	0.00444	NA			07/27/2005
E05-0210-86464	DXS-SW-T01009-0-050721 LS	0.0532	110			07/27/2005
E05-0210-86465	DXS-SW-T01009-0-050721 HS	0.535	120			07/27/2005
E05-0210-86466	DXS-SW-T01010-0-050721	0.00395	NA	**0.00390**	**2.56**	07/27/2005
E05-0210-86467	DXS-SW-T01010-0-050721 Dup	0.00385	NA			07/27/2005
E05-0210-86468	DXS-SW-T01010-0-050721 LS	0.0543	114			07/27/2005
E05-0210-86469	DXS-SW-T01010-0-050721 HS	0.501	113			07/27/2005
E05-0210-86470	DXS-SW-T02001-0-050721	0.0414	NA	**0.0419**	**2.15**	07/27/2005
E05-0210-86471	DXS-SW-T02001-0-050721 Dup	0.0423	NA			07/27/2005
E05-0210-86472	DXS-SW-T02001-0-050721 LS	0.0856	99.2			07/27/2005
E05-0210-86473	DXS-SW-T02001-0-050721 HS	0.499	104			07/27/2005

Table 16. PFBS Sample Results Continued.

3M Sample Number	*Sample Description*	*[1]PFBS Conc. (ng/mL)*	*[2]Field Matrix Spike % Recovery*	*Average Result Sample/Sample Duplicate*	*%RPD*	*Extraction Date*
E05-0210-86474	DXS-SW-T02002-0-050721	0.0306	NA	**0.0311**	**3.22**	07/27/2005
E05-0210-86475	DXS-SW-T02002-0-050721 Dup	0.0316	NA			07/27/2005
E05-0210-86476	DXS-SW-T02002-0-050721 LS	0.0783	107			07/27/2005
E05-0210-86477	DXS-SW-T02002-0-050721 HS	0.508	108			07/27/2005
E05-0210-86478	DXS-SW-T02003-0-050721	< 0.00221	NA	**< 0.00221**	**[3]NA**	07/27/2005
E05-0210-86479	DXS-SW-T02003-0-050721 Dup	< 0.00221	NA			07/27/2005
E05-0210-86480	DXS-SW-T02003-0-050721 LS	0.0479	109			07/27/2005
E05-0210-86481	DXS-SW-T02003-0-050721 HS	0.476	108			07/27/2005
E05-0210-86482	DXS-SW-T02004-0-050721	< 0.00221	NA	**< 0.00221**	**[3]NA**	07/27/2005
E05-0210-86483	DXS-SW-T02004-0-050721 Dup	< 0.00221	NA			07/27/2005
E05-0210-86484	DXS-SW-T02004-0-050721 LS	0.0544	122			07/27/2005
E05-0210-86485	DXS-SW-T02004-0-050721 HS	0.476	108			07/27/2005
E05-0210-86486	DXS-SW-T02005-0-050721	< 0.000883	NA	**< 0.00221**	**[3]NA**	07/27/2005
E05-0210-86487	DXS-SW-T02005-0-050721 Dup	< 0.00221	NA			07/28/2005 centrifuged
E05-0210-86488	DXS-SW-T02005-0-050721 LS	0.0511	116			07/27/2005
E05-0210-86489	DXS-SW-T02005-0-050721 HS	0.600	136			07/28/2005 centrifuged
E05-0210-86490	DXS-SW-T02006-0-050721	< 0.000883	NA	**[5]0.00101**	**NA**	07/27/2005
E05-0210-86491	DXS-SW-T02006-0-050721 Dup	0.00101	NA			07/27/2005
E05-0210-86492	DXS-SW-T02006-0-050721 LS	0.0534	119			07/27/2005
E05-0210-86493	DXS-SW-T02006-0-050721 HS	0.545	123			07/27/2005
E05-0210-86494	DXS-SW-T02007-0-050721	< 0.000883	NA	**< 0.000883**	**[3]NA**	07/27/2005
E05-0210-86495	DXS-SW-T02007-0-050721 Dup	< 0.000883	NA			07/27/2005
E05-0210-86496	DXS-SW-T02007-0-050721 LS	0.0470	106			07/27/2005
E05-0210-86497	DXS-SW-T02007-0-050721 HS	0.450	102			07/27/2005
E05-0210-86498	DXS-SW-T02008-0-050721	0.00109	NA	**0.00112**	**5.36**	07/27/2005
E05-0210-86499	DXS-SW-T02008-0-050721 Dup	0.00115	NA			07/27/2005
E05-0210-86500	DXS-SW-T02008-0-050721 LS	0.0508	112			07/27/2005
E05-0210-86501	DXS-SW-T02008-0-050721 HS	0.468	106			07/27/2005
E05-0210-86502	DXS-SW-T02009-0-050721	0.00288	NA	**0.00266**	**16.5**	07/27/2005
E05-0210-86503	DXS-SW-T02009-0-050721 Dup	0.00244	NA			07/27/2005
E05-0210-86504	DXS-SW-T02009-0-050721 LS	0.0541	117			07/27/2005
E05-0210-86505	DXS-SW-T02009-0-050721 HS	0.498	112			07/27/2005
E05-0210-86506	DXS-SW-T02010-0-050721	0.00628	NA	**0.00591**	**12.7**	07/27/2005
E05-0210-86507	DXS-SW-T02010-0-050721 Dup	0.00553	NA			07/27/2005
E05-0210-86508	DXS-SW-T02010-0-050721 LS	0.0533	107			07/27/2005
E05-0210-86509	DXS-SW-T02010-0-050721 HS	0.344	76.7			07/27/2005
E05-0210-86510	DXS-SW-T03001-0-050721	0.818	NA	**0.836**	**4.31**	07/27/2005
E05-0210-86511	DXS-SW-T03001-0-050721 Dup	0.854	NA			07/27/2005
E05-0210-86512	DXS-SW-T03001-0-050721 LS	0.911	[6]NR			07/27/2005
E05-0210-86513	DXS-SW-T03001-0-050721 HS	1.33	112			07/27/2005

Table 16. PFBS Sample Results Continued.

3M Sample Number	*Sample Description*	*[1]PFBS Conc. (ng/mL)*	*[2]Field Matrix Spike % Recovery*	*Average Result Sample/Sample Duplicate*	*%RPD*	*Extraction Date*
E05-0210-86514	DXS-SW-T03002-0-050721	0.00519	NA	**0.00472**	**20.1**	07/27/2005
E05-0210-86515	DXS-SW-T03002-0-050721 Dup	0.00424	NA			07/27/2005
E05-0210-86516	DXS-SW-T03002-0-050721 LS	0.0521	107			07/27/2005
E05-0210-86517	DXS-SW-T03002-0-050721 HS	0.480	108			07/27/2005
E05-0210-86518	DXS-SW-T03003-0-050721	< 0.000883	NA	**< 0.000883**	**[3]NA**	07/27/2005
E05-0210-86519	DXS-SW-T03003-0-050721 Dup	< 0.000883	NA			07/27/2005
E05-0210-86520	DXS-SW-T03003-0-050721 LS	0.0519	118			07/27/2005
E05-0210-86521	DXS-SW-T03003-0-050721 HS	0.487	110			07/27/2005
E05-0210-86522	DXS-SW-T03004-0-050722	0.00430	NA	**0.00268**	**121**	07/27/2005
E05-0210-86523	DXS-SW-T03004-0-050722 Dup	0.00106	NA			07/27/2005
E05-0210-86524	DXS-SW-T03004-0-050722 LS	0.0536	115			07/27/2005
E05-0210-86525	DXS-SW-T03004-0-050722 HS	0.516	116			07/27/2005
E05-0210-86526	DXS-SW-T03005-0-050722	< 0.000883	NA	**[5]0.00171**	**NA**	07/27/2005
E05-0210-86527	DXS-SW-T03005-0-050722 Dup	0.00171	NA			07/28/2005 centrifuged
E05-0210-86528	DXS-SW-T03005-0-050722 LS	0.0588	133			07/27/2005
E05-0210-86529	DXS-SW-T03005-0-050722 HS	0.536	122			07/27/2005
E05-0210-86530	DXS-SW-T03006-0-050722	< 0.000883	NA	**< 0.000883**	**[3]NA**	07/27/2005
E05-0210-86531	DXS-SW-T03006-0-050722 Dup	< 0.000883	NA			07/27/2005
E05-0210-86532	DXS-SW-T03006-0-050722 LS	0.0430	97.5			07/28/2005 centrifuged
E05-0210-86533	DXS-SW-T03006-0-050722 HS	0.591	134			07/27/2005
E05-0210-86534	DXS-SW-T03007-0-050722	< 0.000883	NA	**[5]0.00107**	**NA**	07/27/2005
E05-0210-86535	DXS-SW-T03007-0-050722 Dup	0.00107	NA			07/28/2005 centrifuged
E05-0210-86536	DXS-SW-T03007-0-050722 LS	0.0564	128			07/27/2005
E05-0210-86537	DXS-SW-T03007-0-050722 HS	0.513	116			07/27/2005
E05-0210-86538	DXS-SW-T03008-0-050722	< 0.000883	NA	**< 0.000883**	**[3]NA**	07/27/2005
E05-0210-86539	DXS-SW-T03008-0-050722 Dup	< 0.000883	NA			07/27/2005
E05-0210-86540	DXS-SW-T03008-0-050722 LS	0.0513	116			07/27/2005
E05-0210-86541	DXS-SW-T03008-0-050722 HS	0.507	115			07/27/2005
E05-0210-86542	DXS-SW-T03009-0-050722	< 0.000883	NA	**< 0.000883**	**[3]NA**	07/27/2005
E05-0210-86543	DXS-SW-T03009-0-050722 Dup	< 0.000883	NA			07/27/2005
E05-0210-86544	DXS-SW-T03009-0-050722 LS	0.0505	114			07/27/2005
E05-0210-86545	DXS-SW-T03009-0-050722 HS	0.460	104			07/27/2005
E05-0210-86546	DXS-SW-T03010-0-050722	0.000908	NA	**[5]0.000908**	**NA**	07/27/2005
E05-0210-86547	DXS-SW-T03010-0-050722 Dup	< 0.000883	NA			07/27/2005
E05-0210-86548	DXS-SW-T03010-0-050722 LS	0.0498	111			07/27/2005
E05-0210-86549	DXS-SW-T03010-0-050722 HS	0.449	102			07/27/2005

Table 16. PFBS Sample Results Continued.

3M Sample Number	*Sample Description*	*(1)PFBS Conc. (ng/mL)*	*(2)Field Matrix Spike % Recovery*	*Average Result Sample/Sample Duplicate*	*%RPD*	*Extraction Date*
E05-0210-86550	DLS-SW-TRIP01	< 0.000883	NA	**< 0.000883**	**NA**	07/27/2005
E05-0210-86551	DLS-SW-TRIP01 LS	0.04710	107			07/27/2005
E05-0210-86552	DLS-SW-TRIP01 HS	0.444	101			07/27/2005
E05-0210-86553	DXS-SW-TRIP02	< 0.000883	NA	**< 0.000883**	**NA**	07/27/2005
E05-0210-86554	DXS-SW-TRIP02 LS	0.0478	108			07/27/2005
E05-0210-86555	DXS-SW-TRIP02 HS	0.440	99.8			07/27/2005
E05-0210-86556	DXS-SW-TRIP03	< 0.000883	NA	**< 0.000883**	**NA**	07/27/2005
E05-0210-86557	DXS-SW-TRIP03 LS	0.0495	112			07/27/2005
E05-0210-86558	DXS-SW-TRIP03 HS	0.080	18.0			07/27/2005

(1) The analytical uncertainty of the PFBS resuts is 100±10.6% based on method accuracy and precision. All results and calculations in this table are presented with three significant figures. Sample concentrations, averages, and %RPD values may vary slightly from the raw data.

(2) Low field matrix spike concentration = 0.0441 ng/mL. High field matrix spike concentration = 0.441 ng/mL.

(3) NA: Not applicable. %RPD value was not determined when concentrations for both the sample and sample duplicate were below the stated LOQ.

(4) Sample descriptions were misidentified when checked into LIMS. Samples with LIMS ID numbers 86370 and 86371 were in bottles labeled low spike and high spike, respectively. Bottles with LIMS ID numbers 86372 and 86372 were surrogate spiked only (sample and sample duplicate bottles).

(5) The average value listed is the concentration for the sample or sample duplicate that produced a value above the LOQ. A true average and %RPD between the sample and sample duplicate was not determined.

(6) NR: Not reported. Spike recovery not calculated as the endogenous sample concentration was at least three times the spiked amount.

Table 17. PFHS Sample Results.

3M Sample Number	*Sample Description*	*[1]PFHS Conc. (ng/mL)*	*[2]Field Matrix Spike % Recovery*	*Average Result Sample/Sample Duplicate*	*%RPD*	*Extraction Date*
E05-0210-86358	DLS-SW-TRM307-0-050718	< 0.00104	NA	**< 0.00104**	**[3]NA**	07/26/2005
E05-0210-86359	DLS-SW-TRM307-0-050718 Dup	< 0.00104	NA			07/26/2005
E05-0210-86360	DLS-SW-TRM307-0-050718 LS	0.0581	112			07/26/2005
E05-0210-86361	DLS-SW-TRM307-0-050718 HS	0.584	112			07/26/2005
E05-0210-86362	DLS-SW-TRM301-0-050718	< 0.00104	NA	**0.00134**	**[4]NA**	07/26/2005
E05-0210-86363	DLS-SW-TRM301-0-050718 Dup	0.00134	NA			07/26/2005
E05-0210-86364	DLS-SW-TRM301-0-050718 LS	0.0542	101			07/26/2005
E05-0210-86365	DLS-SW-TRM301-0-050718 HS	0.600	115			07/26/2005
E05-0210-86366	DLS-SW-TRM301-F-050718	< 0.00104	NA	**< 0.00104**	**[3]NA**	07/26/2005
E05-0210-86367	DLS-SW-TRM301-F-050718 Dup	< 0.00104	NA			07/26/2005
E05-0210-86368	DLS-SW-TRM301-F-050718 LS	0.0577	111			07/26/2005
E05-0210-86369	DLS-SW-TRM301-F-050718 HS	0.576	110			07/26/2005
E05-0210-86370	DLS-SW-TRM295-0-050719[5]	0.0719	116	**0.0117**	**2.58**	07/26/2005
E05-0210-86371	DLS-SW-TRM295-0-050719 Dup[5]	0.5490	103			07/26/2005
E05-0210-86372	DLS-SW-TRM295-0-050719 LS[5]	0.0115	NA			07/26/2005
E05-0210-86373	DLS-SW-TRM295-0-050719 HS[5]	0.0118	NA			07/26/2005
E05-0210-86374	DLS-SW-TRM289-0-050719	0.0133	NA	**0.01280**	**7.81**	07/26/2005
E05-0210-86375	DLS-SW-TRM289-0-050719 Dup	0.0123	NA			07/26/2005
E05-0210-86376	DLS-SW-TRM289-0-050719 LS	0.0666	103			07/26/2005
E05-0210-86377	DLS-SW-TRM289-0-050719 HS	0.493	92.2			07/26/2005
E05-0210-86378	DLS-SW-TRM289-F-050719	0.0129	NA	**0.01245**	**7.23**	07/26/2005
E05-0210-86379	DLS-SW-TRM289-F-050719 Dup	0.0120	NA			07/26/2005
E05-0210-86380	DLS-SW-TRM289-F-050719 LS	0.0706	112			07/26/2005
E05-0210-86381	DLS-SW-TRM289-F-050719 HS	0.582	109			07/26/2005
E05-0210-86382	DLS-SW-TRM283-0-050719	0.00888	NA	**0.00886**	**0.565**	07/26/2005
E05-0210-86383	DLS-SW-TRM283-0-050719 Dup	0.00883	NA			07/26/2005
E05-0210-86384	DLS-SW-TRM283-0-050719 LS	0.0645	107			07/26/2005
E05-0210-86385	DLS-SW-TRM283-0-050719 HS	0.572	108			07/26/2005
E05-0210-86386	DLS-SW-TRM277-0-050719	0.00579	NA	**0.00642**	**19.5**	07/26/2005
E05-0210-86387	DLS-SW-TRM277-0-050719 Dup	0.00704	NA			07/26/2005
E05-0210-86388	DLS-SW-TRM277-0-050719 LS	0.0637	110			07/26/2005
E05-0210-86389	DLS-SW-TRM277-0-050719 HS	0.574	109			07/26/2005

Table 17. PFHS Sample Results Continued.

3M Sample Number	*Sample Description*	*[1]PFHS Conc. (ng/mL)*	*[2]Field Matrix Spike % Recovery*	*Average Result Sample/Sample Duplicate*	*%RPD*	*Extraction Date*
E05-0210-86390	DLS-SW-TRM277-F-050719	0.00609	NA	**0.00641**	**9.84**	07/26/2005
E05-0210-86391	DLS-SW-TRM277-F-050719 Dup	0.00672	NA			07/26/2005
E05-0210-86392	DLS-SW-TRM277-F-050719 LS	0.0637	110			07/26/2005
E05-0210-86393	DLS-SW-TRM277-F-050719 HS	0.529	100			07/26/2005
E05-0210-86394	DLS-SW-TRM271-0-050719	0.00512	NA	**0.00543**	**11.4**	07/26/2005
E05-0210-86395	DLS-SW-TRM271-0-050719 Dup	0.00574	NA			07/26/2005
E05-0210-86396	DLS-SW-TRM271-0-050719 LS	0.0573	99.6			07/26/2005
E05-0210-86397	DLS-SW-TRM271-0-050719 HS	0.558	106			07/26/2005
E05-0210-86398	DLS-SW-TRM265-0-050719	0.00525	NA	**0.00534**	**3.19**	07/26/2005
E05-0210-86399	DLS-SW-TRM265-0-050719 Dup	0.00542	NA			07/26/2005
E05-0210-86400	DLS-SW-TRM265-0-050719 LS	0.0568	98.8			07/26/2005
E05-0210-86401	DLS-SW-TRM265-0-050719 HS	0.561	107			07/26/2005
E05-0210-86402	DLS-SW-TRM261-2-050720	< 0.00104	NA	**< 0.00104**	**[3]NA**	07/26/2005
E05-0210-86403	DLS-SW-TRM261-2-050720 Dup	< 0.00104	NA			07/26/2005
E05-0210-86404	DLS-SW-TRM261-2-050720 LS	0.0604	116			07/26/2005
E05-0210-86405	DLS-SW-TRM261-2-050720 HS	0.576	110			07/26/2005
E05-0210-86406	DLS-SW-TRM261-0-050720	0.00520	NA	**0.00501**	**7.79**	07/26/2005
E05-0210-86407	DLS-SW-TRM261-0-050720 Dup	0.00481	NA			07/26/2005
E05-0210-86408	DLS-SW-TRM261-0-050720 LS	0.0568	99.4			07/26/2005
E05-0210-86409	DLS-SW-TRM261-0-050720 HS	0.530	101			07/26/2005
E05-0210-86410	DLS-SW-TRM261-F-050720	0.00542	NA	**0.00514**	**10.9**	07/26/2005
E05-0210-86411	DLS-SW-TRM261-F-050720 Dup	0.00486	NA			07/26/2005
E05-0210-86412	DLS-SW-TRM261-F-050720 LS	0.0586	103			07/27/2005
E05-0210-86413	DLS-SW-TRM261-F-050720 HS	0.512	97.3			07/27/2005
E05-0210-86414	DLS-SW-TRM256-0-050720	0.00485	NA	**0.00478**	**3.14**	07/27/2005
E05-0210-86415	DLS-SW-TRM256-0-050720 Dup	0.00470	NA			07/27/2005
E05-0210-86416	DLS-SW-TRM256-0-050720 LS	0.0611	108			07/27/2005
E05-0210-86417	DLS-SW-TRM256-0-050720 HS	0.559	106			07/27/2005
E05-0210-86418	DLS-SW-TRM254-0-050720	0.00550	NA	**0.00516**	**13.4**	07/27/2005
E05-0210-86419	DLS-SW-TRM254-0-050720 Dup	0.00481	NA			07/27/2005
E05-0210-86420	DLS-SW-TRM254-0-050720 LS	0.0623	110			07/27/2005
E05-0210-86421	DLS-SW-TRM254-0-050720 HS	0.555	106			07/27/2005
E05-0210-86422	DLS-SW-TRM254-F-050720	0.00533	NA	**0.00529**	**1.51**	07/27/2005
E05-0210-86423	DLS-SW-TRM254-F-050720 Dup	0.00525	NA			07/27/2005
E05-0210-86424	DLS-SW-TRM254-F-050720 LS	0.0639	112			07/27/2005
E05-0210-86425	DLS-SW-TRM254-F-050720 HS	0.585	111			07/27/2005

Table 17. PFHS Sample Results Continued

3M Sample Number	*Sample Description*	*[1]PFHS Conc. (ng/mL)*	*[2]Field Matrix Spike % Recovery*	*Average Result Sample/Sample Duplicate*	*%RPD*	*Extraction Date*
E05-0210-86426	DLS-SW-TRM254-2-050720	< 0.00104	NA	**< 0.00104**	[3]NA	07/27/2005
E05-0210-86427	DLS-SW-TRM254-2-050720 Dup	< 0.00104	NA			07/27/2005
E05-0210-86428	DLS-SW-TRM254-2-050720 LS	0.0578	111			07/27/2005
E05-0210-86429	DLS-SW-TRM254-2-050720 HS	0.575	110			07/27/2005
E05-0210-86430	DXS-SW-T01001-0-050721	0.0121	NA	**0.0119**	**4.22**	07/27/2005
E05-0210-86431	DXS-SW-T01001-0-050721 Dup	0.0116	NA			07/27/2005
E05-0210-86432	DXS-SW-T01001-0-050721 LS	0.0691	110			07/27/2005
E05-0210-86433	DXS-SW-T01001-0-050721 HS	0.570	107			07/27/2005
E05-0210-86434	DXS-SW-T01002-0-050721	0.0101	NA	**0.00985**	**5.18**	07/27/2005
E05-0210-86435	DXS-SW-T01002-0-050721 Dup	0.00959	NA			07/27/2005
E05-0210-86436	DXS-SW-T01002-0-050721 LS	0.0637	103			07/27/2005
E05-0210-86437	DXS-SW-T01002-0-050721 HS	0.593	112			07/27/2005
E05-0210-86438	DXS-SW-T01003-0-050721	0.00827	NA	**0.00884**	**12.9**	07/27/2005
E05-0210-86439	DXS-SW-T01003-0-050721 Dup	0.00941	NA			07/27/2005
E05-0210-86440	DXS-SW-T01003-0-050721 LS	0.0625	103			07/27/2005
E05-0210-86441	DXS-SW-T01003-0-050721 HS	0.517	99.2			07/28/2005 centrifuged
E05-0210-86442	DXS-SW-T01004-0-050721	0.0097	NA	**0.00989**	**4.35**	07/27/2005
E05-0210-86443	DXS-SW-T01004-0-050721 Dup	0.0101	NA			07/27/2005
E05-0210-86444	DXS-SW-T01004-0-050721 LS	0.0692	114			07/27/2005
E05-0210-86445	DXS-SW-T01004-0-050721 HS	0.512	96.4			07/27/2005
E05-0210-86446	DXS-SW-T01005-0-050721	0.00633	NA	**0.00650**	**5.23**	07/27/2005
E05-0210-86447	DXS-SW-T01005-0-050721 Dup	0.00667	NA			07/27/2005
E05-0210-86448	DXS-SW-T01005-0-050721 LS	0.0951	170			07/27/2005
E05-0210-86449	DXS-SW-T01005-0-050721 HS	0.541	102			07/27/2005
E05-0210-86450	DXS-SW-T01006-0-050721	0.00346	NA	**0.00340**	**3.83**	07/27/2005
E05-0210-86451	DXS-SW-T01006-0-050721 Dup	0.00333	NA			07/27/2005
E05-0210-86452	DXS-SW-T01006-0-050721 LS	0.0731	134			07/27/2005
E05-0210-86453	DXS-SW-T01006-0-050721 HS	0.611	117			07/27/2005
E05-0210-86454	DXS-SW-T01007-0-050721	0.00419	NA	**0.00424**	**2.36**	07/27/2005
E05-0210-86455	DXS-SW-T01007-0-050721 Dup	0.00429	NA			07/27/2005
E05-0210-86456	DXS-SW-T01007-0-050721 LS	0.0628	112			07/27/2005
E05-0210-86457	DXS-SW-T01007-0-050721 HS	0.559	106			07/27/2005
E05-0210-86458	DXS-SW-T01008-0-050721	0.00316	NA	**0.00322**	**3.73**	07/27/2005
E05-0210-86459	DXS-SW-T01008-0-050721 Dup	0.00328	NA			07/27/2005
E05-0210-86460	DXS-SW-T01008-0-050721 LS	0.0686	125			07/27/2005
E05-0210-86461	DXS-SW-T01008-0-050721 HS	0.507	96.7			07/27/2005

Table 17. PFHS Sample Results Continued.

3M Sample Number	*Sample Description*	*[1]PFHS Conc. (ng/mL)*	*[2]Field Matrix Spike % Recovery*	*Average Result Sample/Sample Duplicate*	*%RPD*	*Extraction Date*
E05-0210-86462	DXS-SW-T01009-0-050721	0.00301	NA	**0.00316**	**9.19**	07/27/2005
E05-0210-86463	DXS-SW-T01009-0-050721 Dup	0.00330	NA			07/27/2005
E05-0210-86464	DXS-SW-T01009-0-050721 LS	0.0595	108			07/27/2005
E05-0210-86465	DXS-SW-T01009-0-050721 HS	0.601	115			07/27/2005
E05-0210-86466	DXS-SW-T01010-0-050721	0.00332	NA	**0.00305**	**18.1**	07/27/2005
E05-0210-86467	DXS-SW-T01010-0-050721 Dup	0.00277	NA			07/27/2005
E05-0210-86468	DXS-SW-T01010-0-050721 LS	0.0607	111			07/27/2005
E05-0210-86469	DXS-SW-T01010-0-050721 HS	0.561	107			07/27/2005
E05-0210-86470	DXS-SW-T02001-0-050721	0.0205	NA	**0.0196**	**9.18**	07/27/2005
E05-0210-86471	DXS-SW-T02001-0-050721 Dup	0.0187	NA			07/27/2005
E05-0210-86472	DXS-SW-T02001-0-050721 LS	0.0729	102			07/27/2005
E05-0210-86473	DXS-SW-T02001-0-050721 HS	0.560	104			07/27/2005
E05-0210-86474	DXS-SW-T02002-0-050721	0.0124	NA	**0.0125**	**1.60**	07/27/2005
E05-0210-86475	DXS-SW-T02002-0-050721 Dup	0.0126	NA			07/27/2005
E05-0210-86476	DXS-SW-T02002-0-050721 LS	0.0661	103			07/27/2005
E05-0210-86477	DXS-SW-T02002-0-050721 HS	0.552	104			07/27/2005
E05-0210-86478	DXS-SW-T02003-0-050721	< 0.00104	NA	**< 0.00104**	**[3]NA**	07/27/2005
E05-0210-86479	DXS-SW-T02003-0-050721 Dup	< 0.00104	NA			07/27/2005
E05-0210-86480	DXS-SW-T02003-0-050721 LS	0.0553	106			07/27/2005
E05-0210-86481	DXS-SW-T02003-0-050721 HS	0.528	101			07/27/2005
E05-0210-86482	DXS-SW-T02004-0-050721	< 0.00104	NA	**< 0.00104**	**[3]NA**	07/27/2005
E05-0210-86483	DXS-SW-T02004-0-050721 Dup	< 0.00104	NA			07/27/2005
E05-0210-86484	DXS-SW-T02004-0-050721 LS	0.0619	117			07/27/2005
E05-0210-86485	DXS-SW-T02004-0-050721 HS	0.534	102			07/27/2005
E05-0210-86486	DXS-SW-T02005-0-050721	< 0.0026	NA	**< 0.0026**	**[3]NA**	07/27/2005
E05-0210-86487	DXS-SW-T02005-0-050721 Dup	< 0.0026	NA			07/28/2005 centrifuged
E05-0210-86488	DXS-SW-T02005-0-050721 LS	0.0544	104			07/27/2005
E05-0210-86489	DXS-SW-T02005-0-050721 HS	0.675	119			07/28/2005 centrifuged
E05-0210-86490	DXS-SW-T02006-0-050721	< 0.0026	NA	**< 0.0026**	**[3]NA**	07/27/2005
E05-0210-86491	DXS-SW-T02006-0-050721 Dup	< 0.0026	NA			07/27/2005
E05-0210-86492	DXS-SW-T02006-0-050721 LS	0.0595	114			07/27/2005
E05-0210-86493	DXS-SW-T02006-0-050721 HS	0.617	118			07/27/2005
E05-0210-86494	DXS-SW-T02007-0-050721	< 0.0026	NA	**< 0.0026**	**[3]NA**	07/27/2005
E05-0210-86495	DXS-SW-T02007-0-050721 Dup	< 0.0026	NA			07/27/2005
E05-0210-86496	DXS-SW-T02007-0-050721 LS	0.0529	102			07/27/2005
E05-0210-86497	DXS-SW-T02007-0-050721 HS	0.526	101			07/27/2005

Table 17. PFHS Sample Results Continued.

3M Sample Number	*Sample Description*	*[1]PFHS Conc. (ng/mL)*	*[2]Field Matrix Spike % Recovery*	*Average Result Sample/Sample Duplicate*	*%RPD*	*Extraction Date*
E05-0210-86498	DXS-SW-T02008-0-050721	< 0.0026	NA	**< 0.0026**	[3]NA	07/27/2005
E05-0210-86499	DXS-SW-T02008-0-050721 Dup	< 0.0026	NA			07/27/2005
E05-0210-86500	DXS-SW-T02008-0-050721 LS	0.0578	111			07/27/2005
E05-0210-86501	DXS-SW-T02008-0-050721 HS	0.528	101			07/27/2005
E05-0210-86502	DXS-SW-T02009-0-050721	< 0.0026	NA	**< 0.0026**	[3]NA	07/27/2005
E05-0210-86503	DXS-SW-T02009-0-050721 Dup	< 0.0026	NA			07/27/2005
E05-0210-86504	DXS-SW-T02009-0-050721 LS	0.0608	117			07/27/2005
E05-0210-86505	DXS-SW-T02009-0-050721 HS	0.570	109			07/27/2005
E05-0210-86506	DXS-SW-T02010-0-050721	0.00363	NA	**0.00353**	**5.96**	07/27/2005
E05-0210-86507	DXS-SW-T02010-0-050721 Dup	0.00342	NA			07/27/2005
E05-0210-86508	DXS-SW-T02010-0-050721 LS	0.0554	99.6			07/27/2005
E05-0210-86509	DXS-SW-T02010-0-050721 HS	0.357	67.8			07/27/2005
E05-0210-86510	DXS-SW-T03001-0-050721	0.176	NA	**0.181**	**4.99**	07/27/2005
E05-0210-86511	DXS-SW-T03001-0-050721 Dup	0.185	NA			07/27/2005
E05-0210-86512	DXS-SW-T03001-0-050721 LS	0.250	133			07/27/2005
E05-0210-86513	DXS-SW-T03001-0-050721 HS	0.742	108			07/27/2005
E05-0210-86514	DXS-SW-T03002-0-050721	< 0.0026	NA	**< 0.0026**	[3]NA	07/27/2005
E05-0210-86515	DXS-SW-T03002-0-050721 Dup	< 0.0026	NA			07/27/2005
E05-0210-86516	DXS-SW-T03002-0-050721 LS	0.0568	109			07/27/2005
E05-0210-86517	DXS-SW-T03002-0-050721 HS	0.549	105			07/27/2005
E05-0210-86518	DXS-SW-T03003-0-050721	< 0.0026	NA	**< 0.0026**	[3]NA	07/27/2005
E05-0210-86519	DXS-SW-T03003-0-050721 Dup	< 0.0026	NA			07/27/2005
E05-0210-86520	DXS-SW-T03003-0-050721 LS	0.0581	112			07/27/2005
E05-0210-86521	DXS-SW-T03003-0-050721 HS	0.558	107			07/27/2005
E05-0210-86522	DXS-SW-T03004-0-050722	0.00756	NA	[4]**0.00756**	**NA**	07/27/2005
E05-0210-86523	DXS-SW-T03004-0-050722 Dup	< 0.0026	NA			07/27/2005
E05-0210-86524	DXS-SW-T03004-0-050722 LS	0.0597	100			07/27/2005
E05-0210-86525	DXS-SW-T03004-0-050722 HS	0.570	108			07/27/2005
E05-0210-86526	DXS-SW-T03005-0-050722	< 0.0026	NA	[4]**0.00331**	**NA**	07/27/2005
E05-0210-86527	DXS-SW-T03005-0-050722 Dup	0.00331	NA			07/28/2005 centrifuged
E05-0210-86528	DXS-SW-T03005-0-050722 LS	0.0649	118			07/27/2005
E05-0210-86529	DXS-SW-T03005-0-050722 HS	0.589	112			07/27/2005
E05-0210-86530	DXS-SW-T03006-0-050722	< 0.0026	NA	**< 0.0026**	[3]NA	07/27/2005
E05-0210-86531	DXS-SW-T03006-0-050722 Dup	< 0.0026	NA			07/27/2005
E05-0210-86532	DXS-SW-T03006-0-050722 LS	0.0285	54.7			07/28/2005 centrifuged
E05-0210-86533	DXS-SW-T03006-0-050722 HS	0.643	123			07/27/2005

Table 17. PFHS Sample Results Continued.

3M Sample Number	*Sample Description*	*[1]PFHS Conc. (ng/mL)*	*[2]Field Matrix Spike % Recovery*	*Average Result Sample/Sample Duplicate*	*%RPD*	*Extraction Date*
E05-0210-86534	DXS-SW-T03007-0-050722	< 0.0026	NA			07/27/2005
E05-0210-86535	DXS-SW-T03007-0-050722 Dup	0.00366	NA	**[4]0.00366**	**NA**	07/28/2005 centrifuged
E05-0210-86536	DXS-SW-T03007-0-050722 LS	0.0640	123			07/27/2005
E05-0210-86537	DXS-SW-T03007-0-050722 HS	0.579	111			07/27/2005
E05-0210-86538	DXS-SW-T03008-0-050722	< 0.0026	NA			07/27/2005
E05-0210-86539	DXS-SW-T03008-0-050722 Dup	< 0.0026	NA	**< 0.0026**	**[3]NA**	07/27/2005
E05-0210-86540	DXS-SW-T03008-0-050722 LS	0.0551	106			07/27/2005
E05-0210-86541	DXS-SW-T03008-0-050722 HS	0.567	109			07/27/2005
E05-0210-86542	DXS-SW-T03009-0-050722	< 0.0026	NA			07/27/2005
E05-0210-86543	DXS-SW-T03009-0-050722 Dup	< 0.0026	NA	**< 0.0026**	**[3]NA**	07/27/2005
E05-0210-86544	DXS-SW-T03009-0-050722 LS	0.0568	109			07/27/2005
E05-0210-86545	DXS-SW-T03009-0-050722 HS	0.530	102			07/27/2005
E05-0210-86546	DXS-SW-T03010-0-050722	< 0.0026	NA			07/27/2005
E05-0210-86547	DXS-SW-T03010-0-050722 Dup	< 0.0026	NA	**< 0.0026**	**[3]NA**	07/27/2005
E05-0210-86548	DXS-SW-T03010-0-050722 LS	0.0547	105			07/27/2005
E05-0210-86549	DXS-SW-T03010-0-050722 HS	0.533	102			07/27/2005
E05-0210-86550	DLS-SW-TRIP01	< 0.0026	NA			07/27/2005
E05-0210-86551	DLS-SW-TRIP01 LS	0.0534	102	**< 0.0026**	**NA**	07/27/2005
E05-0210-86552	DLS-SW-TRIP01 HS	0.508	97.5			07/27/2005
E05-0210-86553	DXS-SW-TRIP02	< 0.0026	NA			07/27/2005
E05-0210-86554	DXS-SW-TRIP02 LS	0.0530	102	**< 0.0026**	**NA**	07/27/2005
E05-0210-86555	DXS-SW-TRIP02 HS	0.506	97.1			07/27/2005
E05-0210-86556	DXS-SW-TRIP03	< 0.0026	NA			07/27/2005
E05-0210-86557	DXS-SW-TRIP03 LS	0.0528	101	**< 0.0026**	**NA**	07/27/2005
E05-0210-86558	DXS-SW-TRIP03 HS	0.531	102			07/27/2005

(1) The analytical uncertainty of the PFHS resuts is 100±15.2% based on method accuracy and precision. All results and calculations in this table are presented with three significant figures. Sample concentrations, averages, and %RPD values may vary slightly from the raw data.

(2) Low field matrix spike concentration = 0.0521 ng/mL. High field matrix spike concentration = 0.521 ng/mL.

(3) NA: Not applicable. %RPD value was not determined when concentrations for the both the sample and sample duplicate were below the stated LOQ.

(4) The average value listed is the concentration for the sample or sample duplicate that produced a value above the LOQ. A true average and %RPD between the sample and sample duplicate was not determined.

(5) Sample descriptions were misidentified when checked into LIMS. Samples with LIMS ID numbers 86370 and 86371 were in bottles labeled low spike and high spike, respectively. Bottles with LIMS ID numbers 86372 and 86372 were surrogate spiked only (sample and sample duplicate bottles).

Table 18. PFOS Sample Results.

3M Sample Number	*Sample Description*	*[1]PFOS Conc. (ng/mL)*	*[2]Field Matrix Spike % Recovery*	*Average Result Sample/Sample Duplicate*	*%RPD*	*Extraction Date*
E05-0210-86358	DLS-SW-TRM307-0-050718	0.00670	NA	[3]0.00670	NA	07/26/2005
E05-0210-86359	DLS-SW-TRM307-0-050718 Dup	< 0.00496	NA			07/26/2005
E05-0210-86360	DLS-SW-TRM307-0-050718 LS	0.05960	107			07/26/2005
E05-0210-86361	DLS-SW-TRM307-0-050718 HS	0.564	112			07/26/2005
E05-0210-86362	DLS-SW-TRM301-0-050718	< 0.00496	NA	< 0.00496	[4]NA	07/26/2005
E05-0210-86363	DLS-SW-TRM301-0-050718 Dup	< 0.00496	NA			07/26/2005
E05-0210-86364	DLS-SW-TRM301-0-050718 LS	0.0574	116			07/26/2005
E05-0210-86365	DLS-SW-TRM301-0-050718 HS	0.607	122			07/26/2005
E05-0210-86366	DLS-SW-TRM301-F-050718	< 0.00496	NA	< 0.00496	[4]NA	07/26/2005
E05-0210-86367	DLS-SW-TRM301-F-050718 Dup	< 0.00496	NA			07/26/2005
E05-0210-86368	DLS-SW-TRM301-F-050718 LS	0.0604	122			07/26/2005
E05-0210-86369	DLS-SW-TRM301-F-050718 HS	0.558	112			07/26/2005
E05-0210-86370	DLS-SW-TRM295-0-050719[5]	0.12900	111	0.0742	1.48	07/26/2005
E05-0210-86371	DLS-SW-TRM295-0-050719 Dup[5]	0.59000	104			07/26/2005
E05-0210-86372	DLS-SW-TRM295-0-050719 LS[5]	0.0736	NA			07/26/2005
E05-0210-86373	DLS-SW-TRM295-0-050719 HS[5]	0.0747	NA			07/26/2005
E05-0210-86374	DLS-SW-TRM289-0-050719	0.07630	NA	0.0743	5.52	07/26/2005
E05-0210-86375	DLS-SW-TRM289-0-050719 Dup	0.07220	NA			07/26/2005
E05-0210-86376	DLS-SW-TRM289-0-050719 LS	0.1340	121			07/26/2005
E05-0210-86377	DLS-SW-TRM289-0-050719 HS	0.544	94.7			07/26/2005
E05-0210-86378	DLS-SW-TRM289-F-050719	0.0588	NA	0.0525	24.0	07/26/2005
E05-0210-86379	DLS-SW-TRM289-F-050719 Dup	0.0462	NA			07/26/2005
E05-0210-86380	DLS-SW-TRM289-F-050719 LS	0.120	136			07/26/2005
E05-0210-86381	DLS-SW-TRM289-F-050719 HS	0.631	117			07/26/2005
E05-0210-86382	DLS-SW-TRM283-0-050719	0.0528	NA	0.0616	28.4	07/26/2005
E05-0210-86383	DLS-SW-TRM283-0-050719 Dup	0.0703	NA			07/26/2005
E05-0210-86384	DLS-SW-TRM283-0-050719 LS	0.0973	72.2			07/26/2005
E05-0210-86385	DLS-SW-TRM283-0-050719 HS	0.605	110			07/26/2005
E05-0210-86386	DLS-SW-TRM277-0-050719	0.0336	NA	0.0433	44.8	07/26/2005
E05-0210-86387	DLS-SW-TRM277-0-050719 Dup	0.0530	NA			07/26/2005
E05-0210-86388	DLS-SW-TRM277-0-050719 LS	0.0881	90.5			07/26/2005
E05-0210-86389	DLS-SW-TRM277-0-050719 HS	0.575	107			07/26/2005
E05-0210-86390	DLS-SW-TRM277-F-050719	0.0304	NA	0.0347	24.8	07/26/2005
E05-0210-86391	DLS-SW-TRM277-F-050719 Dup	0.0390	NA			07/26/2005
E05-0210-86392	DLS-SW-TRM277-F-050719 LS	0.0861	104			07/26/2005
E05-0210-86393	DLS-SW-TRM277-F-050719 HS	0.515	96.8			07/26/2005

Table 18. PFOS Sample Results Continued.

3M Sample Number	*Sample Description*	*(1)PFOS Conc. (ng/mL)*	*(2)Field Matrix Spike % Recovery*	*Average Result Sample/Sample Duplicate*	*%RPD*	*Extraction Date*
E05-0210-86394	DLS-SW-TRM271-0-050719	0.0320	NA	**0.0326**	**3.68**	07/26/2005
E05-0210-86395	DLS-SW-TRM271-0-050719 Dup	0.0332	NA			07/26/2005
E05-0210-86396	DLS-SW-TRM271-0-050719 LS	0.0837	103			07/26/2005
E05-0210-86397	DLS-SW-TRM271-0-050719 HS	0.563	107			07/26/2005
E05-0210-86398	DLS-SW-TRM265-0-050719	0.0377	NA	**0.0376**	**0.532**	07/26/2005
E05-0210-86399	DLS-SW-TRM265-0-050719 Dup	0.0375	NA			07/26/2005
E05-0210-86400	DLS-SW-TRM265-0-050719 LS	0.0820	89.7			07/26/2005
E05-0210-86401	DLS-SW-TRM265-0-050719 HS	0.596	112			07/26/2005
E05-0210-86402	DLS-SW-TRM261-2-050720	< 0.00496	NA	**< 0.00496**	**(4)NA**	07/26/2005
E05-0210-86403	DLS-SW-TRM261-2-050720 Dup	< 0.00496	NA			07/26/2005
E05-0210-86404	DLS-SW-TRM261-2-050720 LS	0.0593	120			07/26/2005
E05-0210-86405	DLS-SW-TRM261-2-050720 HS	0.571	115			07/26/2005
E05-0210-86406	DLS-SW-TRM261-0-050720	0.0324	NA	**0.0327**	**1.83**	07/26/2005
E05-0210-86407	DLS-SW-TRM261-0-050720 Dup	0.0330	NA			07/26/2005
E05-0210-86408	DLS-SW-TRM261-0-050720 LS	0.0839	103			07/26/2005
E05-0210-86409	DLS-SW-TRM261-0-050720 HS	0.562	107			07/26/2005
E05-0210-86410	DLS-SW-TRM261-F-050720	0.0333	NA	**0.0283**	**35.8**	07/26/2005
E05-0210-86411	DLS-SW-TRM261-F-050720 Dup	0.0232	NA			07/26/2005
E05-0210-86412	DLS-SW-TRM261-F-050720 LS	0.0783	101			07/27/2005
E05-0210-86413	DLS-SW-TRM261-F-050720 HS	0.525	100			07/27/2005
E05-0210-86414	DLS-SW-TRM256-0-050720	0.0326	NA	**0.0334**	**4.79**	07/27/2005
E05-0210-86415	DLS-SW-TRM256-0-050720 Dup	0.0342	NA			07/27/2005
E05-0210-86416	DLS-SW-TRM256-0-050720 LS	0.0856	105			07/27/2005
E05-0210-86417	DLS-SW-TRM256-0-050720 HS	0.558	106			07/27/2005
E05-0210-86418	DLS-SW-TRM254-0-050720	0.0352	NA	**0.0347**	**3.17**	07/27/2005
E05-0210-86419	DLS-SW-TRM254-0-050720 Dup	0.0341	NA			07/27/2005
E05-0210-86420	DLS-SW-TRM254-0-050720 LS	0.0927	117			07/27/2005
E05-0210-86421	DLS-SW-TRM254-0-050720 HS	0.594	113			07/27/2005
E05-0210-86422	DLS-SW-TRM254-F-050720	0.0300	NA	**0.0321**	**13.1**	07/27/2005
E05-0210-86423	DLS-SW-TRM254-F-050720 Dup	0.0342	NA			07/27/2005
E05-0210-86424	DLS-SW-TRM254-F-050720 LS	0.0903	118			07/27/2005
E05-0210-86425	DLS-SW-TRM254-F-050720 HS	0.626	120			07/27/2005
E05-0210-86426	DLS-SW-TRM254-2-050720	< 0.00992	NA	**< 0.00992**	**(4)NA**	07/27/2005
E05-0210-86427	DLS-SW-TRM254-2-050720 Dup	< 0.00992	NA			07/27/2005
E05-0210-86428	DLS-SW-TRM254-2-050720 LS	0.0577	116			07/27/2005
E05-0210-86429	DLS-SW-TRM254-2-050720 HS	0.525	106			07/27/2005

Table 18. PFOS Sample Results Continued.

3M Sample Number	*Sample Description*	*(1)PFOS Conc. (ng/mL)*	*(2)Field Matrix Spike % Recovery*	*Average Result Sample/Sample Duplicate*	*%RPD*	*Extraction Date*
E05-0210-86430	DXS-SW-T01001-0-050721	0.0739	NA	**0.0710**	**8.32**	07/27/2005
E05-0210-86431	DXS-SW-T01001-0-050721 Dup	0.0680	NA			07/27/2005
E05-0210-86432	DXS-SW-T01001-0-050721 LS	0.1230	105			07/27/2005
E05-0210-86433	DXS-SW-T01001-0-050721 HS	0.602	107			07/27/2005
E05-0210-86434	DXS-SW-T01002-0-050721	0.0607	NA	**0.0601**	**2.16**	07/27/2005
E05-0210-86435	DXS-SW-T01002-0-050721 Dup	0.0594	NA			07/27/2005
E05-0210-86436	DXS-SW-T01002-0-050721 LS	0.1050	90.8			07/27/2005
E05-0210-86437	DXS-SW-T01002-0-050721 HS	0.635	116			07/27/2005
E05-0210-86438	DXS-SW-T01003-0-050721	0.0542	NA	**0.0549**	**2.37**	07/27/2005
E05-0210-86439	DXS-SW-T01003-0-050721 Dup	0.0555	NA			07/27/2005
E05-0210-86440	DXS-SW-T01003-0-050721 LS	0.107	105			07/27/2005
E05-0210-86441	DXS-SW-T01003-0-050721 HS	0.580	117			07/28/2005 centrifuged
E05-0210-86442	DXS-SW-T01004-0-050721	0.0560	NA	**0.0598**	**12.7**	07/27/2005
E05-0210-86443	DXS-SW-T01004-0-050721 Dup	0.0636	NA			07/27/2005
E05-0210-86444	DXS-SW-T01004-0-050721 LS	0.114	109			07/27/2005
E05-0210-86445	DXS-SW-T01004-0-050721 HS	0.521	93.0			07/27/2005
E05-0210-86446	DXS-SW-T01005-0-050721	0.0383	NA	**0.0387**	**1.81**	07/27/2005
E05-0210-86447	DXS-SW-T01005-0-050721 Dup	0.0390	NA			07/27/2005
E05-0210-86448	DXS-SW-T01005-0-050721 LS	0.133	191			07/27/2005
E05-0210-86449	DXS-SW-T01005-0-050721 HS	0.605	114			07/27/2005
E05-0210-86450	DXS-SW-T01006-0-050721	0.0209	NA	**0.0214**	**4.67**	07/27/2005
E05-0210-86451	DXS-SW-T01006-0-050721 Dup	0.0219	NA			07/27/2005
E05-0210-86452	DXS-SW-T01006-0-050721 LS	0.0903	139			07/27/2005
E05-0210-86453	DXS-SW-T01006-0-050721 HS	0.650	127			07/27/2005
E05-0210-86454	DXS-SW-T01007-0-050721	0.0273	NA	**0.0271**	**1.85**	07/27/2005
E05-0210-86455	DXS-SW-T01007-0-050721 Dup	0.0268	NA			07/27/2005
E05-0210-86456	DXS-SW-T01007-0-050721 LS	0.0865	120			07/27/2005
E05-0210-86457	DXS-SW-T01007-0-050721 HS	0.586	113			07/27/2005
E05-0210-86458	DXS-SW-T01008-0-050721	0.0219	NA	**0.0218**	**0.917**	07/27/2005
E05-0210-86459	DXS-SW-T01008-0-050721 Dup	0.0217	NA			07/27/2005
E05-0210-86460	DXS-SW-T01008-0-050721 LS	0.0892	136			07/27/2005
E05-0210-86461	DXS-SW-T01008-0-050721 HS	0.523	101			07/27/2005
E05-0210-86462	DXS-SW-T01009-0-050721	0.0202	NA	**0.0203**	**0.494**	07/27/2005
E05-0210-86463	DXS-SW-T01009-0-050721 Dup	0.0203	NA			07/27/2005
E05-0210-86464	DXS-SW-T01009-0-050721 LS	0.0770	115			07/27/2005
E05-0210-86465	DXS-SW-T01009-0-050721 HS	0.631	123			07/27/2005

Table 18. PFOS Sample Results Continued.

3M Sample Number	*Sample Description*	*[1]PFOS Conc. (ng/mL)*	*[2]Field Matrix Spike % Recovery*	*Average Result Sample/Sample Duplicate*	*%RPD*	*Extraction Date*
E05-0210-86466	DXS-SW-T01010-0-050721	0.0216	NA	**0.0218**	**1.38**	07/27/2005
E05-0210-86467	DXS-SW-T01010-0-050721 Dup	0.0219	NA			07/27/2005
E05-0210-86468	DXS-SW-T01010-0-050721 LS	0.0772	112			07/27/2005
E05-0210-86469	DXS-SW-T01010-0-050721 HS	0.553	107			07/27/2005
E05-0210-86470	DXS-SW-T02001-0-050721	0.129	NA	**0.123**	**9.76**	07/27/2005
E05-0210-86471	DXS-SW-T02001-0-050721 Dup	0.117	NA			07/27/2005
E05-0210-86472	DXS-SW-T02001-0-050721 LS	0.170	94.9			07/27/2005
E05-0210-86473	DXS-SW-T02001-0-050721 HS	0.640	104			07/27/2005
E05-0210-86474	DXS-SW-T02002-0-050721	0.0707	NA	**0.0735**	**7.49**	07/27/2005
E05-0210-86475	DXS-SW-T02002-0-050721 Dup	0.0762	NA			07/27/2005
E05-0210-86476	DXS-SW-T02002-0-050721 LS	0.1260	106			07/27/2005
E05-0210-86477	DXS-SW-T02002-0-050721 HS	0.606	107			07/27/2005
E05-0210-86478	DXS-SW-T02003-0-050721	< 0.00992	NA	**< 0.00992**	**[4]NA**	07/27/2005
E05-0210-86479	DXS-SW-T02003-0-050721 Dup	< 0.00992	NA			07/27/2005
E05-0210-86480	DXS-SW-T02003-0-050721 LS	0.0548	111			07/27/2005
E05-0210-86481	DXS-SW-T02003-0-050721 HS	0.511	103			07/27/2005
E05-0210-86482	DXS-SW-T02004-0-050721	< 0.00992	NA	**< 0.00992**	**NA**	07/27/2005
E05-0210-86483	DXS-SW-T02004-0-050721 Dup	< 0.00992	NA			07/27/2005
E05-0210-86484	DXS-SW-T02004-0-050721 LS	0.0659	119			07/27/2005
E05-0210-86485	DXS-SW-T02004-0-050721 HS	0.523	104			07/27/2005
E05-0210-86486	DXS-SW-T02005-0-050721	< 0.00744	NA	**< 0.0496**	**[4]NA**	07/27/2005
E05-0210-86487	DXS-SW-T02005-0-050721 Dup	< 0.0496	NA			07/28/2005 centrifuged
E05-0210-86488	DXS-SW-T02005-0-050721 LS	0.0560	113			07/27/2005
E05-0210-86489	DXS-SW-T02005-0-050721 HS	0.684	138			07/28/2005 centrifuged
E05-0210-86490	DXS-SW-T02006-0-050721	< 0.00744	NA	**[3][6]0.00799**	**NA**	07/27/2005
E05-0210-86491	DXS-SW-T02006-0-050721 Dup	0.00799	NA			07/27/2005
E05-0210-86492	DXS-SW-T02006-0-050721 LS	0.0728	131			07/27/2005
E05-0210-86493	DXS-SW-T02006-0-050721 HS	0.667	133			07/27/2005
E05-0210-86494	DXS-SW-T02007-0-050721	< 0.00744	NA	**< 0.00744**	**[4]NA**	07/27/2005
E05-0210-86495	DXS-SW-T02007-0-050721 Dup	< 0.00744	NA			07/27/2005
E05-0210-86496	DXS-SW-T02007-0-050721 LS	0.0513	104			07/27/2005
E05-0210-86497	DXS-SW-T02007-0-050721 HS	0.479	96.6			07/27/2005
E05-0210-86498	DXS-SW-T02008-0-050721	< 0.00744	NA	**< 0.00744**	**[4]NA**	07/27/2005
E05-0210-86499	DXS-SW-T02008-0-050721 Dup	< 0.00744	NA			07/27/2005
E05-0210-86500	DXS-SW-T02008-0-050721 LS	0.0579	117			07/27/2005
E05-0210-86501	DXS-SW-T02008-0-050721 HS	0.493	99.4			07/27/2005

Table 18. PFOS Sample Results Continued.

3M Sample Number	*Sample Description*	*[1]PFOS Conc. (ng/mL)*	*[2]Field Matrix Spike % Recovery*	*Average Result Sample/Sample Duplicate*	*%RPD*	*Extraction Date*
E05-0210-86502	DXS-SW-T02009-0-050721	0.00872	NA	**0.00878**	**1.25**	07/27/2005
E05-0210-86503	DXS-SW-T02009-0-050721 Dup	0.00883	NA			07/27/2005
E05-0210-86504	DXS-SW-T02009-0-050721 LS	0.0725	129			07/27/2005
E05-0210-86505	DXS-SW-T02009-0-050721 HS	0.524	104			07/27/2005
E05-0210-86506	DXS-SW-T02010-0-050721	0.0426	NA	**[6]0.0356**	**39.7**	07/27/2005
E05-0210-86507	DXS-SW-T02010-0-050721 Dup	0.0285	NA			07/27/2005
E05-0210-86508	DXS-SW-T02010-0-050721 LS	0.0590	47.4			07/27/2005
E05-0210-86509	DXS-SW-T02010-0-050721 HS	0.293	51.9			07/27/2005
E05-0210-86510	DXS-SW-T03001-0-050721	0.782	NA	**0.795**	**3.15**	07/27/2005
E05-0210-86511	DXS-SW-T03001-0-050721 Dup	0.807	NA			07/27/2005
E05-0210-86512	DXS-SW-T03001-0-050721 LS	0.909	[7]NR			07/27/2005
E05-0210-86513	DXS-SW-T03001-0-050721 HS	1.330	108			07/27/2005
E05-0210-86514	DXS-SW-T03002-0-050721	0.0235	NA	**0.0202**	**32.7**	07/27/2005
E05-0210-86515	DXS-SW-T03002-0-050721 Dup	0.0169	NA			07/27/2005
E05-0210-86516	DXS-SW-T03002-0-050721 LS	0.0711	103			07/27/2005
E05-0210-86517	DXS-SW-T03002-0-050721 HS	0.543	105			07/27/2005
E05-0210-86518	DXS-SW-T03003-0-050721	0.0111	NA	**0.0115**	**6.11**	07/27/2005
E05-0210-86519	DXS-SW-T03003-0-050721 Dup	0.0118	NA			07/27/2005
E05-0210-86520	DXS-SW-T03003-0-050721 LS	0.0715	121			07/27/2005
E05-0210-86521	DXS-SW-T03003-0-050721 HS	0.549	108			07/27/2005
E05-0210-86522	DXS-SW-T03004-0-050722	0.0226	NA	**0.0197**	**30.0**	07/27/2005
E05-0210-86523	DXS-SW-T03004-0-050722 Dup	0.0167	NA			07/27/2005
E05-0210-86524	DXS-SW-T03004-0-050722 LS	0.0696	101			07/27/2005
E05-0210-86525	DXS-SW-T03004-0-050722 HS	0.561	109			07/27/2005
E05-0210-86526	DXS-SW-T03005-0-050722	< 0.00744	NA	**[3]0.0773**	**NA**	07/27/2005
E05-0210-86527	DXS-SW-T03005-0-050722 Dup	0.0773	NA			07/28/2005 centrifuged
E05-0210-86528	DXS-SW-T03005-0-050722 LS	0.0762	[8]NR			07/27/2005
E05-0210-86529	DXS-SW-T03005-0-050722 HS	0.594	104			07/27/2005
E05-0210-86530	DXS-SW-T03006-0-050722	0.00763	NA	**[3]0.00763**	**NA**	07/27/2005
E05-0210-86531	DXS-SW-T03006-0-050722 Dup	< 0.00744	NA			07/27/2005
E05-0210-86532	DXS-SW-T03006-0-050722 LS	< 0.0496	[9]NR			07/28/2005 centrifuged
E05-0210-86533	DXS-SW-T03006-0-050722 HS	0.665	132			07/27/2005
E05-0210-86534	DXS-SW-T03007-0-050722	< 0.00744	NA	**< 0.0496**	**[4]NA**	07/27/2005
E05-0210-86535	DXS-SW-T03007-0-050722 Dup	< 0.0496	NA			07/28/2005 centrifuged
E05-0210-86536	DXS-SW-T03007-0-050722 LS	0.0664	134			07/27/2005
E05-0210-86537	DXS-SW-T03007-0-050722 HS	0.576	116			07/27/2005

Table 18. PFOS Sample Results Continued.

3M Sample Number	*Sample Description*	*(1)PFOS Conc. (ng/mL)*	*(2)Field Matrix Spike % Recovery*	*Average Result Sample/Sample Duplicate*	*%RPD*	*Extraction Date*
E05-0210-86538	DXS-SW-T03008-0-050722	< 0.00744	NA	**< 0.00744**	**NA**	07/27/2005
E05-0210-86539	DXS-SW-T03008-0-050722 Dup	< 0.00744	NA			07/27/2005
E05-0210-86540	DXS-SW-T03008-0-050722 LS	0.0600	121			07/27/2005
E05-0210-86541	DXS-SW-T03008-0-050722 HS	0.561	113			07/27/2005
E05-0210-86542	DXS-SW-T03009-0-050722	0.00809	NA	**(3)0.00809**	**NA**	07/27/2005
E05-0210-86543	DXS-SW-T03009-0-050722 Dup	< 0.00744	NA			07/27/2005
E05-0210-86544	DXS-SW-T03009-0-050722 LS	0.0608	106			07/27/2005
E05-0210-86545	DXS-SW-T03009-0-050722 HS	0.508	101			07/27/2005
E05-0210-86546	DXS-SW-T03010-0-050722	0.00749	NA	**(3)0.00749**	**NA**	07/27/2005
E05-0210-86547	DXS-SW-T03010-0-050722 Dup	< 0.00744	NA			07/27/2005
E05-0210-86548	DXS-SW-T03010-0-050722 LS	0.0556	97.2			07/27/2005
E05-0210-86549	DXS-SW-T03010-0-050722 HS	0.506	100			07/27/2005
E05-0210-86550	DLS-SW-TRIP01	< 0.00744	NA	**< 0.00744**	**NA**	07/27/2005
E05-0210-86551	DLS-SW-TRIP01 LS	0.0551	111			07/27/2005
E05-0210-86552	DLS-SW-TRIP01 HS	0.457	92.1			07/27/2005
E05-0210-86553	DXS-SW-TRIP02	< 0.00744	NA	**< 0.00744**	**NA**	07/27/2005
E05-0210-86554	DXS-SW-TRIP02 LS	0.0516	104			07/27/2005
E05-0210-86555	DXS-SW-TRIP02 HS	0.491	99.0			07/27/2005
E05-0210-86556	DXS-SW-TRIP03	< 0.00744	NA	**< 0.00744**	**NA**	07/27/2005
E05-0210-86557	DXS-SW-TRIP03 LS	0.0552	112			07/27/2005
E05-0210-86558	DXS-SW-TRIP03 HS	0.537	108			07/27/2005

(1) The analytical uncertainty of the PFOS results is 100±13.8 % based on method accuracy and precision. All results and calculations in this table are presented with three significant figures. Sample concentrations, averages, and %RPD values may vary slightly from the raw data.

(2) Low field matrix spike concentration = 0.0496 ng/mL. High field matrix spike concentration = 0.496 ng/mL.

(3) The average value listed is the concentration for the sample or sample duplicate that produced a value above the LOQ. A true average and %RPD between the sample and sample duplicate was not determined.

(4) NA: Not applicable. %RPD value was not determined when concentrations for the both the sample and sample duplicate were below the stated LOQ.

(5) Sample descriptions were misidentified when checked into LIMS. Samples with LIMS ID numbers 86370 and 86371 were in bottles labeled low spike and high spike, respectively. Bottles with LIMS ID numbers 86372 and 86372 were surrogate spiked only (sample and sample duplicate bottles).

(6) Both field matrix spikes associated with this sampling location exceeded method acceptance criteria of 100±30%. Analytical accuracy for this location should be considered 100±50% due matrix contributions.

(7) NR: Not reported. Spike recovery not calculated as the endogenous sample concentration was at least three times the spiked amount.

(8) NR: Not reported. Concentration of spiked sample roughly equivalent to sample replicate producing a concentration above the stated LOQ. Reported sample concentration should be considered accurate to within 100±50% based on high field matrix spike recovery only (poor precision between sample/sample duplicate).

(9) NR: Not reported. PFOS not quantitated above the stated LOQ for the low matrix spike. Reported sample concentration should be considered accurate to within 100±50% based on high field matrix spike recovery only.

Table 19. PFOA[1,2 ^{13}C] Surrogate Results.

3M Sample Number	*Sample Description*	*(1)PFOA [1,2 ^{13}C] Concentration (ng/mL)*	*(2)Non-Corrected Surrogate Percent Recovery*	*(3)Corrected Surrogate Percent Recovery*	*Extraction Date*
E05-0210-86358	DLS-SW-TRM307-0-050718	0.177	64.6	115	07/26/2005
E05-0210-86359	DLS-SW-TRM307-0-050718 Dup	0.162	59.1	105	07/26/2005
E05-0210-86360	DLS-SW-TRM307-0-050718 LS	0.160	63.0	112	07/26/2005
E05-0210-86361	DLS-SW-TRM307-0-050718 HS	0.154	60.6	108	07/26/2005
E05-0210-86362	DLS-SW-TRM301-0-050718	0.155	56.6	101	07/26/2005
E05-0210-86363	DLS-SW-TRM301-0-050718 Dup	0.155	56.6	101	07/26/2005
E05-0210-86364	DLS-SW-TRM301-0-050718 LS	0.146	57.5	102	07/26/2005
E05-0210-86365	DLS-SW-TRM301-0-050718 HS	0.148	58.3	104	07/26/2005
E05-0210-86366	DLS-SW-TRM301-F-050718	0.160	58.4	104	07/26/2005
E05-0210-86367	DLS-SW-TRM301-F-050718 Dup	0.172	62.8	112	07/26/2005
E05-0210-86368	DLS-SW-TRM301-F-050718 LS	0.153	60.2	107	07/26/2005
E05-0210-86369	DLS-SW-TRM301-F-050718 HS	0.146	57.5	102	07/26/2005
E05-0210-86370	DLS-SW-TRM295-0-050719	0.158	62.2	111	07/26/2005
E05-0210-86371	DLS-SW-TRM295-0-050719 Dup	0.137	53.9	96.1	07/26/2005
E05-0210-86372	DLS-SW-TRM295-0-050719 LS	0.152	55.5	98.9	07/26/2005
E05-0210-86373	DLS-SW-TRM295-0-050719 HS	0.158	57.7	103	07/26/2005
E05-0210-86374	DLS-SW-TRM289-0-050719	0.156	56.9	101	07/26/2005
E05-0210-86375	DLS-SW-TRM289-0-050719 Dup	0.154	56.2	100	07/26/2005
E05-0210-86376	DLS-SW-TRM289-0-050719 LS	0.142	55.9	99.6	07/26/2005
E05-0210-86377	DLS-SW-TRM289-0-050719 HS	0.131	51.6	91.9	07/26/2005
E05-0210-86378	DLS-SW-TRM289-F-050719	0.150	54.7	97.6	07/26/2005
E05-0210-86379	DLS-SW-TRM289-F-050719 Dup	0.165	60.2	107	07/26/2005
E05-0210-86380	DLS-SW-TRM289-F-050719 LS	0.154	60.6	108	07/26/2005
E05-0210-86381	DLS-SW-TRM289-F-050719 HS	0.145	57.1	102	07/26/2005
E05-0210-86382	DLS-SW-TRM283-0-050719	0.164	59.8	107	07/26/2005
E05-0210-86383	DLS-SW-TRM283-0-050719 Dup	0.154	56.2	100	07/26/2005
E05-0210-86384	DLS-SW-TRM283-0-050719 LS	0.149	58.7	104	07/26/2005
E05-0210-86385	DLS-SW-TRM283-0-050719 HS	0.146	57.5	102	07/26/2005
E05-0210-86386	DLS-SW-TRM277-0-050719	0.160	58.4	104	07/26/2005
E05-0210-86387	DLS-SW-TRM277-0-050719 Dup	0.153	55.8	99.5	07/26/2005
E05-0210-86388	DLS-SW-TRM277-0-050719 LS	0.159	62.6	112	07/26/2005
E05-0210-86389	DLS-SW-TRM277-0-050719 HS	0.133	52.4	93.3	07/26/2005
E05-0210-86390	DLS-SW-TRM277-F-050719	0.161	58.8	105	07/26/2005
E05-0210-86391	DLS-SW-TRM277-F-050719 Dup	0.169	61.7	110	07/26/2005
E05-0210-86392	DLS-SW-TRM277-F-050719 LS	0.157	61.8	110	07/26/2005
E05-0210-86393	DLS-SW-TRM277-F-050719 HS	0.122	48.0	85.6	07/26/2005
E05-0210-86394	DLS-SW-TRM271-0-050719	0.153	55.8	99.5	07/26/2005
E05-0210-86395	DLS-SW-TRM271-0-050719 Dup	0.158	57.7	103	07/26/2005
E05-0210-86396	DLS-SW-TRM271-0-050719 LS	0.135	53.1	94.7	07/26/2005
E05-0210-86397	DLS-SW-TRM271-0-050719 HS	0.136	53.5	95.4	07/26/2005

Table 19. PFOA[1,2 ^{13}C] Surrogate Results Continued.

3M Sample Number	*Sample Description*	*(1)PFOA [1,2 ^{13}C] Concentration (ng/mL)*	*(2)Non-Corrected Surrogate Percent Recovery*	*(3)Corrected Surrogate Percent Recovery*	*Extraction Date*
E05-0210-86398	DLS-SW-TRM265-0-050719	0.148	54.0	96.3	07/26/2005
E05-0210-86399	DLS-SW-TRM265-0-050719 Dup	0.157	57.3	102	07/26/2005
E05-0210-86400	DLS-SW-TRM265-0-050719 LS	0.133	52.4	93.3	07/26/2005
E05-0210-86401	DLS-SW-TRM265-0-050719 HS	0.138	54.3	96.8	07/26/2005
E05-0210-86402	DLS-SW-TRM261-2-050720	0.158	57.7	103	07/26/2005
E05-0210-86403	DLS-SW-TRM261-2-050720 Dup	0.159	58.0	103	07/26/2005
E05-0210-86404	DLS-SW-TRM261-2-050720 LS	0.150	59.0	105	07/26/2005
E05-0210-86405	DLS-SW-TRM261-2-050720 HS	0.129	50.8	90.5	07/26/2005
E05-0210-86406	DLS-SW-TRM261-0-050720	0.147	53.6	95.6	07/26/2005
E05-0210-86407	DLS-SW-TRM261-0-050720 Dup	0.156	56.9	101	07/26/2005
E05-0210-86408	DLS-SW-TRM261-0-050720 LS	0.141	55.5	99.0	07/26/2005
E05-0210-86409	DLS-SW-TRM261-0-050720 HS	0.134	52.8	94.0	07/26/2005
E05-0210-86410	DLS-SW-TRM261-F-050720	0.154	56.2	100	07/26/2005
E05-0210-86411	DLS-SW-TRM261-F-050720 Dup	0.141	51.4	91.7	07/26/2005
E05-0210-86412	DLS-SW-TRM261-F-050720 LS	0.140	55.1	98.2	07/27/2005
E05-0210-86413	DLS-SW-TRM261-F-050720 HS	0.123	48.4	86.3	07/27/2005
E05-0210-86414	DLS-SW-TRM256-0-050720	0.143	52.2	93.0	07/27/2005
E05-0210-86415	DLS-SW-TRM256-0-050720 Dup	0.148	54.0	96.3	07/27/2005
E05-0210-86416	DLS-SW-TRM256-0-050720 LS	0.145	57.1	102	07/27/2005
E05-0210-86417	DLS-SW-TRM256-0-050720 HS	0.133	52.4	93.3	07/27/2005
E05-0210-86418	DLS-SW-TRM254-0-050720	0.158	57.7	103	07/27/2005
E05-0210-86419	DLS-SW-TRM254-0-050720 Dup	0.154	56.2	100	07/27/2005
E05-0210-86420	DLS-SW-TRM254-0-050720 LS	0.158	62.2	111	07/27/2005
E05-0210-86421	DLS-SW-TRM254-0-050720 HS	0.132	52.0	92.6	07/27/2005
E05-0210-86422	DLS-SW-TRM254-F-050720	0.160	58.4	104	07/27/2005
E05-0210-86423	DLS-SW-TRM254-F-050720 Dup	0.164	59.8	107	07/27/2005
E05-0210-86424	DLS-SW-TRM254-F-050720 LS	0.159	62.6	112	07/27/2005
E05-0210-86425	DLS-SW-TRM254-F-050720 HS	0.147	57.9	103	07/27/2005
E05-0210-86426	DLS-SW-TRM254-2-050720	0.162	59.1	105	07/27/2005
E05-0210-86427	DLS-SW-TRM254-2-050720 Dup	0.157	57.3	102	07/27/2005
E05-0210-86428	DLS-SW-TRM254-2-050720 LS	0.145	57.1	102	07/27/2005
E05-0210-86429	DLS-SW-TRM254-2-050720 HS	0.138	54.3	96.8	07/27/2005
E05-0210-86430	DXS-SW-T01001-0-050721	0.172	62.8	112	07/27/2005
E05-0210-86431	DXS-SW-T01001-0-050721 Dup	0.164	59.8	107	07/27/2005
E05-0210-86432	DXS-SW-T01001-0-050721 LS	0.159	62.6	112	07/27/2005
E05-0210-86433	DXS-SW-T01001-0-050721 HS	0.142	55.9	99.6	07/27/2005
E05-0210-86434	DXS-SW-T01002-0-050721	0.167	60.9	109	07/27/2005
E05-0210-86435	DXS-SW-T01002-0-050721 Dup	0.164	59.8	107	07/27/2005
E05-0210-86436	DXS-SW-T01002-0-050721 LS	0.139	54.7	97.6	07/27/2005
E05-0210-86437	DXS-SW-T01002-0-050721 HS	0.146	57.5	102	07/27/2005

Table 19. PFOA[1,2 ^{13}C] Surrogate Results Continued.

3M Sample Number	*Sample Description*	*(1)PFOA [1,2 ^{13}C] Concentration (ng/mL)*	*(2)Non-Corrected Surrogate Percent Recovery*	*(3)Corrected Surrogate Percent Recovery*	*Extraction Date*
E05-0210-86438	DXS-SW-T01003-0-050721	0.158	57.7	103	07/27/2005
E05-0210-86439	DXS-SW-T01003-0-050721 Dup	0.161	58.8	105	07/27/2005
E05-0210-86440	DXS-SW-T01003-0-050721 LS	0.142	55.9	99.6	07/27/2005
E05-0210-86441	DXS-SW-T01003-0-050721 HS	0.135	53.1	94.7	07/28/2005 centrifuged
E05-0210-86442	DXS-SW-T01004-0-050721	0.175	63.9	114	07/27/2005
E05-0210-86443	DXS-SW-T01004-0-050721 Dup	0.160	58.4	104	07/27/2005
E05-0210-86444	DXS-SW-T01004-0-050721 LS	0.162	63.8	114	07/27/2005
E05-0210-86445	DXS-SW-T01004-0-050721 HS	0.126	49.6	88.4	07/27/2005
E05-0210-86446	DXS-SW-T01005-0-050721	0.167	60.9	109	07/27/2005
E05-0210-86447	DXS-SW-T01005-0-050721 Dup	0.171	62.4	111	07/27/2005
E05-0210-86448	DXS-SW-T01005-0-050721 LS	0.151	59.4	106	07/27/2005
E05-0210-86449	DXS-SW-T01005-0-050721 HS	0.137	53.9	96.1	07/27/2005
E05-0210-86450	DXS-SW-T01006-0-050721	0.157	57.3	102	07/27/2005
E05-0210-86451	DXS-SW-T01006-0-050721 Dup	0.162	59.1	105	07/27/2005
E05-0210-86452	DXS-SW-T01006-0-050721 LS	0.178	70.1	125	07/27/2005
E05-0210-86453	DXS-SW-T01006-0-050721 HS	0.151	59.4	106	07/27/2005
E05-0210-86454	DXS-SW-T01007-0-050721	0.148	54.0	96.3	07/27/2005
E05-0210-86455	DXS-SW-T01007-0-050721 Dup	0.159	58.0	103	07/27/2005
E05-0210-86456	DXS-SW-T01007-0-050721 LS	0.152	59.8	107	07/27/2005
E05-0210-86457	DXS-SW-T01007-0-050721 HS	0.144	56.7	101	07/27/2005
E05-0210-86458	DXS-SW-T01008-0-050721	0.149	54.4	96.9	07/27/2005
E05-0210-86459	DXS-SW-T01008-0-050721 Dup	0.149	54.4	96.9	07/27/2005
E05-0210-86460	DXS-SW-T01008-0-050721 LS	0.180	70.9	126	07/27/2005
E05-0210-86461	DXS-SW-T01008-0-050721 HS	0.123	48.4	86.3	07/27/2005
E05-0210-86462	DXS-SW-T01009-0-050721	0.163	59.5	106	07/27/2005
E05-0210-86463	DXS-SW-T01009-0-050721 Dup	0.163	59.5	106	07/27/2005
E05-0210-86464	DXS-SW-T01009-0-050721 LS	0.144	56.7	101	07/27/2005
E05-0210-86465	DXS-SW-T01009-0-050721 HS	0.141	55.5	99.0	07/27/2005
E05-0210-86466	DXS-SW-T01010-0-050721	0.168	61.3	109	07/27/2005
E05-0210-86467	DXS-SW-T01010-0-050721 Dup	0.170	62.0	110	07/27/2005
E05-0210-86468	DXS-SW-T01010-0-050721 LS	0.145	57.1	102	07/27/2005
E05-0210-86469	DXS-SW-T01010-0-050721 HS	0.134	52.8	94.0	07/27/2005
E05-0210-86470	DXS-SW-T02001-0-050721	0.152	55.5	98.9	07/27/2005
E05-0210-86471	DXS-SW-T02001-0-050721 Dup	0.165	60.2	107	07/27/2005
E05-0210-86472	DXS-SW-T02001-0-050721 LS	0.141	55.5	99.0	07/27/2005
E05-0210-86473	DXS-SW-T02001-0-050721 HS	0.131	51.6	91.9	07/27/2005
E05-0210-86474	DXS-SW-T02002-0-050721	0.148	54.0	96.3	07/27/2005
E05-0210-86475	DXS-SW-T02002-0-050721 Dup	0.145	52.9	94.3	07/27/2005
E05-0210-86476	DXS-SW-T02002-0-050721 LS	0.138	54.3	96.8	07/27/2005
E05-0210-86477	DXS-SW-T02002-0-050721 HS	0.137	53.9	96.1	07/27/2005

Table 19. PFOA[1,2 ^{13}C] Surrogate Results Continued.

3M Sample Number	*Sample Description*	*(1)PFOA [1,2 ^{13}C] Concentration (ng/mL)*	*(2)Non-Corrected Surrogate Percent Recovery*	*(3)Corrected Surrogate Percent Recovery*	*Extraction Date*
E05-0210-86478	DXS-SW-T02003-0-050721	0.149	54.4	96.9	07/27/2005
E05-0210-86479	DXS-SW-T02003-0-050721 Dup	0.165	60.2	107	07/27/2005
E05-0210-86480	DXS-SW-T02003-0-050721 LS	0.136	53.5	95.4	07/27/2005
E05-0210-86481	DXS-SW-T02003-0-050721 HS	0.133	52.4	93.3	07/27/2005
E05-0210-86482	DXS-SW-T02004-0-050721	0.172	62.8	112	07/27/2005
E05-0210-86483	DXS-SW-T02004-0-050721 Dup	0.154	56.2	100	07/27/2005
E05-0210-86484	DXS-SW-T02004-0-050721 LS	0.161	58.8	105	07/27/2005
E05-0210-86485	DXS-SW-T02004-0-050721 HS	0.131	47.8	85.2	07/27/2005
E05-0210-86486	DXS-SW-T02005-0-050721	0.178	70.1	125	07/27/2005
E05-0210-86487	DXS-SW-T02005-0-050721 Dup	0.170	62.0	110	07/28/2005 centrifuged
E05-0210-86488	DXS-SW-T02005-0-050721 LS	0.139	54.7	97.6	07/27/2005
E05-0210-86489	DXS-SW-T02005-0-050721 HS	0.177	69.7	124	07/28/2005 centrifuged
E05-0210-86490	DXS-SW-T02006-0-050721	0.151	55.1	98.2	07/27/2005
E05-0210-86491	DXS-SW-T02006-0-050721 Dup	0.156	56.9	101	07/27/2005
E05-0210-86492	DXS-SW-T02006-0-050721 LS	0.151	59.4	106	07/27/2005
E05-0210-86493	DXS-SW-T02006-0-050721 HS	0.143	56.3	100	07/27/2005
E05-0210-86494	DXS-SW-T02007-0-050721	0.142	51.8	92.4	07/27/2005
E05-0210-86495	DXS-SW-T02007-0-050721 Dup	0.154	56.2	100	07/27/2005
E05-0210-86496	DXS-SW-T02007-0-050721 LS	0.139	54.7	97.6	07/27/2005
E05-0210-86497	DXS-SW-T02007-0-050721 HS	0.146	57.5	102	07/27/2005
E05-0210-86498	DXS-SW-T02008-0-050721	0.151	55.1	98.2	07/27/2005
E05-0210-86499	DXS-SW-T02008-0-050721 Dup	0.161	58.8	105	07/27/2005
E05-0210-86500	DXS-SW-T02008-0-050721 LS	0.147	57.9	103	07/27/2005
E05-0210-86501	DXS-SW-T02008-0-050721 HS	0.128	50.4	89.8	07/27/2005
E05-0210-86502	DXS-SW-T02009-0-050721	0.159	58.0	103	07/27/2005
E05-0210-86503	DXS-SW-T02009-0-050721 Dup	0.151	55.1	98.2	07/27/2005
E05-0210-86504	DXS-SW-T02009-0-050721 LS	0.153	60.2	107	07/27/2005
E05-0210-86505	DXS-SW-T02009-0-050721 HS	0.138	54.3	96.8	07/27/2005
E05-0210-86506	DXS-SW-T02010-0-050721	0.143	52.2	93.0	07/27/2005
E05-0210-86507	DXS-SW-T02010-0-050721 Dup	0.143	52.2	93.0	07/27/2005
E05-0210-86508	DXS-SW-T02010-0-050721 LS	0.131	51.6	91.9	07/27/2005
E05-0210-86509	DXS-SW-T02010-0-050721 HS	0.086	33.8	60.2	07/27/2005
E05-0210-86510	DXS-SW-T03001-0-050721	0.144	52.6	93.7	07/27/2005
E05-0210-86511	DXS-SW-T03001-0-050721 Dup	0.146	53.3	95.0	07/27/2005
E05-0210-86512	DXS-SW-T03001-0-050721 LS	0.141	55.5	99.0	07/27/2005
E05-0210-86513	DXS-SW-T03001-0-050721 HS	0.127	50.0	89.1	07/27/2005
E05-0210-86514	DXS-SW-T03002-0-050721	0.165	60.2	107	07/27/2005
E05-0210-86515	DXS-SW-T03002-0-050721 Dup	0.142	51.8	92.4	07/27/2005
E05-0210-86516	DXS-SW-T03002-0-050721 LS	0.142	55.9	99.6	07/27/2005
E05-0210-86517	DXS-SW-T03002-0-050721 HS	0.126	49.6	88.4	07/27/2005

Table 19. PFOA[1,2 ^{13}C] Surrogate Results Continued.

3M Sample Number	*Sample Description*	*(1)PFOA [1,2 ^{13}C] Concentration (ng/mL)*	*(2)Non-Corrected Surrogate Percent Recovery*	*(3)Corrected Surrogate Percent Recovery*	*Extraction Date*
E05-0210-86518	DXS-SW-T03003-0-050721	0.153	55.8	99.5	07/27/2005
E05-0210-86519	DXS-SW-T03003-0-050721 Dup	0.136	49.6	88.5	07/27/2005
E05-0210-86520	DXS-SW-T03003-0-050721 LS	0.142	55.9	99.6	07/27/2005
E05-0210-86521	DXS-SW-T03003-0-050721 HS	0.124	48.8	87.0	07/27/2005
E05-0210-86522	DXS-SW-T03004-0-050722	0.154	56.2	100	07/27/2005
E05-0210-86523	DXS-SW-T03004-0-050722 Dup	0.142	51.8	92.4	07/27/2005
E05-0210-86524	DXS-SW-T03004-0-050722 LS	0.146	57.5	102	07/27/2005
E05-0210-86525	DXS-SW-T03004-0-050722 HS	0.135	53.1	94.7	07/27/2005
E05-0210-86526	DXS-SW-T03005-0-050722	0.139	50.7	90.4	07/27/2005
E05-0210-86527	DXS-SW-T03005-0-050722 Dup	0.048	17.7	31.5	07/28/2005 centrifuged
E05-0210-86528	DXS-SW-T03005-0-050722 LS	0.165	65.0	116	07/27/2005
E05-0210-86529	DXS-SW-T03005-0-050722 HS	0.138	54.3	96.8	07/27/2005
E05-0210-86530	DXS-SW-T03006-0-050722	0.151	55.1	98.2	07/27/2005
E05-0210-86531	DXS-SW-T03006-0-050722 Dup	0.138	50.4	89.8	07/27/2005
E05-0210-86532	DXS-SW-T03006-0-050722 LS	0.012	4.61	8.21	07/28/2005 centrifuged
E05-0210-86533	DXS-SW-T03006-0-050722 HS	0.155	61.0	109	07/27/2005
E05-0210-86534	DXS-SW-T03007-0-050722	0.164	59.8	107	07/27/2005
E05-0210-86535	DXS-SW-T03007-0-050722 Dup	0.179	65.3	116	07/28/2005 centrifuged
E05-0210-86536	DXS-SW-T03007-0-050722 LS	0.155	61.0	109	07/27/2005
E05-0210-86537	DXS-SW-T03007-0-050722 HS	0.127	50.0	89.1	07/27/2005
E05-0210-86538	DXS-SW-T03008-0-050722	0.162	59.1	105	07/27/2005
E05-0210-86539	DXS-SW-T03008-0-050722 Dup	0.158	57.7	103	07/27/2005
E05-0210-86540	DXS-SW-T03008-0-050722 LS	0.141	55.5	99.0	07/27/2005
E05-0210-86541	DXS-SW-T03008-0-050722 HS	0.132	52.0	92.6	07/27/2005
E05-0210-86542	DXS-SW-T03009-0-050722	0.161	58.8	105	07/27/2005
E05-0210-86543	DXS-SW-T03009-0-050722 Dup	0.144	52.6	93.7	07/27/2005
E05-0210-86544	DXS-SW-T03009-0-050722 LS	0.147	57.9	103	07/27/2005
E05-0210-86545	DXS-SW-T03009-0-050722 HS	0.132	52.0	92.6	07/27/2005
E05-0210-86546	DXS-SW-T03010-0-050722	0.148	54.0	96.3	07/27/2005
E05-0210-86547	DXS-SW-T03010-0-050722 Dup	0.140	51.1	91.1	07/27/2005
E05-0210-86548	DXS-SW-T03010-0-050722 LS	0.145	57.1	102	07/27/2005
E05-0210-86549	DXS-SW-T03010-0-050722 HS	0.127	50.0	89.1	07/27/2005

Table 19. PFOA[1,2 ^{13}C] Surrogate Results Continued.

3M Sample Number	*Sample Description*	*(1)PFOA [1,2 ^{13}C] Concentration (ng/mL)*	*(2)Non-Corrected Surrogate Percent Recovery*	*(3)Corrected Surrogate Percent Recovery*	*Extraction Date*
E05-0210-86550	DLS-SW-TRIP01	0.139	50.7	90.4	07/27/2005
E05-0210-86551	DLS-SW-TRIP01 LS	0.138	50.4	89.8	07/27/2005
E05-0210-86552	DLS-SW-TRIP01 HS	0.117	46.1	82.1	07/27/2005
E05-0210-86553	DXS-SW-TRIP02	0.137	50.0	89.1	07/27/2005
E05-0210-86554	DXS-SW-TRIP02 LS	0.130	51.2	91.2	07/27/2005
E05-0210-86555	DXS-SW-TRIP02 HS	0.112	44.1	78.6	07/27/2005
E05-0210-86556	DXS-SW-TRIP03	0.144	52.6	93.7	07/27/2005
E05-0210-86557	DXS-SW-TRIP03 LS	0.128	50.4	89.8	07/27/2005
E05-0210-86558	DXS-SW-TRIP03 HS	0.129	50.8	90.5	07/27/2005

(1) All results and calculations in this table are presented with three significant figures. Sample concentrations, values may vary slightly from the raw data.

(2) Surrogate concentration in sample/sample duplicates = 0.274 ng/mL. Surrogate concentration in low and high field matrix spikes = 0.254 ng/mL.

(3) A correction factor of 56.1% was applied to all surrogate recoveries. The overall average raw surrogate recovery was used to determine the correction factor.

$$\text{Corrected Surrogate Percent Recovery} = \frac{\text{Non-Corrected Surrogate Percent Recovery}}{56.1}$$

STATISTICAL METHODS AND CALCULATIONS

Statistical methods used to interpret sample results include averages and standard deviations. The Analyst software program calculated sample concentrations using resultant analyte peak areas and the established quadratic, 1/x weighted, calibration curve. None of the samples analyzed for this interim report required dilution. Sample calculations and equations used to report method accuracy and precision are described below.

Accuracy and Precision Equations

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

$$\text{Sample Spike Recovery} = \frac{(\text{Spiked Sample Concentration} - \text{Average Concentration : Field Sample \& Field Sample Dup.})}{\text{Spike Concentraton}} * 100\%$$

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

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

Determination of Analytical Uncertainty

Both the accuracy (percent recovery) and precision (%RSD) of the lab control spikes are used to estimate the analytical uncertainty for a given analyte. For example, the overall accuracy and precision for PFBS based on LCS results was 107%±3.49% (three significant figures). The measured precision (%RSD) is then used to determine the range of the accuracy.

Example:

106.8*(0.0349) = 3.73

106.8 + 3.73 = 110.6; 107 – 3.73 = 103

Thus, LCS accuracy results range from 103% to 110.6%. The absolute difference of the low and high ends of this range, when compared 100%, are then calculated.

110.6%-100%= 10.6%

103%-100 = 3%.

The most conservative (largest) absolute difference is then used as the analytical uncertainty for the given analyte. Therefore, the analytical uncertainty for PFBS is given as 100±10.6% for this set of data. For PFHS, the overall project accuracy and precision of the the LCS results was 110%±4.72%. This produced an estimated analytical uncertainty of 100±15.2%. For PFOS, the overall project accuracy and precision was 108%%±5.79% resulting in an estimated analytical accuracy of 100±13.8%.

STATEMENT OF CONCLUSION

Sample results for PFBS, PFHS, and PFOS were presented in Table 1. Laboratory control spikes were used to determine the method accuracy and precision for each analyte. The accuracy and precision were then used to estimate the analytical uncertainty. Recoveries of field matrix spiked samples within 100±30% demonstrated that the overall analytical method was appropriate for the matrix collected. Analytical accuracy for select PFOS results was adjusted to 100±50% for samples whose associated field matrix spikes produced recoveries exceeding 100±30%.

LIST OF ATTACHMENTS

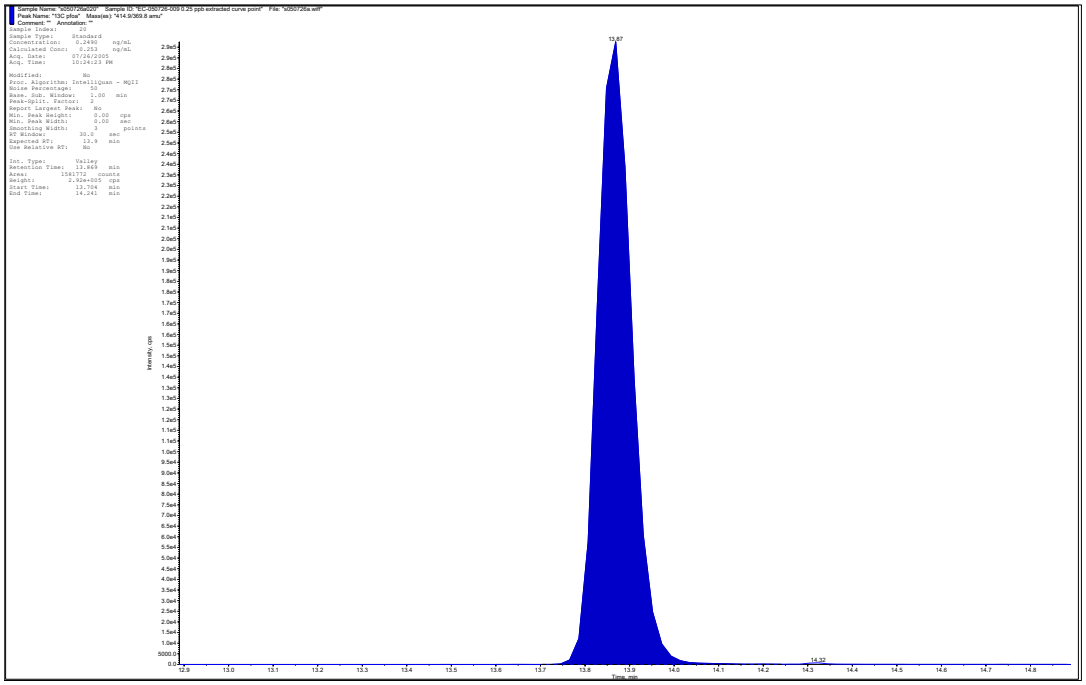
- **Attachment A: Sample Chromatograms and Calibration Curves**
- **Attachment B: Extraction and Analytical Methods**
- **Attachment C: Protocol and Protocol Amendments**

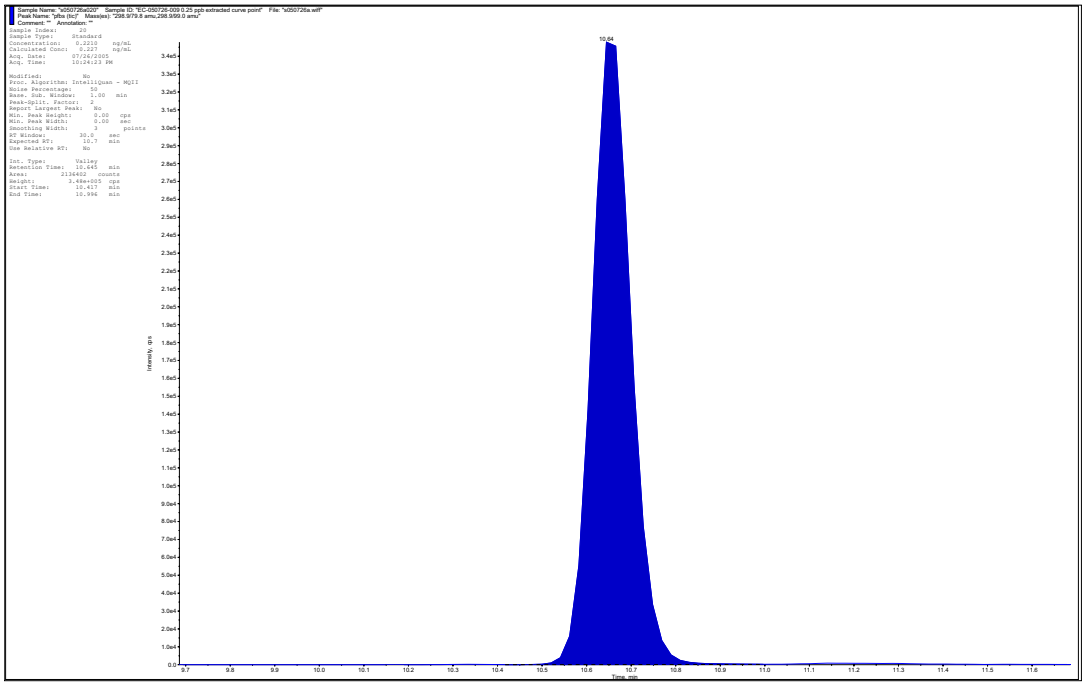
SIGNATURE PAGE

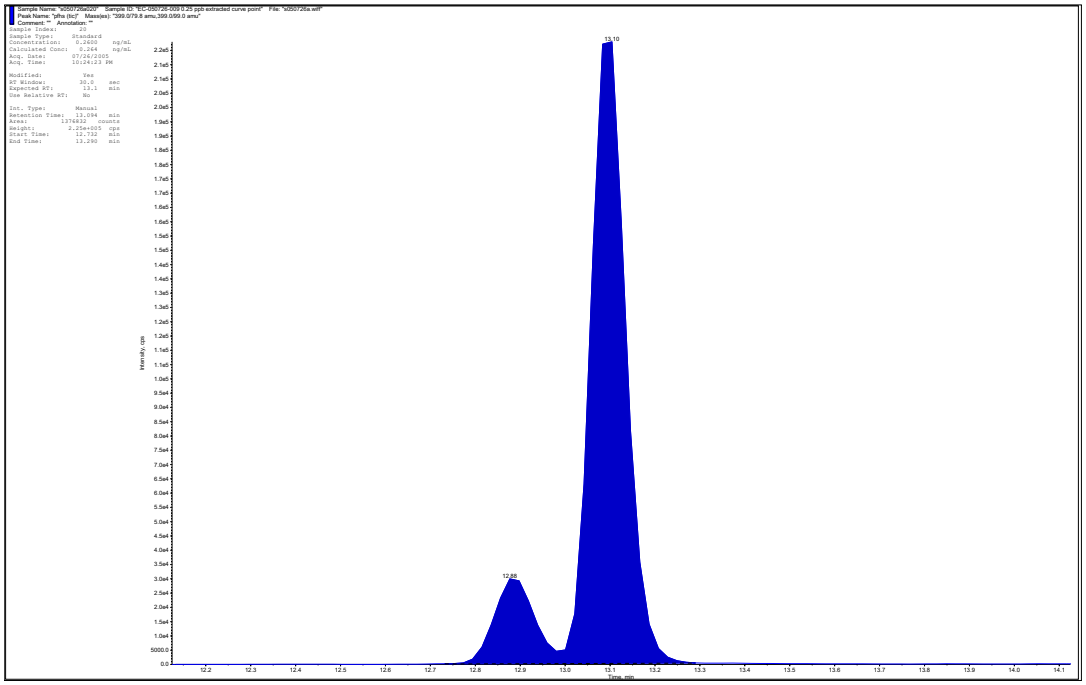
We certify that this report is a true and complete representation of the data for this study:

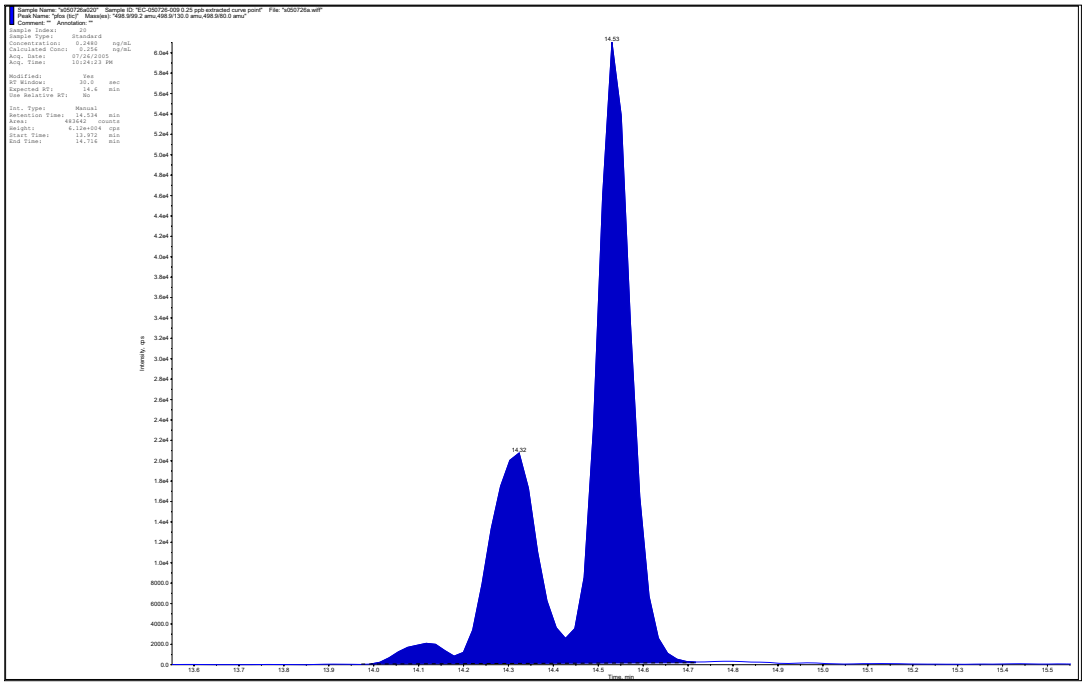
Jaisimha Kesari, P.E., DEE ,	Study Director	3/21/06 Date
Michelle D. Malinsky, Ph.D.,	3M Senior Chemist	3/17/06 Date
William K. Reagen, Ph.D.,	Testing Facility Management	03/20/06 Date
Michael A. Santoro,	Sponsor Representative	03/23/06 Date

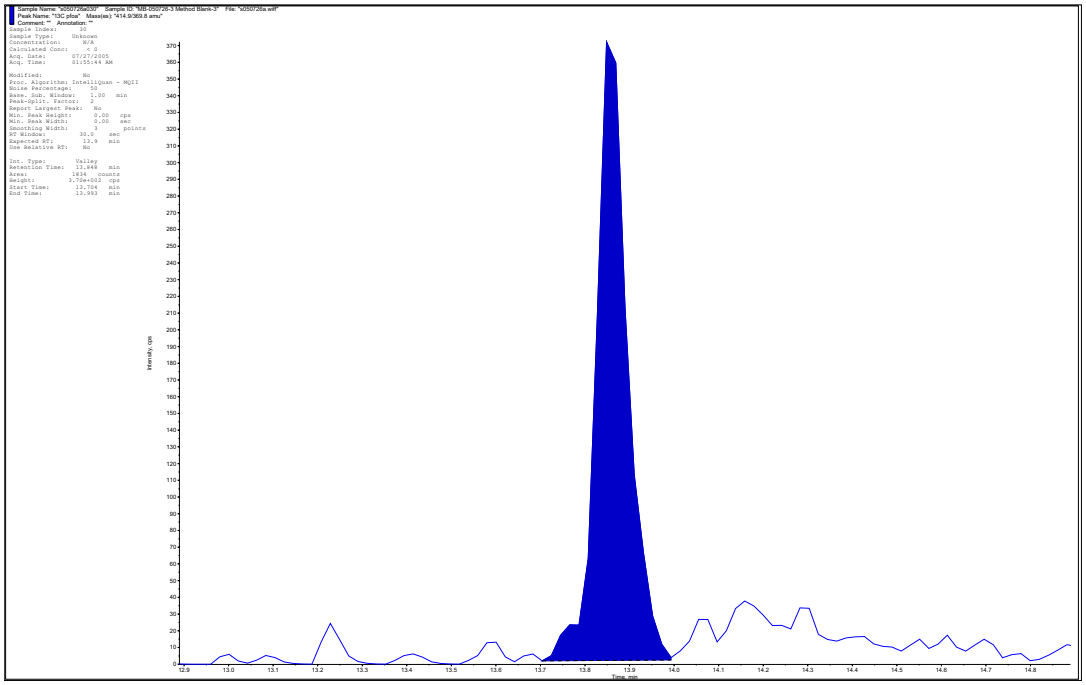
ATTACHMENT A: SAMPLE CHROMATOGRAMS AND CALIBRATION CURVES

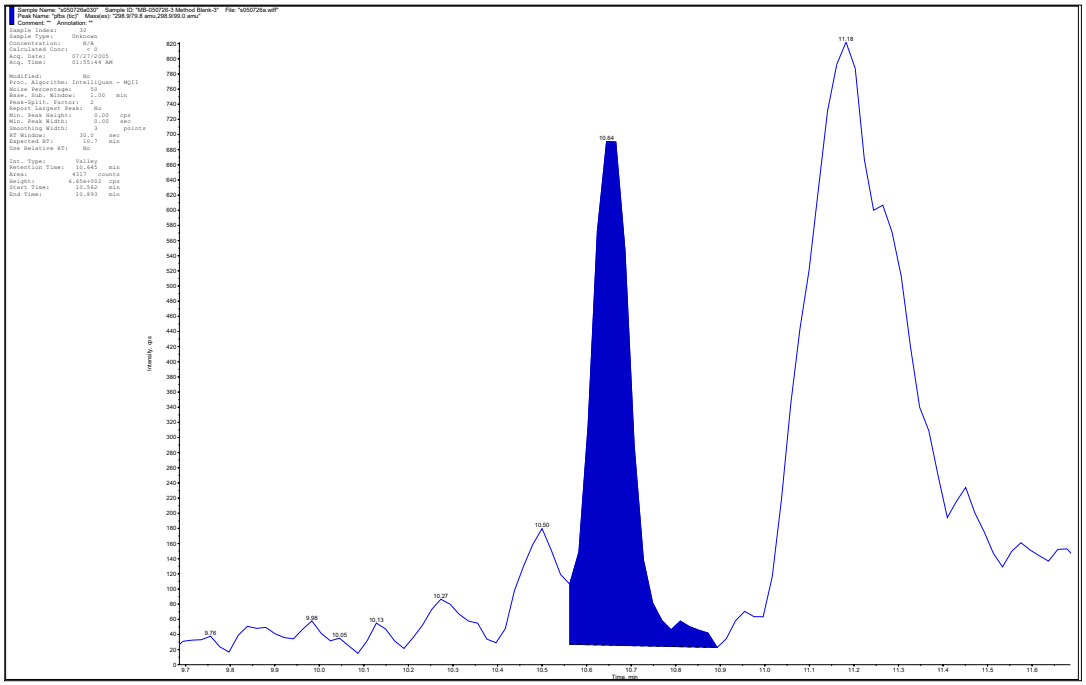

Sample Name: "w050726a020" Sample ID: "EC-050726-039 0.25 ppb extracted curve point" File: "w050726a.wiff"
Peak Name: "13C pfoa" Mass(es): "414.9/369.8 amu"
Comment: "" Annotation: ""
sample Index: 20
Sample Type: Standard
Concentration: 0.2490 ng/mL
Calculated Conc: 0.253 ng/mL
Acq. Date: 07/26/2005
Acq. Time: 10:24:23 PM
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
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: 13.9 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 13.869 min
Area: 1581772 counts
Height: 2.92e+005 cps
Start Time: 13.704 min
End Time: 14.241 min
13.87
14.32
Intensity, cps
Time, min

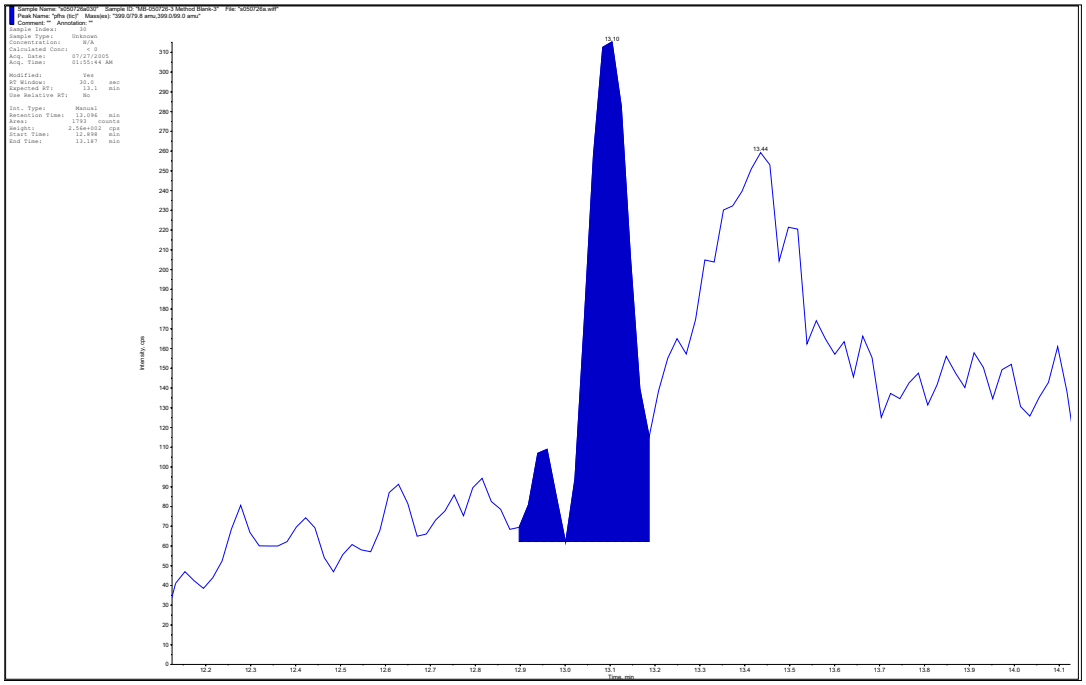

Sample Name: "w050726a020" Sample ID: "EC-050726-039 0.25 ppb extracted curve point" File: "w050726a.wiff"
Peak Name: "pfhx (hc)" Mass(es): "298.9/79.8 amu,298.9/99.0 amu"
Comment: "" Annotation: ""
sample Index: 20
Sample Type: Standard
Concentration: 0.2210 ng/mL
Calculated Conc: 0.227 ng/mL
Acq. Date: 07/26/2005
Acq. Time: 10:24:23 PM
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
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: 10.7 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 10.645 min
Area: 2134402 counts
Height: 3.48e+005 cps
Start Time: 10.417 min
End Time: 10.996 min
10.64
Intensity, cps
Time, min

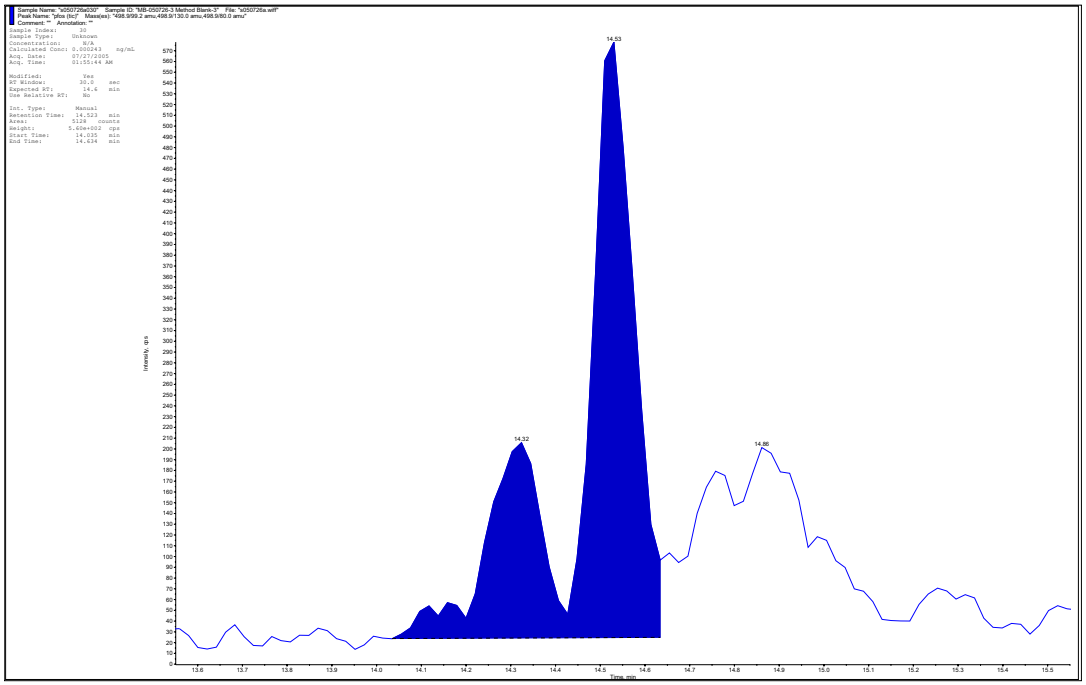

Sample Name: "w050726a020" Sample ID: "EC-050726-009 0.25 ppb extracted curve point" File: "w050726a.wiff"
Peak Name: "pfhs (tic)" Mass(es): "399.0/79.8 amu,399.0/99.0 amu"
Comment: "" Annotation: ""
Sample Index: 20
Sample Type: Standard
Concentration: 0.2600 ng/mL
Calculated Conc: 0.264 ng/mL
Acq. Date: 07/26/2005
Acq. Time: 10:24:23 PM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 13.1 min
Use Relative RT: No
Int. Type: Manual
Integration Time: 12.094 min
Area: 1376832 counts
Height: 2.25e+005 cps
Start Time: 12.732 min
End Time: 13.290 min
13.10
12.88
Intensity, cps
Time, min

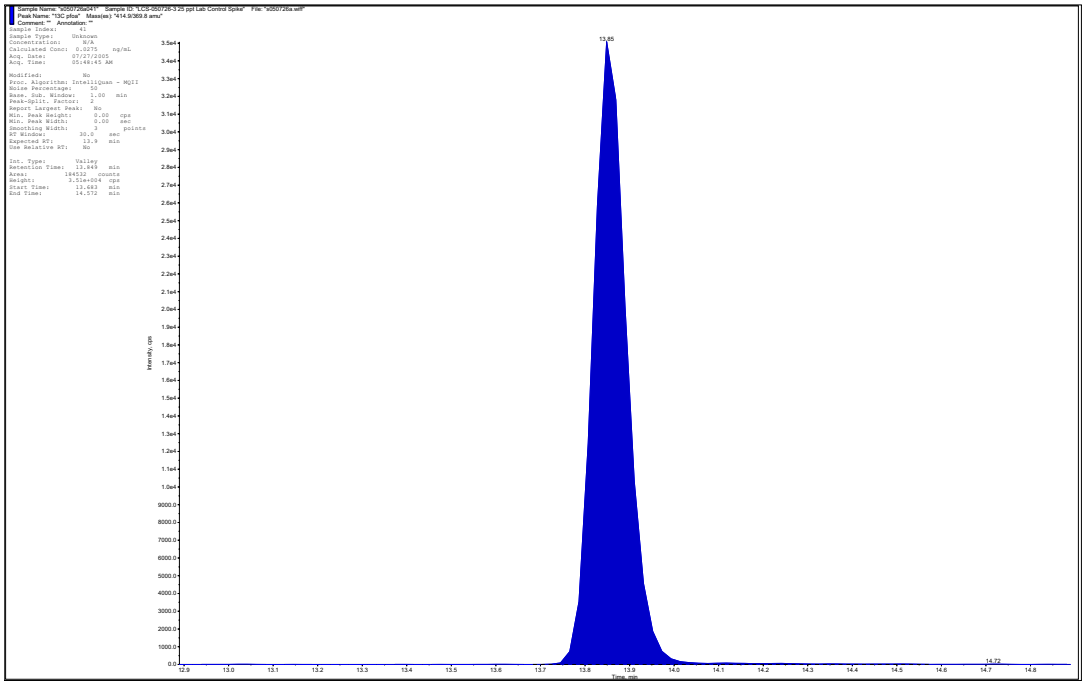

Sample Name: "w050726a020" Sample ID: "EC-050726-009 0.25 ppb extracted curve point" File: "w050726a.wiff"
Peak Name: "pfhs (tic)" Mass(es): "498.9/99.2 amu,498.9/130.0 amu,498.9/80.0 amu"
Comment: "" Annotation: ""
Sample Index: 20
Sample Type: Standard
Concentration: 0.2480 ng/mL
Calculated Conc: 0.256 ng/mL
Acq. Date: 07/26/2005
Acq. Time: 10:24:23 PM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 14.4 min
Use Relative RT: No
Int. Type: Manual
Integration Time: 14.174 min
Area: 483442 counts
Height: 6.12e+004 cps
Start Time: 13.972 min
End Time: 14.716 min
14.60
14.32
Intensity, cps
Time, min

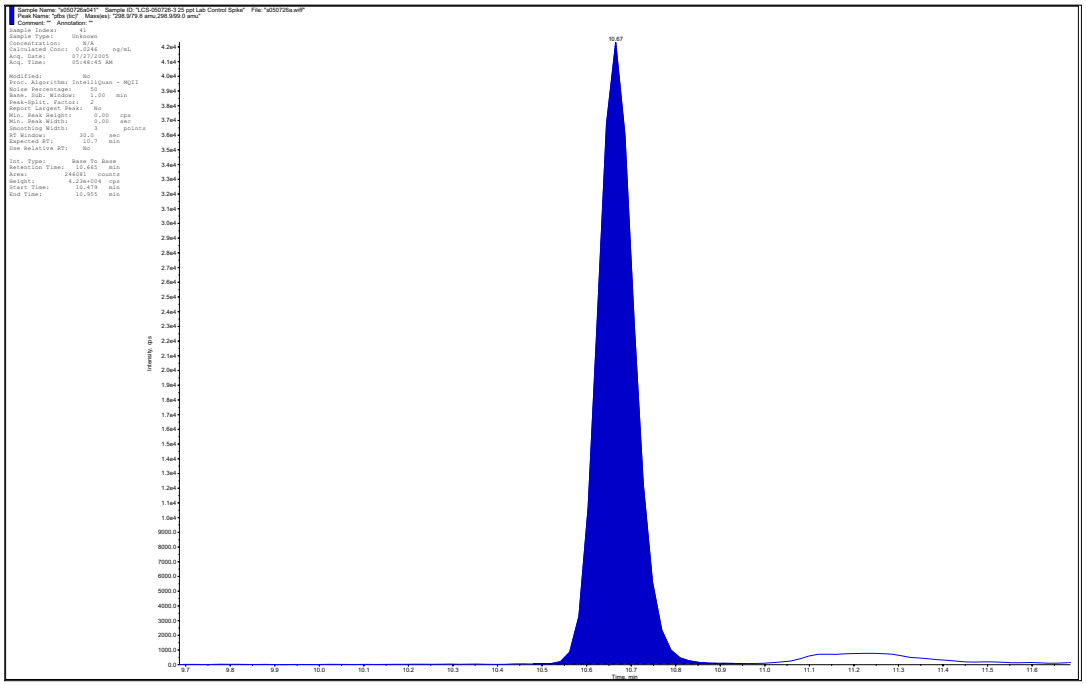

Sample Name: "w050726a030" Sample ID: "MB-050726-3 Method Blank-3" File: "w050726a.wiff"
Peak Name: "13C pfoa" Mass(es): "414.9/369.8 amu"
Comment: "" Annotation: ""
Sample Index: 30
Sample Type: Unknown
Concentration: N/A
Calculated Conc: < 0
Acq. Date: 07/27/2005
Acq. Time: 01:55:44 AM
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
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: 13.9 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 13.848 min
Area: 1834 counts
Height: 3.70e+002 cps
Start Time: 13.704 min
End Time: 13.993 min
Intensity, cps
Time, min

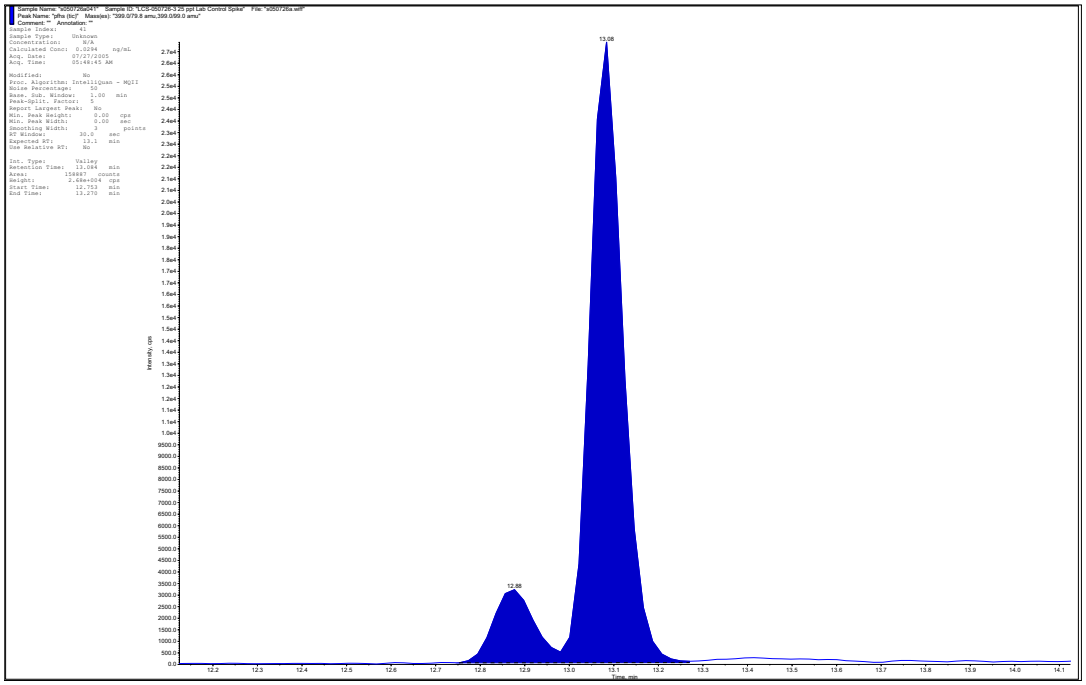

Sample Name: "w050726a030" Sample ID: "MB-050726-3 Method Blank-3" File: "w050726a.wiff"
Peak Name: "pfhx (hz)" Mass(es): "298.9/79.8 amu,298.9/99.0 amu"
Comment: "" Annotation: ""
Sample Index: 30
Sample Type: Unknown
Concentration: N/A
Calculated Conc: < 0
Acq. Date: 07/27/2005
Acq. Time: 01:55:44 AM
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
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: 10.7 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 10.645 min
Area: 4317 counts
Height: 6.45e+002 cps
Start Time: 10.562 min
End Time: 10.893 min
9.76
9.98
10.05
10.13
10.27
10.50
10.64
11.18
Intensity, cps
Time, min

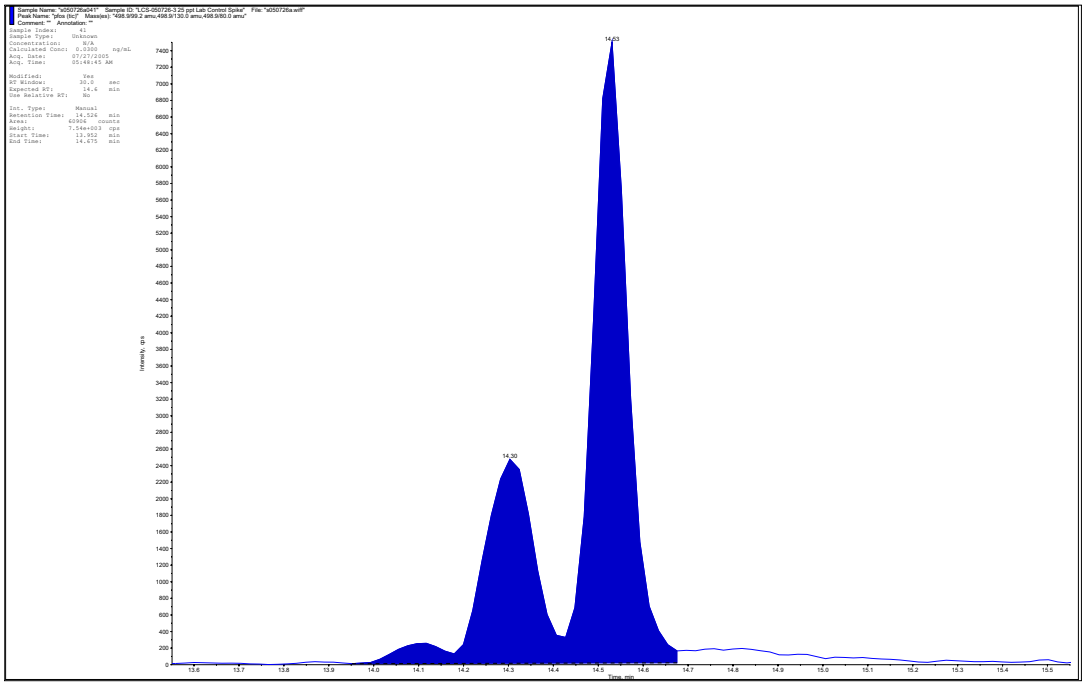

Sample Name: "w050726a030" Sample ID: "MB-050726-3 Method Blank-3" File: "w050726a.wiff"
Peak Name: "pfhs (tic)" Mass(es): "399.0/79.8 amu,399.0/99.0 amu"
Comment: "" Annotation: ""
Sample Index: 30
Sample Type: Unknown
Concentration: N/A
Calculated Conc: < 0
Acq. Date: 07/27/2005
Acq. Time: 01:55:44 AM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 13.1 min
Use Relative RT: No
Int. Type: Manual
Integration Time: 12.996 min
Area: 1791 counts
Height: 2.56e+002 cps
Start Time: 12.898 min
End Time: 13.187 min
13.19
13.44
Intensity, cps
Time, min

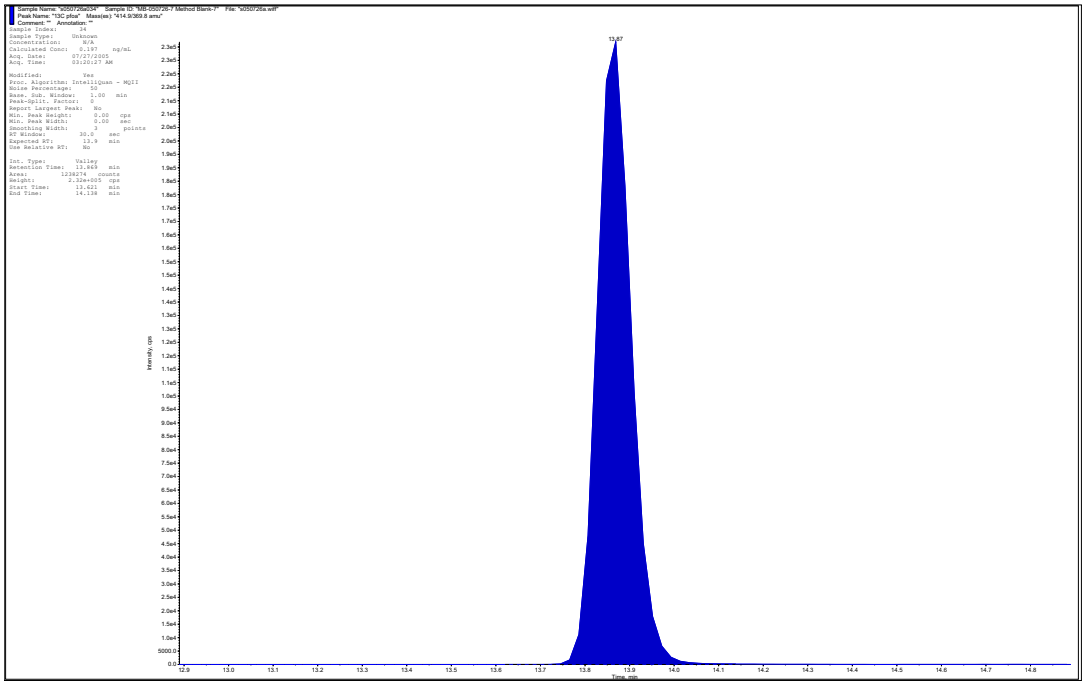

Sample Name: "w050726a030" Sample ID: "MB-050726-3 Method Blank-3" File: "w050726a.wiff"
Peak Name: "pfhs (tic)" Mass(es): "498.9/99.2 amu,498.9/130.0 amu,498.9/80.0 amu"
Comment: "" Annotation: ""
Sample Index: 30
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.000243 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 01:55:44 AM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 14.4 min
Use Relative RT: No
Int. Type: Manual
Integration Time: 14.327 min
Area: 5126 counts
Height: 5.60e+002 cps
Start Time: 14.035 min
End Time: 14.634 min
14.53
14.32
14.86
Intensity, cps
Time, min

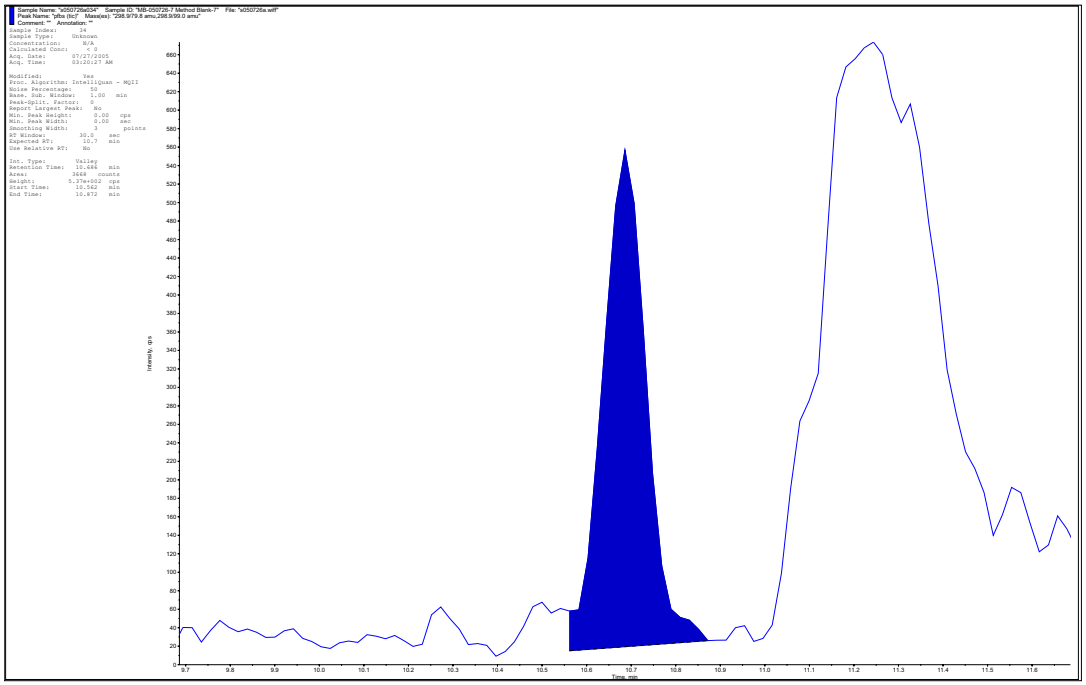

Sample Name: "w050726a041" Sample ID: "LCS-050726-3.25 ppt Lab Control Spike" File: "w050726a.wiff"
Peak Name: "13C pfoa" Mass(es): "414.9/369.8 amu"
Comment: "" Annotation: ""
Sample Index: 41
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.0275 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 05:48:45 AM
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
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: 13.9 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 13.849 min
Area: 194532 counts
Height: 3.51e+004 cps
Start Time: 13.683 min
End Time: 14.572 min
13.85
14.72
Intensity, cps
Time, min

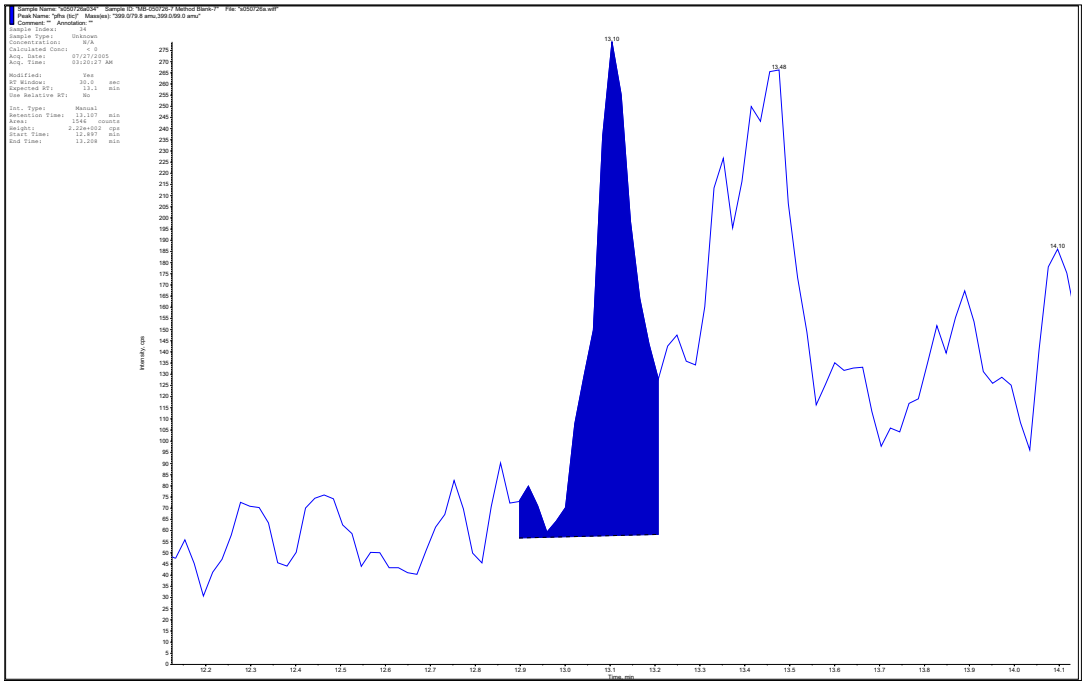

Sample Name: "w050726a041" Sample ID: "LCS-050726-3.25 ppt Lab Control Spike" File: "w050726a.wiff"
Peak Name: "pfhx (hc)" Mass(es): "298.9/79.8 amu,298.9/99.0 amu"
Comment: "" Annotation: ""
Sample Index: 41
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.0244 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 05:48:45 AM
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
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: 10.7 min
Use Relative RT: No
Int. Type: Base To Base
Retention Time: 10.665 min
Area: 244081 counts
Height: 4.23e+004 cps
Start Time: 10.479 min
End Time: 10.955 min
10.67
Intensity, cps
Time, min

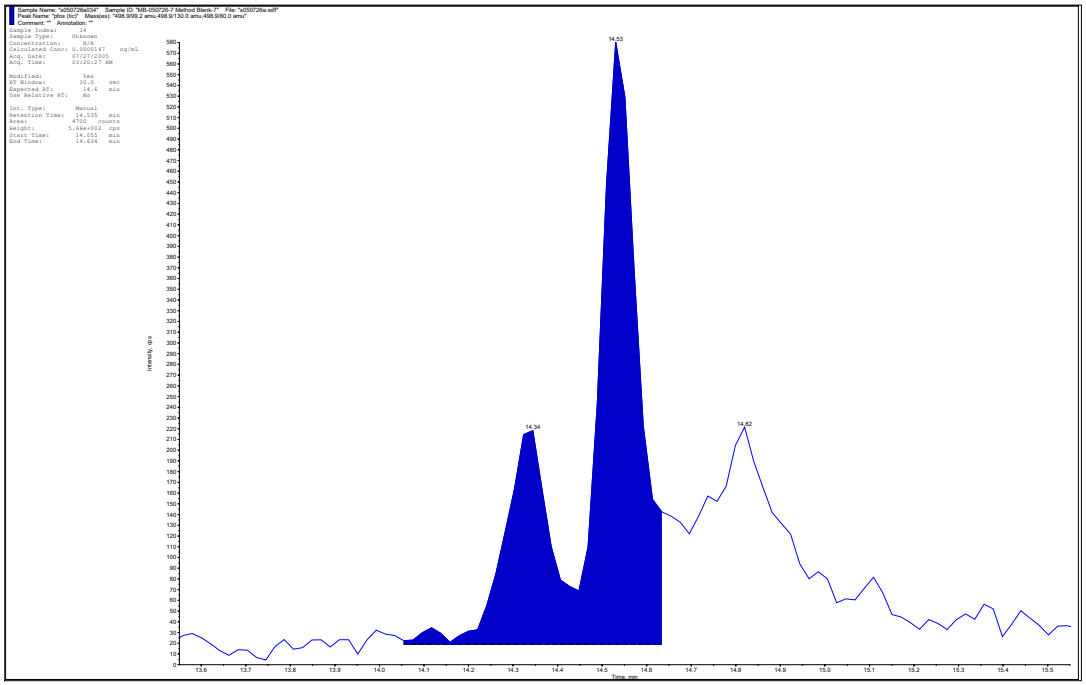

Sample Name: "w050726a041" Sample ID: "LCS-050726-3 25 ppt Lab Control Spike" File: "w050726a.wiff"
Peak Name: "pfhx (tic)" Mass(es): "399.0/79.8 amu,399.0/99.0 amu"
Comment: "" Annotation: ""
Sample Index: 41
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.0294 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 05:48:45 AM
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 5
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: 13.1 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 13.084 min
Area: 156687 counts
Height: 2.68e+004 cps
Start Time: 12.753 min
End Time: 13.270 min
13.08
12.88
Intensity, cps
Time, min

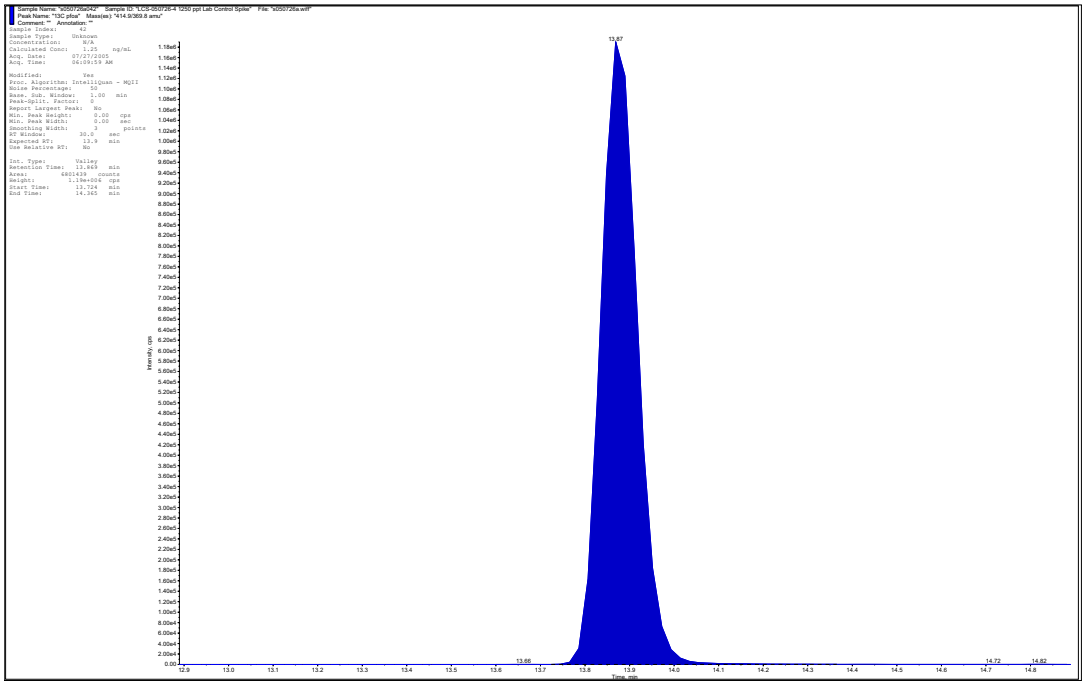

Sample Name: "w050726a041" Sample ID: "LCS-050726-3 25 ppt Lab Control Spike" File: "w050726a.wiff"
Peak Name: "pfhx (tic)" Mass(es): "498.9/99.2 amu,498.9/130.0 amu,498.9/80.0 amu"
Comment: "" Annotation: ""
Sample Index: 41
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.0300 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 05:48:45 AM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 14.4 min
Use Relative RT: No
Int. Type: Manual
Retention Time: 14.324 min
Area: 60861 counts
Height: 7.54e+003 cps
Start Time: 13.952 min
End Time: 14.675 min
14.60
14.30
Intensity, cps
Time, min

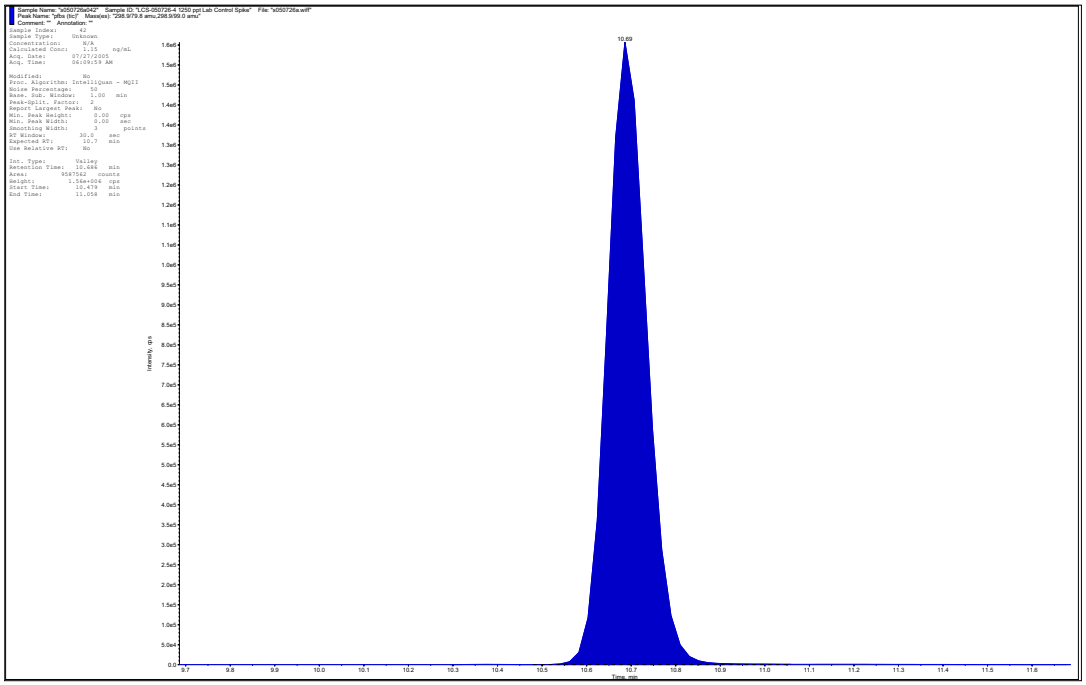

Sample Name: "w050726a034" Sample ID: "MB-050726-7 Method Blank-7" File: "w050726a.wiff"
Peak Name: "13C pfoa" Mass(es): "414.9/369.8 amu"
Comment: "" Annotation: ""
Sample Index: 34
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.197 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 03:20:27 AM
Modified: Yes
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 0
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: 13.9 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 13.869 min
Area: 1238274 counts
Height: 2.32e+005 cps
Start Time: 13.621 min
End Time: 14.138 min
13.87
Intensity, cps
Time, min

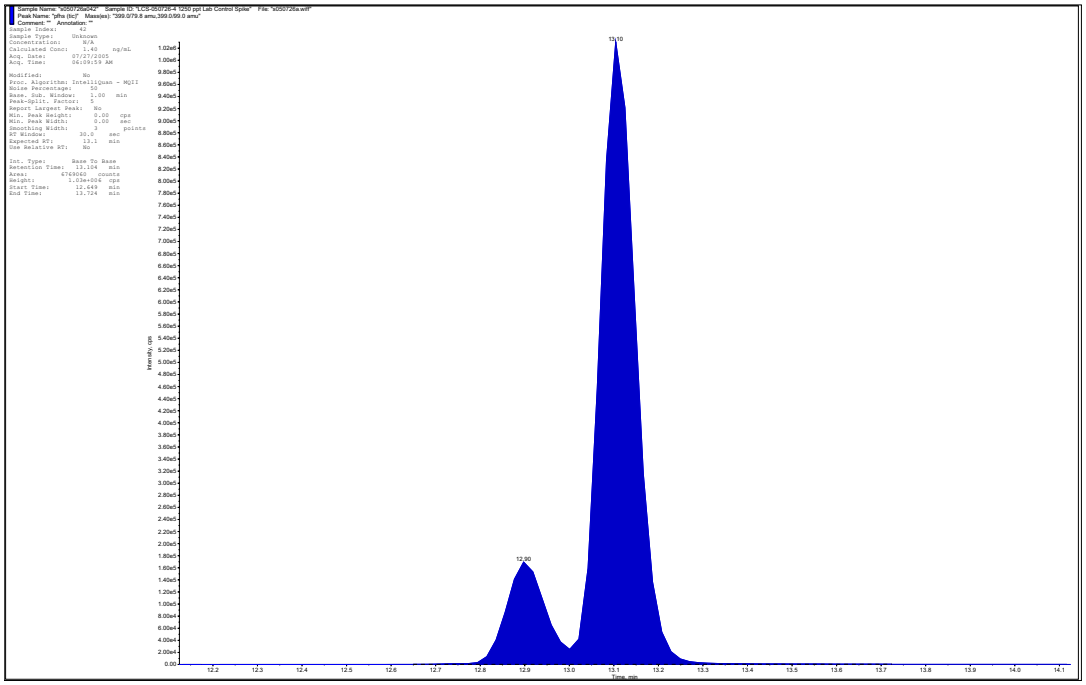

Sample Name: "w050726a034" Sample ID: "MB-050726-7 Method Blank-7" File: "w050726a.wiff"
Peak Name: "pfhx (hc)" Mass(es): "298.9/79.8 amu,298.9/99.0 amu"
Comment: "" Annotation: ""
Sample Index: 34
Sample Type: Unknown
Concentration: N/A
Calculated Conc: < 0
Acq. Date: 07/27/2005
Acq. Time: 03:20:27 AM
Modified: Yes
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 0
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: 10.7 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 10.686 min
Area: 3648 counts
Height: 5.37e+002 cps
Start Time: 10.562 min
End Time: 10.872 min
Intensity, cps
Time, min

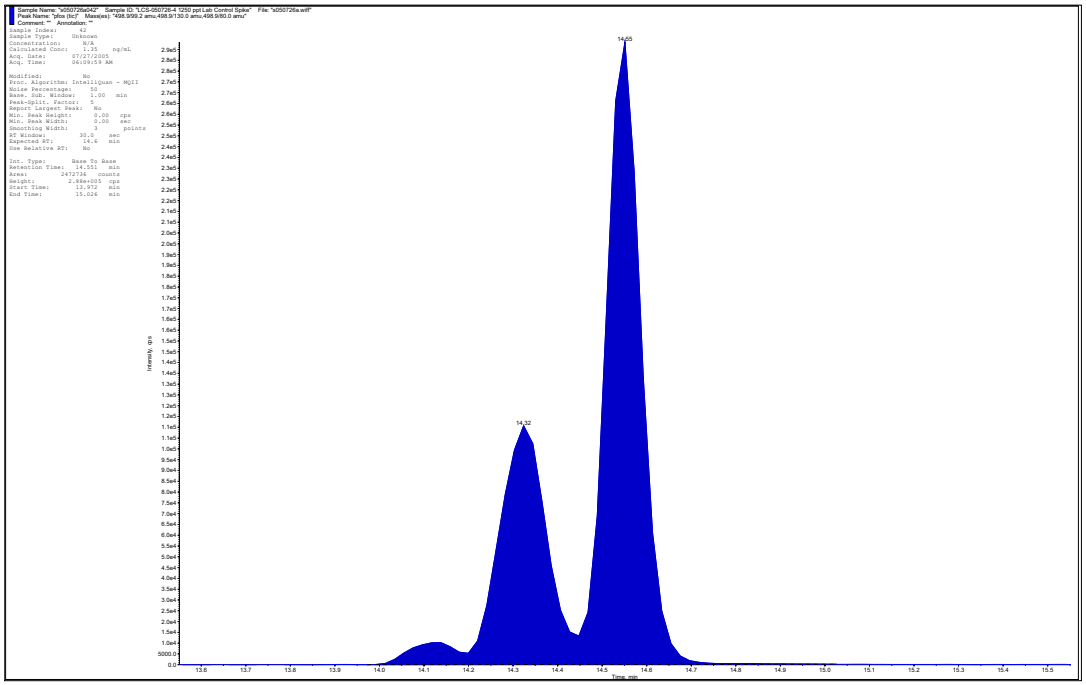

Sample Name: "w050726a034" Sample ID: "MB-050726-7 Method Blank-7" File: "w050726a.wiff"
Peak Name: "pfhx (hc)" Mass(es): "399.0/79.8 amu,399.0/99.0 amu"
Comment: "" Annotation: ""
Sample Index: 34
Sample Type: Unknown
Concentration: N/A
Calculated Conc: < 0
Acq. Date: 07/27/2005
Acq. Time: 03:20:27 AM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 13.1 min
Use Relative RT: No
Int. Type: Manual
Integration Time: 12.897 min
Area: 1546 counts
Height: 2.22e+002 cps
Start Time: 12.897 min
End Time: 13.208 min
13.10
13.48
14.10
Intensity, cps
Time, min

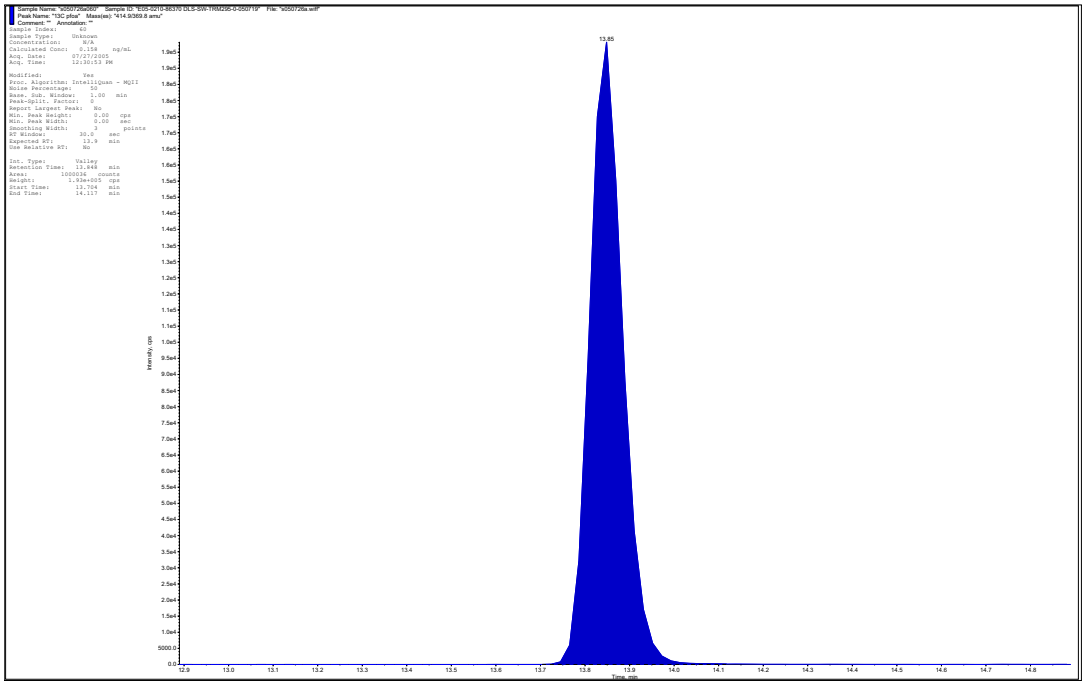

Sample Name: "w050726a034" Sample ID: "MB-050726-7 Method Blank-7" File: "w050726a.wiff"
Peak Name: "pfhx (hc)" Mass(es): "498.9/99.2 amu,498.9/130.0 amu,498.9/80.0 amu"
Comment: "" Annotation: ""
Sample Index: 34
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.0000147 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 03:20:27 AM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 14.4 min
Use Relative RT: No
Int. Type: Manual
Integration Time: 14.555 min
Area: 4761 counts
Height: 5.66e+002 cps
Start Time: 14.055 min
End Time: 14.634 min
14.53
14.34
14.82
Intensity, cps
Time, min

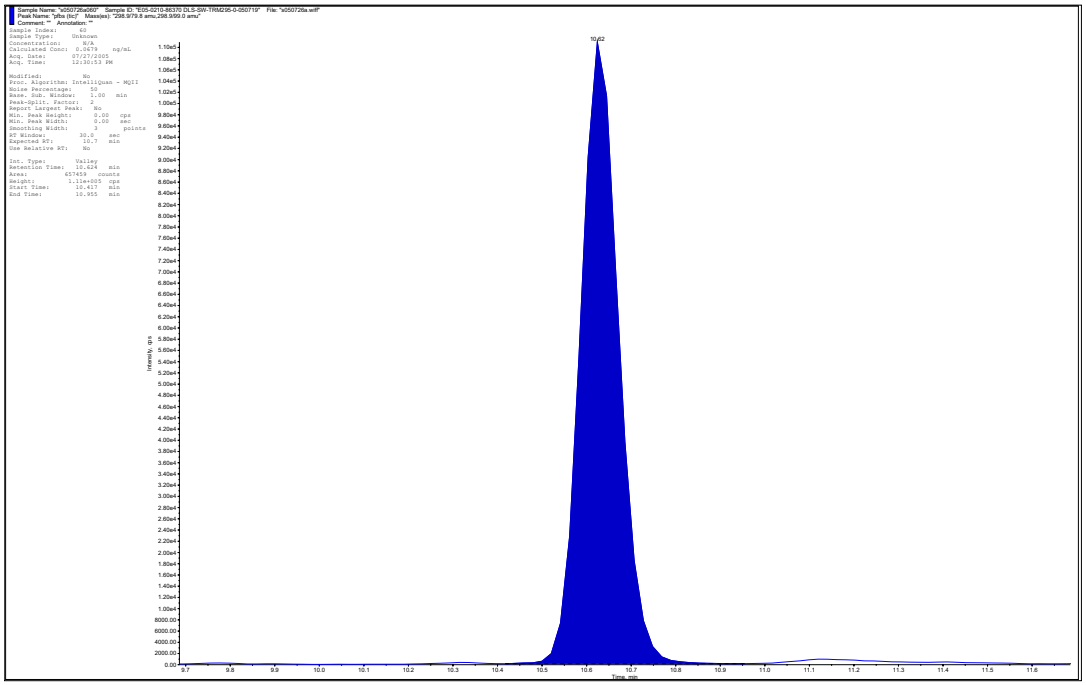

Sample Name: "w050726a042" Sample ID: "LCS-050726-4 1250 ppt Lab Control Spike" File: "w050726a.wiff"
Peak Name: "13C pfoa" Mass(es): "414.9/369.8 amu"
Comment: "" Annotation: ""
Sample Index: 42
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 1.25 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 04:09:59 AM
Modified: Yes
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 8
Report Largest Peak: No
Min. Peak Height: 0.00 cps
Min. Peak Area: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 13.9 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 13.869 min
Area: 6801439 counts
Height: 1.19e+004 cps
Start Time: 13.724 min
End Time: 14.345 min
13.87
13.66
14.72
14.82
Intensity, cps
Time, min

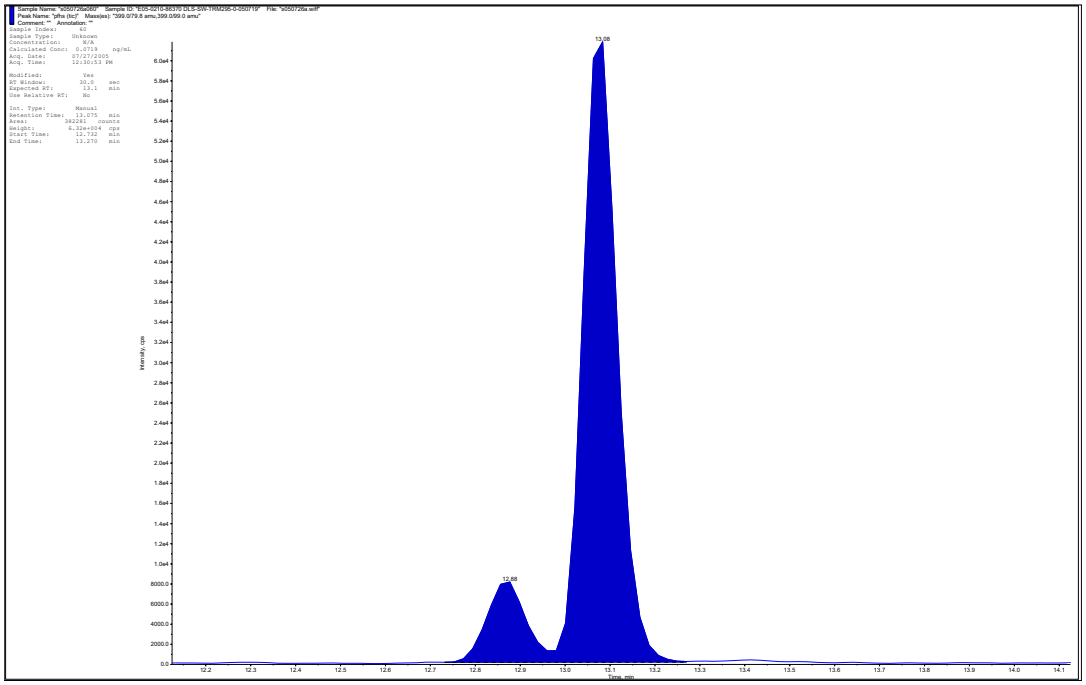

Sample Name: "w050726a042" Sample ID: "LCS-050726-4 1250 ppt Lab Control Spike" File: "w050726a.wiff"
Peak Name: "pfhx (hc)" Mass(es): "298.9/79.8 amu,298.9/99.0 amu"
Comment: "" Annotation: ""
Sample Index: 42
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 1.15 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 04:09:59 AM
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 2
Report Largest Peak: No
Min. Peak Height: 0.00 cps
Min. Peak Area: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 10.7 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 10.686 min
Area: 9587562 counts
Height: 1.56e+004 cps
Start Time: 10.479 min
End Time: 11.058 min
10.69
Intensity, cps
Time, min


Sample Name: "w050726a042" Sample ID: "LCS-050726-4 1250 ppt Lab Control Spike" File: "w050726a.wiff"
Peak Name: "pfhs (Iic)" Mass(es): "399.0/79.8 amu,399.0/99.0 amu"
Comment: "" Annotation: ""
Sample Index: 42
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 1.40 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 04:09:59 AM
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base, Sub. Window: 1.00 min
Peak-Split. Factor: 5
Report Largest Peak: No
Min. Peak Height: 0.00 cps
Min. Peak Area: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 13.1 min
Use Relative RT: No
Int. Type: Base To Base
Retention Time: 13.104 min
Area: 4763040 counts
Height: 1.03e+006 cps
Start Time: 12.649 min
End Time: 13.724 min
13.10
12.90
Intensity, cps
Time, min


Sample Name: "w050726a042" Sample ID: "LCS-050726-4 1250 ppt Lab Control Spike" File: "w050726a.wiff"
Peak Name: "pfhs (Iic)" Mass(es): "498.9/99.2 amu,498.9/130.0 amu,498.9/80.0 amu"
Comment: "" Annotation: ""
Sample Index: 42
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 1.35 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 04:09:59 AM
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base, Sub. Window: 1.00 min
Peak-Split. Factor: 5
Report Largest Peak: No
Min. Peak Height: 0.00 cps
Min. Peak Area: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 14.6 min
Use Relative RT: No
Int. Type: Base To Base
Retention Time: 14.551 min
Area: 2472736 counts
Height: 2.88e+005 cps
Start Time: 13.972 min
End Time: 15.026 min
14.55
14.32
Intensity, cps
Time, min


Sample Name: "w050728a0607" Sample ID: "E05-0210-86370 DLS-SW-TRM295-0-050719" File: "w050728a.wiff"
Peak Name: "13C pfoa" Mass(es): "414.9/369.8 amu"
Comment: "" Annotation: ""
Sample Index: 60
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.158 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 12:30:53 PM
Modified: Yes
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 0
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: 13.9 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 13.848 min
Area: 1000036 counts
Height: 1.93e+005 cps
Start Time: 13.704 min
End Time: 14.117 min
13.85
Intensity, cps
Time, min


Sample Name: "w050728a0607" Sample ID: "E05-0210-86370 DLS-SW-TRM295-0-050719" File: "w050728a.wiff"
Peak Name: "pfhx (hc)" Mass(es): "298.9/79.8 amu,298.9/99.0 amu"
Comment: "" Annotation: ""
Sample Index: 60
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.0479 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 12:30:53 PM
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
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: 10.7 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 10.624 min
Area: 657459 counts
Height: 1.11e+005 cps
Start Time: 10.417 min
End Time: 10.955 min
10.62
Intensity, cps
Time, min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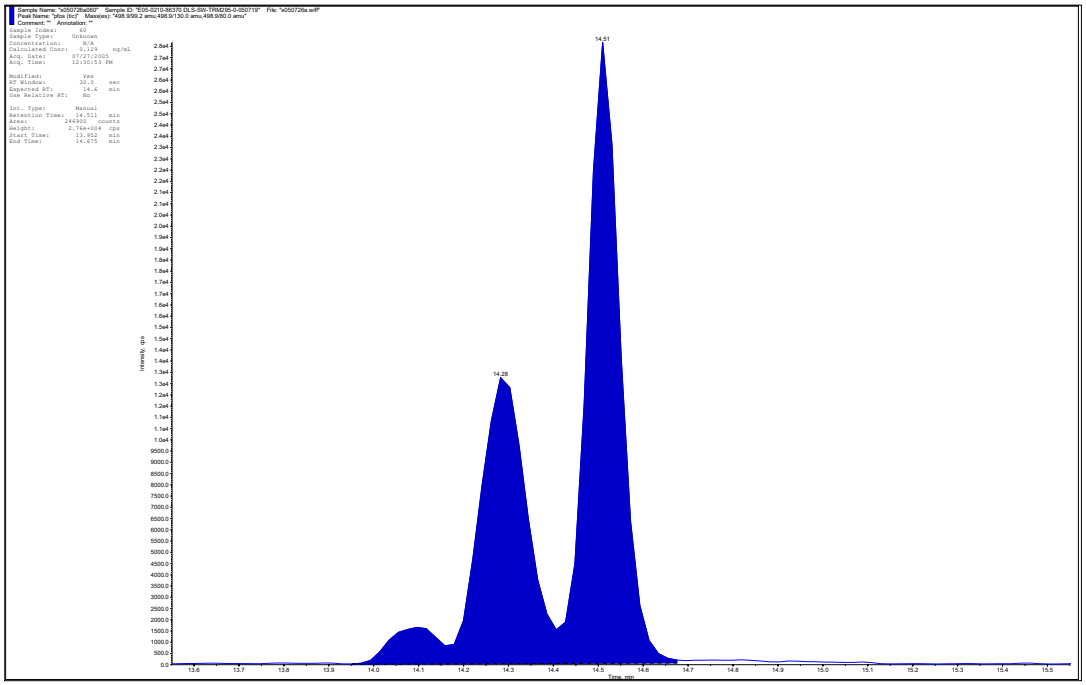
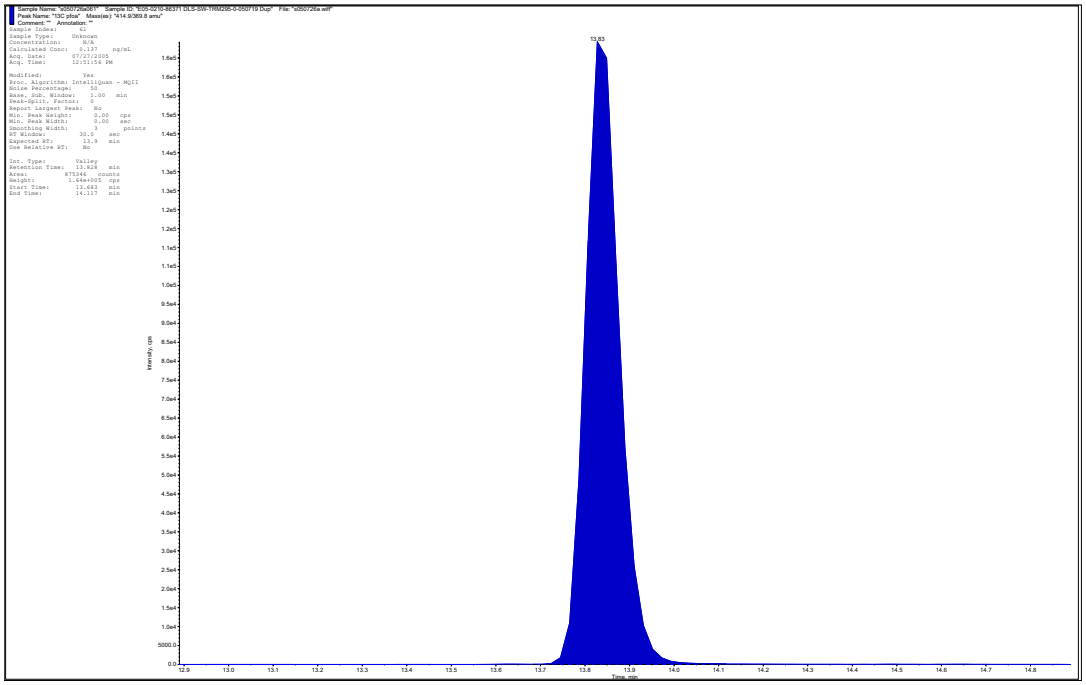
Peak Name: "pfhx (tic)" Mass(es): "399.0/79.8 amu,399.0/99.0 amu"
Comment: "" Annotation: ""
Sample Index: 60
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.0719 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 12:30:53 PM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 13.1 min
Use Relative RT: No
Int. Type: Manual
Integration Time: 12.975 min
Area: 382281 counts
Height: 6.32e+004 cps
Start Time: 12.732 min
End Time: 13.270 min
13.08
12.88
Intensity, cps
Time, min


Sample Name: "w050726a060" Sample ID: "E05-0210-86370 DLS-SW-TRM295-0-050719" File: "w050726a.wiff"
Peak Name: "pfhx (tic)" Mass(es): "498.9/99.2 amu,498.9/130.0 amu,498.9/80.0 amu"
Comment: "" Annotation: ""
Sample Index: 60
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.129 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 12:30:53 PM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 14.4 min
Use Relative RT: No
Int. Type: Manual
Integration Time: 14.311 min
Area: 246861 counts
Height: 2.76e+004 cps
Start Time: 13.952 min
End Time: 14.675 min
14.51
14.28
Intensity, cps
Time, min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Peak Name: "13C pfoa" Mass(es): "414.9/369.8 amu"
Comment: "" Annotation: ""
Sample Index: 61
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.137 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 12:51:56 PM
Modified: Yes
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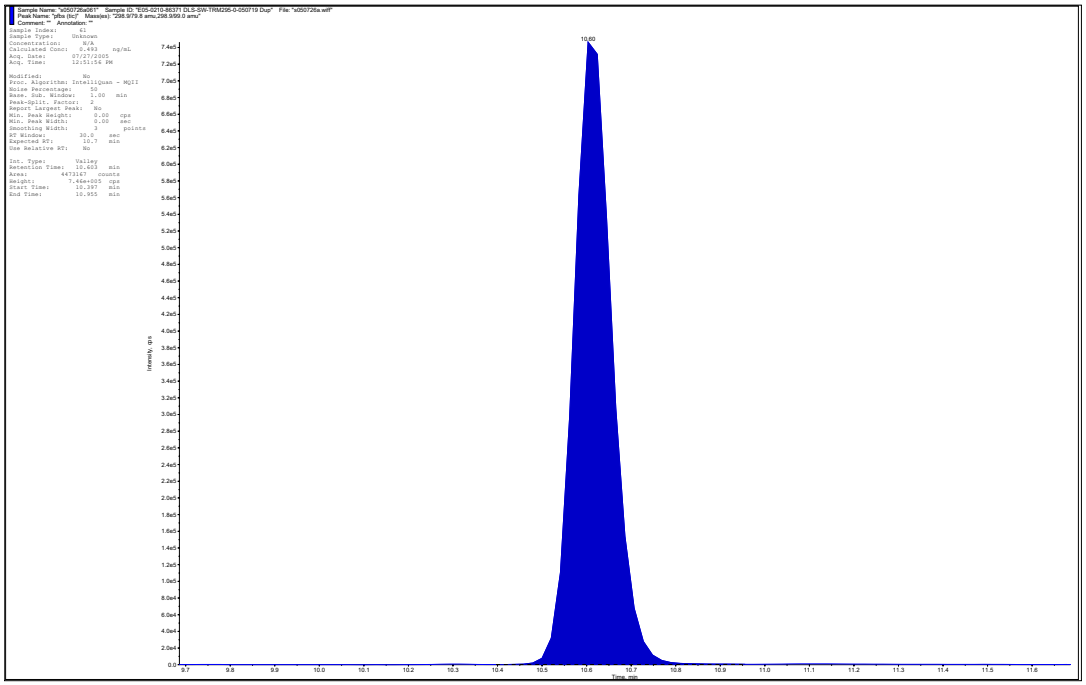
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 0
Report Largest Peak: No
Min. Peak Height: 0.00 cps
Min. Peak Width: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 13.9 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 13.828 min
Area: 875346 counts
Height: 1.44e+005 cps
Start Time: 13.683 min
End Time: 14.117 min
13.83
Intensity, cps
Time, min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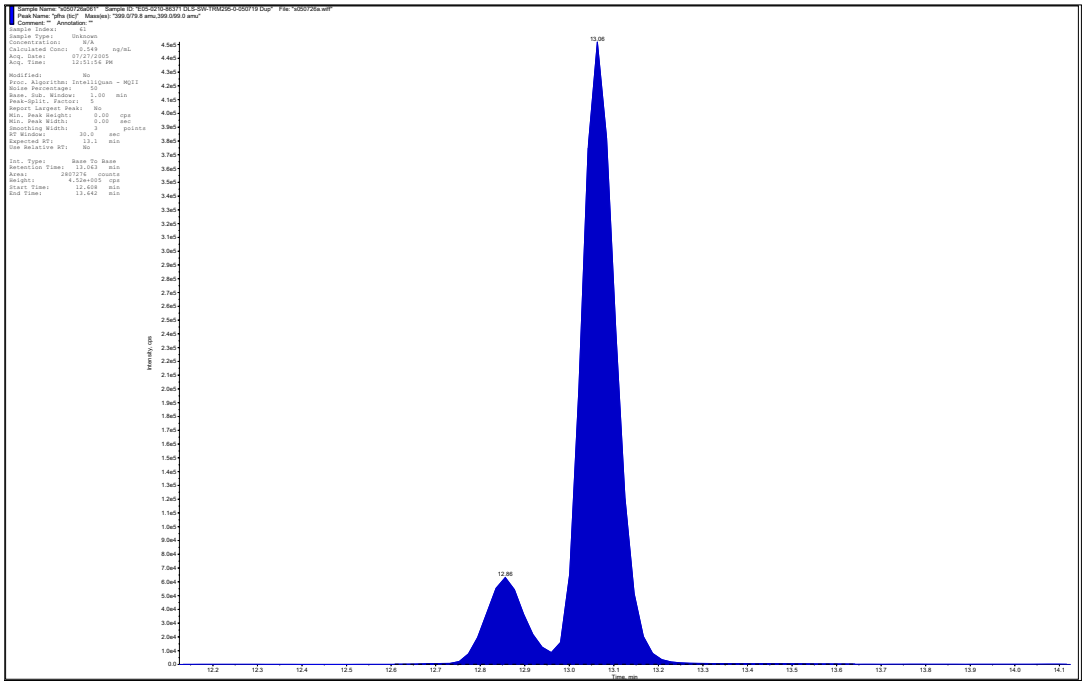
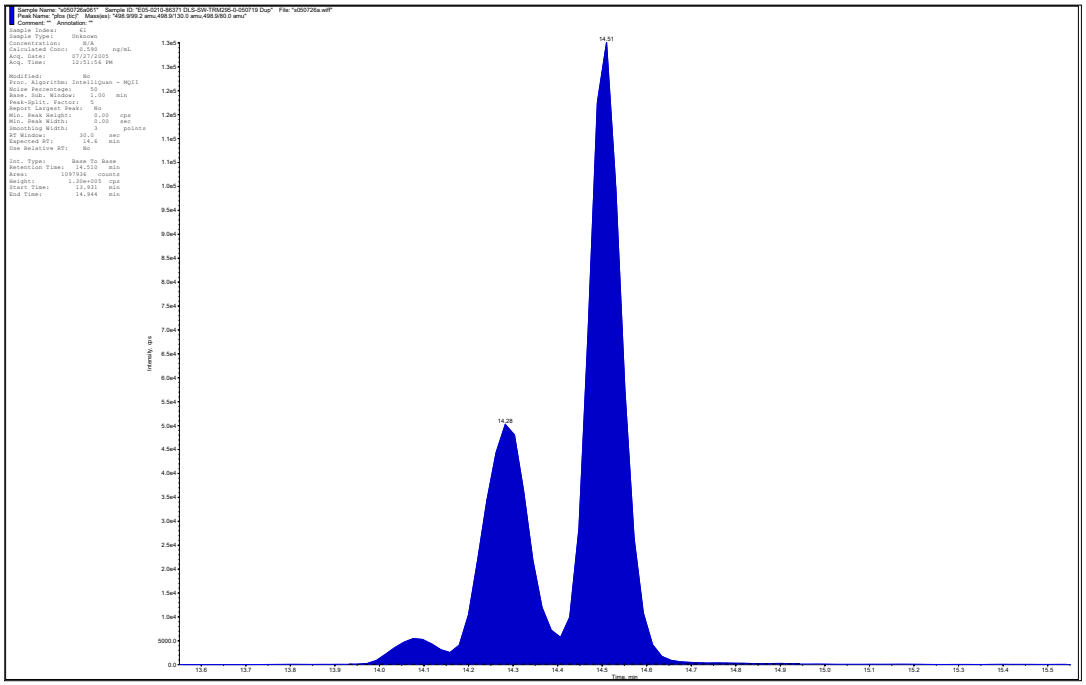
Peak Name: "pfhx (hc)" Mass(es): "298.9/79.8 amu,298.9/99.0 amu"
Comment: "" Annotation: ""
Sample Index: 61
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.493 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 12:51:56 PM
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. 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: 10.7 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 10.603 min
Area: 4473167 counts
Height: 7.46e+005 cps
Start Time: 10.397 min
End Time: 10.955 min
10.60
Intensity, cps
Time, min


Sample Name: "w050726a061" Sample ID: "E05-0210-86371 DLS-SW-TRM295-0-050719 Dup" File: "w050726a.wiff"
Peak Name: "pfhs (5c)" Mass(es): "399.0/79.8 amu,399.0/99.0 amu"
Comment: "" Annotation: ""
Sample Index: 61
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.549 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 12:51:56 PM
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 5
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: 13.1 min
Use Relative RT: No
Int. Type: Base To Base
Retention Time: 13.063 min
Area: 2807276 counts
Height: 4.52e+005 cps
Start Time: 12.808 min
End Time: 13.442 min
13.06
12.86
Intensity, cps
Time, min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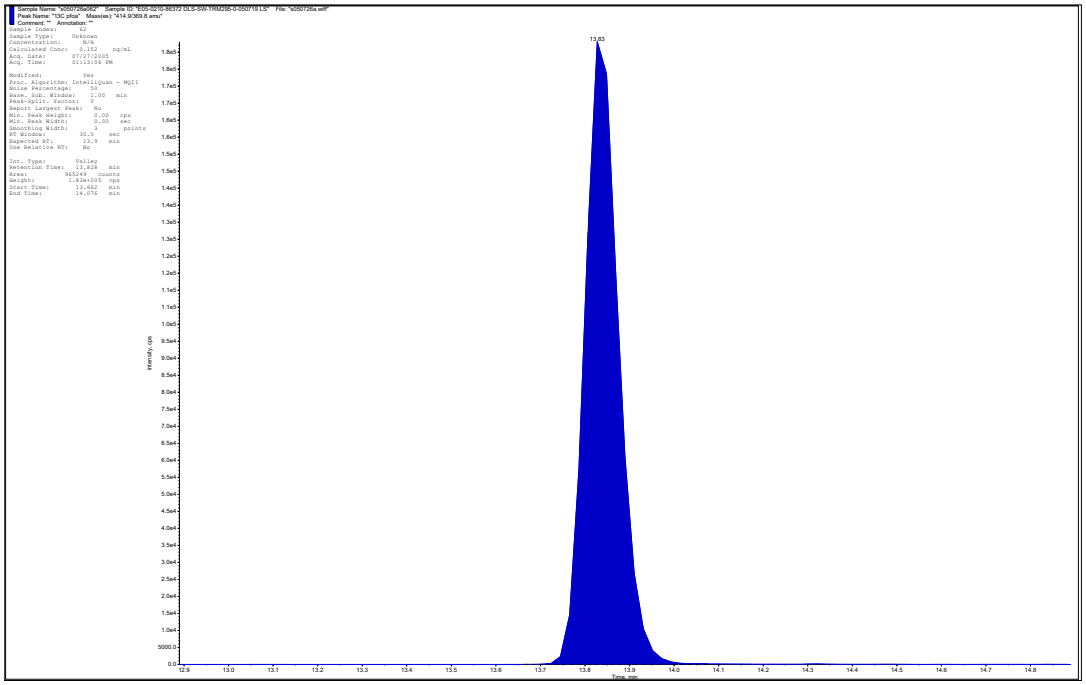
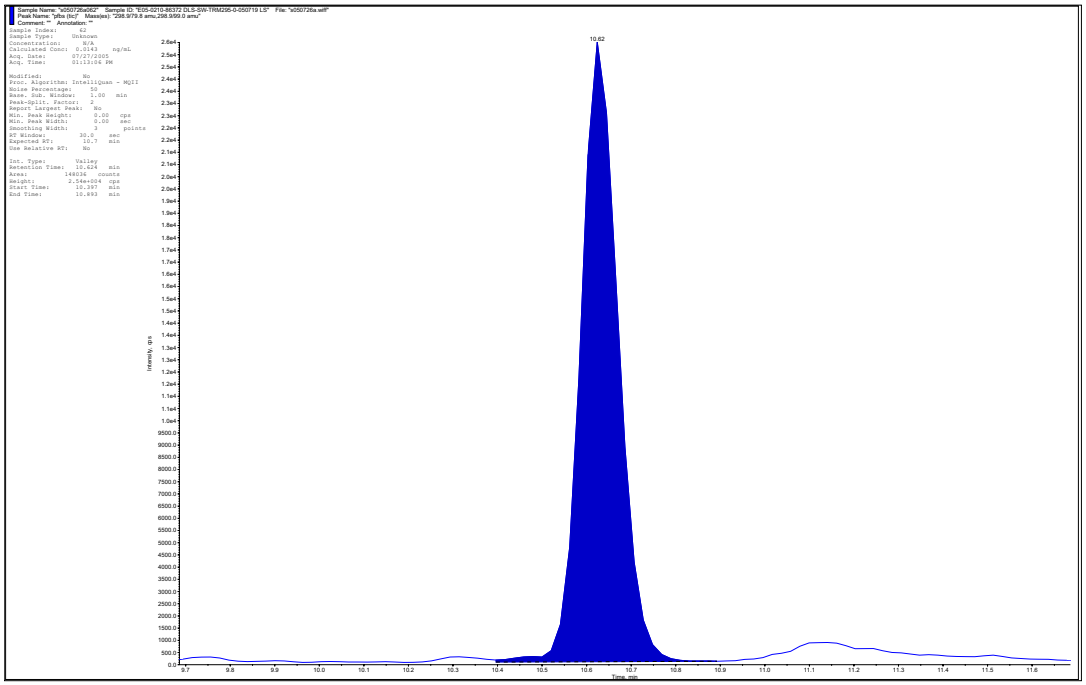
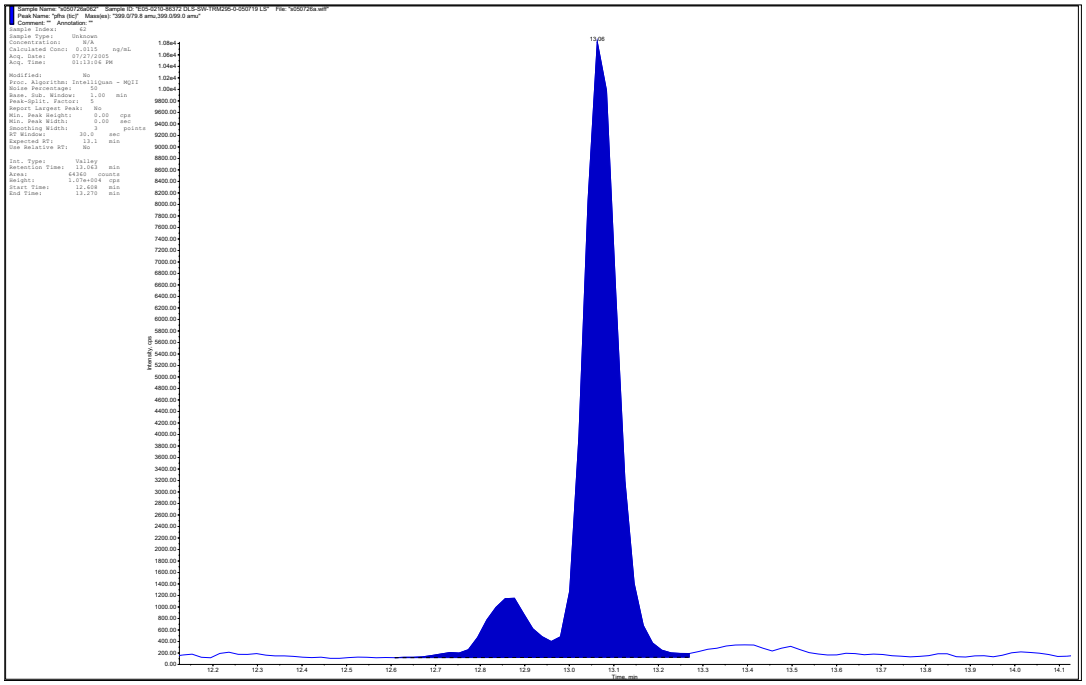
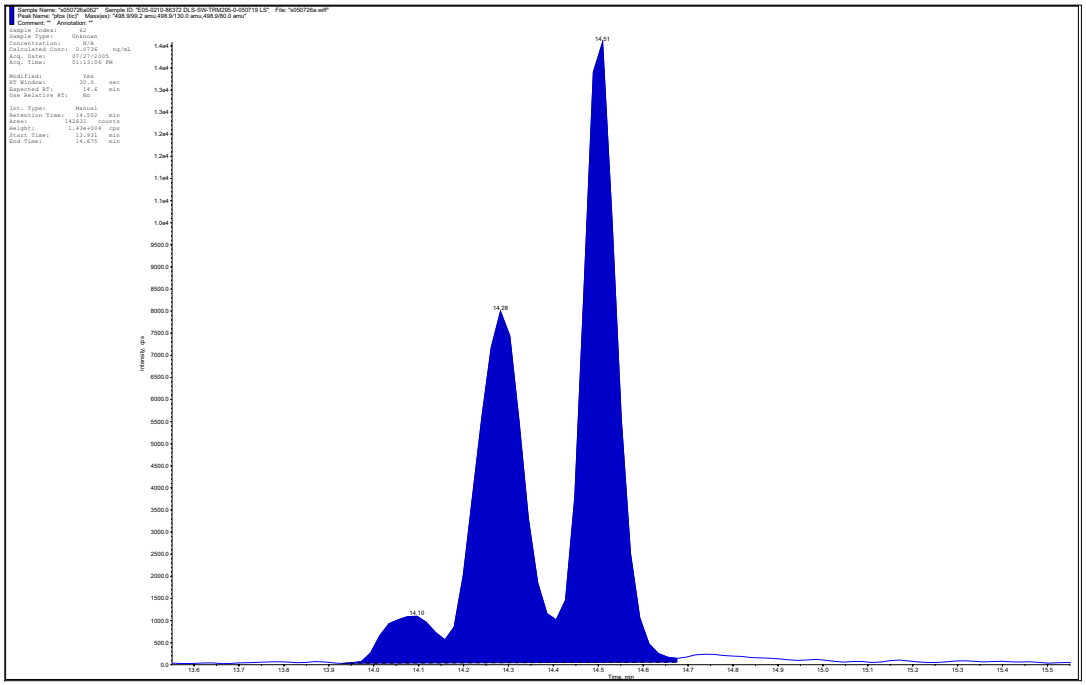
Peak Name: "pfhs (5c)" Mass(es): "498.9/99.2 amu,498.9/130.0 amu,498.9/80.0 amu"
Comment: "" Annotation: ""
Sample Index: 61
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.590 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 12:51:56 PM
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 5
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: 14.6 min
Use Relative RT: No
Int. Type: Base To Base
Retention Time: 14.510 min
Area: 1097936 counts
Height: 1.30e+005 cps
Start Time: 13.931 min
End Time: 14.944 min
14.51
14.28
Intensity, cps
Time, min


Sample Name: "a050725a062" Sample ID: "E05-0210-86372 DLS-SW-TRM295-0-050719 LS" File: "a050725a.wiff"
Peak Name: "13C pfox" Mass(es): "414.9/369.8 amu"
Comment: "" Annotation: ""
Sample Index: 62
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.152 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 01:13:06 PM
Modified: Yes
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 0
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: 13.9 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 13.828 min
Area: 945249 counts
Height: 1.83e+005 cps
Start Time: 13.662 min
End Time: 14.076 min
13.83
Intensity, cps
Time, min


Sample Name: "a050725a062" Sample ID: "E05-0210-86372 DLS-SW-TRM295-0-050719 LS" File: "a050725a.wiff"
Peak Name: "pfhx (hc)" Mass(es): "298.9/79.8 amu,298.9/99.0 amu"
Comment: "" Annotation: ""
Sample Index: 62
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.0143 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 01:13:06 PM
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
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: 10.7 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 10.624 min
Area: 148036 counts
Height: 2.54e+004 cps
Start Time: 10.397 min
End Time: 10.893 min
10.62
Intensity, cps
Time, min


Sample Name: "a050725a062" Sample ID: "E05-0210-86372 DLS-SW-TRM295-0-050719 LS" File: "a050725a.wiff"
Peak Name: "pfhs (9cl" Mass(es): "399.0/79.8 amu,399.0/99.0 amu"
Comment: "" Annotation: ""
Sample Index: 62
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.0115 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 01:13:06 PM
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 5
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: 13.1 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 13.063 min
Area: 64360 counts
Height: 1.07e+004 cps
Start Time: 12.808 min
End Time: 13.270 min
13.06
Intensity, cps
Time, min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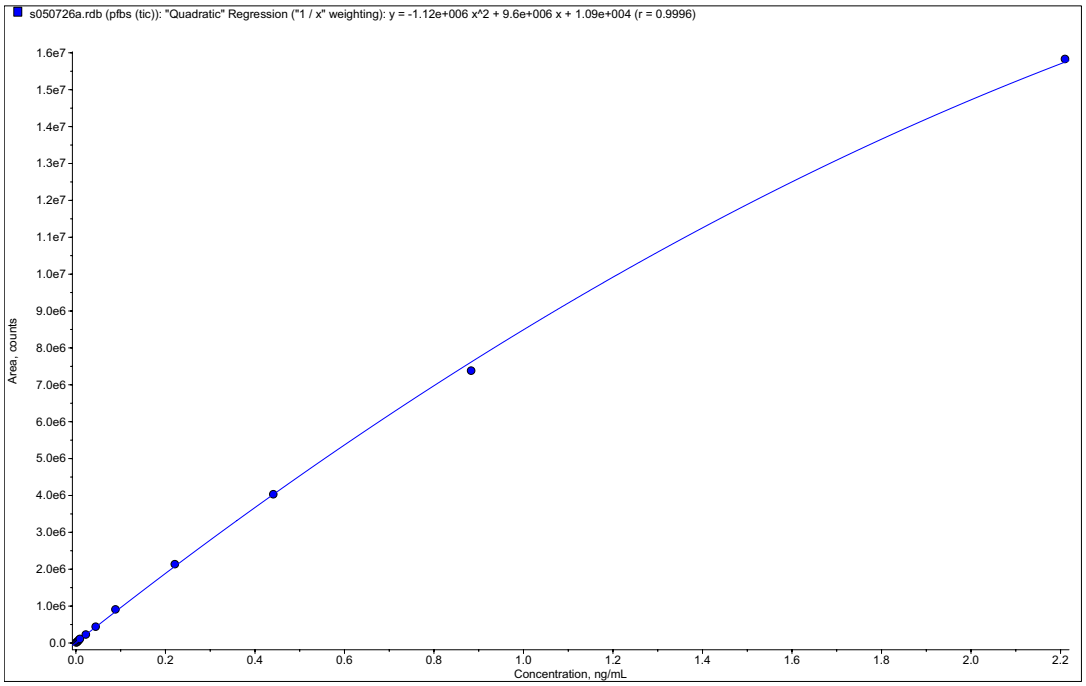
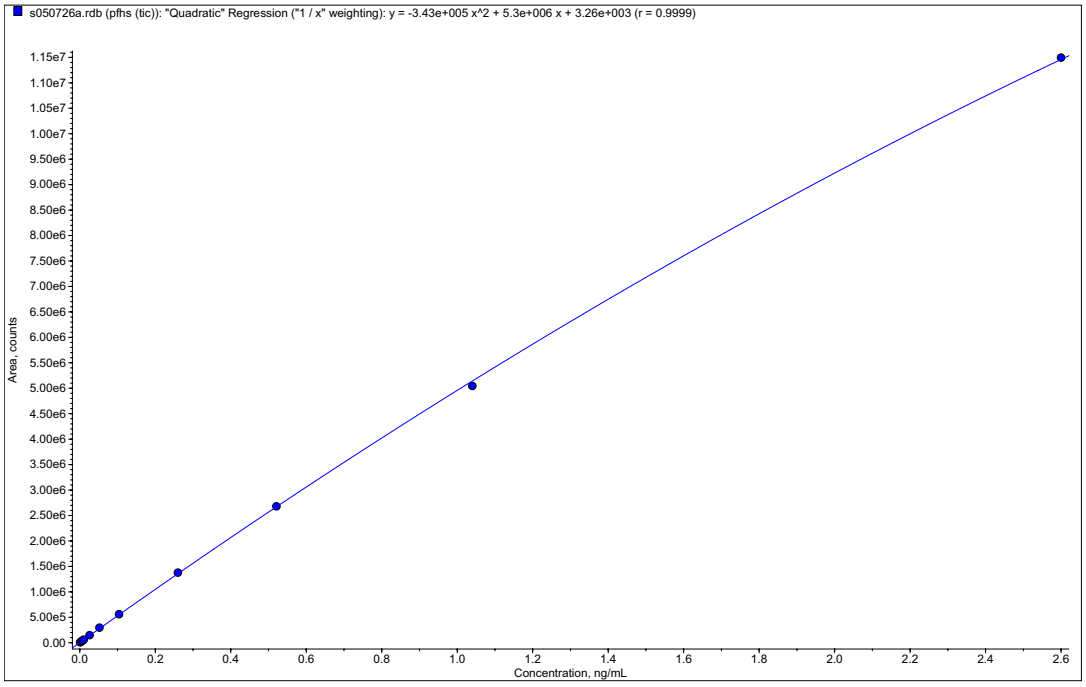
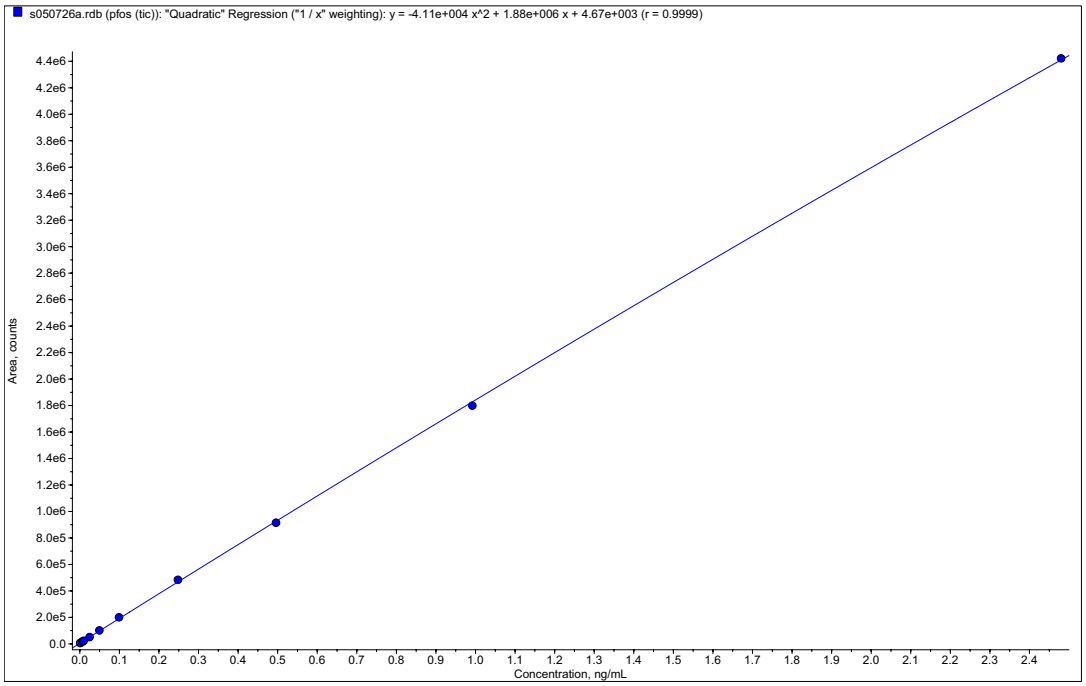
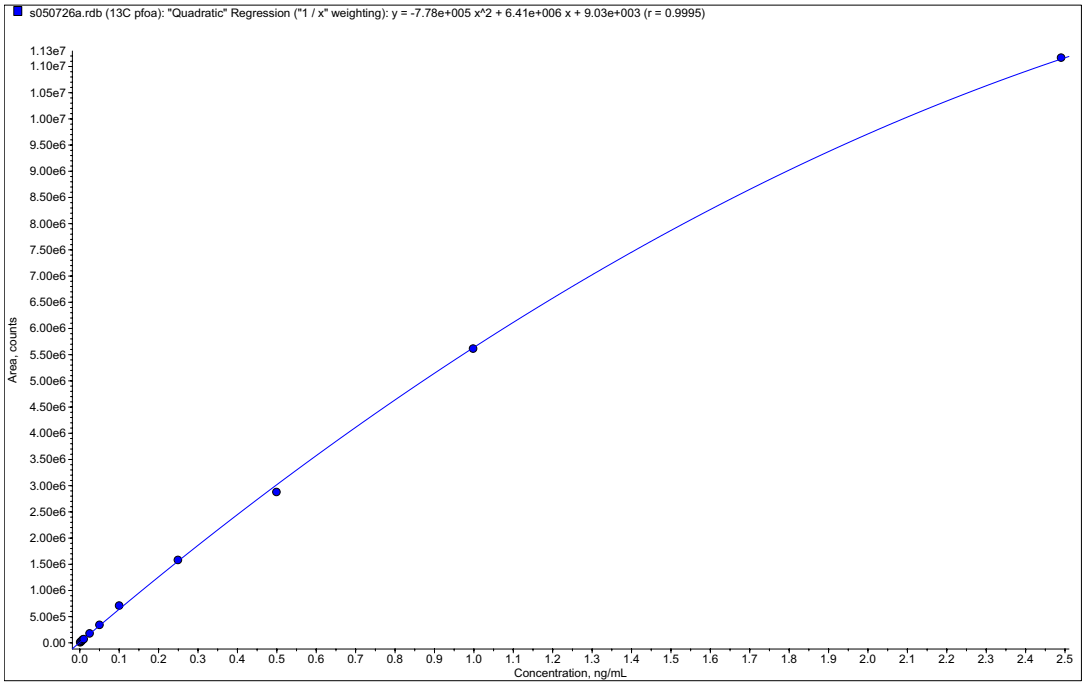
Peak Name: "pfhs (9cl" Mass(es): "498.9/99.2 amu,498.9/130.0 amu,498.9/80.0 amu"
Comment: "" Annotation: ""
Sample Index: 62
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 0.0734 ng/mL
Acq. Date: 07/27/2005
Acq. Time: 01:13:06 PM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 14.4 min
Use Relative RT: No
Int. Type: Manual
Retention Time: 14.502 min
Area: 142431 counts
Height: 1.43e+004 cps
Start Time: 13.931 min
End Time: 14.675 min
14.51
14.28
14.10
Intensity, cps
Time, min


s050726a.rdb (pfbs (tic)): "Quadratic" Regression ("1 / x" weighting): y = -1.12e+006 x^2 + 9.6e+006 x + 1.09e+004 (r = 0.9996)
Area, counts
Concentration, ng/mL


s050726a.rdb (pfhs (tic)): "Quadratic" Regression ("1 / x" weighting): y = -3.43e+005 x^2 + 5.3e+006 x + 3.26e+003 (r = 0.9999)
Area, counts
Concentration, ng/mL


s050726a.rdb (pfos (tic)): "Quadratic" Regression ("1 / x" weighting): y = -4.11e+004 x^2 + 1.88e+006 x + 4.67e+003 (r = 0.9999)
Area, counts
Concentration, ng/mL


s050726a.rdb (13C pfoa): "Quadratic" Regression ("1 / x" weighting): y = -7.78e+005 x^2 + 6.41e+006 x + 9.03e+003 (r = 0.9995)
Area, counts
Concentration, ng/mL

ATTACHMENT B: EXTRACTION AND ANALYTICAL METHODS

3M Environmental Laboratory

Method

Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates In Water By Solid Phase Extraction and High Performance Liquid Chromatography/Mass Spectrometry

Method Number: ETS-8-154.1

Adoption Date: 28 Apr 2000

Revision Date: 5 May, 2003

Effective Date: 5 May, 2003

Approved By:

05/05/03

William K. Reagen
Manager

Date

1 Scope and Application

This method was validated for the collection, extraction, and analytical procedure for the determination of Perfluorooctane sulfonate (PFOS), Perfluorooctane sulfonylamide (FOSA), and Perfluorooctanoate (PFOA) in groundwater, surface water, and drinking water samples. This method may also be applied to the determination of other perfluorinated acids, alcohols, amides, and sulfonates in similar matrices, as long as the defined QC elements are satisfied and with the understanding that the method is not validated for compounds outside the scope of the original protocol

This method is based in part on the report "Method of Analysis for the Determination of Perfluorooctane sulfonate (PFOS), Perfluorooctane sulfonylamide (PFOSA), and Perfluorooctanoate (POAA) in Water" (see Section 17), as developed and validated by Exygen Research (formerly Centre Analytical Laboratories, Inc.).

2 Method Summary

Water samples are collected from a site of interest and shipped cold to an analytical facility. Perfluorinated acids, alcohols, amides, and sulfonates are extracted from 40mL water samples using C18 solid phase extraction (SPE) cartridges. The compounds are eluted from the C18 cartridge, using methanol. Separation, identification, and measurement are accomplished by high-performance liquid chromatography/ tandem mass spectrometry (HPLC/MS/MS) analysis. High-performance liquid chromatography/mass spectrometry (HPLC/MS) may be used if the defined QC elements are satisfied.

The concentration of each identified component is measured by comparing the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by the same compound in an extracted calibration standard (external standard).

3 Definitions

3.1 Analytical Sample

A portion of an extracted Laboratory Sample prepared for analysis.

3.2 Calibration Standard

A solution prepared from the Working Standard (WS) and extracted according to this method. The calibration standard solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 Duplicate Sample (DS)

A DS is a separate aliquot of a sample, taken in the analytical laboratory that is extracted and analyzed separately with identical procedures. Analysis of DSs compared to that of the first aliquot give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 Field Blank Control Sample (FB)

ASTM Type I water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FB is to determine if test substances or other interferences are present in the field environment.

3.5 Field Duplicate (FD)

A sample collected in duplicate at the same time as the sample and placed under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analysis of FD compared to that of the first sample gives a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.6 Field Matrix Spike (FMS)

A sample collected in duplicate to which known quantities of the target analytes are added in the field at the time of sample collection. Alternatively, the known quantity of target analytes may be added to the sample bottle in the laboratory before the bottles are sent to the field. A known, specific volume of sample must be added to sample container without rinsing. This may be accomplished by making a "fill to this level" line on the outside of the sample container. The FMS should be spiked at approximately 50–150% of the expected analyte concentration in the sample. If the expected range of analyte concentrations is unknown, a low and a high spike may be prepared to increase the likelihood that a spike at an appropriate range is made. The FMS is analyzed to ascertain if any matrix effects, interferences, or stability issues may complicate the interpretation of the sample analysis.

3.7 Field Spike Control Sample (FSCS)

An aliquot of ASTM Type I water to which known quantities of the target analytes are added in the field at the time of sample collection (at an appropriate concentration to be determined by the project lead) or in the laboratory prior to the shipment of the collection bottles. The FSCS is extracted and analyzed exactly like a sample to determine whether a loss of analyte could be attributed to sample storage and/or shipment. A low and high FSCS may be appropriate when expected sample concentrations are not known.

3.8 Laboratory Control Sample (LCS)

An aliquot of ASTM Type I water to which known quantities of the target analytes are added in the laboratory. Two levels are included, one at the LLOQ (approx. 25 pg/mL), the other at a concentration of approx. 100–250 pg/mL or another concentration to be determined by the project lead. The LCS is extracted and analyzed exactly like a laboratory sample to determine whether the methodology is in control, and whether the laboratory is capable of making accurate measurements at the required method detection limit and higher.

3.9 Laboratory Sample

A portion of a sample received from the field for testing.

3.10 Limit of Detection (LOD)

The LOD is the lowest concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. If required, the LOD may be determined in several ways, including signal-to-noise ratio and statistical calculations.

3.11 Limit of Quantitation (LOQ)

The LOQ for a dataset is the lowest concentration (LLOQ) or highest concentration (ULOQ) that can be reliably achieved within the specified limits of precision and accuracy during routine operating conditions.

Note: For many analytes, the LLOQ analyte concentration is selected as the lowest non-zero standard in the calibration curve to simplify data reporting. Sample LLOQs are matrix-dependent.

3.12 Matrix Spike (MS)

A matrix spike is an aliquot of a sample, to which known quantities of target analytes are added in the laboratory. The MS is extracted and analyzed exactly like a laboratory sample to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS corrected for background concentrations.

3.13 Method Blank

An aliquot of ASTM Type I water that is treated exactly like a laboratory sample including exposure to all glassware, equipment, solvents, and reagents that are used with other laboratory samples. The method blank is used to determine if test substances or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.14 Method Detection Limit (MDL) Determination

A MDL is the statistically calculated minimum amount of an analyte that can be measured with 99% confidence that the reported value is greater than zero. One of several processes that may be used to establish a LOD value is found in 40 CFR Part 136 Appendix B.

3.15 Sample

A sample is a small portion collected from a larger quantity of material intended to represent the original source material.

3.16 Spiking Stock Standard (SSS)

A solution prepared from stock standards used to prepare the working standard.

3.17 Stock Standard (SS)

A concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound.

3.18 Working Standard (WS)

A solution of several analytes prepared in the laboratory from SSs and diluted as needed to prepare calibration standards and other required analyte solutions.

4 Warnings and Cautions

4.1 Health and Safety

The acute and chronic toxicity of the standards for this method have not been precisely determined; however, each should be treated as a potential health hazard.

Unknown samples may contain high concentrations of volatile toxic compounds. Sample containers should be opened in a hood and handled with gloves to prevent exposure.

The laboratory is responsible for maintaining a safe work environment and a current awareness of local regulations regarding the handling of the chemicals used in this method. A reference file of material safety data sheets (MSDS) should be available to all personnel involved in these analyses.

4.2 Cautions

None

5 Interferences

During extraction and analysis, major potential contaminant sources are reagents and solid phase extraction devices.

All materials used in the analyses shall be demonstrated to be free from interferences under conditions of analysis by running method blanks.

Parts and supplies that contain Teflon® should be avoided due to the possibility of interference and/or contamination. These may include, but are not limited to: wash bottles, Teflon® lined caps, autovial caps, HPLC parts, etc.

The use of disposable micropipettes or pipettes to aliquot standard solutions is recommended to make calibration standards and matrix spikes.

6 Instrumentation, Supplies, and Materials

Note: Brand names, suppliers, and part numbers are for illustrative purposes only. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory performing the analysis.

6.1 Instrumentation

Balance, analytical (display at least 0.0001g), Mettler

HPLC/MS/MS or HPLC/MS system, as described in Section 10.

6.2 Supplies and Materials.

Sample collection bottles—LDPE (e.g., Nalgene™) narrow-mouth bottles with screw cap. **Note:** Do not use Teflon bottles or Teflon lined caps.

Coolers for sample shipment.

Ice for sample shipment.

Vacuum pump, Bűchi.

Visiprep vacuum manifold, Supelco.

Sep Pak Vac 6cc (1g) tC18 cartridges (part # WAT 036795),Waters.

50mL disposable polypropylene centrifuge tubes, VWR.

15mL disposable polypropylene centrifuge tubes, VWR.

Disposable micropipettes (50–100µL, 100–200µL), Drummond.

Class A pipettes and volumetric flasks, various.

Hypercarb drop-in guard column (4mm) (part # 844017–400), Keystone.

Stand-alone drop-in guard cartridge holder, Keystone.

125mL LDPE narrow-mouth bottles, Nalgene.

2mL clear HPLC vial kit (cat # 5181–3400), Agilent/Hewlett Packard.

Standard lab equipment (graduated cylinders, disposable tubes, etc.), various.

7 Reagents and Standards

Note: Suppliers and catalog numbers are for illustrative purposes only. Equivalent performance may be achieved using chemicals obtained from other suppliers. Do not use a lesser grade of chemical than those listed.

7.1 Chemicals

Methanol (MeOH), HPLC grade, JT Baker, Catalog No. JT9093–2.

Ammonium Acetate, Reagent grade, Sigma-Aldrich, Catalog No. A–7330.

ASTM Type I Water, prepared in-house.

Sodium Thiosulfate, Reagent grade, JT Baker.

7.2 Standards

Potassium perfluorooctane sulfonate

Perfluorooctane sulfonylamide

Ammonium perfluorooctanoate

Others as required.

7.3 Reagent Preparation

250mg/mL sodium thiosulfate solution — Dissolve 25g of sodium thiosulfate in 100mL reagent water.

40% methanol wash solution – Measure 400mL methanol and adjust volume to 1.0L with reagent water.

100mM ammonium acetate solution (Analysis)—Weigh 7.71g of ammonium acetate and dissolve in 1.0L of reagent water. Dilute the 100mM solution by a factor of 50 to make the 2mM ammonium acetate solution used for mobile phase A.

Note: Alternative volumes may be prepared as long as the ratios of the solvent to solute ratios are maintained.

7.4 Spiking Stock Standard (SSS) Preparation

The following standard preparation procedure serves as an example and may be changed to suit the needs of a particular study. For example, µL volumes may be spiked into volumetric flasks when diluting stock solutions to appropriate levels.

100µg/mL each PFOS, PFOSA, and POAA SSSs—Weigh out 10mg of analytical standard (corrected for percent salt and purity—i.e., 10 mg $C_8F_{17}SO_3K$ purity 90% = 8.35mg $C_8F_{17}SO_3^-$) and dilute to 100mL with methanol in a 100mL volumetric flask. Transfer to a 125mL LDPE bottle or other suitable container. Prepare a separate solution for each analyte. Solutions may be stored in a refrigerator at 4°±2°C for a maximum period of 6 months from the date of preparation.

1µg/mL mixed SSS—Add 1.0mL each of the 100µg/mL SSSs (from 7.4.1) to a 100mL volumetric flask and bring up to volume with methanol.

0.1µg/mL mixed SSS—Add 10.0mL of the 1.0µg/mL-mixed solution (from 7.4.2) to a 100mL volumetric flask and bring up to volume with methanol.

0.01µg/mL mixed SSS—Add 10.0mL of the 0.1µg/mL-mixed solution (from 7.4.3) to a 100mL volumetric flask and bring up to volume with methanol.

Storage Conditions—Store all SSSs in a refrigerator at 4°±2°C for a maximum period of 6 months from the date of preparation.

7.5 Calibration Standards

The following standard preparation procedure serves as an example and may be changed to suit the needs of a particular study, provided the concentrations are calculated correctly.

100µg/mL each PFOS, PFOSA, and POAA stock standard solutions—Weigh out 10mg of analytical standard (corrected for percent salt and purity) and dilute to 100mL with methanol in a 100mL volumetric flask. Transfer to a 125mL LDPE bottle or other suitable container. Prepare a separate solution for each analyte. Store solutions in a refrigerator at 4°±2°C for a maximum period of 6 months from the date of preparation.

1µg/mL Working Standard—Add 1.0mL each of the 100µg/mL SS solutions (from 7.5.1) to a 100mL volumetric flask and bring up to volume with methanol.

0.1µg/mL Working Standard —Add 10.0mL of the 1.0µg/mL mixed solution (from 7.5.2) to a 100mL volumetric flask and bring up to volume with methanol.

0.01µg/mL Working Standard —Add 10.0mL of the 0.1µg/mL mixed solution (from 7.5.3) to a 100mL volumetric flask and bring up to volume with methanol.

Storage Conditions—Store all WSs in a refrigerator at 4°±2°C for a maximum period of 6 months from the date of preparation.

Calibration Standard—Prepare calibration solutions in ASTM Type I using the following table as a guideline:

Concentration of WS, µg/mL	Volume of WS, µL	Final Calibration Standard Volume, mL , of ASTM Type I Water	Final Concentration of Calibration Standard, pg/mL, in ASTM Type I Water
0.0	0	40	0
0.010	100	40	25
0.010	200	40	50
0.010	400	40	100
0.10	100	40	250
0.10	200	40	500
0.10	300	40	750
0.10	400	40	1000
1.0	100	40	2500
1.0	400	40	10000
1.0	1000	40	25000

The standards are processed through the extraction procedure (Section 11), identical to the laboratory samples. The concentration of the calibration standard in the final extract is equal to 8X the initial concentration, due to the concentration of the standard during the extraction process.

Storage Conditions—Store all extracted calibration standards in 15mL polypropylene tubes at 4°±2°C, for a maximum period of two weeks from the date of preparation

8 Sample Collection and Handling

Note: Sampling equipment, including automatic samplers, must be free of Teflon tubing, gaskets, and other parts that may leach interfering analytes into the water sample. Automatic samplers that composite samples over time should use refrigerated polypropylene sample containers if possible. Sample bottles should not be rinsed before sample collection.

Labeling: Each sample bottle must display information regarding the collection of that sample, the individual collecting the sample, and any matrix spike that has been added to the sample.

This includes the volume and concentration of any spiking solution added and the volume and identification of any preservatives added in the field.

Spiking: The spiking scheme will be clearly outlined in the sampling plan, including whether the samples will be spiked in the field or in the laboratory prior to the shipment of the bottles to the site. If spiking is to be performed in the field, materials and specific instructions will be included in the sampling kit. Be sure to clearly label each bottle with spiking information if applicable.

Tap Water: Open the tap and allow the system to flush until the water temperature (15°±10°C) has stabilized (usually about two minutes). Adjust the flow to about 500mL/min and collect samples from the flowing stream.

Ground Water: Purge the well of standing water using a pump or a bailer. Collect the sample directly from the pump or from the bailer.

Surface Water: When sampling from an open body of water, fill the sample container with water from a representative area.

Sample Dechlorination: All samples should be iced or refrigerated at 4°±2°C and kept in the dark from the time of collection until extraction. Residual chlorine should be eliminated by adding 200µL of a 250mg/mL sodium thiosulfate solution to each tap-water sample and associated FB and FSCS (which may be placed in each bottle before leaving for the sampling site or done in the field.).

Holding Time (HT): Results of the time/storage study of all target analytes showed that the three compounds are stable for 14 days in water samples when the samples are dechlorinated and stored as described in the previous section (see also references in section 17). Therefore, laboratory samples must be extracted within 14 days and the extracts analyzed within 30 days of sample collection. If the HT exceeds 14 days, great care is used when evaluating field spikes to avoid misrepresentation of the sample concentration.

8.1 Field Blanks

Process a Field Blank Control Sample (FB) along with each sample set (samples collected from the same general sample site at approximately the same time). At the laboratory, prior to sample collection, fill a sample container with ASTM Type I water, seal, and ship the FB to the sampling site along with the empty sample containers. Return the FB to the laboratory with the filled sample bottles.

When sodium thiosulfate is added to samples, use the same procedure to preserve the FB.

8.2 Field Duplicates

Collect a Field Duplicate (FD) for every ten (10) samples collected or per each sampling set, if less than 10 samples are collected.

Separate FDs must be collected for each type of water sample (ground, tap, etc.) collected.

Collect the FD immediately after the sample.

Preserve, store and ship FD using the same procedures as used for the samples.

8.3 Field Spike Control Sample (FSCS)

A Field Spike Control Sample (FSCS) must be prepared for each sample shipment. If multiple coolers are used to ship a set of samples, each cooler must contain a FSCS.

At the laboratory, fill a sample container with 100mL of ASTM Type I water. Seal and ship to the sampling site along with the empty sample containers and FBs. Samples may either be spiked in the field or in the laboratory prior to shipment. The method employed should be consistent throughout the study. If the samples are to be spiked in the field, be sure to send appropriate supplies and instructions for the field personnel to follow.

Seal and gently invert the FSCS to mix. Store and ship the FSCS using the same procedures as used for the samples

Provide information on sample collection, preservation, shipment and storage. List applicable holding times. Include sample stability and extract storage requirements. Reference the method used for sample preparation, if applicable.

8.4 Field Matrix Spike (FMS)

A Field Matrix Spike (FMS) must be prepared for each sampling location. One unspiked sample from the same location must accompany the FMS to determine endogenous levels in the sample. The samples should be clearly identifiable as being from the same location.

Samples may either be spiked in the field or in the laboratory prior to shipment. The method employed should be consistent throughout the study. If the samples are to be spiked in the field, be sure to send appropriate supplies and instructions for the field personnel to follow.

9 Quality Control and Data Quality Objectives

Analytical results of the FB, FMS, FD, and FSCS should be evaluated at the conclusion of the study to help interpret the quality of sample data. Analytical results for these control/duplicate samples must be reported with the sample data.

9.1 Solvent Blanks

Solvent blanks are analyzed with each sample set to determine contamination or carryover. Aliquots of methanol represent the solvent used for the standard curve and the sample extraction. Solvent blanks should have area counts that are less than 50% of the area count of the lowest calibration standard.

Solvent blanks should be analyzed prior to and following each calibration curve, each set of system suitability samples, and after no more than 10 unknown sample extracts. If instrument carryover is a problem consecutive solvent blanks may be necessary. In this case the area counts of the solvent blanks should return to <50% of the lowest calibration standard prior to the injection of further standards or samples.

9.2 Method Blanks

A method blank consists of an aliquot of ASTM Type I water, equal in volume to the samples, and extracted in the same manner as the samples. At least two method blanks should be prepared and analyzed each day that extractions are performed for a particular study or project. When analyzed the area counts of these samples must be less than 50% of the area count of the lowest calibration standard.

9.3 Sample Replicates

All samples, including field spikes, trip blanks, etc., should be extracted at least in duplicate, and in triplicate if difficulties were encountered in the sampling and/or holding conditions of the samples. The relative percent difference (RPD) of duplicate samples or relative standard deviation (RSD) should be less than 15% for the precision of sample preparation and analysis to be considered in control.

9.4 Matrix Spike

Matrix spikes are prepared for each sample type and analyzed to determine the matrix effect on the recovery efficiency. Matrix spike recoveries should fall within ± 25% of expected values. If the matrix spikes fail, evaluate the lab control spikes. If the LCS are within acceptance criteria there may be matrix issues in the samples. Discuss these in the final report.

Matrix spike duplicates are prepared periodically to measure the precision associated with the analysis.

Analyze a matrix spike and matrix spike duplicate (if prepared) in the same run as the original sample.

Matrix spike and matrix spike duplicate concentrations should fall in the mid-range of the initial calibration curve or should be prepared at 1.5-5 times the endogenous concentration of the analyte. Spike concentrations should fall in the low-range of the initial calibration curve if extremely low-levels are expected. Generally two or more levels are prepared, one in the low range of the curve and one in the mid-range. This avoids the need to pre-screen unknown samples prior to preparation.

9.5 Laboratory Control Spike

Lab control spikes are prepared for each study to ensure recovery of the target analytes. These should be prepared at a minimum of 2 levels and in duplicate or triplicate. Recovery of these samples should be within ± 25% of expected values, and the RPD (or RSD) be ≤ 15%. If recoveries fall outside these limits the samples should be addressed in the final report.

10 Calibration and Standardization

10.1 Instrument Setup

Note: In this example, a MicroMass Ultima™ Liquid Chromatography Tandem Mass Spectrometer (LC/MS/MS) is used. Other brands of LC/MS/MSs as well as single quadrupole mass spectrometers (LC/MS) may be used as long as the method criteria are met. Brand names, suppliers, part numbers, and models are for illustrative purposes only. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory. The operator must optimize and document the equipment and settings used.

Establish the LC/MS/MS system and operating conditions equivalent to the following:

Mass Spec: Micromass Ultima (Micromass)

Interface: Electrospray (Micromass)

Mode: Electrospray Negative, Multiple Response Monitoring (MRM)

Harvard infusion pump (Harvard Instruments), for tuning

Computer: COMPAQ Professional Workstation AP200

Software: Windows NT, MassLynx 3.3

HPLC: Hewlett Packard (HP) Series 1100

HP Quaternary Pump

HP Vacuum Degasser

HP Autosampler

HP Column Oven

Note: A 4 × 10mm Hypercarb drop-in guard cartridge (Keystone, part # 844017–400) may be attached on-line after the purge valve and before the sample injector port to trap any residue contaminants that may be in the mobile phase and/or HPLC system.

HPLC Column: Genesis C8 (Jones Chromatography), 2.1mm x 50mm, 4µm

Column Temperature: 35°C

Injection Volume: 15µL

Mobile Phase (A): 2mM Ammonium Acetate in ASTM Type I water (See 7.3.1)

Mobile Phase (B): Methanol

Time, min	Percent Mobile Phase A	Percent Mobile Phase B	Flow Rate, mL/min
0.0	60	40	0.3
0.4	60	40	0.3
1.0	10	90	0.3
7.0	10	90	0.3
7.5	0	100	0.3
9.0	0	100	0.4
9.5	60	40	0.4
13.5	60	40	0.4
14.0	60	40	0.3

Note: Other HPLC gradients may be used as long as the method criteria are met.

It may be necessary to adjust the HPLC gradient in order to optimize instrument performance. Columns with different dimensions (e.g. 2.1mm x 30mm) and columns from different manufacturers (Keystone Betasil C18 etc.) may be used.

Ions Monitored:

Analyte	Primary Ion	Product Ion	Approximate Retention Time (minutes)
PFOA	413	169	5.0
PFOS	499	99	5.2
FOSA	498	78	5.8

Other product ions may be chosen at the discretion of the analyst, although m/z 99 is suggested for PFOS. Use of the suggested primary ion is recommended. Retention times may vary slightly, on a day-to-day basis, depending on the batch of mobile phase etc. Drift in retention times is acceptable within an analytical run, as long as the drift continues through the entire analysis and the standards are interspersed throughout the analytical run.

10.2 Tune File Parameters

The following values are provided as an example. Actual values may vary from instrument to instrument. Also, these values may be changed from time to time in order to optimize for greatest sensitivity.

Analyte	Dwell, sec	Collision Energy, eV	Cone, V
PFOA	0.2–0.4	10–25	20–30
PFOS	0.2–0.4	30–60	50–80
FOSA	0.2–0.4	20–50	30–60

Source	Set
Capillary	2.6–3.5kV
Hexapole 1	0.5V
Aperture 1	0.2V
Hexapole 2	0.8V
Source Block Temp.	100–150°C
Desolvation Temp.	250–400°C

Analyzer	Set
LM Res 1	12.5–15.0V
HM Res 1	12.5–15.0V
IEnergy 1	0.7V
Entrance	–2V
Exit	1V
LM Res 2	11.0V
HM Res 2	11.0V
IEnergy 2	1.0V
Multiplier	650V

Gas Flows	Set
Cone Gas	150L/hr
Desolvation	700L/hr

Pressures	Set
Gas Cell	3.0e–3mbar

10.3 Calibration Curve

Analyze the standard curves prior to each set of samples. The validated method specifies that the standard curve should be plotted using a linear fit, weighted 1/x or unweighted. However, the standard curve may also be plotted by quadratic fit ($y = ax^2 + bx + c$), weighted 1/x or unweighted, using suitable software. The calibration curves may include but should not be forced through zero. The mathematical method used to calculate the calibration curve should be applied consistently throughout a study. Any change should be thoroughly documented in the raw data.

If the calibration curve does not meet acceptance criteria perform routine maintenance or prepare a new standard curve (if necessary) and reanalyze.

For purposes of accuracy when quantitating low levels of analyte, it may be necessary to use the low end of the calibration curve rather than the full range. For example, when attempting to quantitate approximately 50 pg/mL of analyte, generate a calibration curve consisting of the standards from 25 pg/mL to 1000 pg/mL rather than the full range of the curve (25 pg/mL to 25000 pg/mL). This will reduce inaccuracy attributed to linear regression weighting of high concentration standards.

High and/or low points may be excluded from the calibration curves to provide a better fit over the linear range appropriate to the data or because they did not meet the pre-determined acceptance criteria. Low-level curve points should also be excluded if their area counts are not at least twice that of the method and/or solvent blanks. Any curve point may be rejected due to a bad injection or failing to meet accuracy requirements of ± 25% (and ± 30% for the LLOQ). Justification for exclusion of calibration curve points will be noted in the raw data. A minimum of 6 points will be used to construct the calibration curve.

10.4 Continuing Calibration Verification (CCV)

Continuing calibration verifications (CCV) are analyzed to verify the accuracy of the calibration curve. Analyze a mid-range calibration standard, one of the same standards used to construct the calibration curve, at a minimum after every tenth sample, not including solvent blanks, with a minimum of one per sample set. Calibration verification injections must be within ±25% to be considered acceptable. The calibration curve and the last passing CCV will then bracket acceptable samples. Multiple CCV levels may be used.

10.5 System Suitability

A minimum of three system suitability samples will be injected at the beginning and end of each analytical run. Typically these samples are run prior to the calibration curve. The system suitability injections must have area counts with an RSD of ≤5% and a retention time RSD of ≤2% when evaluated independently.

11 Procedures

11.1 Extraction Scheme

Allow samples to equilibrate to room temperature. Thoroughly mix samples by gently inverting the sample bottle.

Measure 40mL of sample into 50mL polypropylene centrifuge tubes (Spike the Matrix spikes as required*, replace lid and mix well).

Note: * Samples may need to be prescreened to determine an appropriate matrix spike level (typically 50–150% of sample concentration). Alternatively the samples could be spiked at more than one level, allowing for the inappropriate spike level to be eliminated.

Condition the C18 SPE cartridges (1g, 6mL) by passing approximately 10mL methanol followed by approximately 50mL ASTM Type I water (flow rate approximately 2 drop/sec). Do not let column run dry.

Note: For the following steps, maintain a ~1drop/sec flow rate. Do not allow the column to run dry at any time.

Load the analytical sample onto the C18 SPE cartridge. Discard eluate.

Ten mL of the 40% methanol in water wash mixture is passed through the C18 SPE cartridge to rinse away potential interferences and then discarded. This step must be omitted if perfluorinated compounds with chain lengths less than C8 are targeted since these will be lost during this wash step.

Elute with exactly 5mL of 100% methanol. Collect eluate into graduated 15mL polypropylene centrifuge tubes. This is the target elution fraction (final volume approximately 4.5 mL as not all of the solvent will leave the SPE column. This will not affect the calculations in any way since the curve is also extracted).

Analyze a portion of the target elution fraction eluent using negative electrospray HPLC/MS/MS or HPLC/MS.

Note: Samples are concentrated by a factor of eight during the extraction; Initial Vol = 40mL → Final Vol. = 5mL.

Samples are stable at room temperature for at least 24 hours. Analytical samples may be stored in a refrigerator at 4°±2°C until analysis.

Standardization of C18 SPE columns—If poor recoveries are observed, it may be necessary to standardize the C18 SPE columns in the following manner before analyzing samples.

Use a standard with an analyte concentration between 1000 and 4000 pg/mL. Repeat the extraction scheme from the beginning up through the eluting with ~5mL 100% methanol.

After the eluting with ~5mL 100% methanol step, collect an additional post-elution fraction by eluting with an additional 5mL of 100% methanol.

Analyze both fractions by HPLC/MS/MS or HPLC/MS. If the target fraction contains a minimum of 85% of the respective analytes, it may be considered acceptable.

If the wash contains significant standard (>15%), either the wash volume or percentage of MeOH should be decreased.

If the post-elution fraction contains significant standard (>15%), the target elution volume should be increased.

11.2 Sample Analysis

Set up analysis sample queue.

Inject the same volume (between 5–25µL) of each standard, analytical sample and blank into the instrument.

All samples with a concentration > ULOQ must be diluted and reanalyzed. If dilution of the final extract fails to produce acceptable results (e.g. poor MS recoveries) dilute the original sample and re-extract.

12 Data Analysis and Calculations

Calculate the analytical sample (extract) concentration from the standard curve using the following equation:

Extract Concentration, pg/mL = (Peak area – intercept)
(slope)

Calculate the percent recovery of the FSCS using the following equation:

FSCS % rec. = (FSCS conc., pg/mL) x 100
(Conc. added, pg/mL)

Calculate the percent recovery of the MSs using the following equation:

MS % rec. = (MS conc., pg/mL – Sample conc., pg/mL) x 100
(Conc. added, pg/mL)

13 Method Performance

Note: Any method performance parameters that are not achieved must be considered in the evaluation of the data. Nonconformance to any specified parameters must be described and discussed in any reporting of the data.

If criteria listed in this method performance section are not met, maintenance may be performed on the system and samples reanalyzed, or other actions taken as determined by the analyst. Document all actions in the raw data.

If data are to be reported when performance criteria have not been met, the data must be footnoted on tables and discussed in the text of the report.

13.1 System Suitability

A minimum of three system suitability samples will be injected at the beginning and end of each analytical run. Typically these samples are run prior to the calibration curve. The system suitability injections must have area counts with an RSD of ≤5% and a retention time RSD of ≤2% when evaluated independently.

13.2 Quantitation

Calibration Curve: The coefficient of determination (r^2) value for the calibration curve must be greater than or equal to 0.990. Each point in the curve must be within ±25% of the theoretical concentration with the exception of the LLOQ, which may be within ±30%.

Demonstration of Specificity: Specificity is demonstrated by chromatographic retention time (within 3% of standard) and the mass spectral response of unique ions.

13.3 Sensitivity

Solvent Blanks and Method Blanks: Solvent and method blank area counts must be < 50% that of the lowest standard used in the calibration curve.

Limits of Quantitation (LOQ): The lower LOQ (LLOQ) is the lowest non-zero active standard in the calibration curve; the peak area of the LLOQ must be at least 2X that of the extraction blank. By definition, the measured value of the LLOQ must be within 30% of the theoretical value.

13.4 Accuracy

CCV Performance: Calibration verification injections must be within ±25% to be considered acceptable. The calibration curve and the last passing CCV will then bracket acceptable samples. Multiple CCV levels may be used.

Matrix Spikes: Matrix spike percent recoveries must be within ± 25% of the spiked concentration. If matrix effects are suspected, evaluate the LCS results to determine if a matrix effects are present and if the method is in control based on compliant LCS results. Discuss all results in the analytical report.

13.5 Precision

Reproducibility: Reproducibility of the method is defined by the results of duplicate or triplicate analysis of samples. A RPD or RSD of ≤ 15% will be considered acceptable.

System Suitability: The system suitability injections must have area counts with an RSD of ≤5% and a retention time RSD of ≤2% when evaluated independently.

14 Pollution Prevention and Waste Management

Sample extract waste and flammable solvent is discarded in high BTU containers, and glass pipette waste is discarded in broken glass containers located in the laboratory.

15 Records

Each data package generated for a study must have the following information included: study or project number, acquisition method, integration method, sample name, extraction date, dilution factor (if applicable), and analyst.

Print the tune page, sample list, and acquisition method to include in the appropriate study folder. Copy these pages and tape into the instrument run log.

Plot the calibration curves as described in this method, then print these graphs and store in the study folder.

Print data integration summary, integration method, and chromatograms and store in the study folder.

Summarize data using suitable software and store in the study folder.

16 Attachments

None.

17 References

"Method of Analysis for the Determination of Perfluorooctane sulfonate (PFOS), Perfluorooctane sulfonylamide (PFOSA), and Perfluorooctanoate (POAA) in Water", E. Wickremesinhe and J. Flaherty, Study Number 023–002, Centre Analytical Laboratories, Inc., State College, Pennsylvania, January 2000.

Validation report for the "Method of Analysis for the Determination of Perfluorooctane sulfonate (PFOS), Perfluorooctane sulfonylamide (PFOSA), and Perfluorooctanoate (POAA) in Water", E. Wickremesinhe and J. Flaherty, Study Number 023–002, Centre Analytical Laboratories, Inc., State College, Pennsylvania.

18 Affected Documents

None.

19 Revisions

Revision Number	Revision Number	Revision Date
1	*Updated to the new format. Changed Title.* *Section 1: States the validation of 3 analytes, removes reference to EPA document that's no longer applicable.* *Section 2: Provided for the extraction of more than the 3 validated analytes, allows the use of a LC/MS system, not only the LS/MS/MS previously mentioned.* *Section 3: Revised definitions for field matrix spike, field control spike, LLOQ, method blank, and MDL.* *Section 5: Reworded the interferences, added recommendation to use disposable pipettes.* *Section 6: Recategorized and pared down.* *Section 7: Changed storage time to 6 months. Added more calibration points to the table.* *Section 8:Added statement addressing labeling requirements and spiking procedures. Expanded section 8.8.* *Section 9: New Section* *Section 10: Changed some of the parameters in the tables. Allowed for use of different instrumentation. Added information from section 12 of previous version, extensively revised.* *Section 11 (section 9 in previous version): Clarification of wash step, stated exact volume of eluate is 5 mL, revised standardization process, removed requirement to use LC/MS/MS.* *Section 12 (section 13 in previous version: no changes* *Section 13 (section 14 in previous version): Extensively rewritten.* *Section 14 (section 15 in previous version): no changes* *Section 15 (section 16 in previous version): Minor changes to recording requirements.* *Section 16 (section 17 in previous version): Removed attachment.* *Section 17 (section 18 in previous version): Removed reference to EPA document that no longer applied to this SOP.* *Section 18: New section.*	7

ATTACHMENT C: PROTOCOL AND PROTOCOL AMENDMENTS

Exygen Protocol Number: P0001131

STUDY PROTOCOL

Study Title:

Analysis of Perfluorobutanesulfonate (PFBS), Perfluorohexanesulfonate (PFHS), and Perfluorooctanesulfonate (PFOS) in Water, Soil, Sediment, Fish, Clams, Vegetation, Small Mammal Liver and Small Mammal Serum Using LC/MS/MS for the 3M Decatur Monitoring Program

Exygen Protocol Number: P0001131

Performing Laboratory:
Exygen Research
3058 Research Drive
State College, PA 16801
Phone: (814) 272-1039

Sponsor Representative:
Michael A. Santoro
Director of Regulatory Affairs
3M Building 0236-01-B-10
St. Paul, MN 55144
Phone: (651) 733-6374

Exygen Protocol Number: P0001131

DISTRIBUTION:

1) Jaisimha Kesari, Study Director, Weston Solutions

2) John M. Flaherty, Principal Investigator, Exygen Research

3) Michael A. Santoro, Sponsor Representative, 3M Company

4) Exygen Research Quality Assurance Unit

Exygen Protocol Number: P0001131

PROTOCOL APPROVAL

Study Title: Analysis of Perfluorobutanesulfonate (PFBS), Perfluorohexanesulfonate (PFHS), and Perfluorooctanesulfonate (PFOS) in Water, Soil, Sediment, Fish, Clams, Vegetation, Small Mammal Livers and Small Mammal Serum Using LC/MS/MS for the 3M Decatur Monitoring Program

Exygen Protocol Number: P0001131

APPROVALS

Jaisimha Kesari, Study Director
Weston Solutions — 11/5/04 Date

Michael A. Santoro, Sponsor Representative
3M Company — 11/11/04 Date

John M. Flaherty, Principal Investigator
Exygen Research — 10/29/04 Date

Richard A. Grazzini, President, Facility Management
Exygen Research — 29-OCT-2004 Date

Lydia Shaffer, Technical Lead, Quality Assurance Unit
Exygen Research — 10/29/04 Date

Exygen Protocol Number: P0001131

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Exygen Protocol Number: P0001131

INTRODUCTION

The purpose of this study is to perform analysis for perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHS) and perfluorooctanesulfonate (PFOS) in water, soil, sediment, fish, clams, vegetation, small mammal livers and small mammal serum using LC/MS/MS for the 3M Decatur Monitoring Program.

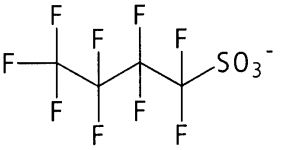
The study will be audited for compliance with EPA TSCA Good Laboratory Practice Standards 40 CFR 792 by the Quality Assurance Unit of Exygen Research.

TEST MATERIALS

The test materials are perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHS) and perfluorooctanesulfonate (PFOS) and are all supplied by 3M.

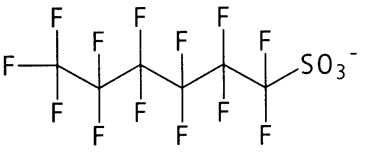
PFBS

Chemical Name: Perfluorobutanesulfonate
Molecular Weight: 338 supplied as the potassium salt ($C_4F_9SO_3^-K^+$)
Lot Number: 101
Purity: 96.7%
Transitions Monitored: 299 → 99
Structure:



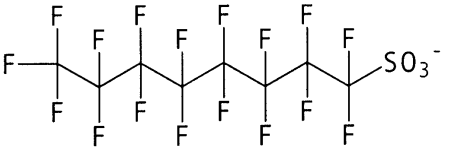
PFHS

Chemical Name: Perfluorohexanesulfonate
Molecular Weight: 438 supplied as the potassium salt ($C_6F_{13}SO_3^-K^+$)
Lot Number: SE036
Purity: 98.6%
Transitions Monitored: 399 → 80
Structure:



PFOS

Chemical Name: Perfluorooctanesulfonate
Molecular Weight: 538 supplied as the potassium salt ($C_8F_{17}SO_3^-K^+$)
Lot Number: 217
Purity: 86.9%
Transitions Monitored: 499 → 99
Structure:



OBJECTIVE

The purpose of this study is to perform analysis for perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHS) and perfluorooctanesulfonate (PFOS) in water, soil, sediment, fish, clams, vegetation, small mammal livers and small mammal serum for the 3M Decatur Monitoring Program using the current versions of the following Exygen analytical methods:

V0001780: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Water by LC/MS/MS"
V0001781: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Soil by LC/MS/MS"
V0001782: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Sediment by LC/MS/MS"
V0001783: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Fish and Clams by LC/MS/MS"
V0001784: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Vegetation by LC/MS/MS"
V0001785: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Small Mammal Liver by LC/MS/MS"
V0001786: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Small Mammal Serum by LC/MS/MS"

TESTING FACILITY

Exygen Research
3058 Research Drive
State College, PA 16801
Phone: (814) 272-1039

Exygen Protocol Number: P0001131

STUDY DIRECTOR

Jaisimha Kesari P.E., DEE
Weston Solutions, Inc.
1400 Weston Way
West Chester, PA 19380
Phone: (610) 701-3761
Fax: (610) 701-7401
j.kesari@westonsolutions.com

SPONSOR REPRESENTATIVE

Michael A. Santoro
3M Company
Director of Regulatory Affairs
3M Building 0236-01-B-10
St. Paul, MN 55144
Phone: (651) 733-6374

PRINCIPAL INVESTIGATOR

John M. Flaherty
Exygen Research
3058 Research Drive
State College, PA 16801
Phone: (814) 272-1039
john.flaherty@exygen.com

PROPOSED EXPERIMENTAL START AND TERMINATION DATES

It is proposed that the analytical portion of this study be conducted from October 01, 2004 to December 31, 2005. The actual experimental start and termination dates will be included in the final report.

IDENTIFICATION AND JUSTIFICATION OF THE TEST SYSTEM

The following are the test systems for this study:

- Water (groundwater and surface water)
- Soil
- Sediment
- Fish
- Clams
- Vegetation
- Small Mammal Liver
- Small Mammal Serum

The samples will be collected by Weston Solutions. The control samples will be purchased and prepared by the testing facility. Purchase and processing details for the control samples will be included in the final report associated with this study.

The test systems were chosen to access the environmental impact of PFBS, PFHS and PFOS in the Decatur, Alabama area.

SAMPLE PROCUREMENT, RECEIPT AND RETENTION

Water, soil, sediment, fish, clam, vegetation, small mammal liver and small mammal serum samples will be received at Exygen directly from Weston Solutions. The details of sample procurement for this study are outlined in the 3M work plan entitled "Phase 2 Work Plan for Sampling Environmental Media." The number and types of samples collected will vary depending availability in the field. The total number of samples received and analyzed for each matrix will be documented in the final report associated with this study.

Water, soil, and sediment samples will be used as received without further processing at Exygen. These samples will be stored refrigerated at 2°C-8°C. Fish, clam, vegetation and small mammal liver samples will be processed according to the appropriate analytical method (see Appendix I). These samples will be stored frozen at ≤ -10°C. Small mammal whole blood samples will be centrifuged in the field at the time of collection and the serum fraction will be used for the study. Small mammal serum will be stored frozen at ≤ -10°C.

The receipt and processing of the samples will be documented in the final report and raw data associated with the study.

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SAMPLE IDENTIFICATION

Prior to analysis, each sample will be assigned a laboratory sample reference number. The reference number will be unique and will distinguish each laboratory sample that is processed throughout the analytical procedure. Chromatographic data will be identified by the laboratory sample reference number.

Sample storage conditions and locations will be documented throughout the study.

ANALYTICAL PROCEDURE SUMMARY

References:

V0001780: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Water by LC/MS/MS"

V0001781: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Soil by LC/MS/MS"

V0001782: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Sediment by LC/MS/MS"

V0001783: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Fish and Clams by LC/MS/MS"

V0001784: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Vegetation by LC/MS/MS"

V0001785: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Small Mammal Liver by LC/MS/MS"

V0001786: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Small Mammal Serum by LC/MS/MS"

The above methods use analytical conditions capable of separating the isomers of PFBS, PFHS and PFOS. The final report will include the isomers summed into total PFBS, total PFHS, and total PFOS found.

VERIFICATION OF ANALYTICAL PROCEDURE

A laboratory control sample will be used for the preparation of fortified control samples. The test substance will be made into solutions as per the method, and added to the matrices via a micropipette.

For water sampling, Exygen will supply one bottle per sample collected. The bottles will be 500 mL precleaned Sci/Spec Premier wide mouth HDPE bottles. These bottles have been routinely used for fluorochemical sample

collection at the testing facility and have been shown to be free of PFBS, PFHS and PFOS. Samples will be added to each container to a volumetric fill line at 200 mL. A field duplicate, a low field spike and a high field spike of each sample will be collected. The low and high field spike bottles will contain PFBS, PFHS and PFOS as well as perfluorooctanoic acid (PFOA) and 1.2-13C perfluorooctanoic acid (^{13}C PFOA). PFOA and ^{13}C PFOA are included in the solutions used to spike the samples. The results for PFOA and ^{13}C PFOA will not be reported in this study. Exygen will supply one field blank (control water) and two field blank spikes (control water fortified with PFBS, PFHS and PFOS at a low and high level) for every twenty samples collected. At the testing facility, each water sample (excluding field duplicates and field spikes) will be extracted in duplicate and will also be fortified at a low and high concentration with PFBS, PFHS and PFOS and processed through the described procedure to determine method accuracy and to check for bias.

For soil, sediment, clams, and vegetation, Exygen will supply one 500 mL precleaned Sci/Spec Premier wide mouth HDPE bottle per sample collected or a zip-seal bag. All containers/bags used for sample collection will be shipped to the sample location. Samples will be added to each container or bag in the field. At the testing facility, each sample will be extracted in duplicate and will also be fortified at a known concentration with PFBS, PFHS and PFOS at both a low and high level and processed through the described procedure to determine method accuracy and to check for bias.

For small mammal liver, Exygen will supply a 50 mL polypropylene centrifuge tube. For small mammal serum, Exygen will supply a collection kit for each sample containing serum separator tubes (red top), vacutainers, needle holders and needles, transfer pipettes, and polypropylene tubes. At the testing facility, each liver and serum sample will be extracted in duplicate and will also be fortified at a known concentration with PFBS, PFHS and PFOS at both a low and high level and processed through the described procedure to determine method accuracy and to check for bias.

Low and high spiking levels for each matrix are defined below:

Matrix	Low Spiking Level	High Spiking Level
Water	500 ng/L	5000 ng/L
Soil	4 ng/g	40 ng/g
Sediment	4 ng/g	40 ng/g
Fish	10 ng/g	100 ng/g
Clams	10 ng/g	100 ng/g
Vegetation	10 ng/g	100 ng/g
Small Mammal Liver	10 ng/g	100 ng/g
Small Mammal Serum	10 ng/mL	100 ng/mL

Recoveries are anticipated to be between 70% and 130% of the fortified levels; however, the exact precision and accuracy will be determined by the analysis of the quality control samples described above. A statement of accuracy will be included in the final report.

METHOD FOR CONTROL OF BIAS

Control of bias will be addressed by taking representative sub-samples from a homogeneous mixture of each matrix from untreated control samples, and by analyzing at least two levels of fortifications.

STATISTICAL METHODS

Statistics will be limited to those specified in the subject methods and to the calculation of average recoveries, as applicable.

GLP STATEMENT

All aspects of this study shall be performed and reported in compliance with EPA TSCA Good Laboratory Practice Standards 40 CFR 792. The final report or data package (supplied to the Sponsor) shall contain a statement that the study was conducted in compliance with current and applicable GLP standards and will outline any deviations in the study from those standards. This statement will be signed by the Study Director and Sponsor Representative.

REPORT

A final report will be prepared by the principal investigator or their designee at the conclusion of the study. The report will include, but will not be limited to, the following:

- The name and address of the Study Director, Sponsor Representative, and of the testing facility.
- A statement of GLP compliance (any related documentation, such as chain-of-custody records, must be in the study records).

- The signed and dated statement by the Exygen Research Quality Assurance Unit regarding dates of study inspections and dates findings were reported to the Study Director and Management.
- A description of the exact analytical conditions employed in the study. If the subject method was followed exactly, it is necessary to include only a copy of the analytical method. Any modifications to this method will be incorporated into the report. If the method is photo-reduced, the project number and page number must be included on each page.
- Description of the instrumentation used and operating conditions.
- All results from all sets analyzed. Control and fortified samples will be identified and the data table will include sample number and fortification level.
- Representative chromatograms for each analyte in each matrix, including chromatograms of a standard and a control sample, and a chromatogram at a fortification level. The location of the analyte peaks will be clearly identified in all chromatograms.
- All circumstances that may have affected the quality or integrity of the data will be documented in the report.
- Locations where raw data and the final report are to be archived.
- Additions or corrections to the final report shall be in the form of an amendment signed by the Study Director. The amendment shall clearly identify that part of the report that is being altered and the reasons for the alterations. The amendment will be signed and dated by the Study Director and the Sponsor Representative.
- All applicable requirements for reporting of study results as per 40 CFR 792.185.

SAFETY AND HEALTH

- Laboratory personnel will practice good sanitation and health habits.
- Every reasonable precaution shall be taken to prevent inadvertent exposure of personnel and the environment to the test or reference substance(s).

AMENDMENTS TO PROTOCOL

All significant changes to the analytical protocol outlined here will be expressed in writing, signed and dated by the Study Director and Sponsor Representative. Amendments usually will be issued prior to initiation of study plan change. However, when a change is required without sufficient time for the issue of a written amendment, that change may be effected verbally with supporting documentation signed and dated by the Study Director and followed with a written amendment as soon as possible. In this case, the effective date of the written amendment will be the date of the documented change. Copies of the signed amendments will be appended to all distributed study plan copies. The original amendment will be maintained with the original study plan. Any deviations from the study plan or from the analytical method as provided will be documented and reported promptly to the Sponsor Representative.

DATA RECORD KEEPING

Records to be maintained include the following (as appropriate):

- Sample tracking sheet(s)
- Sample receipt records, storage history, and chains of custody
- History and preparation of standards (stock, fortification, calibration)
- Description of any modifications to the method
- Instrument run sheets, bench-sheets or logs
- Analytical data tables
- All chromatographic and instrumental conditions
- Sample extraction and analysis dates
- A complete listing of study personnel, signatures and initials
- Chronological presentation of all study correspondence
- Any other documentation necessary for the reconstruction of the study

Chromatograms- All chromatograms will contain the following:

- Sample identification, injection date, arrow or other indication of the area of interest, and injection number corresponding to the run.
- Additionally, fortifications will include the amount of analyte added and the sample number of the sample that was fortified.
- Analytical standard chromatograms will additionally include the concentration (e.g., µg/mL).

- As part of the documentation the following sheets will be included in each analytical set: a run sheet listing the samples to be run in the set, and an instrument conditions sheet describing the instrument type and operating conditions.

QUALITY ASSURANCE

The QA Unit of Exygen Research will inspect the study at intervals adequate to assure compliance with GLP's, and will report the findings of audits to the Study Director, Exygen Management, and the Sponsor Representative.

RETENTION OF DATA AND ARCHIVING

All hard copy raw data, including, but not limited to, the original chromatograms, worksheets, correspondence, and results shall be included with the data package submitted to the Study Director. These will be archived with the original study plan, amendments, final report, and all pertinent information from the Sponsor.

The testing facility shall keep all electronic raw data and any instrument, equipment, and storage logs for the period of time specified in 40 CFR 792.195. An exact copy of the materials submitted to the study director will also be kept at Exygen Research.

Exygen will obtain permission from the study director before discarding or returning samples.

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APPENDIX I

ANALYTICAL METHODS

V0001780: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Water by LC/MS/MS"
V0001781: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Soil by LC/MS/MS"
V0001782: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Sediment by LC/MS/MS"
V0001783: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Fish and Clams by LC/MS/MS"
V0001784: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Vegetation by LC/MS/MS"
V0001785: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Small Mammal Liver by LC/MS/MS"
V0001786: "Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Small Mammal Serum by LC/MS/MS"

Exygen Protocol Number: P0001131

ANALYTICAL METHOD
Method Number: V0001780

Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Water by LC/MS/MS

Analytical Testing Facility:

Exygen Research
3058 Research Drive
State College, PA 16801

Approved By:

Paul Connolly
Technical Leader, LC-MS, Exygen Research

10/26/04
Date

John Flaherty
Vice President, Operations, Exygen Research

10/26/04
Date

Total Pages: 7

Exygen Protocol Number: P0001131

Exygen Research Method Number V0001780

ANALYTICAL METHOD

Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Water by LC/MS/MS

1.0 Scope

This method is to be employed for the isolation and quantitation of perfluorooctanoic acid by High Performance Liquid Chromatography coupled to a tandem Mass Spectrometric Detector (LC/MS/MS) in water.

2.0 Safety

2.1 Always observe safe laboratory practices.
2.2 Consult the appropriate MSDS before handling any chemical for proper safety precautions.

3.0 Sample Requirement

3.1 At least 40 mL of test sample for extraction.
3.2 No sample processing is needed for water samples.
3.3 Samples stored refrigerated should be allowed to equilibrate to room temperature.
3.4 All samples must be thoroughly mixed before being sampled for extraction.
3.5 Any samples containing particles should be centrifuged at ~3000 rpm for ~5 minutes and the supernatant used for the extraction.
3.6 Sample collection procedures will be specified in the sampling plan for this project.

4.0 Reagents and Standards

4.1 Water – HPLC grade
4.2 Methanol – HPLC grade
4.3 Ammonium Acetate – A.C.S. Reagent Grade
4.4 Perfluorooctanoic Acid – Sigma-Aldrich

5.0 Instrument and Equipment

5.1 A high performance liquid chromatograph capable of pumping up to 2 solvents equipped with a variable volume injector capable of injecting 5-200 µL connected to a tandem Mass Spectrometer (LC/MS/MS).
5.2 A device to collect raw data for peak integration and quantitation.
5.3 Analytical balance capable of reading to 0.00001 g.
5.4 50 mL disposable polypropylene centrifuge tubes.
5.5 15 mL disposable polypropylene centrifuge tubes.
5.6 Disposable micropipets (50-100uL, 100-200uL).
5.7 125-mL LDPE narrow-mouth bottles.
5.8 2 mL clear HPLC vial kit.
5.9 Disposable pipettes.
5.10 Autopipettes (100-1000 µL and 10-100 µL), with disposable tips.
5.11 Waters Sep Pak Vac 6 cc (1g) tC18 SPE cartridges.

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5.12 SPE vacuum manifold.
5.13 Centrifuge capable of spinning 50 mL polypropylene tubes at 3000 rpm.

6.0 Chromatographic System

6.1 Analytical Column: Fluophase RP (Keystone Scientific), 2.1 mm x 50 mm, 5µ (P/N: 82505-052130)
6.2 Temperature: 30°C
6.3 Mobile Phase (A) : 2 mM Ammonium Acetate in Water
6.4 Mobile Phase (B) : Methanol
6.5 Gradient Program:

Time (min)	% A	% B	Flow Rate (mL/min)
0.0	65	35	0.3
1.0	65	35	0.3
8.0	25	75	0.3
20.0	25	75	0.3
22.5	65	35	0.3

6.6 Injection Volume: 15 µL (can be increased to as much as 50 µL).
6.7 Quantitation: Peak Area – external standard calibration curve.
6.8 Run Time: ~ 23 minutes.

The above conditions are intended as a guide and may be changed in order to optimize the HPLC system.

7.0 MS/MS System

7.1 Mode: Electrospray Negative MRM mode, monitoring 413 → 369 m/z.

The above conditions are intended as a guide and may be changed in order to optimize the MSMS system.

8.0 Preparation of Solutions

8.1 Mobile Phase

8.1.1 2 mM ammonium acetate in water is prepared by adding 0.154 g of ammonium acetate to 1000 mL of water.

Alternate volumes may be prepared.

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9.0 Standard Preparation

9.1 Standard Stock/Fortification Solution

9.1.1 Prepare a stock solution of ~100 µg/mL of PFOA by weighing 10 mg of analytical standard (corrected for purity) and dilute to 100 mL with methanol in a 125-mL LDPE bottle.

9.1.2 A 10 µg/mL fortification solution of PFOA is prepared by bringing 10 mL of the 100 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.3 A 1.0 µg/mL fortification solution of PFOA is prepared by bringing 10 mL of the 10 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.4 A 0.1 µg/mL fortification solution of PFOA is prepared by bringing 10 mL of the 1.0 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.5 A 0.01 µg/mL fortification solution of PFOA is prepared by bringing 10 mL of the 0.1 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.6 The stock and fortification solutions are to be stored in a refrigerator at approximately 4°C and are stable for a maximum period of 6 months from the date of preparation.

9.2 Standard Calibration Solutions

9.2.1 LC/MS/MS calibration standards are prepared in HPLC water. The calibration standards are processed through the extraction procedure, identical to samples.

9.2.2 The following is a typical example: additional concentrations may be prepared as needed.

Concentration of Fortification Solution (ppb)	Fortification Volume (µL)	Volume of Fortified Control Sample (mL)	Final Concentration of Calibration Standard (ppt)*	Calibration Standard ID (example)
0	0	40	0	XCmmddyy-0
10	100	40	25	XCmmddyy-1
10	200	40	50	XCmmddyy-2
10	400	40	100	XCmmddyy-3
100	100	40	250	XCmmddyy-4
100	200	40	500	XCmmddyy-5
100	400	40	1000	XCmmddyy-6

* The extracted concentration of the calibration standard is equal to 8× its initial concentration, due to the concentration of the standard during the extraction (SPE). XC = extracted calibration standard.

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9.2.3 A zero standard solution (reagent blank) must be prepared with each set of standards extracted.
9.2.4 Store all extracted calibration standards in 15-mL polypropylene tubes at 2°C to 6°C, up to two weeks.
9.2.5 Alternate volumes and concentrations of standards may be prepared as needed.

10.0 Batch Set Up

10.1 Each batch of samples extracted (typically 20 or less) must include at least one reagent control (method blank using HPLC water) and two reagent controls fortified at known concentrations (lab control spike) to verify procedural recovery for the batch.
10.2 Requirements for field and laboratory duplicates and spikes will be specified in the quality assurance plan for this project.

11.0 Sample Extraction

11.1 Measure 40 mL of sample or a portion of sample diluted to 40 mL with water into 50 mL polypropylene centrifuge tubes (fortify as needed, replace lid and mix well).
11.2 Condition the C_{18} SPE cartridges (1 g, 6 mL) by passing 10 mL methanol followed by 5 mL of HPLC water (~ 2 drop/sec). Do not let column run dry
11.3 Load sample on conditioned C_{18} SPE cartridge. Discard eluate.
11.4 Elute with ~5 mL 100% methanol. Collect 5 mL of eluate into graduated 15 mL polypropylene centrifuge tubes (final volume = 5 mL).
11.5 Analyze samples using electrospray LC/MS/MS.

12.0 Chromatography

12.1 Inject the same amount of each standard, sample and fortified sample into the LC/MS/MS system. A calibration standard must precede and follow all analyzed samples.
12.2 Standards of PFOA corresponding to at least five or more concentration levels must be included in an analytical set.
12.3 An entire set of extracted calibration standards must be included at the beginning and at the end of a sample set. Extracted standards must be interspersed between every 5-10 samples. As an alternative, an entire set of extracted calibration standards may be injected at the beginning of a set followed by extracted calibration standards interspersed every 5-10 samples (to account for a second set of extracted standards). In either case, extracted calibration standards must be the first and last injection in a sample set.
12.4 Use linear standard curves for quantitation. Linear standard curves are generated for the analyte by linear regression using 1/x weighting of peak area

versus calibration standard concentration using MassLynx 3.3 (or equivalent) software system.

12.5 Sample response should not exceed standard responses. Any samples that exceed standard responses should be further diluted and reanalyzed.

13.0 Acceptance Criteria

13.1 Chromatogram must show a peak of a daughter ion at 369 amu from a parent of 413 amu. The 413 amu parent corresponds to the PFOA anion, while the daughter ion (369 amu) represents the loss of carbon dioxide.

13.2 Method blanks must not contain PFOA at levels greater than the LOQ. If a blank contains PFOA at levels greater than 50 ng/L, then a new blank sample must be obtained and the entire set must be re-extracted.

13.3 Recoveries of control spikes and matrix spikes must be between 70-130% of their known values. If a control spike falls outside the acceptable limits, the entire set of samples should be re-extracted. Any matrix spike outside 70-130% should be evaluated by the analyst to determine if re-extraction is warranted.

13.4 Any calibration standard found to be a statistical outlier by using the Huge Error Test, may be excluded from the calculation of the calibration curve. However, the total number of extracted calibration standards that could be excluded must not exceed 20% of the total number of extracted standards injected.

13.5 The correlation coefficient (R) for calibration curves generated must be ≥ 0.992 ($R^2 \geq 0.985$). If calibration results fall outside these limits, then appropriate steps must be taken to adjust instrument operation, and the standards or the relevant set of samples should be reanalyzed.

13.6 Retention times between standards and samples must not drift more than ± 4 % within an analytical run. If retention time drift exceeds this limit within an analytical run then the set must be reanalyzed.

14.0 Calculations

14.1 Use the following equation to calculate the amount of PFOA found (in ng/L, based on peak area) using the standard curve (linear regression parameters) generated by the Mass Lynx software program:

$$\text{PFOA found (ng/L)} = \frac{(\text{Peak area} - \text{intercept})}{\text{slope}} \times \text{DF}$$

DF = factor by which the final volume was diluted, if necessary.

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14.2 For samples fortified with known amounts of PFOA prior to extraction, use the following equation to calculate the percent recovery.

Recovery (%) =

$$\frac{\left[\text{total analyte found (ng/L)} - \text{analyte found in control (ng/L)}\right]}{\text{analyte added (ng/L)}} \times 100$$

Exygen Protocol Number: P0001131

ANALYTICAL METHOD
Method Number: V0001781

Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Soil by LC/MS/MS

Analytical Testing Facility: Exygen Research
3058 Research Drive
State College, PA 16801

Approved By:

Paul Connolly
Technical Leader, LC-MS, Exygen Research

10/26/04
Date

John Flaherty
Vice President, Operations, Exygen Research

10/26/04
Date

Total Pages: 7

Exygen Protocol Number: P0001131

Exygen Research Method Number V0001781

ANALYTICAL METHOD

Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Soil by LC/MS/MS

1.0 Scope

This method is to be employed for the isolation and quantitation of perfluorooctanoic acid by High Performance Liquid Chromatography coupled to a tandem Mass Spectrometric Detector (LC/MS/MS) in soil.

2.0 Safety

2.1 Always observe safe laboratory practices.
2.2 Consult the appropriate MSDS before handling any chemical for proper safety precautions.

3.0 Sample Requirement

3.1 At least 15 g of test sample for extraction.
3.2 No sample processing is needed for soil samples.
3.3 Samples stored refrigerated should be allowed to equilibrate to room temperature.
3.4 All samples must be thoroughly mixed before being sampled for extraction.
3.5 Sample collection procedures will be specified in the sampling plan for this project.

4.0 Reagents and Standards

4.1 Water – HPLC grade
4.2 Methanol – HPLC grade
4.3 Ammonium Acetate – A.C.S. Reagent Grade
4.4 Perfluorooctanoic Acid – Sigma-Aldrich

5.0 Instrument and Equipment

5.1 A high performance liquid chromatograph capable of pumping up to 2 solvents equipped with a variable volume injector capable of injecting 5-200 µL connected to a tandem Mass Spectrometer (LC/MS/MS).
5.2 A device to collect raw data for peak integration and quantitation.
5.3 Analytical balance capable of reading to 0.00001 g.
5.4 50 mL disposable polypropylene centrifuge tubes.
5.5 15 mL disposable polypropylene centrifuge tubes.
5.6 Disposable micropipets (50-100uL, 100-200uL).
5.7 125-mL LDPE narrow-mouth bottles.
5.8 2 mL clear HPLC vial kit.
5.9 Disposable pipettes.
5.10 Autopipettes (100-1000 µL and 10-100 µL), with disposable tips.
5.11 Waters Sep Pak Vac 6 cc (1g) tC18 SPE cartridges.
5.12 SPE vacuum manifold.
5.13 Ultrasonic bath.

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5.14 Wrist-action shaker.
5.15 Centrifuge capable of spinning 50 mL polypropylene tubes at 5000 rpm.

6.0 Chromatographic System

6.1 Analytical Column: Fluophase RP (Keystone Scientific), 2.1 mm x 50 mm, 5µ (P/N: 82505-052130)
6.2 Temperature: 30°C
6.3 Mobile Phase (A) : 2 mM Ammonium Acetate in Water
6.4 Mobile Phase (B) : Methanol
6.5 Gradient Program:

Time (min)	% A	% B	Flow Rate (mL/min)
0.0	65	35	0.3
1.0	65	35	0.3
8.0	25	75	0.3
20.0	25	75	0.3
22.5	65	35	0.3

6.6 Injection Volume: 15 µL (can be increased to as much as 50 µL).
6.7 Quantitation: Peak Area – external standard calibration curve.
6.8 Run Time: ~ 23 minutes.

The above conditions are intended as a guide and may be changed in order to optimize the HPLC system.

7.0 MS/MS System

7.1 Mode: Electrospray Negative MRM mode, monitoring 413 → 369 m/z for PFOA.

The above conditions are intended as a guide and may be changed in order to optimize the MSMS system.

8.0 Preparation of Solutions

8.1 Mobile Phase

8.1.1 2 mM ammonium acetate in water is prepared by adding 0.154 g of ammonium acetate to 1000 mL of water.

Alternate volumes may be prepared.

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9.0 Standard Preparation

9.1 Standard Stock/Fortification Solution

9.1.1 Prepare a stock solution of ~100 µg/mL of PFOA by weighing 10 mg of analytical standard (corrected for purity) and dilute to 100 mL with methanol in a 125-mL LDPE bottle.

9.1.2 A 10 µg/mL fortification solution of PFOA is prepared by bringing 10 mL of the 100 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.3 A 1.0 µg/mL fortification solution of PFOA is prepared by bringing 10 mL of the 10 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.4 A 0.1 µg/mL fortification solution of PFOA is prepared by bringing 10 mL of the 1.0 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.5 A 0.01 µg/mL fortification solution of PFOA is prepared by bringing 10 mL of the 0.1 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.6 The stock and fortification solutions are to be stored in a refrigerator at approximately 4°C and are stable for a maximum period of 6 months from the date of preparation.

9.2 Standard Calibration Solutions

9.2.1 LC/MS/MS calibration standards are prepared in HPLC water. The calibration standards are processed through the extraction procedure, identical to samples.

9.2.2 The following is a typical example: additional concentrations may be prepared as needed.

Concentration of Fortification Solution (ppb)	Fortification Volume (µL)	Volume of Fortified Control Sample (mL)	Final Concentration of Calibration Standard (ppt)*	Calibration Standard ID (example)
0	0	40	0	XCmmddyy-0
10	100	40	25	XCmmddyy-1
10	200	40	50	XCmmddyy-2
10	400	40	100	XCmmddyy-3
100	100	40	250	XCmmddyy-4
100	200	40	500	XCmmddyy-5
100	400	40	1000	XCmmddyy-6

* The extracted concentration of the calibration standard is equal to 8× its initial concentration, due to the concentration of the standard during the extraction (SPE). XC = extracted calibration standard.

9.2.3 A zero standard solution (reagent blank) must be prepared with each set of standards extracted.
9.2.4 Store all extracted calibration standards in 15-mL polypropylene tubes at 2°C to 6°C, up to two weeks.
9.2.5 Alternate volumes and concentrations of standards may be prepared as needed.

10.0 Batch Set Up

10.1 Each batch of samples extracted (typically 20 or less) must include at least one reagent control (method blank using 5 mL of methanol) and two reagent controls fortified at known concentrations (lab control spike) to verify procedural recovery for the batch.
10.2 Requirements for field and laboratory duplicates and spikes will be specified in the quality assurance plan for this project.

11.0 Sample Extraction

11.1 Weigh 5 g of sample into 50 mL polypropylene centrifuge tubes (fortify as needed, replace lid and mix well).
11.2 Add 5 mL of methanol and shake on a wrist action shaker for ~15 minutes.
11.3 Transfer the tubes to an ultrasonic bath and sonicate for ~15 minutes.
11.4 Bring the volume up to 40 mL with water in the 50 mL polypropylene centrifuge tube.
11.5 Centrifuge for ~10 minutes at ~3000 rpm.
11.6 Condition the C_{18} SPE cartridges (1 g, 6 mL) by passing 10 mL methanol followed by 5 mL of HPLC water (~ 2 drop/sec). Do not let column run dry
11.7 Load (decant) the sample on the conditioned C_{18} SPE cartridge. Discard eluate.
11.8 Elute with ~5 mL 100% methanol. Collect 5 mL of eluate into graduated 15 mL polypropylene centrifuge tubes (final volume = 5 mL).
11.9 Analyze samples using electrospray LC/MS/MS.

12.0 Chromatography

12.1 Inject the same amount of each standard, sample and fortified sample into the LC/MS/MS system. A calibration standard must precede and follow all analyzed samples.
12.2 Standards of PFOA corresponding to at least five or more concentration levels must be included in an analytical set.
12.3 An entire set of extracted calibration standards must be included at the beginning and at the end of a sample set. Extracted standards must be interspersed between every 5-10 samples. As an alternative, an entire set of

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extracted calibration standards may be injected at the beginning of a set followed by extracted calibration standards interspersed every 5-10 samples (to account for a second set of extracted standards). In either case, extracted calibration standards must be the first and last injection in a sample set.

12.4 Use linear standard curves for quantitation. Linear standard curves are generated for the analyte by linear regression using 1/x weighting of peak area versus calibration standard concentration using MassLynx 3.3 (or equivalent) software system.

12.5 Sample response should not exceed standard responses. Any samples that exceed standard responses should be further diluted and reanalyzed.

13.0 Acceptance Criteria

13.1 Chromatogram must show a peak of a daughter ion at 369 amu from a parent of 413 amu. The 413 amu parent corresponds to the PFOA anion, while the daughter ion (369 amu) represents the loss of carbon dioxide.

13.2 Method blanks must not contain PFOA at levels greater than the LOQ. If a blank contains PFOA at levels greater than 50 ng/L, then a new blank sample must be obtained and the entire set must be re-extracted.

13.3 Recoveries of control spikes and matrix spikes must be between 70-130% of their known values. If a control spike falls outside the acceptable limits, the entire set of samples should be re-extracted. Any matrix spike outside 70-130% should be evaluated by the analyst to determine if re-extraction is warranted.

13.4 Any calibration standard found to be a statistical outlier by using the Huge Error Test, may be excluded from the calculation of the calibration curve. However, the total number of extracted calibration standards that could be excluded must not exceed 20% of the total number of extracted standards injected.

13.5 The correlation coefficient (R) for calibration curves generated must be ≥ 0.992 ($R^2 \geq 0.985$). If calibration results fall outside these limits, then appropriate steps must be taken to adjust instrument operation, and the standards or the relevant set of samples should be reanalyzed.

13.6 Retention times between standards and samples must not drift more than ± 4 % within an analytical run. If retention time drift exceeds this limit within an analytical run then the set must be reanalyzed.

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14.0 Calculations

14.1 Use the following equation to calculate the amount of PFOA found (in ng/L, based on peak area) using the standard curve (linear regression parameters) generated by the Mass Lynx software program:

$$\text{PFOA found (ng/L)} = \frac{\text{(Peak area - intercept)}}{\text{slope}} \times \text{DF}$$

DF = factor by which the final volume was diluted, if necessary.

14.2 For samples fortified with known amounts of PFOA prior to extraction, use the following equation to calculate the percent recovery.

Recovery (%) =

$$\frac{[\text{total analyte found (ng/L)} - \text{analyte found in control (ng/L)}]}{\text{analyte added (ng/L)}} \times 100$$

14.3 Use the following equation to convert the amount of PFOA found in ng/L to ng/g (ppb).

$$\text{PFOA found (ppb)} = \frac{\text{[PFOA found (ng/L) x volume extracted (0.04L)]}}{\text{sample weight (5 g)}}$$

14.4 Use the following equation to calculate the amount of PFOA found in ppb based on dry weight.

PFOA found (ppb) dry weight = PFOA found (ppb) x [100% / total solids(%)]

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ANALYTICAL METHOD
Method Number: V0001782

Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Sediment by LC/MS/MS

Analytical Testing Facility:

Exygen Research
3058 Research Drive
State College, PA 16801

Approved By:

Paul Connolly
Technical Leader, LC-MS, Exygen Research

10/26/04
Date

John Flaherty
Vice President, Operations, Exygen Research

10/26/04
Date

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ANALYTICAL METHOD

Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Sediment by LC/MS/MS

1.0 Scope

This method is to be employed for the isolation and quantitation of perfluorooctanoic acid by High Performance Liquid Chromatography coupled to a tandem Mass Spectrometric Detector (LC/MS/MS) in sediment.

2.0 Safety

2.1 Always observe safe laboratory practices.
2.2 Consult the appropriate MSDS before handling any chemical for proper safety precautions.

3.0 Sample Requirement

3.1 At least 30 g of test sample for extraction.
3.2 No sample processing is needed for sediment samples.
3.3 Samples stored refrigerated should be allowed to equilibrate to room temperature.
3.4 All samples must be thoroughly mixed before being sampled for extraction.
3.5 Sample collection procedures will be specified in the sampling plan for this project.

4.0 Reagents and Standards

4.1 Water – HPLC grade
4.2 Methanol – HPLC grade
4.3 Acetic Acid – Reagent grade
4.4 Ammonium Acetate – A.C.S. Reagent Grade
4.5 Perfluorooctanoic Acid – Sigma-Aldrich

5.0 Instrument and Equipment

5.1 A high performance liquid chromatograph capable of pumping up to 2 solvents equipped with a variable volume injector capable of injecting 5-200 µL connected to a tandem Mass Spectrometer (LC/MS/MS).
5.2 A device to collect raw data for peak integration and quantitation.
5.3 Analytical balance capable of reading to 0.00001 g.
5.4 50 mL disposable polypropylene centrifuge tubes.
5.5 15 mL disposable polypropylene centrifuge tubes.
5.6 Disposable micropipets (50-100uL, 100-200uL).
5.7 125-mL LDPE narrow-mouth bottles.
5.8 2 mL clear HPLC vial kit.
5.9 Disposable pipettes.
5.10 Autopipettes (100-1000 µL and 10-100 µL), with disposable tips.
5.11 Waters Sep Pak Vac 6 cc (1g) tC18 SPE cartridges.
5.12 SPE vacuum manifold.

5.13 Vortexer.
5.14 Wrist-action shaker.
5.15 Centrifuge capable of spinning 50 mL polypropylene tubes at 3000 rpm.

6.0 Chromatographic System

6.1 Analytical Column: Fluophase RP (Keystone Scientific), 2.1 mm x 50 mm, 5µ (P/N: 82505-052130)
6.2 Temperature: 30°C
6.3 Mobile Phase (A) : 2 mM Ammonium Acetate in Water
6.4 Mobile Phase (B) : Methanol
6.5 Gradient Program:

Time (min)	% A	% B	Flow Rate (mL/min)
0.0	65	35	0.3
1.0	65	35	0.3
8.0	25	75	0.3
20.0	25	75	0.3
22.5	65	35	0.3

6.6 Injection Volume: 15 µL (can be increased to as much as 50 µL).
6.7 Quantitation: Peak Area – external standard calibration curve.
6.8 Run Time: ~ 23 minutes.

The above conditions are intended as a guide and may be changed in order to optimize the HPLC system.

7.0 MS/MS System

7.1 Mode: Electrospray Negative MRM mode, monitoring 413 → 369 m/z for PFOA.

The above conditions are intended as a guide and may be changed in order to optimize the MSMS system.

8.0 Preparation of Solutions

8.1 Mobile Phase

8.1.1 2 mM ammonium acetate in water is prepared by adding 0.154 g of ammonium acetate to 1000 mL of water.

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8.2 Extraction Solutions

8.2.1 1% acetic acid in water is prepared by adding 10 mL of acetic acid to 1000 mL of water.

Alternate volumes may be prepared.

9.0 Standard Preparation

9.1 Standard Stock/Fortification Solution

9.1.1 Prepare a stock solution of ~100 µg/mL of PFOA by weighing 10 mg of analytical standard (corrected for purity) and dilute to 100 mL with methanol in a 125-mL LDPE bottle.

9.1.2 A 10 µg/mL fortification solution of PFOA is prepared by bringing 10 mL of the 100 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.3 A 1.0 µg/mL fortification solution of PFOA is prepared by bringing 10 mL of the 10 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.4 A 0.1 µg/mL fortification solution of PFOA is prepared by bringing 10 mL of the 1.0 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.5 A 0.01 µg/mL fortification solution of PFOA is prepared by bringing 10 mL of the 0.1 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.6 The stock and fortification solutions are to be stored in a refrigerator at approximately 4°C and are stable for a maximum period of 6 months from the date of preparation.

9.2 Standard Calibration Solutions

9.2.1 LC/MS/MS calibration standards are prepared in methanol via dilution of the 0.1 µg/mL fortification solution.

9.2.2 The following is a typical example: additional concentrations may be prepared as needed.

Concentration of Fortification Solution (ng/mL)	Volume (mL)	Diluted to (mL)	Final Concentration (ng/mL)
100	10	100	10.0
100	5	100	5.0
100	2	100	2.0
10	10	100	1.0
5	10	100	0.5
2	10	100	0.2

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9.2.3 Store all calibration standards in 125-mL LDPE narrow-mouth bottles at 2°C to 6°C, up to six months.

9.2.4 Alternate volumes and concentrations of standards may be prepared as needed.

10.0 Batch Set Up

10.1 Each batch of samples extracted (typically 20 or less) must include at least one untreated control and two untreated controls fortified at known concentrations (lab control spike) to verify procedural recovery for the batch.

10.2 Requirements for field and laboratory duplicates and spikes will be specified in the quality assurance plan for this project.

11.0 Sample Extraction

11.1 Weigh 5 g of sample into 50 mL polypropylene centrifuge tubes (fortify as needed, replace lid and mix well).

11.2 Add 35 mL of 1% acetic acid, cap, vortex and shake on a wrist action shaker for ~60 minutes.

11.3 Centrifuge the tubes at ~3000 rpm for ~20 minutes.

11.4 Condition the C_{18} SPE cartridges (1 g, 6 mL) by passing 10 mL methanol followed by 20 mL of HPLC water (~ 2 drop/sec). Do not let column run dry

11.5 Load (decant) the sample on the conditioned C_{18} SPE cartridge. Discard eluate.

11.6 Add 20 mL of methanol to the sediment left in the bottom of the 50 mL centrifuge tube. Cap, vortex and shake on a wrist action shaker for ~30 minutes.

11.7 Centrifuge the tubes at ~3000 rpm for ~20 minutes.

11.8 Decant the methanol onto the same SPE cartridge. Collect the eluate.

11.9 Wash the column with 4 mL of methanol. Collect the eluate and add it to the eluate collected in step 11.8.

11.10 Condition a second C_{18} SPE cartridge (1 g, 6 mL) by passing 10 mL methanol followed by 20 mL of HPLC water (~ 2 drop/sec). Do not let column run dry

11.11 Add the methanol to ~200 mL of water and load on the second conditioned SPE cartridge.

11.12 Elute with ~5 mL 100% methanol. Collect 5 mL of eluate into graduated 15 mL polypropylene centrifuge tubes (final volume = 5 mL).

11.13 Analyze samples using electrospray LC/MS/MS.

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12.0 Chromatography

12.1 Inject the same amount of each standard, sample and fortified sample into the LC/MS/MS system. A calibration standard must precede and follow all analyzed samples.

12.2 Standards of PFOA corresponding to at least five or more concentration levels must be included in an analytical set.

12.3 An entire set of extracted calibration standards must be included at the beginning and at the end of a sample set. Standards must be interspersed between every 5-10 samples. As an alternative, an entire set of calibration standards may be injected at the beginning of a set followed by calibration standards interspersed every 5-10 samples (to account for a second set of standards). In either case, calibration standards must be the first and last injection in a sample set.

12.4 Use linear standard curves for quantitation. Linear standard curves are generated for the analyte by linear regression using 1/x weighting of peak area versus calibration standard concentration using MassLynx 3.3 (or equivalent) software system.

12.5 Sample response should not exceed standard responses. Any samples that exceed standard responses should be further diluted and reanalyzed.

13.0 Acceptance Criteria

13.1 Chromatogram must show a peak of a daughter ion at 369 amu from a parent of 413 amu. The 413 amu parent corresponds to the PFOA anion, while the daughter ion (369 amu) represents the loss of carbon dioxide.

13.2 Method blanks must not contain PFOA at levels greater than the LOQ. If a blank contains PFOA at levels greater than 0.2 ng/mL, then a new blank sample must be obtained and the entire set must be re-extracted.

13.3 Recoveries of control spikes and matrix spikes must be between 70-130% of their known values. If a control spike falls outside the acceptable limits, the entire set of samples should be re-extracted. Any matrix spike outside 70-130% should be evaluated by the analyst to determine if re-extraction is warranted.

13.4 Any calibration standard found to be a statistical outlier by using the Huge Error Test, may be excluded from the calculation of the calibration curve. However, the total number of extracted calibration standards that could be excluded must not exceed 20% of the total number of extracted standards injected.

13.5 The correlation coefficient (R) for calibration curves generated must be ≥ 0.992 ($R^2 \geq 0.985$). If calibration results fall outside these limits, then appropriate steps must be taken to adjust instrument operation, and the standards or the relevant set of samples should be reanalyzed.

13.6 Retention times between standards and samples must not drift more than ± 4 % within an analytical run. If retention time drift exceeds this limit within an analytical run then the set must be reanalyzed.

14.0 Calculations

14.1 Use the following equation to calculate the amount of PFOA found (in ng/mL, based on peak area) using the standard curve (linear regression parameters) generated by the Mass Lynx software program:

$$\text{PFOA found (ng/mL)} = \frac{\text{(Peak area - intercept)}}{\text{slope}} \times \text{DF}$$

DF = factor by which the final volume was diluted, if necessary.

14.2 For samples fortified with known amounts of PFOA prior to extraction, use the following equation to calculate the percent recovery.

Recovery (%) =

$$\frac{[\text{total analyte found (ng/mL)} - \text{analyte found in control (ng/mL)}]}{\text{analyte added (ng/mL)}} \times 100$$

14.3 Use the following equation to convert the amount of PFOA found in ng/mL to ng/g (ppb).

$$\text{PFOA found (ppb)} = \frac{[\text{PFOA found (ng/mL) x final volume (5 mL)}]}{\text{sample weight (5 g)}}$$

14.4 Use the following equation (if necessary) to calculate the amount of PFOA found in ppb based on dry weight.

PFOA found (ppb) dry weight = PFOA found (ppb) x [100% / total solids(%)]

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ANALYTICAL METHOD
Method Number: V0001783

Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Fish and Clams by LC/MS/MS

Analytical Testing Facility: Exygen Research
3058 Research Drive
State College, PA 16801

Approved By:

Paul Connolly
Technical Leader, LC-MS, Exygen Research

10/26/04
Date

John Flaherty
Vice President, Operations, Exygen Research

10/26/04
Date

Total Pages: 8

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ANALYTICAL METHOD

Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Fish and Clams by LC/MS/MS

1.0 Scope

This method is to be employed for the isolation and quantitation of perfluorooctanoic acid by High Performance Liquid Chromatography coupled to a tandem Mass Spectrometric Detector (LC/MS/MS) in fish and clams.

2.0 Safety

2.1 Always observe safe laboratory practices.
2.2 Consult the appropriate MSDS before handling any chemical for proper safety precautions.

3.0 Sample Requirement

3.1 At least 20 g of test sample for extraction.
3.2 Samples should be processed before extraction. Place the frozen sample in a food processor and homogenize with dry ice. Place the samples in containers and leave open in frozen storage overnight to allow for carbon dioxide sublimation. Seal and place the samples in frozen storage until time of analysis.
3.3 Sample collection procedures will be specified in the sampling plan for this project.

4.0 Reagents and Standards

4.1 Water – HPLC grade
4.2 Acetonitrile – HPLC grade
4.3 Carbon (120-400 mesh) – Reagent grade
4.4 Methanol – HPLC grade
4.5 Silica gel (60-200 mesh) – Reagent grade
4.6 Florisil (60-100 mesh) – Reagent grade
4.7 Superclean LC-NH_2 – Reagent grade
4.8 1-Octanol – HPLC grade
4.9 L-Ascorbic acid – Reagent grade
4.10 Dimethyldichlorosilane – Reagent grade
4.11 Toluene – Reagent grade
4.12 Ammonium Acetate – A.C.S. Reagent Grade
4.13 Perfluorooctanoic Acid – Sigma-Aldrich

5.0 Instrument and Equipment

5.1 A high performance liquid chromatograph capable of pumping up to 2 solvents equipped with a variable volume injector capable of injecting 5-200 µL connected to a tandem Mass Spectrometer (LC/MS/MS).
5.2 A device to collect raw data for peak integration and quantitation.
5.3 Analytical balance capable of reading to 0.00001 g.

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5.4 Rotary evaporator.
5.5 Tissumizer.
5.6 125 mL pear-shaped flasks.
5.7 50 mL disposable polypropylene centrifuge tubes.
5.8 15 mL disposable polypropylene centrifuge tubes.
5.9 Disposable micropipets (50-100uL, 100-200uL).
5.10 125-mL LDPE narrow-mouth bottles.
5.11 2 mL clear HPLC vial kit.
5.12 Disposable pipettes.
5.13 Autopipettes (100-1000 µL and 10-100 µL), with disposable tips.
5.14 SPE tubes (20mL) (Supelco cat. no. N057177).
5.15 Wrist action shaker.
5.16 Centrifuge capable of spinning 50 mL polypropylene tubes at 2000 rpm.

6.0 Chromatographic System

6.1 Analytical Column: Fluophase RP (Keystone Scientific), 2.1 mm x 50 mm, 5µ (P/N: 82505-052130)
6.2 Temperature: 30°C
6.3 Mobile Phase (A) : 2 mM Ammonium Acetate in Water
6.4 Mobile Phase (B) : Methanol
6.5 Gradient Program:

Time (min)	% A	% B	Flow Rate (mL/min)
0.0	65	35	0.3
1.0	65	35	0.3
8.0	25	75	0.3
20.0	25	75	0.3
22.5	65	35	0.3

6.6 Injection Volume: 15 µL (can be increased to as much as 50 µL).
6.7 Quantitation: Peak Area – external standard calibration curve.
6.8 Run Time: ~ 23 minutes.

The above conditions are intended as a guide and may be changed in order to optimize the HPLC system.

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7.0 MS/MS System

7.1 Mode: Electrospray Negative MRM mode, monitoring 413 → 369 m/z for PFOA.

The above conditions are intended as a guide and may be changed in order to optimize the MSMS system.

8.0 Preparation of Solutions

8.1 Mobile Phase

8.1.1 2 mM ammonium acetate in water is prepared by adding 0.154 g of ammonium acetate to 1000 mL of water.

8.2 Extraction Solutions

8.2.1 2% ascorbic acid in methanol is prepared by dissolving 2 g of ascorbic acid in 100 mL of methanol.

8.2.2 30% Dimethyldichlorosilane in toluene is prepared by bringing 3 mL of dimethyldichlorosilane to a final volume of 10 mL with toluene.

Alternate volumes may be prepared.

9.0 Standard Preparation

9.1 Standard Stock/Fortification Solution

9.1.1 Prepare a stock solution of ~100 µg/mL of PFOA by weighing 10 mg of analytical standard (corrected for purity) and dilute to 100 mL with methanol in a 125-mL LDPE bottle.

9.1.2 A 1.0 µg/mL fortification solution of PFOA is prepared by bringing 1 mL of the 100 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.3 A 0.1 µg/mL fortification solution of PFOA is prepared by bringing 10 mL of the 1.0 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.4 A 0.01 µg/mL fortification solution of PFOA is prepared by bringing 10 mL of the 0.1 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.5 The stock and fortification solutions are to be stored in a refrigerator at approximately 4°C and are stable for a maximum period of 6 months from the date of preparation.

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9.2 Standard Calibration Solutions

9.2.1 LC/MS/MS calibration standards are prepared in methanol via dilution of the 1.0 µg/mL fortification solution.

9.2.2 The following is a typical example: additional concentrations may be prepared as needed.

Concentration of Fortification Solution (µg/mL)	Volume (mL)	Diluted to (mL)	Final Concentration (µg/mL)
1.0	5.0	100	0.05
1.0	2.5	100	0.025
1.0	1.0	100	0.01
0.05	10	100	0.005
0.025	10	100	0.0025
0.1	10	100	0.001
0.005	10	100	0.0005

9.2.3 Store all calibration standards in 125-mL LDPE narrow-mouth bottles at 2°C to 6°C, up to six months.

9.2.4 Alternate volumes and concentrations of standards may be prepared as needed.

10.0 Batch Set Up

10.1 Each batch of samples extracted (typically 20 or less) must include at least one untreated control and two untreated controls fortified at known concentrations (lab control spike) to verify procedural recovery for the batch.

10.2 Requirements for field and laboratory duplicates and spikes will be specified in the quality assurance plan for this project.

11.0 Sample Extraction

11.1 Weigh 5 g of frozen sample into 50 mL polypropylene centrifuge tubes (fortify as needed, replace lid and mix well).

11.2 Add 30 mL of acetonitrile and shake on a wrist action shaker for ~15 minutes.

11.3 Place the tubes in a freezer for ~1 hour.

11.4 Pack and condition the SPE tubes and silanize the pear-shaped flasks.

11.5 Pack the 20 mL SPE tubes in sequence with 2 g florisil, 2 g silica gel, 2 g carbon, and 1 g LC-NH_2. Condition the columns with 20 mL of methanol, then 20 mL of acetonitrile. Discard all washes. Do not allow the column to dry.

11.6 Silanize the 125 mL pear-shaped flasks by rinsing with the 30% dimethyldichlorosilane in toluene solution. Rinse the flask with toluene once, followed by methanol (three times). Dry the flasks completely before use, either by air-drying or with a stream of nitrogen.

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11.7 Centrifuge the 50 mL polypropylene tubes containing sample at ~2000 rpm for ~10 minutes.

11.8 Decant the extract on to a conditioned SPE column fitted inside the mouth of the pear-shaped flask. Collect the eluate in the 125 mL silanized pear-shape flask.

11.9 Add 10 mL of acetonitrile to the sample in the 50 mL centrifuge tube. Homogenize the frozen fat phase using a tissumizer for ~30 seconds and rinse the tissumizer with ~10 mL of acetonitrile into the tube.

11.10 Shake the sample again for ~10 minutes on a wrist-action shaker.

11.11 Place the tubes in a freezer for ~ 1 hour more.

11.12 Centrifuge the 50 mL polypropylene tubes containing sample at ~2000 rpm for ~10 minutes.

11.13 Decant the extract onto the same SPE column. Collect the eluate into the same pear-shaped flask and combine with the eluent from the initial extraction.

11.14 Pass 20 mL of acetonitrile through the SPE column and combine the eluate in the same pear-shaped flask.

11.15 Add 3-4 drops of 1-octanol to the extract in the pear-shaped flask and evaporate at reduced pressure using a rotary evaporator (at < 40°C).

11.16 Make the final volume, by adding 2 mL of 2% ascorbic acid in methanol to the pear-shaped flask and swirl to mix/dissolve.

11.17 Transfer the extracts to HPLC vials using disposable pipets.

11.18 Analyze samples using electrospray LC/MS/MS.

12.0 Chromatography

12.1 Inject the same amount of each standard, sample and fortified sample into the LC/MS/MS system. A calibration standard must precede and follow all analyzed samples.

12.2 Standards of PFOA corresponding to at least five or more concentration levels must be included in an analytical set.

12.3 An entire set of calibration standards must be included at the beginning and at the end of a sample set. Standards must be interspersed between every 5-10 samples. As an alternative, an entire set of calibration standards may be injected at the beginning of a set followed by calibration standards interspersed every 5-10 samples (to account for a second set of standards). In either case, calibration standards must be the first and last injection in a sample set.

12.4 Use linear standard curves for quantitation. Linear standard curves are generated for the analyte by linear regression using 1/x weighting of peak area versus calibration standard concentration using MassLynx 3.3 (or equivalent) software system.

12.5 Sample response should not exceed standard responses. Any samples that exceed standard responses should be further diluted and reanalyzed.

13.0 Acceptance Criteria

13.1 Chromatogram must show a peak of a daughter ion at 369 amu from a parent of 413 amu. The 413 amu parent corresponds to the PFOA anion, while the daughter ion (369 amu) represents the loss of carbon dioxide.

13.2 Method blanks must not contain PFOA at levels greater than the LOQ. If a blank contains PFOA at levels greater than 0.5 ppb, then a new blank sample must be obtained and the entire set must be re-extracted.

13.3 Recoveries of control spikes and matrix spikes must be between 70-130% of their known values. If a control spike falls outside the acceptable limits, the entire set of samples should be re-extracted.

13.4 Any calibration standard found to be a statistical outlier by using the Huge Error Test, may be excluded from the calculation of the calibration curve. However, the total number of calibration standards that could be excluded must not exceed 20% of the total number of standards injected.

13.5 The correlation coefficient (R) for calibration curves generated must be ≥ 0.992 ($R^2 \geq 0.985$). If calibration results fall outside these limits, then appropriate steps must be taken to adjust instrument operation, and the standards or the relevant set of samples should be reanalyzed.

13.6 Retention times between standards and samples must not drift more than ± 4 % within an analytical run. If retention time drift exceeds this limit within an analytical run then the set must be reanalyzed.

14.0 Calculations

14.1 Use the following equation to calculate the amount of PFOA found (in ng/mL, based on peak area) using the standard curve (linear regression parameters) generated by the Mass Lynx software program:

$$\text{PFOA found (ng/mL)} = \frac{\text{(Peak area - intercept)}}{\text{slope}}$$

14.2 Use the following equation to convert the amount of PFOA found in ng/mL to ng/g (ppb).

$$\text{PFOA found (ppb)} = \frac{\text{[PFOA found (ng/mL) x final volume (mL) x DF]}}{\text{sample weight (g)}}$$

DF = factor by which the final volume was diluted, if necessary.

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14.3 For samples fortified with known amounts of PFOA prior to extraction, use the following equation to calculate the percent recovery.

Recovery (%) =

$$\frac{[\text{total analyte found (ng/g)} - \text{analyte found in control (ng/g)}]}{\text{analyte added (ng/g)}} \times 100$$

Exygen Protocol Number: P0001131

ANALYTICAL METHOD
Method Number: V0001784

Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Vegetation by LC/MS/MS

Analytical Testing Facility: Exygen Research
3058 Research Drive
State College, PA 16801

Approved By:

Paul Connolly
Technical Leader, LC-MS, Exygen Research

10/26/04
Date

John Flaherty
Vice President, Operations, Exygen Research

10/26/04
Date

Total Pages: 7

Exygen Protocol Number: P0001131

Exygen Research Method Number V0001784

ANALYTICAL METHOD

Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Vegetation by LC/MS/MS

1.0 Scope

This method is to be employed for the isolation and quantitation of perfluorooctanoic acid by High Performance Liquid Chromatography coupled to a tandem Mass Spectrometric Detector (LC/MS/MS) in vegetation.

2.0 Safety

2.1 Always observe safe laboratory practices.
2.2 Consult the appropriate MSDS before handling any chemical for proper safety precautions.

3.0 Sample Requirement

3.1 At least 20 g of test sample for extraction.
3.2 Samples should be processed before extraction. Place the frozen sample in a food processor and homogenize with dry ice. Place the samples in containers and leave open in frozen storage overnight to allow for carbon dioxide sublimation. Seal and place the samples in frozen storage until time of analysis.
3.3 Sample collection procedures will be specified in the sampling plan for this project.

4.0 Reagents and Standards

4.1 Water – HPLC grade
4.2 Acetonitrile – HPLC grade
4.3 Carbon (120-400 mesh) – Reagent grade
4.4 Methanol – HPLC grade
4.5 Silica gel (60-200 mesh) – Reagent grade
4.6 Florisil (60-100 mesh) – Reagent grade
4.7 Superclean LC-NH_2 – Reagent grade
4.8 1-Octanol – HPLC grade
4.9 L-Ascorbic acid – Reagent grade
4.10 Dimethyldichlorosilane – Reagent grade
4.11 Toluene – Reagent grade
4.12 Ammonium Acetate – A.C.S. Reagent Grade
4.13 Perfluorooctanoic Acid – Sigma-Aldrich

5.0 Instrument and Equipment

5.1 A high performance liquid chromatograph capable of pumping up to 2 solvents equipped with a variable volume injector capable of injecting 5-200 µL connected to a tandem Mass Spectrometer (LC/MS/MS).
5.2 A device to collect raw data for peak integration and quantitation.
5.3 Analytical balance capable of reading to 0.00001 g.

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5.4 Rotary evaporator.
5.5 125 mL pear-shaped flasks.
5.6 50 mL disposable polypropylene centrifuge tubes.
5.7 15 mL disposable polypropylene centrifuge tubes.
5.8 Disposable micropipets (50-100uL, 100-200uL).
5.9 125-mL LDPE narrow-mouth bottles.
5.10 2 mL clear HPLC vial kit.
5.11 Disposable pipettes.
5.12 Autopipettes (100-1000 µL and 10-100 µL), with disposable tips.
5.13 SPE tubes (20mL) (Supelco cat. no. N057177).
5.14 Wrist action shaker.
5.15 Centrifuge capable of spinning 50 mL polypropylene tubes at 2000 rpm.

6.0 Chromatographic System

6.1 Analytical Column: Fluophase RP (Keystone Scientific), 2.1 mm x 50 mm, 5µ (P/N: 82505-052130)
6.2 Temperature: 30°C
6.3 Mobile Phase (A) : 2 mM Ammonium Acetate in Water
6.4 Mobile Phase (B) : Methanol
6.5 Gradient Program:

Time (min)	% A	% B	Flow Rate (mL/min)
0.0	65	35	0.3
1.0	65	35	0.3
8.0	25	75	0.3
20.0	25	75	0.3
22.5	65	35	0.3

6.6 Injection Volume: 15 µL (can be increased to as much as 50 µL).
6.7 Quantitation: Peak Area – external standard calibration curve.
6.8 Run Time: ~ 23 minutes.

The above conditions are intended as a guide and may be changed in order to optimize the HPLC system.

7.0 MS/MS System

7.1 Mode: Electrospray Negative MRM mode, monitoring 413 → 369 m/z for PFOA.

The above conditions are intended as a guide and may be changed in order to optimize the MSMS system.

8.0 Preparation of Solutions

8.1 Mobile Phase

8.1.1 2 mM ammonium acetate in water is prepared by adding 0.154 g of ammonium acetate to 1000 mL of water.

8.2 Extraction Solutions

8.2.1 2% ascorbic acid in methanol is prepared by dissolving 2 g of ascorbic acid in 100 mL of methanol.

8.2.2 30% Dimethyldichlorosilane in toluene is prepared by bringing 3 mL of dimethyldichlorosilane to a final volume of 10 mL with toluene.

Alternate volumes may be prepared.

9.0 Standard Preparation

9.1 Standard Stock/Fortification Solution

9.1.1 Prepare a stock solution of ~100 µg/mL of PFOA by weighing 10 mg of analytical standard (corrected for purity) and dilute to 100 mL with methanol in a 125-mL LDPE bottle.

9.1.2 A 1.0 µg/mL fortification solution of PFOA is prepared by bringing 1 mL of the 100 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.3 A 0.1 µg/mL fortification solution of PFOA is prepared by bringing 10 mL of the 1.0 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.4 A 0.01 µg/mL fortification solution of PFOA is prepared by bringing 10 mL of the 0.1 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.5 The stock and fortification solutions are to be stored in a refrigerator at approximately 4°C and are stable for a maximum period of 6 months from the date of preparation.

9.2 Standard Calibration Solutions

9.2.1 LC/MS/MS calibration standards are prepared in methanol via dilution of the 1.0 µg/mL fortification solution.

9.2.2 The following is a typical example: additional concentrations may be prepared as needed.

Concentration of Fortification Solution (µg/mL)	Volume (mL)	Diluted to (mL)	Final Concentration (µg/mL)
1.0	5.0	100	0.05
1.0	2.5	100	0.025
1.0	1.0	100	0.01
0.05	10	100	0.005
0.025	10	100	0.0025
0.1	10	100	0.001
0.005	10	100	0.0005

9.2.3 Store all calibration standards in 125-mL LDPE narrow-mouth bottles at 2°C to 6°C, up to six months.

9.2.4 Alternate volumes and concentrations of standards may be prepared as needed.

10.0 Batch Set Up

10.1 Each batch of samples extracted (typically 20 or less) must include at least one untreated control and two untreated controls fortified at known concentrations (lab control spike) to verify procedural recovery for the batch.

10.2 Requirements for field and laboratory duplicates and spikes will be specified in the quality assurance plan for this project.

11.0 Sample Extraction

11.1 Weigh 5 g of frozen sample into 50 mL polypropylene centrifuge tubes (fortify as needed, replace lid and mix well).

11.2 Add 30 mL of acetonitrile and shake on a wrist action shaker for ~15 minutes.

11.3 Centrifuge the 50 mL polypropylene tubes containing sample at ~2000 rpm for ~10 minutes.

11.4 Pack and condition the SPE tubes and silanize the pear-shaped flasks.

11.5 Pack the 20 mL SPE tubes in sequence with 2 g florisil, 2 g silica gel, 2 g carbon, and 1 g LC-NH_2. Condition the columns with 20 mL of methanol, then 20 mL of acetonitrile. Discard all washes. Do not allow the column to dry.

11.6 Silanize the 125 mL pear-shaped flasks by rinsing with the 30% dimethyldichlorosilane in toluene solution. Rinse the flask with toluene once, followed by methanol (three times). Dry the flasks completely before use, either by air-drying or with a stream of nitrogen.

11.7 Decant the extract on to a conditioned SPE column fitted inside the mouth of the pear-shaped flask. Collect the eluate in the 125 mL silanized pear-shape flask.

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11.8 Add 20 mL of acetonitrile to the sample in the 50 mL centrifuge tube.
11.9 Shake the sample again for ~10 minutes on a wrist-action shaker.
11.10 Centrifuge the 50 mL polypropylene tubes containing sample at ~2000 rpm for ~5 minutes.
11.11 Decant the extract onto the same SPE column. Collect the eluate into the same pear-shaped flask and combine with the eluent from the initial extraction.
11.12 Repeat steps 11.8 through 11.11 again.
11.13 Add 3-4 drops of 1-octanol to the extract in the pear-shaped flask and evaporate at reduced pressure using a rotary evaporator (at < 40°C).
11.14 Make the final volume, by adding 2 mL of 2% ascorbic acid in methanol to the pear-shaped flask and swirl to mix/dissolve.
11.15 Transfer the extracts to HPLC vials using disposable pipets.
11.16 Analyze samples using electrospray LC/MS/MS.

12.0 Chromatography

12.1 Inject the same amount of each standard, sample and fortified sample into the LC/MS/MS system. A calibration standard must precede and follow all analyzed samples.
12.2 Standards of PFOA corresponding to at least five or more concentration levels must be included in an analytical set.
12.3 An entire set of extracted calibration standards must be included at the beginning and at the end of a sample set. Extracted standards must be interspersed between every 5-10 samples. As an alternative, an entire set of extracted calibration standards may be injected at the beginning of a set followed by extracted calibration standards interspersed every 5-10 samples (to account for a second set of extracted standards). In either case, extracted calibration standards must be the first and last injection in a sample set.
12.4 Use linear standard curves for quantitation. Linear standard curves are generated for the analyte by linear regression using 1/x weighting of peak area versus calibration standard concentration using MassLynx 3.3 (or equivalent) software system.
12.5 Sample response should not exceed standard responses. Any samples that exceed standard responses should be further diluted and reanalyzed.

13.0 Acceptance Criteria

13.1 Chromatogram must show a peak of a daughter ion at 369 amu from a parent of 413 amu. The 413 amu parent corresponds to the PFOA anion, while the daughter ion (369 amu) represents the loss of carbon dioxide.

13.2 Method blanks must not contain PFOA at levels greater than the LOQ. If a blank contains PFOA at levels greater than 0.5 ppb, then a new blank sample must be obtained and the entire set must be re-extracted.

13.3 Recoveries of control spikes and matrix spikes must be between 70-130% of their known values. If a control spike falls outside the acceptable limits, the entire set of samples should be re-extracted.

13.4 Any calibration standard found to be a statistical outlier by using the Huge Error Test, may be excluded from the calculation of the calibration curve. However, the total number of calibration standards that could be excluded must not exceed 20% of the total number of standards injected.

13.5 The correlation coefficient (R) for calibration curves generated must be ≥ 0.992 ($R^2 \geq 0.985$). If calibration results fall outside these limits, then appropriate steps must be taken to adjust instrument operation, and the standards or the relevant set of samples should be reanalyzed.

13.6 Retention times between standards and samples must not drift more than ± 4 % within an analytical run. If retention time drift exceeds this limit within an analytical run then the set must be reanalyzed.

14.0 Calculations

14.1 Use the following equation to calculate the amount of PFOA found (in ng/mL, based on peak area) using the standard curve (linear regression parameters) generated by the Mass Lynx software program:

$$\text{PFOA found (ng/mL)} = \frac{\text{(Peak area - intercept)}}{\text{slope}}$$

14.2 Use the following equation to convert the amount of PFOA found in ng/mL to ng/g (ppb).

$$\text{PFOA found (ppb)} = \frac{\text{[PFOA found (ng/mL) x final volume (mL) x DF]}}{\text{sample weight (g)}}$$

DF = factor by which the final volume was diluted, if necessary.

14.3 For samples fortified with known amounts of PFOA prior to extraction, use the following equation to calculate the percent recovery.

$$\text{Recovery (\%)} = \frac{\text{[total analyte found (ng/g) - analyte found in control (ng/g)]}}{\text{analyte added (ng/g)}} \times 100$$

Exygen Protocol Number: P0001131

ANALYTICAL METHOD
Method Number: V0001785

Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Small Mammal Liver by LC/MS/MS

Analytical Testing Facility: Exygen Research
3058 Research Drive
State College, PA 16801

Approved By:

Paul Connolly
Technical Leader, LC-MS, Exygen Research

10/26/04
Date

John Flaherty
Vice President, Operations, Exygen Research

10/26/04
Date

Total Pages: 7

Exygen Protocol Number: P0001131

Exygen Research | Method Number V0001785

ANALYTICAL METHOD

Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Small Mammal Liver by LC/MS/MS

1.0 Scope

This method is to be employed for the isolation and quantitation of perfluorooctanoic acid by High Performance Liquid Chromatography coupled to a tandem Mass Spectrometric Detector (LC/MS/MS) in small mammal liver.

2.0 Safety

2.1 Always observe safe laboratory practices.
2.2 Consult the appropriate MSDS before handling any chemical for proper safety precautions.

3.0 Sample Requirement

3.1 At least 5 g of test sample for extraction.
3.2 Samples should be processed before extraction. Place the frozen sample in a food processor and homogenize with dry ice. Place the samples in containers and leave open in frozen storage overnight to allow for carbon dioxide sublimation. Seal and place the samples in frozen storage until time of analysis. Alternately, if there is an insufficient amount of sample (~less than 5 g), then no processing is necessary and the sample can be used as supplied.
3.3 Sample collection procedures will be specified in the sampling plan for this project.

4.0 Reagents and Standards

4.1 Water – HPLC grade
4.2 Methanol – HPLC grade
4.3 Acetonitrile – HPLC grade
4.4 Ammonium Acetate – A.C.S. Reagent Grade
4.5 Perfluorooctanoic Acid – Sigma-Aldrich

5.0 Instrument and Equipment

5.1 A high performance liquid chromatograph capable of pumping up to 2 solvents equipped with a variable volume injector capable of injecting 5-200 µL connected to a tandem Mass Spectrometer (LC/MS/MS).
5.2 A device to collect raw data for peak integration and quantitation.
5.3 Analytical balance capable of reading to 0.00001 g.
5.4 50 mL disposable polypropylene centrifuge tubes.
5.5 15 mL disposable polypropylene centrifuge tubes.
5.6 Disposable micropipets (50-100uL, 100-200uL).
5.7 125-mL LDPE narrow-mouth bottles.
5.8 2 mL clear HPLC vial kit.

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5.9 Disposable pipettes.
5.10 Autopipettes (100-1000 µL and 10-100 µL), with disposable tips.
5.11 Waters Sep Pak Vac 6 cc (1g) tC18 SPE cartridges.
5.12 SPE vacuum manifold.
5.13 Tissuemizer.
5.14 Wrist-action shaker.
5.15 Centrifuge capable of spinning 15 mL polypropylene tubes at 3000 rpm.

6.0 Chromatographic System

6.1 Analytical Column: Fluophase RP (Keystone Scientific), 2.1 mm x 50 mm, 5µ (P/N: 82505-052130)
6.2 Temperature: 30°C
6.3 Mobile Phase (A) : 2 mM Ammonium Acetate in Water
6.4 Mobile Phase (B) : Methanol
6.5 Gradient Program:

Time (min)	% A	% B	Flow Rate (mL/min)
0.0	65	35	0.3
1.0	65	35	0.3
8.0	25	75	0.3
20.0	25	75	0.3
22.5	65	35	0.3

6.6 Injection Volume: 15 µL (can be increased to as much as 50 µL).
6.7 Quantitation: Peak Area – external standard calibration curve.
6.8 Run Time: ~ 23 minutes.

The above conditions are intended as a guide and may be changed in order to optimize the HPLC system.

7.0 MS/MS System

7.1 Mode: Electrospray Negative MRM mode, monitoring 413 → 369 m/z for PFOA.

The above conditions are intended as a guide and may be changed in order to optimize the MSMS system.

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8.0 Preparation of Solutions

8.1 Mobile Phase

8.1.1 2 mM ammonium acetate in water is prepared by adding 0.154 g of ammonium acetate to 1000 mL of water.

Alternate volumes may be prepared.

9.0 Standard Preparation

9.1 Standard Stock/Fortification Solution

9.1.1 Prepare a stock solution of ~100 µg/mL of PFOA by weighing 10 mg of analytical standard (corrected for purity) and dilute to 100 mL with methanol in a 125-mL LDPE bottle.

9.1.2 A 1.0 µg/mL fortification solution of PFOA is prepared by bringing 1 mL of the 100 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.3 A 0.1 µg/mL fortification solution of PFOA is prepared by bringing 10 mL of the 1.0 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.4 The stock and fortification solutions are to be stored in a refrigerator at approximately 4°C and are stable for a maximum period of 6 months from the date of preparation.

9.2 Standard Calibration Solutions

9.2.1 LC/MS/MS calibration standards are prepared in methanol via dilution of the 0.1 µg/mL fortification solution.

9.2.2 The following is a typical example: additional concentrations may be prepared as needed.

Concentration of Fortification Solution (ng/mL)	Volume (mL)	Diluted to (mL)	Final Concentration (ng/mL)
100	5.0	100	5.0
100	2.0	100	2.0
100	1.0	100	1.0
5.0	10	100	0.5
2.0	10	100	0.2
1.0	10	100	0.1

9.2.3 Store all calibration standards in 125-mL LDPE narrow-mouth bottles at 2°C to 6°C, up to six months.

9.2.4 Alternate volumes and concentrations of standards may be prepared as needed.

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10.0 Batch Set Up

10.1 Each batch of samples extracted (typically 20 or less) must include at least one untreated control and two untreated controls fortified at known concentrations (lab control spike) to verify procedural recovery for the batch.

10.2 Requirements for field and laboratory duplicates and spikes will be specified in the quality assurance plan for this project.

11.0 Sample Extraction

11.1 Weigh 1 g of sample into a 50 mL polypropylene centrifuge tubes (fortify as needed, replace lid and mix well). Note that alternate weights of liver may be measured depending on the sample size available for use.

11.2 Add water to the sample for a final volume of 10 mL.

11.3 Homogenize sample using a tissuemizer for ~1 minute.

11.4 Transfer 1 mL of the sample using a disposable pipette into a 15 mL disposable centrifuge tube.

11.5 Add 5 mL of acetonitrile and shake for ~20 minutes on a wrist-action shaker.

11.6 Centrifuge the tubes at ~3000 rpm for ~5 minutes.

11.7 Decant the supernatant into a 50 mL disposable centrifuge tube and add 35 mL of water.

11.8 Condition the C_{18} SPE cartridges (1 g, 6 mL) by passing 10 mL methanol followed by 5 mL of HPLC water (~ 2 drop/sec). Do not let column run dry

11.9 Load the sample on conditioned C_{18} SPE cartridge. Discard eluate.

11.10 Elute with ~2 mL of methanol. Collect 2 mL of eluate into a graduated 15 mL polypropylene centrifuge tube (final volume = 2 mL).

11.11 Analyze samples using electrospray LC/MS/MS.

12.0 Chromatography

12.1 Inject the same amount of each standard, sample and fortified sample into the LC/MS/MS system. A calibration standard must precede and follow all analyzed samples.

12.2 Standards of PFOA corresponding to at least five or more concentration levels must be included in an analytical set.

12.3 An entire set of calibration standards must be included at the beginning and at the end of a sample set. Standards must be interspersed between every 5-10 samples. As an alternative, an entire set of calibration standards may be injected at the beginning of a set followed by calibration standards interspersed every 5-10 samples (to account for a second set of standards). In either case, calibration standards must be the first and last injection in a sample set.

12.4 Use linear standard curves for quantitation. Linear standard curves are generated for the analyte by linear regression using 1/x weighting of peak area

versus calibration standard concentration using MassLynx 3.3 (or equivalent) software system.

12.5 Sample response should not exceed standard responses. Any samples that exceed standard responses should be further diluted and reanalyzed.

13.0 Acceptance Criteria

13.1 Chromatogram must show a peak of a daughter ion at 369 amu from a parent of 413 amu. The 413 amu parent corresponds to the PFOA anion, while the daughter ion (369 amu) represents the loss of carbon dioxide.

13.2 Method blanks must not contain PFOA at levels greater than the LOQ. If a blank contains PFOA at levels greater than 10 ng/g, then a new blank sample must be obtained and the entire set must be re-extracted.

13.3 Recoveries of control spikes and matrix spikes must be between 70-130% of their known values. If a control spike falls outside the acceptable limits, the entire set of samples should be re-extracted. Any matrix spike outside 70-130% should be evaluated by the analyst to determine if re-extraction is warranted.

13.4 Any calibration standard found to be a statistical outlier by using the Huge Error Test, may be excluded from the calculation of the calibration curve. However, the total number of calibration standards that could be excluded must not exceed 20% of the total number of standards injected.

13.5 The correlation coefficient (R) for calibration curves generated must be ≥ 0.992 ($R^2 \geq 0.985$). If calibration results fall outside these limits, then appropriate steps must be taken to adjust instrument operation, and the standards or the relevant set of samples should be reanalyzed.

13.6 Retention times between standards and samples must not drift more than ± 4 % within an analytical run. If retention time drift exceeds this limit within an analytical run then the set must be reanalyzed.

14.0 Calculations

14.1 Use the following equation to calculate the amount of PFOA found (in ng/mL, based on peak area) using the standard curve (linear regression parameters) generated by the Mass Lynx software program:

$$\text{PFOA found (ng/mL)} = \frac{\text{(Peak area - intercept)}}{\text{slope}} \times \text{DF} \times \text{aliquot factor}$$

DF = factor by which the final volume was diluted, if necessary.
Aliquot factor = 10

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14.2 For samples fortified with known amounts of PFOA prior to extraction, use the following equation to calculate the percent recovery.

$$\text{Recovery (\%)} = \frac{[\text{total analyte found (ng/mL)} - \text{analyte found in control (ng/mL)}]}{\text{analyte added (ng/mL)}} \times 100$$

14.3 Use the following equation to convert the amount of PFOA found in ng/mL to ng/g (ppb).

$$\text{PFOA found (ppb)} = \frac{[\text{PFOA found (ng/mL)} \times \text{final volume (mL)}]}{\text{sample weight (g)}}$$

Exygen Protocol Number: P0001131

ANALYTICAL METHOD
Method Number: V0001786

Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Small Mammal Serum by LC/MS/MS

Analytical Testing Facility: Exygen Research
3058 Research Drive
State College, PA 16801

Approved By:

Paul Connolly
Technical Leader, LC-MS, Exygen Research

10/26/04
Date

John Flaherty
Vice President, Operations, Exygen Research

10/26/04
Date

Total Pages: 7

Exygen Protocol Number: P0001131

Exygen Research | Method Number V0001786

ANALYTICAL METHOD

Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Small Mammal Serum by LC/MS/MS

1.0 Scope

This method is to be employed for the isolation and quantitation of perfluorooctanoic acid by High Performance Liquid Chromatography coupled to a tandem Mass Spectrometric Detector (LC/MS/MS) in small mammal serum.

2.0 Safety

2.1 Always observe safe laboratory practices.
2.2 Consult the appropriate MSDS before handling any chemical for proper safety precautions.

3.0 Sample Requirement

3.1 At least 1 mL of test sample for extraction.
3.2 No sample processing is needed for serum samples. However, frozen serum samples must to allowed to completely thaw to room temperature before use.
3.3 Sample collection procedures will be specified in the sampling plan for this project.

4.0 Reagents and Standards

4.1 Water – HPLC grade
4.2 Methanol – HPLC grade
4.3 Acetonitrile – HPLC grade
4.4 Ammonium Acetate – A.C.S. Reagent Grade
4.5 Perfluorooctanoic Acid – Sigma-Aldrich

5.0 Instrument and Equipment

5.1 A high performance liquid chromatograph capable of pumping up to 2 solvents equipped with a variable volume injector capable of injecting 5-200 µL connected to a tandem Mass Spectrometer (LC/MS/MS).
5.2 A device to collect raw data for peak integration and quantitation.
5.3 Analytical balance capable of reading to 0.00001 g.
5.4 50 mL disposable polypropylene centrifuge tubes.
5.5 15 mL disposable polypropylene centrifuge tubes.
5.6 Disposable micropipets (50-100uL, 100-200uL).
5.7 125-mL LDPE narrow-mouth bottles.
5.8 2 mL clear HPLC vial kit.
5.9 Disposable pipettes.
5.10 Autopipettes (100-1000 µL and 10-100 µL), with disposable tips.
5.11 Waters Sep Pak Vac 6 cc (1g) tC18 SPE cartridges.
5.12 SPE vacuum manifold.
5.13 Vortexer.

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5.14 Wrist-action shaker.
5.15 Centrifuge capable of spinning 15 mL polypropylene tubes at 3000 rpm.

6.0 Chromatographic System

6.1 Analytical Column: Fluophase RP (Keystone Scientific), 2.1 mm x 50 mm, 5µ (P/N: 82505-052130)
6.2 Temperature: 30°C
6.3 Mobile Phase (A) : 2 mM Ammonium Acetate in Water
6.4 Mobile Phase (B) : Methanol
6.5 Gradient Program:

Time (min)	% A	% B	Flow Rate (mL/min)
0.0	65	35	0.3
1.0	65	35	0.3
8.0	25	75	0.3
20.0	25	75	0.3
22.5	65	35	0.3

6.6 Injection Volume: 15 µL (can be increased to as much as 50 µL).
6.7 Quantitation: Peak Area – external standard calibration curve.
6.8 Run Time: ~ 23 minutes.

The above conditions are intended as a guide and may be changed in order to optimize the HPLC system.

7.0 MS/MS System

7.1 Mode: Electrospray Negative MRM mode, monitoring 413 → 369 m/z for PFOA.

The above conditions are intended as a guide and may be changed in order to optimize the MSMS system.

8.0 Preparation of Solutions

8.1 Mobile Phase

8.1.1 2 mM ammonium acetate in water is prepared by adding 0.154 g of ammonium acetate to 1000 mL of water.

Alternate volumes may be prepared.

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9.0 Standard Preparation

9.1 Standard Stock/Fortification Solution

9.1.1 Prepare a stock solution of ~100 µg/mL of PFOA by weighing 10 mg of analytical standard (corrected for purity) and dilute to 100 mL with methanol in a 125-mL LDPE bottle.

9.1.2 A 1.0 µg/mL fortification solution of PFOA is prepared by bringing 1 mL of the 100 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.3 A 0.1 µg/mL fortification solution of PFOA is prepared by bringing 10 mL of the 1.0 µg/mL solution to a final volume of 100 with methanol in a 125 mL LDPE bottle.

9.1.4 The stock and fortification solutions are to be stored in a refrigerator at approximately 4°C and are stable for a maximum period of 6 months from the date of preparation.

9.2 Standard Calibration Solutions

9.2.1 LC/MS/MS calibration standards are prepared in methanol via dilution of the 0.1 µg/mL fortification solution.

9.2.2 The following is a typical example: additional concentrations may be prepared as needed.

Concentration of Fortification Solution (ng/mL)	Volume (mL)	Diluted to (mL)	Final Concentration (ng/mL)
100	5.0	100	5.0
100	2.0	100	2.0
100	1.0	100	1.0
5.0	10	100	0.5
2.0	10	100	0.2
1.0	10	100	0.1

9.2.3 Store all calibration standards in 125-mL LDPE narrow-mouth bottles at 2°C to 6°C, up to six months.

9.2.4 Alternate volumes and concentrations of standards may be prepared as needed.

10.0 Batch Set Up

10.1 Each batch of samples extracted (typically 20 or less) must include at least one untreated control and two untreated controls fortified at known concentrations (lab control spike) to verify procedural recovery for the batch.

10.2 Requirements for field and laboratory duplicates and spikes will be specified in the quality assurance plan for this project.

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ANALYTICAL METHOD

Method of Analysis for the Determination of Perfluorooctanoic Acid (PFOA) in Small Mammal Serum by LC/MS/MS

11.0 Sample Extraction

11.1 Measure 1 mL of sample into a 50 mL polypropylene centrifuge tubes (fortify as needed, replace lid and mix well). Note that alternate volumes of serum may be measured depending on the sample size available for use.
11.2 Add water to the sample for a final volume of 20 mL. Cap tightly
11.3 Vortex for ~1 minute.
11.4 Transfer 1 mL of the sample using a disposable pipette into a 15 mL disposable centrifuge tube.
11.5 Add 5 mL of acetonitrile and shake for ~20 minutes on a wrist-action shaker.
11.6 Centrifuge the tubes at ~3000 rpm for ~5 minutes.
11.7 Decant the supernatant into a 50 mL disposable centrifuge tube and add 35 mL of water.
11.8 Condition the C_{18} SPE cartridges (1 g, 6 mL) by passing 10 mL methanol followed by 5 mL of HPLC water (~ 2 drop/sec). Do not let column run dry
11.9 Load the sample on conditioned C_{18} SPE cartridge. Discard eluate.
11.10 Elute with ~2 mL of methanol. Collect 2 mL of eluate into a graduated 15 mL polypropylene centrifuge tube (final volume = 2 mL).
11.11 Analyze samples using electrospray LC/MS/MS.

12.0 Chromatography

12.1 Inject the same amount of each standard, sample and fortified sample into the LC/MS/MS system. A calibration standard must precede and follow all analyzed samples.
12.2 Standards of PFOA corresponding to at least five or more concentration levels must be included in an analytical set.
12.3 An entire set of calibration standards must be included at the beginning and at the end of a sample set. Standards must be interspersed between every 5-10 samples. As an alternative, an entire set of calibration standards may be injected at the beginning of a set followed by calibration standards interspersed every 5-10 samples (to account for a second set of standards). In either case, calibration standards must be the first and last injection in a sample set.
12.4 Use linear standard curves for quantitation. Linear standard curves are generated for the analyte by linear regression using 1/x weighting of peak area versus calibration standard concentration using MassLynx 3.3 (or equivalent) software system.
12.5 Sample response should not exceed standard responses. Any samples that exceed standard responses should be further diluted and reanalyzed.

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13.0 Acceptance Criteria

13.1 Chromatogram must show a peak of a daughter ion at 369 amu from a parent of 413 amu. The 413 amu parent corresponds to the PFOA anion, while the daughter ion (369 amu) represents the loss of carbon dioxide.

13.2 Method blanks must not contain PFOA at levels greater than the LOQ. If a blank contains PFOA at levels greater than 10 ng/mL, then a new blank sample must be obtained and the entire set must be re-extracted.

13.3 Recoveries of control spikes and matrix spikes must be between 70-130% of their known values. If a control spike falls outside the acceptable limits, the entire set of samples should be re-extracted. Any matrix spike outside 70-130% should be evaluated by the analyst to determine if re-extraction is warranted.

13.4 Any calibration standard found to be a statistical outlier by using the Huge Error Test, may be excluded from the calculation of the calibration curve. However, the total number of calibration standards that could be excluded must not exceed 20% of the total number of standards injected.

13.5 The correlation coefficient (R) for calibration curves generated must be ≥ 0.992 ($R^2 \geq 0.985$). If calibration results fall outside these limits, then appropriate steps must be taken to adjust instrument operation, and the standards or the relevant set of samples should be reanalyzed.

13.6 Retention times between standards and samples must not drift more than ± 4 % within an analytical run. If retention time drift exceeds this limit within an analytical run then the set must be reanalyzed.

14.0 Calculations

14.1 Use the following equation to calculate the amount of PFOA found (in ng/mL, based on peak area) using the standard curve (linear regression parameters) generated by the Mass Lynx software program:

$$\text{PFOA found (ng/mL)} = \frac{\text{(Peak area - intercept)}}{\text{slope}} \times \text{DF} \times \text{aliquot factor}$$

DF = factor by which the final volume was diluted, if necessary.
Aliquot factor = 20

14.2 For samples fortified with known amounts of PFOA prior to extraction, use the following equation to calculate the percent recovery.

$$\text{Recovery (\%)} = \frac{[\text{total analyte found (ng/mL)} - \text{analyte found in control (ng/mL)}]}{\text{analyte added (ng/mL)}} \times 100$$

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14.3 Use the following equation to convert the amount of PFOA found in ng/mL to ppb.

$$\text{PFOA found (ppb)} = \frac{[\text{PFOA found (ng/mL)} \times \text{final volume (mL)}]}{\text{sample volume (mL)}}$$

Protocol Exygen P0001131; 3M Study Number E05-0210
Amendment 3

Study Title

ANALYSIS OF PERFLUOROBUTANESULFONATE (PFBS), PERFLUOROHEXANESULFONATE (PFHS), AND PERFLUOROOCTANESULFONATE (PFOS) IN WATER, SOIL, SEDIMENT, FISH, CLAMS, VEGETATION, SMALL MAMMAL LIVER AND SMALL MAMMAL SERUM USING LC/MS/MS FOR THE 3M DECATUR MONITORING PROGRAM

PROTOCOL AMENDMENT NO. 3

Amendment Date:
May 16, 2005

Performing Laboratory
3M Environmental, Health, and Safety Operations
3M Environmental Laboratory
935 Bush Avenue
St. Paul, MN 55106

Laboratory Project Identification
E05-0210

Protocol Exygen P0001131; 3M Study Number E05-0210
Amendment 3

This amendment modifies the following portion(s) of the protocol:

PROTOCOL READS:
TESTING FACILITY

Exygen Research
3058 Research Drive
State College, PA 15801
Phone: (814) 272-1039

AMEND TO READ:

TESTING FACILITIES

Exygen Research
3058 Research Drive
State College, PA 15801
Phone: (814) 272-1039

3M Environmental Laboratory
Building 2-3E-09
935 Bush Avenue
St. Paul, MN 55106

REASON:

Addition of 3M Environmental Laboratory as a testing facility allows selected water samples to be sent to the 3M facility for analysis of PFBS, PFHS, and PFOS using the most current version of ETS 8-154 "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates in Water by Solid Phase Extractions and High Performance Liquid Chromatography/Mass Spectrometry".

The following modifications to ETS 8-154.1 will be incorporated into the study:

(1) The sample volume extracted and the final SPE elution volume may be adjusted, at the analyst's discretion, to better achieve the detection limits specified in study objectives. As written, ETS 8-154.1 calls for a 40 mL extraction volume with a 5 mL elution volume which results in an eight-fold sample concentration. The actual volumes used and the resulting overall concentration factor will be given in the final report. Associated method quality control samples will demonstrate that the volume modifications do not impact method accuracy and precision.
(2) A solvent (unextracted) calibration curve may be analyzed with the extracted calibration curve to ascertain extraction efficiency. Samples will be analyzed using the extracted curve unless otherwise stated in the final report. Data from the solvent calibration curve will not be included or discussed in the final report unless it is used to strengthen experimental observations/explanations.
(3) ETS 8-154.1 makes no mention of sample surrogate spikes; however, all samples will be spiked with at least one of the following radiolabeled surrogates, PFOA [1,2 ^{13}C] (perfluorooctanoic acid), PFOS [^{18}O2] and/or PFNA [1,2 ^{13}C] (perfluorononanoic acid – C9).The concentration of the surrogate spike may vary depending on the collection event, but typical samples are spiked with a nominal concentration of 0.05 ng/mL. Surrogate spike recoveries will be documented and discussed in the final report. Surrogate recoveries between 100±25% will be deemed as meeting method criteria for accuracy.
(4) Several method blanks may be prepared and analyzed to better determine a "representative" area count value for the method blank. The method blank area count is instrumental in determining the method limit of quantitation and understanding the average and range of area counts possible is critical. If a method blank value is used as a "zero point" in the final calibration curve, then a brief explanation in the final report or in the raw data as a Note to File must be

included to describe why that specific method blank was selected as the zero point (closest to the average value, most conservative (largest) value, etc.)

(5) The overall analytical uncertainty for each target (non-surrogate) analyte will be estimated using both the method accuracy and precision. The method accuracy and precision will be calculated using data from laboratory contorl spike (LCS) samples prepared and analyzed with the sample set(s). Replicate LCSs must be prepared each day samples and/or other quality control samples are prepared. A sample calculation of how the analytical uncertainty was determined will be provided in the final report and/or raw data.

A new revision of ETS 8-154 may incorporate all or several of the modifications listed above. If a new version of ETS 8-154 is issued during the course of this study, sample results must meet the new method requirements regardless if they are listed above.

3M Environmental Laboratory management will approve all documented deviations to the 3M Environmental Laboratory quality system (SOPs, methods, etc.) that occur during the course of this investigation.

Protocol Exygen P0001131; 3M Study Number E05-0210
Amendment 3

Amendment Approval

Michael A. Santoro, 3M,	Sponsor Representative	Date 06/02/05
William K. Reagen, Ph.D.	3M Environmental Laboratory Manager	Date 05/17/05
Jaisimha Kesari, Weston Solutions,	Study Director	Date 5/26/05