ORIGINAL

TSCA NON-CONFIDENTIAL BUSINESS INFORMATION

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8EHQ- 598-373	89120000492	7/10/12

COMMENTS:

DOES NOT CONTAIN CBI

3M Environmental, Health and Safety Operations

3M Center, Building 0224-05-W-03
St. Paul, MN 55144-1000

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3M

July 5, 2012

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Document Processing Center
EPA East – Room 6428 Attn: Section 8(e)
Office of Pollution Prevention and Toxics, U.S. EPA
1200 Pennsylvania Avenue NW
Washington, DC 20460-0001

Re: TSCA 8(e) Substantial Risk Notice: Sulfonate-based and Carboxylic-based Fluorochemicals, Docket 8EHQ-0598-373 - Results from Analysis of Sediments, Surface Water and Groundwater in the Decatur, Alabama Area

Dear Sir or Madam:

3M is submitting this notice to supplement its previous submissions on sulfonate and carboxylic-based fluorochemicals. More specifically, the data contained in this submittal have been generated as part of a site-related environmental assessment for fluorochemicals that 3M is performing for its 3M Decatur, Alabama manufacturing facility. As part of this effort, 3M has recently received the enclosed final analytical reports and summary figures for sampling activities conducted at a regional landfill that previously operated in the vicinity of our Decatur manufacturing facility and also from the wastewater treatment plant area at our Decatur site (due to the size of some of the files pertaining to this submittal, they have been placed on a CD for the reader's convenience):

Regional Landfill

3M recently completed sampling and analytical efforts pertaining to samples of sediments, surface water and groundwater collected at a former disposal site commonly referred to as the former Bert Jeffries landfill. Figure 1, attached, depicts the general location of this site. Figure 2, also attached, illustrates the sample locations at the site itself. It should be noted that the sediment sampling locations, while not specifically referenced on the figure, correspond identically to the surface water sampling points. Furthermore, the monitoring well designations "MWxR" and "MWxL" refer to shallow (residuum) and limestone bedrock water-bearing units, respectively.

The analytical reports summarizing and documenting the data for the referenced sampling efforts are attached and identified as follows:

- GLP10-01-01 Interim Report 26: Analysis for PFOA in Sediments Collected from the Jeffries Property in February 2012
- GLP10-01-01, Interim Report 27: Analysis of PFOA in Surface Water Samples Collected at Bert Jeffries Landfill in Decatur, AL in February 2012
- GLP10-01-01 Interim Report 31: Analysis of PFOA in Groundwater Samples Collected at Off-Site Wells on Bert Jeffries Property in Decatur, AL in April 2012

CONTAINS NO CBI CONTAINS NO CBI

- GLP10-01-02 Interim Report 25: Analysis of PFOS, PFHS and PFBS in Sediments Collected from the Jeffries Property
- GLP10-01-02; Interim Report 26 – Analysis of PFBS, PFHS, and PFOS in Surface Water Samples Collected at Bert Jeffries Landfill in Decatur, AL in February 2012
- GLP10-01-02; Interim Report 30 – Analysis of PFBS, PFHS, and PFOS in Groundwater Samples Collected at Off-Site Wells on Bert Jeffries Property in Decatur, AL in April 2012

While some of the data has been summarized on Figure 2, it should be noted that the complete data set is contained within the attached analytical reports.

3M Decatur Wastewater Treatment Plant (WWTP) Area

On-site groundwater monitoring was recently expanded through the construction and sampling of six (6) temporary monitoring wells in and around the 3M Decatur wastewater treatment plant area. These sampling locations are depicted on Figure 3, attached, and all represent groundwater from the shallow (residuum) water-bearing unit at the site.

The analytical reports summarizing and documenting the data for the referenced sampling efforts are attached and identified as follows:

- GLP10-01-01, Interim Report 32: Analysis for PFOA in Groundwater Samples from New On-Site Wells – Adjacent to the 3M Decatur Wastewater Treatment Plant (WWTP) April 2012
- GLP10-01-02, Interim Report 31: Analysis for PFBS, PFHS, and PFOS in Groundwater Samples from New On-Site Wells – Adjacent to the 3M Decatur Wastewater Treatment Plant (WWTP) April 2012

While some of the data has been summarized on Figure 3, it should be noted that the complete data set is contained within the attached analytical reports.

While 3M does not believe that any of these data taken alone or cumulatively meet the "substantial risk" reporting threshold, we nevertheless recognize the ongoing work by U.S. EPA to assess fluorochemical exposure pathways. Therefore, we are placing these results in the 8(e) docket as a supplement to previous submissions.

If you have any questions, please contact Deanna Luebker at 651-737-1374 or djluebker@mmm.com .

Sincerely,

Jean B. Sweeney (DL)

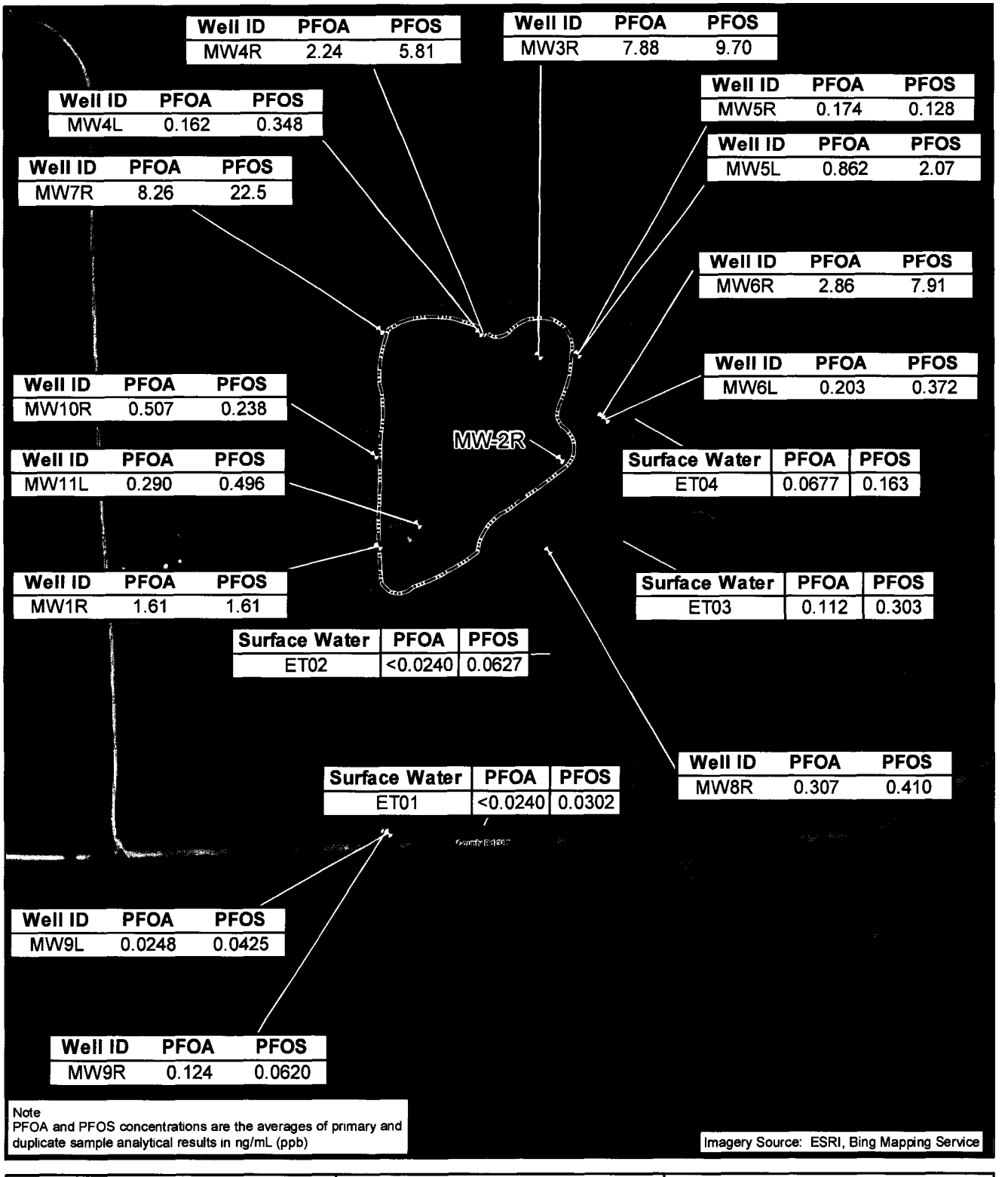
Jean B. Sweeney
Vice President
Environmental, Health and Safety Operations

List of Attachments:

Figure 1 – Regional Map
Figure 2 – Former Bert Jeffries Landfill
Figure 3 – 3M Decatur, AL Wastewater Treatment Plant Area

GLP10-01-01, Interim Report 26
GLP10-01-01, Interim Report 27
GLP10-01-01, Interim Report 31
GLP10-01-01, Interim Report 32
GLP10-01-02, Interim Report 25
GLP10-01-02, Interim Report 26
GLP10-01-02, Interim Report 30
GLP10-01-02, Interim Report 31

cc: Glenda Dean, ADEM



Legend

- Property Line
- Area of Suspected Waste Disposal
- Abandoned Monitoring Wells
- Existing Monitoring Wells
- New Monitoring Wells
- Surface Water Sampling Locations

0 100 200 Feet

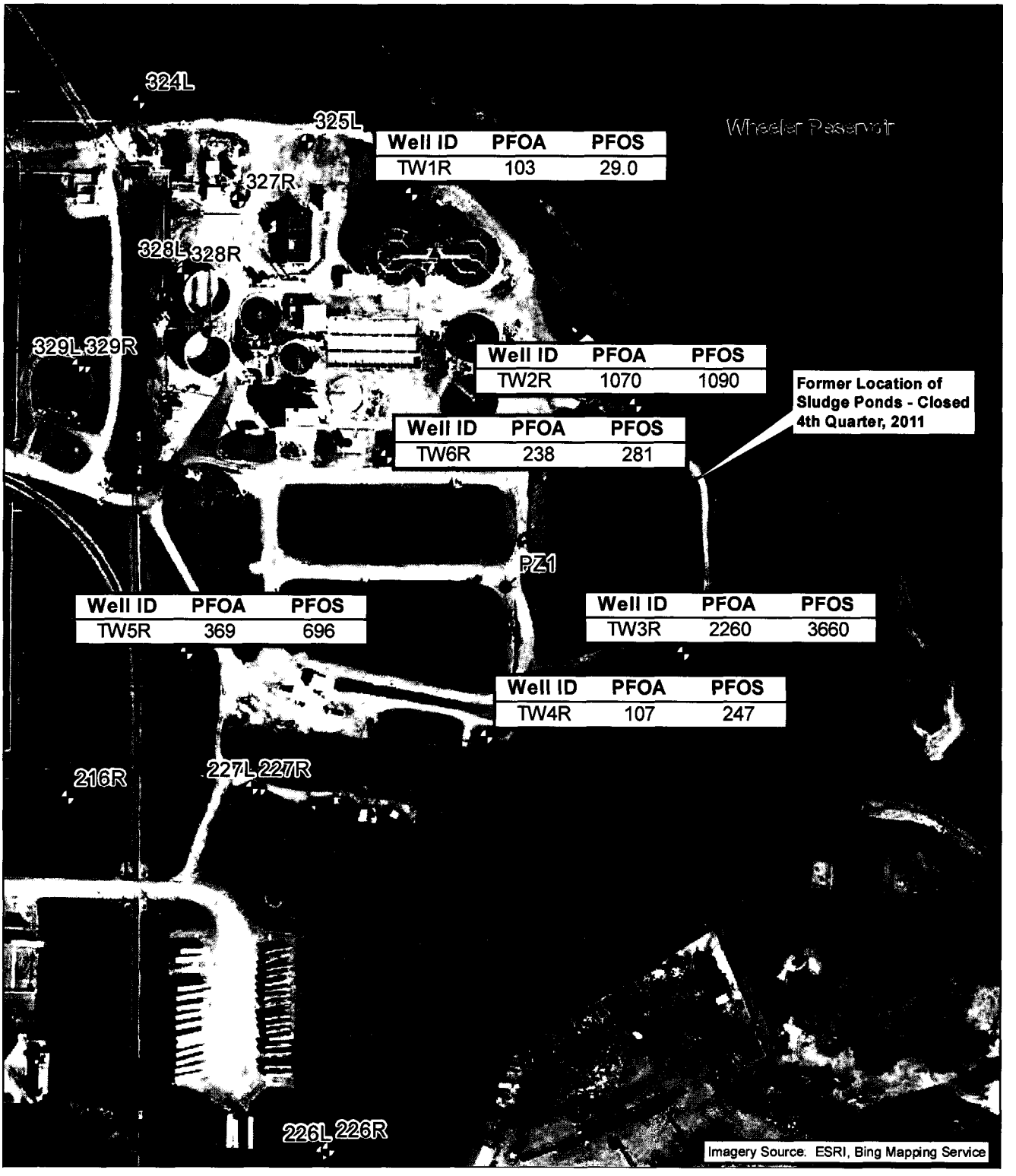
N W E S

WESTON SOLUTIONS

Figure 1
Former Bert Jeffries Landfill
Groundwater and Surface Water
Average PFOA and PFOS Concentrations
April 2012

Decatur, AL

File Y:\3M Dec\MXD\BertJeffries_landfill_PFOA_PFOS_SW.mxd, 5/30/2012 10:42:41 AM, ricksc



Legend

- Existing Monitoring Wells
- Temporary Monitoring Wells (TW)
- Temporary Piezometer (PZ)

Note
-PFOA and PFOS concentrations are the averages of primary and duplicate sample analytical results in ng/mL (ppb)

225 112.5 0 Feet

N W E S

WESTON SOLUTIONS

Figure 2
Wastewater Treatment Plant Area
Groundwater Average PFOA and PFOS Concentrations
April 2012

Decatur, AL

File Y:\3MDec\MXD\WWTP_locs_PFOA_PFOS.mxd, 5/30/2012 10:45:14 AM, ricksc



Legend:

- Facility Boundary
- ★ Landfill

9,000 4,500 0 Feet

N W E S

WESTON SOLUTIONS

Figure 1
Regional Landfill Map

Decatur, AL

File: \\Fsfed01\TIG\3MDec\MXD\Phase3_landfills.mxd, 26-Mar-09 16:15, ricksc

GLP10-01-02 Interim Report 25: Analysis of PFOS, PFHS and PFBS in Sediments Collected from the Jeffries Property

Study Title

3M Environmental Laboratory Analytical Protocol GLP10-01-02: Analysis of Perfluorooctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane Sulfonate (PFBS) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program

Data Requirement

EPA TSCA Good Laboratory Practice Standards 40 CFR Part 792

Study Director

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Principal Analytical Investigator

Cleston C. Lange, Ph.D.
3M Environmental Laboratory

Interim Report Completion Date

Upon Signing

Performing Laboratory

3M Environmental Health and Safety Operations
Environmental Laboratory
3M Center, Bldg 260-05-N-17
St. Paul, MN 55144

Project Identification

GLP10-01-02-25

Total Number of Pages

24

This page has been reserved for specific country requirements.

GLP COMPLIANCE STATEMENT

Report Title: GLP10-01-02 Interim Report 25: Analysis for PFOS, PFHS and PFBS in Sediments Collected from the Jeffries Property. 3M Environmental Laboratory Analytical Protocol GLP-10-01-02: Analysis of Perfluorcoctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane Sulfonate (PFBS) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program.

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

Exceptions to GLP compliance:

- The reference substances were not all characterized under GLPs.
- Because these are environmental samples and the study analytical in nature only, there was no specific test substance or control substance for this study.

Gary Hohenstein, Sponsor Representative — 6/22/12
Date

Jaisimha Kesari, P.E., DEE, Study Director — 6/25/12
Date

QUALITY ASSURANCE STATEMENT

Report Title: GLP10-01-02 Interim Report 25: Analysis for PFOS, PFHS and PFBS in Sediments Collected from the Jeffries Property. 3M Environmental Laboratory Analytical Protocol GLP-10-01-02: Analysis of Perfluorooctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane Sulfonate (PFBS) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program.

This interim analytical report and the accompanying data were audited by the 3M Environmental Laboratory Quality Assurance Unit (QAU), as indicated below. The findings were reported to the principal investigator (P.I.), laboratory management and study director.

Study Inspection Dates	Phase		Date Reported to	
		P.I.	Study Director Management	Study Director
6/7/2012-6/8/2012	Interim Report and Data	6/8/2012	6/13/2012	6/13/2012

QAU Representative

6/19/12
Date

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1 Study Information

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Study Dates

Study Initiation: March 08, 2010
Interim Analytical Initiation: March 12, 2012
Interim Analytical Completion: May 29, 2012
Interim Report Completion: Upon final Signatures

Location of Archives

All original raw data and analytical reports 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.

2 Summary

This interim report provides the PFOS, PFHS and PFBS concentration results for five sediment samples collected in March 2012 at the Jeffries property in northern Alabama. In addition, one travel blank (trip blank), containing between10-25 grams of control soil in a sample bottle, accompanied the sample bottles to and from the site and was also analyzed for quality control purposes. Samples were logged into the 3M Environmental Laboratory information management system (LIMS) under project GLP10-01-01-26 and cross referenced to this project GLP10-01-02-25 for additional fluorochemical sulfonates analysis. Four aliquots of sample were removed from each sample bottle and accurately weighed for extraction. The first and second aliquot served as analytical sample and duplicate analytical sample. The third and fourth aliquots were fortified with nominal 20.0 and 200 ng each of PFOS (linear isomer), PFHS (linear isomer) and PFBS as a low and high laboratory matrix spike (LMS), respectively. Three aliquots of the trip blank were taken, with the third prepared as a single LMS that was fortified with nominal 1.00 ng each of PFOS (linear isomer), PFHS (linear isomer) and PFBS. Samples were extracted and analyzed per method ETS-8-053 by liquid chromatography with triple quadrapole mass spectrometric detection (LC/MS/MS). The LMS recovery results provided a measure of the data accuracy. The relative percent difference (RPD) of the duplicate analytical sample results was used to assess the data precision. The percent moisture of each soil was also determined as part of the study. The PFOS, PFHS and PFBS concentrations are summarized in **Table 1**. The PFOS, PFHS and PFBS recoveries from the LMS samples are summarized in **Table 2**. The average data accuracy and standard deviation determined from LMS results was 107% ± 7.9% for PFOS, 105% ± 7.2% for PFHS and 106% ± 5.2% for PFBS. The analytical method uncertainty (95% CI) was determined at ± 7.3% for PFOS, ± 10% for PFHS and ± 12% for PFBS.

Table 1. Results for Jeffries Property Sediments

3M LIMS ID [d]	Sample ID	Average Concentration (ng/g; dry)		
		PFOS	PFHS	PFBS
GLP10-01-01-26-001	JPAL SD TRIP1 0 0000	BLQ	BLQ	BLQ
GLP10-01-01-26-002	JPAL SD ET01 0 0000	3.95	BLQ	BLQ
GLP10-01-01-26-003	JPAL SD ET02 0 0000	8.59	BLQ	BLQ
GLP10-01-01-26-004	JPAL SD ET02 DB 0000	10.0	BLQ	BLQ
GLP10-01-01-26-005	JPAL SD ET03 0 0000	12.1	BLQ	BLQ
GLP10-01-01-26-006	JPAL SD ET04 0 0000	23.8	BLQ	BLQ

All LMS recovery results were within acceptance criteria of 100 ± 30%
Average concentration of duplicate analytical result reported; RPDs of duplicates were less than 10%
The analytical method uncertainty was determined from LCS results at ± 12% for PFBS, ± 10% for PFHS and ± 7.2% for PFOS
Concentration values are shown at 3 significant figures, but more precise data was used for data calculations.
BLQ; analyte response was lower than the analyte response of the lowest standard (LLOQ) which was the nominal 0.500 ng calibration standard (i.e. less than nominal 0.50 ng/g)

Table 2. LMS Recovery for Jeffries Property Sediments

3M LIMS ID [b]	Sample ID	LMS Recovery (%)		
		PFOS	PFHS	PFBS
GLP10-01-01-26-001 Low	JPAL SD TRIP1 0 0000 LMS	130%	125%	105%
GLP10-01-01-26-002 Low	JPAL SD ET01 0 0000 LMS Low	102%	105%	114%
GLP10-01-01-26-002 High	JPAL SD ET01 0 0000 LMS High	103%	103%	103%
GLP10-01-01-26-003 Low	JPAL SD ET02 0 0000 LMS Low	104%	102%	110%
GLP10-01-01-26-003 High	JPAL SD ET02 0 0000 LMS High	104%	105%	103%
GLP10-01-01-26-004 Low	JPAL SD ET02 DB 0000 LMS Low	105%	100%	105%
GLP10-01-01-26-004 High	JPAL SD ET02 DB 0000 LMS High	104%	103%	98.5%
GLP10-01-01-26-005 Low	JPAL SD ET03 0 0000 LMS Low	111%	105%	108%
GLP10-01-01-26-005 High	JPAL SD ET03 0 0000 LMS High	108%	107%	104%
GLP10-01-01-26-006 Low	JPAL SD ET04 0 0000 LMS Low	105%	108%	115%
GLP10-01-01-26-006 High	JPAL SD ET04 0 0000 LMS High	104%	97.0%	101%
Average Recovery		**107%**	**105%**	**106%**
Standard Deviation		**7.9%**	**7.2%**	**5.2%**
RSD		**7.4%**	**6.8%**	**4.9%**

LMSs were fortified with PFOS, PFHS and PFBS (linear isomers only) at nominal 20.0 ng (low) and 200 ng (high).
The LMS for the trip blank was fortified at nominal 1.0 ng each of PFOS, PFHS and PFBS
Recovery values are shown at 3 significant figures, but more precise data was used for data calculations.

3 Introduction

The soil analyses results reported herein were conducted as part of the Phase 3 Environmental Monitoring and Assessment Program for the 3M facility located in Decatur, Alabama. The objective of the overall program is to gain information regarding concentrations of perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHS) and perfluorobutane sulfonate (PFBS) in various environmental media such as groundwater, soils and sediments that are associated with and near the Decatur facility. Reported herein are the results from analysis of sediments collected from the Jeffries property. The samples were collected by Weston Solutions, Inc. personnel in February 2012 and shipped to the 3M Environmental Laboratory for quantitative analysis of PFOS, PFHS and PFBS. One soil travel blank (trip blank) accompanied the sample bottles to the site, during collection and during samples shipment and was analyzed to evaluate for any potential contamination of samples during the sample shipment and collection period.

This report describes the sample shipment, receipt, extraction and quantitative LC/MS/MS analysis procedures conducted for determination of PFOS, PFHS and PFBS in the sediment samples that were received. Additionally, included in this report are the assessment of the analytical precision and accuracy for the reported PFOS, PFHS and PFBS concentration results based on duplicate analytical sample results and laboratory matrix spike (LMS) recovery results, respectively. The recovery results for a stable isotope labeled $^{13}C_4$-PFOS surrogate recovery standard (SRS) that was added to each soil aliquot prior to extraction, and the determined percent moisture content of each soil, are also included herein.

4 Test, Control and Reference Substances

This study does not have a test substance in the classic sense of a GLP study because this study was purely analytical in nature. The reference and control substances are listed in **Table 3.**

Table 3. Reference Substances

Reference ID	PFOS (linear)	PFOS (linear + branched)	PFHS (linear)
Chemical Name	n-Perfluorooctane-1-Sulfonate Potassium Salt	Perfluorooctane Sulfonate Potassium Salt	n-Perfluorohexane-1-sulfonate Sodium Salt
Chemical Formula	n-$C_8F_{17}SO_3$ K	$C_8F_{17}SO_3$ K	n-$C_6F_{13}SO_3$ Na
Use	Reference Standard for Calibration and LMSs	Reference Standard for LCSs	Reference Standard for Calibration and LMSs
Source	Wellington Laboratories	3M	Wellington Laboratories
Expiration Date	10/18/18	12/14/16	3/25/18
Storage Conditions	Frozen	Frozen	Frozen
Chemical Lot Number	LPFOSKBM06	171	LPFHxSAM08
TCR Number	TCR08-0001-1/1	TCR-696	TCR08-0018-1/1
Physical Description	Crystalline	White Powder	Crystalline
Purity	98%	86.4%	>98%
Reference ID	PFHS (linear + branched)	PFBS (predominantly linear)	$^{13}C_4$-PFOS
Chemical Name	n-Perfluorohexane-1-sulfonate Potassium Salt	Perfluorobutane-1-sulfonate Potassium Salt	[1,2,3,4-$^{13}C_4$]-Perfluorooctane-1-Sulfonate Sodium Salt
Chemical Formula	n-$C_6F_{13}SO_3$ K	n-$C_4F_9SO_3$ K	$^{13}C_4{}^{12}C_4F_{17}SO_3$ Na
Use	Reference Standard for LCSs	Reference Standard for All PFBS	Surrogate
Source	3M	3M	Wellington Laboratories
Expiration Date	2/12/17	1/10/17	9/8/2013
Storage Conditions	Frozen	Frozen	Frozen
Chemical Lot Number	NB 120067-69	101	MPFOS0910
TCR Number	TCR-083	TCR-121	TCR10-0044-2/9
Physical Description	White Powder	White Powder	Liquid; Methanol solution
Purity	98.6%	96.7%	>98% [a]

Reference ID	$^{13}C_8$-PFOS	$^{13}C_3$-PFHS	$^{18}O_2$-PFBS
Chemical Name	[$^{13}C_8$]-Perfluorooctane-1-Sulfonate Sodium Salt	[$^{13}C_3$]-Perfluorohexane-1-Sulfonate Sodium Salt	[$^{18}O_2$]-Perfluorobutane-1-Sulfonate Ammonium Salt
Chemical Formula	$^{13}C_8F_{17}SO_3$ Na	$^{13}C_3{}^{12}C_3F_{13}SO_3Na$	$C_4F_9S^{18}O_2{}^{16}O$ NH_4
Use	Internal Standard for PFOS	Internal Standard for PFHS	Internal Standard for PFBS
Source	Wellington Laboratories	Wellington Laboratories	RTI International
Expiration Date	9/28/2013	9/28/2013	3/9/15
Storage Conditions	-20°C	-20°C	-20°C
Chemical Lot Number	092310	092310	11546-107-2
TCR Number	TCR10-0048-3/16, 4/16	TCR10-0048-3/16, 4/16	TCR-1042
Physical Description	Liquid; Methanol solution	Liquid; Methanol solution	Liquid; Methanol solution
Purity	>98% [a]	>98% [a]	>99% [a]
[a] The commercially provided material was a methanol solutions and labeled with a weight/volume concentration purity value. However, the concentration of further dilutions was based on the certified concentration of the stock material.			

5 Test System

There was not a test system for this study in the classic sense of a GLP study. This study was conducted for analysis of sediments collected from the Jeffries property that is located in Northern Alabama. Samples for this study are "real world" environmental samples.

6 Method Summary

6.1 Methods

The sample extractions and quantitative LC/MS/MS analyses were performed following method ETS-8-053.0. The results reported herein were obtained from analytical run j120507b. Two analytical runs were conducted as o120312a and o120313a, but result not used due to QC results that did not meet method acceptance criteria.

6.2 Sample Receipt

On February 21, 2012 seven empty 250-mL HDPE Nalgene™ sample bottles, and one travel blank (trip blank) containing approximately 10-25 grams of a control soil TCR-455, were sent from the 3M Environmental Laboratory to Weston Solutions, Inc. field personnel for collection of sediments from the property known as the Jeffries Property, formerly the Bert Jeffries landfill. Following the sample

collections by Weston Solutions, Inc. personnel, five sediment-filled sample bottles and the trip blank were returned in the bottles to the 3M Environmental Laboratory for quantitative analysis of PFOS, PFHS and PFBS. The samples were received with sample chains of custody numbers 15290 on March 02, 2012.

Soil samples from Alabama are regulated and the sediments for this study were shipped in accordance with USDA/APHIS soil permit number P330-09-00125.

Sample nomenclature follows the form JPAL-SD-ET-xxxx where the first string defines the Jeffries Property Alabama (JPAL), the second string defines the sample media (i.e., SD= sediment, SB –field sample duplicate), the third string defines the site location (ET = eastern tributary), the fourth string defines the field sample (1,2,3… or DB = duplicate field sample) . The fourth string defines the sediment sampling depth (0000 = 0 ft to 0.5 ft interval).

6.3 Sample Preparation

Each soil or sediment extraction involved removal of a 1 cubic centimeter (1 cc; 1 mL) aliquot of field sample (typically ~ 1 gram) from each sample bottle using a fixed volume 1 cc spoon, transferring it to a 15 mL conical centrifuge tube, followed by accurate weight determination of the aliquot on a 5-place balance. Then, nominal 3.0 ng of internal standard (IS; nominal 3.0 ng) and 3.0ng of surrogate recovery standard (SRS) was added to each soil aliquot and a known quantity of PFOS (linear isomer), PFHS (linear isomer) and PFBS was added to each LMS. Then each was extracted by addition of 8 mL of a 4:1 acetonitrile:water solution followed by sonication for 1 to 2 hours followed by centrifugation to remove solids. The supernatant from each was then transferred to an autovial for analysis. An accurately measured volume of each supernatant was analyzed by LC/MS/MS.

During preparation, each sample and quality control sample received nominal 3.0 ng of a stable isotope labeled $^{13}C_4$-PFOS surrogate recovery standard (SRS). Although not included as part of the data accuracy assessment for this study, SRS recovery determinations were included as part of an ongoing method validation aspect for SRS behavior in environmental soil and sediment samples for potential future applications. The SRS was quantified from a SRS calibration curve constructed from analysis of calibration standards prepared from the SRS in calibration standards. The SRS recovery was determined based on the calculated concentration of SRS from the analysis and recovery of SRS from each sample is included in **Tables 15, 16 and 17** but was not used for evaluation of data accuracy for this study and is otherwise excluded from the discussions in the report.

Each analytical sample was prepared in duplicate for analysis of PFOS, PFHS and PFBS in the sample. Additionally, a third and/or fourth replicate was weighed out and used to prepare LMSs. The LMS results were used for determination of data accuracy. RPD of duplicate samples results was used for determination of data precision. Appropriate LMS levels are considered those that are within 0.5-times to 10-times the measured endogenous analyte level in the equivalent non-fortified soil/sediment sample, and the fortification of 20 ng and 200 ng was sufficient in at least one of the LMSs to be considered appropriate for determination of the data accuracy for PFOS, but was greater than 10-times the PFBS and PFHS endogenous levels which were less than the LLOQ (BLQ) in all samples.

Calibration standards were prepared by spiking known quantities of PFOS (linear isomer), PFHS (linear isomer), PFBS and $^{13}C_4$-PFOS into 1-cubic centimeter (1 cc, 1 mL) aliquots of 3M Environmental Laboratory control soil TCR-455. The nominal mass of 1 cc of control soil TCR-455 is 1.0 gram (dry), therefore, the nominal calibration standard range prepared and analyzed was 0.200 ng/g to 500 ng/g.

Laboratory control spike (LCS) samples were prepared with each sample preparation batch; prepared at three levels (nominal 3.00 ng/g, 30.0 ng/g and 300 ng/g) and each level in triplicate. The LCSs were prepared using control soil TCR-455, same as calibration standards, and were fortified with PFOS (mixed linear + branched isomers), PFHS (mixed linear + branched isomers) and PFBS. The LCS results were used to estimate the analytical method uncertainty.

6.4 Percent Soil Moisture Determination

The percent moisture of sediment samples was determined by gravimetric analysis. Dry weights were determined from separate weighings than the sample aliquot weighings used for extractions. To determine the percent moisture, duplicate aliquots of each soil sample were removed and the accurate "wet" weight determined for each. Each aliquot was then dried at ≥ 100°C until no further mass loss occurred from water evaporation, at which time the accurate dry sample weights were determined. The difference in mass, attributed to water evaporation, was used to calculate the percent moisture of the original sample. The averaged percent moisture result for each was then used to report the PFOS, PFHS and PFBS concentration on a dry weight basis.

6.5 LC/MS/MS Analysis

The analysis of sample extracts for PFOS, PFHS and PFBS was performed by LC/MS/MS as described in method ETS-8-053.0. The relative percent difference (RPD) of duplicate prepared sample results was used as a measure of the analytical precision. The determined recovery of fortified PFOS, PFHS and PFBS from LMS samples was used as a measure of analytical accuracy. Surrogate recoveries are reported in **Tables 15, 16 and 17**, but were not used for evaluating analyte recovery for this study. The surrogate data was collected as part of an on-going evaluation of surrogate recovery from environmental field samples for supporting a method validation of ETS-8-053.

Details of the specific instrument parameters, the liquid chromatography gradient program, and the specific mass transitions analyzed are detailed in the raw data, and are briefly described below in **Table 4**, **Table 5** and **Table 6**.

Table 4. Instrument Information

Instrument Name	ETS-Jonas (j)
Analytical Method ID	ETS-8-053.0
Liquid Chromatograph	Agilent 1100 with Binary Pump
Guard column	Pre-Autosampler; Prism RP (2.1 x 50 mm, 5 µm)
Extraction column	Oasis HLB (3 x 20 mm, 25 µ); 30°C
Analytical column	Betasil C18 (2.1 x 100 mm, 5µ)
Injection Volume	25 µL
Mass Spectrometer	API 5000
Ion Source	Turbolon Spray
Polarity	Negative
Software	Analyst 1.4.2

Table 5. Gradient Liquid Chromatography Conditions (ETS-8-053)

Step Number	*Total Time [min]*	*Flow Rate [mL/min]*	*Percent A [2 mm Aqueous Ammonium Acetate]*	*Percent B [Acetonitrile]*
1	0.0	0.400	97.0	3.0
2	3.0	0.400	97.0	3.0
3	3.5	0.400	70.0	30.0
4	17.0	0.400	40.0	60.0
5	17.5	0.400	10.0	90.0
6	19.5	0.400	10.0	90.0
7	20.0	0.400	97.0	3.0
8	23.0	0.400	97.0	3.0

Table 6. Mass Transitions

Analyte	*Mass Transitions Monitored*
PFBS	*299>99, 299>80*
$^{18}O_2$-PFBS (IS)	*303>84*
PFHS	*399>99, 399>80*
$^{13}C_3$-PFHS (IS)	*402>80*
PFOS	*499>130, 499>99, 499>80*
$^{13}C_8$-PFOS (IS)	*507>80*
$^{13}C_4$-PFOS (Surrogate)	*503>80*

Note: Multiple mass transitions are summed to give the instrument response for that analyte.

7 Analytical Results

Concentration values are rounded to three significant figures according to EPA rounding rules. Because of rounding some calculated values may vary slightly from those found in the raw data. Samples with RPDs for duplicate results of less than 50% and LMS results meeting the method criterion of within 100 ± 30% demonstrated that the method was appropriate for those samples and were reported without footnotes in results tables. The nominal 20.0 ng and 200 ng fortified quantities of PFOS, PFHS and PFBS into LMSs for field samples were at an appropriate level for evaluating sample-specific analyte recoveries for PFOS. Results for PFHS and PFBS were all less than the LLOQ (BLQ) and therefore LMS fortifications were greater than 10-times the endogenous level measured in the samples.

7.1 Calibration

A set of calibration standards were prepared by spiking varying known quantities of PFOS (linear), PFHS (linear), PFBS and surrogate ($^{13}C_4$-PFOS), and a fixed quantity of stable isotope labeled internal standards, into one cubic centimeter (1 cc, 1 mL) aliquots of 3M Environmental Laboratory control soil TCR-455 (nominal soil mass of 1.0 g/mL). A total of twelve (12) calibration standards were prepared as a set. The prepared standards were fortified from nominal 0.200 ng to 500 ng in 1 cubic centimeter of

control soil TCR-455; equivalent to nominal 0.200 ng/g to 500 ng/g in soil TCR-455. Following analysis of the calibration standards, the concentration of each standard was plotted against the measured analyte /IS peak area ratio. A quadratic equation with 1/x weighting was used to fit the data for each analyte. Calibration curves were not forced through zero. Determining the standard concentration using the resultant calibration curve and comparing to the known concentration confirmed accuracy of each curve point at within 100 ± 30% (± 35% at the LLOQ). The correlation coefficient (r) was greater than 0.999 for all calibration curves, and the coefficient of determination (r^2) was greater than 0.990. Calibration results for PFOS, PFHS and PFBS are summarized in **Table 7**, **Table 8** and **Table 9**, respectively.

Because soil and sediment weights can vary significantly for a 1 cc (1 mL) field sample, depending on composition and moisture content, the instrument response was calibrated for the known concentrations of target analytes based on the mass quantity of reference substance added to a 1 cc soil (1 mL) calibration standard prior to extraction (*e.g.* calibrated in this study for a range of 0.500 ng to 500 ng PFOS, PFHS and PFBS; the 0.200 ng standard was excluded). Because a 1cc aliquot of control soil TCR-455 weighs nominally 1.0 gram (dry weight) and has less than 5% moisture content, the nominal concentration range of the calibration was essentially 0.200 ng/g to 500 ng/g. However, because sample soil aliquots may weigh more than 1.0 gram and contain significant moisture, the determined concentrations during the analysis on an ng per sample aliquot basis from the calibration curve and then adjusted for the accurate determined weight and percent moisture so they could be reported on a ng/g (dry weight) basis.

Table 7. PFOS Calibration Summary

Analytical Run	PFOS (ng)												r
	STD 1	STD 2	STD 3	STD 4	STD 5	STD 6	STD 7	STD 8	STD 9	STD 10	STD 11	STD 12	
Actual	0.199	0.499	0.748	0.997	2.49	4.99	9.97	24.9	49.9	99.7	199	499	N/A
s111007a	excluded	0.478	0.791	0.888	2.51	5.42	10.1	24.5	50.6	98.9	199	499	0.9999
Recovery	N/A	95.8%	106%	89.1%	101%	109%	101%	98.4%	101%	99.2%	100%	100%	N/A

Table 8. PFHS Calibration Summary

Analytical Run	PFHS (ng)												r
	STD 1	STD 2	STD 3	STD 4	STD 5	STD 6	STD 7	STD 8	STD 9	STD 10	STD 11	STD 12	
Actual	0.200	0.500	0.750	1.00	2.50	5.00	10.0	25.0	50.0	100	200	500	N/A
s111007a	excluded	0.473	0.801	0.908	2.41	5.57	9.95	26.2	47.5	99.9	201	500	0.9998
Recovery	N/A	94.6%	107%	90.8%	96.4%	111%	99.5%	105%	95.0%	99.9%	101%	100%	N/A

Table 9. PFBS Calibration Summary

Analytical Run	PFBS (ng)												r
	STD 1	STD 2	STD 3	STD 4	STD 5	STD 6	STD 7	STD 8	STD 9	STD 10	STD 11	STD 12	
Actual	0.200	0.500	0.750	1.00	2.50	5.00	10.0	25.0	50.0	100	200	500	N/A
s111007a	excluded	0.415	0.773	0.944	2.54	5.90	9.76	25.5	51.5	97.7	199	501	0.9998
Recovery	N/A	83.0%	103%	94.4%	102%	118%	97.6%	102%	103%	97.7%	99.5%	100%	N/A

7.2 Limits of Quantitation (LOQs)

The lower limit of quantitation (LLOQ) was the lowest non-zero calibration standard in the curve that met the linearity and accuracy requirement for a low standard (100 ± 35%) and for which the area counts were at least twice that of the average response determined for the method blank injected just prior to the calibration standards . The LLOQ for this study was the nominal 0.500 ng calibration standard (nominal 0.500 ng/g in soil TCR-455) for PFOS, PFHS and PFBS. All sample analyte responses less than the response of the 0.500 ng calibration standard were reported as BLQ (below the limits of quantitation). The upper limit of quantitation (ULOQ) was the nominal 500 ng calibration standard.

7.3 Continuing Calibration

During the course of each analysis, continuing calibration verifications (CCVs) were performed by regular injection of a mid-level calibration standard after approximately every 15th sample injected in the analytical run. The back calculated concentration results were used to confirm that the instrument response and the initial calibration curve were still in control. All CCVs flanking reported data met the method criteria of 100% ± 30% accuracy.

7.4 Blanks

Three types of blanks were analyzed during this analysis: method blanks were prepared with blank matrix soil TCR-455 and were spiked with IS and surrogate; travel blanks (trip blanks) prepared from aliquots of soil TCR-455 sealed in s ample bottle that accompanied the bottle order to and from the sampling site; and solvent blanks containing extraction solvent. The different blank results were reviewed to evaluate potential contamination during shipment, and to evaluate method performance parameters such as injector carry over and to establish the LLOQ. All blanks were below the LLOQ (BLQ)

7.5 Laboratory Control Spikes (LCSs)

Laboratory control spikes were prepared by spiking know quantities of PFOS (linear + branched), PFHS (linear + branched) and PFBS into 1 cc aliquots of soil TCR-455, fortified at nominal 3.0 ng and 30 ng and 300 ng levels, with each level prepared in triplicate. The results of the LCS analyses and calculation of analyte measurement accuracies (percent recovery) for PFOS, PFHS and PFBS are shown in **Table 10, Table 11** and **Table 12** respectively. The analytical method uncertainty calculated from LCS results is shown in **Table 13.**

$$\text{LCS Recovery} = \frac{(\text{Determined Concentration of LCS})}{\text{Spike Concentration}} * 100\%$$

Table 10. LCS Results (PFOS, linear + branched isomer)

Sample ID	PFOS Recovery		
	3.00 LCS	30.0 LCS	300 LCS
LCSs (j120507b)	114%	109%	118%
	112%	109%	117%
	108%	114%	113%
Average Recovery	**111%**	**111%**	**116%**
Std Dev.	**2.9%**	**3.1%**	**2.8%**
RSD	**2.6%**	**2.8%**	**2.4%**

Nominal LCS concentrations were 3.00 ng/g. 30.0 ng/g and 300 ng/g of PFOS (linear + branched isomers), each prepared and analyzed in triplicate.

Table 11. LCS Results (PFHS, linear + branched isomer)

Sample ID	PFHS Recovery		
	3.00 LCS	30.0 LCS	300 LCS
LCSs (j120507b)	118%	109%	108%
	116%	107%	113%
	103%	107%	105%
Average Recovery	**113%**	**108%**	**109%**
Std Dev.	**8.3%**	**1.1%**	**3.9%**
RSD	**7.4%**	**0.99%**	**3.5%**

Nominal LCS concentrations were 3.00 ng/g. 30.0 ng/g and 300 ng/g of PFHS (linear + branched isomers), each prepared and analyzed in triplicate.

Table 12. LCS Results (PFBS)

Sample ID	PFBS Recovery		
	3.00 LCS	30.0 LCS	300 LCS
LCSs (j120507b)	116%	106%	98.3%
	117%	114%	112%
	113%	109%	106%
Average Recovery	**116%**	**110%**	**106%**
Std Dev.	**2.1%**	**4.2%**	**7.0%**
RSD	**1.8%**	**3.8%**	**6.6%**

Nominal LCS concentrations were 3.00 ng/g. 30.0 ng/g and 300 ng/g of PFBS, each prepared and analyzed in triplicate.

Table 13. Analytical Method Uncertainties

Sample ID	LCS Results		
	PFOS	PFHS	PFBS
3.00 LCSs	114%	118%	116%
	112%	116%	117%
	109%	103%	113%
30.0 LCSs	109%	109%	106%
	109%	107%	114%
	115%	107%	109%
300 LCSs	119%	108%	98.3%
	118%	113%	112%
	113%	105%	106%
Average Recovery	**113%**	**110%**	**110%**
Std Dev.	**3.7%**	**5.1%**	**6.1%**
RSD	**3.3%**	**4.7%**	**5.5%**
Method Uncertainty (2 x Std. Dev.); 95% CI	**7.3%**	**10%**	**12%**

7.6 Laboratory Matrix Spikes (LMSs)

Laboratory matrix spikes (LMSs) were generated by adding a known quantity of PFOS (linear), PFHS (linear) and PFBS to an aliquot of sediment sample, and then preparing the sample the same as non-spiked samples. Spikes for this study, LMSs were spiked at levels that were appropriate for the endogenous analyte levels in the soils, determined from screening analysis and fortified with the target analytes from 0.5-times to 10-times the endogenous analyte levels determined in the soil/sediment samples during the range finding analysis. The LMS method acceptance criterion of within 100 ± 30% were met for all LMS recoveries. The LMS recovery results are summarized in **Table 2**. The nominal 20.0 ng and 200 ng fortified quantities of PFOS, PFHS and PFBS into LMSs for field samples were at an appropriate level for evaluating sample-specific analyte recoveries for PFOS. Results for PFHS and PFBS were all less than the LLOQ (BLQ) and therefore LMS fortifications were greater than 10-times the endogenous level measured in the samples. The PFOS, PFHS and PFBS recovery calculations for LMSs used the following equation:

$$\text{LMS Recovery} = \frac{(\text{Determined Concentration of LMS} - \text{Determined Concentration of Field Sample})}{\text{Spike Concentration}} * 100\%$$

7.7 Percent Moisture Determinations

The percent moisture was determined for each soil sample. Duplicate aliquots of each were taken and accurately weighed to determine the "wet" weight. Then each aliquot was dried at > 100°C until no further loss in mass occurred due to water evaporation, after which the dry weight was accurately determined. The average percent moisture and RPD of the duplicate determinations for each soil are reported in **Table 14**. The percent moisture was calculated by the following equation:

$$\text{Percent Moisture} = \frac{(\text{Original Soil Wet Mass} - \text{Dried Soil Mass})}{\text{Original Soil Wet Mass}} * 100\%$$

Table 14. Percent Moistures for Jeffries Property Sediments

LIMS ID	Sample ID	Average Percent Moisture (w/w) [a]	Relative Percent Difference [a]
GLP10-01-01-26-001	JPAL SD TRIP1 0 0000	2.7%	2.5%
GLP10-01-01-26-002	JPAL SD ET01 0 0000	28%	0.78%
GLP10-01-01-26-003	JPAL SD ET02 0 0000	30%	1.5%
GLP10-01-01-26-004	JPAL SD ET02 DB 0000	30%	0.78%
GLP10-01-01-26-005	JPAL SD ET03 0 0000	40%	3.6%
GLP10-01-01-26-006	JPAL SD ET04 0 0000	61%	0.096%

[a] Percent moisture determined for duplicate sample aliquots taken from each sample bottle

7.8 Individual Analytical Sample Results

The individual analytical sample results for PFOS, PFHS and PFBS concentrations are shown in **Table 15, Table 16** and **Table 17,** respectively.

Table 15. Individual PFOS Results for Jeffries Property Sediments

Sample Description	Surrogate ($^{13}C_4$-PFOS) Recovery	LMS Spike Concentration (ng/g; dry weight)	Measured PFOS Concentration (ng/g; dry weight)	LMS Recovery	Average PFOS Concentration (ng/g; dry wt.) and RPD (%)
GLP10-01-01-21-001	109%	N/A	BLQ	N/A	BLQ
GLP10-01-01-21-001 Dup	110%		BLQ		
GLP10-01-01-21-001 LMS	105%	1.04	1.35	130%	N/A
GLP10-01-01-21-002	101%	N/A	3.81	N/A	3.95
GLP10-01-01-21-002 Dup	103%		4.09		
GLP10-01-01-21-002 Low LMS	102%	14.6	18.8	102%	7.0%
GLP10-01-01-21-002 High LMS	104%	143	152	103% [a]	
GLP10-01-01-21-003	106%	N/A	8.99	N/A	8.59
GLP10-01-01-21-003 Dup	110%		8.20		
GLP10-01-01-21-003 Low LMS	107%	15.0	24.1	104%	9.1%
GLP10-01-01-21-003 High LMS	103%	151	166	104% [a]	
GLP10-01-01-26-004	106%	N/A	9.8	N/A	10.0
GLP10-01-01-26-004 Dup	104%		10.2		

Table 15. Individual PFOS Results for Jeffries Property Sediments

Sample Description	Surrogate ($^{13}C_4$-PFOS) Recovery	LMS Spike Concentration (ng/g; dry weight)	Measured PFOS Concentration (ng/g; dry weight)	LMS Recovery	Average PFOS Concentration (ng/g; dry wt.) and RPD (%)
GLP10-01-01-26-004 Low LMS	105%	16.6	27.5	105%	3.6%
GLP10-01-01-26-004 High LMS	105%	152	168	104% [a]	
GLP10-01-01-21-005	104%	N/A	11.9	N/A	12.1
GLP10-01-01-21-005 Dup	106%		12.2		
GLP10-01-01-21-005 Low LMS	104%	19.6	33.8	111%	2.9%
GLP10-01-01-21-005 High LMS	104%	198	227	108% [a]	
GLP10-01-01-21-006	104%	N/A	23.5	N/A	23.8
GLP10-01-01-21-006 Dup	102%		24.1		
GLP10-01-01-21-006 Low LMS	106%	35.8	61.4	105%	2.5%
GLP10-01-01-21-006 High LMS	104%	380	418	104%	

N/A; not applicable
BLQ; analyte response was lower than the analyte response of the LLOQ which was nominal 0.500 ng/g low standard.
[a] LMS fortification level was greater than 10-times the endogenous analyte level.

Table 16. Individual PFHS Results for Jeffries Property Sediments

Sample Description	Surrogate ($^{13}C_4$-PFOS) Recovery	LMS Spike Concentration (ng/g; dry weight)	Measured PFHS Concentration (ng/g; dry weight)	LMS Recovery	Average PFHS Concentration (ng/g; dry wt.) and RPD (%)
GLP10-01-01-21-001	109%	N/A	BLQ	N/A	BLQ
GLP10-01-01-21-001 Dup	110%		BLQ		
GLP10-01-01-21-001 LMS	105%	1.04	1.30	125%	N/A
GLP10-01-01-21-002	101%	N/A	BLQ	N/A	BLQ
GLP10-01-01-21-002 Dup	103%		BLQ		
GLP10-01-01-21-002 Low LMS	102%	14.6	15.3	105% [a]	N/A
GLP10-01-01-21-002 High LMS	104%	144	148	103% [a]	
GLP10-01-01-21-003	106%	N/A	BLQ	N/A	BLQ
GLP10-01-01-21-003 Dup	110%		BLQ		
GLP10-01-01-21-003 Low LMS	107%	15.1	15.4	102% [a]	N/A
GLP10-01-01-21-003 High LMS	103%	151	158	105% [a]	

Table 16. Individual PFHS Results for Jeffries Property Sediments

Sample Description	Surrogate ($^{13}C_4$-PFOS) Recovery	LMS Spike Concentration (ng/g; dry weight)	Measured PFHS Concentration (ng/g; dry weight)	LMS Recovery	Average PFHS Concentration (ng/g; dry wt.) and RPD (%)
GLP10-01-01-26-004	106%	N/A	BLQ	N/A	BLQ
GLP10-01-01-26-004 Dup	104%		BLQ		
GLP10-01-01-26-004 Low LMS	105%	16.7	16.7	100% [a]	N/A
GLP10-01-01-26-004 High LMS	105%	153	157	103% [a]	
GLP10-01-01-21-005	104%	N/A	BLQ	N/A	BLQ
GLP10-01-01-21-005 Dup	106%		BLQ		
GLP10-01-01-21-005 Low LMS	104%	19.7	20.7	105% [a]	N/A
GLP10-01-01-21-005 High LMS	104%	199	212	107% [a]	
GLP10-01-01-21-006	104%	N/A	BLQ	N/A	BLQ
GLP10-01-01-21-006 Dup	102%		BLQ		
GLP10-01-01-21-006 Low LMS	106%	36.0	38.7	108% [a]	N/A
GLP10-01-01-21-006 High LMS	104%	382	371	97.0% [a]	

N/A; not applicable
BLQ; analyte response was lower than the analyte response of the LLOQ which was nominal 0.500 ng/g low standard.
[a] LMS fortification level was too low relative to the endogenous analyte level to make an accurate determination of recovery.

Table 17. Individual PFBS Results for Jeffries Property Sediments

Sample Description	Surrogate ($^{13}C_4$-PFOS) Recovery	LMS Spike Concentration (ng/g; dry weight)	Measured PFBS Concentration (ng/g; dry weight)	LMS Recovery	Average PFBS Concentration (ng/g; dry wt.) and RPD (%)
GLP10-01-01-21-001	109%	N/A	BLQ	N/A	BLQ
GLP10-01-01-21-001 Dup	110%		BLQ		
GLP10-01-01-21-001 LMS	105%	1.04	1.09	105%	N/A
GLP10-01-01-21-002	101%	N/A	BLQ	N/A	BLQ
GLP10-01-01-21-002 Dup	103%		BLQ		
GLP10-01-01-21-002 Low LMS	102%	14.6	16.6	114% [a]	N/A
GLP10-01-01-21-002 High LMS	104%	144	148	103% [a]	
GLP10-01-01-21-003	106%	N/A	BLQ	N/A	BLQ
GLP10-01-01-21-003 Dup	110%		BLQ		
GLP10-01-01-21-003 Low LMS	107%	15.1	16.6	110% [a]	N/A

Table 17. Individual PFBS Results for Jeffries Property Sediments

Sample Description	Surrogate ($^{13}C_4$-PFOS) Recovery	LMS Spike Concentration (ng/g; dry weight)	Measured PFBS Concentration (ng/g; dry weight)	LMS Recovery	Average PFBS Concentration (ng/g; dry wt.) and RPD (%)
GLP10-01-01-21-003 High LMS	103%	151	148	103% [a]	
GLP10-01-01-26-004	106%	N/A	BLQ	N/A	BLQ
GLP10-01-01-26-004 Dup	104%		BLQ		
GLP10-01-01-26-004 Low LMS	105%	16.7	17.4	105% [a]	N/A
GLP10-01-01-26-004 High LMS	105%	153	150	98.5% [a]	
GLP10-01-01-21-005	104%	N/A	BLQ	N/A	BLQ
GLP10-01-01-21-005 Dup	106%		BLQ		
GLP10-01-01-21-005 Low LMS	104%	19.7	21.2	108% [a]	N/A
GLP10-01-01-21-005 High LMS	104%	199	206	104% [a]	
GLP10-01-01-21-006	104%	N/A	BLQ	N/A	BLQ
GLP10-01-01-21-006 Dup	102%		BLQ		
GLP10-01-01-21-006 Low LMS	106%	36.0	41.4	115% [a]	N/A
GLP10-01-01-21-006 High LMS	104%	382	384	101% [a]	

N/A; not applicable
BLQ; analyte response was lower than the analyte response of the LLOQ which was nominal 0.500 ng/g low standard.

8 Conclusion

Sediments collected from the Jeffries Property in March 2012 were successfully analyzed for PFOS, PFHS and PFBS following 3M Environmental Laboratory method ETS-8-053.0 and conducted as 3M study GLP10-01-02-25. The average PFOS, PFHS and PFBS concentration results for the soil samples are summarized in **Table 1** and the LMS recoveries are summarized in **Table 2**. The individual analytical sample results are shown in **Table 15**, **Table 16**, and **Table 17** for PFOS, PFHS and PFBS, respectively. The soil trip blank that accompanied the sample bottles to the site and then accompanied samples back to the laboratory was sufficiently devoid of PFOS, PFHS and PFBS, indicating that no contamination of the samples occurred during sample shipment or sample to the laboratory. The PFHS and PFBS levels in the samples were all less than the 0.5 ng/g calibration standard that defined the lower limit of quantitation. The PFOS concentrations in the sediment samples ranged from 3.95 ng/g to 23.8 ng/g.

The data accuracy was within 100 $\pm$ 30% and the data precision was excellent with RPDs less than 10%.

The analytical method uncertainties (95% CI) were determined by statistical examination of the LCS results for PFOS, PFHS and PFBS and were $\pm$ 7.3% for PFOS, $\pm$ 10% for PFHS and $\pm$ 12% for PFBS, respectively, at the 95% confidence interval (95% CI).

9 Data/Sample Retention

All associated project data (hardcopy and electronic) will be archived as project GLP10-01-02-25 according to 3M Environmental Laboratory standard operating procedures. The percent moisture raw data was determined for the samples as part of study GLP10-01-01-26 and that raw data are archived with that interim study data packet and report.

10 List of Attachments

Attachment A: Preparation Forms, Raw Data and Chromatograms

11 Signatures

Report Approval:

6/19/2012

Cleston C. Lange, Ph.D., Principal Analytical Investigator — Date

19 JUNE 2012

William K. Reagen, Ph.D., 3M Environmental Laboratory Management — Date

6/22/12

Gary A. Hohenstein, Sponsor Representative — Date

6/25/12

Jaisimha Kesari, Study Director — Date

Attachment A

Preparation Forms, Raw Data and Chromatograms

GLP10-01-01 Interim Report 26: Analysis for PFOA in Sediments Collected from the Jeffries Property in February 2012

Study Title

3M Environmental Laboratory Analytical Protocol GLP10-01-01: Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program

Data Requirement

EPA TSCA Good Laboratory Practice Standards 40 CFR Part 792

Study Director

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Principal Analytical Investigator

Cleston C. Lange, Ph.D.
3M Environmental Laboratory

Interim Report Completion Date

Upon Signing

Performing Laboratory

3M Environmental Health and Safety Operations
Environmental Laboratory
3M Center, Bldg 260-05-N-17
St. Paul, MN 55144

Project Identification

GLP10-01-01-26

Total Number of Pages

19

This page has been reserved for specific country requirements.

GLP Compliance Statement

Report Title: GLP10-01-01 Interim Report 26: Analysis for PFOA in Sediments Collected from the Jeffries Property in February 2012. 3M Environmental Laboratory Analytical Protocol GLP10-01-01: Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program.

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

Exceptions to GLP compliance:

- **Test, control and reference substances were not all characterized under GLPs.**
- **Samples environmental samples, there was no dosing and no specific test substance for this study.**

Gary Hohenstein, Sponsor Representative — Date 4/17/12

Jaisimha Kesari, P.E., DEE, Study Director — Date 4/24/12

QUALITY ASSURANCE STATEMENT

Report Title: GLP10-01-01 Interim Report 26: Analysis for PFOA in Sediments Collected from the Jeffries Property in February 2012. 3M Environmental Laboratory Analytical Protocol GLP10-01-01: Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program.

This interim study report and the accompanying data were audited by the 3M Environmental Laboratory Quality Assurance Unit (QAU), as indicated below. The findings were reported to the principal investigator (P.I.), laboratory management and study director.

Study Inspection Dates	Phase		Date Reported to	
		P.I.	Study Director Management	Study Director
4/3/2012– 4/5/2012	Interim Report and Data	4/9/2012	4/10/2012	4/10/2012

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QAU Representative Date

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Study Dates

Study Initiation: March 08, 2010
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Interim Analytical Completion: March 23, 2012
Interim Report Completion: Upon final Signatures

Location of Archives

All original raw data and analytical reports 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.

2 Summary

This interim report provides the PFOA concentration results for five sediments collected from the Jeffries property (Bert Jeffries Landfill) located in Northern Alabama. One travel blank (trip blank), containing approximately 10-25 grams of control soil in a sample bottle, accompanied the sample bottles to and from the collection site and was also analyzed. Samples were received on March 02, 2012 and logged into the 3M Environmental Laboratory electronic LIMS system under project GLP10-01-01-26. Prior to extraction, sediments were aliquoted from each sample bottle in triplicate into extraction vessels and accurately weighed. The first and second aliquot served as analytical sample and duplicate sample. The third replicate of each was fortified with nominal 2.00 ng of PFOA as a laboratory matrix spike (LMS). A single LMS for the trip blank was also prepared and fortified with nominal 1.00 ng of PFOA. Each aliquot was extracted and analyzed per method ETS-8-053 by liquid chromatography with triple quadrapole mass spectrometric detection (LC/MS/MS). The PFOA recovery results from LMSs provided a measure of sample-specific accuracy for the results. The relative percent difference (RPD) of the duplicate sample results was used to assess the analytical precision of the sample results. The percent moisture of each soil was also determined as part of the study and results reported on a dry sediment weight basis. The PFOA concentrations and RPDs are summarized in **Table 1**. The LMS fortification concentrations and recoveries for PFOA are summarized in **Table 2**.

Table 1. PFOA Results for Sediments from Jeffries Property, February 2012

3M LIMS ID	Sample ID	Avg. PFOA Concentration (ng/g; dry weight)	Relative Percent Difference
GLP10-01-01-26-001	JPAL SD TRIP1 0 0000	BLQ	NA
GLP10-01-01-26-002	JPAL SD ET01 0 0000	0.629	14%
GLP10-01-01-26-003	JPAL SD ET02 0 0000	0.671	23%
GLP10-01-01-26-004	JPAL SD ET02 DB 0000	0.819	42%
GLP10-01-01-26-005	JPAL SD ET03 0 0000	1.06	1.4%
GLP10-01-01-26-006	JPAL SD ET04 0 0000	2.39	11%

BLQ; The integrated peak area response for PFOA in the sample was below the PFOA peak area response for the lowest standard that was used to construct the calibration curve (< nominal 0.200 ng/g).
NA; not applicable

Table 2. LMS PFOA Recovery Results for Sediments from Jeffries Property, February 2012

3M LIMS ID	Sample ID	PFOA Spike Concentration (ng/g; dry weight)	PFOA Recovery (Data Accuracy)
GLP10-01-01-26-001 LMS	JPAL SD TRIP1 0 0000, LMS 1.00 ng	0.980	89.6%
GLP10-01-01-26-002 LMS	JPAL SD ET01 0 0000, LMS 2.00 ng	1.38	92.5%
GLP10-01-01-26-003 LMS	JPAL SD ET02 0 0000, LMS 2.00 ng	1.67	89.3%
GLP10-01-01-26-004 LMS	JPAL SD ET02 DB 0000, LMS 2.00 ng	1.45	85.0%
GLP10-01-01-26-005 LMS	JPAL SD ET04 0 0000, LMS 2.00 ng	2.13	91.8%
GLP10-01-01-26-006 LMS	JPAL SD TRIP1 0 0000, LMS 2.00 ng	3.34	101%

[a] Samples with an endogenous PFOA level of BLQ were treated as a concentration of zero to calculate recovery.

3 Introduction

The analyses reported herein were conducted as part of the Phase 3 Environmental Monitoring and Assessment Program for the 3M facility located in Decatur, Alabama. The objective of the overall program is to gain information regarding concentrations of perfluorooctanoate (PFOA) in various environmental media such as groundwater, soils and sediments that are associated with and near the Decatur facility. Reported herein are the results from analysis of sediments collected from the Jeffries property. The samples were collected by Weston Solutions, Inc. personnel in February 2012 and shipped to the 3M Environmental Laboratory for quantitative analysis of PFOA. One soil travel blank (trip blank) accompanied the sample bottles to the site, during collection and during samples shipment and was analyzed to evaluate for any potential contamination of samples during the sample shipment and collection period.

This report describes the sample shipment, receipt, extraction and quantitative LC/MS/MS analysis procedures conducted for determination of PFOA in the soils for project GLP10-01-01-26. Additionally, included in this report are the assessment of the analytical precision and accuracy for the reported PFOA concentration results, the recovery results for a stable isotope labeled $^{13}C_4$-PFOA surrogate recovery standard (SRS) that was added to each soil aliquot prior to extraction, and the determined percent moisture content of each soil.

4 Test, Control and Reference Substances

This study does not have a test substance in the classic sense of a GLP study because this study was purely analytical in nature. The analytical reference substances are listed in **Table 3.**

Table 3. Reference Substances

Test Substance	PFOA (linear isomer), free acid	Technical PFOA (linear + branched isomers), ammonium salt	$^{13}C_4$-PFOA	$^{13}C_8$-PFOA
Use	Calibration & LMSs	LCSs	Surrogate	Internal Standard
Source	Oakwood	3M	Wellington Labs	Wellington Labs
Expiration Date	Jan.17, 2018	Feb. 27, 2017	Dec. 07, 2013	May 24, 2014
Storage Conditions	Frozen	Frozen	Frozen	Frozen
Chemical Lot	3440	332	MPFOA1210	052411
TCR Number	TCR07-0041-1/1	TCR-123	TCR11-0001-11/14	TCR11-0016-13/17 & TC R11-0016-14/17
Physical Description	Powder	White Powder	Methanol Solution [a]	Methanol Solution [a]
Purity	99.6%	95%	>98%	>98%

[a] Stable isotope labeled materials are typically provided as methanol solutions by the commercial vendor and are treated as 100% pure; the vendor's reported methanol stock concentration is used for calculating concentrations of diluted standards made from them.

5 Test System

There was not a test system for this study in the classic sense of a GLP study. This study was conducted for analysis of sediments collected from the Jeffries property that is located in Northern Alabama. Samples for this study are "real world" environmental samples.

6 Method Summary

6.1 Methods

The sample extractions and quantitative LC/MS/MS analyses were performed following validated method ETS-8-053.0. Two analytical batches were prepared for this study as o120309c and o120316a. The result for the trip blank was reported from batch o120309c and results for field samples were reported from run 120316a.

6.2 Sample Receipt

On February 21, 2012 seven empty 250-mL HDPE Nalgene™ sample bottles, and one travel blank (trip blank) containing approximately 10-25 grams of a control soil TCR-455, were sent from the 3M Environmental Laboratory to Weston Solutions, Inc. field personnel for collection of sediments from the property known as the Bert Jeffries landfill. Following the sample collections by Weston Solutions, Inc. personnel, five sediment-filled sample bottles and the trip blank were returned in the bottles to the 3M Environmental Laboratory for quantitative analysis of PFOA. The samples were received with sample chains of custody numbers 15290 on March 02, 2012.

Soil samples from Alabama are regulated and the sediments for this study were shipped in accordance with USDA/APHIS soil permit number P330-09-00125.

Sample nomenclature follows the form JPAL-SD-ET-xxxx where the first string defines the Jeffries Property Alabama (JPAL), the second string defines the sample media (i.e., SD= sediment, SB –field sample duplicate), the third string defines the site location (ET = eastern tributary), the fourth string defines the field sample (1,2,3… or DB = duplicate field sample) . The fourth string defines the sediment sampling depth (0000 = 0 ft to 0.5 ft interval).

6.3 Sample Preparation

Sample preparation was conducted as two analytical batches, o120309c and o120316a. The first batch was prepared with LMSs fortified at 20 and 200 ng of PFOA, which was later determined to be too high for a proper evaluation of PFOA recovery from the sediments which contained much lower PFOA levels. The trip blank was prepared with a 1 ng PFOA LMS and was reported from that batch. The samples were prepared a second time as o120316a with a 2 ng fortified LMS for each sample, and the sample results reported from that batch.

Each soil or sediment extraction involved removal of a 1 cubic centimeter (1 cc; 1 mL) aliquot of field sample (typically ~ 1 gram) from each sample bottle using a fixed volume 1 cc spoon, transferring it to a 15 mL conical centrifuge tube, followed by accurate weight determination of the aliquot on a 5-place balance. Then, nominal 3.0 ng of internal standard (IS; nominal 3.0 ng) and 3.0ng of surrogate recovery standard (SRS) was added to each soil aliquot and a known quantity of PFOA was added to each LMS. Then each was extracted by addition of 8 mL of a 4:1 acetonitrile:water solution followed by sonication for 1 to 2 hours followed by centrifugation to remove solids. The supernatant from each was then transferred to an autovial

for analysis. An accurately measured volume of each supernatant was analyzed by LC/MS/MS.

During preparation, each sample additionally received nominal 3.0 ng of a stable isotope labeled surrogate recovery standard (SRS) as $^{13}C_4$-PFOA. Although not included as part of the data accuracy assessment for this study, SRS recovery determinations were included as part of an ongoing method validation aspect for SRS behavior in environmental soil samples for potential future applications. The SRS was quantified from a SRS calibration curve constructed from analysis of calibration standards prepared from the SRS in calibration standards. The SRS recovery was determined based on the calculated concentration of SRS from the analysis and recovery of SRS from each sample is included in **Table 10**, but was not used for evaluation of data accuracy for this study and is otherwise excluded from the discussions in the report.

Each analytical sample was prepared in duplicate for analysis of PFOA in the sample. Additionally, a third and/or fourth replicate was weighed out and used to prepare LMSs. The LMS results were used for determination of data accuracy. RPD of duplicate samples results was used for determination of data precision. Appropriate LMS levels are considered those that are within 0.5-times to 10-times the measured endogenous PFOA level in the equivalent non-fortified soil/sediment sample.

Calibration standards were prepared by spiking known quantities of PFOA (linear isomer) into 1-cubic centimeter (1 cc, 1 mL) aliquots of 3M Environmental Laboratory control soil TCR-455. The nominal mass of 1 cc of control soil TCR-455 is 1.0 gram (dry), therefore, the nominal calibration standard range prepared and analyzed was 0.200 ng/g to 500 ng/g.

Laboratory control spike (LCS) samples were prepared with each sample preparation batch; prepared at three levels (nominal 3.00 ng/g, 30.0 ng/g and 300 ng/g) and each level in triplicate. The LCSs were prepared using control soil TCR-455, same as calibration standards, and were fortified with technical PFOA (linear + branched isomer). The LCS results were used to estimate the analytical method uncertainty.

6.4 Percent Soil Moisture Determination

The percent moisture of sediments and soils were used to calculate the dry weight of the wet soil and sediment samples weighed during sample preparations for PFOA analysis, and was determined by gravimetric analysis. Dry weights were determined for separate weighings than the weighings used for PFOA extraction and analysis procedures. To determine the percent moisture, duplicate aliquots of each soil sample were removed and the accurate "wet" weight determined for each. All aliquots were dried at $\geq$ 100°C until no further mass loss occurred from wate r evaporation, at which time the accurate dried weights were determined. The difference in mass, attributed to water evaporation, was used to calculate the percent moisture of the original soil. The averaged percent moisture result for each was then used to calculate the soil PFOA concentration on a dry weight basis, and is reported for each sample in **Table 9**.

6.5 LC/MS/MS Analysis

The LC/MS/MS analysis was performed as described in method ETS-8-053.0

The relative percent difference (RPD) of the duplicate sample results was used as a measure of the analytical precision. The determined recovery of fortified PFOA from the LMS samples was used as a measure of sample-specific analytical accuracy. Recovery of the surrogate ($^{13}C_4$-PFOA) is included within this report in **Table 10** as an indirect measure of analytical data accuracy, and is not considered in the accuracy assessment for this study and is only included as part of an on-going method validation aspect in which surrogate recovery behavior is being evaluated in "real world" environmental samples for possible future applications.

Details of the specific instrument parameters, the liquid chromatography gradient program, and the specific mass transitions analyzed are detailed in the raw data, and are briefly described below in **Table 4**, **Table 5** and **Table 6**.

Table 4. Instrument Information

Instrument Name	ETS-Ollie
Analytical Method ID	ETS-8-053.0
Liquid Chromatograph	Agilent 1100 with Binary Pump
Guard column	Pre-Autosampler; Prism RP (2.1 x 50 mm, 5 µ)
Extraction column	Oasis HLB (3 x 20 mm, 25 µ); 30°C
Analytical column	Betasil C18 (2.1 x 100 mm, 5µ)
Injection Volume	25 µL
Mass Spectrometer	API 4000
Ion Source	Turbolon Spray
Polarity	Negative
Software	Analyst 1.4.2

Table 5. Gradient Liquid Chromatography Conditions (ETS-8-053)

Step Number	*Total Time [min]*	*Flow Rate [mL/min]*	*Percent A [2 mm Aqueous Ammonium Acetate]*	*Percent B [Acetonitrile]*
1	0.0	0.400	97.0	3.0
2	3.0	0.400	97.0	3.0
3	3.5	0.400	70.0	30.0
4	17.0	0.400	40.0	60.0
5	17.5	0.400	10.0	90.0
6	19.5	0.400	10.0	90.0
7	20.0	0.400	97.0	3.0
8	23.0	0.400	97.0	3.0

Table 6. Mass Transitions

Analyte	*Mass Transitions Monitored*
PFOA	*413>169, 413>219, 413>369*
$^{13}C_4$-PFOA (Surrogate)	*417>169, 417>219, 417>372*
$^{13}C_8$-PFOA (IS)	*421>172, 421>223, 421>376*

Note: Multiple mass transitions are summed to give the instrument response for that analyte.

7 Analytical Results

All results are rounded to three significant figures according to EPA rounding rules. Because of rounding, values may vary slightly from those found in the raw data. All results were calculated from accurate values in the raw data. Laboratory matrix spikes (LMS) meeting the method acceptance criteria of 100 ± 30%, demonstrate that the method was appropriate.

7.1 Calibration

Calibration standards were prepared by spiking varying known quantities of PFOA (linear isomer) and surrogate, and a fixed quantity of internal standard, into separate 1-cubic centimeter (1 cc, 1 mL) aliquots of 3M Environmental Laboratory matrix soil TCR-455 (nominal 1.0 gram per mL). A total of twelve (12) soil matrix calibration standards ranging from nominal PFOA concentration 0.200 ng/g to 500 ng/g were prepared and analyzed. Following the analysis of calibration standards, the nominal concentration of each standard was plotted versus the measured analyte peak area/IS peak area response ratio. A quadratic equation with 1/x weighting was used to fit the calibration response data. Calibration curves were not forced through zero. Calculating the determined standard concentration using the resultant calibration curve and comparing to the known concentration confirmed accuracy of each curve point within 100 ± 30% (± 35% at the LLOQ). The correlation coefficient (r) was greater than 0.998, and coefficient of determination (r^2) was greater than 0.990. Calibration results for PFOA are summarized in **Table 7**.

Because soil weights vary significantly for a 1 cc (1 mL) soil sample, depending on soil type and moisture content, the instrument response was calibrated for the known concentrations of PFOA based on the mass quantity of PFOA added to each 1 cc soil calibration standard prior to extraction (*e.g.* calibrated in this study for a range of 0.200 ng/g to 200 ng/g PFOA). Because a 1cc aliquot of control soil TCR-455 weighs approximately 1.0 gram (dry weight) and has less than 5% moisture content, the nominal concentration range of the calibration was essentially 0.200 ng/g to 200 ng/g. However, because the sample soils and sediments can vary in moisture content, composition and density, 1 cc aliquots of field soil and sediment samples typically weigh more or less than 1.0 gram. Therefore, the final measured results from the analysis were adjusted for the accurate determined dry weight of the 1 cc sample aliquot that was extracted.

Table 7. PFOA Calibration Summary (Calibrated with linear PFOA)

Analytical Run	PFOA (ng) [a]												r
	STD 1	STD 2	STD 3	STD 4	STD 5	STD 6	STD 7	STD 8	STD 9	STD 10	STD 11	STD 12	
Actual Conc.	*0.200*	*0.500*	*0.750*	*1.00*	*2.50*	*5.00*	*9.99*	*25.0*	*50.0*	*100*	*200*	*500*	*N/A*
o120309c	excluded	0.342	0.651	1.01	2.78	5.13	11.9	27.2	53.5	101	183	512	0.9984
o120316a	0.166	0.511	0.763	0.911	2.62	5.45	10.4	26.3	51.7	96.8	198	502	0.9998
Average (ng)	0.166	0.427	0.707	0.961	2.70	5.29	11.2	26.8	52.6	98.9	191	507	0.9991
Avg. Recovery (%)	83.0%	85.3%	94.3%	96.1 %	108%	106%	112%	107%	105%	98.9%	95.3%	101%	NA

NA; not applicable
[a] PFOA concentrations are nominal ng/g (dry soil wt) concentration based on a nominal mass of 1.0 gram (dry wt.) for each 1 cubic centimeter of control soil used to prepare each calibration standard.

7.2 Limits of Quantitation (LOQs)

The lower limit of quantitation (LLOQ) was the lowest non-zero calibration standard in the curve that met linearity and accuracy requirements (100 ± 35%) and for which the area counts were at least 2X that of the average response determined from the method blanks. The LLOQ for analytical run o120309c, from which the trip blank result was reported, was nominal 0.500 ng/g calibration standard. The LLOQ for analytical batch o120316a, from which the study sample results were reported, was nominal 0.200 ng/g. All sample analyte responses less than the response of the 0.200 ng/g calibration standard were reported as BLQ (below the limits of quantitation).

7.3 Continuing Calibration

During the course of each analysis, continuing calibration verifications (CCVs) was performed by regular injection of a mid-level calibration standard after approximately every 15 samples in the analytical run. The back calculated concentration results for PFOA from CCVs were used to confirm that the instrument response and the initial calibration curve were still in control. All CCVs flanking reported PFOA data met the method criteria of 100% ± 30% accuracy, except for in o120309c where one of the CCVs for PFOA was at 131% and the PFOA result for the trip blank in that run reported with a method deviation.

7.4 Blanks

Three types of blanks were analyzed during this analysis: solvent blanks; and method blanks, which were prepared with blank matrix soil TCR-455 and were spiked with IS and surrogate; and travel blanks (trip blanks) prepared from aliquots of soil TCR-455 contained in sealed sample bottles that accompanied the bottle order to Decatur, AL and the collection site, and returned with the sample shipment back to 3M Environmental Laboratory. The different blanks results were reviewed to evaluate potential contamination during shipment and sampling, to evaluate method performance parameters such as injector carry over and also to establish the LLOQ and the performance of the blanks were considered in the reporting of all results.

7.5 Laboratory Control Spikes (LCSs)

Laboratory control spikes were prepared by spiking known quantities of PFOA (linear + branched isomers) into 1 cc aliquots of soil TCR-455, fortified with nominal 3.0 ng, 30 ng and 300 ng PFOA (linear + branched isomer). The linear + branched isomer quantitation using a linear PFOA calibration curve provided a measure of accuracy in quantifying the sum of potential linear + branched PFOA isomers that are commonly associated with environmental samples. Each LCS level was prepared in triplicate. The averaged results of the LCS analyses are shown in **Table 8** and calculated analytical method uncertainty is shown in **Table 9.** The method acceptance criteria of 100 ± 30% was met for all LCSs. The LCS recoveries were calculated using the following equation:

$$\text{LCS Recovery} = \frac{(\text{Determined Concentration of LCS})}{\text{Spike Concentration}} * 100\%$$

Table 8. LCS Results

Sample ID	PFOA Recovery		
	3.00 ng LCS	30.0 ng LCS	300 ng LCS
LCSs (o120309c)	114%	114%	129%
	97.0%	108%	104%
	108%	110%	107%
LCSs (o120316a)	89.7%	93.7%	102%
	97.0%	93.7%	95.0%
	95.3%	88.3%	96.3%
Average Recovery	100%	101%	106%
Std Dev.	9.1%	10%	12%
RSD	9.1%	10%	12%
Overall Average	102%		
Overall Std. Dev.	10%		
Overall RSD	10%		
Method Uncertainty (95% CI) = 2 x Std Dev. all levels	**21%**		

LCS concentrations were 3.00 ng, 30.0 ng and 300 ng of PFOA (linear + branched isomers) added to each nominal 1 gram of control soil used to prepare the LCSs (1 cc of soil TCR-455 equal to nominal 1.0 gram; dry weight).

7.6 Laboratory Matrix Spikes (LMSs)

Laboratory matrix spikes (LMSs) were generated by spiking a known quantity of PFOA (linear) to an aliquot of each soil/sediment sample and then preparing the sample the same as regular non-fortified samples. For this study, LMSs were prepared for each field sample at 20 and 200 ng PFOA as a low LMS and high LMS, respectively, in run o120309c. However, those LMS levels were too high and samples re-prepared in o120316a with LMSs fortified with 2 ng PFOA. One LMS was prepared for the trip blank and fortified with nominal 1.00 ng PFOA in run o120309c and was reported from that run. The LMS recoveries for PFOA are shown in **Table 2**. The method acceptance criteria of 100 ± 30% was met for all LMSs. The PFOA recovery calculations for LMS samples used the following equation:

$$\text{LMS Recovery} = \frac{(\text{Determined Concentration of LMS} - \text{Determined Concentration of Field Sample})}{\text{Spike Concentration}} * 100\%$$

7.7 Percent Moisture Determinations

The percent moisture was determined in duplicate for each soil sample. For each replicate, a sample aliquot is accurately weighed to determine the "wet" weight. Then the aliquot is dried at > 100°C unt il no further loss in mass occurs (due to water evaporation), and then the dry weight is accurately determined. The average percent moisture and RPD of the duplicate determinations for each is reported in **Table 10.** The percent moisture was calculated by the following equation:

$$\text{Percent Moisture} = \frac{(\text{Original Soil Wet Mass} - \text{Dried Soil Mass})}{\text{Original Soil Wet Mass}} * 100\%$$

Table 10. Percent Moistures for Jeffries Property Sediments, February 2012

LIMS ID	Sample ID	Average Percent Moisture (w/w) [a]	Relative Percent Difference [a]
GLP10-01-01-26-001	JPAL SD TRIP1 0 0000	2.72%	2.5%
GLP10-01-01-26-002	JPAL SD ET01 0 0000	28%	0.78%
GLP10-01-01-26-003	JPAL SD ET02 0 0000	30%	1.5%
GLP10-01-01-26-004	JPAL SD ET02 DB 0000	30%	0.78%
GLP10-01-01-26-005	JPAL SD ET03 0 0000	40%	3.6%
GLP10-01-01-26-006	JPAL SD ET04 0 0000	61%	0.096%

[a] Percent moisture determined for duplicate samples of soil/sediment taken from each sample bottle

7.8 Individual Sample Results

The individual sample concentration results are shown in **Table 11.**

Table 11. Individual PFOA Results for Jeffries Property Sediments, February 2012

Sample Description	Surrogate ($^{13}C_4$-PFOA) Recovery [a]	LMS Spike Concentration (ng/g; dry weight)	Measured PFOA Concentration (ng/g; dry weight)	LMS Recovery (Data Accuracy) [b]	Average PFOA Concentration (ng/g; dry wt.) and RPD (Data Precision)
JPAL SD TRIP1 0 0000	101%	NA	BLQ	NA	BLQ
JPAL SD TRIP1 0 0000 Duplicate	113%		BLQ		
JPAL SD TRIP1 0 0000 LMS [c]	113%	0.980	0.878	89.6%	NA
JPAL SD ET01 0 0000	98.2%	NA	0.671	NA	0.629
JPAL SD ET01 0 0000 Duplicate	103%		0.586		
JPAL SD ET01 0 0000 LMS	94.5%	1.38	1.91	92.5%	14%
JPAL SD ET02 0 0000	109%	NA	0.592	NA	0.671
JPAL SD ET02 0 0000 Duplicate	106%		0.749		
JPAL SD ET02 0 0000 LMS	97.2%	1.67	2.16	89.3%	23%
JPAL SD ET02 DB 0000	96.2%	NA	0.990	NA	0.819

Table 11. Individual PFOA Results for Jeffries Property Sediments, February 2012

Sample Description	Surrogate ($^{13}C_4$-PFOA) Recovery [a]	LMS Spike Concentration (ng/g; dry weight)	Measured PFOA Concentration (ng/g; dry weight)	LMS Recovery (Data Accuracy) [b]	Average PFOA Concentration (ng/g; dry wt.) and RPD (Data Precision)
JPAL SD ET02 DB 0000 Duplicate	94.5%		0.649		
JPAL SD ET02 DB 0000 LMS	104%	1.45	2.05	85.0%	42%
JPAL SD ET03 0 0000	109%	NA	1.07	NA	1.06
JPAL SD ET03 0 0000 Duplicate	104%		1.05		
JPAL SD ET03 0 0000 LMS	101%	2.13	3.02	91.8%	1.4%
JPAL SD ET04 0 0000	100%	NA	2.25	NA	2.39
JPAL SD ET04 0 0000 Duplicate	108%		2.53		
JPAL SD ET04 0 0000 LMS	104%	3.34	5.76	101%	11%

NA; Not applicable
BLQ; Below the lower limit of quantitation
[a] Surrogate recovery determined for samples fortified with 3.0 ng of $^{13}C_4$-PFOA and quantified from a $^{13}C_4$-PFOA calibration curve,
[b] LMSs prepared using PFOA (linear isomer).
[c] Values below the LLOQ (BLQ) were treated as a concentration of zero for LMS recovery calculations

8 Conclusion

Analysis of the sediments collected from the Jeffries property was successfully completed following 3M Environmental Laboratory method ETS-8-053.0 and conducted as 3M study GLP10-01-01-26. The average PFOA concentration results for the samples and trip blank are summarized in **Table 1** and associated LMS recoveries are summarized in **Table 2**. The PFOA results for each individual analytical sample replicate used for reporting are provided in **Table 10**.

All sample results were reported with LMS recoveries within 100 ± 15%, and duplicate results gave RPDs of less than 50%. The travel blank that accompanied the sample bottles shipments was below the low limit of quantitation (BLQ, less than nominal 0.500 ng/g), indicating there wasn't any contamination of samples during sample shipment, storage and preparation for analysis.

9 Data/Sample Retention

All soil samples and associated project data (hardcopy and electronic) will be archived as project GLP10-01-01-26 according to 3M Environmental Laboratory standard operating procedures.

10 List of Attachments

Attachment A: Preparation Forms, Raw Data and Chromatograms

11 Signatures

Report Approval:

Cleston C. Lange, Ph.D., Principal Analytical Investigator — Date: 4/13/2012

William K. Reagen, Ph.D., 3M Environmental Laboratory Management — Date: 13 April 2012

Gary A. Hohenstein, Sponsor Representative — Date: 4/17/12

Jaisimha Kesari, Study Director — Date: 4/24/12

Attachment A

Preparation Forms, Raw Data and Chromatograms

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GLP10-01-01, Interim Report 27: Analysis of PFOA in Surface Water Samples Collected at Bert Jeffries Landfill in Decatur, AL in February 2012

Study Title

Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program

Data Requirement

EPA TSCA Good Laboratory Practice Standards 40 CFR Part 792

Study Director

Jaisimha Kesari P.E., DEE
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3M Environmental Laboratory

Interim Report Completion Date

Date of signing

Performing Laboratory

3M Environmental Health and Safety Operations
Environmental Laboratory
3M Center, Bldg 260-05-N-17
St. Paul, MN 55144

Project Identification

GLP10-01-01-27

Total Number of Pages

61

A2LA ACCREDITED

The testing reported herein meet the requirements of ANSI/ISO/IEC 17025:2005 "General Requirements for the Competence of Testing and Calibration Laboratories", in accordance with the A2LA Testing Certificate # 2052.01. Testing that complies with this International Standard also meets principles of ISO 9001:2000.

Testing Cert #2052.01

This page has been reserved for specific country requirements.

GLP COMPLIANCE STATEMENT

Report Title: GLP10-01-01, Interim Report 27. Analysis of PFOA in Surface Water Samples Collected at Bert Jeffries Landfill in Decatur, AL in February 2012

Study: Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program.

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

- These are environmental samples where there is no specific test substance, no specific test system and no dosing of a test system.
- The reference substances have not been characterized under the GLPs and the stability under storage conditions at the test site have not been determined under GLPs.

Gary Hohenstein, Sponsor Representative — Date 4/16/12

Jaisimha Kesari, P.E., DEE, Study Director — Date 4/19/12

QUALITY ASSURANCE STATEMENT

Report Title: GLP10-01-01, Interim Report 27. Analysis of PFOA in Surface Water Samples Collected at Bert Jeffries Landfill in Decatur, AL in February 2012

Study: Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program.

This report and the accompanying data were audited by the 3M Environmental Laboratory Quality Assurance Unit (QAU), as indicated below. The findings were reported to the principal analytical investigator (P.A.I.), laboratory management and study director.

Inspection Dates	Phase	Date Reported to	
		Testing Facility Management	Study Director
3/30/12 and 4/2/12	Data and Report	4/9/12	4/6/12

Casey Howell 4-11-12

QAU Representative Date

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1 Study Information

Sponsor

3M Company

Sponsor Representative

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Study Location

Testing Facility

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Cleston Lange, Ph.D., Principal Analytical Investigator. (clange@mmm.com); phone (651)-733-9860
Susan Wolf, 3M Analyst
Chelsie Grochow, Analyst
Kevin Eich, Analyst
Kelly Ukes, Analyst
Jonathan Steege, Analyst

Study Dates

Study Initiation: March 8, 2010
Interim Report 27 Experimental Termination: March 7, 2012
Interim Report Completion: Date of Interim Report Signing

Location of Archives

All original raw data and the analytical report have been archived at the 3M Environmental Laboratory according to 40 CFR Part 792. The test substance and analytical reference standard reserve samples are archived at the 3M Environmental Laboratory according to 40 CFR Part 792

2 Summary

The 3M Environmental Laboratory received surface water samples from four different locations located at Jeffries Landfill in Decatur, AL. A total of nineteen sample bottles were received at the 3M Environmental Laboratory for perfluorooctanoate (PFOA) analysis and included duplicate surface water samples and two field matrix spike (FMS) samples from each sampling location. A set of trip blank samples; single trip blank containing Milli-Q™ water and two trip blank spikes, were included with the sample bottles. All samples were logged into the laboratory information management system (LIMS) under project GLP10-01-01-27. The surface water samples and trip blanks were received from Weston personnel on March 2, 2012. All of the samples were prepared and analyzed for PFOA and the surrogate recovery standard $^{13}C_4$-PFOA, following 3M Environmental Laboratory Method ETS-8-044.1.

The average measured PFOA concentrations are summarized in **Table 1.** The trip blank was below the lower limit of quantitation (LLOQ) of 0.0240 ng/mL, indicating adequate control of sample contamination during shipping and sample collection. The analytical uncertainty was estimated at 100±17%.

Table 1. Summarized PFOA Results (Jeffries Landfill Site, February 2012)

3M LIMS ID	Sample Description	PFOA Concentration (ng/mL)
GLP10-01-01-027-005	JPAL-SW-ET01-0-120228	<0.0240
GLP10-01-01-027-006	JPAL-SW-ET01-DB-120228	<0.0240
	Average	**<0.0240**
	%RPD Sample/Sample Dup	**NA**
GLP10-01-01-027-009	JPAL-SW-ET02-0-120228	<0.0240
GLP10-01-01-027-010	JPAL-SW-ET02-DB-120228	<0.0240
	Average	**<0.0240**
	%RPD Sample/Sample Dup	**NA**
GLP10-01-01-027-013	JPAL-SW-ET03-0-120228	0.114
GLP10-01-01-027-014	JPAL-SW-ET03-DB-120228	0.110
	Average	**0.112**
	%RPD Sample/Sample Dup	**3.6**
GLP10-01-01-027-017	JPAL-SW-ET04-0-120228	0.0644
GLP10-01-01-027-018	JPAL-SW-ET04-DB-120228	0.0709
	Average	**0.0677**
	%RPD Sample/Sample Dup	**9.6**
GLP10-01-01-027-025	JPAL-SW-TRIP1-0-120228	**<0.0240**

NA = Not Applicable
The analytical method uncertainty for PFOA is ±17%.

3 Introduction

This analytical study was conducted as part of the Phase 3 Environmental Monitoring and Assessment Program for the 3M facility located in Decatur, Alabama. The objective of the overall program is to gain information regarding concentrations of perfluorooctanoate (PFOA) in various environmental media such as groundwater, soils and sediments that are associated with and near the Decatur facility. This analytical study was conducted to analyze surface water samples collected from four locations near Jeffries Landfill in Decatur, AL for PFOA.

The 3M Environmental Laboratory prepared sample bottles (250 mL high-density polyethylene) which were shipped to Decatur, AL Weston personnel prior to field sampling. Sample bottle sets for each sampling location included a field sample, field sample duplicate, and two field spike samples. Each empty container for samplings was marked with a "fill to here" line to produce a final sample volume of 200 mL. Containers designated for field matrix samples were fortified with an appropriate matrix spike solution containing PFOA prior to being sent to the field for sample collection. All sample bottles included the addition of $^{13}C_8$-PFOA (internal standard) at a nominal concentration of 1 ng/mL, and $^{13}C_4$-PFOA (surrogate recovery standard) at a nominal concentration of 0.1 ng/mL. See section 8.8 of the report for field matrix spike levels.

Samples were prepared and analyzed according to the procedure defined in 3M Environmental Laboratory method ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds in Water by LC/MS/MS; Direct Injection Analysis". The use of an internal standard was used to aid in the data quality objectives.

Table 1 summarizes the average PFOA concentration for the duplicate surface water samples collected and the trip blank sample. **Tables 10-14** summarize the individual sample results and the associated FMS recoveries. All results for the quality control samples prepared and analyzed with the samples are reported and discussed elsewhere in this report.

4 Test & Control Substances

There was not a test substance or control substances in the classic sense of a GLP study. This study was purely analytical in nature.

5 Reference Substances

The analytical reference substances used for this study are listed below.

Reference Substance	PFOA (Linear+Branched)	$^{13}C_4$-PFOA	$^{13}C_8$-PFOA	$^{13}C_8$-PFOA
Chemical Name	Perfluorooctanoate	Perfluorooctanoate	Perfluorooctanoate	Perfluorooctanoate
Chemical Formula	$C_7F_{15}COOH$	$^{13}C_4HF_{15}O_2$	$^{13}C_8HF_{15}O_2$	$^{13}C_8HF_{15}O_2$
Identifier	CAS # 95328-99-7	MPFOA	MPFC-C-0511	MPFC-C-0112
Use	Target Analyte Reference Standard	Surrogate	Internal Standard	Internal Standard
Source	Wellington	Wellington	Wellington	Wellington
Expiration Date	03/17/2014	12/07/2013	05/25/2014	01/24/2015
Storage Conditions	Frozen	Frozen	Frozen	Frozen
Chemical Lot Number	TPFOA0311	MPFOA1210	052411	012312
TCR Number	TCR11-0009, TCR11-0042	TCR11-0001	TCR11-0016	TCR12-0004
Physical Description	Liquid	Liquid	Liquid	Liquid
Purity	98.3%	>98%	NA (1)	NA (1)

(1) Compound is part of a custom mixture of mass-labeled perfluorinated compounds at a concentration of 5.0 µg/mL.

6 Test System

There was not a test system for this study in the classic sense of a GLP study. This study was conducted for analysis of surface water samples collected from the Jeffries property located near Decatur, AL by Weston Solutions, Inc. personnel. Samples for this study are "real world" environmental samples.

Table 2. Sample Description Key Code.

String Number	String Descriptor	Example
Example	*JPAL-SW-ET01-0-120228*	
1	*Sample Location*	*JPAL = Jeffries Property, Alabama*
2	*Sample Type*	*SW = Surface Water*
3	*Well ID*	*Example: ET01* *ET = Eastern tributary to Mallard Creek*
4	*Sampling Date*	*120228– February 28, 2012*
5	*Sample Type*	*0=primary sample* *DB=duplicate sample* *LS = low spike* *HS = high spike*

7 Method Summary

7.1 Method

Analysis for all analytes was completed following 3M Environmental Laboratory method ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds In Water by High Performance Liquid Chromatography/Mass Spectrometry Direct Injection Analysis".

7.2 Sample Collection

Samples were collected in 250 mL Nalgene™ (high-density polyethylene) bottles prepared at the 3M Environmental Laboratory. Sample bottles associated with GLP10-01-01-27 were returned to the laboratory at ambient conditions on March 2, 2012. Samples were stored refrigerated at the laboratory after receipt. A set of laboratory prepared Trip Blank and Trip Blank field matrix spikes were sent with the set of sample collection bottles.

7.3 Sample Preparation

Samples were prepared by removing an aliquot of the well mixed sample and placing it in an autovial for analysis.

During the preparation of the laboratory control samples, an aliquot of a separate internal standard spiking solution was added to the laboratory control samples (nominal concentration of 1 ng/mL). The samples bottles were spiked with an internal standard mix at a nominal concentration of 1 ng/mL prior to being sent to the field for sample collection.

7.4 Analysis

All study samples and quality control samples were analyzed for PFOA using high performance liquid chromatography/ tandem mass spectrometry (HPLC/MS/MS). Detailed instrument parameters, the liquid chromatography gradient program, and the specific mass transitions analyzed are described in the raw data hard copies placed in the final data packet, and are briefly described below in **Table 3**, **Table 4** and **Table 5**.

Table 3. Instrument Parameters.

Instrument Name	**ETS Ginger**
Analytical Method Followed	ETS-8-044.1
Analysis Date	3/6/12
Liquid Chromatograph	Agilent 1100
Guard column	Betasil C18 (4.6 mm X 100 mm), 5µ
Analytical column	Betasil C18 (4.6 mm X 100 mm), 5µ
Injection Volume	25 µL
Mass Spectrometer	Applied Biosystems API 5000
Ion Source	Turbo Spray
Electrode	Turbo ion electrode
Polarity	Negative
Software	Analyst 1.4.2

Table 4. Liquid Chromatography Conditions.

Step Number	Total Time (min)	Flow Rate (µL/min)	Percent A (2 mM ammonium acetate)	Percent B (Methanol)
ETS-8-044.1 Analysis				
0	0.0	750	97.0	3.0
1	2.0	750	97.0	3.0
2	14.5	750	5.0	95.0
3	15.5	750	5.0	95.0
4	16.5	750	97.0	3.0
5	20.0	750	97.0	3.0

Table 5. Mass Transitions.

Analyte	Mass Transition Q1/Q3	Internal Standard	Mass Transition Q1/Q3
PFOA	413/369	[$^{13}C_8$]-PFOA	421/376
	413/219		
	413/169		
[$^{13}C_4$]-PFOA	417/372	[$^{13}C_8$]-PFOA	421/376

Dwell time was 50 msec for each transition. The individual transitions were summed to produce a "total ion chromatogram" (TIC), which was used for quantitation.

8 Analytical Results

8.1 Calibration

Samples were analyzed using a stable isotope internal standard calibration curve. Calibration standards were prepared by spiking known amounts of the stock solution containing PFOA (reference standard containing both linear and branched isomers) into a laboratory-prepared synthetic groundwater containing calcium and magnesium. A separate internal standard spiking solution was prepared and an aliquot was added at the same level to all calibration standards and laboratory control samples at a nominal concentration of 1 ng/mL. A calibration curve ranging from approximately 0.025 ng/mL to 100 ng/mL (0.025 ng/mL to 10 ng/mL for $^{13}C_4$-PFOA surrogate) was prepared. A quadratic, 1/x weighted, calibration curve of the standard peak area/peak area ratios was used to fit the data for each analyte. The data were not forced through zero during the fitting process. Calculating the standard concentrations using the peak area/ peak area ratios and the resultant calibration curve confirmed accuracy of each curve point.

Each curve point was quantitated using the overall calibration curve and reviewed for accuracy. Method calibration accuracy requirements of 100 ± 25% (100 ± 30% for the lowest curve point) were met for PFOA and $^{13}C_4$-PFOA surrogate. The correlation coefficient (r) was greater than 0.995 for both analytes.

8.2 System Suitability

A calibration standard was analyzed four times at the beginning of the analytical sequence to demonstrate overall system suitability. The acceptance criteria of less than or equal to 5% relative standard deviation (RSD) for peak area and retention time criteria of less than or equal to 2% RSD was met for PFOA and $^{13}C_4$-PFOA surrogate.

8.3 Limit of Quantitation (LOQ)

The LOQ for this analysis is the lowest non-zero calibration standard in the curve that meets linearity and accuracy requirements and for which the area counts are at least twice those of the appropriate blanks. The nominal LOQ for PFOA can be found in **Table 6**.

Table 6. Limit of Quantitation (LOQ).

Analysis Date	*PFOA ng/mL*
3/6/12	0.0240

8.4 Continuing Calibration

During the course of each analytical sequence, continuing calibration verification samples (CCVs) were analyzed to confirm that the instrument response and the initial calibration curve were still in control. All CCVs met method criteria of 100% ± 25% for PFOA and $^{13}C_4$-PFOA surrogate.

8.5 Blanks

Two types of blanks were prepared and analyzed with the samples: procedural blanks and trip blanks. Procedural blank results were reviewed and used to evaluate method performance to determine the LOQ. Trip blanks reflect the shipping and sample collection conditons the sample bottles and samples experience.

8.6 Lab Control Spikes (LCSs)

Low, mid, and high lab control spikes were prepared for the target analytes and analyzed in triplicate, while only low and high lab control spikes were prepared for the $^{13}C_4$-PFOA surrogate. LCSs were prepared by spiking known amounts of the analyte into 10 mL of synthetic groundwater to produce the desired concentration. The spiked water samples were then analyzed in the same manner as the samples. The method acceptance criteria, average of LCS at each level should be within 100% ± 20% with an RSD ≤20%, were met for both PFOA and $^{13}C_4$-PFOA surrogate.

The following calculations were used to generate data in **Table 7** for laboratory control spikes:

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

$$\text{LCS\% RSD} = \frac{\text{standard deviation LCS replicates}}{\text{average LCS recovery}} * 100\%$$

Table 7. Laboratory Control Spike Recovery.

ETS-8-044.1 Analyzed 3/6/12	PFOA (Linear + Branched)			$^{13}C_4$-PFOA surrogate		
Lab ID	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery
LCS-120306-1	0.190	0.162	85.5	0.198	0.229	116
LCS-120306-2	0.190	0.166	87.6	0.198	0.223	112
LCS-120306-3	0.190	0.164	86.1	0.198	0.219	110
Average ± %RSD	86.4% ± 1.3%			113% ± 2.7%		
LCS-120306-4	1.90	1.88	99.1	1.98	2.24	113
LCS-120306-5	1.90	1.96	103	1.98	2.31	116
LCS-120306-6	1.90	1.86	97.9	1.98	2.33	118
Average ± %RSD	100% ± 2.7%			116% ± 2.2%		
LCS-120306-7	19.0	18.0	95.0	NA	NA	NA
LCS-120306-8	19.0	17.8	93.8	NA	NA	NA
LCS-120306-9	19.0	16.9	89.1	NA	NA	NA
Average ± %RSD	92.6% ± 3.4%			NA		

NA = Not Applicable

8.7 Analytical Method Uncertainty

Analytical uncertainty is based on historical QC data that is control charted and used to evaluate method accuracy and precision. The method uncertainty is calculated following ETS-12-012.2. The standard deviation is calculated for the set of accuracy results (in %) obtained for the QC samples. The expanded uncertainty is calculated by multiplying the standard deviation by a factor of 2, which corresponds to a confidence level of 95%.

Table 8. Analytical Method Uncertainty.

Analyte	Method	Standard Deviation	Method Uncertainty
PFOA	ETS-8-044.1	8.68	±17%

8.8 Field Matrix Spikes (FMS)

Low and high field matrix spikes were collected at each sampling point to verify that the analytical method is applicable to the collected matrix. Field matrix spikes were generated by adding a measured volume of field sample to a container spiked by the laboratory with PFOA (reference standard containing both linear and branched isomers) prior to shipping sample containers for sample collection. Field matrix spike recoveries within method acceptance criteria of 100±30% confirm that "unknown" components in the sample matrix do not significantly interfere with the extraction and analysis of the analytes of interest. Field matrix spike concentrations must be 50% of the sample concentration to be considered an appropriate field spike. Field matrix spikes are presented in section 9 of this report.

Table 9. Field Matrix Spike Levels.

Sampling Location	Spike Level	PFOA, ng/mL
All Locations and Trip Blank	Low	0.998
	High	9.98

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

8.9 Data Summary and Discussion

The tables below summarize the sample results and field matrix spike recoveries for the sampling locations as well as the Trip Blanks. Results and average values are rounded to three significant figures according to EPA rounding rules. Because of rounding, values may vary slightly from those listed in the raw data. Field matrix spike recoveries meeting the method acceptance criteria of ± 30%, demonstrate that the method was appropriate for the given matrix and their respective quantitative ranges.

Table 10. JPAL SW ET01 120228

		PFOA		$^{13}C_4$ PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-27-005	JPAL-SW-ET01-0-120228	<0.0240	NA	111
GLP10-01-01-27-006	JPAL-SW-ET01-DB-120228	<0.0240	NA	108
GLP10-01-01-27-007	JPAL-SW-ET01-LS-120228	0.950	95.2	110
GLP10-01-01-27-008	JPAL-SW-ET01-HS-120228	9.44	94.6	118
Average Concentration (ng/mL) ± %RPD/RSD		<0.0240 ng/mL		112% ± 3.9%

NA = Not Applicable

Table 11. JPAL SW ET02 120228

		PFOA		$^{13}C_4$ PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-27-009	JPAL-SW-ET02-0-120228	<0.0240	NA	109
GLP10-01-01-27-010	JPAL-SW-ET02-DB-120228	<0.0240	NA	115
GLP10-01-01-27-011	JPAL-SW-ET02-LS-120228	0.938	94.0	106
GLP10-01-01-27-012	JPAL-SW-ET02-HS-120228	9.02	90.4	111
Average Concentration (ng/mL) ± %RPD/RSD		<0.0240 ng/mL		110% ± 3.4%

NA = Not Applicable

Table 12. JPAL SW ET03 120228

		PFOA		$^{13}C_4$ PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-27-013	JPAL-SW-ET03-0-120228	0.114	NA	107
GLP10-01-01-27-014	JPAL-SW-ET03-DB-120228	0.110	NA	108
GLP10-01-01-27-015	JPAL-SW-ET03-LS-120228	1.10	99.0	110
GLP10-01-01-27-016	JPAL-SW-ET03-HS-120228	9.37	92.8	110
Average Concentration (ng/mL) ± %RPD/RSD		0.112 ng/mL ± 3.6%		109% ± 1.4%

NA = Not Applicable

Table 13. JPAL SW ET04 120228

		PFOA		$^{13}C_4$ PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-27-017	JPAL-SW-ET04-0-120228	0.0644	NA	112
GLP10-01-01-27-018	JPAL-SW-ET04-DB-120228	0.0709	NA	111
GLP10-01-01-27-019	JPAL-SW-ET04-LS-120228	1.02	95.4	111
GLP10-01-01-27-020	JPAL-SW-ET04-HS-120228	8.96	89.1	109
Average Concentration (ng/mL) ± %RPD/RSD		0.0677 ng/mL ± 9.6%		111% ± 1.1%

NA = Not Applicable

Table 14. Trip Blank 120228

		PFOA		$^{13}C_4$ PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-27-025	JPAL-SW-TRIP1-0-120228	<0.0240	NA	101
GLP10-01-01-27-026	JPAL-SW-TRIP1-LS-120228	0.955	95.7	118
GLP10-01-01-27-027	JPAL-SW-TRIP1-HS-120228	9.16	91.8	112

NA = Not Applicable

9 Conclusion

Laboratory control spikes and field matrix spikes were used to determine the analytical method accuracy and precision for PFOA. Analysis was successfully completed following 3M Environmental Laboratory method ETS-8-044.1 described herein.

10 Data/Sample Retention

All remaining samples and associated project data (hardcopy and electronic) will be archived according to 3M Environmental Laboratory standard operating procedures.

11 Attachments

Attachment A: Protocol Amendment 27 (General Project Outline)

Attachment B: Representative Chromatograms and Calibration Curves

Attachment C: Analytical Method – ETS-8-044.1

12 Signatures

4/11/2012
Cleston Lange, Ph.D., 3M Principal Analytical Investigator — Date

13 April 2012
William K. Reagen, Ph.D., 3M Environmental Laboratory Manager — Date

Gary Hohenstein
4/16/12
Gary Hohenstein, 3M Sponsor Representative — Date

4/19/12
Jaisimha Kesari, Study Director — Date

ATTACHMENT A: PROTOCOL AMENDMENT

Analytical Protocol: GLP10-01-01
Amendment 27

Study Title

Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program

PROTOCOL AMENDMENT NO. 27

Amendment Date:
February 21, 2012

Performing Laboratory
3M Environmental, Health, and Safety Operations
3M Environmental Laboratory
Building 260-5N-17
Maplewood, MN 55144-1000

Laboratory Project Identification
GLP10-01-01-27

Sampling Event

Bert Jeffries Landfill –Surface Water Sampling

Analytical Protocol: GLP10-01-01
Amendment 27

This amendment modifies the following portion of protocol:

"Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program"

PROTOCOL READS:

No changes to the wording of the protocol are required.

AMEND TO READ:

No changes to the wording of the protocol are required. This amendment only addresses and documents the addition of the General Project Outline (GPO) for the collection and analysis of groundwater samples at Decatur, AL, and conducted as part of the 3M Decatur Phase 3 Program for PFOA (GLP10-01-01). Sampling activities at and near the Bert Jeffries landfill are scheduled for the week of February 27, 2012 and will consist of 6 paired surface water and sediment samples. This protocol amendment addresses the sampling and analysis of the surface water samples. Surface water samples collected under this sampling event will be entered into the 3M Environmental Laboratory LIMS as project GLP10-01-01-27 and reported as interim report GLP10-01-01-27, (reflecting study GLP10-01-01 and amendment -27).

Reason:

The reason for this amendment is to document the General Project Outline (GPO) which describes the anticipated surface water sample collection event to be conducted at and near the Bert Jeffries landfill in Lawrence County, AL.

The GPO is three pages in length and included as attached to this amendment form.

Analytical Protocol: GLP10-01-01
Amendment 27

Amendment Approval

Gary Hohenstein, Sponsor Representative	7/29/12 Date
Cleston C. Lange, Principal Analytical Investigator	2/21/2012 Date
William Reagen, EHS Opns Environmental Lab Management	24 FEB 2012 Date
Jaisimha Kesari P.E., DEE, Study Director	3/14/12 Date

Analytical Protocol: GLP10-01-01
Amendment 27

3M Environmental Health & Safety Operations, Environmental Laboratory

General Project Outline

To:	Gary Hohenstein, 3M EHS&Opns
From:	Susan Wolf, 3M EHS&Opns; Environmental Lab
cc:	William Reagen, 3M EHS&Opns; Environmental Lab
	Jai Kesari, Weston Solutions
	Charles Young, Weston Solutions
Date:	February 21, 2012
Subject:	Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program; GLP Interim Report 27 – Bert Jeffries Landfill; Surface Water sampling the week of February 27, 2012.

1 General Project Information

Contacts	**3M Sponsor Representative** Gary Hohenstein 3M EHS Operations 3M Building 224-6W-03 Saint Paul, MN 55144-1000 Phone: (651) 737-3570 gahohenstein@mmm.com **3M Environmental Laboratory Management** William K. Reagen 3M EHS Opns, Environmental Laboratory 260-5N-17 651 733-9739 wkreagen@mmm.com **Principal Analytical Investigator** Cleston Lange 3M EHS Opns, Environmental Laboratory 260-5N-17 651 733-9660 cclange@mmm.com **Sampling Coordinator** Timothy Frinak Weston Solutions Timothy.frinak@westonsolutions.com Phone: (334)-332-9123
Lab Request Number	GLP10-01-01-27
Six Digit Department Number	Dept #530711, Project #0022674449
Project Schedule/Test Dates	Tentatively scheduled for the week of February 27, 2012.

All verbal and written correspondence will be directed to Gary Hohenstein and Jai Kesari.

Analytical Protocol: GLP10-01-01
Amendment 27

2 Background Information and Project Objective(s)

The 3M EHS Operations Laboratory (3M Environmental Lab) will receive and analyze surface water samples collected from six (6) locations at and near the Bert Jeffries landfill. Surface water samples will be collected by Weston. The 3M Environmental Laboratory will prepare the sample bottles. Samples will be analyzed for Perfluorooctanoic Acid (PFOA). Analyses will be conducted under the GLP requirements of EPA TSCA Good Laboratory Practice Standards 40 CFR 792.

The final report will be submitted to Gary Hohenstein and Jai Kesari upon completion under interim report GLP10-01-01-27.

3 Project Schedule

Sample collection bottles will be prepared by the 3M Environmental Laboratory. Sample bottles will be shipped in coolers overnight to 3M Decatur for arrival by Friday, February 24, 2012. Sample bottles should be stored refrigerated on-site until sample collection.

Martin Smith \ Weston Trailer
3M Decatur Plant
1400 State Docks Road
Decatur, Alabama 35601

4 Test Parameters

The targeted limit of quantitation will be **0.025 ng/mL** (ppb) for PFOA.

A total of six sampling locations have been specified. For each sampling location, a total of four sample bottles will be collected (sample, sample duplicate, low-level field matrix spike, and high-level field matrix spike). The "fill to here" line on each 250 mL Nalgene bottle will be 200 mL. One set of trip blanks consisting of reagent-grade water, a low-level trip blank spike, and a high-level trip blank spike will be prepared at the 3M Environmental Laboratory and sent to the sampling location with the other bottles. No previous data on fluorochemicals in groundwater, surface water or sediment media exist for the site. The low field matrix spike will be prepared at 1 ng/mL and the high field matrix spike at 10 ng/mL.

All sample bottles will include the addition of $^{13}C_8$-PFOA (internal standard) at a nominal concentration of 1 ng/mL and $^{13}C_4$-PFOA (surrogate recovery standard) at a nominal concentration of 0.1 ng/mL.

To aid in sample collection, a non-spiked 1-L sample bottle will be provided for each sampling location. Sample collection will consist of direct immersion. Aliquots will be decanted from the collection bottle to the primary, duplicate and matrix spike bottles. No rinseate blank will be collected.

5 Test Methods

Samples will be prepared and analyzed by LC/MS/MS following ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds in Water by High Performance Liquid Chromatography/Mass Spectrometry Direct Injection Analysis". Alternately, samples may be analyzed by ETS 8-154.3 "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates in Water By Solid Phase Extraction and High Performance Liquid Chromatography/Mass Spectrometry.

Where applicable, samples will be analyzed against an internal standard calibration curve. Each curve point will contain isotopically-labeled PFOA at a nominal concentration of 1 ng/mL. The calibration curve will be

generated by taking the ratio of the standard peak area counts over the internal standard peak area counts to fit the data for each analyte.

Laboratory control samples prepared with the samples must have an average recovery within 100±20% and a RSD ≤20%. The data quality objective for this study is quantitative results for the target analytes with an analytical accuracy of 100±30%. Field matrix spikes not yielding recoveries within 100±30% will be addressed in the report and the final accuracy statement may be adjusted accordingly.

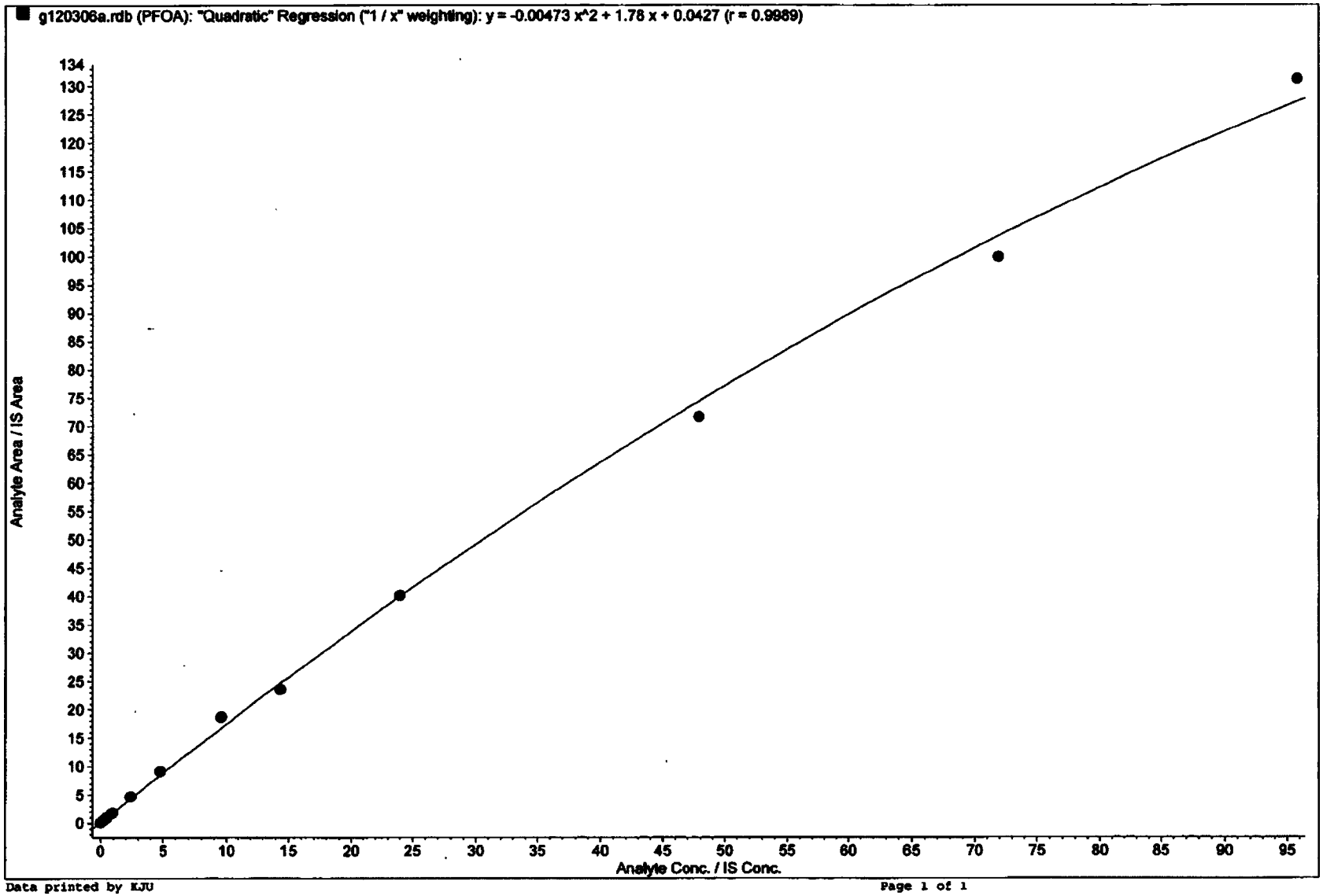
6 Reporting Requirements

For each sampling location, the report will contain the results for the sample, sample duplicate, and the two field matrix spikes. Trip blank and trip blank spikes will be reported for the sampling event. Laboratory control spikes of reagent water prepared at the time of sample extraction will also be reported and used to evaluate the overall method accuracy and precision. Method blanks of reagent water prepared at the time of sample preparation will be used to determine the method detection limit. For those sampling locations where the field matrix spike level was not appropriate due to higher than expected analyte concentrations, a target analyte laboratory matrix spike may be prepared and will be included in the final report.

ATTACHMENT B: REPRESENTATIVE SAMPLE CHROMATOGRAMS AND CALIBRATION CURVE(S)

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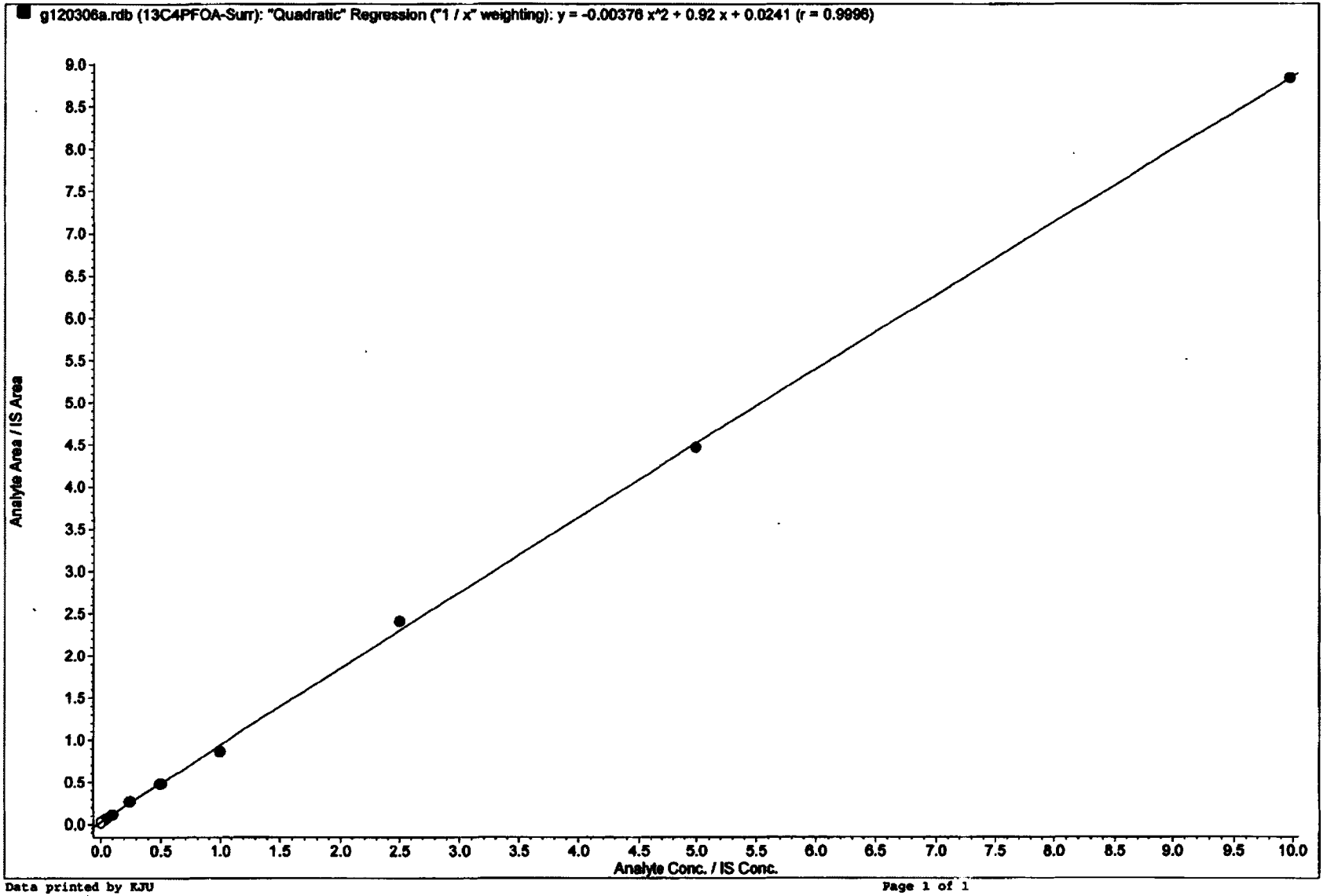


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Page 1 of 1

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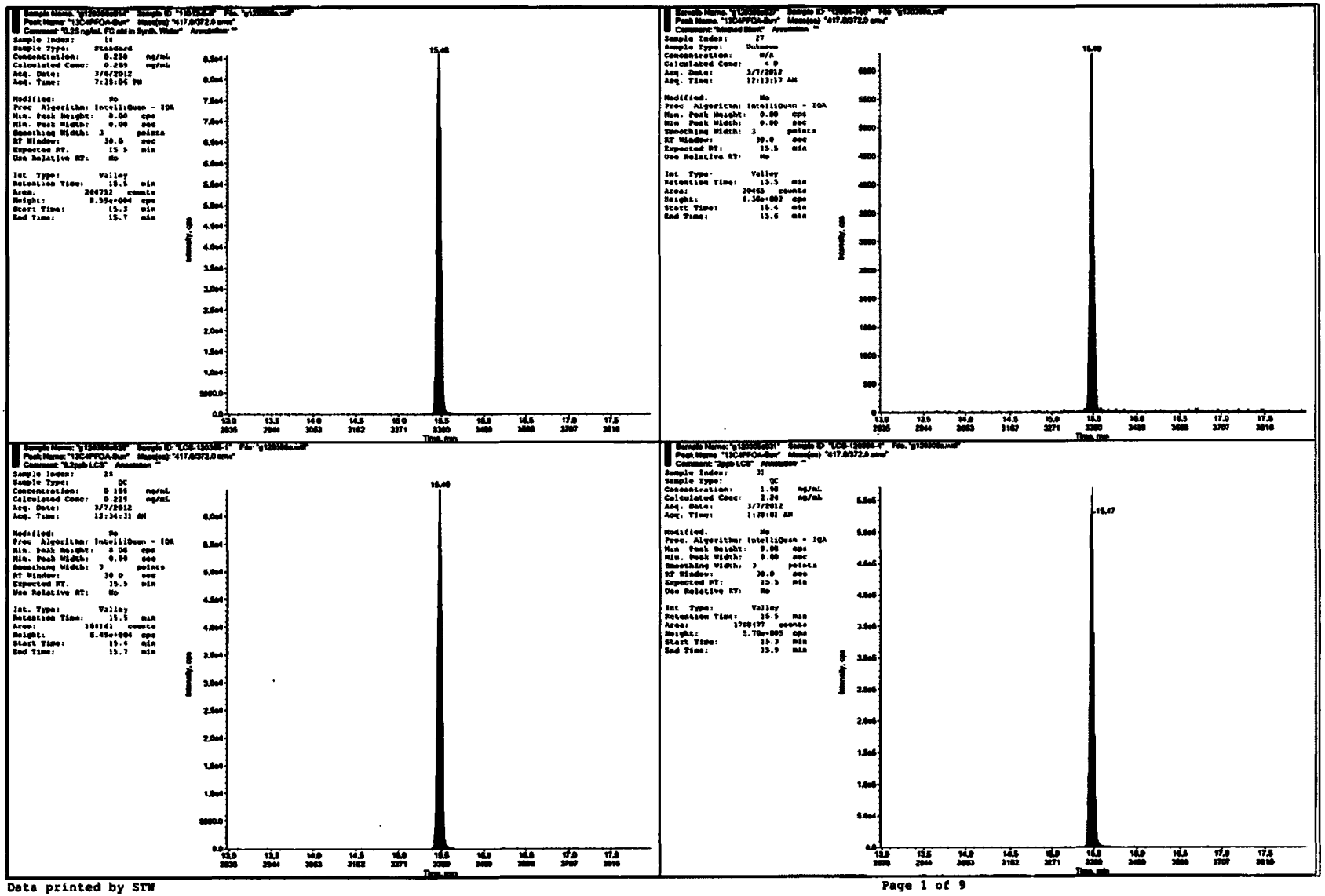


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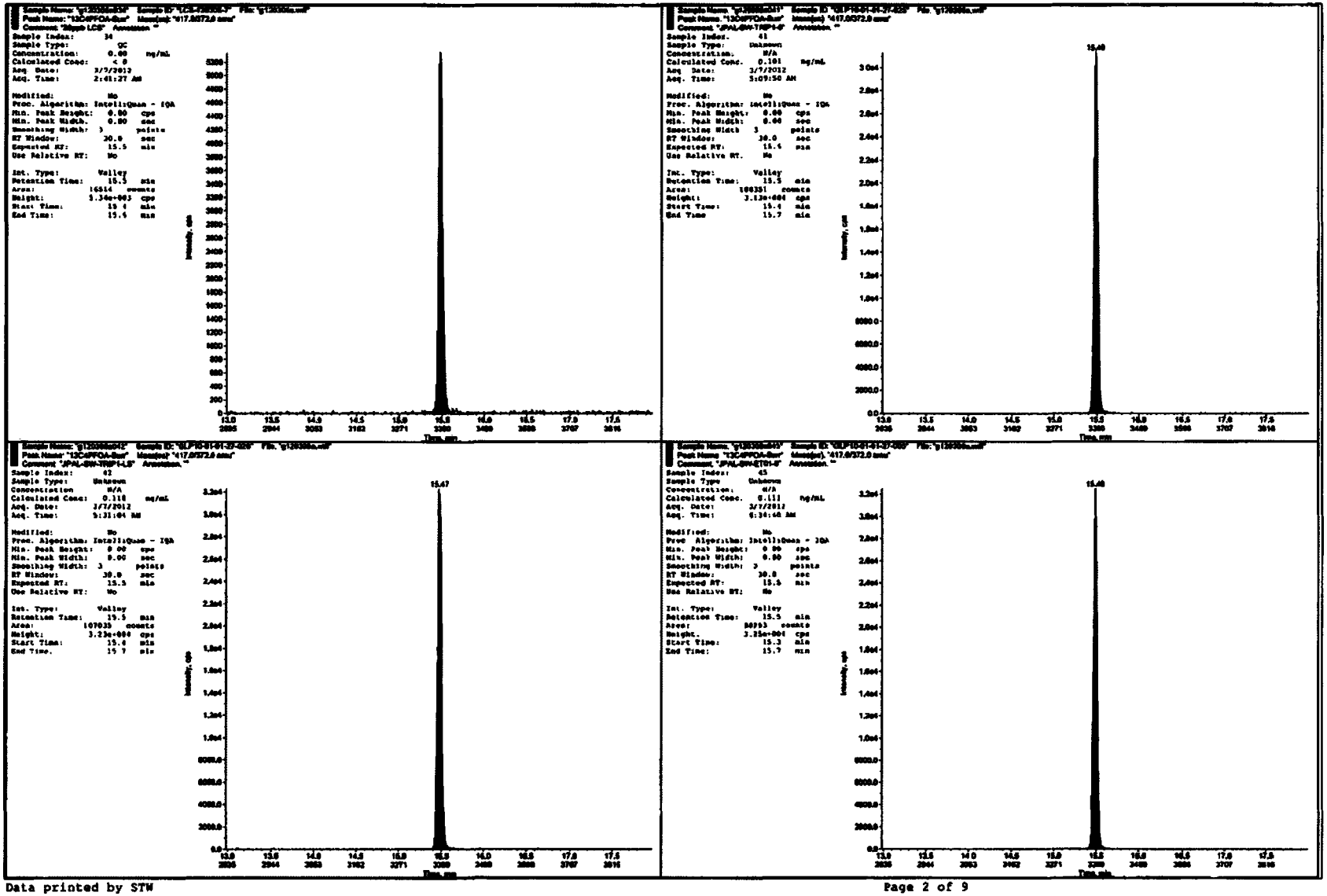
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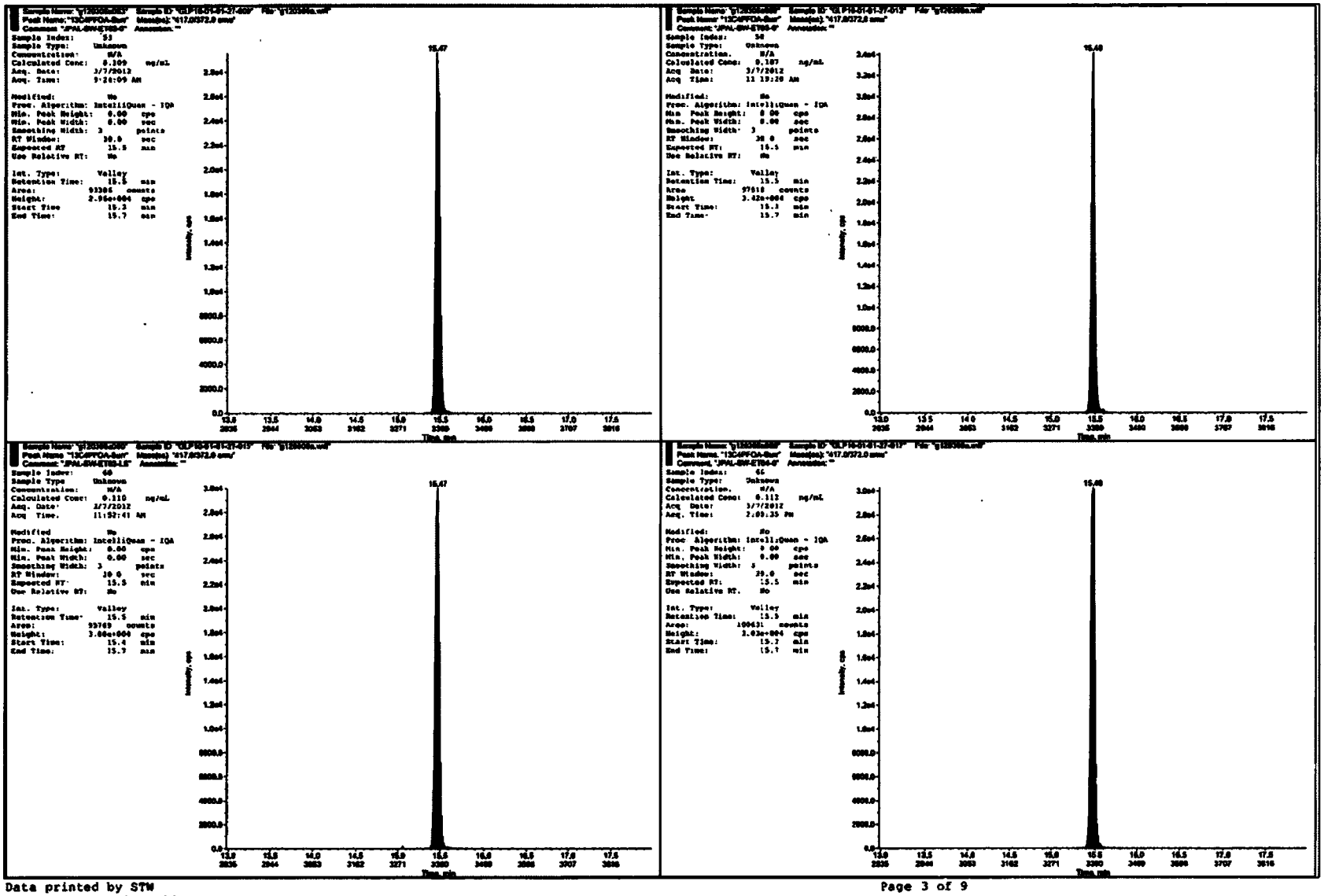
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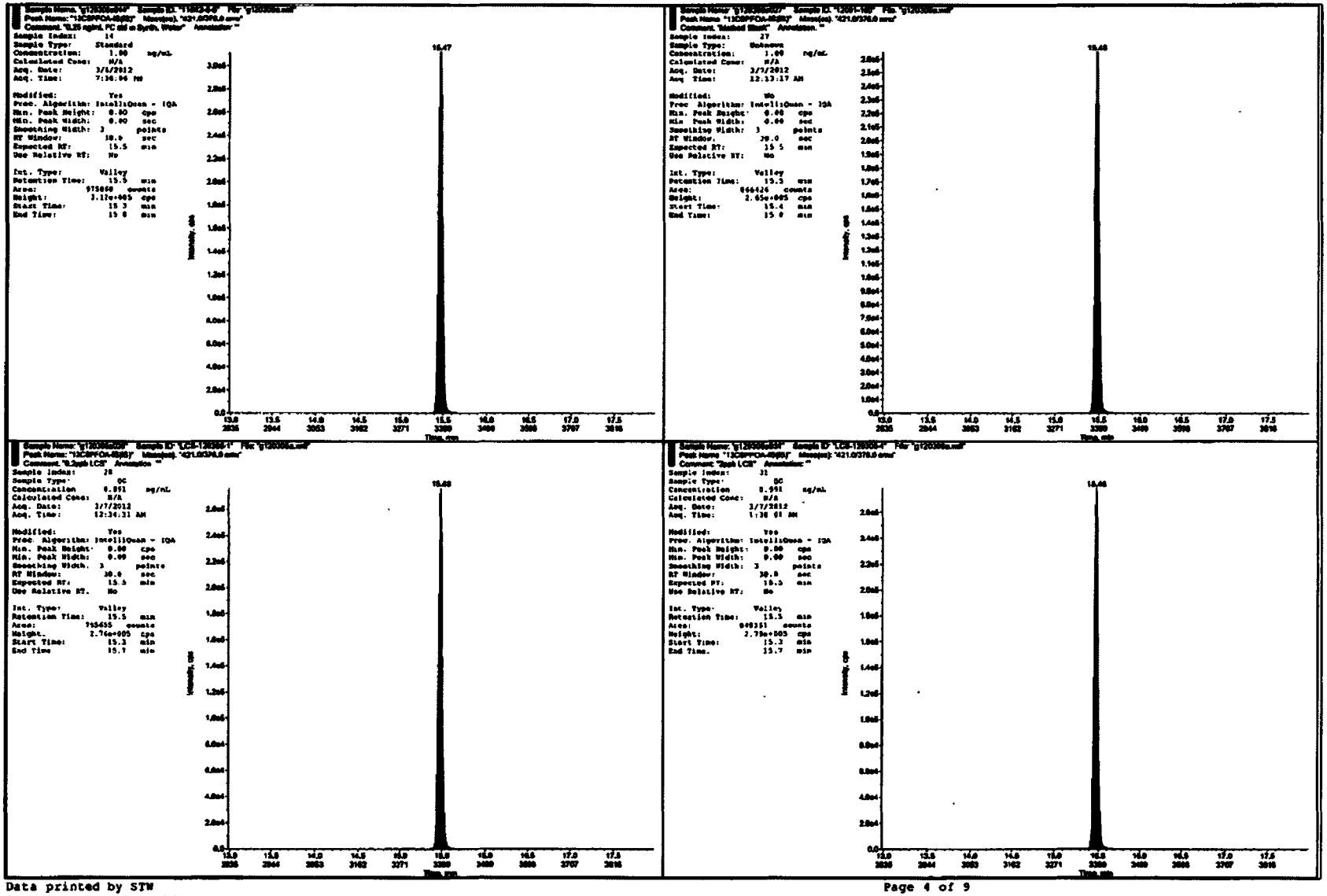
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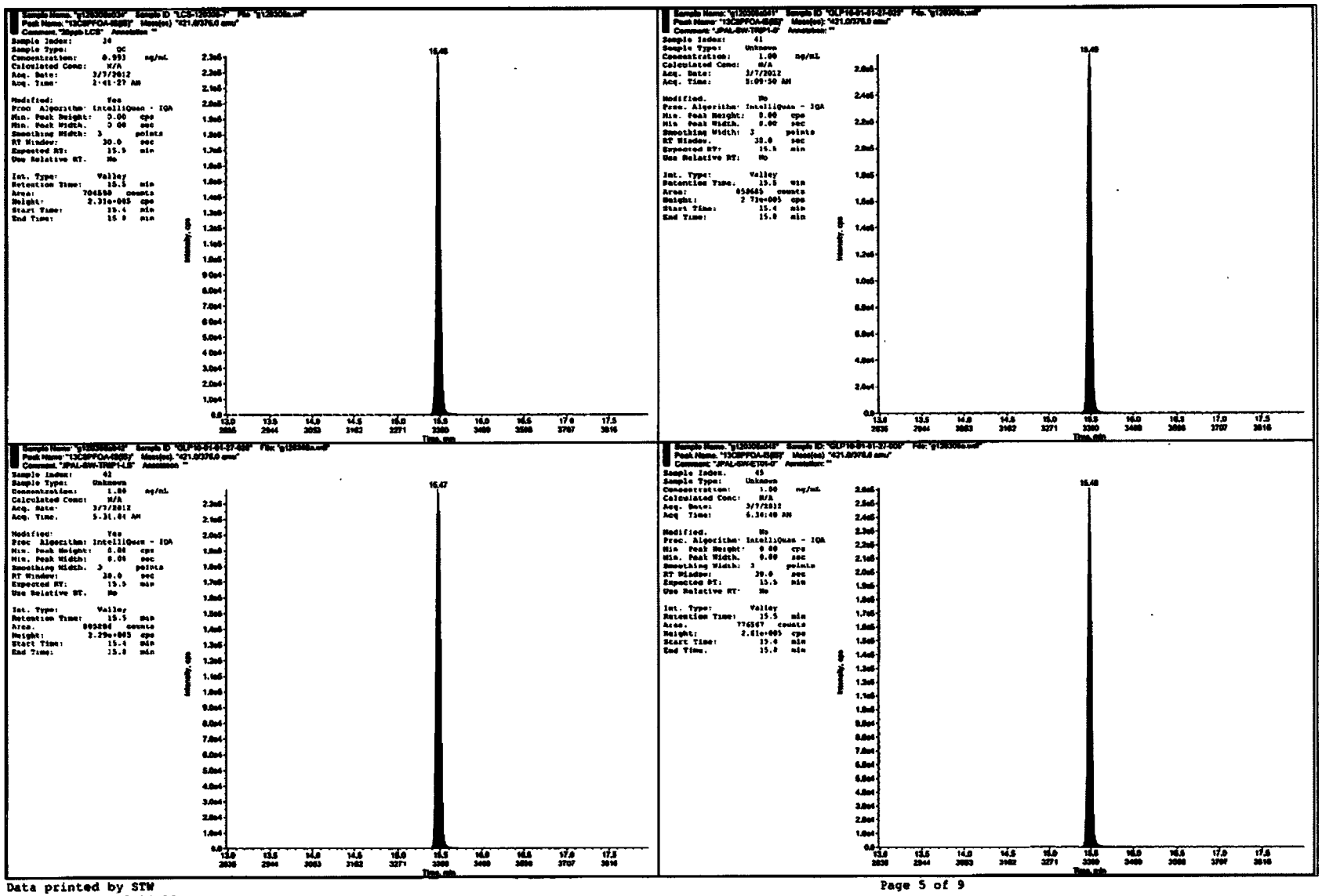
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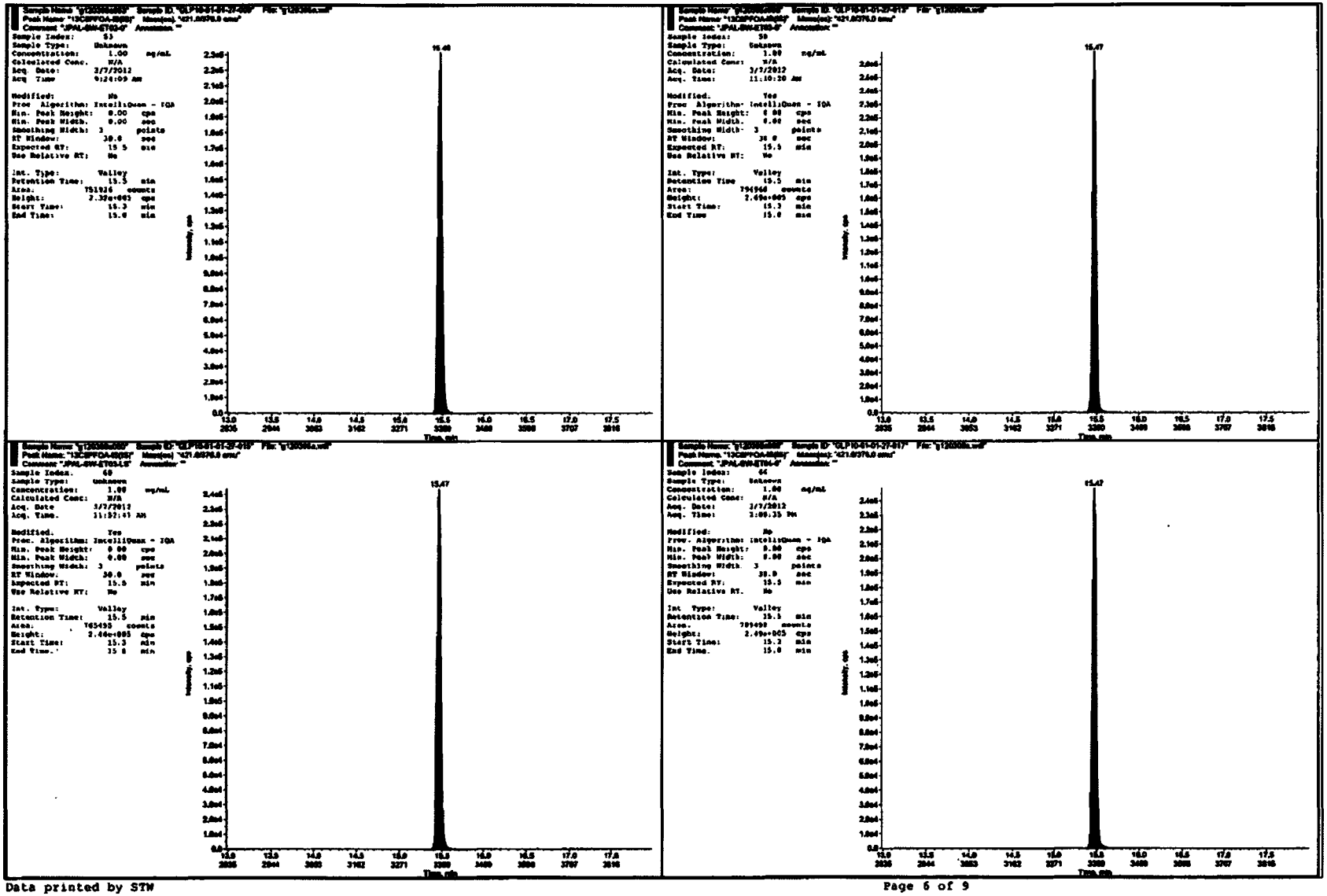
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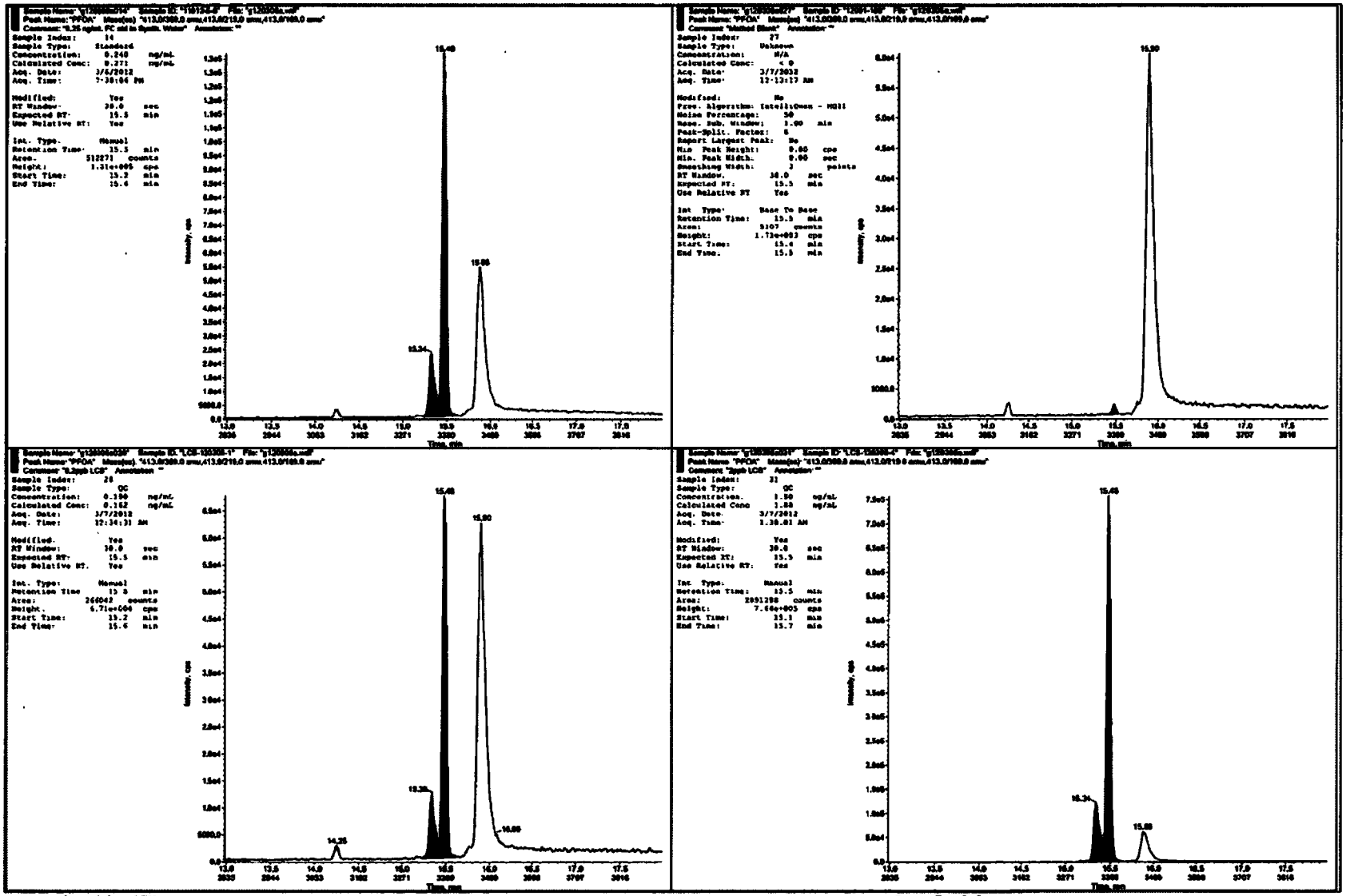
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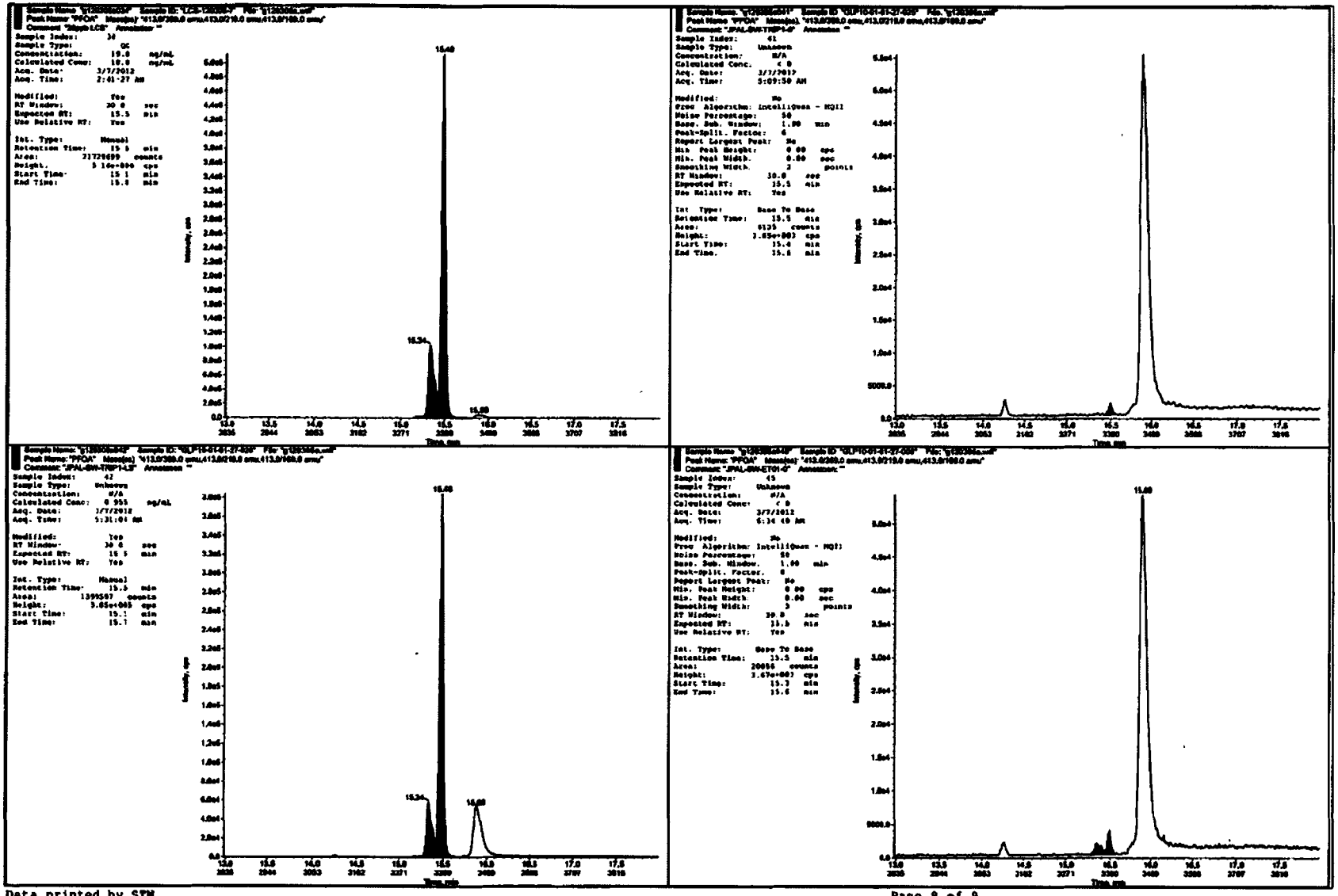
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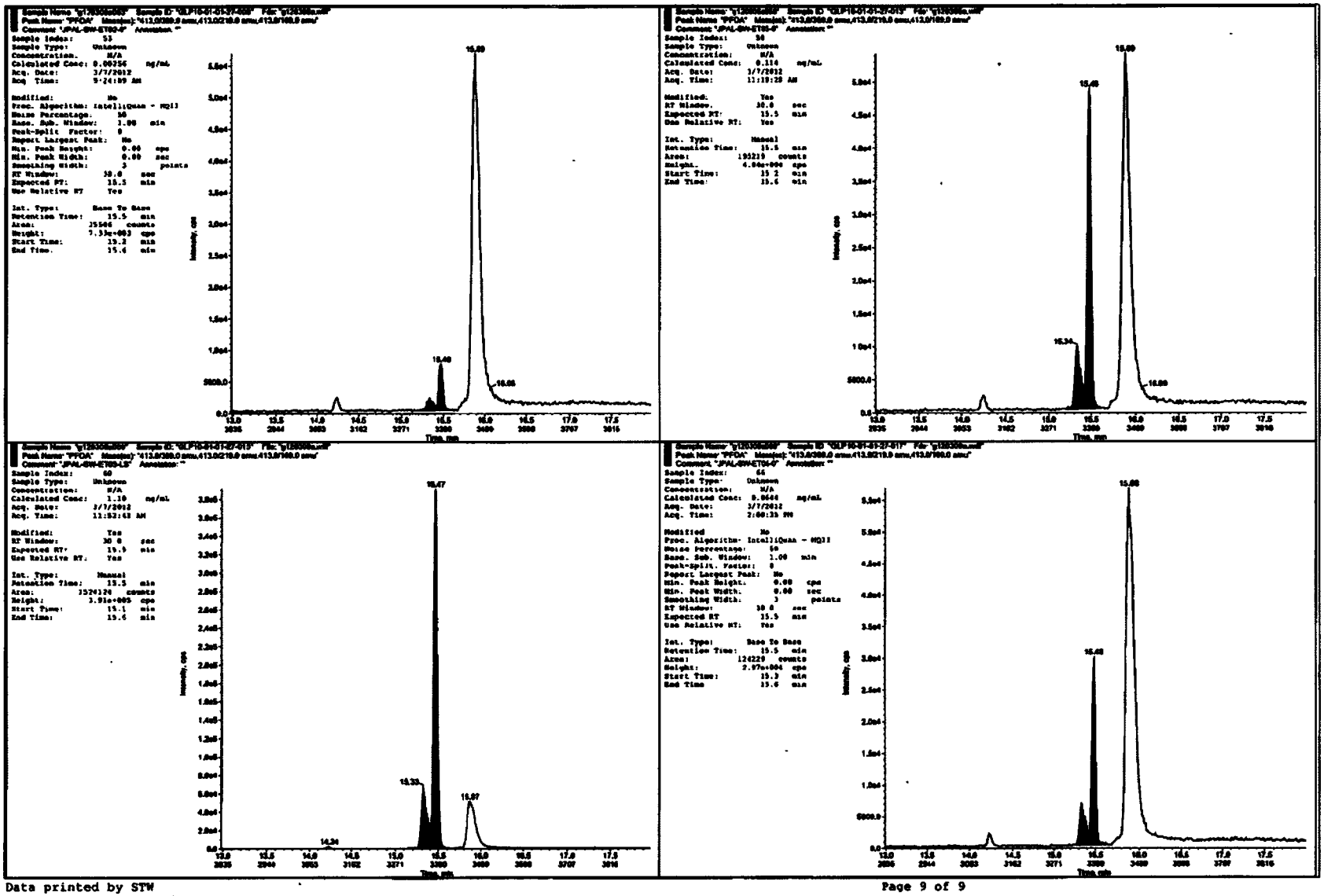
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ATTACHMENT C: ANALYTICAL METHOD(S)

3M Environmental Laboratory

Method

Method of Analysis for the Determination of Perfluorinated Compounds in Water by LC/MS/MS; Direct Injection Analysis

Method Number: ETS-8-044.1

Adoption Date: 4/12/07

Effective Date: 11/9/11

Approved By:

9 NOV 2011

William K. Reagen, Technical Director, Environmental Laboratory — Date

1 Scope and Application

This method describes the direct injection analysis of perfluorinated compounds (PFCs) from water matrices using high-performance liquid chromatography tandem mass spectrometry (HPLC/MS/MS). The method is generally applicable but not limited to the measurement of perfluoroalkyl sulfonamides and perfluorinated alkyl acids (PFAAs) such as perfluorosulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs) (Table 1). Water samples containing heavy particulate may require preparation by an alternate method such as ETS-8-154 "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates In Water By Solid Phase Extraction and High Performance Liquid Chromatography/Mass Spectrometry". The method is applicable to both external standard and internal standard calibration[1].

Table 1. Representative Target Analytes

Acronym	*Analyte*	*Chemical Abstract Services Registry Number (CASRN)*
PFBA (C4 Acid)	Perfluorobutanoic acid	375-22-4
PFPeA (C5 Acid)	Perfluoropentanoic acid	2706-90-3
PFHxA (C6 Acid)	Perfluorohexanoic acid	307-24-4
PFHpA (C7 Acid)	Perfluoroheptanoic acid	375-85-9
PFOA (C8 Acid)	Perfluorooctanoic acid	335-67-1
PFNA (C9 Acid)	Perfluorononanoic acid	375-95-1
PFDA (C10 Acid)	Perfluorodecanoic acid	335-76-2
PFUnA (C11 Acid)	Perfluoroundecanoic acid	2058-94-8
PFDoA (C12 Acid)	Perfluorododecanoic acid	307-55-1
PFTrDA (C13 Acid)	Perfluorotridecanoic acid	72629-94-8
PFBS (C4 Sulfonate)	Perfluorobutanesulfonic acid	375-73-5
PFHS (C6 Sulfonate)	Perfluorohexanesulfonic acid	355-46-4
PFOS (C8 Sulfonate)	Perfluorooctanesulfonic acid	1763-23-1
FBSA (C4 Sulfonamide	Perfluorobutanesulfonamide	30334-69-1
FOSA (C8 Sulfonamide)	Pefluorooctanesulfonamide	754-91-6

The Minimum Reporting Level (MRL) is the Limit of Quantitation (LOQ) that meets Data Quality Objectives (DQOs) that are developed based on the intended use of this method.

Method Flexibility – This is a performance-based method and may be generally applied to the determination of perfluorinated compounds in water matrices when analysis batch quality control (QC) criteria are met[2]. Each set of samples are prepared in an analysis batch with calibration standards, LCSs, blanks, and continuing calibration check standards analyzed on the same instrument during a time period that begins and ends with the analysis of the appropriate continuing calibration check standards. The laboratory is permitted to modify the LC column, mobile phase composition, LC conditions, and MS/MS conditions. Method modifications should be considered to improve method performance or to meet data quality objectives for the study. In all cases where method modifications are implemented, the batch

[1] The method is supported by validation with internal standard calibration for C4-C13 PFCAs, C4, C6, and C8 PFSAs, and C8 perfluoroalkane sulfonamide in laboratory control samples under 3M method validation E11-0667.

[2] Guidance for establishing method QC Criteria based on a.) FDA May 2001, "Guidance for Industry, Bioanalytical Method Validation", b.) EPA Method 537, and c.) European Commission: Guidance for Generating and Reporting Methods of Analysis in Support of Pre-registration Data Requirements for Annex II (Part A, section 4) and Annex III (Part A,section 5) of Directive 91/414, SANCO/3029/99 rev. 4 (11/07/00).

analytical QCs (section 9) must be completed and pass QC acceptance criteria (section 13) if the data from the analytical batch are to be reported.

2 Method Summary

Water samples are analyzed as neat aqueous sample or as solvent diluted aqueous samples by direct injection using LC/MS/MS. Samples containing heavy particulate may not be suitable for analysis by this method. Samples containing suspended particulate should be centrifuged or filtered prior to removing a sample aliquot or diluting with solvent. The water sample is mixed well prior to removing an aliquot or diluting, if necessary, with ASTM Type I water, HPLC water, other suitable water, or solvent (methanol).

Quantitation is by stable isotope internal standard calibration in laboratory reagent water. All perfluorinated compounds (PFCs) target analyte concentrations of perfluorosulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs) are reported as anions and corrected for their salt or free acid forms. Alternatively, quantitation may be performed by external standard calibration.

This is a performance-based method. Method uncertainty for each target analyte is determined for each analytical batch using multiple laboratory control spikes at multiple concentrations. This method also requires that the precision and accuracy for each sample be determined using field matrix spikes to verify that the method is applicable to each sample matrix.

Calibration standards for PFUnA, PFDoA, PFTrDA, and FOSA have been found to be unstable for more than 2 days in 100% water. Samples requiring analysis for these compounds by this method should be diluted 1:1 with methanol and analyzed against a calibration curve prepared in 1:1 synthetic groundwater:MeOH.

3 Definitions

3.1 Analysis Batch

A set of study samples that are prepared with calibration standards, laboratory control samples, and procedural blanks, and analyzed on the same instrument during a time period that begins and ends with the analysis of the appropriate continuing calibration check standards.

3.2 Analytical Sample

A portion of a laboratory sample prepared for analysis.

3.3 Calibration Standard

A solution prepared by spiking a known volume of the Working Standard (WS) into a predetermined amount of ASTM Type I, HPLC grade water, or other suitable water (i.e. matrix water), and analyzed according to this method. Calibration standards are used to calibrate the instrument response with respect to analyte concentration.

3.4 Laboratory Duplicate Sample (LDS, or Lab Dup)

A laboratory duplicate sample is a separate aliquot of a sample taken in the analytical laboratory that is analyzed separately with identical procedures. Analysis of LDSs 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.

3.5 Field Blank (FB)/Trip Blank (TB)

ASTM Type I, HPLC grade water, or other suitable 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 TB is to determine if test substances or other interferences are present in the field environment. This sample is also referred to as a Trip Blank.

3.6 Field Duplicate Sample (FDS, Field Dup)

A sample collected in duplicate at the same time from the same location as the sample. The FDS is handled under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analysis of the FDS 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.

3.7 Field Matrix Spike (FMS)

A sample to which known quantities of the target analytes, ISs and SRSs are added to the sample bottle in the laboratory before the bottles are sent to the field for collection of aqueous samples. A known, specific volume of sample must be added to the 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 is analyzed to ascertain if any matrix effects, interferences, or stability issues may complicate the interpretation of the sample analysis.

3.8 Trip Blank Matrix Spike (TBMS)

An aliquot of ASTM Type I, HPLC grade water, or other suitable water, to which known quantities of the target analytes, ISs and SRSs are added in the laboratory prior to the shipment of the collection bottles. The TBMS is analyzed exactly like a study sample to help determine if the method is in control and whether a loss of analyte or analytical bias could be attributed to sample holding time, sample storage and/or shipment issues. A low and high TBMS are appropriate when expected sample concentrations are not known or may vary.

3.9 Internal Standard (IS)

A compound added to each study sample, calibration standard, laboratory control samples, and procedural blanks at a consistent level (typically around 1 ng/mL). The internal standard(s) are stable isotope labeled versions of the target analytes. The area count ratio of the target analyte to the internal standard is used for calibration. Surrogate ISs are applied when stable isotope ISs of target analytes are unavailable. A surrogate IS is not necessarily a stable isotope labeled version of the target analyte, but is treated as an internal standard for quantitation.

3.10 Laboratory Control Sample (LCS)

An aliquot of control matrix to which known quantities of the target analytes, ISs and SRSs (when applicable) are added in the laboratory at the time when samples are aliquotted. At least three levels (two levels for SRSs) in triplicate are included, one generally at the low end of the calibration curve and one near the mid range and the upper end of the curve. The LCSs are analyzed exactly like a laboratory sample to determine whether the stability of the standards. LCSs should be prepared each day samples are aliquoted.

3.11 Laboratory Matrix Spike (LMS)

A laboratory matrix spike is an aliquot of a sample to which known quantities of target analytes, ISs and SRSs (when applicable) are added in the laboratory. The LMS is analyzed exactly like a laboratory sample to determine whether the sample matrix contributes bias to the analytical results. The endogenous concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LMS corrected for these concentrations. LMSs are optional for analysis of aqueous samples.

3.12 Laboratory Sample

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

3.13 Limit of Quantitation (LOQ)

The lower limit of quantitation (LLOQ) for an analytical batch is the lowest concentration that can be reliably quantitated within the specified limits of precision and accuracy. The LLOQ is generally selected as the lowest non-zero standard in the calibration curve that meets method acceptance criteria. The LLOQ for each target analyte is established for each analysis batch as the lowest calibration standard with area counts at least twice that of the average area counts of the procedural blanks.

The upper limit of quantitation (ULOQ) for an analytical batch is the highest concentration that can be reliably quantitated within the specified limits of precision and accuracy. The highest standard in the calibration curve that meets method acceptance criteria is defined as the ULOQ.

3.14 Method/Procedural Blank

An aliquot of control matrix 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.

3.15 Sample

A sample is an aliquot removed from a larger quantity of material intended to represent the original source material.

3.16 Stock Standard Solution (SSS)

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

3.17 Surrogate Internal Standard

An IS that is not necessarily a stable isotopically labeled target analyte, but is treated as an internal standard for quantitation. Surrogate ISs are used when isotopically labeled counterparts of the target analyte are not commercially or readily available.

3.18 Surrogate Recovery Standard (SRS)

An isotopically labeled standard, not used as an internal standard, that is added to each sample and appropriate QC sample as a means to evaluate the method performance for a chemical class of compounds (e.g., PFSAs, PFCAs).

3.19 Working Standard (WS)

A solution of several analytes prepared in the laboratory from SSSs 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. The analyst should wear gloves, a lab coat, and safety glasses to prevent exposure to chemicals that might be present.

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

The analyst must be familiar with the laboratory equipment and potential hazards including, but not limited to, the use of solvents, pressurized gas and solvent lines, high voltage, and vacuum systems. Refer to the appropriate equipment procedure or operator manual for additional information and cautions.

5 Interferences

During sample preparation and analysis, major potential contaminant sources are reagents and glassware. 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 or minimized 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

6.1 Instrumentation

Analytical balance capable of reading to 0.0001g

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

6.2 Supplies and Materials

Sample collection bottles—HDPE (e.g., Nalgene™) wide-mouth bottles with screw cap.
Note: Do not use fluorinated or Teflon® bottles or lined caps.

Coolers or boxes for sample shipment.

15-mL and 50-mL disposable polypropylene centrifuge tubes.

Class A pipettes and volumetric flasks, various.

2 mL HPLC autovials

Disposable pipettes, polypropylene or glass as appropriate

Centrifuge capable of spinning 15-mL and 50-mL polypropylene tubes at 3000 rpm.

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

Water – Milli-Q, HPLC grade, or other suitably appropriate sources

Calcium Acetate - A.C.S. Reagent Grade

Magnesium Acetate - A.C.S. Reagent Grade

Methanol – HPLC grade

Ammonium Acetate – A.C.S. Reagent Grade

7.2 Representative Target Analytes, ISs, and SRSs

PFBA, Heptafluorobutyric Acid, (C_4 Perfluorinated Acid)

PFPeA, Nonafluoropentanoic Acid (C_5 Perfluorinated Acid)

PFHxA, Perfluorohexanoic Acid (C_6 Perfluorinated Acid)

PFHpA, Tridecafluoroheptanoic Acid, (C_7 Perfluorinated Acid)

PFOA, Ammonium perfluorooctanoate, (C_8 Perfluorinated Acid)

PFNA, Heptadecafluorononanoic Acid, (C_9 Perfluorinated Acid)

PFDA, Nonadecafluorodecanoic Acid (C_{10} Perfluorinated Acid)

PFUnA, Perfluoroundecanoic Acid, (C_{11} Perfluorinated Acid)

PFDoA, Perfluorododecanoic Acid, (C_{12} Perfluorinated Acid)

PFTrDA, Perfluorotridecanoic Acid, (C_{13} Perfluorinated Acid)

FBSA, Perfluorobutanesulfonamide

FOSA, Perfluorooctanesulfonylamide

PFBS, Potassium Perfluorobutanesulfonate

PFHS, Perfluorohexanesulfonate

PFOS, Potassium perfluorooctanesulfonate

PFOA [1,2, 3, 4-^{13}C], $^{13}C_4$-isotopically labeled perfluorooctanoic acid (SRS)

PFOS [1,2, 3, 4-^{13}C], $^{13}C_4$-isotopically labeled Perfluorooctanesulfonate (SRS)

PFUnA [1,2-^{13}C], $^{13}C_2$-isotopically labeled Perfluoroundecanoic acid (SRS)

A custom mix of ISs in a methanolic solution containing ([1,2,3,4-$^{13}C_4$]PFBA, [1,2-$^{13}C_2$]PFHxA, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA, [1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA, [1,2-$^{13}C_2$]PFDA, [1,2,3,4,5,6,7-$^{13}C_7$]PFUnA, [1,2-$^{13}C_2$]PFDoA, [1,2,3-$^{13}C_3$]PFHS, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOS, and [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOSA (Wellington Laboratories, Guelph, ON) in combination with added ([1,2,3,4,5-$^{13}C_5$]PFPeA, ([1,2,3,4-$^{13}C_4$]PFHpA, and [$^{18}O_2$]PFBS can be used to prepare a stock IS solution. Alternatively, individual stable isotope ISs can be used to prepare a stock IS mixture.

Other ISs can be applied.

7.3 Reagent Preparation

2 mM Ammonium acetate solution (Analysis)—Weigh 0.3 g of Ammonium acetate and dissolve in 2.0 L of reagent water.

Synthetic Groundwater (containing 25 ppm Ca and Mg) – Weigh 0.61 g of Calcium Acetate and 0.92 g of Magnesium Acetate and dissolve in 6.0 L of reagent water.

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

7.4 Stock Standard Solution (SSS) and Working Standard Solution Preparation

The following standard preparation procedure serves as an example. Weighed amounts and final volumes 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.

100 µg/mL target analyte SSSs—Weigh out 10 mg of analytical standard ***(corrected for percent salt, acid [ETS-4-031] and purity)*** and dilute to 100 mL with methanol or other suitable solvent, in a 100 mL volumetric flask. Transfer to a 125 mL LDPE bottle or other suitable container. Prepare a separate solution for each analyte. Expiration dates and storage conditions of stock solutions should be assigned in accordance with laboratory standard operating procedure. An example of purity and salt correction is given below for PFOS.

$$\text{salt correction factor} = \frac{\text{molecular weight of anion}}{\text{moclecular weight of salt}}$$

$$\text{PFOS } (K^+) \text{salt correction factor} = \frac{499}{538} = 0.9275$$

10 mg $C_8F_{17}SO_3^-K^+$ with purity 90% = 8.35 mg $C_8F_{17}SO_3^-$ (10 mg*0.90*0.9275=8.35 mg)

10 µg/mL (10,000 ng/mL) mixed working standard—Add 5.0 mL each of the 100 µg/mL SSSs to a 50 mL volumetric flask and bring up to volume with solvent.

1 µg/mL (1,000 ng/mL) mixed working standard—Add 0.5 mL of the 100 µg/mL SSSs to a 50 mL volumetric flask and bring up to volume with solvent.

0.1 µg/mL (100 ng/mL) mixed standard—Add 0.05 mL of the 100 µg/mL SSSs to a 50 mL volumetric flask and bring up to volume with solvent.

Storage Conditions—Store all SSSs and working standards in accordance with laboratory standard operating procedure or in a refrigerator at 4°±2°C for a maximum period of 6 months from the date of preparation.

7.5 Calibration Standards

Calibration can be performed by IS or external calibration. Using the working standards described above, prepare calibration solutions in ASTM Type I water, HPLC water, other suitable water, or a mixture of solvent and water using the information in Table 2 as a guideline. Note: Volumes of water or water/solvent mixtures and working standards may be adjusted to meet the data quality objectives addressed in the general project outline. Calibration levels other than those listed below can be prepared as needed.

For the quantitation of PFOA and PFOS, reference materials of certified mixed linear and branched isomer are preferred. Alternately, reference materials of primarily linear isomers of PFOA and/or PFOS may be used, however, when quantitating with predominantly linear reference standards, additional LCS samples containing both linear and branched isomers of PFOA and PFOS are required[3].

7.5.1 Internal Standard (IS) and Surrogate Recovery Standard (SRS)

For IS calibration, stable isotope internal standards of each target analyte or appropriate surrogate ISs should be spiked at the same level in all calibration standards. Once the calibration standards have been prepared as stated above in Section 7.5, all calibration standards are spiked with a separate internal standard spiking solution. Typically the

[3] A report summarizing an assessment of the use of reference standards containing certified linear and branched isomers of PFOA/PFOS can be found in 3M report E11-0560.

concentration of the internal standard is consistent with the internal standard concentration expected in the samples being prepared, usually 1 ng/mL. The concentration of the internal standard spiking solution is typically 2 µg/mL. A separate zero point or method blank is typically prepared at the same time as the calibration standards, using the same solution used to prepare the standards (ASTM Type I water, HPLC water, other suitable water, or a solvent/water mixture), and is spiked with the internal standard at the same concentration as the calibration curve, typically at 1 ng/mL.

If the samples being analzyed were pre-spiked with SRSs, the calibration curve prepared in Section 7.5 is spiked with a separate SRS spiking solution. Typically, the sample bottles are spiked with a SRS at 0.1 ng/mL. The final calibration curve must consist of at least six calibration points after analysis. The following table provides an example of spike concentrations and volumes used to achieve a multi-point extracted calibration curve with internal standard and surrogate standard.

Table 1 lists recommended stable isotope internal standards for several PFSA and PFCA target compounds. A custom mix of isotopically labeled target analytes in a methanolic solution containing ([1,2,3,4-$^{13}C_4$]PFBA, [1,2 -$^{13}C_2$]PFHxA, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA, [1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA, [1,2,3,4,5,6 -$^{13}C_6$]PFDA, [1,2,3,4,5,6,7 -$^{13}C_7$]PFUnA, [1,2 -$^{13}C_2$]PFDoA, [1,2,3-$^{13}C_3$]PFHS, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOS, and [1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA (Wellington Laboratories, Guelph, ON) in combination with added ([1,2,3,4,5-$^{13}C_5$]PFPeA, ([1,2,3,4-$^{13}C_4$]PFHpA, and [$^{18}O_2$]PFBS can be used to prepare a stock IS solution. Alternative sources of certified stable isotope labeled target analytes are applicable. Alternatively, individual stable isotope ISs can be used to prepare a stock IS mixture. The table below lists the recommended stable isotope ISs and SRSs applied in the method. Other stable isotope ISs and SRSs of target analytes not listed in the table may be used if supported by validation and/or analysis batch QCs meeting method acceptance criteria (e.g., [$^{13}C_2$]-PFOA). The same internal standard should be used for a given analyte throughout the entire project/study. Note: some of the compounds listed below are appropriate to use as surrogate ISs when a stable isotope IS of a target analyte is not available. Generally, surrogate isotopically labeled PFCAs are used for PFCAs, and surrogate isotopically labeled PFSAs are used for PFSAs.

Table 2 provides examples of spike concentrations and volumes used to achieve a multi-point calibration curve with ISs and SRSs.

Table 1. Stable Isotope PFCAs and PFSAs used for ISs and SRSs

Compound Name	*Synonym or Acronym*	*Analytical Purpose*	*Reference Standard Source*
$^{13}C_4$-Perfluorobutanoic acid	[1,2,3,4-$^{13}C_4$]PFBA	IS for PFBA	Wellington Labs (Mix or Individual)
$^{13}C_4$-Perfluoropentanoic acid	[1,2,3,4,5-$^{13}C_5$]PFPeA	IS for PFPeA	Wellington Labs (Mix or Individual)
$^{13}C_2$-Perfluorohexanoic acid	[1,2 -$^{13}C_2$]PFHxA	IS for PFHxA	Wellington Labs (Mix or Individual)
$^{13}C_4$-Perfluoroheptanoic acid	[1,2,3,4-$^{13}C_4$]PFHpA	IS for PFHpA	Wellington Labs (Mix or Individual)
$^{13}C_8$-Perfluorooctanoic acid	[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA	IS for PFOA and [1,2,3,4 $^{13}C_4$]PFOA	Wellington Labs (Mix or Individual)
$^{13}C_9$-Perfluorononanoic acid	[1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA	IS for PFNA	Wellington Labs (Mix or Individual)
$^{13}C_6$-Perfluorodecanoic acid	[1,2,3,4,5,6 -$^{13}C_6$]PFDA	IS for PFDA	Wellington Labs (Mix or Individual)
$^{13}C_7$-Perfluoroundecanoic acid	[1,2,3,4,5,6,7 -$^{13}C_7$]PFUnA	IS for PFUnA	Wellington Labs (Mix or Individual)
$^{13}C_2$-Perfluorododecanoic acid	[1,2 -$^{13}C_2$]PFDoA	IS for PFDoA, *PFTA	Wellington Labs (Mix or Individual)
$^{18}O_2$-Ammonium Perfluorobutane sulfonate	[$^{18}O_2$]PFBS	IS for PFBS	RTI International (Individual)
$^{13}C_3$-Ammonium Perfluorohexane sulfonate	[1,2,3-$^{13}C_3$]PFHS	IS for PFHS	Wellington Labs (Mix or Individual)
$^{13}C_8$-Sodium Perfluorooctane sulfonate	[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOS	IS for PFOS and PFOS[1,2,3,4 $^{13}C_4$],	Wellington Labs (Mix or Individual)
$^{13}C_8$-Perfluorooctanesulfonamide	[1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA	IS for FOSA	Wellington Labs (mix) RTI International (Individual)
$^{13}C_4$-Perfluorooctanoic acid	[1,2,3,4-$^{13}C_4$]PFOA	SRS for all PFCAs: C4-C8	Wellington
$^{13}C_2$-Perfluoroundecanoic acid	[1,2 -$^{13}C_2$]PFUnA	SRS for all PFCAs C9-C13	Wellington
$^{13}C_8$-Perfluorooctane sulfonate	[1,2,3,4-$^{13}C_4$]PFOS	SRS for all PFSAs: C4, C6, and C8	Wellington

Table 2. Example Preparation of Calibration Curve with ISs and SRSs

Sample Description	*Concentration of WS, µg/mL*	*Volume of WS, µL*	*Volume of IS (2 µg/mL), µL*	*Concentration of Surrogate, µg/mL*	*Volume of Surrogate, µL*	*Volume of ASTM Type I Water, or other suitable solvent [1], mL*
0.025 ng/mL curve point	0.10	25	50	0.20	12.5	100
0.030 ng/mL curve point	0.10	30	50	0.20	15	100
0.04 ng/mL curve point	0.10	40	50	0.20	20	100
0.05 ng/mL curve point	0.10	50	50	0.20	25	100
0.1 ng/mL curve point	0.10	100	50	0.20	50	100
0.25 ng/mL curve point	0.10	250	50	0.20	125	100
0.5 ng/mL curve point	1.0	50	50	0.20	250	100
1 ng/mL curve point	1.0	100	50	0.20	500	100
2.5 ng/mL curve point	10.0	25	50	10.0	25	100
5.0 ng/mL curve point	10.0	50	50	10.0	50	100
10.0 ng/mL curve point	10.0	100	50	10.0	100	100
25.0 ng/mL curve point	10.0	250	50	10.0	NA	100
50.0 ng/mL curve point	10.0	500	50	10.0	NA	100
75.0 ng/mL curve point	10.0	750	50	10.0	NA	100
100 ng/mL curve point	10.0	1000	50	10.0	NA	100

N/A - Not Applicable
(1) Samples requiring analysis for PFUnA, PFDoA, PFTrDA, and FOSA should be analyzed against a calibration curve prepared in 1:1 synthetic groundwater:MeOH.

8 Sample Collection and Bottle Preparation

Sample collection bottles are prepared by 3M Environmental Laboratory (or subcontract supplier) personnel for shipment at ambient temperature to the collection site. Typically, four separate collection bottles are associated with a single collection site: sample, field duplicate sample, low field matrix spike, and high field matrix spike. Alternatively, the sample and field duplicate sample may contain SRSs in lieu of additional target analyte low field matrix spike and target analyte high field matrix spike samples. Depending on the scope of the project, additional replicates of the field sample and field matrix spikes may be added. Also, it is not uncommon for additional mid-level field matrix spikes to be collected if the expected sample concentrations are truly unknown or could span a large concentration range.

High-density polyethylene (HDPE) wide-mouth Nalgene bottles are used for the sample collection containers. (Volumes of the bottles may vary depending on how much sample is required to meet data quality objectives.) Sample collection volumes are project specific and based on data quality objectives. The Nalgene bottles do not require any pretreatment prior to use. Typically, placement of a sample bottle volumetric "fill to here" line is done by using a sample bottle marker template. Alternatively, bottles may be weighed prior to bottle preparation and weighed again after samples have been collected.

All bottles should be clearly labeled to indicate its intended use as a sample, field sample duplicate, low field matrix spike, high field matrix spike, sample/SRS field matrix spike, field duplicate sample/SRS field matrix spike, trip blank, or trip blank matrix spike. If each location has different designated spike levels, the label should also clearly indicate the sample location designation. Generally, a set of bottles for a given collection site are prepared then grouped together in plastic bags for organizational purposes. For each sample collection event, at least one set of trip blank and trip blank matrix spikes are prepared.

Bottle preparation should be documented in a Note to File or on a sample preparation worksheet and should include the following information: date prepared, total number of bottles prepared, number of sample sites, the standard identification numbers and spike volumes used to prepare spiked bottles, the "fill to here" volume, and any other pertinent information needed for reconstructibility of the data. The Note to File will be included in the final data package for the project.

Samples are collected in the field and shipped to the laboratory at ambient temperature.

8.1 Field Matrix Spike Sample (FMS)

Field matrix spike samples are a requirement of the method. A FMS sample is defined as a QC sample to which known quantities of appropriate target analytes are added to the sample bottle in the field or in the laboratory before the bottles are sent to the field. The sample and field duplicate sample may contain appropriate SRSs in lieu of target analyte FMS samples. Sample quantities are determined volumetrically or gravimetrically. A known, specific volume or weight of sample is added to the sample container without rinsing. Volumetric sample measurements may be acquired by a laboratory applied "fill to this level" line on the outside of the sample container. Target analyte FMS samples should be spiked at approximately 0.5-10 times the expected analyte concentration in the sample. If the expected range of analyte concentrations is unknown, multiple spikes at varying levels may be prepared to increase the likelihood that a spike at an appropriate level is made. Typically a low and a high target analyte spike are prepared for each sampling location. In those instances where SRSs are to be used in lieu of target analyte FMS samples, the sample and field duplicate sample are spiked at approximately 2-5 times the target LOQ. The FMS is analyzed to ascertain if matrix effects or sample holding time contributes bias to the analytical results. For the sample bottles designated for matrix spikes, an appropriate volume of matrix spiking solution is added to the empty bottle prior to sampling. The volume of spike solution added should produce the desired final concentration of target analytes once the bottle is filled with sample to the "fill to here line". The matrix spiking solution(s) should be prepared in a suitable solvent and contain all of the appropriate target analytes, ISs, and SRSs. The target analyte matrix spiking solution is often the same as the working standards used to create the calibration standards. An example of a bottle spike is given below.

"Fill to here" volume = 200 mL (A 250 mL Nalgene bottle is used)

Desired Field Spike Concentration = 0.25 ng/mL

500 µL of a 0.1 µg/mL spiking solution (containing the target analytes) is added to the bottle and the bottle cap promptly sealed.

8.2 Internal Standard and Surrogate Recovery Standard

If analysis of a surrogate recovery standard (SRS) is included in the project objectives, an appropriate volume of a surrogate standard solution is added to all the bottles prior to sampling and SPE. Typically sample bottles are spiked with surrogate recovery standards at a final desired spike concentration of 0.1 ng/mL.

If quantitation by internal standard (IS) is included in the project objective, an appropriate volume of internal standard solution is added to all the bottles prior to sampling and SPE. Typically sample bottles are spiked with internal standard at a final desired spike concentration of 1 ng/mL.

For the trip blank, the SRS spike and IS spike is added to the bottle and then ASTM Type I water (HPLC grade reagent water or other suitable water may used) is added to the "fill to here" line. The bottle is capped and sealing tape may be placed around the outer edge of the cap. Trip blank matrix spikes are prepared by adding the appropriate volume of target analyte spiking solution, IS, and SRS spiking solutions and filling the bottle to the desired volume with the appropriate water and capping and sealing the cap.

9 Quality Control and Data Quality Objectives

9.1 Data Quality Objectives

This method and required quality control samples is designed to generate data accurate to ±30% with a targeted LOQ of 0.025 ng/mL. Any deviations from the quality control measures spelled out below will be documented in the raw data and footnoted in the final report.

9.2 Method/Procedural Blanks

The method/procedural blank is zero point calibration standard (which includes ISs) analyzed in a regular basis with each analysis batch. At a minimum, method blanks are analyzed prior to instrument calibration, prior to the analysis of CCV samples, after every 10 sample injections, and at the end of the analytical run.

The mean area count or area ratios when using internal standard calibration, for each analyte in the method blanks must be less than 50% of the area count counts or area ratios when using internal standard calibration, of the LOQ standard. The standard deviation of the area counts, or area ratios when using internal standard calibration, of these method blanks should be calculated. A specific %RSD acceptance criteria is not specified but is assessed on an analytical batch basis. If the mean area counts or area ratios when using internal standard calibration, of the method blanks exceed 50% of the LOQ standard, then the LOQ must be raised to the first standard level in the curve that meets criteria. Method blanks may be eliminated if technical justification can be provided (e.g. the procedural blank was analyzed after an unexpectedly high level sample). If any procedural blanks are removed from the LOQ determination, document in the raw data and report as appropriate. Laboratory Sample Replicates / Field Duplicate Sample

Typically, samples are collected in duplicates in the field. The relative percent difference (RPD) of duplicate samples should be ≤20% for the precision of sample preparation and analysis to be considered in control. Replicate samples not meeting the ≤20% RPD criteria are flagged and reported as outside of QC acceptance criteria.

9.3 Laboratory Matrix Spikes (LMSs)

LMSs may be performed in lieu of FMSs if FMSs have previously been performed for the sample matrix. Additionally, LMSs may be performed in lieu of FMSs for a sample matrix if the FMS levels were not appropriate for determining spike recoveries relative to endogenous levels of target analytes and appropriate SRSs. Generally, each sample location represents a different sample and sample matrix. LMSs are prepared for each sample and analyzed to determine the matrix effect on spike recovery efficiency of each target analyte and appropriate SRSs. LMSs should be prepared at a minimum of one level and in duplicate. LMS concentrations should be prepared at approximately 0.5-10 times the endogenous concentration or approximately 4-10 times the LOQ concentration of each target analyte.

Lab matrix spike recoveries should fall within ± 30% of expected values. Sample data with LMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria. Data with LMS recovery outside of ±50% of the expected value are reported as NR, where NR is defined as "Not Reportable" data outside of QC acceptance criteria.

9.4 Lab Control Sample

Lab control spikes are prepared for each analysis batch to determine method accuracy and precision. LCSs should be prepared at three levels in triplicate for each target analyte and at a minimum of two levels in triplicate for appropriate SRSs. Low lab control spikes should be prepared at a concentration in the range of approximately four to ten times higher than the targeted lower LOQ, the mid lab control spikes should be prepared at a concentration near the mid-point of the calibration curve and the high lab control spikes at approximately 80% of the upper LOQ. For each target analyte and SRSs, the percent relative standard deviation (method precision) for each control spike level must be less than or equal to 20% and the average recovery (method accuracy) for each control spike level must be 80-120%. Sample data for target analytes outside of the laboratory control spike acceptance criteria will be handled as follows:

If the average recovery of a spiking level falls outside method acceptance, but at least 67% (6 out of 9) of LCS samples are within 20% of their respective nominal value (33% of the QC samples, not all replicates at the same concentration, may be outside 20% of nominal value), the average recovery will be flagged as outside method acceptance criteria. All LCS samples will be control charted as per ETS-4-026. If the average recovery of one of the spiking levels exceeded the analytical method uncertainty as determined by ETS-12-012, that analytical batch uncertainty will be expanded for that particular study.

If more than 67% of the LCS samples fail to meet method acceptance criteria, the data will not be reported.

Calibration standards consisting of mixed branched and linear isomer PFOS/PFOA are preferred. However, for PFOS/PFOA target analytes, if the calibration standards are comprised of predominantly linear isomers only, at least one level of triplicate LCSs should be prepared using PFOS/PFOA which contains a mix of linear and branched isomers. These LCSs will be used to demonstrate quantitative equivalency (or quantitative bias) of the isomeric mix when using a predominantly linear standard for calibration. The mixed linear and branched isomer PFOS/PFOA LCSs recoveries should fall within ± 30% of expected values. Alternatively, in lieu of mixed branched and linear isomer PFOS/PFOA LCSs, mixed branched and linear isomer PFOS/PFOA TBMSs may be applied to demonstrate method accuracy and precision.

9.5 Field Matrix Spikes (FMSs) / Surrogate Recovery Standards (SRSs)

FMSs are prepared for each sampling location and analyzed to determine the matrix effect and sample holding time on the spike recovery of each target analyte and/or appropriate SRS. Generally, each sample location represents a different sample and sample matrix.

FMSs are QC samples to which known quantities of appropriate target analytes are added to the sample bottle in the laboratory before the bottles are sent to the field. Typically a low and a high target analyte FMS are prepared for each sampling location. The sample and field duplicate sample may contain appropriate SRSs in lieu of target analyte low field matrix spike and target analyte high field matrix spike samples.

Field matrix spike method acceptance criteria are recoveries within ±30% of the expected value. If FMS recovery (target analyte or SRS spike) is outside of ±30% of the expected value or could not be assessed because the FMS (target analyte) was spiked at an inappropriate level, the sample result is reported as follows:

1.) If target analyte FMS recovery could not be assessed because the FMS's were at an inappropriate level, then Laboratory Matrix Spikes (LMS) may be substituted. If LMS recoveries are within ±30% the data are reportable and flagged to indicate that the FMS spikes levels were inappropriate.

2.) If multiple target analyte FMS's were prepared on a sample and the closest FMS level to the reported sample meets the ±30% acceptance criteria but additional FMS's are outside the ±30% acceptance range, the data are reportable and flagged to indicate that while there were failing FMS's, the uncertainty will not be expanded since the most appropriate spike level passed.

3.) If the target analyte FMS recoveries are outside of the ±30% acceptance range but at least 30 acceptable historical reportable FMS sample results are available, the data may be reported but flagged with an expanded uncertainty and as not meeting FMS criteria.

4.) Sample data with FMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria with an expanded uncertainty.

5.) If FMS recovery is outside of ±50%, the sample result is reported as NR, where NR is defined as "Not Reportable" due to noncompliant QC results.

The targeted fortification levels should be at least 50% of the endogenous level and less than 10 times the endogenous level to be used without justification to determine the statement of accuracy for analytical results.

Note: It is possible for bottles utilized for Field Matrix Spike samples to be under-filled or over-filled during sample collection. Since this scenario will effect the actual concentration of the FMS sample (surrogate and internal standard concentrations will also be effected, if used), it is important that any obvious under-filling or over-filling of sample bottles be documented in the data package and taken into account in the FMS, ISs, or SRSs recovery calculations. Samples over-filled or under-filled by more than 10% will be require recalculation of the FMS, ISs, and SRS true values.

The average of the sample and the field duplicate should be used to calculate the recovery.

10 Procedures

10.1 Water Sample Preparation

This method is applicable to water samples. Samples containing heavy particulate may not be suitable for analysis by this method. Samples containing suspended particulate should be centrifuge prior to removing a sample aliquot, or filtered.

- Thoroughly mix sample before removing an aliquot and placing in a labeled autovial.
- Dilute sample, if necessary, with ASTM Type I water, HPLC water, other suitable water, or solvent (methanol).
- Lab control spikes are prepared for each analysis batch to determine method accuracy and precision. LCSs should be prepared at three levels in triplicate for each target analyte and at a minimum of two levels in triplicate for appropriate SRSs. Low lab control spikes should be prepared at a concentration in the range of approximately four to ten times higher than the targeted lower LOQ, the mid lab control spikes should be prepared at a concentration near the mid-point of the calibration curve and the high lab control spikes at approximately 80% of the upper LOQ. For IS quantitation, stable isotope internal standards of each target analyte or appropriate surrogate ISs should be spiked at the same level as the samples being analyzed, in all LCSs.
- If LCSs are being prepared using synthetic groundwater, allow the LCSs samples to equilibrate for a minimum of 4 hours before aliquoting for analysis or diluting with solvent (methanol).

11 Sample Analysis - LC/MS/MS

11.1 Instrument Setup

Note: In this example, an Applied Biosystems Sciex API 4000 (API 5000 or API 5500) Tandem Mass Spectrometer (LC/MS/MS) is used. Other brands/models of LC/MS/MS instruments as well as single quadrupole mass spectrometers (LC/MS) may be used as long as the method acceptance 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: Applied Biosystems API 4000, API 5000, or API 5500

Ion Source: Turbo Ion Spray (ABS)

Mode: Electrospray Negative

Scan Type: MRM (Multiple Reaction Monitoring)

Computer: Dell DHM

Software: Windows 2000 or Windows XP, Analyst 1.4.2 or higher versions

HPLC: Agilent Series 1100,1200, or 1290

Agilent Quaternary Pump

Agilent Vacuum Degasser

Agilent Autosampler

Agilent Column Oven

Note: One or more C18 HPLC analytical columns (2.1 mm x 100 mm, 5µm or 2.1 mm x 50 mm, 5µm) may be attached on-line after the purge valve and before the sample injection port to retard and separate any residue contaminants that may be in the mobile phase and/or HPLC system.

HPLC Column: Betasil C18, 4.6mm x 100mm, 5µm (ThermoElectron Corporation)

Column Temperature: 35°C

Injection Volume: 5µL

Mobile Phase (A): 2mM Ammonium Acetate in ASTM Type I water (See 7.3)

Mobile Phase (B): Methanol

Table 3. Liquid Chromatography Gradient Program.

Step Number	*Total Time (min)*	*Flow Rate (µL/min)*	*Percent A (2 mM ammonium acetate)*	*Percent B (Methanol)*
0	0	750	97.0	3.0
1	2.0	750	97.0	3.0
2	14.5	750	5.0	95.0
3	15.5	750	5.0	95.0
4	16.5	750	97.0	3.0
5	20.0	750	97.0	3.0

Note: Other HPLC gradients may be used as long as the method criteria and project data quality objectives 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.

Table 4 Suggested MRM Transitions for Target Analytes, Surrogates, and Internal Standards

Analyte	*Analyte Description*	*Mass Transition Q1 (amu)*	*Mass Transition Q3 (amu)*
PFBA (C4 Acid)	Target	213	169
PFPeA (C5 Acid)	Target	263	219
PFHxA (C6 Acid)	Target	313	269, 119
PFHpA (C7 Acid)	Target	363	319, 169
PFOA (C8 Acid)	Target	413	369, 219, 169
PFNA (C9 Acid)	Target	463	419, 169, 219
PFDA (C10 Acid)	Target	513	469, 269, 219
PFUnA (C11 Acid)	Target	563	519, 269, 219
PFDoA (C12 Acid)	Target	613	569, 169, 319
PFTA (C13 Acid)	Target	663	619, 369, 319
FBSA (C4 Sulfonamide)	Target	298	78
FOSA (C8 Sulfonamide)	Target	498	78
PFBS (C4 Sulfonate)	Target	299	99, 80
PFHS (C6 Sulfonate)	Target	399	99, 80
PFOS (C8 Sulfonate)	Target	499	80, 99, 130
[1,2,3,4 -$^{13}C_4$]PFBA	IS for PFBA	217	172
[1,2,3,4,5 -$^{13}C_5$]PFPeA	IS for PFPeA	268	223
[1,2 -$^{13}C_2$]PFHxA	IS for PFHxA	315	270
[1,2,3,4- $^{13}C_4$]PFHpA	IS for PFHpA	367	322
[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA	IS for PFOA	421	376
[1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA	IS for PFNA	472	427
[1,2,3,4,5,6 -$^{13}C_6$]PFDA	IS for PFDA	519	474
[1,2,3,4,5,6,7 -$^{13}C_7$]PFUnA	IS for PFUnA	570	525
[1,2 -$^{13}C_2$]PFDoA	IS for PFDoA and PFTA	615	570
[$^{18}O_2$]PFBS	IS for PFBS	303	84
[1,2,3-$^{13}C_3$]PFHS	IS for PFHS	402	80
[1,2,3,4- $^{13}C_4$]PFOS	IS for PFOS	503	80
[1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA	IS for FOSA	507	80
[1,2,3,4-$^{13}C_4$]PFOA	Surrogate (C4-C8 Acids)	417	372
[1,2,3,4- $^{13}C_4$]PFOS	Surrogate(Sulfonates, FOSA)	503	80
[1,2 -$^{13}C_2$]PFUnA	Surrogate (C9-C13 Acids)	565	520

Multiple transitions for monitoring the analytes is an option. The use of one daughter ion is acceptable if data sensitivity and selectivity is achieved and provided that retention time criteria are met to assure adequate specificity. While the daughter ions may be chosen at the discretion of the analyst, mass transition 99 is suggested for PFOS. Quantitation may be performed using the total ion chromatogram (TIC, or summed MRMs) for a given analyte. For example, the PFOA TIC would sum all three of the monitored transitions. 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 and the gradient, column, guard column(s) used 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.

11.2 Calibration Curve

Quantitation is by internal standard or external standard calibration. Calibration standards may be prepared in ASTM Type I, HPLC water, other suitable water, or a solvent/water mixture. If internal standard calibration does not meet calibration acceptance criteria, external calibration can be applied. See Table 1 for

Table 4 Suggested MRM Transitions for Target Analytes, Surrogates, and Internal Standards

Analyte	*Analyte Description*	*Mass Transition Q1 (amu)*	*Mass Transition Q3 (amu)*
PFBA (C4 Acid)	Target	213	169
PFPeA (C5 Acid)	Target	263	219
PFHxA (C6 Acid)	Target	313	269, 119
PFHpA (C7 Acid)	Target	363	319, 169
PFOA (C8 Acid)	Target	413	369, 219, 169
PFNA (C9 Acid)	Target	463	419, 169, 219
PFDA (C10 Acid)	Target	513	469, 269, 219
PFUnA (C11 Acid)	Target	563	519, 269, 219
PFDoA (C12 Acid)	Target	613	569, 169, 319
PFTA (C13 Acid)	Target	663	619, 369, 319
FBSA (C4 Sulfonamide)	Target	298	78
FOSA (C8 Sulfonamide)	Target	498	78
PFBS (C4 Sulfonate)	Target	299	99, 80
PFHS (C6 Sulfonate)	Target	399	99, 80
PFOS (C8 Sulfonate)	Target	499	80, 99, 130
[1,2,3,4 -$^{13}C_4$]PFBA	IS for PFBA	217	172
[1,2,3,4,5 -$^{13}C_5$]PFPeA	IS for PFPeA	268	223
[1,2 -$^{13}C_2$]PFHxA	IS for PFHxA	315	270
[1,2,3,4- $^{13}C_4$]PFHpA	IS for PFHpA	367	322
[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA	IS for PFOA	421	376
[1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA	IS for PFNA	472	427
[1,2,3,4,5,6 -$^{13}C_6$]PFDA	IS for PFDA	519	474
[1,2,3,4,5,6,7 -$^{13}C_7$]PFUnA	IS for PFUnA	570	525
[1,2 -$^{13}C_2$]PFDoA	IS for PFDoA and PFTA	615	570
[$^{18}O_2$]PFBS	IS for PFBS	303	84
[1,2,3-$^{13}C_3$]PFHS	IS for PFHS	402	80
[1,2,3,4- $^{13}C_4$]PFOS	IS for PFOS	503	80
[1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA	IS for FOSA	507	80
[1,2,3,4-$^{13}C_4$]PFOA	Surrogate (C4-C8 Acids)	417	372
[1,2,3,4- $^{13}C_4$]PFOS	Surrogate(Sulfonates, FOSA)	503	80
[1,2 -$^{13}C_2$]PFUnA	Surrogate (C9-C13 Acids)	565	520

Multiple transitions for monitoring the analytes is an option. The use of one daughter ion is acceptable if data sensitivity and selectivity is achieved and provided that retention time criteria are met to assure adequate specificity. While the daughter ions may be chosen at the discretion of the analyst, mass transition 99 is suggested for PFOS. Quantitation may be performed using the total ion chromatogram (TIC, or summed MRMs) for a given analyte. For example, the PFOA TIC would sum all three of the monitored transitions. 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 and the gradient, column, guard column(s) used 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.

11.2 Calibration Curve

Quantitation is by internal standard or external standard calibration. Calibration standards may be prepared in ASTM Type I, HPLC water, other suitable water, or a solvent/water mixture. If internal standard calibration does not meet calibration acceptance criteria, external calibration can be applied. See Table 1 for

recommended application of available internal standards. Quantitation of PFOA and PFOS is by summed analyte-specific mass transitions.

Analyze the standard curve prior to each set of samples. If internal standards were added to the calibration standards area ratios are used to generate the calibration curve. The standard curve may be plotted using a linear regression ($y = mx + b$), weighted 1/x or unweighted, or by quadratic fit ($y = ax^2 + bx + c$), weighted 1/x or unweighted, using suitable software. 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.

High and/or low points may be excluded from the calibration curves to provide a better fit over the 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 (or area ratio if quantitating by IS) are not at least twice that of the average area counts (or area ratio if quantitating by IS) of method and/or solvent blanks. The coefficient of determination (r^2) value for the calibration curve must be greater than or equal to 0.990 (or a correlation coefficient (r) of 0.995). Each point in the curve must be within ±25% of the theoretical concentration with the exception of the LLOQ, which may be within ±30%. 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.

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

11.3 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. Samples must be bracketed by passing CCVs or the calibration curve and a passing CCV to be reportable.

11.4 System Suitability

A minimum of three system suitability samples should be injected at the beginning of each analytical run, prior to the analysis of the calibration curve. Typically these samples are at a concentration near the mid-level of the calibration curve and are repeated injections from one autosampler vial. It is suggested that the system suitability injections have area counts or area ratios when using internal standard calibration, with a target RSD of ≤5% and a target retention time RSD of ≤2%. There is no defined acceptability limit on these results as the %RSD value is dependent on the number of MRM transitions being monitored in the LC/MS/MS run or time period. Ultimately, any effects on these parameters for the System Suitability samples will also be evident on all standards and QC samples analyzed as part of the analysis batch. Any effect of system suitability is incorporated within QC acceptance criteria.[4]

11.5 Sample Analysis and QCs

For each analysis batch, the instrument analysis run sequence should include an initial calibration curve, samples, FDSs, interspersed blanks, interspersed CCVs, appropriate QCs (i.e., LCSs, LMSs, FMSs, TBMSs, and TBs), and a final CCV or calibration curve bracketing samples and appropriate QCs

Inject the same volume (between 5 - 100µL) of each standard, analytical sample and blank into the instrument (unless an on-instrument sample dilution is desired).

Samples containing analytes that are quantitated above the concentration of the highest standard in the curve should be further diluted and reanalyzed.

[4] 3M Environmental Laboratory study E08-0096 evaluated the effect on these results as a function of the number of MRMs being monitored.

12 Data Analysis and Calculations

The chromatography analysis software will typically calculate the amount of target analyte in the sample extracts using the established calibration curve.

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

$$\text{LCS\% recovery} = \frac{\text{LCS Concentration } (\frac{ng}{mL})}{\text{Spike Concentration } (\frac{ng}{mL})} * 100\%$$

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

$$\text{LMS \% recovery} = \frac{\text{LMS Concentration } (\frac{ng}{mL}) - \text{Concentration of Sample } (\frac{ng}{mL})}{\text{Spike Concentration } (\frac{ng}{mL})} * 100\%$$

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

$$\text{Recovery} = \frac{\text{Total analyte found (ng/mL) - Average analyte found in sample (ng/mL)}}{\text{Analyte added (ng/mL)}} \times 100$$

13 Analysis Batch Method Performance Criteria

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 the final report if the Technical Manager (non-GLP study) or Study Director (GLP study) chooses to report 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 appropriate. 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 – Analysis Batch

A minimum of three system suitability samples should be injected at the beginning of each analytical run. These samples are run prior to the calibration curve. It is suggested that the system suitability injections have area counts with a target RSD of ≤5% and a target retention time RSD of ≤2%. There is no defined acceptability limit on these results as the %RSDs are dependent on the number of MRM transitions being monitored in the LC/MS/MS run or time period. Any effect of system suitability is incorporated in the QC acceptance criteria.

13.2 Calibration and Limit of Quantitation (LOQ) – Analysis Batch

Calibration Curve: The coefficient of determination (r^2) value for the calibration curve must be greater than or equal to 0.990 corresponding to a correlation coefficient (r) = 0.995. Each point in the curve must be within ±25% of the theoretical concentration with the exception of the LLOQ, which may be within ±30%.

CCV Performance: The calibration standards that are interspersed throughout the analytical sequence are evaluated as continuing calibration verifications in addition to being part of the calibration curve. The accuracy

of each curve point must be within 25% of the theoretical value (within 30% for lowest curve point). Samples that are bracketed by CCVs not meeting these criteria must be reanalyzed.

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 average area counts for all prepared procedural blank(s). By definition, the measured value of the LLOQ must be within 30% of the theoretical value.

Demonstration of Specificity: Specificity is demonstrated by chromatographic retention time (within 4% of standard) and the mass spectral response of unique ions.

13.3 Blanks – Method/Procedural Blanks and Trip

Method/Procedural Blanks: Multiple procedural blanks should be interspersed throughout the analysis batch and the analytical sequence. At a minimum, method blanks are analyzed prior to instrument calibration, prior to the analysis of CCV samples, after every 10 sample injections, and at the end of the analytical run.

The mean area counts (or area ratios when using IS calibration) for each analyte must be less than 50% of the area count of the LOQ standard. If the area counts of the procedural blanks exceed 50% of the LOQ standard, then the LOQ must be raised to the first standard level that meets criteria.

Trip Blank: A trip blank of ASTM Type I water (or lab equivalent) is prepared in a sample container in the laboratory and treated as a sample, including exposure to shipping, sampling site conditions, storage, preservation and all analytical procedures. The trip blanks results for each analyte are included with the reported sample results.

13.4 Data Accuracy and Precision – Analysis Batch

Lab Control Spikes: The average recovery at each LCS level for each target analyte and appropriate SRS should be within 80-120% and the percent relative standard deviation of the recoveries must be less than or equal to 20%. If the average recovery of a spiking level falls outside method acceptance, but at least 67% (6 out of 9) of LCS samples are within 20% of their respective nominal value (33% of the QC samples, not all replicates at the same concentration, may be outside 20% of nominal value), the average recovery will be flagged as outside method acceptance criteria. All LCS samples will be control charted as per ETS-12-012. If the average recovery of one of the spiking levels exceeded the analytical method uncertainty as determined by ETS-12-012, that analytical batch uncertainty will be expanded for that particular study. The average recovery at each LCS level for mixed branched/linear isomer PFOA and PFOS should be within 70-130% and the percent relative standard deviation of the recoveries must be less than or equal to 20%.

Field Duplicates: The relative percent difference (RPD) of duplicate samples should be less than 20% for the precision of sample preparation and analysis to be considered in control. Replicate samples not meeting the 20% RPD criteria are flagged and reported as outside of QC acceptance criteria.

Field Matrix Spikes: FMS acceptance criteria are recoveries within ±30% of the expected value for each target analyte and appropriate SRS. Sample data with FMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria. Data with FMS recovery outside of ±50% of the expected value are reported as NR, where NR is defined as "Not Reportable" data outside of QC acceptance criteria. If FMS recovery could not be assessed because FMSs were at an inappropriate level, then Laboratory Matrix Spikes (LMSs) may be substituted. If LMS recoveries are within ±30% for each target analyte and SRSs the data are reportable but flagged as not meeting the FMS method acceptance criteria.

13.5 Analytical Method Uncertainty

Analytical method uncertainty for each target analyte and SRS is determined with control charted historical analysis batch LCS data for the method and reported with each analysis batch.[5] Uncertainty determinations

[5] Method uncertainty based on INTERNATIONAL ANS/ISO/IED STANDARD 17025 reference (GUM, Guide to the Expression of Uncertainty in Measurement). Method application demonstrated in ETS-12-012, citing references: a.) EURACHEM/CITAC Guide, "Quantifying Uncertainty in Analytical Measurement," Second Edition; Editors: S.L.R. Ellison, M. Rosslein, and A. Williams. b.)Georgian, Thomas, "Estimation of Laboratory Analytical Uncertainty Using Laboratory Control Samples," Environmental Testing &

are based on INTERNATIONAL ANS/ISO/IED STANDARD 17025 reference (GUM, Guide to the Expression of Uncertainty in Measurement) and described in ETS-12-012. At least thirty data points are required for determining analytical method uncertainty. The method uncertainty is defined as 2x the standard deviation of the percent recoveries of the pooled lab control spikes. While all LCS data points are control charted, only the most recent fifty data points are used for determining the method uncertainty.

When less than thirty LCS data points have been generated for a given analyte, the analysis batch LCSs are used to determine the data uncertainty. If FMSs meet the ±30% recovery criteria at a level appropriate to the endogenous level, and the LCS meet the ±20% recovery criteria, then the uncertainty of the data is determined as within 100±20%.

Analysis batch sample data with FMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria with expanded uncertainties. Data with FMS recovery outside of ±50% of the expected value are reported as NR, where NR is defined as "Not Reportable" data outside of QC acceptance criteria. If FMS recovery could not be assessed because FMSs were at an inappropriate level, then Laboratory Matrix Spikes (LMSs) may be substituted. If LMS recoveries are within ±30% for each target analyte and appropriate SRSs the data are reportable but flagged as not meeting the FMS method acceptance criteria with uncertainties of ±30%. If FMS do not meet the ±30% recovery criteria, and historical FMS data does not exist, the analytical uncertainty is evaluated on a sample-by-sample basis, the data may be reported with expanded uncertainty and are flagged.

13.6 Quantitation of PFOA/PFOS – Analysis Batch

Calibration standards consisting of mixed branched and linear isomer PFOS/PFOA are preferred. Quantitation is performed by integrating the linear and branched isomers together. Alternately, the linear and branched isomers can be integrated separately, applying the appropriate true value to each calibration curve point for each isomer. The LCS and samples are then quantitated by integrating the linear and branched isomers separately (requires separate analytical results files) and quantitating the resulting peak against the linear or branched calibration curve. The results from both integrations are then summed to produce the final result. Integrating the linear and branched isomers separately may be helpful for those samples where the linear/branched ratios do not closely match those of the reference standards.

However, for PFOS/PFOA target analytes, if the calibration standards are comprised of predominantly linear isomers only the method requires the addition of LCSs of mixed branched/linear isomer PFOS/PFOA. The purpose of including these LCSs is to demonstrate quantitative equivalency (or quantitative bias) of the isomeric mix when using a predominantly linear PFOS or PFOA standard for calibration. Alternatively, in lieu of mixed branched and linear isomer PFOS/PFOA LCSs, mixed branched and linear isomer PFOS/PFOA TBMSs may be applied to demonstrate method accuracy and precision.

An alternate method of quantitation can be performed whereby only the linear isomer of PFOS/PFOA is integrated and used for generating the calibration curve. The LCS and samples are then quantitated by integrating the linear and branched isomers separately (requires separate analytical results files) and quantitating the resulting peak against the linear calibration curve. The results from both integrations are then summed to produce the final result. Integrating the linear and branched isomers separately reduces the on-column concentration for those samples that contain both linear and branched isomers of PFOA/PFOS. This ensures that the concentration detected is within the a range of the calibration curve that is comparable regardless of whether the calibration curve was generated using predominantly linear isomers of PFOS/PFOA or linear plus branched isomers of PFOS/PFOA.

14 Pollution Prevention and Waste Management

Waste generated when performing this method will be disposed of appropriately. The original samples will be archived at the 3M Environmental Laboratory in accordance with internal procedures.

Analysis, November/December 2000. c.)Taylor, B.N. and CE. Kuyatt, NIST Technical Note 1297, 1994 Edition: "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results."d.)Adams, T.M., "A2LA Guide for the Estimation of Measurement Uncertainty in Testing", July 2002.

15 Records

Each data package generated for a study must include all supporting information for reconstruction of the data. Information for the data package must include, but is not limited to the following items: study or project number, sample and standard prep sheets/records, instrument run log (instrument batch records, instrument acquisition method, summary pages), instrument results files, chromatograms, calibration curves, and data calculations.

16 Affected Documents

None.

17 Revisions

Revision Number	Summary of Changes
1	*Section 1. Included the use of internal standard calibration by this method.* *Section 2. Included the use of internal standard calibration by this method. Included the use of a solvent/water mixture when analyzing for PFUnA, PFDoA, PFTrDA, and FOSA.* *Section 3. Added definitions for internal standard, surrogate internal standard, and surrogate recovery standard.* *Section 6.Removed the details regarding the instrument parameters to section 10 of the method.* *Section 7. Updated reference standards to include internal standards and surrogates. Changed concentration levels for working standards and included the use of internal standards and surrogates.* *Section 8. Inserted a new section on sample bottle preparation.* *Section 9 Quality Control. This section was previously section 10 in ETS-8-044.0. Updated QC criteria to be consistent with method ETS-8-154.4.* *Section 10 Procedures. This section was previously section 8 (Sample Handling) in ETS-8-044.0. Added detail regarding the preparation of LCSs. Included the use of methanol as a dilution solvent.* *Section 11 Sample Analysis. This section was previously section 10 in ETS-8-044.0. Included the details regarding the instrument parameters.* *Section 12 Data Analysis and Calculations. This section was previously section 11 in ETS-8-044.0. Removed the equation for calculating the analytes concentration, indicating that this is done by the instrument software.* *Section 13 Method Performance. This section was previously section 12 in ETS-8-044.0. Updated QC criteria to be consistent with ETS-8-154.4. Added information on the determination of analytical method uncertainty and quantitation of PFOA/PFOS.* *Section 14 Pollution Prevention. This section was previously section 13 in ETS-8-044.0.* *Section 15 Records. This section was previously section 14 in ETS-8-044.0.* *Section 16 Affected Documents. This section was previously section 15 in ETS-8-044.0.* *Section 17 Revisions. This section was previously section 16 in ETS-8-044.0.*

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GLP10-01-02; Interim Report 26 - Analysis of PFBS, PFHS, and PFOS in Surface Water Samples Collected at Bert Jeffries Landfill in Decatur, AL in February 2012

Study Title

Analysis of Perfluorooctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane Sulfonate (PFBS) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program

Data Requirement

EPA TSCA Good Laboratory Practice Standards 40 CFR Part 792

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Interim Report Completion Date

Date of signing

Performing Laboratory

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Environmental Laboratory
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Project Identification

GLP10-01-02-26

Total Number of Pages

77

ACCREDITED

The testing reported herein meet the requirements of ANSI/ISO/IEC 17025:2005 "General Requirements for the Competence of Testing and Calibration Laboratories", in accordance with the A2LA Testing Certificate # 2052.01. Testing that complies with this International Standard also meets principles of ISO 9001:2000.

Testing Cert #2052.01

This page has been reserved for specific country requirements.

GLP COMPLIANCE STATEMENT

Report Title: Interim Report 26 - Analysis of PFBS, PFHS, and PFOS in Surface Water Samples Collected at Bert Jeffries Landfill in Decatur, AL in February 2012

Study: Analysis of Perfluorooctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane Sulfonate (PFBS) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program.

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

- These are environmental samples where there is no specific test substance, no specific test system and no dosing of a test system.
- The reference substances have not been characterized under the GLPs and the stability under storage conditions at the test site have not been determined under GLPs.

Gary Hohenstein 4/16/12

Gary Hohenstein, Sponsor Representative — Date

Jaisimha Kesari 4/19/12

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

QUALITY ASSURANCE STATEMENT

Report Title: Interim Report 26 - Analysis of PFBS, PFHS, and PFOS in Surface Water Samples Collected at Bert Jeffries Landfill in Decatur, AL in February 2012

Study: Analysis of Perfluorooctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane Sulfonate (PFBS) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program.

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

Inspection Dates	Phase	Date Reported to	
		Testing Facility Management	Study Director
4/2/12 – 4/3/12	Data and Report	4/9/12	4/6/12

Casey Hom 4-11-12

QAU Representative Date

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1 Study Information

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Kevin Eich, Analyst
Kelly Ukes, Analyst
Jonathan Steege, Analyst

Study Dates

Study Initiation: March 8, 2010
Interim 26 Experimental Termination: March 14, 2012
Interim Report Completion: Date of Interim Report Signing

Location of Archives

All original raw data and the analytical report have been archived at the 3M Environmental Laboratory according to 40 CFR Part 792. The test substance and analytical reference standard reserve samples are archived at the 3M Environmental Laboratory according to 40 CFR Part 792

2 Summary

The 3M Environmental Laboratory received surface water samples from four different locations located at Jeffries Landfill in Decatur, AL. A total of nineteen sample bottles were received at the 3M Environmental Laboratory for perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHS) and perfluorobutane sulfonate (PFBS), and included duplicate surface water samples and two field matrix spike (FMS) samples from each sampling location. A set of trip blank samples; single trip blank containing Milli-Q™ water and two trip blank spikes, were included with the sample bottles. All samples were logged into the laboratory information management system (LIMS) under project GLP10-01-02-26. The surface water samples and trip blanks were received from Weston personnel on March 2, 2012. All of the samples were prepared and analyzed for PFBS, PFHS, PFOS, and the surrogate recovery standard $^{13}C_4$-PFOS, following 3M Environmental Laboratory Method ETS-8-044.1.

The average measured PFBS, PFHS, and PFOS concentrations are summarized in **Table 1.** The trip blank sample was below the lower limit of quantitation (LLOQ) for all analytes, indicating adequate control of sample contamination during shipping and sample collections. The analytical method uncertainties associated with the reported results are: PFBS ± 22%, PFHS ± 19% and PFOS ± 15%.

Table 1. Summarized PFBS, PFHS, and PFOS Results (Jeffries Landfill Site, Feb 2012).

3M LIMS ID	Sample Description	PFBS Concentration (ng/mL)	PFHS Concentration (ng/mL)	PFOS Concentration (ng/mL)
GLP10-01-02-026-005	JPAL-SW-ET01-0-120228	0.0345	<0.0250	0.0302
GLP10-01-02-026-006	JPAL-SW-ET01-DB-120228	0.0362	<0.0250	0.0302
	Average	**0.0354**	**<0.0250**	**0.0302**
	%RPD Sample/Sample Dup	**4.8**	**NA**	**0.0**
GLP10-01-02-026-009	JPAL-SW-ET02-0-120228	<0.0250	<0.0250	0.0661
GLP10-01-02-026-010	JPAL-SW-ET02-DB-120228	<0.0250	<0.0250	0.0593
	Average	**<0.0250**	**<0.0250**	**0.0627**
	%RPD Sample/Sample Dup	**NA**	**NA**	**11**
GLP10-01-02-026-013	JPAL-SW-ET03-0-120228	<0.0250	<0.0250	0.303
GLP10-01-02-026-014	JPAL-SW-ET03-DB-120228	<0.0250	0.0252	0.303
	Average	**<0.0250**	**0.0252**	**0.303**
	%RPD Sample/Sample Dup	**NA**	**NA (1)**	**0.0**
GLP10-01-02-026-017	JPAL-SW-ET04-0-120228	<0.0250	<0.0250	0.166
GLP10-01-02-026-018	JPAL-SW-ET04-DB-120228	<0.0250	<0.0250	0.159
	Average	**<0.0250**	**<0.0250**	**0.163**
	%RPD Sample/Sample Dup	**NA**	**NA**	**4.3**
GLP10-01-02-026-025	JPAL-SW-TRIP1-0-120228	**<0.0250**	**<0.0250**	**<0.0232**

NA = Not Applicable

The analytical method uncertainties associated with the reported results are: PFBS ± 22%, PFHS ± 19 %, and PFOS ± 15%.

(1) A sample/sample duplicate RPD could not be determined since the concentration for the primary sample was BLOQ for PFHS.

3 Introduction

This analytical study was conducted as part of the Phase 3 Environmental Monitoring and Assessment Program for the 3M facility located in Decatur, Alabama. The objective of the overall program is to gain information regarding concentrations of perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHS) and perfluorobutane sulfonate (PFBS), in various environmental media such as groundwater, soils and sediments that are associated with and near the Decatur facility. This analytical study was conducted to analyze surface water samples collected from four locations at or near Jeffries Landfill in Decatur, AL for PFBS, PFHS, and PFOS in an effort to characterize surface water conditions.

The 3M Environmental Laboratory prepared sample containers (250 mL high-density polyethylene bottles) which were shipped to Decatur, AL Weston personnel prior to field sampling. Sample containers for each sampling location included a field sample, field sample duplicate, and two field matrix spike samples. Each empty container was marked with a "fill to here" line to produce a final sample volume of 200 mL. Containers designated for field matrix samples were fortified with an appropriate matrix spike solution containing PFBS (linear isomer), PFHS (linear isomer), and PFOS (linear and branched isomers) prior to being sent to the field for sample collection. All sample bottles included the addition of $^{18}O_2$-PFBS, $^{13}C_3$-PFHS, and $^{13}C_8$-PFOS (internal standard) at a nominal concentration of 1 ng/mL. All sample bottles also included the addition of $^{13}C_4$-PFOS (surrogate recovery standard) at a nominal concentration of 0.1 ng/mL. See section 8.8 of the report for field matrix spike levels.

Samples were prepared and analyzed according to the procedure defined in 3M Environmental Laboratory method ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds In Water by LC/MS/MS; Direct Injection Analysis". The use of internal standards was used to aid in the data quality objectives.

Table 1 summarizes the average PFBS, PFHS, and PFOS concentrations for the duplicate surface water samples collected and the trip blank sample. **Tables 10-14** summarize the individual sample results and the associated field matrix spike recoveries. All results for the quality control samples prepared and analyzed with the samples are reported and discussed elsewhere in this report

4 Test & Control Substances

There was not a test substance or control substances in the classic sense of a GLP study. This study was purely analytical in nature.

5 Reference Substances

Reference Substance	PFBS (predominantly linear)	$^{18}O_2$-PFBS
Chemical Name	Potassium Perfluorobutane sulfonate	[$^{18}O_2$]-Ammonium Perfluorobutanesulfonate
Chemical Formula	$C_4F_9SO_3^-K^+$	$C_4F_9S[^{18}O_2]O\text{-}NH_4^+$
Identifier	NA	NA
Use	Target Analyte Reference Standard	Internal Standard
Source	3M	RTI International
Expiration Date	01/10/2017	03/09/2015
Storage Conditions	Frozen	Frozen
Chemical Lot Number	41-2600-8442-5	11546-107-2
TCR Number	TCR-121	TCR-1044, TCR-1040
Physical Description	White Powder	Liquid
Purity	96.7%	>99%

Reference Substance	PFHS (Linear)	$^{13}C_3$-PFHS	$^{13}C_3$-PFHS
Chemical Name	Sodium Perfluorohexane sulfonate	Sodium Perfluorohexanesulfonate	Sodium Perfluorohexanesulfonate
Chemical Formula	$C_6F_{13}SO_3^-Na^+$	$^{13}C_3{}^{12}C_3F_{13}SO_3^-Na^+$	$^{13}C_3{}^{12}C_3F_{13}SO_3^-Na^+$
Identifier	L-PFHXS	MPFC-C-0511	MPFC-C-0112
Use	Target Analyte Reference Standard	Internal Standard	Internal Standard
Source	Wellington	Wellington	Wellington
Expiration Date	03/25/2018	05/25/2014	01/24/2015
Storage Conditions	Frozen	Frozen	Frozen
Chemical Lot Number	LPFHxSAM08	MPFC-C-0511	MPFC-C-0112
TCR Number	TCR08-0018	TCR11-0016	TCR12-0004
Physical Description	Crystalline	Liquid	Liquid
Purity	100%	5 µg/mL (1)	5 µg/mL (1)

(1) Custom mixture of seven mass-labeled (^{13}C) perfluoroalkylcarboxylic acids, two mass labeled (^{13}C) perfluoroalkylsulfonates and one mass-labeled (^{13}C) perfluoro-1-octanesulfonamide.

Reference Substance	PFOS (Linear + Branched)	$^{13}C_4$-PFOS	$^{13}C_8$-PFOS	$^{13}C_8$-PFOS
Chemical Name	Potassium Perfluorooctane sulfonate	Sodium Perfluorooctane sulfonate	Sodium Perfluorooctane sulfonate	Sodium Perfluorooctane sulfonate
Chemical Formula	$C_8F_{17}SO_3^-K^+$	$^{13}C_4{}^{12}C_4F_{17}SO_3^-Na^+$	$^{13}C_8F_{17}SO_3^-Na^+$	$^{13}C_8F_{17}SO_3^-Na^+$
Identifier	Br-PFOSK	MPFOS	MPFC-C-0511	MPFC-C-0112
Use	Target Analyte Reference Standard	Surrogate	Internal Standard	Internal Standard
Source	Wellington	Wellington	Wellington	Wellington
Expiration Date	03/17/2014; 12/01/2014	09/08/2013	05/25/2014	01/24/2015
Storage Conditions	Frozen	Frozen	Frozen	Frozen
Chemical Lot Number	brPFOSK0708; brPFOSK1111	MPFOS0910	MPFC-C-0511	MPFC-C-0112
TCR Number	TCR11-0010; TCR11-0041	TCR10-0044-7/9	TCR11-0016	TCR12-0004
Physical Description	Liquid	Liquid	Liquid	Liquid
Purity	99.9%	>98%	5 µg/mL (1)	5 µg/mL (1)

(1) Custom mixture of seven mass-labeled (^{13}C) perfluoroalkylcarboxylic acids, two mass labeled (^{13}C) perfluoroalkylsulfonates and one mass-labeled (^{13}C) perfluoro-1-octanesulfonamide.

6 *Test System*

The test systems for this study are surface water samples collected from wells located in Decatur, AL by Weston Solutions, Inc. personnel. Samples for this study are "real world" samples, not dosed with a specific lot of test substance.

Table 2. Sample Description Key Code.

String Number	String Descriptor	Example
Example	*JPAL-SW-ET01-0-120228*	
1	*Sample Location*	*JPAL= Jeffries Property, Alabama*
2	*Sample Type*	*SW = Surface Water*
3	*Well ID*	*Example: ET01* *ET = Eastern tributary to Mallard Creek*
4	*Sampling Date*	*120228– February 28, 2012*
5	*Sample Type*	*0 = primary sample* *DB = duplicate sample* *LS = low spike* *HS = high spike*

7 *Method Summary*

7.1 Method

Analysis for all analytes was completed following 3M Environmental Laboratory method ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds In Water by High Performance Liquid Chromatography/Mass Spectrometry Direct Injection Analysis".

7.2 Sample Collection

Samples were collected in 250 mL Nalgene™ (high-density polyethylene) bottles prepared at the 3M Environmental Laboratory. Sample bottles associated with GLP10-01-02-26 were returned to the laboratory at ambient conditions on March 2, 2012. Samples were stored refrigerated at the laboratory after receipt. A set of laboratory prepared Trip Blank and Trip Blank field matrix spikes were sent with the sample collection bottles.

7.3 Sample Preparation

Samples were prepared by removing an aliquot of the well mixed sample and placing it in an autovial for analysis.

During the preparation of the laboratory control samples, an aliquot of a separate internal standard spiking solution was added to the laboratory control samples (nominal concentration of 1 ng/mL). The samples bottles were spiked with an internal standard mix at a nominal concentration of 1 ng/mL prior to being sent to the field for sample collection

7.4 Analysis

All study samples and quality control samples were analyzed for PFBS, PFHS, and PFOS using high performance liquid chromatography/ tandem mass spectrometry (HPLC/MS/MS). Detailed instrument parameters, the liquid chromatography gradient program, and the specific mass transitions analyzed are described in the raw data hard copies placed in the final data packet, and are briefly described below.

Table 3. Instrument Parameters.

Instrument Name	ETS Ginger	ETS McCoy
Analytical Method Followed	ETS-8-044.1	ETS-8-044.1
Analysis Date	3/7/12 – PFBS and PFHS	3/13/12 – PFOS
Liquid Chromatograph	Agilent 1100	Agilent 1290
Guard column	Betasil C18 (4.6 mm X 100 mm), 5µ	Betasil C18 (4.6 mm X 100 mm), 5µ
Analytical column	Betasil C18 (4.6 mm X 100 mm), 5µ	Betasil C18 (4.6 mm X 100 mm), 5µ
Injection Volume	25 µL	50 µL
Mass Spectrometer	Applied Biosystems API 5000	Applied Biosystems API 5500
Ion Source	Turbo Spray	Turbo Spray
Electrode	Turbo ion electrode	Turbo ion electrode
Polarity	Negative	Negative
Software	Analyst 1.4.2	Analyst 1.5.2

Table 4. Liquid Chromatography Conditions.

Step Number	Total Time (min)	Flow Rate (µL/min)	Percent A (2 mM ammonium acetate)	Percent B (methanol)
ETS-8-044.1 Analyzed 3/7/12				
0	0.0	750	97.0	3.0
1	2.0	750	97.0	3.0
2	14.5	750	5.0	95.0
3	15.5	750	5.0	95.0
4	16.5	750	97.0	3.0
5	20.0	750	97.0	3.0
Step Number	**Total Time (min)**	**Flow Rate (µL/min)**	**Percent A (5 mM ammonium acetate: 0.01% acetic acid)**	**Percent B (acetonitrile)**
ETS-8-044.1 Analyzed 3/13/12				
0	0.0	750	97.0	3.0
1	2.0	750	97.0	3.0
2	14.5	750	5.0	95.0
3	15.5	750	5.0	95.0
4	16.5	750	97.0	3.0
5	20.0	750	97.0	3.0

Table 5. Mass Transitions.

Analyte	Mass Transition Q1/Q3	Reference Material Structure	Internal Standard	Mass Transition Q1/Q3
PFBS	299/80	Linear	[$^{18}O_2$]-PFBS	303/84
	299/99			
PFHS	399/80	Linear	[$^{13}C_3$]-PFHS	402/80
	399/99			
PFOS	499/80	Linear + Branched	[$^{13}C_8$]-PFOS	507/80
	499/99			
	499/130			
[$^{13}C_4$]-PFOS	503/80	Linear	[$^{13}C_8$]-PFOS	507/80
Dwell time was 50 msec for each transition. The individual transitions were summed to produce a "total ion chromatogram" (TIC), which was used for quantitation.				

8 Analytical Results

8.1 Calibration

Samples were analyzed using a stable isotope internal standard calibration curve. Calibration standards were prepared by spiking known amounts of the stock solution containing the target analytes into a laboratory-prepared synthetic groundwater containing calcium and magnesium. A separate internal standard spiking solution was prepared and an aliquot was added at the same level to all calibration standards and laboratory control samples at a nominal concentration of 1 ng/mL. A calibration curve ranging from approximately 0.025 ng/mL to 100 ng/mL (0.025 ng/mL to 10 ng/mL for $^{13}C_4$-PFOS surrogate) was prepared. The reference standard used for the calibration standards for PFOS contained both linear and branched isomers.

A quadratic, 1/x weighted, calibration curve of the standard peak area/peak area ratios was used to fit the data for each analyte. The data were not forced through zero during the fitting process. Calculating the standard concentrations using the peak area/peak area ratios and the resultant calibration curve confirmed accuracy of each curve point.

Each curve point was quantitated using the overall calibration curve and reviewed for accuracy. Method calibration accuracy requirements of 100±25% (100±30% for the lowest curve point) were met for all analytes. The correlation coefficient (r) was greater than 0.995 for PFBS, PFHS, PFOS, and $^{13}C_4$-PFOS.

8.2 System Suitability

A calibration standard was analyzed four times at the beginning of each analytical sequence to demonstrate overall system suitability. The acceptance criteria of less than or equal to 5% relative standard deviation (RSD) for peak area and retention time criteria of less than or equal to 2% RSD was met for PFBS, PFHS, PFOS, and $^{13}C_4$-PFOS.

8.3 Limit of Quantitation (LOQ)

The LOQ for this analysis is the lowest non-zero calibration standard in the curve that meets linearity and accuracy requirements and for which the area counts or area ratio are at least twice those of the appropriate blanks. The LOQ for all analytes can be found in Table 6.

Table 6. Limit of Quantitation (LOQ).

PFBS *LOQ, ng/mL*	*PFHS* *LOQ, ng/mL*	*PFOS* *LOQ, ng/mL*
0.0250	0.0250	0.0232

8.4 Continuing Calibration

During the course of each analytical sequence, continuing calibration verification samples (CCVs) were analyzed to confirm that the instrument response and the initial calibration curve were still in control. All CCVs met method criteria of 100% ± 25% for PFBS, PFHS, PFOS, and $^{13}C_4$-PFOS.

8.5 Blanks

Two types of blanks were prepared and analyzed with the samples: procedural blanks and trip blanks. Procedural blank results were reviewed and used to evaluate method performance to determine the LOQ. Trip blanks reflect the shipping and sample collection conditons the sample bottles and samples experience.

8.6 Lab Control Spikes (LCSs)

Low, mid, and high lab control spikes were prepared for the target analytes and analyzed in triplicate, while only low and high lab control spikes were prepared for the $^{13}C_4$-PFOS surrogate. LCSs were prepared by spiking known amounts of the analyte into synthetic groundwater to produce the desired concentration. The spiked water samples were then prepared and analyzed in the same manner as the samples. The method acceptance criteria, average of LCS at each level should be within 100% ± 20% with an RSD ≤20%, was met for all analytes.

The following calculations were used to generate data in Table 7 for laboratory control spikes.

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

$$\text{LCS\% RSD} = \frac{\text{standard deviation LCS replicates}}{\text{average LCS recovery}} * 100\%$$

Table 7. Laboratory Control Spike Recovery.

ETS-8-044.1 Analyzed 3/7/12	PFBS			PFHS		
Lab ID	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery
LCS-120306-1	0.198	0.209	105	0.198	0.191	96.3
LCS-120306-2	0.198	0.209	106	0.198	0.182	91.8
LCS-120306-3	0.198	0.207	104	0.198	0.185	93.3
Average ± %RSD	**105% ± 0.95%**			**93.8% ± 2.4%**		
LCS-120306-4	1.98	2.17	110	1.98	2.08	105
LCS-120306-5	1.98	2.19	111	1.98	1.92	97.1
LCS-120306-6	1.98	2.09	106	1.98	1.94	98.0
Average ± %RSD	**109% ± 2.4%**			**100% ± 4.3%**		
LCS-120306-7	19.9	18.9	95.1	19.8	18.5	93.5
LCS-120306-8	19.9	18.1	91.1	19.8	18.1	91.3
LCS-120306-9	19.9	19.8	99.6	19.8	19.2	96.9
Average ± %RSD	**95.3% ± 4.5%**			**93.9% ± 3.0%**		

ETS-8-044.1 Analyzed 3/13/12	PFOS (Linear + Branched)			$^{13}C_4$-PFOS surrogate		
Lab ID	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery
LCS-120306-1	0.184	0.178	97.0	0.189	0.221	117
LCS-120306-2	0.184	0.170	92.6	0.189	0.215	114
LCS-120306-3	0.184	0.170	92.6	0.189	0.225	119
Average ± %RSD	**94.1% ± 2.7%**			**117% ± 2.2%**		
LCS-120306-4	1.84	1.76	95.6	1.89	2.21	117
LCS-120306-5	1.84	1.72	93.6	1.89	2.14	113
LCS-120306-6	1.84	1.71	92.9	1.89	2.14	113
Average ± %RSD	**94.0% ± 1.5%**			**114% ± 2.0%**		
LCS-120306-7	18.4	17.1	92.8	NA	NA	NA
LCS-120306-8	18.4	16.6	90.4	NA	NA	NA
LCS-120306-9	18.4	17.4	94.3	NA	NA	NA
Average ± %RSD	**92.5% ± 2.1%**			**NA**		

NA = Not Applicable

8.7 Analytical Method Uncertainty

Analytical uncertainty is based on historical QC data that is control charted and used to evaluate method accuracy and precision. The method uncertainty is calculated following ETS-12-012.2. The standard deviation is calculated for the set of accuracy results (in %) obtained for the QC samples. The expanded uncertainty is calculated by multiplying the standard deviation by a factor of 2, which corresponds to a confidence level of 95%.

Table 8. Analytical Uncertainty.

Analyte	Standard Deviation	Method Uncertainty
PFBS	10.8	±22%
PFHS	9.42	±19%
PFOS	7.60	±15%

8.8 Field Matrix Spikes (FMS)

Low, mid, and high field matrix spikes (FMS) were collected at each sampling point to verify that the analytical method is applicable to the collected matrix. Field matrix spikes were generated by adding a measured volume of field sample to a container spiked by the laboratory with PFBS (linear), PFHS (linear), and PFOS (linear+branched) prior to shipping sample containers for sample collection. Field matrix spike recoveries within method acceptance criteria of 100±30% confirm that "unknown" components in the sample matrix do not significantly interfere with the extraction and analysis of the analytes of interest. Field matrix spike concentrations must be 50% of the sample concentration to be considered an appropriate field spike. Field matrix spikes are presented in section 9 of this report.

Table 9. Field Matrix Spike Levels.

Sampling Location	Spike Level	PFBS, ng/mL	PFHS, ng/mL	PFOS, ng/mL
All locations and Trip Blank	Low	1.00	0.998	0.928
	High	10.0	9.98	9.28

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

9 *Data Summary and Discussion*

The tables below summarize the sample results and field matrix spike recoveries for the sampling locations as well as the Trip Blank. Results and average values are rounded to three significant figures according to EPA rounding rules. Because of rounding, values may vary slightly from those listed in the raw data. Field matrix spike recoveries meeting the method acceptance criteria of ± 30%, demonstrate that the method was appropriate for the given matrix and their respective quantitative ranges.

Table 10. JPAL SW ET01 120228

		PFBS		PFHS		PFOS		$^{13}C_4$ PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-26-005	JPAL-SW-ET01-0-120228	0.0345	NA	<0.0250	NA	0.0302	NA	109
GLP10-01-02-26-006	JPAL-SW-ET01-DB-120228	0.0362	NA	<0.0250	NA	0.0302	NA	102
GLP10-01-02-26-007	JPAL-SW-ET01-LS-120228	1.08	104	0.946	94.8	0.863	89.7	110
GLP10-01-02-26-008	JPAL-SW-ET01-HS-120228	10.4	104	8.62	86.4	8.38	90.0	110
Average Concentration (ng/mL) ± %RPD		0.0354 ng/mL ± 4.8%		<0.0250 ng/mL		0.0302 ng/mL ± 0.0%		108% ± 3.3%

NA = Not Applicable

Table 11. JPAL SW ET02 120228

		PFBS		PFHS		PFOS		$^{13}C_4$ PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-26-009	JPAL-SW-ET02-0-120228	<0.0250	NA	<0.0250	NA	0.0661	NA	107
GLP10-01-02-26-010	JPAL-SW-ET02-DB-120228	<0.0250	NA	<0.0250	NA	0.0593	NA	106
GLP10-01-02-26-011	JPAL-SW-ET02-LS-120228	1.08	108	1.030	103	0.924	92.8	109
GLP10-01-02-26-012	JPAL-SW-ET02-HS-120228	9.63	96.3	8.640	86.6	8.45	90.4	107
Average Concentration (ng/mL) ± %RPD		<0.0250 ng/mL		<0.0250 ng/mL		0.0627 ng/mL ± 11%		107% ± 1.2%

NA = Not Applicable

Table 12. JPAL SW ET03 120228

		PFBS		PFHS		PFOS		$^{13}C_4$ PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-26-013	JPAL-SW-ET03-0-120228	<0.0250	NA	<0.0250	NA	0.303	NA	109
GLP10-01-02-26-014	JPAL-SW-ET03-DB-120228	<0.0250	NA	0.0252	NA	0.303	NA	109
GLP10-01-02-26-015	JPAL-SW-ET03-LS-120228	1.05	105	0.992	96.9	1.13	89.1	103
GLP10-01-02-26-016	JPAL-SW-ET03-HS-120228	9.14	91.4	8.820	88.1	8.72	90.7	106
Average Concentration (ng/mL) ± %RPD		<0.0250 ng/mL		0.0252 ng/mL(1)		0.303 ng/mL ± 0.0%		107% ± 2.7%

NA = Not Applicable

(1) A sample/sample duplicate RPD could not be determined since the concentration of the primary sample was BLOQ for PFHS.

Table 13. JPAL SW ET04 120228

		PFBS		PFHS		PFOS		$^{13}C_4$ PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-26-017	JPAL-SW-ET04-0-120228	<0.0250	NA	<0.0250	NA	0.166	NA	113
GLP10-01-02-26-018	JPAL-SW-ET04-DB-120228	<0.0250	NA	<0.0250	NA	0.159	NA	109
GLP10-01-02-26-019	JPAL-SW-ET04-LS-120228	1.14	114	0.931	93.3	1.03	93.5	110
GLP10-01-02-26-020	JPAL-SW-ET04-HS-120228	10.6	106	8.45	84.7	8.47	89.5	105
Average Concentration (ng/mL) ± %RPD		<0.0250 ng/mL		<0.0250 ng/mL		0.163 ng/mL ± 4.3%		109% ± 3.2%

NA = Not Applicable

Table 14. Trip Blank 120228

		PFBS		PFHS		PFOS		$^{13}C_4$ PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-26-025	JPAL-SW-TRIP1-0-120228	<0.0250	NA	<0.0250	NA	<0.0232	NA	108
GLP10-01-02-26-026	JPAL-SW-TRIP1-LS-120228	1.06	106	0.947	94.9	0.809	87.2	109
GLP10-01-02-26-027	JPAL-SW-TRIP1-HS-120228	9.32	93.2	9.21	92.3	8.07	87.0	107

NA = Not Applicable

10 Conclusion

Laboratory control spikes and field matrix spikes were used to determine the analytical method accuracy and precision for PFBS, PFHS, and PFOS. Analysis was successfully completed following 3M Environmental Laboratory method ETS-8-044.1 described herein.

11 Data/Sample Retention

All remaining samples and associated project data (hardcopy and electronic) will be archived according to 3M Environmental Laboratory standard operating procedures.

12 Attachments

Attachment A: Protocol Amendment 26 (General Project Outline)
Attachment B: Representative Chromatograms and Calibration Curves
Attachment C: Analytical Method-ETS-8-044.1

13 Signatures

4/11/2012

Cleston Lange, Ph.D., 3M Principal Analytical Investigator — Date

13 APRIL 2012

William K. Reagen, Ph.D., 3M Environmental Laboratory Department Manager — Date

4/16/12

Gary Hohenstein, Sponsor Representative — Date

4/19/12

Jaisimha Kesari, Study Director — Date

ATTACHMENT A: PROTOCOL AMENDMENT

Analytical Protocol: GLP10-01-02
Amendment 26

Study Title

Analysis of Perfluorooctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane sulfonate (PFBS) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program

PROTOCOL AMENDMENT NO. 26

Amendment Date:
February 21, 2012

Performing Laboratory
3M Environmental, Health, and Safety Operations
3M Environmental Laboratory
Building 260-5N-17
Maplewood, MN 55144-1000

Laboratory Project Identification
GLP10-01-02-26

Sampling Event

Bert Jeffries Landfill –Surface Water Sampling

Analytical Protocol: GLP10-01-02
Amendment 26

This amendment modifies the following portion of protocol:

"Analysis of PFOS, PFHS and PFBS in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program"

PROTOCOL READS:

No changes to the wording of the protocol are required.

AMEND TO READ:

No changes to the wording of the protocol are required. This amendment only addresses and documents the addition of the General Project Outline (GPO) for the collection and analysis of groundwater samples from Decatur, AL, and conducted as part of the 3M Decatur Phase 3 Program for PFOS, PFHS and PFBS (GLP10-01-02). Sampling activities at and near the Bert Jeffries landfill are scheduled for the week of February 27, 2012 and will consist of 6 paired surface water and sediment samples. This protocol amendment addresses the sampling and analysis of the surface water samples. Surface water samples collected under this sampling event will be entered into the 3M Environmental Laboratory LIMS as project GLP10-01-02-26 and reported as interim report GLP10-01-02-26 (reflecting study GLP10-01-02 and amendment -26).

Reason:

The reason for this amendment is to document the General Project Outline (GPO) which describes the anticipated surface water sample collection event to be conducted at and near the Bert Jeffries landfill in Lawrence County, AL.

The GPO is three pages in length and included as attached to this amendment form.

Analytical Protocol: GLP10-01-02
Amendment 26

Amendment Approval

Gary Hohenstein, Sponsor Representative — Date: 2/29/12

Cleston C. Lange, Principal Analytical Investigator — Date: 2/21/2012

William Reagen, EMS Opns Environmental Lab Management — Date: 24 FEB 2012

Jaisimha Kesari P.E., DEE, Study Director — Date: 3/14/12

Analytical Protocol: GLP10-01-02
Amendment 26

3M Environmental Health & Safety Operations, Environmental Laboratory

General Project Outline

To: Gary Hohenstein, 3M EHS&Opns

From: Susan Wolf, 3M EHS&Opns; Environmental Lab

cc: William Reagen, 3M EHS&Opns; Environmental Lab

Jai Kesari, Weston Solutions

Charles Young, Weston Solutions

Date: February 21, 2012

Subject: Analysis of Perfluorooctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane sulfonate (PFBS) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program; GLP Interim Report 26 – Bert Jeffries Landfill; Surface Water sampling the week of February 27, 2012.

1 General Project Information

Contacts	**3M Sponsor Representative** Gary Hohenstein 3M EHS Operations 3M Building 224-5W-03 Saint Paul, MN 55144-1000 Phone: (651) 737-3570 gahohenstein@mmm.com **3M Environmental Laboratory Management** William K. Reagen 3M EHS Opns, Environmental Laboratory 260-5N-17 651 733-9739 wkreagen@mmm.com **Principal Analytical Investigator** Cleston Lange 3M EHS Opns, Environmental Laboratory 260-5N-17 651 733-9860 cclange@mmm.com **Sampling Coordinator** Timothy Frinak Weston Solutions Timothy.frinak@westonsolutions.com Phone: (334)-332-9123
Lab Request Number	GLP10-01-02-26
Six Digit Department Number	Dept #530711, Project #0022674449
Project Schedule/Test Dates	Tentatively scheduled for the week of February 27, 2012.

All verbal and written correspondence will be directed to Gary Hohenstein.

2 Background Information and Project Objective(s)

The 3M EHS Operations Laboratory (3M Environmental Lab) will receive and analyze surface water samples collected from six (6) locations at and near the Bert Jeffries landfill. Surface water samples will be collected by Weston. The 3M Environmental Laboratory will prepare the sample bottles. Samples will be analyzed for Perfluorooctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane Sulfonate (PFBS). Analyses will be conducted under the GLP requirements of EPA TSCA Good Laboratory Practice Standards 40 CFR 792.

The final report will be submitted to Gary Hohenstein and Jai Kesari upon completion under interim report GLP10-01-02-26.

3 Project Schedule

Sample collection bottles will be prepared by the 3M Environmental Laboratory. Sample bottles will be shipped in coolers overnight to 3M Decatur for arrival by Friday, February 24, 2012. Sample bottles should be stored refrigerated on-site until sample collection.

Martin Smith \ Weston Trailer
3M Decatur Plant
1400 State Docks Road
Decatur, Alabama 35601

4 Test Parameters

The targeted limit of quantitation will be **0.025 ng/mL** (ppb) for PFBS, PFHS, and PFOS.

A total of six sampling locations have been specified. For each sampling location, a total of four sample bottles will be collected (sample, sample duplicate, low-level field matrix spike, and high-level field matrix spike). The "fill to here" line on each 250 mL Nalgene bottle will be 200 mL. One set of trip blanks consisting of reagent-grade water, a low-level trip blank spike, and a high-level trip blank spike will be prepared at the 3M Environmental Laboratory and sent to the sampling location with the other bottles. No previous data on fluorochemicals in groundwater, surface water or sediment media exist for the site. The low field matrix spike will be prepared at 1 ng/mL and the high field matrix spike at 10 ng/mL.

All sample bottles will include the addition of $^{18}O_2$-PFBS, $^{13}C_3$-PFHS, and $^{13}C_8$-PFOS, (internal standards) at a nominal concentration of 1 ng/mL. All sample bottles will also include the addition of $^{13}C_4$-PFOS (surrogate recovery standard) at a nominal concentration of 0.1 ng/mL.

To aid in sample collection, a non-spiked 1-L sample bottle will be provided for each sampling location. Sample collection will consist of direct immersion. Aliquots will be decanted from the collection bottle to the primary, duplicate and matrix spike bottles. No rinseate blank will be collected.

Analytical Protocol: GLP10-01-02
Amendment 26

5 Test Methods

Samples will be prepared and analyzed by LC/MS/MS following ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds In Water by High Performance Liquid Chromatography/Mass Spectrometry Direct Injection Analysis". Alternately, samples may be analyzed by ETS 8-154.3 "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates In Water By Solid Phase Extraction and High Performance Liquid Chromatography/Mass Spectrometry".

Where applicable, samples will be analyzed against an internal standard calibration curve. Each curve point will contain isotopically-labeled PFBS, PFHS, and PFOS at a nominal concentration of 1 ng/mL. The calibration curve will be generated by taking the ratio of the standard peak area counts over the internal standard peak area counts to fit the data for each analyte.

Laboratory control samples prepared with the samples must have an average recovery within 100±20% and a RSD ≤20%. The data quality objective for this study is quantitative results for the target analytes with an analytical accuracy of 100±30%. Field matrix spikes not yielding recoveries within 100±30% will be addressed in the report and the final accuracy statement may be adjusted accordingly.

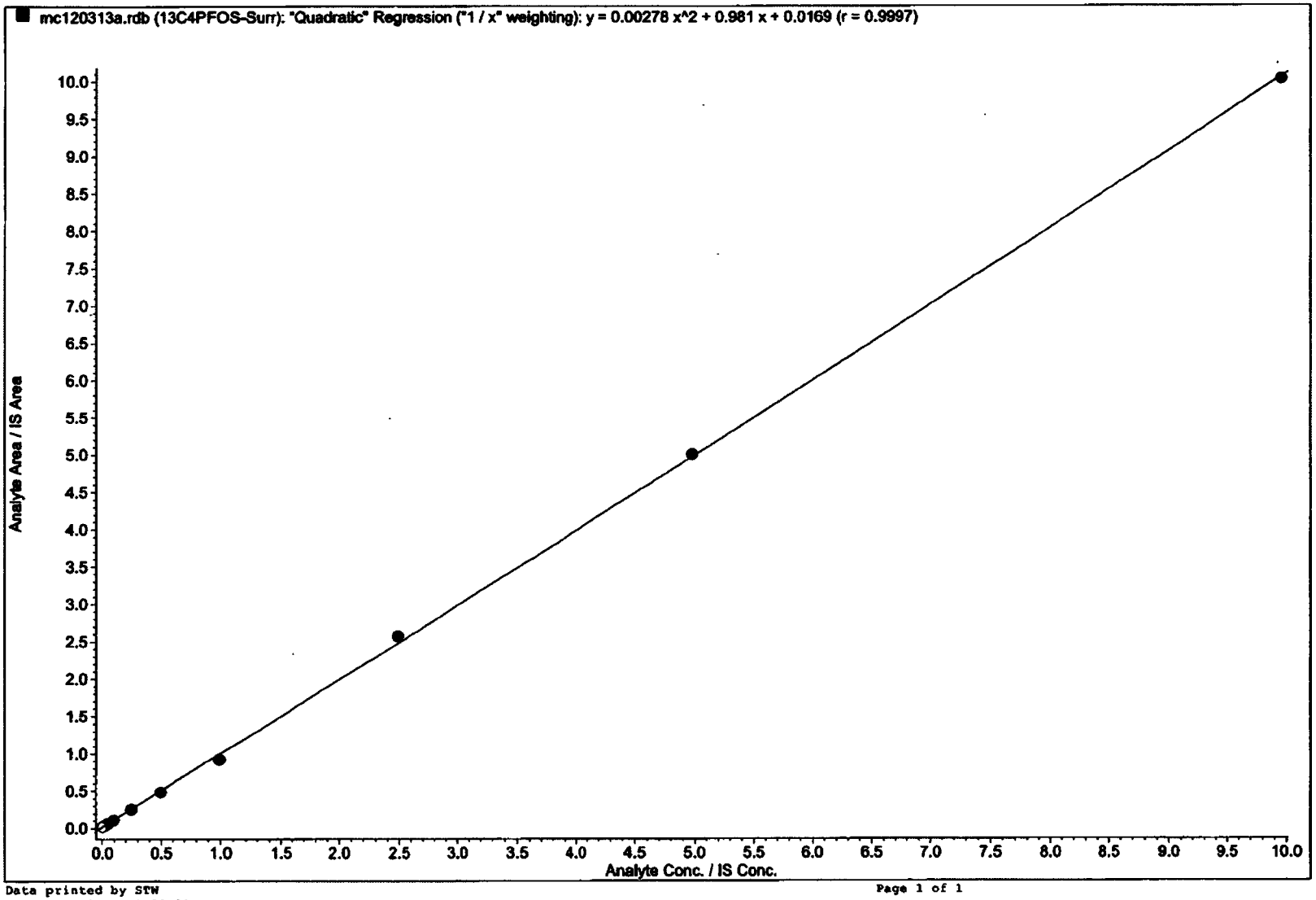
6 Reporting Requirements

For each sampling location, the report will contain the results for the sample, sample duplicate, and the two field matrix spikes. Trip blank and trip blank spikes will be reported for the sampling event. Laboratory control spikes of reagent water prepared at the time of sample extraction will also be reported and used to evaluate the overall method accuracy and precision. Method blanks of reagent water prepared at the time of sample extraction will be used to determine the method detection limit. For those sampling locations where the field matrix spike level was not appropriate due to higher than expected analyte concentrations, a target analyte laboratory matrix spike may be prepared and will be included in the final report.

ATTACHMENT B: REPRESENTATIVE SAMPLE CHROMATOGRAMS AND CALIBRATION CURVE(S)

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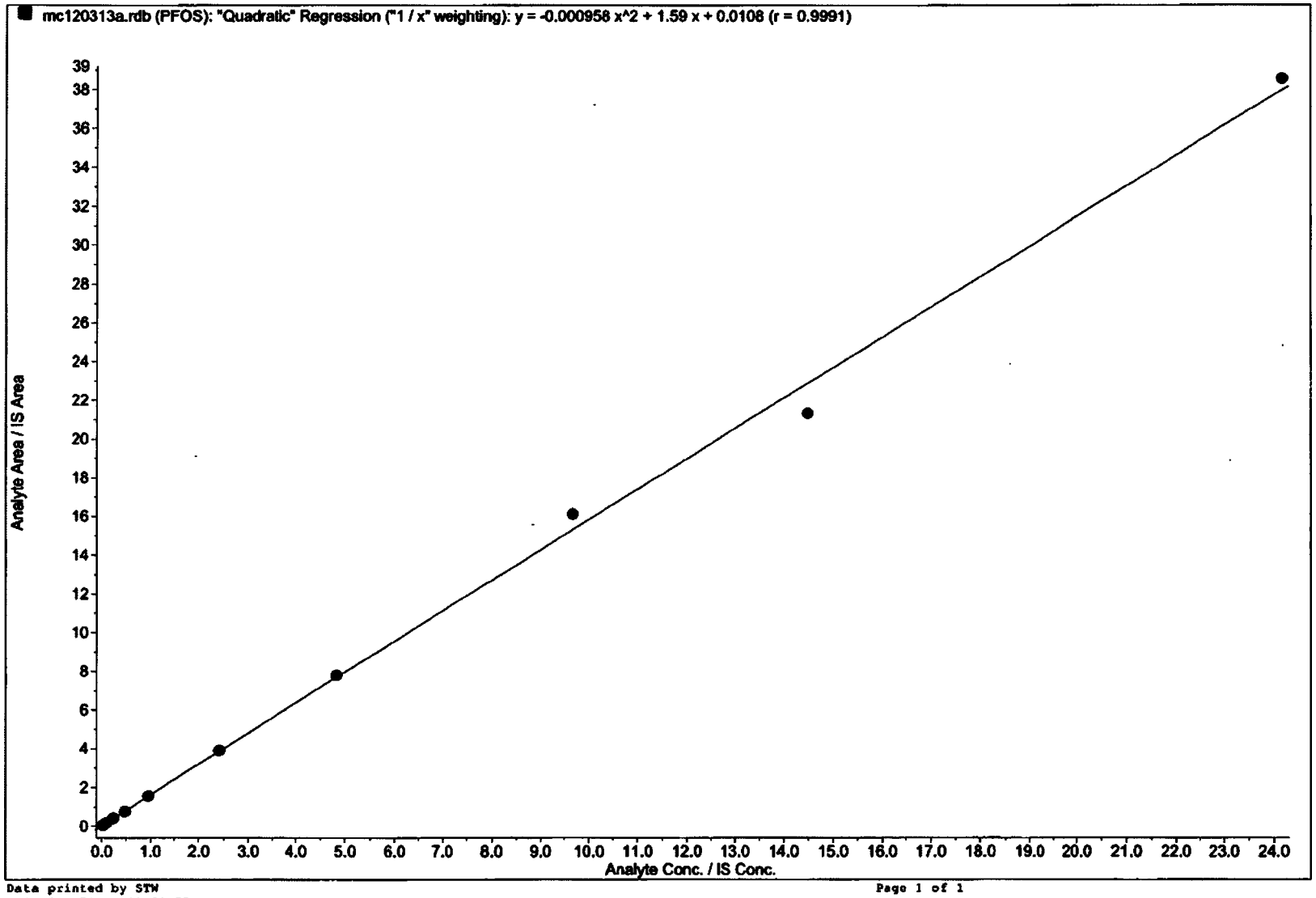


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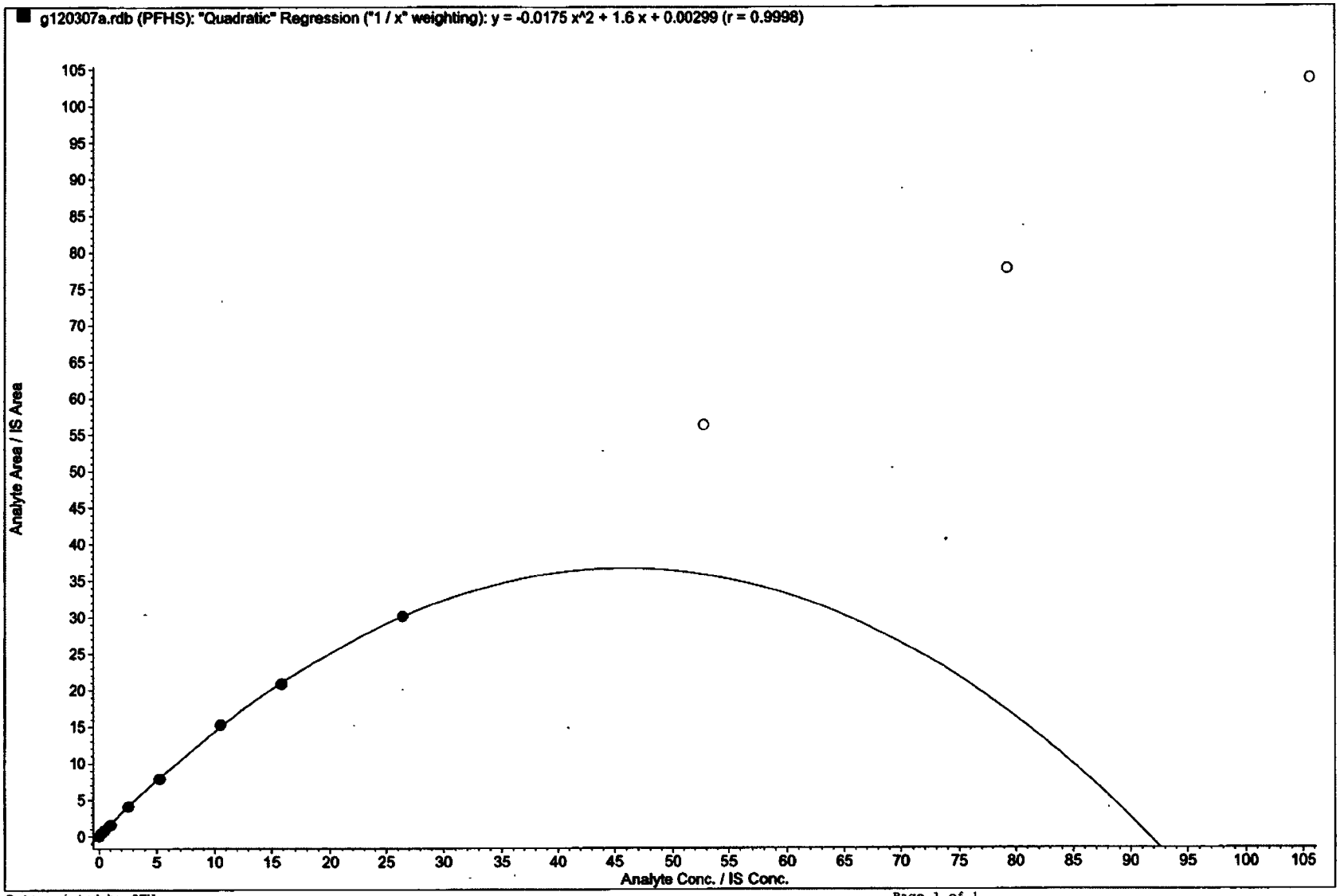


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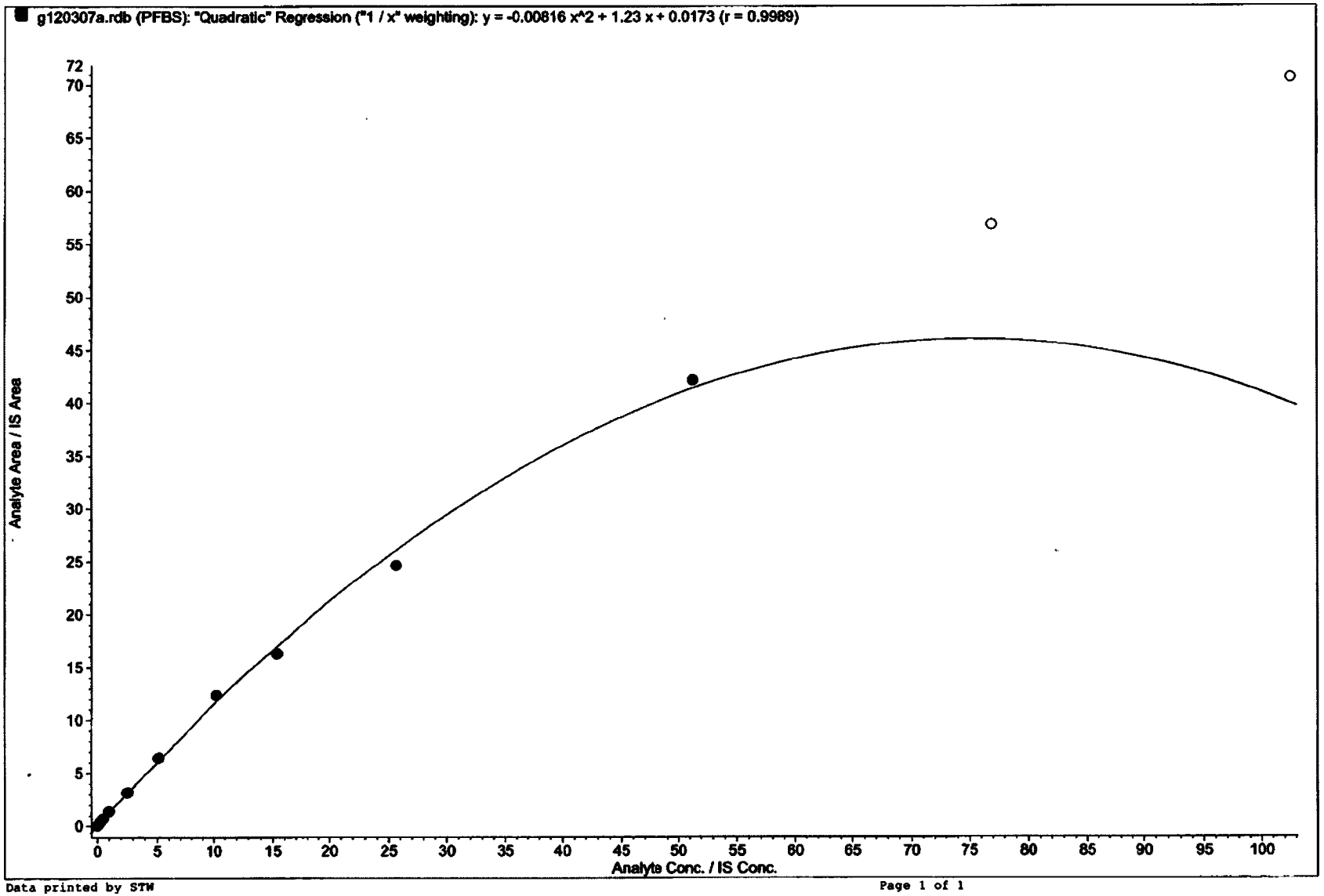


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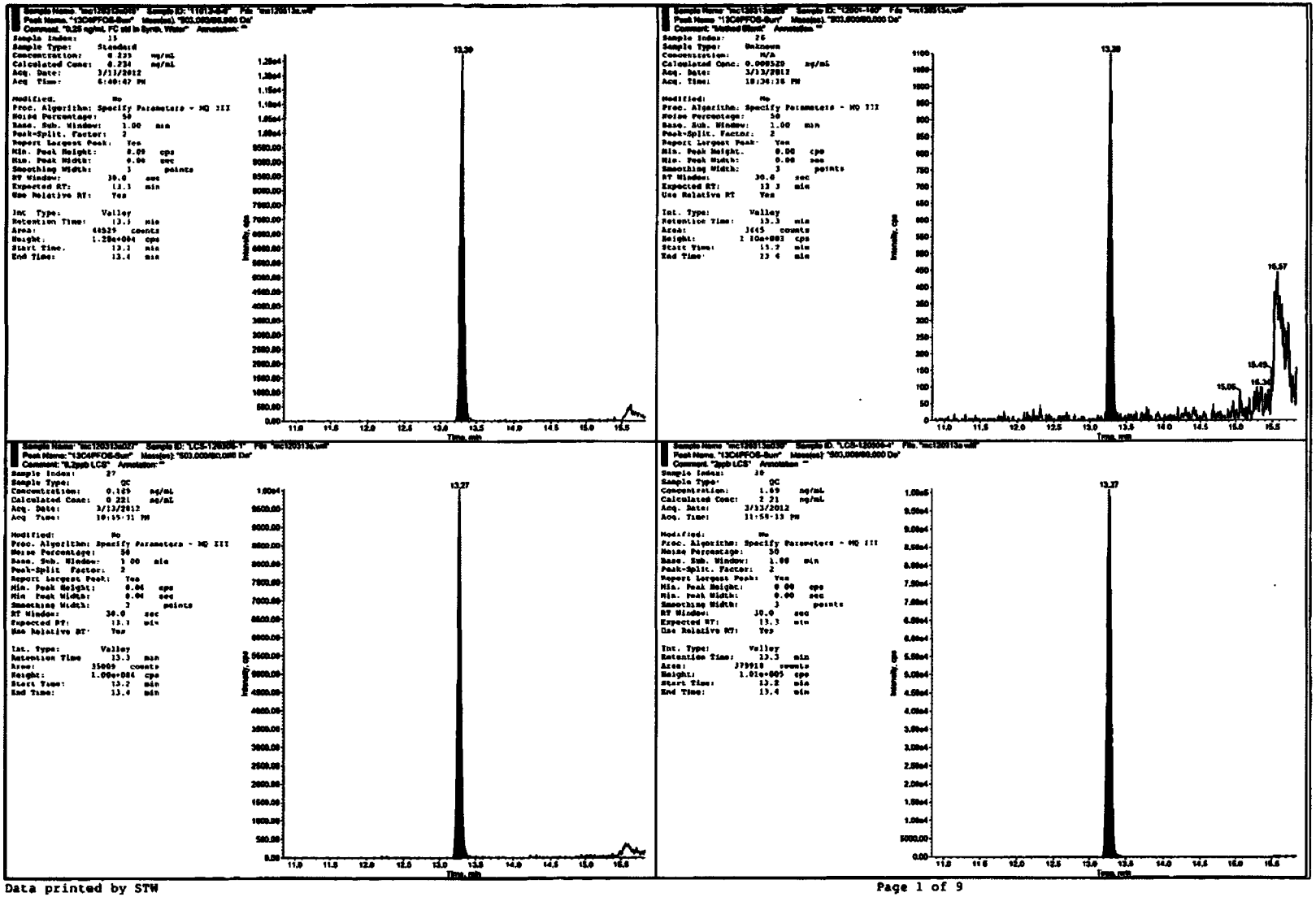


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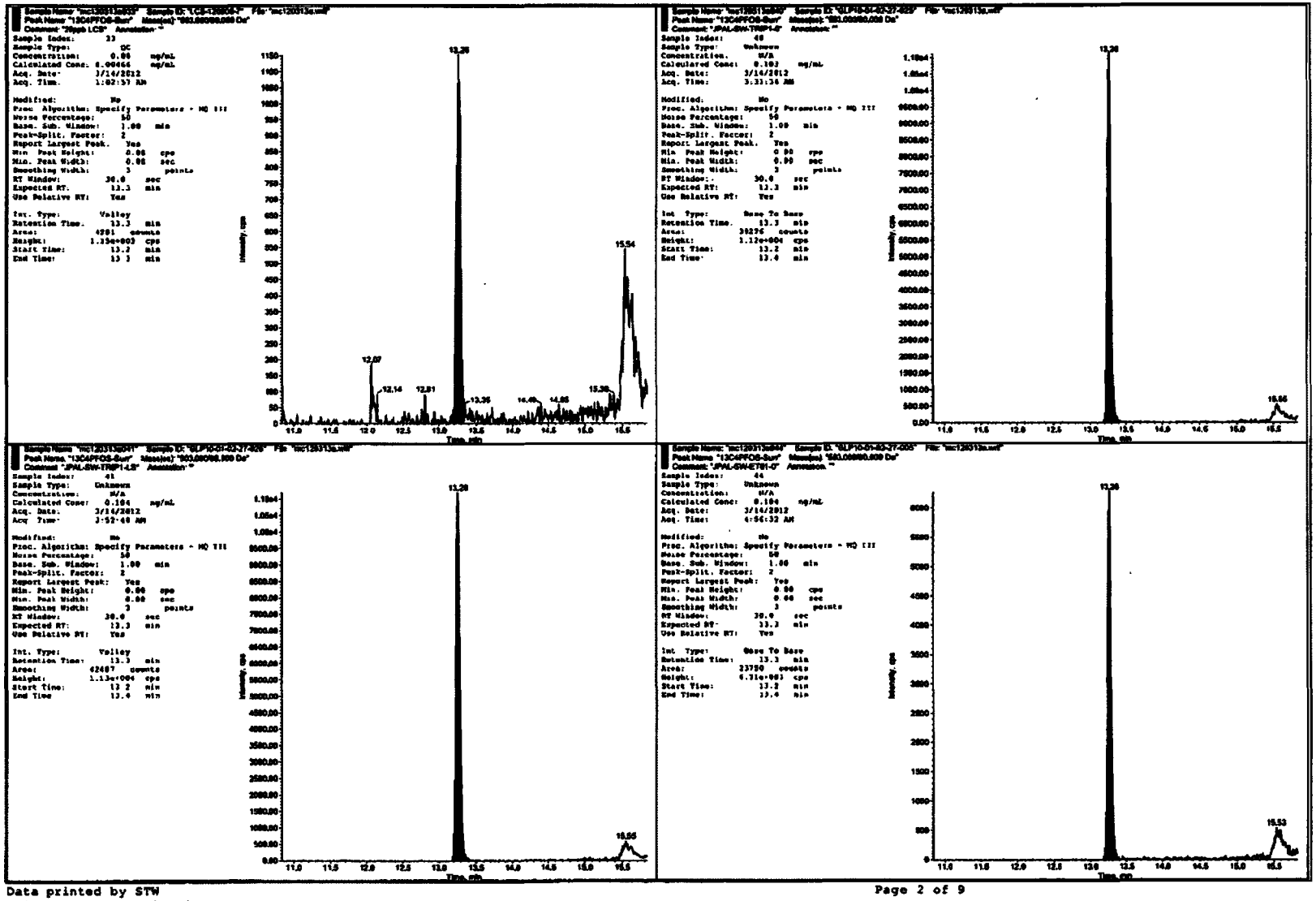
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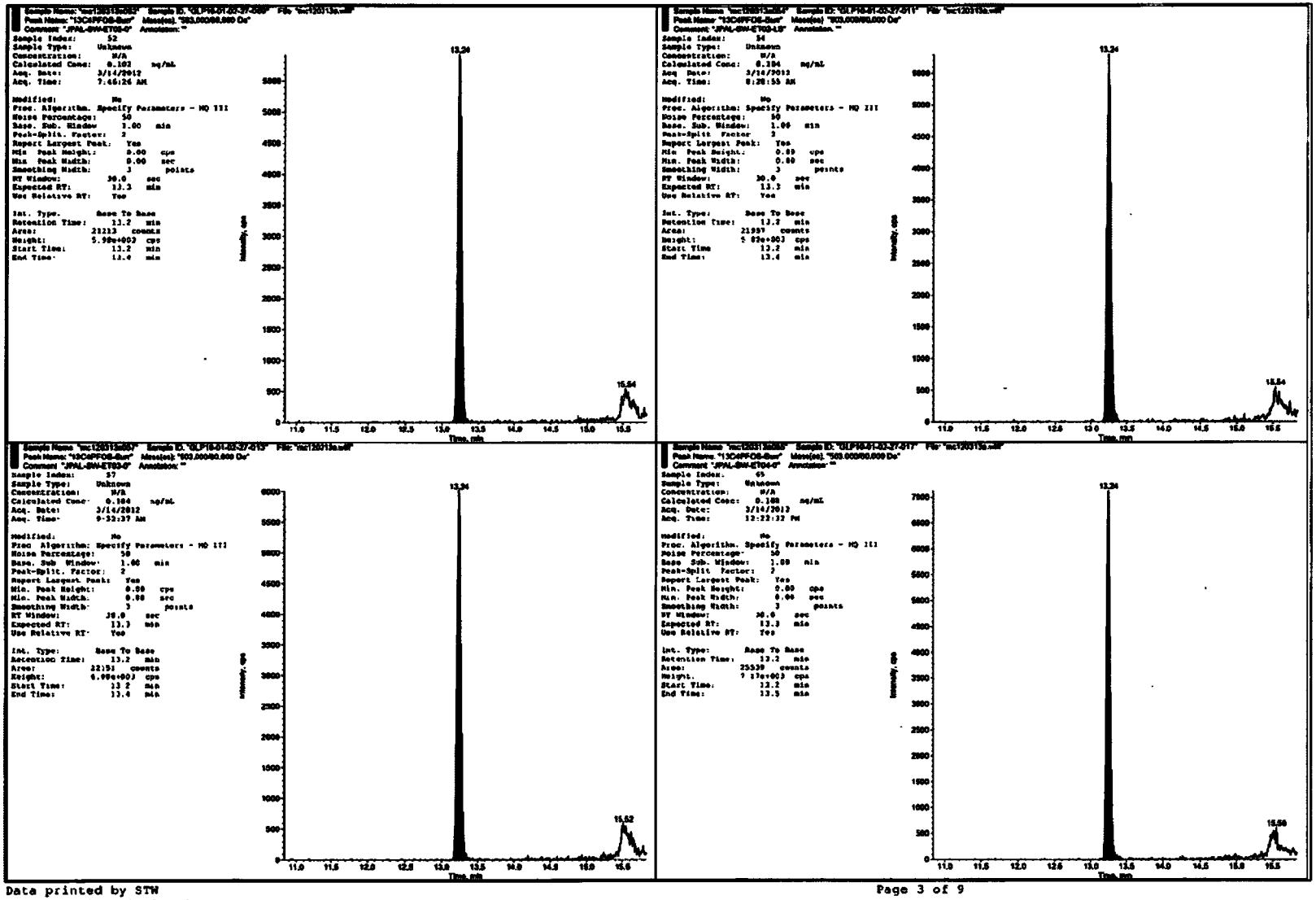
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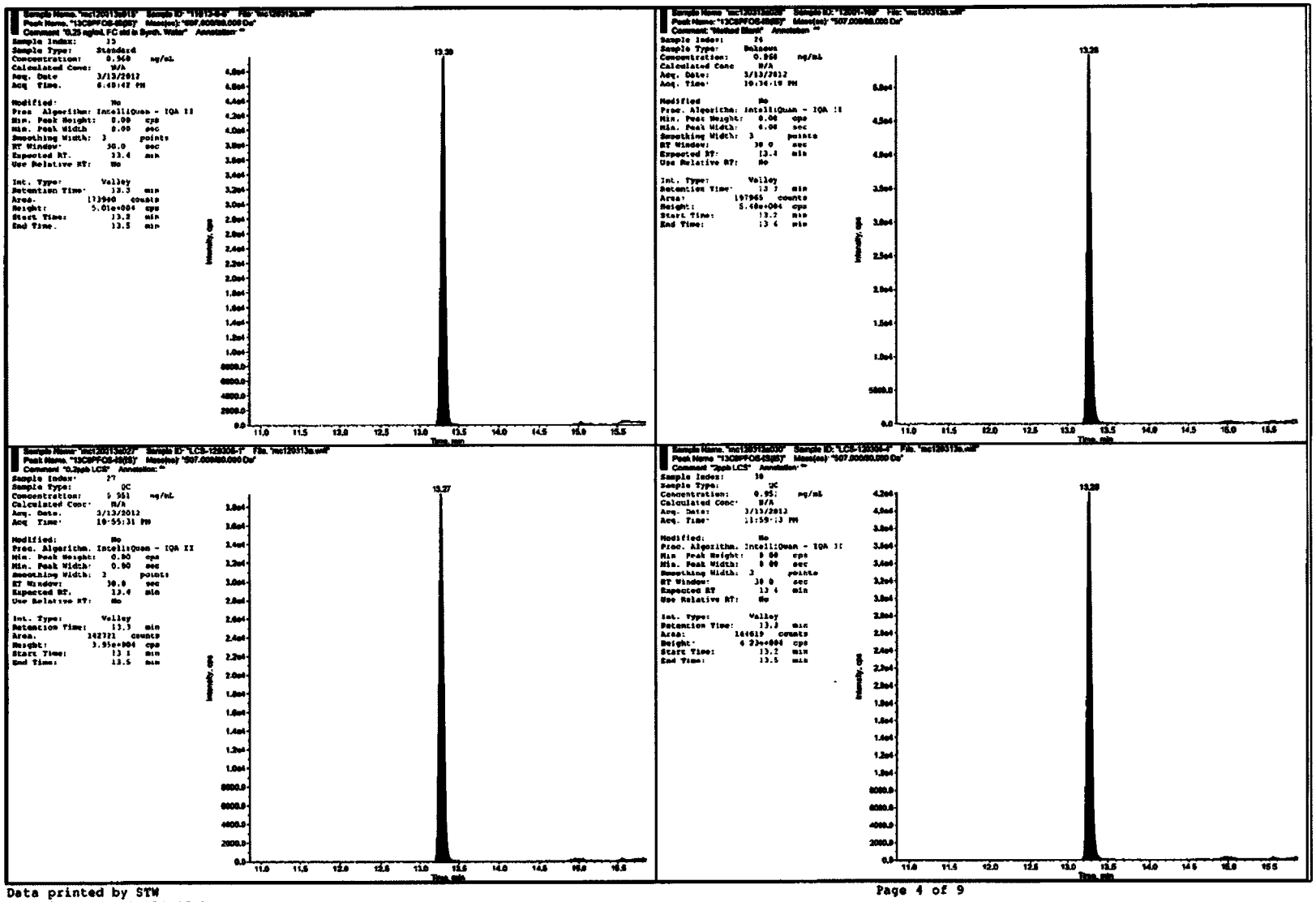
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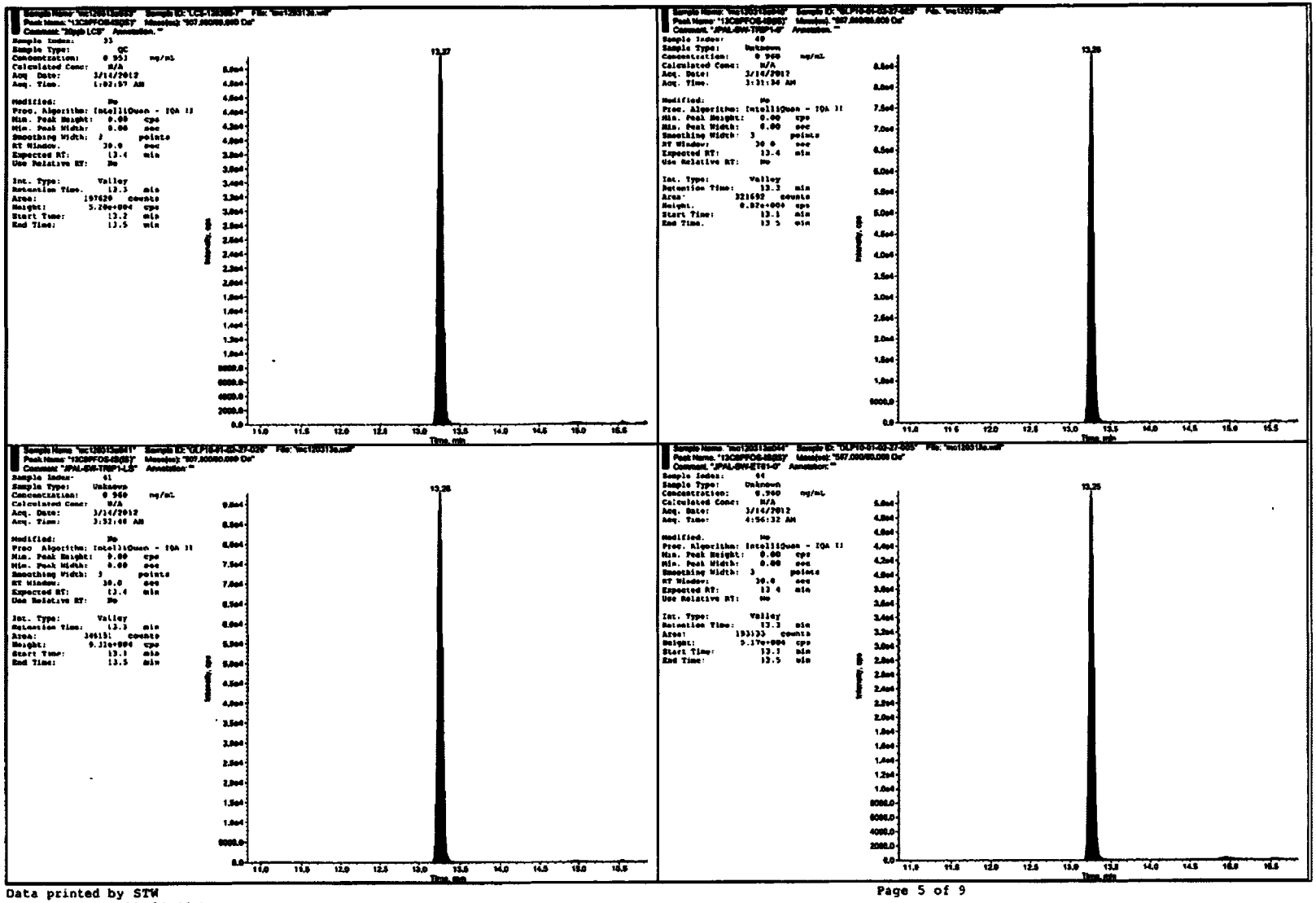


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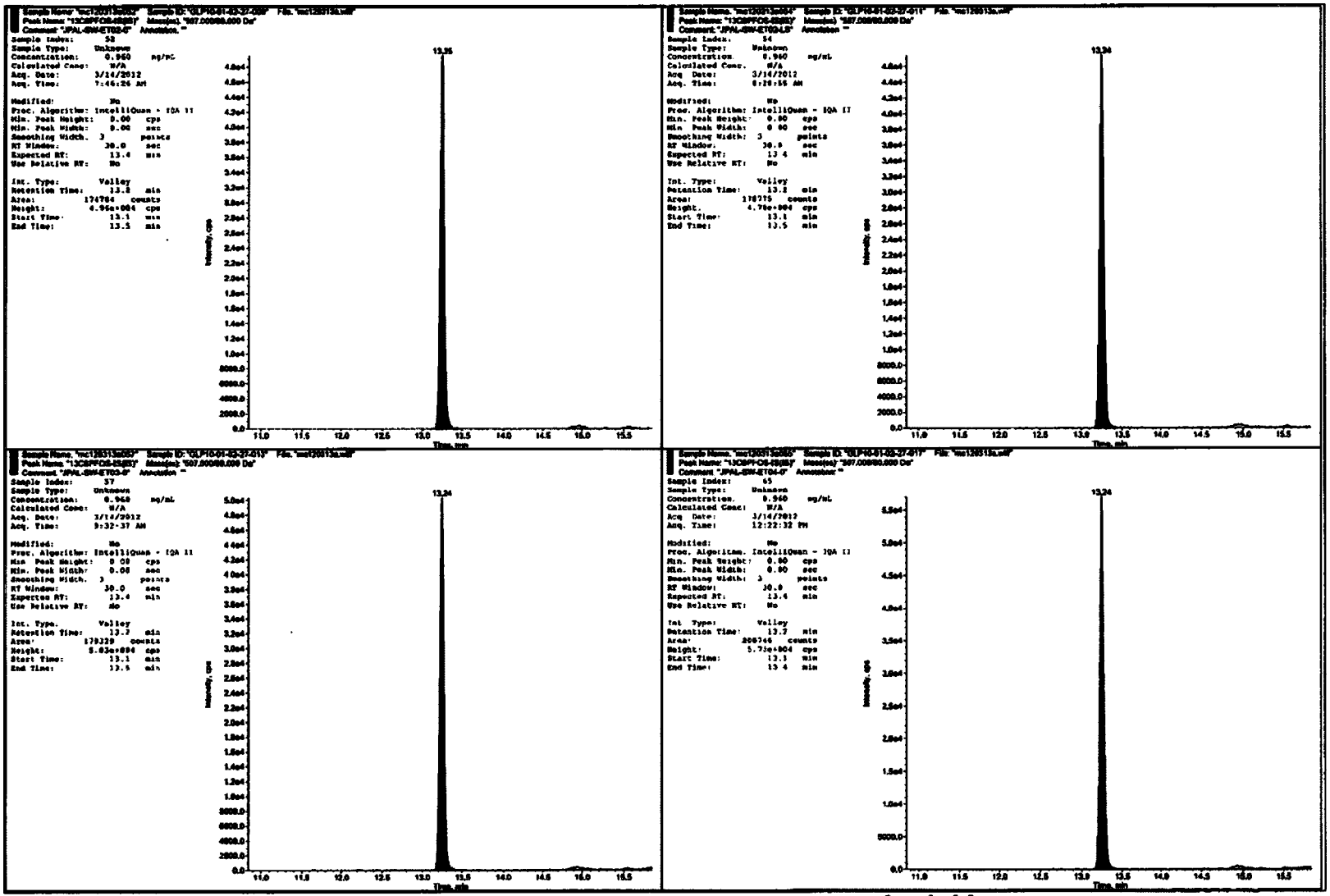
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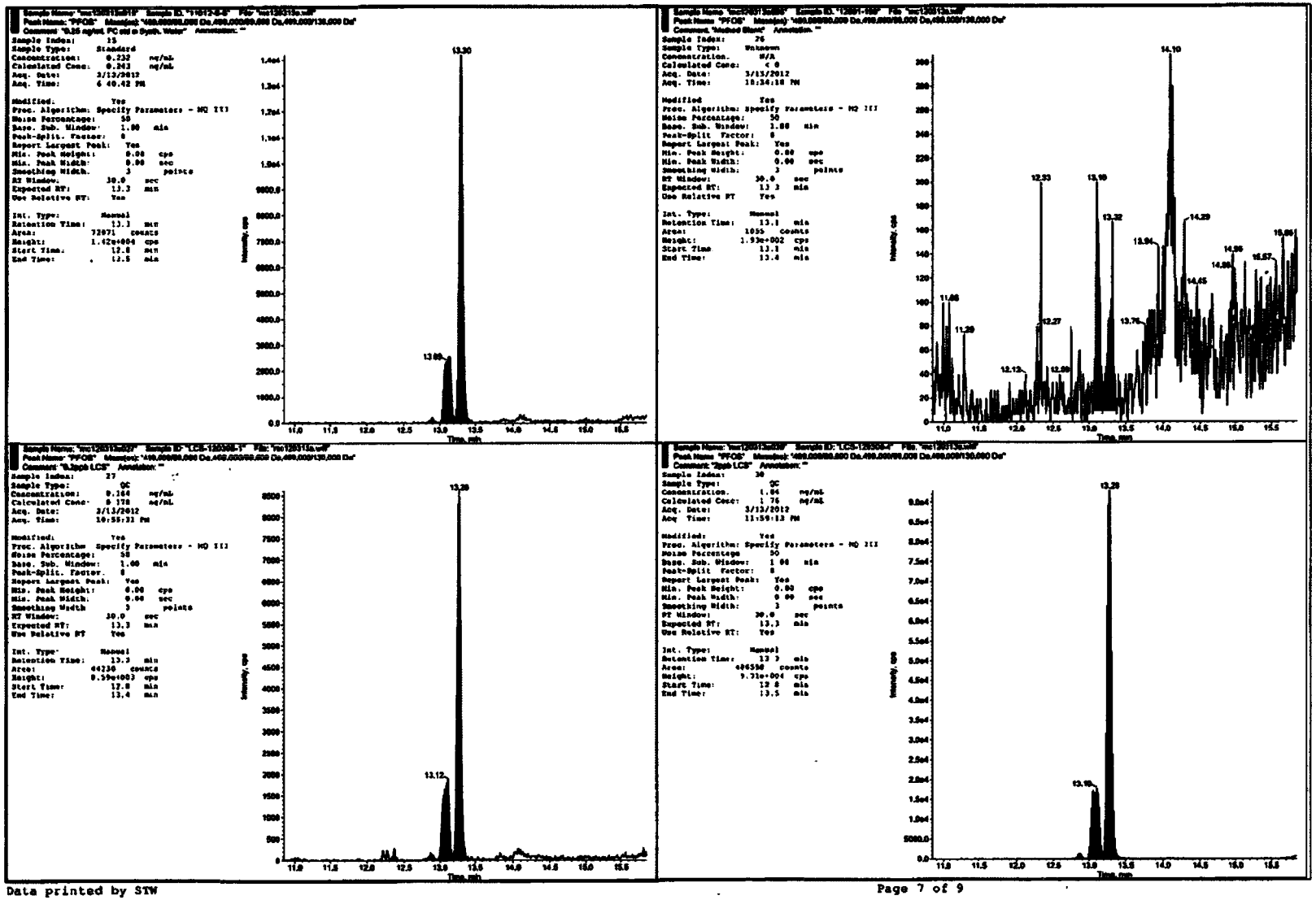


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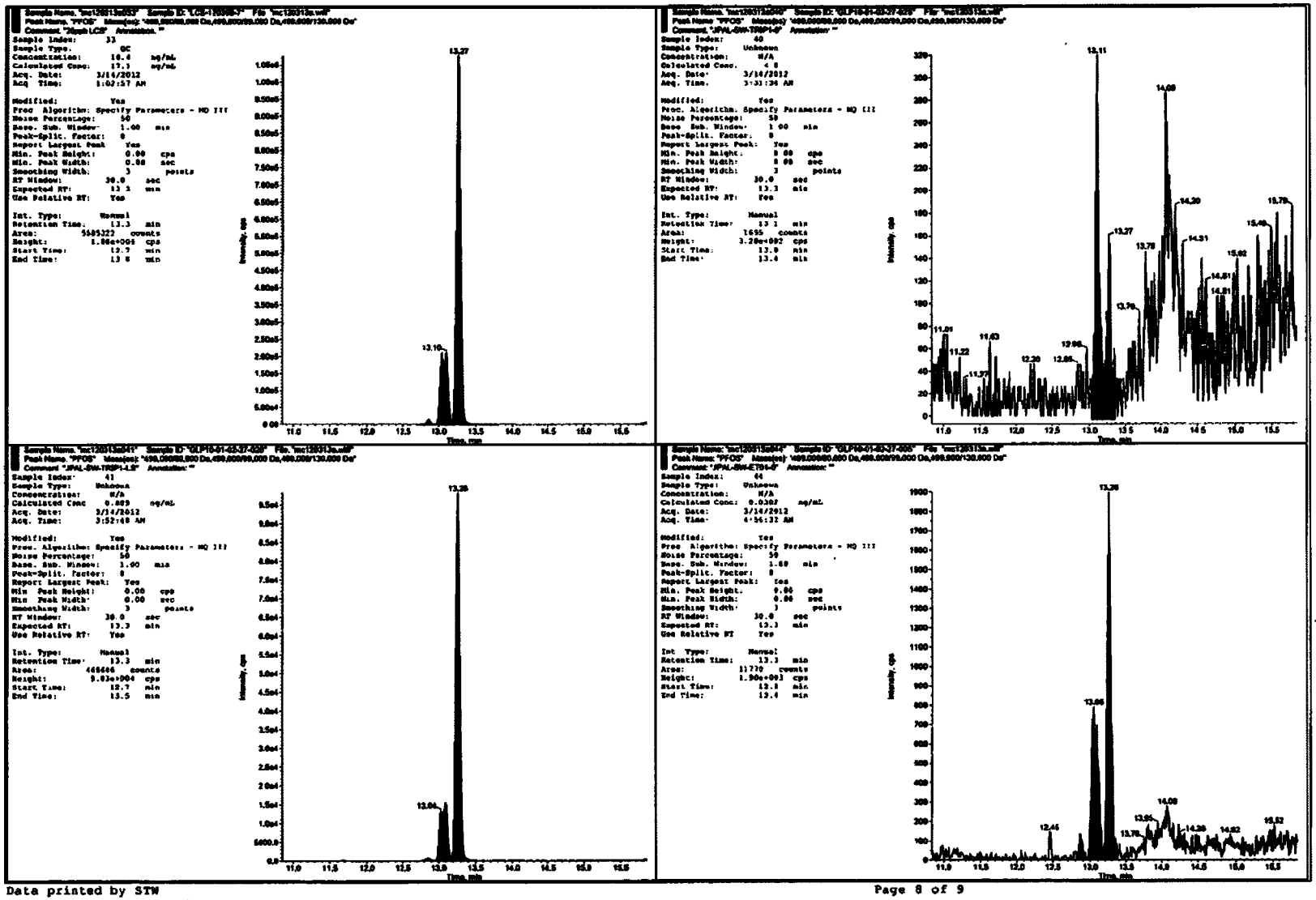
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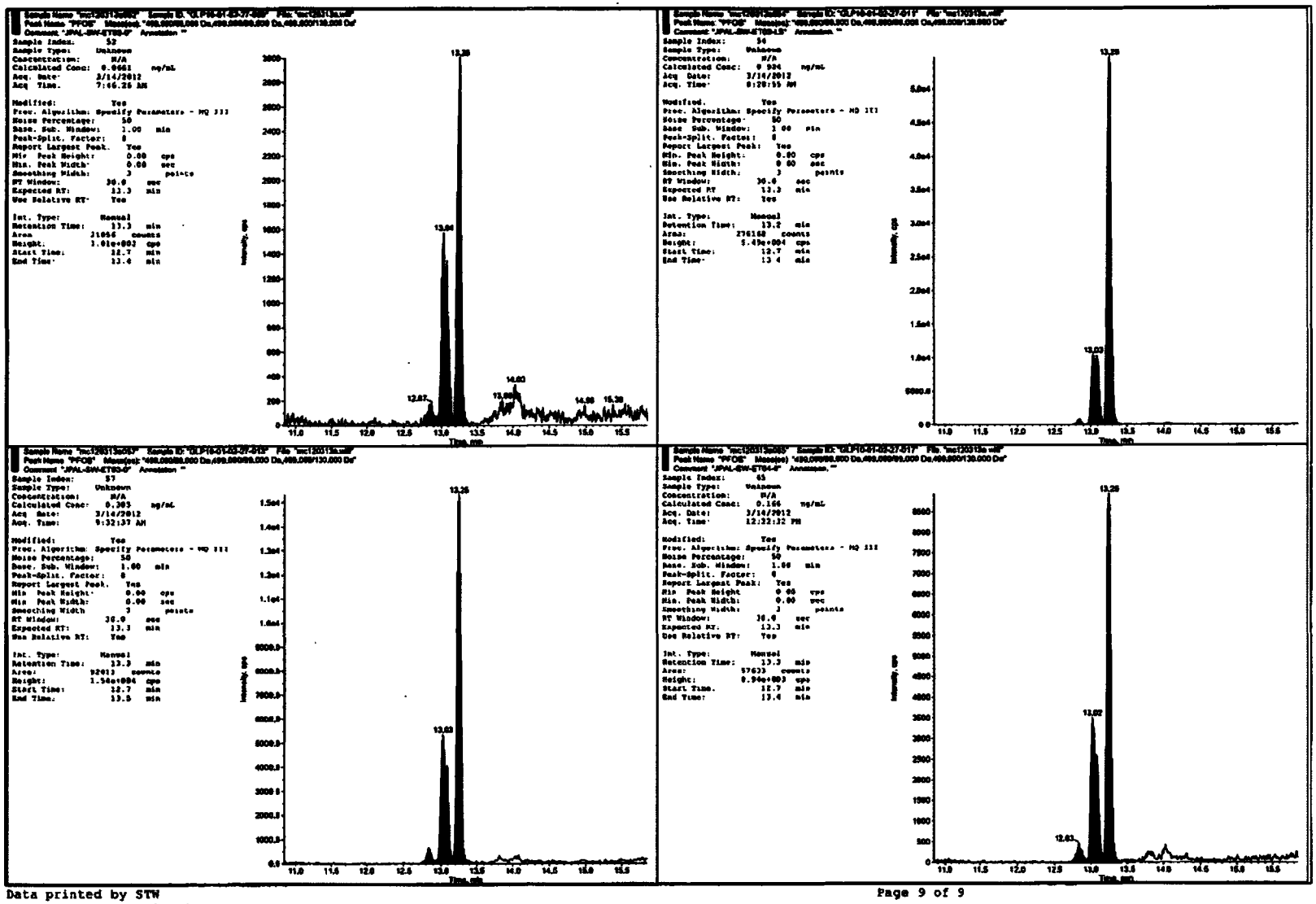


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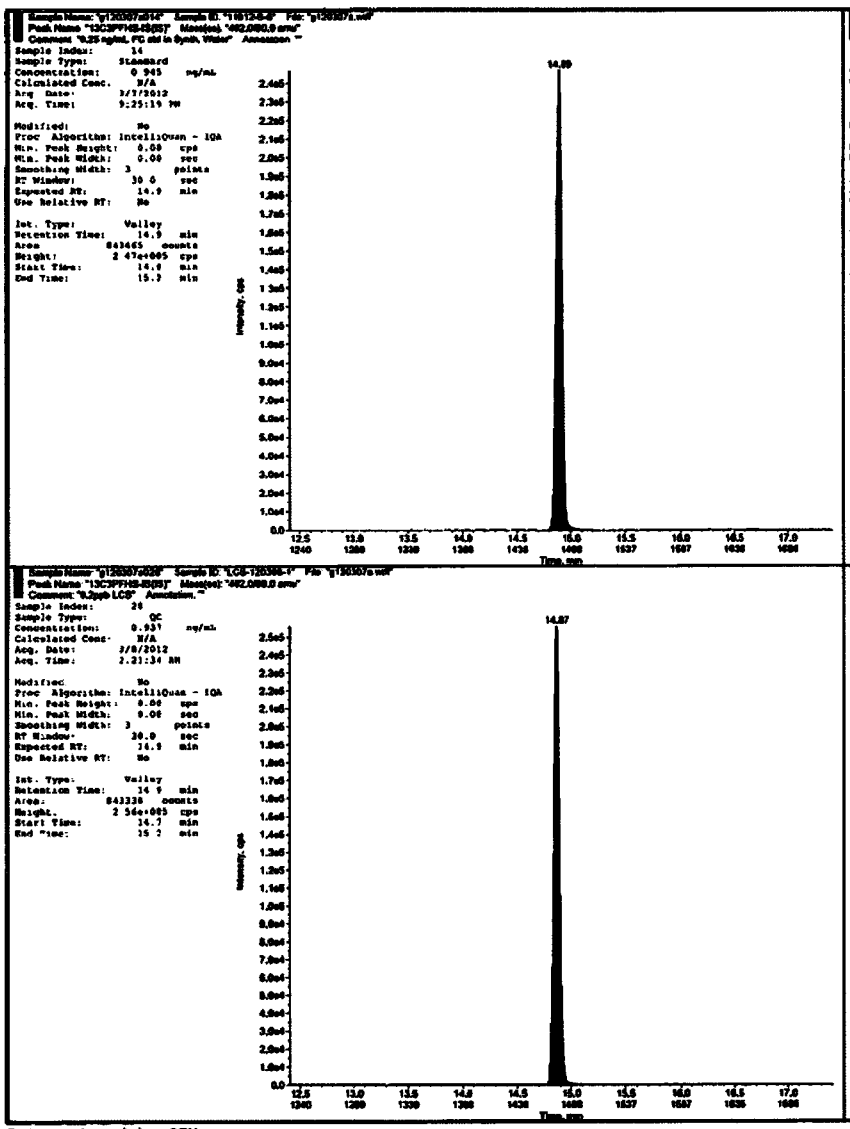


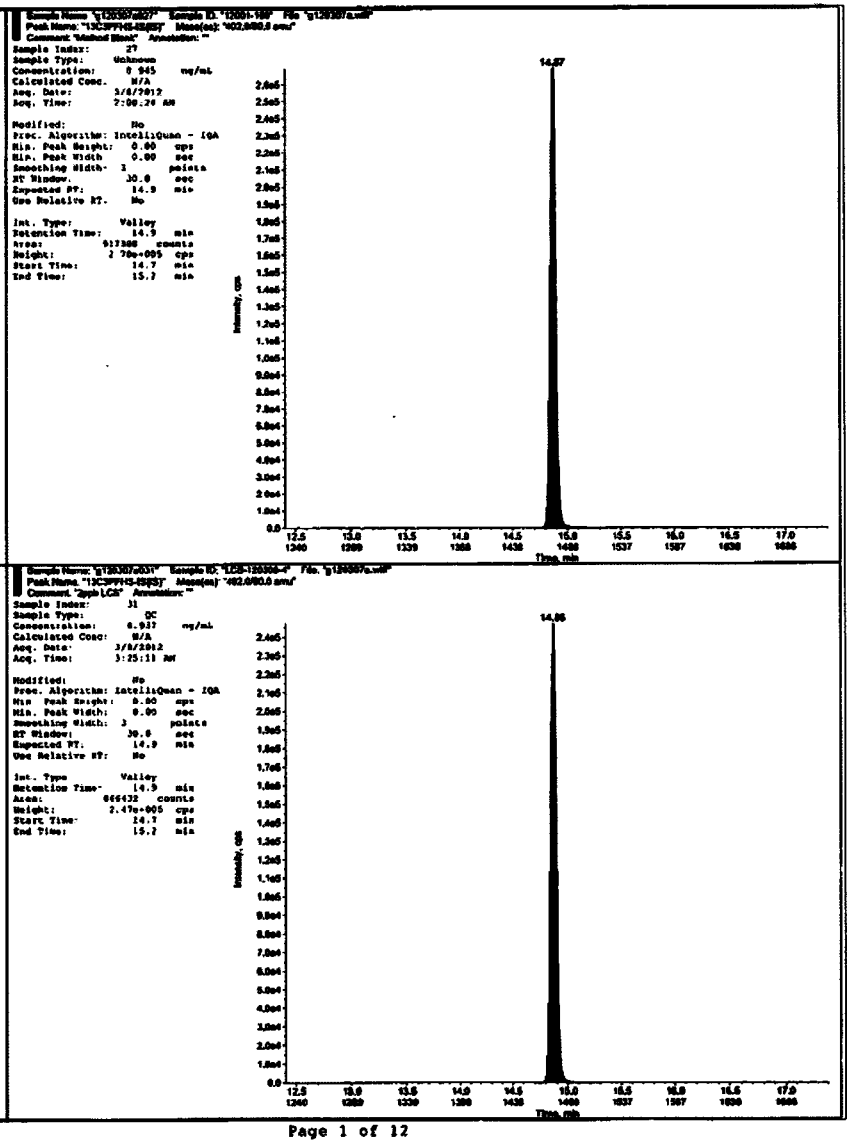
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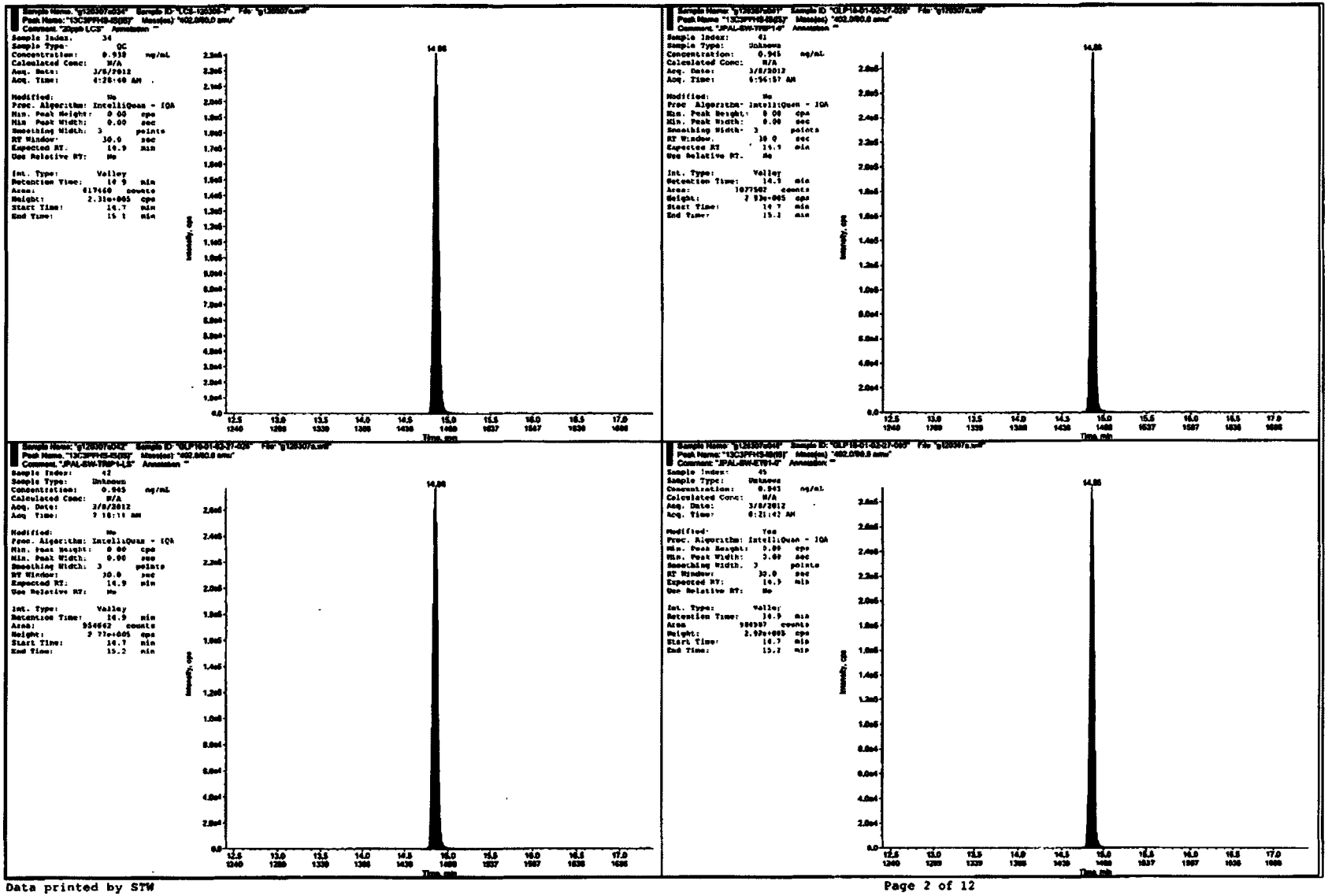




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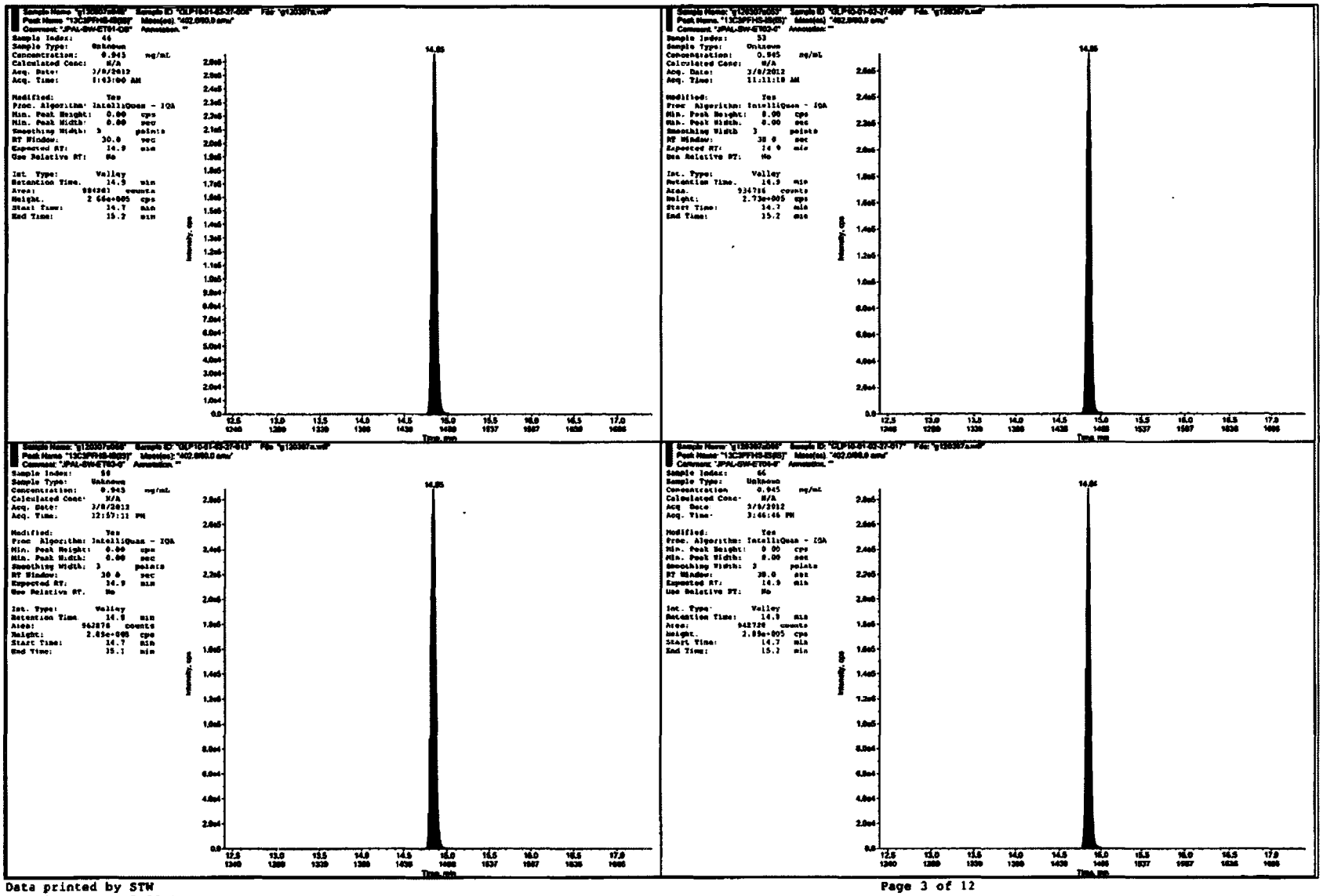
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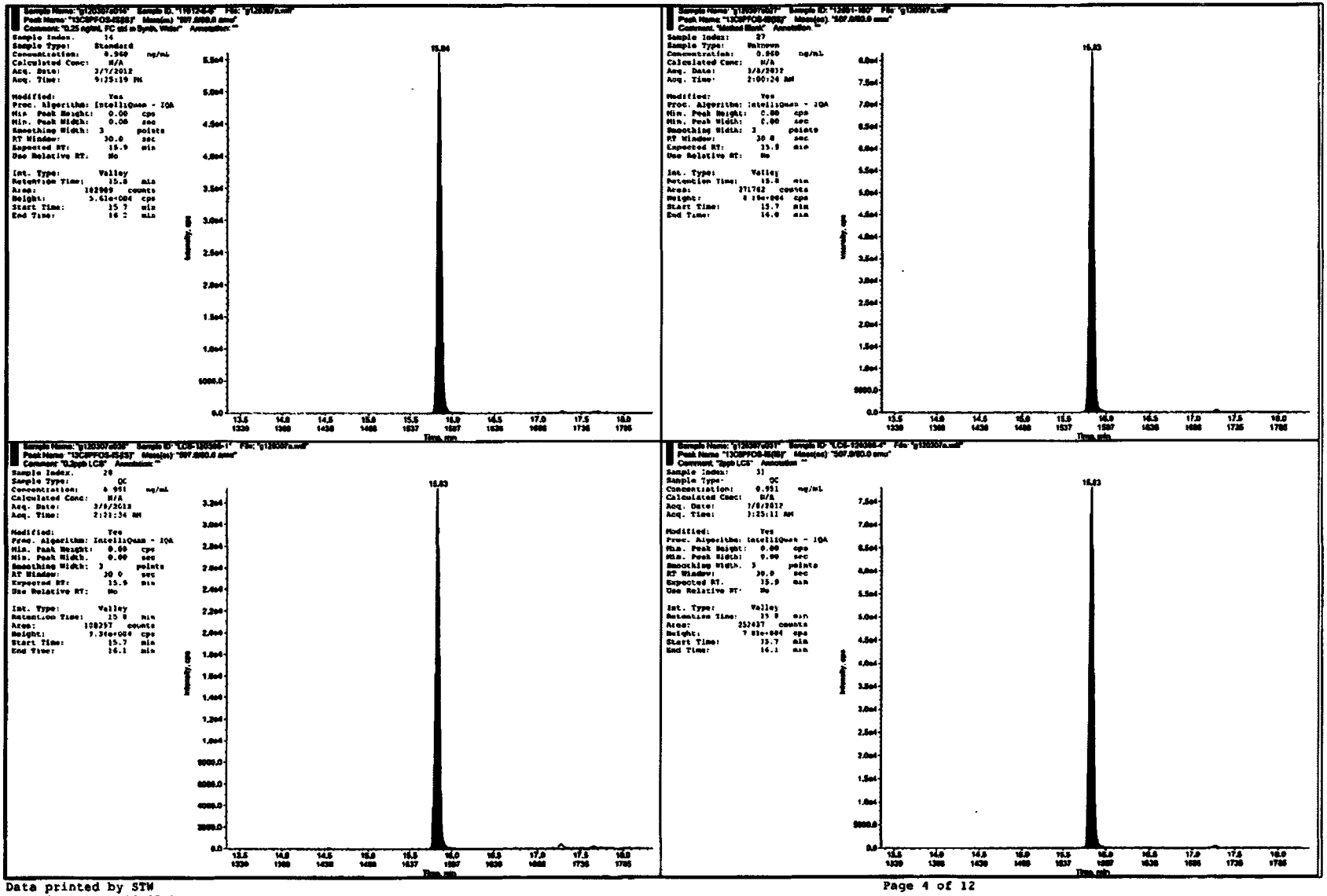
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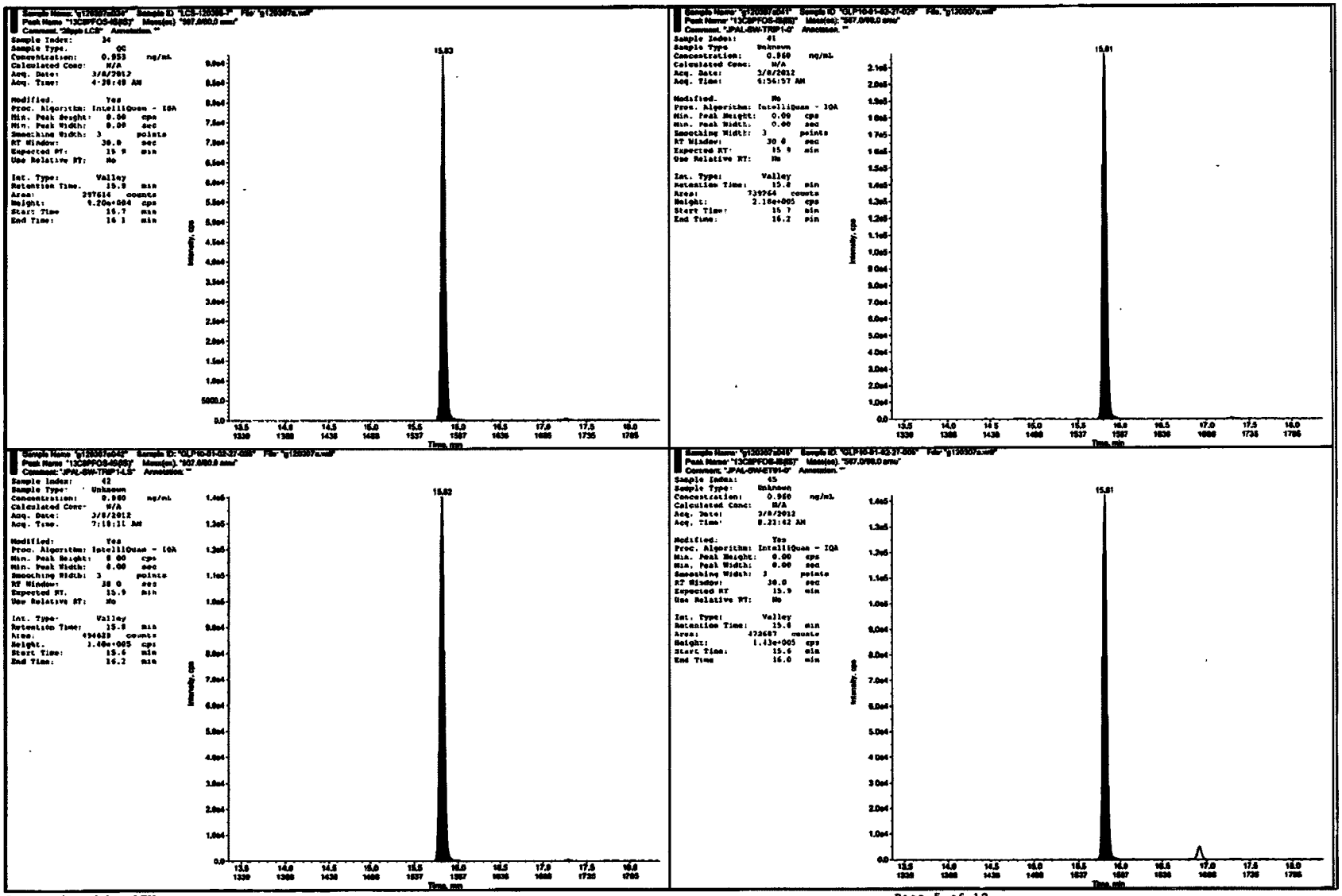
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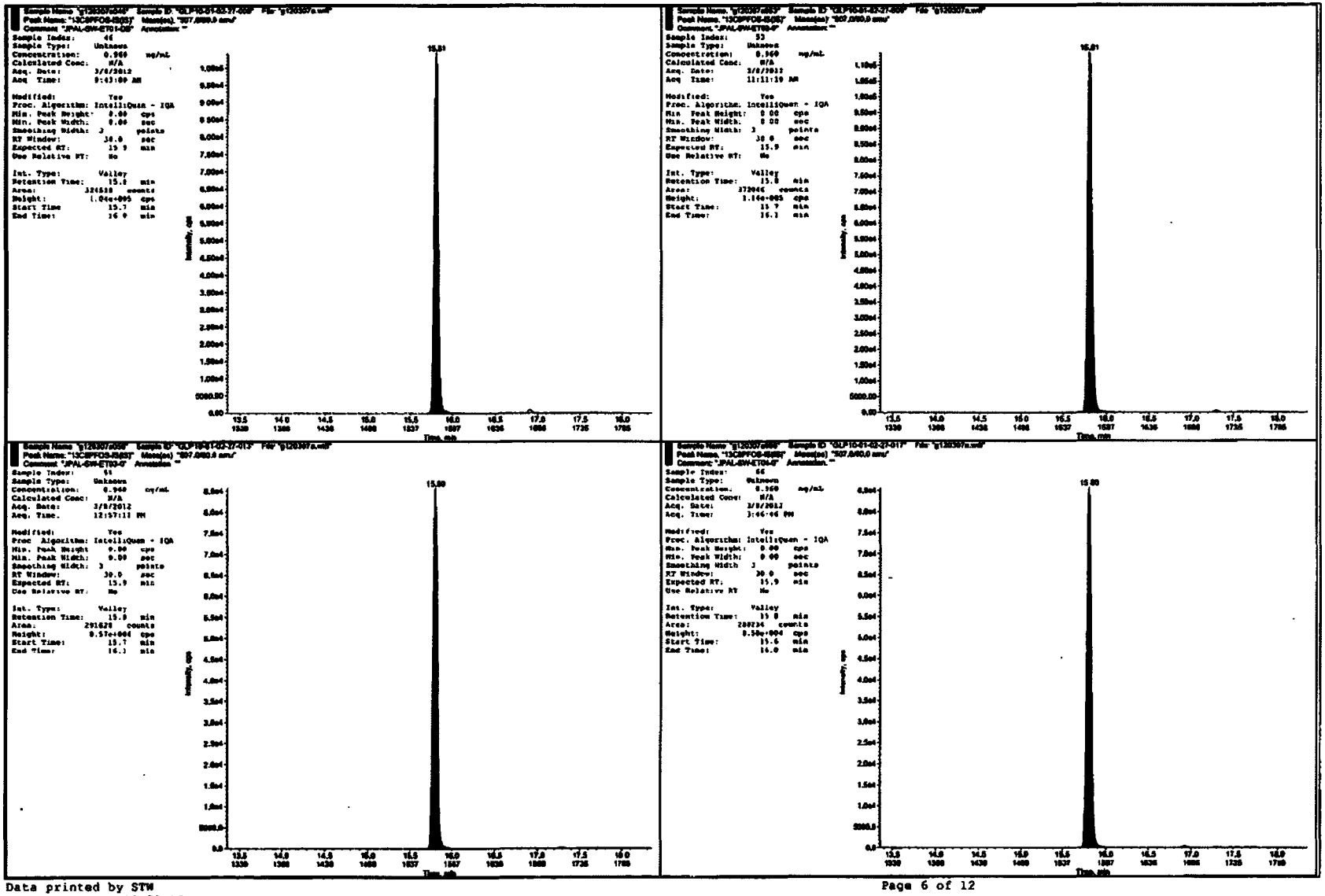
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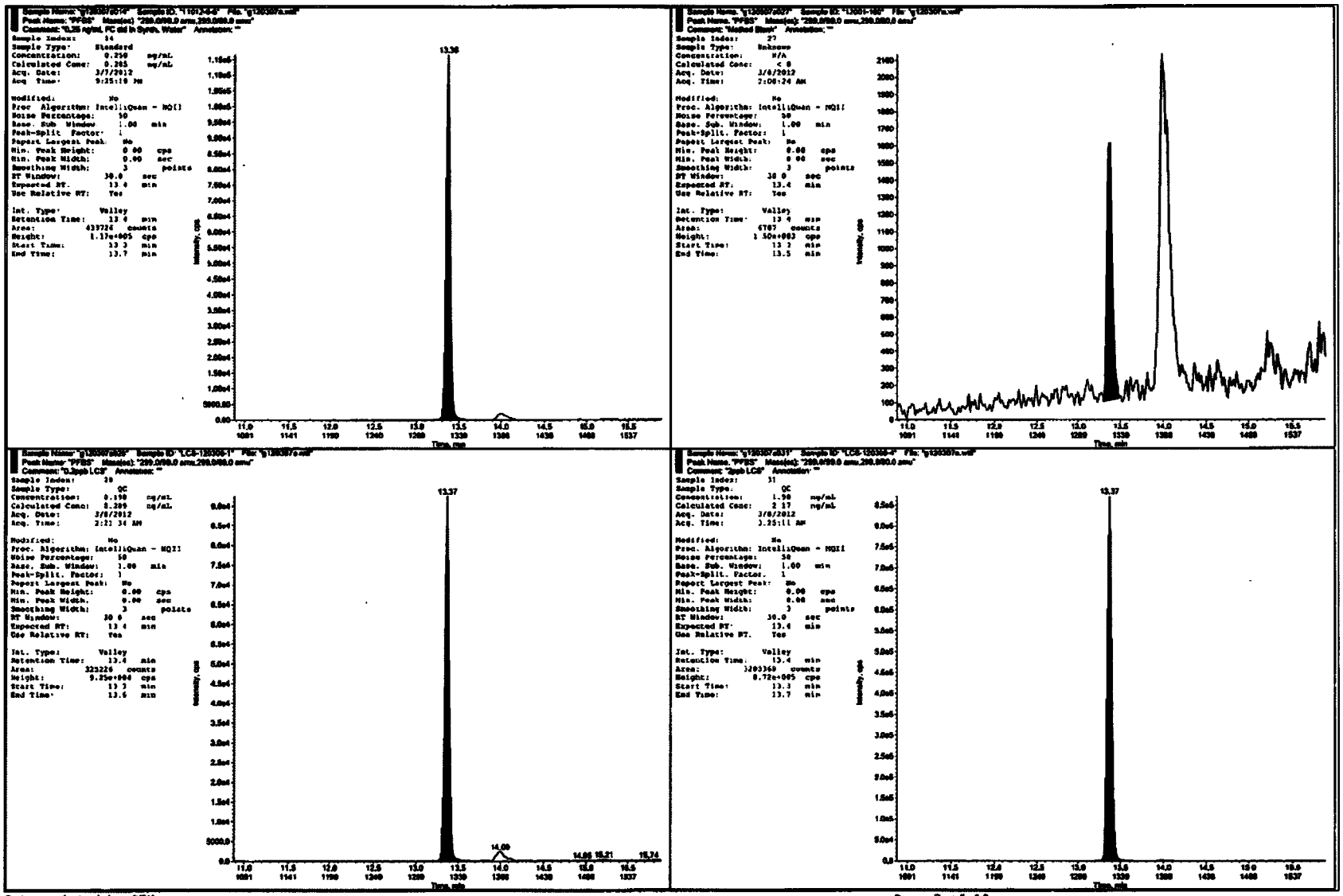
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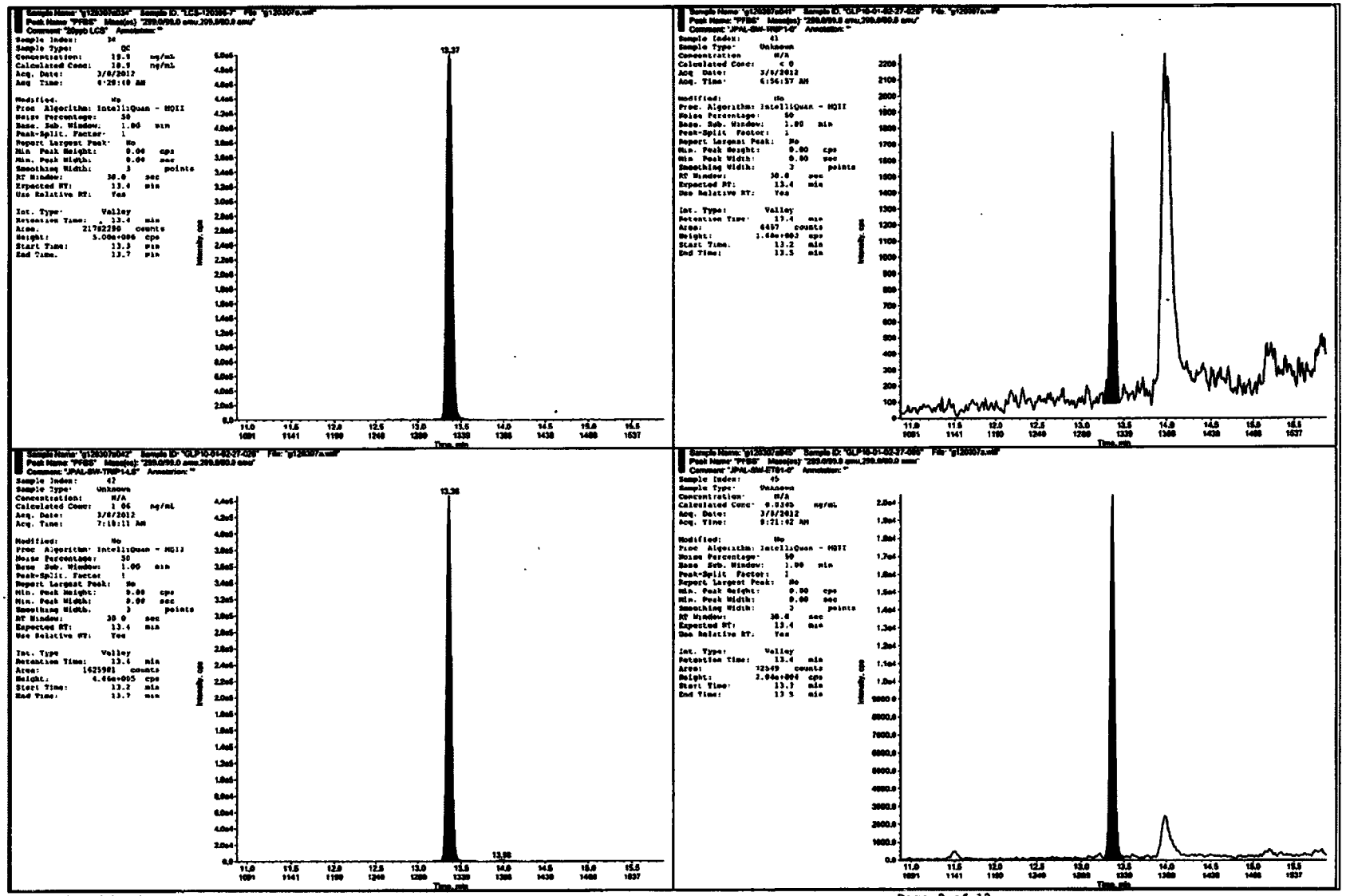
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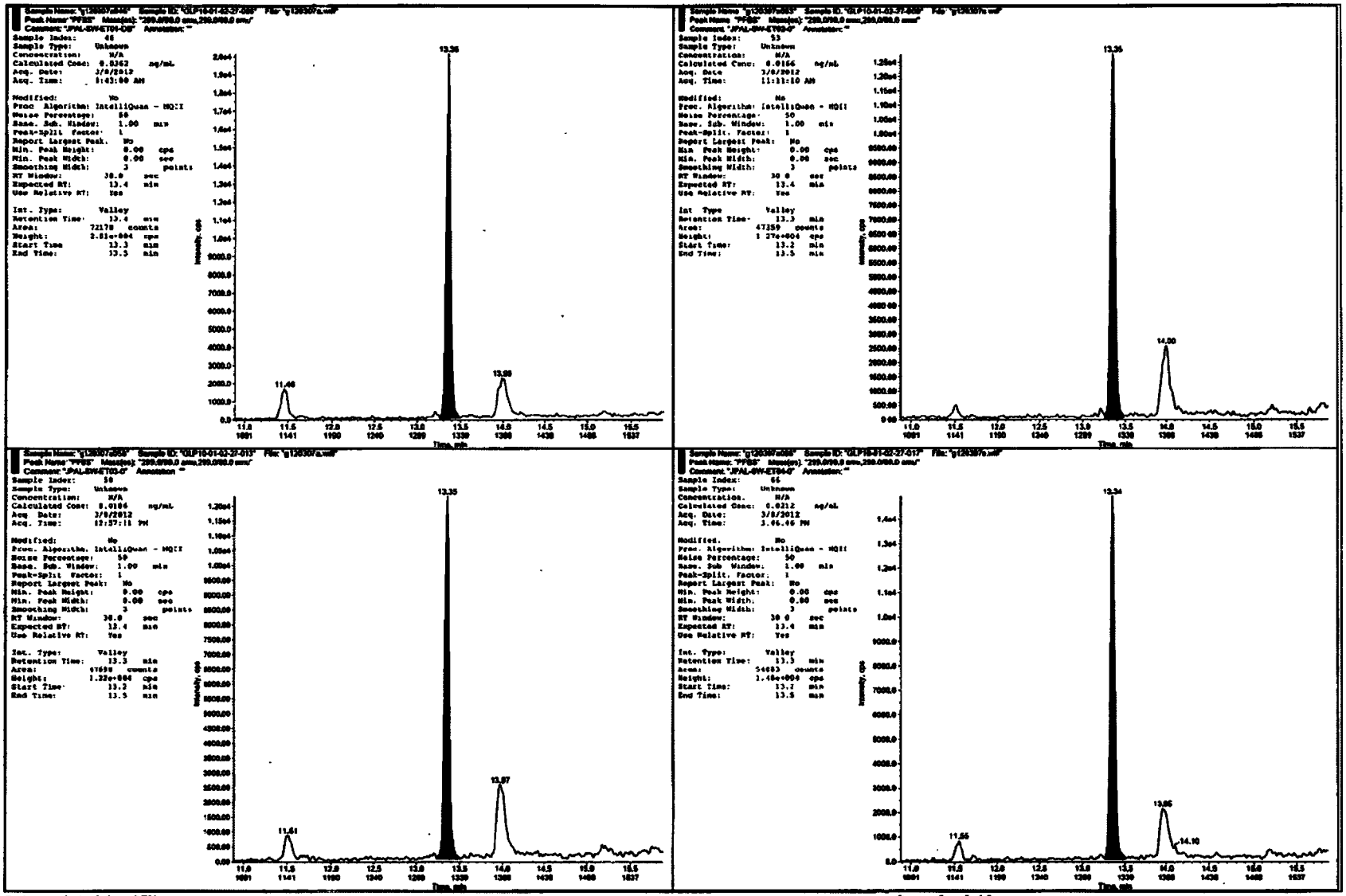
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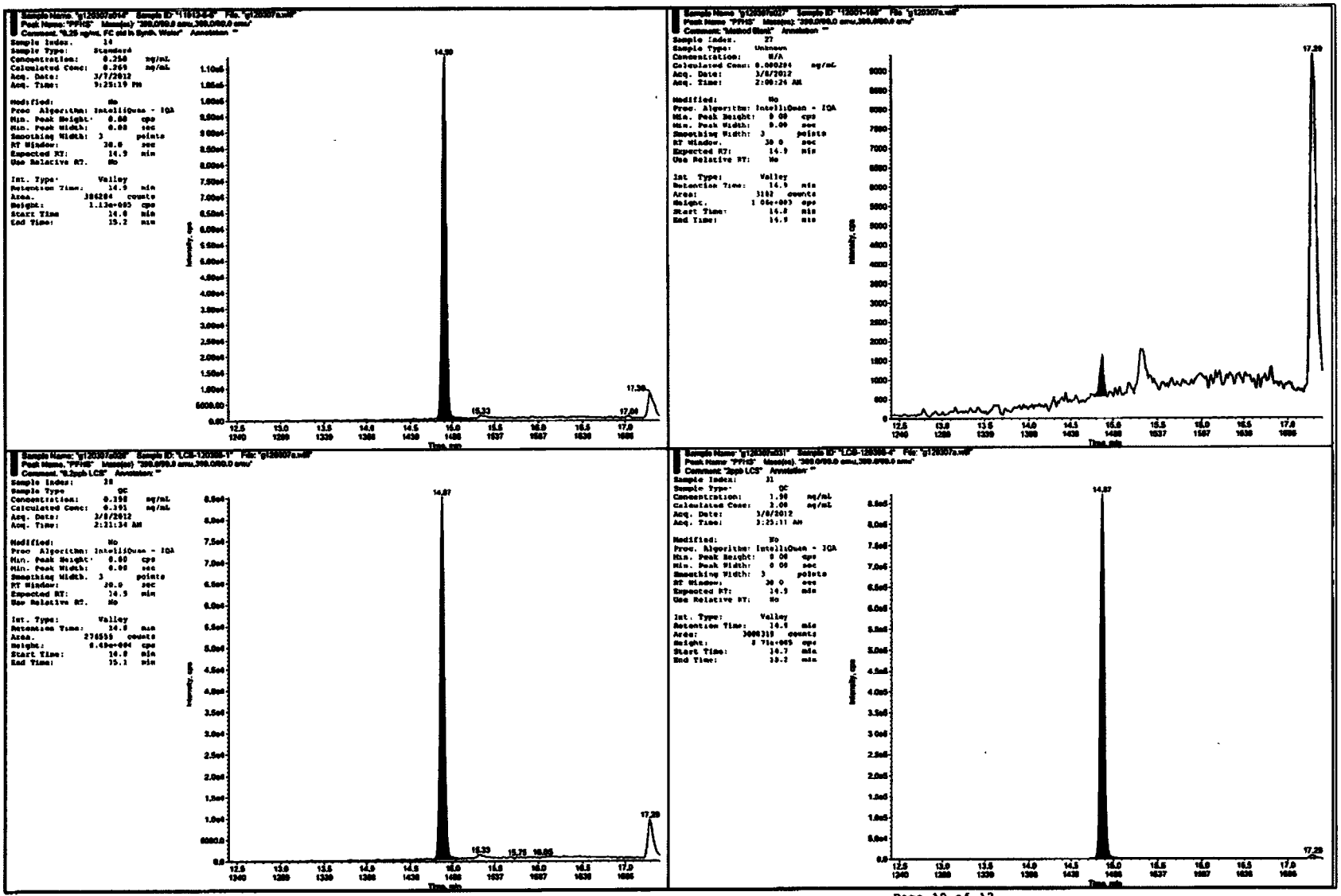
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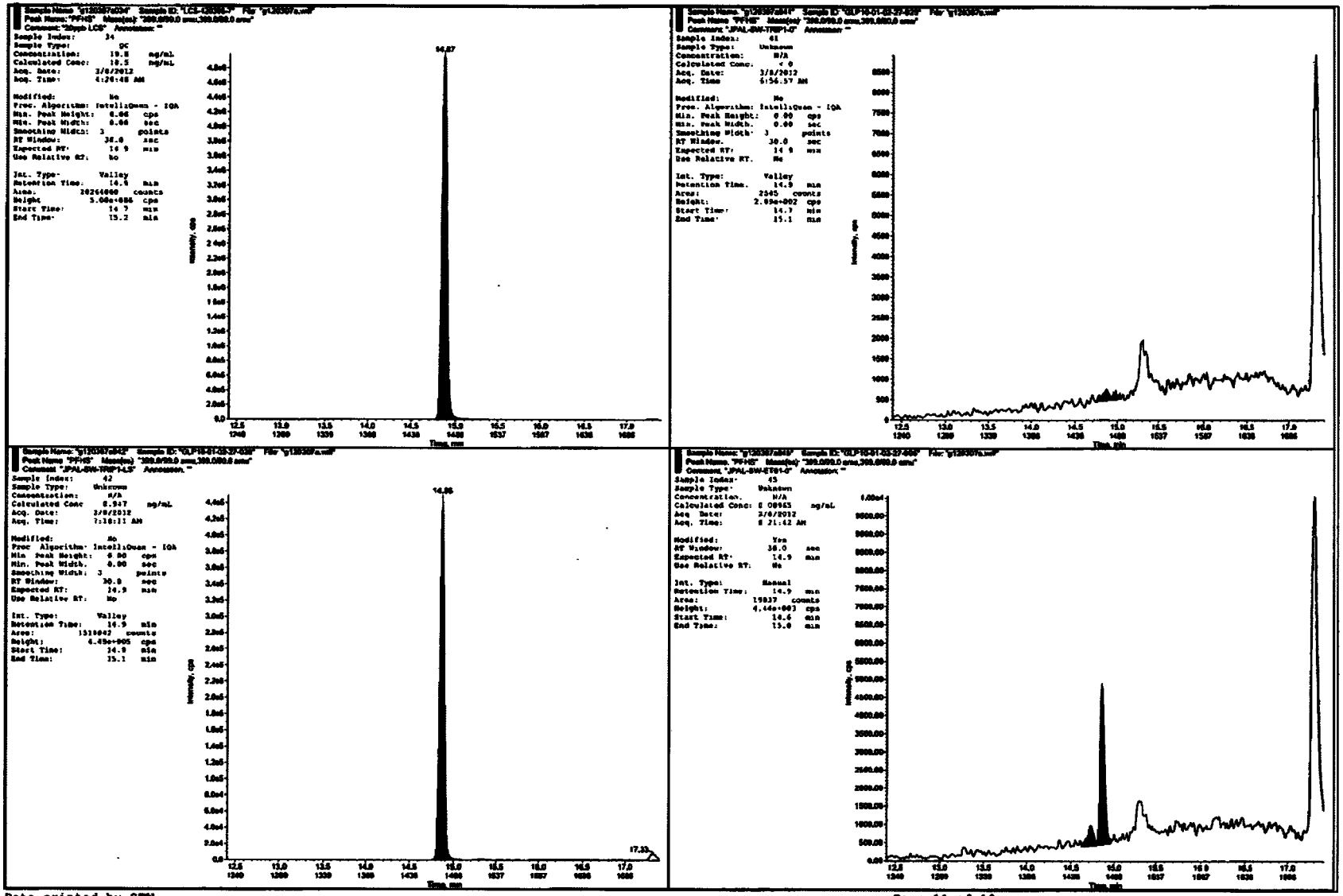
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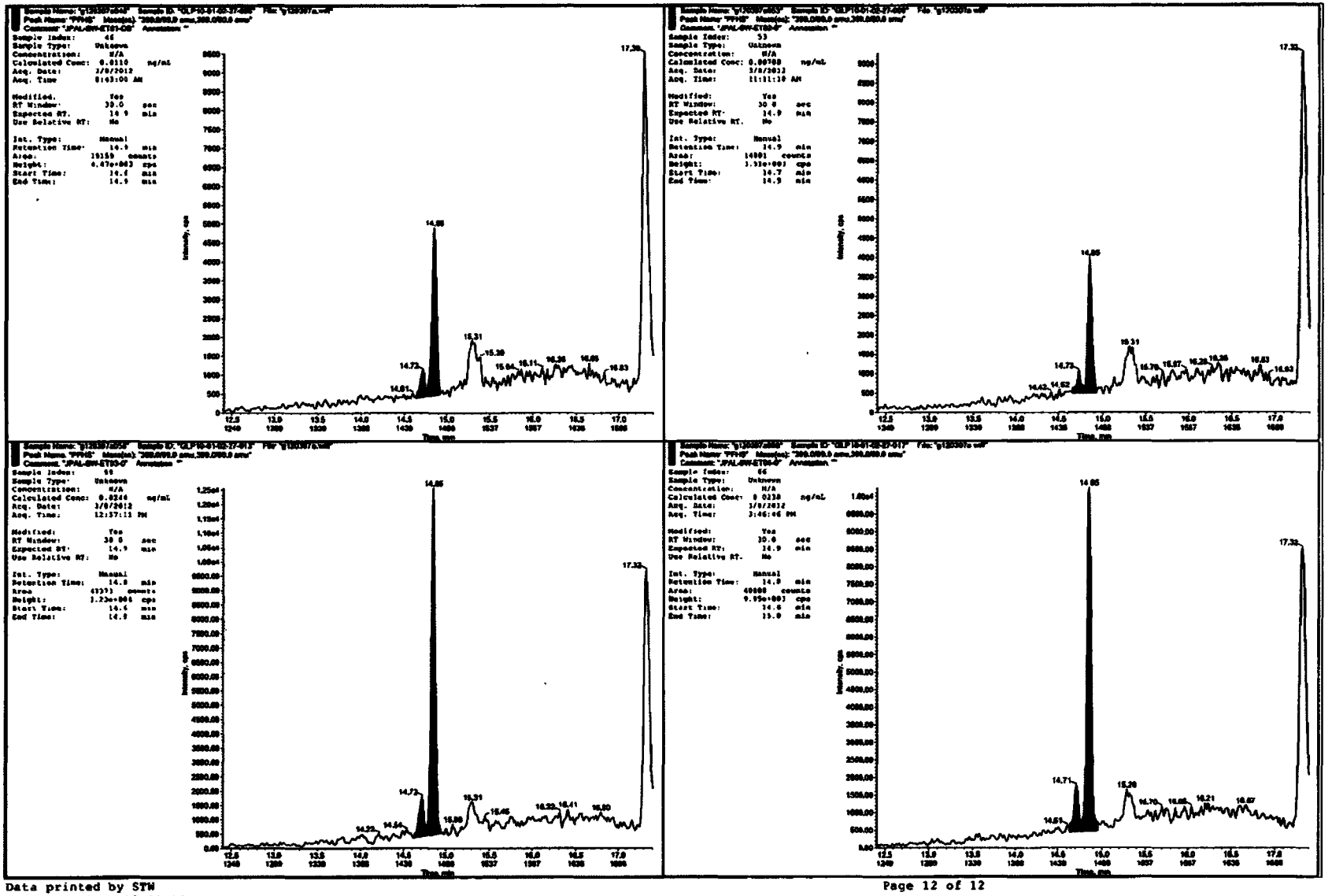
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ATTACHMENT C: ANALYTICAL METHOD(S)

3M Environmental Laboratory

Method

Method of Analysis for the Determination of Perfluorinated Compounds in Water by LC/MS/MS; Direct Injection Analysis

Method Number: ETS-8-044.1

Adoption Date: 4/12/07

Effective Date: 11/9/11

Approved By:

9 NOV 2011

William K. Reagen, Technical Director, Environmental Laboratory — Date

1 Scope and Application

This method describes the direct injection analysis of perfluorinated compounds (PFCs) from water matrices using high-performance liquid chromatography tandem mass spectrometry (HPLC/MS/MS). The method is generally applicable but not limited to the measurement of perfluoroalkyl sulfonamides and perfluorinated alkyl acids (PFAAs) such as perfluorosulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs) (Table 1). Water samples containing heavy particulate may require preparation by an alternate method such as ETS-8-154 "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates In Water By Solid Phase Extraction and High Performance Liquid Chromatography/Mass Spectrometry". The method is applicable to both external standard and internal standard calibration[1].

Table 1. Representative Target Analytes

Acronym	*Analyte*	*Chemical Abstract Services Registry Number (CASRN)*
PFBA (C4 Acid)	Perfluorobutanoic acid	375-22-4
PFPeA (C5 Acid)	Perfluoropentanoic acid	2706-90-3
PFHxA (C6 Acid)	Perfluorohexanoic acid	307-24-4
PFHpA (C7 Acid)	Perfluoroheptanoic acid	375-85-9
PFOA (C8 Acid)	Perfluorooctanoic acid	335-67-1
PFNA (C9 Acid)	Perfluorononanoic acid	375-95-1
PFDA (C10 Acid)	Perfluorodecanoic acid	335-76-2
PFUnA (C11 Acid)	Perfluoroundecanoic acid	2058-94-8
PFDoA (C12 Acid)	Perfluorododecanoic acid	307-55-1
PFTrDA (C13 Acid)	Perfluorotridecanoic acid	72629-94-8
PFBS (C4 Sulfonate)	Perfluorobutanesulfonic acid	375-73-5
PFHS (C6 Sulfonate)	Perfluorohexanesulfonic acid	355-46-4
PFOS (C8 Sulfonate)	Perfluorooctanesulfonic acid	1763-23-1
FBSA (C4 Sulfonamide	Perfluorobutanesulfonamide	30334-69-1
FOSA (C8 Sulfonamide)	Pefluorooctanesulfonamide	754-91-6

The Minimum Reporting Level (MRL) is the Limit of Quantitation (LOQ) that meets Data Quality Objectives (DQOs) that are developed based on the intended use of this method.

Method Flexibility – This is a performance-based method and may be generally applied to the determination of perfluorinated compounds in water matrices when analysis batch quality control (QC) criteria are met[2]. Each set of samples are prepared in an analysis batch with calibration standards, LCSs, blanks, and continuing calibration check standards analyzed on the same instrument during a time period that begins and ends with the analysis of the appropriate continuing calibration check standards. The laboratory is permitted to modify the LC column, mobile phase composition, LC conditions, and MS/MS conditions. Method modifications should be considered to improve method performance or to meet data quality objectives for the study. In all cases where method modifications are implemented, the batch

[1] The method is supported by validation with internal standard calibration for C4-C13 PFCAs, C4, C6, and C8 PFSAs, and C8 perfluoroalkane sulfonamide in laboratory control samples under 3M method validation E11-0667.

[2] Guidance for establishing method QC Criteria based on a.) FDA May 2001, "Guidance for Industry, Bioanalytical Method Validation", b.) EPA Method 537, and c.) European Commission: Guidance for Generating and Reporting Methods of Analysis in Support of Pre-registration Data Requirements for Annex II (Part A, section 4) and Annex III (Part A,section 5) of Directive 91/414, SANCO/3029/99 rev. 4 (11/07/00).

analytical QCs (section 9) must be completed and pass QC acceptance criteria (section 13) if the data from the analytical batch are to be reported.

2 Method Summary

Water samples are analyzed as neat aqueous sample or as solvent diluted aqueous samples by direct injection using LC/MS/MS. Samples containing heavy particulate may not be suitable for analysis by this method. Samples containing suspended particulate should be centrifuged or filtered prior to removing a sample aliquot or diluting with solvent. The water sample is mixed well prior to removing an aliquot or diluting, if necessary, with ASTM Type I water, HPLC water, other suitable water, or solvent (methanol).

Quantitation is by stable isotope internal standard calibration in laboratory reagent water. All perfluorinated compounds (PFCs) target analyte concentrations of perfluorosulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs) are reported as anions and corrected for their salt or free acid forms. Alternatively, quantitation may be performed by external standard calibration.

This is a performance-based method. Method uncertainty for each target analyte is determined for each analytical batch using multiple laboratory control spikes at multiple concentrations. This method also requires that the precision and accuracy for each sample be determined using field matrix spikes to verify that the method is applicable to each sample matrix.

Calibration standards for PFUnA, PFDoA, PFTrDA, and FOSA have been found to be unstable for more than 2 days in 100% water. Samples requiring analysis for these compounds by this method should be diluted 1:1 with methanol and analyzed against a calibration curve prepared in 1:1 synthetic groundwater:MeOH.

3 Definitions

3.1 Analysis Batch

A set of study samples that are prepared with calibration standards, laboratory control samples, and procedural blanks, and analyzed on the same instrument during a time period that begins and ends with the analysis of the appropriate continuing calibration check standards.

3.2 Analytical Sample

A portion of a laboratory sample prepared for analysis.

3.3 Calibration Standard

A solution prepared by spiking a known volume of the Working Standard (WS) into a predetermined amount of ASTM Type I, HPLC grade water, or other suitable water (i.e. matrix water), and analyzed according to this method. Calibration standards are used to calibrate the instrument response with respect to analyte concentration.

3.4 Laboratory Duplicate Sample (LDS, or Lab Dup)

A laboratory duplicate sample is a separate aliquot of a sample taken in the analytical laboratory that is analyzed separately with identical procedures. Analysis of LDSs 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.

3.5 Field Blank (FB)/Trip Blank (TB)

ASTM Type I, HPLC grade water, or other suitable 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 TB is to determine if test substances or other interferences are present in the field environment. This sample is also referred to as a Trip Blank.

3.6 Field Duplicate Sample (FDS, Field Dup)

A sample collected in duplicate at the same time from the same location as the sample. The FDS is handled under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analysis of the FDS 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.

3.7 Field Matrix Spike (FMS)

A sample to which known quantities of the target analytes, ISs and SRSs are added to the sample bottle in the laboratory before the bottles are sent to the field for collection of aqueous samples. A known, specific volume of sample must be added to the 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 is analyzed to ascertain if any matrix effects, interferences, or stability issues may complicate the interpretation of the sample analysis.

3.8 Trip Blank Matrix Spike (TBMS)

An aliquot of ASTM Type I, HPLC grade water, or other suitable water, to which known quantities of the target analytes, ISs and SRSs are added in the laboratory prior to the shipment of the collection bottles. The TBMS is analyzed exactly like a study sample to help determine if the method is in control and whether a loss of analyte or analytical bias could be attributed to sample holding time, sample storage and/or shipment issues. A low and high TBMS are appropriate when expected sample concentrations are not known or may vary.

3.9 Internal Standard (IS)

A compound added to each study sample, calibration standard, laboratory control samples, and procedural blanks at a consistent level (typically around 1 ng/mL). The internal standard(s) are stable isotope labeled versions of the target analytes. The area count ratio of the target analyte to the internal standard is used for calibration. Surrogate ISs are applied when stable isotope ISs of target analytes are unavailable. A surrogate IS is not necessarily a stable isotope labeled version of the target analyte, but is treated as an internal standard for quantitation.

3.10 Laboratory Control Sample (LCS)

An aliquot of control matrix to which known quantities of the target analytes, ISs and SRSs (when applicable) are added in the laboratory at the time when samples are aliquotted. At least three levels (two levels for SRSs) in triplicate are included, one generally at the low end of the calibration curve and one near the mid range and the upper end of the curve. The LCSs are analyzed exactly like a laboratory sample to determine whether the stability of the standards. LCSs should be prepared each day samples are aliquoted.

3.11 Laboratory Matrix Spike (LMS)

A laboratory matrix spike is an aliquot of a sample to which known quantities of target analytes, ISs and SRSs (when applicable) are added in the laboratory. The LMS is analyzed exactly like a laboratory sample to determine whether the sample matrix contributes bias to the analytical results. The endogenous concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LMS corrected for these concentrations. LMSs are optional for analysis of aqueous samples.

3.12 Laboratory Sample

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

3.13 Limit of Quantitation (LOQ)

The lower limit of quantitation (LLOQ) for an analytical batch is the lowest concentration that can be reliably quantitated within the specified limits of precision and accuracy. The LLOQ is generally selected as the lowest non-zero standard in the calibration curve that meets method acceptance criteria. The LLOQ for each target analyte is established for each analysis batch as the lowest calibration standard with area counts at least twice that of the average area counts of the procedural blanks.

The upper limit of quantitation (ULOQ) for an analytical batch is the highest concentration that can be reliably quantitated within the specified limits of precision and accuracy. The highest standard in the calibration curve that meets method acceptance criteria is defined as the ULOQ.

3.14 Method/Procedural Blank

An aliquot of control matrix 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.

3.15 Sample

A sample is an aliquot removed from a larger quantity of material intended to represent the original source material.

3.16 Stock Standard Solution (SSS)

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

3.17 Surrogate Internal Standard

An IS that is not necessarily a stable isotopically labeled target analyte, but is treated as an internal standard for quantitation. Surrogate ISs are used when isotopically labeled counterparts of the target analyte are not commercially or readily available.

3.18 Surrogate Recovery Standard (SRS)

An isotopically labeled standard, not used as an internal standard, that is added to each sample and appropriate QC sample as a means to evaluate the method performance for a chemical class of compounds (e.g., PFSAs, PFCAs).

3.19 Working Standard (WS)

A solution of several analytes prepared in the laboratory from SSSs 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. The analyst should wear gloves, a lab coat, and safety glasses to prevent exposure to chemicals that might be present.

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

The analyst must be familiar with the laboratory equipment and potential hazards including, but not limited to, the use of solvents, pressurized gas and solvent lines, high voltage, and vacuum systems. Refer to the appropriate equipment procedure or operator manual for additional information and cautions.

5 Interferences

During sample preparation and analysis, major potential contaminant sources are reagents and glassware. 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 or minimized 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

6.1 Instrumentation

Analytical balance capable of reading to 0.0001g

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

6.2 Supplies and Materials

Sample collection bottles—HDPE (e.g., Nalgene™) wide-mouth bottles with screw cap.
Note: Do not use fluorinated or Teflon® bottles or lined caps.

Coolers or boxes for sample shipment.

15-mL and 50-mL disposable polypropylene centrifuge tubes.

Class A pipettes and volumetric flasks, various.

2 mL HPLC autovials

Disposable pipettes, polypropylene or glass as appropriate

Centrifuge capable of spinning 15-mL and 50-mL polypropylene tubes at 3000 rpm.

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

Water – Milli-Q, HPLC grade, or other suitably appropriate sources

Calcium Acetate - A.C.S. Reagent Grade

Magnesium Acetate - A.C.S. Reagent Grade

Methanol – HPLC grade

Ammonium Acetate – A.C.S. Reagent Grade

7.2 Representative Target Analytes, ISs, and SRSs

PFBA, Heptafluorobutyric Acid, (C_4 Perfluorinated Acid)

PFPeA, Nonafluoropentanoic Acid (C_5 Perfluorinated Acid)

PFHxA, Perfluorohexanoic Acid (C_6 Perfluorinated Acid)

PFHpA, Tridecafluoroheptanoic Acid, (C_7 Perfluorinated Acid)

PFOA, Ammonium perfluorooctanoate, (C_8 Perfluorinated Acid)

PFNA, Heptadecafluorononanoic Acid, (C_9 Perfluorinated Acid)

PFDA, Nonadecafluorodecanoic Acid (C_{10} Perfluorinated Acid)

PFUnA, Perfluoroundecanoic Acid, (C_{11} Perfluorinated Acid)

PFDoA, Perfluorododecanoic Acid, (C_{12} Perfluorinated Acid)

PFTrDA, Perfluorotridecanoic Acid, (C_{13} Perfluorinated Acid)

FBSA, Perfluorobutanesulfonamide

FOSA, Perfluorooctanesulfonylamide

PFBS, Potassium Perfluorobutanesulfonate

PFHS, Perfluorohexanesulfonate

PFOS, Potassium perfluorooctanesulfonate

PFOA [1,2, 3, 4-^{13}C], $^{13}C_4$-isotopically labeled perfluorooctanoic acid (SRS)

PFOS [1,2, 3, 4-^{13}C], $^{13}C_4$-isotopically labeled Perfluorooctanesulfonate (SRS)

PFUnA [1,2-^{13}C], $^{13}C_2$-isotopically labeled Perfluoroundecanoic acid (SRS)

A custom mix of ISs in a methanolic solution containing ([1,2,3,4-$^{13}C_4$]PFBA, [1,2 - $^{13}C_2$]PFHxA, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA, [1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA, [1,2 - $^{13}C_2$]PFDA, [1,2,3,4,5,6,7 - $^{13}C_7$]PFUnA, [1,2 - $^{13}C_2$]PFDoA, [1,2,3 - $^{13}C_3$]PFHS, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOS, and [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOSA (Wellington Laboratories, Guelph, ON) in combination with added ([1,2,3,4,5-$^{13}C_5$]PFPeA, ([1,2,3,4-$^{13}C_4$]PFHpA, and [$^{18}O_2$]PFBS can be used to prepare a stock IS solution. Alternatively, individual stable isotope ISs can be used to prepare a stock IS mixture.

Other ISs can be applied.

7.3 Reagent Preparation

2 mM Ammonium acetate solution (Analysis)—Weigh 0.3 g of Ammonium acetate and dissolve in 2.0 L of reagent water.

Synthetic Groundwater (containing 25 ppm Ca and Mg) – Weigh 0.61 g of Calcium Acetate and 0.92 g of Magnesium Acetate and dissolve in 6.0 L of reagent water.

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

7.4 Stock Standard Solution (SSS) and Working Standard Solution Preparation

The following standard preparation procedure serves as an example. Weighed amounts and final volumes 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.

100 µg/mL target analyte SSSs—Weigh out 10 mg of analytical standard ***(corrected for percent salt, acid [ETS-4-031] and purity)*** and dilute to 100 mL with methanol or other suitable solvent, in a 100 mL volumetric flask. Transfer to a 125 mL LDPE bottle or other suitable container. Prepare a separate solution for each analyte. Expiration dates and storage conditions of stock solutions should be assigned in accordance with laboratory standard operating procedure. An example of purity and salt correction is given below for PFOS.

$$\text{salt correction factor} = \frac{\text{molecular weight of anion}}{\text{moclecular weight of salt}}$$

$$\text{PFOS } (K^+)\text{salt correction factor} = \frac{499}{538} = 0.9275$$

10 mg $C_8F_{17}SO_3^-K^+$ with purity 90% = 8.35 mg $C_8F_{17}SO_3^-$ (10 mg*0.90*0.9275=8.35 mg)

10 µg/mL (10,000 ng/mL) mixed working standard—Add 5.0 mL each of the 100 µg/mL SSSs to a 50 mL volumetric flask and bring up to volume with solvent.

1 µg/mL (1,000 ng/mL) mixed working standard—Add 0.5 mL of the 100 µg/mL SSSs to a 50 mL volumetric flask and bring up to volume with solvent.

0.1 µg/mL (100 ng/mL) mixed standard—Add 0.05 mL of the 100 µg/mL SSSs to a 50 mL volumetric flask and bring up to volume with solvent.

Storage Conditions—Store all SSSs and working standards in accordance with laboratory standard operating procedure or in a refrigerator at 4°±2°C for a maximum period of 6 months from the date of preparation.

7.5 Calibration Standards

Calibration can be performed by IS or external calibration. Using the working standards described above, prepare calibration solutions in ASTM Type I water, HPLC water, other suitable water, or a mixture of solvent and water using the information in Table 2 as a guideline. Note: Volumes of water or water/solvent mixtures and working standards may be adjusted to meet the data quality objectives addressed in the general project outline. Calibration levels other than those listed below can be prepared as needed.

For the quantitation of PFOA and PFOS, reference materials of certified mixed linear and branched isomer are preferred. Alternately, reference materials of primarily linear isomers of PFOA and/or PFOS may be used, however, when quantitating with predominantly linear reference standards, additional LCS samples containing both linear and branched isomers of PFOA and PFOS are required[3].

7.5.1 Internal Standard (IS) and Surrogate Recovery Standard (SRS)

For IS calibration, stable isotope internal standards of each target analyte or appropriate surrogate ISs should be spiked at the same level in all calibration standards. Once the calibration standards have been prepared as stated above in Section 7.5, all calibration standards are spiked with a separate internal standard spiking solution. Typically the

[3] A report summarizing an assessment of the use of reference standards containing certified linear and branched isomers of PFOA/PFOS can be found in 3M report E11-0560.

concentration of the internal standard is consistent with the internal standard concentration expected in the samples being prepared, usually 1 ng/mL. The concentration of the internal standard spiking solution is typically 2 µg/mL. A separate zero point or method blank is typically prepared at the same time as the calibration standards, using the same solution used to prepare the standards (ASTM Type I water, HPLC water, other suitable water, or a solvent/water mixture), and is spiked with the internal standard at the same concentration as the calibration curve, typically at 1 ng/mL.

If the samples being analzyed were pre-spiked with SRSs, the calibration curve prepared in Section 7.5 is spiked with a separate SRS spiking solution. Typically, the sample bottles are spiked with a SRS at 0.1 ng/mL. The final calibration curve must consist of at least six calibration points after analysis. The following table provides an example of spike concentrations and volumes used to achieve a multi-point extracted calibration curve with internal standard and surrogate standard.

Table 1 lists recommended stable isotope internal standards for several PFSA and PFCA target compounds. A custom mix of isotopically labeled target analytes in a methanolic solution containing ([1,2,3,4-$^{13}C_4$]PFBA, [1,2-$^{13}C_2$]PFHxA, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA, [1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA, [1,2,3,4,5,6-$^{13}C_6$]PFDA, [1,2,3,4,5,6,7-$^{13}C_7$]PFUnA, [1,2-$^{13}C_2$]PFDoA, [1,2,3-$^{13}C_3$]PFHS, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOS, and [1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA (Wellington Laboratories, Guelph, ON) in combination with added ([1,2,3,4,5-$^{13}C_5$]PFPeA, ([1,2,3,4-$^{13}C_4$]PFHpA, and [$^{18}O_2$]PFBS can be used to prepare a stock IS solution. Alternative sources of certified stable isotope labeled target analytes are applicable. Alternatively, individual stable isotope ISs can be used to prepare a stock IS mixture. The table below lists the recommended stable isotope ISs and SRSs applied in the method. Other stable isotope ISs and SRSs of target analytes not listed in the table may be used if supported by validation and/or analysis batch QCs meeting method acceptance criteria (e.g., [$^{13}C_2$]-PFOA). The same internal standard should be used for a given analyte throughout the entire project/study. Note: some of the compounds listed below are appropriate to use as surrogate ISs when a stable isotope IS of a target analyte is not available. Generally, surrogate isotopically labeled PFCAs are used for PFCAs, and surrogate isotopically labeled PFSAs are used for PFSAs.

Table 2 provides examples of spike concentrations and volumes used to achieve a multi-point calibration curve with ISs and SRSs.

Table 1. Stable Isotope PFCAs and PFSAs used for ISs and SRSs

Compound Name	*Synonym or Acronym*	*Analytical Purpose*	*Reference Standard Source*
$^{13}C_4$-Perfluorobutanoic acid	[1,2,3,4-$^{13}C_4$]PFBA	IS for PFBA	Wellington Labs (Mix or Individual)
$^{13}C_4$-Perfluoropentanoic acid	[1,2,3,4,5-$^{13}C_5$]PFPeA	IS for PFPeA	Wellington Labs (Mix or Individual)
$^{13}C_2$-Perfluorohexanoic acid	[1,2 -$^{13}C_2$]PFHxA	IS for PFHxA	Wellington Labs (Mix or Individual)
$^{13}C_4$-Perfluoroheptanoic acid	[1,2,3,4-$^{13}C_4$]PFHpA	IS for PFHpA	Wellington Labs (Mix or Individual)
$^{13}C_8$-Perfluorooctanoic acid	[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA	IS for PFOA and [1,2,3,4 $^{13}C_4$]PFOA	Wellington Labs (Mix or Individual)
$^{13}C_9$-Perfluorononanoic acid	[1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA	IS for PFNA	Wellington Labs (Mix or Individual)
$^{13}C_6$-Perfluorodecanoic acid	[1,2,3,4,5,6 -$^{13}C_6$]PFDA	IS for PFDA	Wellington Labs (Mix or Individual)
$^{13}C_7$-Perfluoroundecanoic acid	[1,2,3,4,5,6,7 -$^{13}C_7$]PFUnA	IS for PFUnA	Wellington Labs (Mix or Individual)
$^{13}C_2$-Perfluorododecanoic acid	[1,2 -$^{13}C_2$]PFDoA	IS for PFDoA, *PFTA	Wellington Labs (Mix or Individual)
$^{18}O_2$-Ammonium Perfluorobutane sulfonate	[$^{18}O_2$]PFBS	IS for PFBS	RTI International (Individual)
$^{13}C_3$-Ammonium Perfluorohexane sulfonate	[1,2,3-$^{13}C_3$]PFHS	IS for PFHS	Wellington Labs (Mix or Individual)
$^{13}C_8$-Sodium Perfluorooctane sulfonate	[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOS	IS for PFOS and PFOS[1,2,3,4 $^{13}C_4$],	Wellington Labs (Mix or Individual)
$^{13}C_8$-Perfluorooctanesulfonamide	[1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA	IS for FOSA	Wellington Labs (mix) RTI International (Individual)
$^{13}C_4$-Perfluorooctanoic acid	[1,2,3,4-$^{13}C_4$]PFOA	SRS for all PFCAs: C4-C8	Wellington
$^{13}C_7$-Perfluoroundecanoic acid	[1,2 -$^{13}C_2$]PFUnA	SRS for all PFCAs C9-C13	Wellington
$^{13}C_8$-Perfluorooctane sulfonate	[1,2,3,4-$^{13}C_4$]PFOS	SRS for all PFSAs: C4, C6, and C8	Wellington

Table 2. Example Preparation of Calibration Curve with ISs and SRSs

Sample Description	*Concentration of WS, µg/mL*	*Volume of WS, µL*	*Volume of IS (2 µg/mL), µL*	*Concentration of Surrogate, µg/mL*	*Volume of Surrogate, µL*	*Volume of ASTM Type I Water, or other suitable solvent (1), mL*
0.025 ng/mL curve point	0.10	25	50	0.20	12.5	100
0.030 ng/mL curve point	0.10	30	50	0.20	15	100
0.04 ng/mL curve point	0.10	40	50	0.20	20	100
0.05 ng/mL curve point	0.10	50	50	0.20	25	100
0.1 ng/mL curve point	0.10	100	50	0.20	50	100
0.25 ng/mL curve point	0.10	250	50	0.20	125	100
0.5 ng/mL curve point	1.0	50	50	0.20	250	100
1 ng/mL curve point	1.0	100	50	0.20	500	100
2.5 ng/mL curve point	10.0	25	50	10.0	25	100
5.0 ng/mL curve point	10.0	50	50	10.0	50	100
10.0 ng/mL curve point	10.0	100	50	10.0	100	100
25.0 ng/mL curve point	10.0	250	50	10.0	NA	100
50.0 ng/mL curve point	10.0	500	50	10.0	NA	100
75.0 ng/mL curve point	10.0	750	50	10.0	NA	100
100 ng/mL curve point	10.0	1000	50	10.0	NA	100

N/A - Not Applicable
(1) Samples requiring analysis for PFUnA, PFDoA, PFTrDA, and FOSA should be analyzed against a calibration curve prepared in 1:1 synthetic groundwater:MeOH.

8 Sample Collection and Bottle Preparation

Sample collection bottles are prepared by 3M Environmental Laboratory (or subcontract supplier) personnel for shipment at ambient temperature to the collection site. Typically, four separate collection bottles are associated with a single collection site: sample, field duplicate sample, low field matrix spike, and high field matrix spike. Alternatively, the sample and field duplicate sample may contain SRSs in lieu of additional target analyte low field matrix spike and target analyte high field matrix spike samples. Depending on the scope of the project, additional replicates of the field sample and field matrix spikes may be added. Also, it is not uncommon for additional mid-level field matrix spikes to be collected if the expected sample concentrations are truly unknown or could span a large concentration range.

High-density polyethylene (HDPE) wide-mouth Nalgene bottles are used for the sample collection containers. (Volumes of the bottles may vary depending on how much sample is required to meet data quality objectives.) Sample collection volumes are project specific and based on data quality objectives. The Nalgene bottles do not require any pretreatment prior to use. Typically, placement of a sample bottle volumetric "fill to here" line is done by using a sample bottle marker template. Alternatively, bottles may be weighed prior to bottle preparation and weighed again after samples have been collected.

All bottles should be clearly labeled to indicate its intended use as a sample, field sample duplicate, low field matrix spike, high field matrix spike, sample/SRS field matrix spike, field duplicate sample/SRS field matrix spike, trip blank, or trip blank matrix spike. If each location has different designated spike levels, the label should also clearly indicate the sample location designation. Generally, a set of bottles for a given collection site are prepared then grouped together in plastic bags for organizational purposes. For each sample collection event, at least one set of trip blank and trip blank matrix spikes are prepared.

Bottle preparation should be documented in a Note to File or on a sample preparation worksheet and should include the following information: date prepared, total number of bottles prepared, number of sample sites, the standard identification numbers and spike volumes used to prepare spiked bottles, the "fill to here" volume, and any other pertinent information needed for reconstructibility of the data. The Note to File will be included in the final data package for the project.

Samples are collected in the field and shipped to the laboratory at ambient temperature.

8.1 Field Matrix Spike Sample (FMS)

Field matrix spike samples are a requirement of the method. A FMS sample is defined as a QC sample to which known quantities of appropriate target analytes are added to the sample bottle in the field or in the laboratory before the bottles are sent to the field. The sample and field duplicate sample may contain appropriate SRSs in lieu of target analyte FMS samples. Sample quantities are determined volumetrically or gravimetrically. A known, specific volume or weight of sample is added to the sample container without rinsing. Volumetric sample measurements may be acquired by a laboratory applied "fill to this level" line on the outside of the sample container. Target analyte FMS samples should be spiked at approximately 0.5-10 times the expected analyte concentration in the sample. If the expected range of analyte concentrations is unknown, multiple spikes at varying levels may be prepared to increase the likelihood that a spike at an appropriate level is made. Typically a low and a high target analyte spike are prepared for each sampling location. In those instances where SRSs are to be used in lieu of target analyte FMS samples, the sample and field duplicate sample are spiked at approximately 2-5 times the target LOQ. The FMS is analyzed to ascertain if matrix effects or sample holding time contributes bias to the analytical results. For the sample bottles designated for matrix spikes, an appropriate volume of matrix spiking solution is added to the empty bottle prior to sampling. The volume of spike solution added should produce the desired final concentration of target analytes once the bottle is filled with sample to the "fill to here line". The matrix spiking solution(s) should be prepared in a suitable solvent and contain all of the appropriate target analytes, ISs, and SRSs. The target analyte matrix spiking solution is often the same as the working standards used to create the calibration standards. An example of a bottle spike is given below.

"Fill to here" volume = 200 mL (A 250 mL Nalgene bottle is used)

Desired Field Spike Concentration = 0.25 ng/mL

500 µL of a 0.1 µg/mL spiking solution (containing the target analytes) is added to the bottle and the bottle cap promptly sealed.

8.2 Internal Standard and Surrogate Recovery Standard

If analysis of a surrogate recovery standard (SRS) is included in the project objectives, an appropriate volume of a surrogate standard solution is added to all the bottles prior to sampling and SPE. Typically sample bottles are spiked with surrogate recovery standards at a final desired spike concentration of 0.1 ng/mL.

If quantitation by internal standard (IS) is included in the project objective, an appropriate volume of internal standard solution is added to all the bottles prior to sampling and SPE. Typically sample bottles are spiked with internal standard at a final desired spike concentration of 1 ng/mL.

For the trip blank, the SRS spike and IS spike is added to the bottle and then ASTM Type I water (HPLC grade reagent water or other suitable water may used) is added to the "fill to here" line. The bottle is capped and sealing tape may be placed around the outer edge of the cap. Trip blank matrix spikes are prepared by adding the appropriate volume of target analyte spiking solution, IS, and SRS spiking solutions and filling the bottle to the desired volume with the appropriate water and capping and sealing the cap.

9 Quality Control and Data Quality Objectives

9.1 Data Quality Objectives

This method and required quality control samples is designed to generate data accurate to ±30% with a targeted LOQ of 0.025 ng/mL. Any deviations from the quality control measures spelled out below will be documented in the raw data and footnoted in the final report.

9.2 Method/Procedural Blanks

The method/procedural blank is zero point calibration standard (which includes ISs) analyzed in a regular basis with each analysis batch. At a minimum, method blanks are analyzed prior to instrument calibration, prior to the analysis of CCV samples, after every 10 sample injections, and at the end of the analytical run.

The mean area count or area ratios when using internal standard calibration, for each analyte in the method blanks must be less than 50% of the area count counts or area ratios when using internal standard calibration, of the LOQ standard. The standard deviation of the area counts, or area ratios when using internal standard calibration, of these method blanks should be calculated. A specific %RSD acceptance criteria is not specified but is assessed on an analytical batch basis. If the mean area counts or area ratios when using internal standard calibration, of the method blanks exceed 50% of the LOQ standard, then the LOQ must be raised to the first standard level in the curve that meets criteria. Method blanks may be eliminated if technical justification can be provided (e.g. the procedural blank was analyzed after an unexpectedly high level sample). If any procedural blanks are removed from the LOQ determination, document in the raw data and report as appropriate. Laboratory Sample Replicates / Field Duplicate Sample

Typically, samples are collected in duplicates in the field. The relative percent difference (RPD) of duplicate samples should be ≤20% for the precision of sample preparation and analysis to be considered in control. Replicate samples not meeting the ≤20% RPD criteria are flagged and reported as outside of QC acceptance criteria.

9.3 Laboratory Matrix Spikes (LMSs)

LMSs may be performed in lieu of FMSs if FMSs have previously been performed for the sample matrix. Additionally, LMSs may be performed in lieu of FMSs for a sample matrix if the FMS levels were not appropriate for determining spike recoveries relative to endogenous levels of target analytes and appropriate SRSs. Generally, each sample location represents a different sample and sample matrix. LMSs are prepared for each sample and analyzed to determine the matrix effect on spike recovery efficiency of each target analyte and appropriate SRSs. LMSs should be prepared at a minimum of one level and in duplicate. LMS concentrations should be prepared at approximately 0.5-10 times the endogenous concentration or approximately 4-10 times the LOQ concentration of each target analyte.

Lab matrix spike recoveries should fall within ± 30% of expected values. Sample data with LMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria. Data with LMS recovery outside of ±50% of the expected value are reported as NR, where NR is defined as "Not Reportable" data outside of QC acceptance criteria.

9.4 Lab Control Sample

Lab control spikes are prepared for each analysis batch to determine method accuracy and precision. LCSs should be prepared at three levels in triplicate for each target analyte and at a minimum of two levels in triplicate for appropriate SRSs. Low lab control spikes should be prepared at a concentration in the range of approximately four to ten times higher than the targeted lower LOQ, the mid lab control spikes should be prepared at a concentration near the mid-point of the calibration curve and the high lab control spikes at approximately 80% of the upper LOQ. For each target analyte and SRSs, the percent relative standard deviation (method precision) for each control spike level must be less than or equal to 20% and the average recovery (method accuracy) for each control spike level must be 80-120%. Sample data for target analytes outside of the laboratory control spike acceptance criteria will be handled as follows:

If the average recovery of a spiking level falls outside method acceptance, but at least 67% (6 out of 9) of LCS samples are within 20% of their respective nominal value (33% of the QC samples, not all replicates at the same concentration, may be outside 20% of nominal value), the average recovery will be flagged as outside method acceptance criteria. All LCS samples will be control charted as per ETS-4-026. If the average recovery of one of the spiking levels exceeded the analytical method uncertainty as determined by ETS-12-012, that analytical batch uncertainty will be expanded for that particular study.

If more than 67% of the LCS samples fail to meet method acceptance criteria, the data will not be reported.

Calibration standards consisting of mixed branched and linear isomer PFOS/PFOA are preferred. However, for PFOS/PFOA target analytes, if the calibration standards are comprised of predominantly linear isomers only, at least one level of triplicate LCSs should be prepared using PFOS/PFOA which contains a mix of linear and branched isomers. These LCSs will be used to demonstrate quantitative equivalency (or quantitative bias) of the isomeric mix when using a predominantly linear standard for calibration. The mixed linear and branched isomer PFOS/PFOA LCSs recoveries should fall within ± 30% of expected values. Alternatively, in lieu of mixed branched and linear isomer PFOS/PFOA LCSs, mixed branched and linear isomer PFOS/PFOA TBMSs may be applied to demonstrate method accuracy and precision.

9.5 Field Matrix Spikes (FMSs) / Surrogate Recovery Standards (SRSs)

FMSs are prepared for each sampling location and analyzed to determine the matrix effect and sample holding time on the spike recovery of each target analyte and/or appropriate SRS. Generally, each sample location represents a different sample and sample matrix.

FMSs are QC samples to which known quantities of appropriate target analytes are added to the sample bottle in the laboratory before the bottles are sent to the field. Typically a low and a high target analyte FMS are prepared for each sampling location. The sample and field duplicate sample may contain appropriate SRSs in lieu of target analyte low field matrix spike and target analyte high field matrix spike samples.

Field matrix spike method acceptance criteria are recoveries within ±30% of the expected value. If FMS recovery (target analyte or SRS spike) is outside of ±30% of the expected value or could not be assessed because the FMS (target analyte) was spiked at an inappropriate level, the sample result is reported as follows:

1.) If target analyte FMS recovery could not be assessed because the FMS's were at an inappropriate level, then Laboratory Matrix Spikes (LMS) may be substituted. If LMS recoveries are within ±30% the data are reportable and flagged to indicate that the FMS spikes levels were inappropriate.

2.) If multiple target analyte FMS's were prepared on a sample and the closest FMS level to the reported sample meets the ±30% acceptance criteria but additional FMS's are outside the ±30% acceptance range, the data are reportable and flagged to indicate that while there were failing FMS's, the uncertainty will not be expanded since the most appropriate spike level passed.

3.) If the target analyte FMS recoveries are outside of the ±30% acceptance range but at least 30 acceptable historical reportable FMS sample results are available, the data may be reported but flagged with an expanded uncertainty and as not meeting FMS criteria.

4.) Sample data with FMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria with an expanded uncertainty.

5.) If FMS recovery is outside of ±50%, the sample result is reported as NR, where NR is defined as "Not Reportable" due to noncompliant QC results.

The targeted fortification levels should be at least 50% of the endogenous level and less than 10 times the endogenous level to be used without justification to determine the statement of accuracy for analytical results.

Note: It is possible for bottles utilized for Field Matrix Spike samples to be under-filled or over-filled during sample collection. Since this scenario will effect the actual concentration of the FMS sample (surrogate and internal standard concentrations will also be effected, if used), it is important that any obvious under-filling or over-filling of sample bottles be documented in the data package and taken into account in the FMS, ISs, or SRSs recovery calculations. Samples over-filled or under-filled by more than 10% will be require recalculation of the FMS, ISs, and SRS true values.

The average of the sample and the field duplicate should be used to calculate the recovery.

10 Procedures

10.1 Water Sample Preparation

This method is applicable to water samples. Samples containing heavy particulate may not be suitable for analysis by this method. Samples containing suspended particulate should be centrifuge prior to removing a sample aliquot, or filtered.

- Thoroughly mix sample before removing an aliquot and placing in a labeled autovial.
- Dilute sample, if necessary, with ASTM Type I water, HPLC water, other suitable water, or solvent (methanol).
- Lab control spikes are prepared for each analysis batch to determine method accuracy and precision. LCSs should be prepared at three levels in triplicate for each target analyte and at a minimum of two levels in triplicate for appropriate SRSs. Low lab control spikes should be prepared at a concentration in the range of approximately four to ten times higher than the targeted lower LOQ, the mid lab control spikes should be prepared at a concentration near the mid-point of the calibration curve and the high lab control spikes at approximately 80% of the upper LOQ. For IS quantitation, stable isotope internal standards of each target analyte or appropriate surrogate ISs should be spiked at the same level as the samples being analyzed, in all LCSs.
- If LCSs are being prepared using synthetic groundwater, allow the LCSs samples to equilibrate for a minimum of 4 hours before aliquoting for analysis or diluting with solvent (methanol).

11 Sample Analysis - LC/MS/MS

11.1 Instrument Setup

Note: In this example, an Applied Biosystems Sciex API 4000 (API 5000 or API 5500) Tandem Mass Spectrometer (LC/MS/MS) is used. Other brands/models of LC/MS/MS instruments as well as single quadrupole mass spectrometers (LC/MS) may be used as long as the method acceptance 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: Applied Biosystems API 4000, API 5000, or API 5500

Ion Source: Turbo Ion Spray (ABS)

Mode: Electrospray Negative

Scan Type: MRM (Multiple Reaction Monitoring)

Computer: Dell DHM

Software: Windows 2000 or Windows XP, Analyst 1.4.2 or higher versions

HPLC: Agilent Series 1100,1200, or 1290

Agilent Quaternary Pump

Agilent Vacuum Degasser

Agilent Autosampler

Agilent Column Oven

Note: One or more C18 HPLC analytical columns (2.1 mm x 100 mm, 5µm or 2.1 mm x 50 mm, 5µm) may be attached on-line after the purge valve and before the sample injection port to retard and separate any residue contaminants that may be in the mobile phase and/or HPLC system.

HPLC Column: Betasil C18, 4.6mm x 100mm, 5µm (ThermoElectron Corporation)

Column Temperature: 35°C

Injection Volume: 5µL

Mobile Phase (A): 2mM Ammonium Acetate in ASTM Type I water (See 7.3)

Mobile Phase (B): Methanol

Table 3. Liquid Chromatography Gradient Program.

Step Number	*Total Time (min)*	*Flow Rate (µL/min)*	*Percent A (2 mM ammonium acetate)*	*Percent B (Methanol)*
0	0	750	97.0	3.0
1	2.0	750	97.0	3.0
2	14.5	750	5.0	95.0
3	15.5	750	5.0	95.0
4	16.5	750	97.0	3.0
5	20.0	750	97.0	3.0

Note: Other HPLC gradients may be used as long as the method criteria and project data quality objectives 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.

Table 4 Suggested MRM Transitions for Target Analytes, Surrogates, and Internal Standards

Analyte	*Analyte Description*	*Mass Transition Q1 (amu)*	*Mass Transition Q3 (amu)*
PFBA (C4 Acid)	Target	213	169
PFPeA (C5 Acid)	Target	263	219
PFHxA (C6 Acid)	Target	313	269, 119
PFHpA (C7 Acid)	Target	363	319, 169
PFOA (C8 Acid)	Target	413	369, 219, 169
PFNA (C9 Acid)	Target	463	419, 169, 219
PFDA (C10 Acid)	Target	513	469, 269, 219
PFUnA (C11 Acid)	Target	563	519, 269, 219
PFDoA (C12 Acid)	Target	613	569, 169, 319
PFTA (C13 Acid)	Target	663	619, 369, 319
FBSA (C4 Sulfonamide)	Target	298	78
FOSA (C8 Sulfonamide)	Target	498	78
PFBS (C4 Sulfonate)	Target	299	99, 80
PFHS (C6 Sulfonate)	Target	399	99, 80
PFOS (C8 Sulfonate)	Target	499	80, 99, 130
[1,2,3,4 -$^{13}C_4$]PFBA	IS for PFBA	217	172
[1,2,3,4,5 -$^{13}C_5$]PFPeA	IS for PFPeA	268	223
[1,2 -$^{13}C_2$]PFHxA	IS for PFHxA	315	270
[1,2,3,4- $^{13}C_4$]PFHpA	IS for PFHpA	367	322
[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA	IS for PFOA	421	376
[1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA	IS for PFNA	472	427
[1,2,3,4,5,6 -$^{13}C_6$]PFDA	IS for PFDA	519	474
[1,2,3,4,5,6,7 -$^{13}C_7$]PFUnA	IS for PFUnA	570	525
[1,2 -$^{13}C_2$]PFDoA	IS for PFDoA and PFTA	615	570
[$^{18}O_2$]PFBS	IS for PFBS	303	84
[1,2,3-$^{13}C_3$]PFHS	IS for PFHS	402	80
[1,2,3,4- $^{13}C_4$]PFOS	IS for PFOS	503	80
[1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA	IS for FOSA	507	80
[1,2,3,4-$^{13}C_4$]PFOA	Surrogate (C4-C8 Acids)	417	372
[1,2,3,4- $^{13}C_4$]PFOS	Surrogate(Sulfonates, FOSA)	503	80
[1,2 -$^{13}C_2$]PFUnA	Surrogate (C9-C13 Acids)	565	520

Multiple transitions for monitoring the analytes is an option. The use of one daughter ion is acceptable if data sensitivity and selectivity is achieved and provided that retention time criteria are met to assure adequate specificity. While the daughter ions may be chosen at the discretion of the analyst, mass transition 99 is suggested for PFOS. Quantitation may be performed using the total ion chromatogram (TIC, or summed MRMs) for a given analyte. For example, the PFOA TIC would sum all three of the monitored transitions. 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 and the gradient, column, guard column(s) used 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.

11.2 Calibration Curve

Quantitation is by internal standard or external standard calibration. Calibration standards may be prepared in ASTM Type I, HPLC water, other suitable water, or a solvent/water mixture. If internal standard calibration does not meet calibration acceptance criteria, external calibration can be applied. See Table 1 for

recommended application of available internal standards. Quantitation of PFOA and PFOS is by summed analyte-specific mass transitions.

Analyze the standard curve prior to each set of samples. If internal standards were added to the calibration standards area ratios are used to generate the calibration curve. The standard curve may be plotted using a linear regression ($y = mx + b$), weighted 1/x or unweighted, or by quadratic fit ($y = ax^2 + bx + c$), weighted 1/x or unweighted, using suitable software. 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.

High and/or low points may be excluded from the calibration curves to provide a better fit over the 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 (or area ratio if quantitating by IS) are not at least twice that of the average area counts (or area ratio if quantitating by IS) of method and/or solvent blanks. The coefficient of determination (r^2) value for the calibration curve must be greater than or equal to 0.990 (or a correlation coefficient (r) of 0.995). Each point in the curve must be within ±25% of the theoretical concentration with the exception of the LLOQ, which may be within ±30%. 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.

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

11.3 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. Samples must be bracketed by passing CCVs or the calibration curve and a passing CCV to be reportable.

11.4 System Suitability

A minimum of three system suitability samples should be injected at the beginning of each analytical run, prior to the analysis of the calibration curve. Typically these samples are at a concentration near the mid-level of the calibration curve and are repeated injections from one autosampler vial. It is suggested that the system suitability injections have area counts or area ratios when using internal standard calibration, with a target RSD of ≤5% and a target retention time RSD of ≤2%. There is no defined acceptability limit on these results as the %RSD value is dependent on the number of MRM transitions being monitored in the LC/MS/MS run or time period. Ultimately, any effects on these parameters for the System Suitability samples will also be evident on all standards and QC samples analyzed as part of the analysis batch. Any effect of system suitability is incorporated within QC acceptance criteria.[4]

11.5 Sample Analysis and QCs

For each analysis batch, the instrument analysis run sequence should include an initial calibration curve, samples, FDSs, interspersed blanks, interspersed CCVs, appropriate QCs (i.e., LCSs, LMSs, FMSs, TBMSs, and TBs), and a final CCV or calibration curve bracketing samples and appropriate QCs

Inject the same volume (between 5 - 100µL) of each standard, analytical sample and blank into the instrument (unless an on-instrument sample dilution is desired).

Samples containing analytes that are quantitated above the concentration of the highest standard in the curve should be further diluted and reanalyzed.

[4] 3M Environmental Laboratory study E08-0096 evaluated the effect on these results as a function of the number of MRMs being monitored.

12 Data Analysis and Calculations

The chromatography analysis software will typically calculate the amount of target analyte in the sample extracts using the established calibration curve.

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

$$\text{LCS\% recovery} = \frac{\text{LCS Concentration } (\frac{ng}{mL})}{\text{Spike Concentration } (\frac{ng}{mL})} * 100\%$$

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

$$\text{LMS \% recovery} = \frac{\text{LMS Concentration } (\frac{ng}{mL}) - \text{Concentration of Sample } (\frac{ng}{mL})}{\text{Spike Concentration } (\frac{ng}{mL})} * 100\%$$

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

$$\text{Recovery} = \frac{\text{Total analyte found (ng/mL) - Average analyte found in sample (ng/mL)}}{\text{Analyte added (ng/mL)}} \times 100$$

13 Analysis Batch Method Performance Criteria

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 the final report if the Technical Manager (non-GLP study) or Study Director (GLP study) chooses to report 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 appropriate. 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 – Analysis Batch

A minimum of three system suitability samples should be injected at the beginning of each analytical run. These samples are run prior to the calibration curve. It is suggested that the system suitability injections have area counts with a target RSD of ≤5% and a target retention time RSD of ≤2%. There is no defined acceptability limit on these results as the %RSDs are dependent on the number of MRM transitions being monitored in the LC/MS/MS run or time period. Any effect of system suitability is incorporated in the QC acceptance criteria.

13.2 Calibration and Limit of Quantitation (LOQ) – Analysis Batch

Calibration Curve: The coefficient of determination (r^2) value for the calibration curve must be greater than or equal to 0.990 corresponding to a correlation coefficient (r) = 0.995. Each point in the curve must be within ±25% of the theoretical concentration with the exception of the LLOQ, which may be within ±30%.

CCV Performance: The calibration standards that are interspersed throughout the analytical sequence are evaluated as continuing calibration verifications in addition to being part of the calibration curve. The accuracy

of each curve point must be within 25% of the theoretical value (within 30% for lowest curve point). Samples that are bracketed by CCVs not meeting these criteria must be reanalyzed.

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 average area counts for all prepared procedural blank(s). By definition, the measured value of the LLOQ must be within 30% of the theoretical value.

Demonstration of Specificity: Specificity is demonstrated by chromatographic retention time (within 4% of standard) and the mass spectral response of unique ions.

13.3 Blanks – Method/Procedural Blanks and Trip

Method/Procedural Blanks: Multiple procedural blanks should be interspersed throughout the analysis batch and the analytical sequence. At a minimum, method blanks are analyzed prior to instrument calibration, prior to the analysis of CCV samples, after every 10 sample injections, and at the end of the analytical run.

The mean area counts (or area ratios when using IS calibration) for each analyte must be less than 50% of the area count of the LOQ standard. If the area counts of the procedural blanks exceed 50% of the LOQ standard, then the LOQ must be raised to the first standard level that meets criteria.

Trip Blank: A trip blank of ASTM Type I water (or lab equivalent) is prepared in a sample container in the laboratory and treated as a sample, including exposure to shipping, sampling site conditions, storage, preservation and all analytical procedures. The trip blanks results for each analyte are included with the reported sample results.

13.4 Data Accuracy and Precision – Analysis Batch

Lab Control Spikes: The average recovery at each LCS level for each target analyte and appropriate SRS should be within 80-120% and the percent relative standard deviation of the recoveries must be less than or equal to 20%. If the average recovery of a spiking level falls outside method acceptance, but at least 67% (6 out of 9) of LCS samples are within 20% of their respective nominal value (33% of the QC samples, not all replicates at the same concentration, may be outside 20% of nominal value), the average recovery will be flagged as outside method acceptance criteria. All LCS samples will be control charted as per ETS-12-012. If the average recovery of one of the spiking levels exceeded the analytical method uncertainty as determined by ETS-12-012, that analytical batch uncertainty will be expanded for that particular study. The average recovery at each LCS level for mixed branched/linear isomer PFOA and PFOS should be within 70-130% and the percent relative standard deviation of the recoveries must be less than or equal to 20%.

Field Duplicates: The relative percent difference (RPD) of duplicate samples should be less than 20% for the precision of sample preparation and analysis to be considered in control. Replicate samples not meeting the 20% RPD criteria are flagged and reported as outside of QC acceptance criteria.

Field Matrix Spikes: FMS acceptance criteria are recoveries within ±30% of the expected value for each target analyte and appropriate SRS. Sample data with FMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria. Data with FMS recovery outside of ±50% of the expected value are reported as NR, where NR is defined as "Not Reportable" data outside of QC acceptance criteria. If FMS recovery could not be assessed because FMSs were at an inappropriate level, then Laboratory Matrix Spikes (LMSs) may be substituted. If LMS recoveries are within ±30% for each target analyte and SRSs the data are reportable but flagged as not meeting the FMS method acceptance criteria.

13.5 Analytical Method Uncertainty

Analytical method uncertainty for each target analyte and SRS is determined with control charted historical analysis batch LCS data for the method and reported with each analysis batch.[5] Uncertainty determinations

[5] Method uncertainty based on INTERNATIONAL ANS/ISO/IED STANDARD 17025 reference (GUM, Guide to the Expression of Uncertainty in Measurement). Method application demonstrated in ETS-12-012, citing references: a.) EURACHEM/CITAC Guide, "Quantifying Uncertainty in Analytical Measurement," Second Edition; Editors: S.L.R. Ellison, M. Rosslein, and A. Williams. b.)Georgian, Thomas, "Estimation of Laboratory Analytical Uncertainty Using Laboratory Control Samples," Environmental Testing &

are based on INTERNATIONAL ANS/ISO/IED STANDARD 17025 reference (GUM, Guide to the Expression of Uncertainty in Measurement) and described in ETS-12-012. At least thirty data points are required for determining analytical method uncertainty. The method uncertainty is defined as 2x the standard deviation of the percent recoveries of the pooled lab control spikes. While all LCS data points are control charted, only the most recent fifty data points are used for determining the method uncertainty.

When less than thirty LCS data points have been generated for a given analyte, the analysis batch LCSs are used to determine the data uncertainty. If FMSs meet the ±30% recovery criteria at a level appropriate to the endogenous level, and the LCS meet the ±20% recovery criteria, then the uncertainty of the data is determined as within 100±20%.

Analysis batch sample data with FMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria with expanded uncertainties. Data with FMS recovery outside of ±50% of the expected value are reported as NR, where NR is defined as "Not Reportable" data outside of QC acceptance criteria. If FMS recovery could not be assessed because FMSs were at an inappropriate level, then Laboratory Matrix Spikes (LMSs) may be substituted. If LMS recoveries are within ±30% for each target analyte and appropriate SRSs the data are reportable but flagged as not meeting the FMS method acceptance criteria with uncertainties of ±30%. If FMS do not meet the ±30% recovery criteria, and historical FMS data does not exist, the analytical uncertainty is evaluated on a sample-by-sample basis, the data may be reported with expanded uncertainty and are flagged.

13.6 Quantitation of PFOA/PFOS – Analysis Batch

Calibration standards consisting of mixed branched and linear isomer PFOS/PFOA are preferred. Quantitation is performed by integrating the linear and branched isomers together. Alternately, the linear and branched isomers can be integrated separately, applying the appropriate true value to each calibration curve point for each isomer. The LCS and samples are then quantitated by integrating the linear and branched isomers separately (requires separate analytical results files) and quantitating the resulting peak against the linear or branched calibration curve. The results from both integrations are then summed to produce the final result. Integrating the linear and branched isomers separately may be helpful for those samples where the linear/branched ratios do not closely match those of the reference standards.

However, for PFOS/PFOA target analytes, if the calibration standards are comprised of predominantly linear isomers only the method requires the addition of LCSs of mixed branched/linear isomer PFOS/PFOA. The purpose of including these LCSs is to demonstrate quantitative equivalency (or quantitative bias) of the isomeric mix when using a predominantly linear PFOS or PFOA standard for calibration. Alternatively, in lieu of mixed branched and linear isomer PFOS/PFOA LCSs, mixed branched and linear isomer PFOS/PFOA TBMSs may be applied to demonstrate method accuracy and precision.

An alternate method of quantitation can be performed whereby only the linear isomer of PFOS/PFOA is integrated and used for generating the calibration curve. The LCS and samples are then quantitated by integrating the linear and branched isomers separately (requires separate analytical results files) and quantitating the resulting peak against the linear calibration curve. The results from both integrations are then summed to produce the final result. Integrating the linear and branched isomers separately reduces the on-column concentration for those samples that contain both linear and branched isomers of PFOA/PFOS. This ensures that the concentration detected is within the a range of the calibration curve that is comparable regardless of whether the calibration curve was generated using predominantly linear isomers of PFOS/PFOA or linear plus branched isomers of PFOS/PFOA.

14 Pollution Prevention and Waste Management

Waste generated when performing this method will be disposed of appropriately. The original samples will be archived at the 3M Environmental Laboratory in accordance with internal procedures.

Analysis, November/December 2000. c.)Taylor, B.N. and CE. Kuyatt, NIST Technical Note 1297, 1994 Edition: "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results."d.)Adams, T.M., "A2LA Guide for the Estimation of Measurement Uncertainty in Testing", July 2002.

15 Records

Each data package generated for a study must include all supporting information for reconstruction of the data. Information for the data package must include, but is not limited to the following items: study or project number, sample and standard prep sheets/records, instrument run log (instrument batch records, instrument acquisition method, summary pages), instrument results files, chromatograms, calibration curves, and data calculations.

16 Affected Documents

None.

17 Revisions

Revision Number	Summary of Changes
1	*Section 1. Included the use of internal standard calibration by this method.* *Section 2. Included the use of internal standard calibration by this method. Included the use of a solvent/water mixture when analyzing for PFUnA, PFDoA, PFTrDA, and FOSA.* *Section 3. Added definitions for internal standard, surrogate internal standard, and surrogate recovery standard.* *Section 6.Removed the details regarding the instrument parameters to section 10 of the method.* *Section 7. Updated reference standards to include internal standards and surrogates. Changed concentration levels for working standards and included the use of internal standards and surrogates.* *Section 8. Inserted a new section on sample bottle preparation.* *Section 9 Quality Control. This section was previously section 10 in ETS-8-044.0. Updated QC criteria to be consistent with method ETS-8-154.4.* *Section 10 Procedures. This section was previously section 8 (Sample Handling) in ETS-8-044.0. Added detail regarding the preparation of LCSs. Included the use of methanol as a dilution solvent.* *Section 11 Sample Analysis. This section was previously section 10 in ETS-8-044.0. Included the details regarding the instrument parameters.* *Section 12 Data Analysis and Calculations. This section was previously section 11 in ETS-8-044.0. Removed the equation for calculating the analytes concentration, indicating that this is done by the instrument software.* *Section 13 Method Performance. This section was previously section 12 in ETS-8-044.0. Updated QC criteria to be consistent with ETS-8-154.4. Added information on the determination of analytical method uncertainty and quantitation of PFOA/PFOS.* *Section 14 Pollution Prevention. This section was previously section 13 in ETS-8-044.0.* *Section 15 Records. This section was previously section 14 in ETS-8-044.0.* *Section 16 Affected Documents. This section was previously section 15 in ETS-8-044.0.* *Section 17 Revisions. This section was previously section 16 in ETS-8-044.0.*

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GLP10-01-02: Interim Report 30 - Analysis of PFBS, PFHS, and PFOS in Groundwater Samples Collected at Off-Site Wells on Bert Jeffries Property in Decatur, AL in April 2012

Study Title

Analysis of Perfluorooctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane Sulfonate (PFBS) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program

Data Requirement
EPA TSCA Good Laboratory Practice Standards 40 CFR Part 792

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The testing reported herein meet the requirements of ANSI/ISO/IEC 17025:2005 "General Requirements for the Competence of Testing and Calibration Laboratories", in accordance with the A2LA Testing Certificate # 2052.01. Testing that complies with this International Standard also meets principles of ISO 9001:2000.

Testing Cert #2052.01

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GLP COMPLIANCE STATEMENT

Report Title: Interim Report 30 - Analysis of PFBS, PFHS, and PFOS in Groundwater Samples Collected at Off-Site Wells on Bert Jeffries Property in Decatur, AL in April 2012.

Study: Analysis of Perfluorooctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane Sulfonate (PFBS) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program.

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

- These are environmental samples where there is no specific test substance, no specific test system and no dosing of a test system.
- The reference substances have not been characterized under the GLPs and the stability under storage conditions at the test site have not been determined under GLPs.

Gary Hohenstein — 5/8/12

Gary Hohenstein, Sponsor Representative — Date

Jaisimha Kesari — 5/14/12

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

QUALITY ASSURANCE STATEMENT

Report Title: Interim Report 30 - Analysis of PFBS, PFHS, and PFOS in Groundwater Samples Collected at Off-Site Wells on Bert Jeffries Property in Decatur, AL in April 2012.

Study: Analysis of Perfluorooctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane Sulfonate (PFBS) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program.

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

Inspection Dates	Phase	Date Reported to	
		Testing Facility Management	Study Director
4/27/12, 4/30/12	Data and Report	5/1/12	5/1/12

Megan Carlson 5/4/12

QAU Representative Date

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1 Study Information

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Kelly Ukes, Analyst

Study Dates

Study Initiation: March 8, 2010
Interim 30 Experimental Termination: April 26, 2012
Interim Report Completion: Date of Interim Report Signing

Location of Archives

All original raw data and the analytical report have been archived at the 3M Environmental Laboratory according to 40 CFR Part 792. The test substance and analytical reference standard reserve samples are archived at the 3M Environmental Laboratory according to 40 CFR Part 792.

2 Summary

The 3M Environmental Laboratory prepared sample containers for fourteen locations on the Bert Jeffries property. A total of forty-five sample bottles were received at the 3M Environmental Laboratory for perfluorobutane sulfonate (PFBS), perfluorobutane sulfonate (PFBS), perfluorooctane sulfonate (PFOS) analysis from Weston personnel on April 9, 2012. All samples were logged into the laboratory information management system (LIMS) under project GLP10-01-02-30.

For each sampling location, a field sample, field duplicate sample and field matrix spike (FMS) sample were collected. Samples also included a trip blank containing Milli-Q™ water and an appropriate trip blank spike. A single equipment rinseate blank was also collected. The equipment rinseate blank did not have FMS samples prepared for determination of PFOA recovery. All sample bottles were fortified with internal standards and surrogate recovery standard $^{13}C_4$-PFOS prior to sample collection. All of the samples were prepared and analyzed for PFBS, PFHS, PFOS, and the surrogate recovery standard $^{13}C_4$-PFOS following 3M Environmental Laboratory Method ETS-8-044.1.

The average measured PFBS, PFHS, and PFOS concentrations are summarized in **Table 1.** The trip blank sample was below the lower limit of quantitation (LLOQ) for all analytes, indicating adequate control of sample contamination during shipping and sample collections. The analytical method uncertainties associated with the reported results are: PFBS $\pm$ 13%, PFHS $\pm$ 14% and PFOS $\pm$ 18%.

Table 1. Summarized PFBS, PFHS, and PFOS Results (Bert Jeffries Property, April 2012).

Sampling Location	PFBS Avg. Conc. (ng/mL) ± %RPD	PFHS Avg. Conc. (ng/mL) ± %RPD	PFOS Avg. Conc. (ng/mL) ± %RPD
JPAL GW MW1R 120405	0.113 ± 2.7%	0.861 ± 1.0%	1.61 ± 1.9%
JPAL GW MW3R 120405	1.79 ± 0.56%	8.73 ± 7.2%	9.70 ± 3.5%
JPAL GW MW4R 120405	0.189 ± 0.53%	4.88 ± 3.1%	5.81 ± 2.2%
JPAL GW MW4L 120405	0.0772 ± 3.2%	0.205 ± 4.4%	0.348 ± 0.57%
JPAL GW MW5R 120405	0.0402 ± 0.75%	0.128 ± 8.6%	0.128 ± 4.7%
JPAL GW MW5L 120405	0.263 ± 2.7%	0.400 ± 0.25%	2.07 ± 6.8%
JPAL GW MW6R 120405	0.334 ± 1.5%	1.06 ± 5.7%	7.91 ± 0.38%
JPAL GW MW6L 120405	0.0551 ± 0.91%	0.0952 ± 0.63%	0.372 ± 3.5%
JPAL GW MW7R 120405	0.536 ± 0.75%	1.87 ± 1.1%	22.5 ± 2.2%
JPAL GW MW8R 120405	0.0508 ± 6.3%	0.128 ± 5.5%	0.410 ± 6.6%
JPAL GW MW9R 120405	<0.0250	0.0650 ± 1.1%	0.0620 ± 10%
JPAL GW MW9L 120405	<0.0250	<0.0250	0.0425 ± 0.71%
JPAL GW MW10R 120405	0.0579 ± 8.1%	0.264 ± 4.2%	0.238 ± 5.0%
JPAL GW MW11L 120405	<0.0250	0.0886 ± 7.6%	0.496 ± 6.5%
Trip Blanks (Milli-Q™ Water)	<0.0250	<0.0250	<0.0232
GLP10-01-02-30 Equipment rinseate blank: JPAL GW MW3R	<0.0250	<0.0250	<0.232
The analytical method uncertainties associated with the reported results are: PFBS ± 13%, PFHS ± 14 %, and PFOS ± 18%.			

3 *Introduction*

This analytical study was conducted as part of the Phase 3 Environmental Monitoring and Assessment Program for the 3M facility located in Decatur, Alabama. The objective of the overall program is to gain information regarding concentrations of perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHS) and perfluorobutane sulfonate (PFBS), in various environmental media such as groundwater, soils and sediments that are associated with and near the Decatur facility. This analytical study was conducted to analyze ground water samples collected from fourteen locations from off-site wells near Jeffries Landfill in Decatur, AL for PFBS, PFHS, and PFOS in an effort to characterize regional groundwater conditions.

The 3M Environmental Laboratory prepared sample containers (250 mL high-density polyethylene bottles) which were shipped to Decatur, AL Weston personnel prior to field sampling. Sample containers for each sampling location included a field sample, field sample duplicate, and one field matrix spike sample. Each empty container was marked with a "fill to here" line to produce a final sample volume of 200 mL. Containers designated for field matrix samples were fortified with an appropriate matrix spike solution containing PFBS (linear isomer), PFHS (linear isomer), and PFOS (linear and branched isomers) prior to being sent to the field for sample collection. All sample bottles included the addition of $^{18}O_2$-PFBS, $^{13}C_3$-PFHS, and $^{13}C_8$-PFOS (internal standard) at a nominal

concentration of 1 ng/mL. All sample bottles also included the addition of $^{13}C_4$-PFOS (surrogate recovery standard) at a nominal concentration of 0.1 ng/mL. See section 8.8 of the report for field matrix spike levels.

Samples were prepared and analyzed according to the procedure defined in 3M Environmental Laboratory method ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds In Water by LC/MS/MS; Direct Injection Analysis". The use of internal standards was used to aid in the data quality objectives.

Table 1 summarizes the average PFBS, PFHS, and PFOS concentrations for the duplicate surface water samples collected and the trip blank sample. Tables 10-25 summarize the individual sample results and the associated field matrix spike recoveries. All results for the quality control samples prepared and analyzed with the samples are reported and discussed elsewhere in this report

4 Test & Control Substances

There was not a test substance or control substances in the classic sense of a GLP study. This study was purely analytical in nature.

5 Reference Substances

Reference Substance	PFBS (predominantly linear)	$^{18}O_2$-PFBS
Chemical Name	Potassium Perfluorobutane sulfonate	[$^{18}O_2$]-Ammonium Perfluorobutanesulfonate
Chemical Formula	$C_4F_9SO_3^-K^+$	$C_4F_9S[^{18}O_2]O\text{-}NH_4^+$
Identifier	NA	NA
Use	Target Analyte Reference Standard	Internal Standard
Source	3M	RTI International
Expiration Date	01/10/2017	03/09/2015
Storage Conditions	Frozen	Frozen
Chemical Lot Number	41-2600-8442-5	11546-107-2
TCR Number	TCR-121	TCR-1024, TCR-1040
Physical Description	White Powder	Liquid
Purity	96.7%	>99%

Reference Substance	PFHS (Linear)	$^{13}C_3$-PFHS
Chemical Name	Sodium Perfluorohexane sulfonate	Sodium Perfluorohexanesulfonate
Chemical Formula	$C_6F_{13}SO_3^-Na^+$	$^{13}C_3{}^{12}C_3F_{13}SO_3^-Na^+$
Identifier	L-PFHXS	MPFC-C-0112
Use	Target Analyte Reference Standard	Internal Standard
Source	Wellington	Wellington
Expiration Date	03/25/2018	01/24/2015
Storage Conditions	Frozen	Frozen
Chemical Lot Number	LPFHxSAM08	MPFC-C-0112
TCR Number	TCR08-0018	TCR12-0004
Physical Description	Crystalline	Liquid
Purity	100%	5 µg/mL (1)

Reference Substance	PFOS (Linear + Branched)	PFOS (Linear + Branched)	$^{13}C_4$-PFOS	$^{13}C_8$-PFOS
Chemical Name	Potassium Perfluorooctane sulfonate	Potassium Perfluorooctane sulfonate	Sodium Perfluorooctane sulfonate	Sodium Perfluorooctane sulfonate
Chemical Formula	$C_8F_{17}SO_3^-K^+$	$C_8F_{17}SO_3^-K^+$	$^{13}C_4{}^{12}C_4F_{17}SO_3^-Na^+$	$^{13}C_8F_{17}SO_3^-Na^+$
Identifier	Br-PFOSK	CAS # 2795-39-3	MPFOS	MPFC-C-0112
Use	Target Analyte Reference Standard	FMS Reference Standard	Surrogate Recovery Standard	Internal Standard
Source	Wellington	Sigma Aldrich	Wellington	Wellington
Expiration Date	12/01/2014	02/04/2014	09/08/2013	01/24/2015
Storage Conditions	Frozen	Ambient	Frozen	Frozen
Chemical Lot Number	brPFOSK1111	1424328V	MPFOS0910	MPFC-C-0112
TCR Number	TCR11-0041	TCR11-0028	TCR10-0044	TCR12-0004
Physical Description	Liquid	White Powder	Liquid	Liquid
Purity	99.9%	99.7%	>98%	5 µg/mL (1)

(1) Custom mixture of seven mass-labeled (^{13}C) perfluoroalkylcarboxylic acids, two mass labeled (^{13}C) perfluoroalkylsulfonates and one mass-labeled (^{13}C) perfluoro-1-octanesulfonamide.

6 Test System

The test systems for this study are groundwater samples collected from wells located in Decatur, AL by Weston Solutions, Inc. personnel. Samples for this study are "real world" samples, not dosed with a specific lot of test substance.

Table 2. Sample Description Key Code.

String Number	String Descriptor	Example
Example	*JPAL-GW-MW1R-0-120405*	
1	*Sample Location*	*JPAL= Jeffries Property, Alabama*
2	*Sample Type*	*GW= Ground Water*
3	*Well Identifier*	*Example: MW1R*
4	*Well Level*	*R = Residuum shallow water-bearing zone* *L = Bedrock water-bearing zone* *S = Epikarst middle water-bearing zone*
5	*Sampling Date*	*120405- April 5, 2012*
6	*Sample Type*	*0=primary sample* *DB=duplicate sample* *FMS = Field Matrix Spike*

7 Method Summary

7.1 Method

Analysis for all analytes was completed following 3M Environmental Laboratory method ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds In Water by High Performance Liquid Chromatography/Mass Spectrometry Direct Injection Analysis".

7.2 Sample Collection

Samples were collected in 250 mL Nalgene™ (high-density polyethylene) bottles prepared at the 3M Environmental Laboratory. Sample bottles associated with GLP10-01-02-30 were returned to the laboratory at ambient conditions on April 9, 2012. Samples were stored refrigerated at the laboratory after receipt. A set of laboratory prepared Trip Blank and Trip Blank field matrix spikes were sent with the sample collection bottles.

7.3 Sample Preparation

Samples were prepared by removing an aliquot of the well mixed sample and placing it in an autovial for analysis.

During the preparation of the laboratory control samples, an aliquot of a separate internal standard spiking solution was added to the laboratory control samples (nominal concentration of 1 ng/mL). The sample bottles were spiked with an internal standard mix at a nominal concentration of 1 ng/mL prior to being sent to the field for sample collection.

7.4 Analysis

All study samples and quality control samples were analyzed for PFBS, PFHS, and PFOS using high performance liquid chromatography/ tandem mass spectrometry (HPLC/MS/MS). Detailed instrument parameters, the liquid chromatography gradient program, and the specific mass transitions analyzed are

described in the raw data hard copies placed in the final data packet, and are briefly described below in Table 3, Table 4 and Table 5..

Table 3. Instrument Parameters.

Instrument Name	ETS Buster
Analytical Method Followed	ETS-8-044.1
Analysis Date	4/23/12
Liquid Chromatograph	Agilent 1100
Guard column	Betasil C18 (4.6 mm X 100 mm), 5µ
Analytical column	Betasil C18 (4.6 mm X 100 mm), 5µ
Injection Volume	50 µL
Mass Spectrometer	Applied Biosystems API 4000
Ion Source	Turbo Spray
Electrode	Turbo ion electrode
Polarity	Negative
Software	Analyst 1.4.2

Table 4. Liquid Chromatography Conditions.

Step Number	*Total Time (min)*	*Flow Rate (µL/min)*	*Percent A (2 mM ammonium acetate)*	*Percent B (methanol)*
ETS-8-044.1				
0	0.0	750	97.0	3.0
1	2.0	750	97.0	3.0
2	14.5	750	5.0	95.0
3	15.5	750	5.0	95.0
4	16.5	750	97.0	3.0
5	20.0	750	97.0	3.0

Table 5. Mass Transitions.

Analyte	*Mass Transition Q1/Q3*	*Reference Material Structure*	*Internal Standard*	*Mass Transition Q1/Q3*
PFBS	*299/80*	*Linear*	*[$^{18}O_2$]-PFBS*	*303/84*
	299/99			
PFHS	*399/80*	*Linear*	*[$^{13}C_3$]-PFHS*	*402/80*
	399/99			
PFOS	*499/80*	*Linear + Branched*	*[$^{13}C_8$]-PFOS*	*507/80*
	499/99			
	499/130			
[$^{13}C_8$]-PFOS	*503/80*	*Linear*	*[$^{13}C_8$]-PFOS*	*507/80*
Dwell time was 50 msec for each transition. The individual transitions were summed to produce a "total ion chromatogram" (TIC), which was used for quantitation.				

8 Analytical Results

8.1 Calibration

Samples were analyzed using a stable isotope internal standard calibration curve. Calibration standards were prepared by spiking known amounts of the stock solution containing the target analytes into a laboratory-prepared synthetic groundwater containing calcium and magnesium. A separate internal standard spiking solution was prepared and an aliquot was added at the same level to all calibration standards and laboratory control samples at a nominal concentration of 1 ng/mL. A calibration curve ranging from approximately 0.025 ng/mL to 25 ng/mL (0.025 ng/mL to 10 ng/mL for $^{13}C_4$-PFOS surrogate) was analyzed. The reference standard used for the calibration standards for PFOS contained both linear and branched isomers. A quadratic, 1/x weighted, calibration curve of the standard peak area/peak area ratios was used to fit the data for each analyte. The data were not forced through zero during the fitting process. Calculating the standard concentrations using the peak area/peak area ratios and the resultant calibration curve confirmed accuracy of each curve point.

Each curve point was quantitated using the overall calibration curve and reviewed for accuracy. Method calibration accuracy requirements of 100±25% (100±30% for the lowest curve point) were met for all analytes. The correlation coefficient (r) was greater than 0.995 for PFBS, PFHS, PFOS, and $^{13}C_4$-PFOS.

8.2 System Suitability

A calibration standard was analyzed four times at the beginning of each analytical sequence to demonstrate overall system suitability. The acceptance criteria of less than or equal to 5% relative standard deviation (RSD) for peak area and retention time criteria of less than or equal to 2% RSD was met for PFBS, PFHS, PFOS, and $^{13}C_4$-PFOS.

8.3 Limit of Quantitation (LOQ)

The LOQ for this analysis is the lowest non-zero calibration standard in the curve that meets linearity and accuracy requirements and for which the area counts or area ratio are at least twice those of the appropriate blanks. The LOQ for all analytes can be found in Table 6.

Table 6. Limit of Quantitation (LOQ).

Analysis Date	*PFBS LOQ, ng/mL*	*PFHS LOQ, ng/mL*	*PFOS LOQ, ng/mL*
4/23/12	0.0250	0.0250	0.0232

8.4 Continuing Calibration

During the course of each analytical sequence, continuing calibration verification samples (CCVs) were analyzed to confirm that the instrument response and the initial calibration curve were still in control. All CCVs met method criteria of 100% ± 25% for PFBS, PFHS, PFOS, and $^{13}C_4$-PFOS.

8.5 Blanks

Three types of blanks were prepared and analyzed with the samples: procedural blanks, trip blanks, and equipment rinseate blanks. Procedural blank results were reviewed and used to evaluate method performance and to determine the LOQ. Trip blanks reflect the shipping and sample collection conditons the sample bottles and samples experience. Equipment rinseate blanks are aqueous samples that reflect the efficiency of equipment cleaning in the field between different sample collections to ensure no cross contamination of samples from the equipment.

8.6 Lab Control Spikes (LCSs)

Low, mid, and high lab control spikes were prepared for the target analytes and analyzed in triplicate, while only low and high lab control spikes were prepared for the $^{13}C_4$-PFOS surrogate. LCSs were prepared by spiking known amounts of the analyte into synthetic groundwater to produce the desired concentration. The spiked water samples were then prepared and analyzed in the same manner as the samples. The method acceptance criteria, average of LCS at each level should be within 100% ± 20% with an RSD ≤20%, were met for all analytes.

The following calculations were used to generate data in Table 7 for laboratory control spikes.

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

$$\text{LCS\% RSD} = \frac{\text{standard deviation LCS replicates}}{\text{average LCS recovery}} * 100\%$$

Table 7. Laboratory Control Spike Recovery.

ETS-8-044.1 Analyzed 4/23/12	PFBS			PFHS		
Lab ID	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery
LCS-120416-1	0.198	0.203	102	0.198	0.201	102
LCS-120416-2	0.198	0.216	109	0.198	0.210	106
LCS-120416-3	0.198	0.222	112	0.198	0.215	108
Average ± %RSD	108% ± 4.8%			105% ± 2.9%		
LCS-120416-4	1.98	2.13	108	1.98	2.10	106
LCS-120416-5	1.98	2.16	109	1.98	2.30	116
LCS-120416-6	1.98	2.10	106	1.98	2.21	112
Average ± %RSD	108% ± 1.4%			111% ± 4.5%		
LCS-120416-7	9.94	9.83	98.9	9.92	10.0	101
LCS-120416-8	9.94	9.58	96.4	9.92	9.16	92.3
LCS-120416-9	9.94	9.41	94.7	9.92	9.39	94.7
Average ± %RSD	96.7% ± 2.2%			96.0% ± 4.7%		

ETS-8-044.1 Analyzed 4/23/12	PFOS (Linear + Branched)			$^{13}C_4$-PFOS surrogate		
Lab ID	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery
LCS-120416-1	0.184	0.179	97.3	0.189	0.202	107
LCS-120416-2	0.184	0.198	107	0.189	0.199	105
LCS-120416-3	0.184	0.199	108	0.189	0.193	102
Average ± %RSD	104% ± 5.7%			105% ± 2.4%		
LCS-120416-4	1.84	1.84	99.8	1.89	1.91	101
LCS-120416-5	1.84	1.91	104	1.89	1.99	105
LCS-120416-6	1.84	1.95	106	1.89	2.01	106
Average ± %RSD	103% ± 3.1%			104% ± 2.5%		
LCS-120416-7	9.22	9.16	99.3	NA	NA	NA
LCS-120416-8	9.22	8.78	95.3	NA	NA	NA
LCS-120416-9	9.22	8.59	93.2	NA	NA	NA
Average ± %RSD	95.9% ± 3.2%			NA		

NA = Not Applicable

8.7 Analytical Method Uncertainty

Analytical uncertainty is based on historical QC data that is control charted and used to evaluate method accuracy and precision. The method uncertainty is calculated following ETS-12-012.2. The standard deviation is calculated for the set of accuracy results (in %) obtained for the QC samples. The expanded uncertainty is calculated by multiplying the standard deviation by a factor of 2, which corresponds to a confidence level of 95%.

Table 8. Analytical Uncertainty.

Analyte	Standard Deviation	Method Uncertainty
PFBS	6.42	±13%
PFHS	7.00	±14%
PFOS	9.10	±18%

8.8 Field Matrix Spikes (FMS)

Low, mid, and high field matrix spikes (FMS) were collected at each sampling point to verify that the analytical method is applicable to the collected matrix. Field matrix spikes were generated by adding a measured volume of field sample to a container spiked by the laboratory with PFBS (linear), PFHS (linear), and PFOS (linear + branched) prior to shipping sample containers for sample collection. Field matrix spike recoveries within method acceptance criteria of 100±30% confirm that "unknown" components in the sample matrix do not significantly interfere with the extraction and analysis of the analytes of interest. Field matrix spike concentrations must be 50% of the sample concentration to be considered an appropriate field spike. Field matrix spikes are presented in section 9 of this report.

Table 9. Field Matrix Spike Levels.

Sampling Location	PFBS, ng/mL	PFHS, ng/mL	PFOS, ng/mL
All Locations and Trip Blank	2.00	2.00	2.00

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

9 *Data Summary and Discussion*

The tables below summarize the sample results and field matrix spike recoveries for the sampling locations as well as the Trip Blank. Results and average values are rounded to three significant figures according to EPA rounding rules. Because of rounding, values may vary slightly from those listed in the raw data. Field matrix spike recoveries meeting the method acceptance criteria of ± 30%, demonstrate that the method was appropriate for the given matrix and their respective quantitative ranges.

JPAL GW MW3R 120405; The field matrix spike level was not appropriate as compared to the PFHS and PFOS concentrations in the samples. However, the $^{13}C_4$-PFOS surrogate recovery added to all sample bottles met method acceptance criteria.

JPAL GW MW4R 120405; The field matrix spike level was not appropriate as compared to the PFHS and PFOS concentrations in the samples. However, the $^{13}C_4$-PFOS surrogate recovery added to all sample bottles met method acceptance criteria.

JPAL GW MW6R 120405; The field matrix spike level was not appropriate as compared to the PFOS concentration in the samples. However, the $^{13}C_4$-PFOS surrogate recovery added to all sample bottles met method acceptance criteria.

JPAL GW MW7R 120405; The field matrix spike level was not appropriate as compared to the PFOS concentration in the samples. However, the $^{13}C_4$-PFOS surrogate recovery added to all sample bottles met method acceptance criteria.

Table 10. JPAL GW MW1R 120405

		PFBS		PFHS		PFOS		$^{13}C_8$-PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-30-001	JPAL-GW-MW1R-0-120405	0.114	NA	0.865	NA	1.62	NA	95.8
GLP10-01-02-30-002	JPAL-GW-MW1R-DB-120405	0.111	NA	0.856	NA	1.59	NA	99.3
GLP10-01-02-30-003	JPAL-GW-MW1R-FMS-120405	2.48	118	3.31	122	4.05	122	110
Average Concentration (ng/mL) ± %RPD/%RSD		*0.113 ng/mL ± 2.7%*		*0.861 ng/mL ± 1.0%*		*1.61 ng/mL ± 1.9%*		*102% ± 7.2%*

NA = Not Applicable

Table 11. JPAL GW MW3R 120405

		PFBS		PFHS		PFOS		$^{13}C_8$-PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-30-004	JPAL-GW-MW3R-0-120405	1.78	NA	9.04	NA	9.53	NA	97.8
GLP10-01-02-30-005	JPAL-GW-MW3R-DB-120405	1.79	NA	8.41	NA	9.87	NA	104
GLP10-01-02-30-006	JPAL-GW-MW3R-FMS-120405	3.63	92.3	10.2	NC	10.9	NC	88.1
Average Concentration (ng/mL) ± %RPD/%RSD		*1.79 ng/mL ± 0.56%*		*8.73 ng/mL ± 7.2%*		*9.70 ng/mL ± 3.5%*		*96.7% ± 8.4%*

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

Table 12. JPAL GW MW4R 120405

		PFBS		PFHS		PFOS		$^{13}C_4$-PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-30-007	JPAL-GW-MW4R-0-120405	0.188	NA	4.95	NA	5.87	NA	93.1
GLP10-01-02-30-008	JPAL-GW-MW4R-DB-120405	0.189	NA	4.80	NA	5.74	NA	93.2
GLP10-01-02-30-009	JPAL-GW-MW4R-FMS-120405	2.15	98.1	6.65	NC	7.85	NC	98.1
Average Concentration (ng/mL) ± %RPD/%RSD		*0.189 ng/mL ± 0.53%*		*4.88 ng/mL ± 3.1%*		*5.81 ng/mL ± 2.2%*		*94.8% ± 3.0%*

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

Table 13. JPAL GW MW4L 120405

		PFBS		PFHS		PFOS		$^{13}C_4$-PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-30-010	JPAL-GW-MW4L-0-120405	0.0759	NA	0.200	NA	0.347	NA	97.1
GLP10-01-02-30-011	JPAL-GW-MW4L-DB-120405	0.0784	NA	0.209	NA	0.349	NA	93.6
GLP10-01-02-30-012	JPAL-GW-MW4L-FMS-120405	2.05	98.6	2.15	97.3	2.21	93.1	91.8
Average Concentration (ng/mL) ± %RPD/%RSD		*0.0772 ng/mL ± 3.2%*		*0.205 ng/mL ± 4.4%*		*0.348 ng/mL ± 0.57%*		*94.2% ± 2.8%*

NA = Not Applicable

Table 14. JPAL GW MW5R 120405

		PFBS		PFHS		PFOS		$^{13}C_4$-PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-30-013	JPAL-GW-MW5R-0-120405	0.0400	NA	0.133	NA	0.125	NA	96.9
GLP10-01-02-30-014	JPAL-GW-MW5R-DB-120405	0.0403	NA	0.122	NA	0.131	NA	98.4
GLP10-01-02-30-015	JPAL-GW-MW5R-FMS-120405	2.03	99.5	2.14	101	1.99	93.1	101
Average Concentration (ng/mL) ± %RPD/%RSD		*0.0402 ng/mL ± 0.75%*		*0.128 ng/mL ± 8.6%*		*0.128 ng/mL ± 4.7%*		*98.9% ± 2.4%*

NA = Not Applicable

Table 15. JPAL GW MW5L 120405

		PFBS		PFHS		PFOS		$^{13}C_4$-PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-30-016	JPAL-GW-MW5L-0-120405	0.259	NA	0.399	NA	2.14	NA	107
GLP10-01-02-30-017	JPAL-GW-MW5L-DB-120405	0.266	NA	0.400	NA	2.00	NA	95.2
GLP10-01-02-30-018	JPAL-GW-MW5L-FMS-120405	2.23	98.4	2.33	96.5	4.00	96.5	99.6
Average Concentration (ng/mL) ± %RPD/%RSD		*0.263 ng/mL ± 2.7%*		*0.400 ng/mL ± 0.25%*		*2.07 ng/mL ± 6.8%*		*100% ± 5.8%*

NA = Not Applicable

Table 16. JPAL GW MW6R 120405

		PFBS		PFHS		PFOS		$^{13}C_8$-PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-30-019	JPAL-GW-MW6R-0-120405	0.336	NA	1.09	NA	7.89	NA	101
GLP10-01-02-30-020	JPAL-GW-MW6R-DB-120405	0.331	NA	1.03	NA	7.92	NA	97.1
GLP10-01-02-30-021	JPAL-GW-MW6R-FMS-120405	2.31	98.8	3.02	98.0	9.47	NC	96.9
Average Concentration (ng/mL) ± %RPD/%RSD		*0.334 ng/mL ± 1.5%*		*1.06 ng/mL ± 5.7%*		*7.91 ng/mL ± 0.38%*		*98.3% ± 2.4%*

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

Table 17. JPAL GW MW6L 120405

		PFBS		PFHS		PFOS		$^{13}C_8$-PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-30-022	JPAL-GW-MW6L-0-120405	0.0548	NA	0.0949	NA	0.365	NA	101
GLP10-01-02-30-023	JPAL-GW-MW6L-DB-120405	0.0553	NA	0.0955	NA	0.378	NA	97.8
GLP10-01-02-30-024	JPAL-GW-MW6L-FMS-120405	2.00	97.2	2.04	97.2	2.21	91.9	88.3
Average Concentration (ng/mL) ± %RPD/%RSD		*0.0551 ng/mL ± 0.91%*		*0.0952 ng/mL ± 0.63%*		*0.372 ng/mL ± 3.5%*		*95.6% ± 6.8%*

NA = Not Applicable

Table 18. JPAL GW MW7R 120405

		PFBS		PFHS		PFOS		$^{13}C_4$-PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-30-025	JPAL-GW-MW7R-0-120405	0.534	NA	1.88	NA	22.7	NA	94.7
GLP10-01-02-30-026	JPAL-GW-MW7R-DB-120405	0.538	NA	1.86	NA	22.2	NA	91.9
GLP10-01-02-30-027	JPAL-GW-MW7R-FMS-120405	2.49	97.7	3.68	90.5	NR (1)	NC	96.4
Average Concentration (ng/mL) ± %RPD/%RSD		*0.536 ng/mL ± 0.75%*		*1.87 ng/mL ± 1.1%*		*22.5 ng/mL ± 2.2%*		*94.4% ± 2.4%*

NA = Not Applicable
NC = Not Calculated; the sample concentration is greater than 2x the spike level.
(1) NR = Not Reported; sample concentration exceeded the calibration range of 23.2 ng/mL for PFOS.

Table 19. JPAL GW MW8R 120405

		PFBS		PFHS		PFOS		$^{13}C_4$-PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-30-028	JPAL-GW-MW8R-0-120405	0.0492	NA	0.124	NA	0.396	NA	91.7
GLP10-01-02-30-029	JPAL-GW-MW8R-DB-120405	0.0524	NA	0.131	NA	0.423	NA	94.6
GLP10-01-02-30-030	JPAL-GW-MW8R-FMS-120405	1.93	94.0	2.06	96.6	2.30	94.5	94.7
Average Concentration (ng/mL) ± %RPD/%RSD		*0.0508 ng/mL ± 6.3%*		*0.128 ng/mL ± 5.5%*		*0.410 ng/mL ± 6.6%*		*93.7% ± 1.8%*

NA = Not Applicable

Table 20. JPAL GW MW9R 120405

		PFBS		PFHS		PFOS		$^{13}C_4$-PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-30-031	JPAL-GW-MW9R-0-120405	<0.0250	NA	0.0653	NA	0.0652	NA	96.0
GLP10-01-02-30-032	JPAL-GW-MW9R-DB-120405	<0.0250	NA	0.0646	NA	0.0588	NA	97.6
GLP10-01-02-30-033	JPAL-GW-MW9R-FMS-120405	2.01	101	2.14	104	1.84	88.9	94.9
Average Concentration (ng/mL) ± %RPD/%RSD		*<0.0250 ng/mL*		*0.0650 ng/mL ± 1.1%*		*0.0620 ng/mL ± 10%*		*96.2% ± 1.4%*

NA = Not Applicable

Table 21. JPAL GW MW9L 120405

		PFBS		PFHS		PFOS		$^{13}C_4$-PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-30-034	JPAL-GW-MW9L-0-120405	<0.0250	NA	<0.0250	NA	0.0423	NA	90.6
GLP10-01-02-30-035	JPAL-GW-MW9L-DB-120405	<0.0250	NA	<0.0250	NA	0.0426	NA	94.4
GLP10-01-02-30-036	JPAL-GW-MW9L-FMS-120405	1.94	97.0	1.99	99.5	1.81	88.4	91.1
Average Concentration (ng/mL) ± %RPD/%RSD		*<0.0250 ng/mL*		*<0.0250 ng/mL*		*0.0425 ng/mL ± 0.71%*		*92.0% ± 2.2%*

NA = Not Applicable

Table 22. JPAL GW MW10R 120405

		PFBS		PFHS		PFOS		$^{13}C_4$-PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-30-037	JPAL-GW-MW10R-0-120405	0.0602	NA	0.269	NA	0.232	NA	93.8
GLP10-01-02-30-038	JPAL-GW-MW10R-DB-120405	0.0555	NA	0.258	NA	0.244	NA	94.8
GLP10-01-02-30-039	JPAL-GW-MW10R-FMS-120405	2.05	99.6	2.20	96.8	2.13	94.6	97.6
Average Concentration (ng/mL) ± %RPD/%RSD		*0.0579 ng/mL ± 8.1%*		*0.264 ng/mL ± 4.2%*		*0.238 ng/mL ± 5.0%*		*95.4% ± 2.1%*

NA = Not Applicable

Table 23. JPAL GW MW11L 120405

		PFBS		PFHS		PFOS		$^{13}C_4$-PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-30-040	JPAL-GW-MW11L-0-120405	<0.0250	NA	0.0919	NA	0.512	NA	86.6
GLP10-01-02-30-041	JPAL-GW-MW11L-DB-120405	<0.0250	NA	0.0852	NA	0.480	NA	98.5
GLP10-01-02-30-042	JPAL-GW-MW11L-FMS-120405	2.03	102	2.16	104	2.46	98.2	100
Average Concentration (ng/mL) ± %RPD/%RSD		*<0.0250 ng/mL*		*0.0886 ng/mL ± 7.6%*		*0.496 ng/mL ± 6.5%*		*95.0% ± 7.7%*

NA = Not Applicable

Table 24. Rinseate Blank

		PFBS	PFHS	PFOS	$^{13}C_4$-PFOS
3M LIMS ID	Description	Concentration (ng/mL)	Concentration (ng/mL)	Concentration (ng/mL)	%Recovery
GLP10-01-02-30-043	JPAL-GW-MW3R-RB-120405	<0.0250	<0.0250	<0.0232	92.1

NA = Not Applicable

Table 25. Trip Blank

		PFBS		PFHS		PFOS		$^{13}C_4$-PFOS
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-02-30-044	JPAL-GW-TRIP01-0-120316	<0.0250	NA	<0.0250	NA	<0.0232	NA	92.8
GLP10-01-02-30-045	JPAL-GW-TRIP01-FMS-120316	2.00	100	2.00	100	1.82	91.0	97.5

NA = Not Applicable

10 Conclusion

Laboratory control spikes and field matrix spikes were used to determine the analytical method accuracy and precision for PFBS, PFHS, and PFOS. Analysis was successfully completed following 3M Environmental Laboratory method ETS-8-044.1 described herein.

11 Data/Sample Retention

All remaining samples and associated project data (hardcopy and electronic) will be archived according to 3M Environmental Laboratory standard operating procedures.

12 Attachments

Attachment A: Protocol Amendment 30 (General Project Outline)
Attachment B: Representative Chromatograms and Calibration Curves
Attachment C: Analytical Method-ETS-8-044.1

13 Signatures

5/4/2012
Cleston Lange, Ph.D., 3M Principal Analytical Investigator — Date

4 May 2012
William K. Reagen, Ph.D., 3M Environmental Laboratory Department Manager — Date

Gary Hohenstein
5/8/12
Gary Hohenstein, Sponsor Representative — Date

5/14/12
Jaisimha Kesari, Study Director — Date

ATTACHMENT A: PROTOCOL AMENDMENT

Study Title

Analysis of Perfluorooctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane sulfonate (PFBS) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program

PROTOCOL AMENDMENT NO. 30

Amendment Date:
March 22, 2012

Performing Laboratory
3M Environmental, Health, and Safety Operations
3M Environmental Laboratory
Building 260-5N-17
Maplewood, MN 55144-1000

Laboratory Project Identification
GLP10-01-02

Sampling Event

Off-Site Wells - Bert Jeffries Property

This amendment modifies the following portion of protocol:

"Analysis of PFOS, PFHS and PFBS in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program"

PROTOCOL READS:

No changes to the wording of the protocol are required.

AMEND TO READ:

No changes to the wording of the protocol are required. This amendment only addresses and documents the addition of the General Project Outline (GPO) for the collection and analysis of groundwater samples as part of the 3M Decatur Phase 3 Program for PFOS, PFHS and PFBS (GLP10-01-02). The anticipated sample collection will occur around the timeframe of the week of March26, 2012. The groundwater samples for this sampling event will be entered into the 3M Environmental Laboratory LIMS as project GLP10-01-02-30 and reported as interim report GLP10-01-02-30, (reflecting study GLP10-01-02 and amendment -30).

Reason:

The reason for this amendment is to document the General Project Outline (GPO) which describes the anticipate groundwater sample collection event for fourteen off-site wells at the Bert Jeffries Property.

The GPO is three pages in length and included as attached to this amendment form.

Amendment Approval

Gary Hohenstein, Sponsor Representative — Date: 3/26/12

Cleston C. Lange, Principal Analytical Investigator — Date: 3/22/2012

William Reagen, EHS Opns Environmental Lab Management — Date: 23 March 2012

Jaisimha Kesari P.E., DEE, Study Director — Date: 3/30/12

3M Environmental Health & Safety Operations, Environmental Laboratory

General Project Outline

To: Gary Hohenstein, 3M EHS&Opns

From: Susan Wolf, 3M EHS&Opns; Environmental Lab

cc: William Reagen, 3M EHS&Opns; Environmental Lab

Cleston Lange, 3M EHS&Opns; Environmental Lab

Jai Kesari, Weston Solutions

Date: March 22, 2012

Subject: Analysis of Perfluorooctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane sulfonate (PFBS) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program; GLP Interim Report 30; Off-Site Wells – Bert Jeffries Property

1 General Project Information

Contacts	**3M Sponsor Representative** Gary Hohenstein 3M EHS Operations 3M Building 224-5W-03 Saint Paul, MN 55144-1000 Phone: (651) 737-3570 gahohenstein@mmm.com **3M Environmental Laboratory Management** William K. Reagen 3M EHS Opns, Environmental Laboratory 260-5N-17 651 733-9739 wkreagen@mmm.com **Principal Analytical Investigator** Cleston Lange 3M EHS Opns, Environmental Laboratory 260-5N-17 651 733-9860 cclange@mmm.com **Sampling Coordinator** Timothy Frinak Weston Solutions Timothy.frinak@westonsolutions.com Phone: (334)-332-9123
Lab Request Number	**GLP10-01-02-30**
Six Digit Department Number	Dept #530711, Project #0022674449
Project Schedule/Test Dates	Sampling scheduled for the week of March 26, 2012

All verbal and written correspondence will be directed to Gary Hohenstein.

2 Background Information and Project Objective(s)

The 3M EHS Operations Laboratory (3M Environmental Lab) will receive and analyze groundwater samples collected from fourteen sampling locations for Perfluorobutanesulfonate (PFBS), Perfluorohexanesulfonate (PFHS), and Perfluorooctanesulfonate (PFOS) from wells located on the Bert Jeffries Property. Analyses will be conducted under the GLP requirements of EPA TSCA Good Laboratory Practice Standards 40 CFR 792.

Groundwater samples will be collected by Weston Solutions personnel the week of March 26, 2012. The 3M Environmental Laboratory will prepare the sample bottles with all required spikes to ensure that results for PFBS, PFHS, and PFOS are of a known precision and accuracy. The final report will be submitted to Gary Hohenstein and Jai Kesari upon completion under interim report GLP10-01-02-30.

3 Project Schedule

Sample collection bottles will be prepared by 3M Environmental Laboratory for sampling the week of March 26, 2012. Sample bottles will be shipped in coolers overnight to 3M Decatur for arrival on Friday, March 23, 2012. Sample bottles should be stored refrigerated on-site until sample collection.

Martin Smith \ Weston Trailer
3M Decatur Plant
1400 State Docks Road
Decatur, Alabama 35601

4 Test Parameters

The targeted limit of quantitation will be **0.025 ng/mL** (ppb) for PFBS, PFHS, and PFOS.

Fourteen sampling locations have been specified. For each sampling location, a total of three sample bottles will be collected (sample, sample duplicate and 2 ng/mL field matrix spike). The "fill to here" line on each 250 mL Nalgene bottle will be 200 mL. One set of trip blanks consisting of reagent-grade water as well as a trip blank spike at 2 ng/mL will be prepared at the 3M Environmental Laboratory and sent to the sampling location with the other bottles. All sample bottles will include the addition of $^{18}O_2$-PFBS, $^{18}O_2$-PFHS, and $^{13}C_8$-PFOS (internal standard) at a nominal concentration of 1 ng/mL. All sample bottles will also include the addition of $^{13}C_4$-PFOS (surrogate spike) at a nominal concentration of 0.1 ng/mL. One additional bottle will be prepared to be used for the preparation of the equipment rinseate blank. A 500-mL bottle of laboratory reagent water will be sent with the sample bottles to be used to generate the rinseate blank sample.

5 Test Methods

Samples will be prepared and analyzed by LC/MS/MS following ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds In Water by LC/MS/MS; Direct Injection Analysis".

The data quality objectives for these studies are quantitative results for the target analytes with an analytical accuracy of 100±30%. Field matrix spikes not yielding recoveries within 100±30% will be addressed in the report and the final accuracy statement may be adjusted accordingly.

Where applicable, samples will be analyzed against an internal standard calibration curve. Each curve point will contain isotopically-labeled perfluorocarboxylic acids and perfluorosulfonic acids at a nominal concentration of 1 ng/mL. The calibration curve will be generated by taking the ratio of the standard peak area counts over the internal standard peak area counts to fit the data for each analyte.

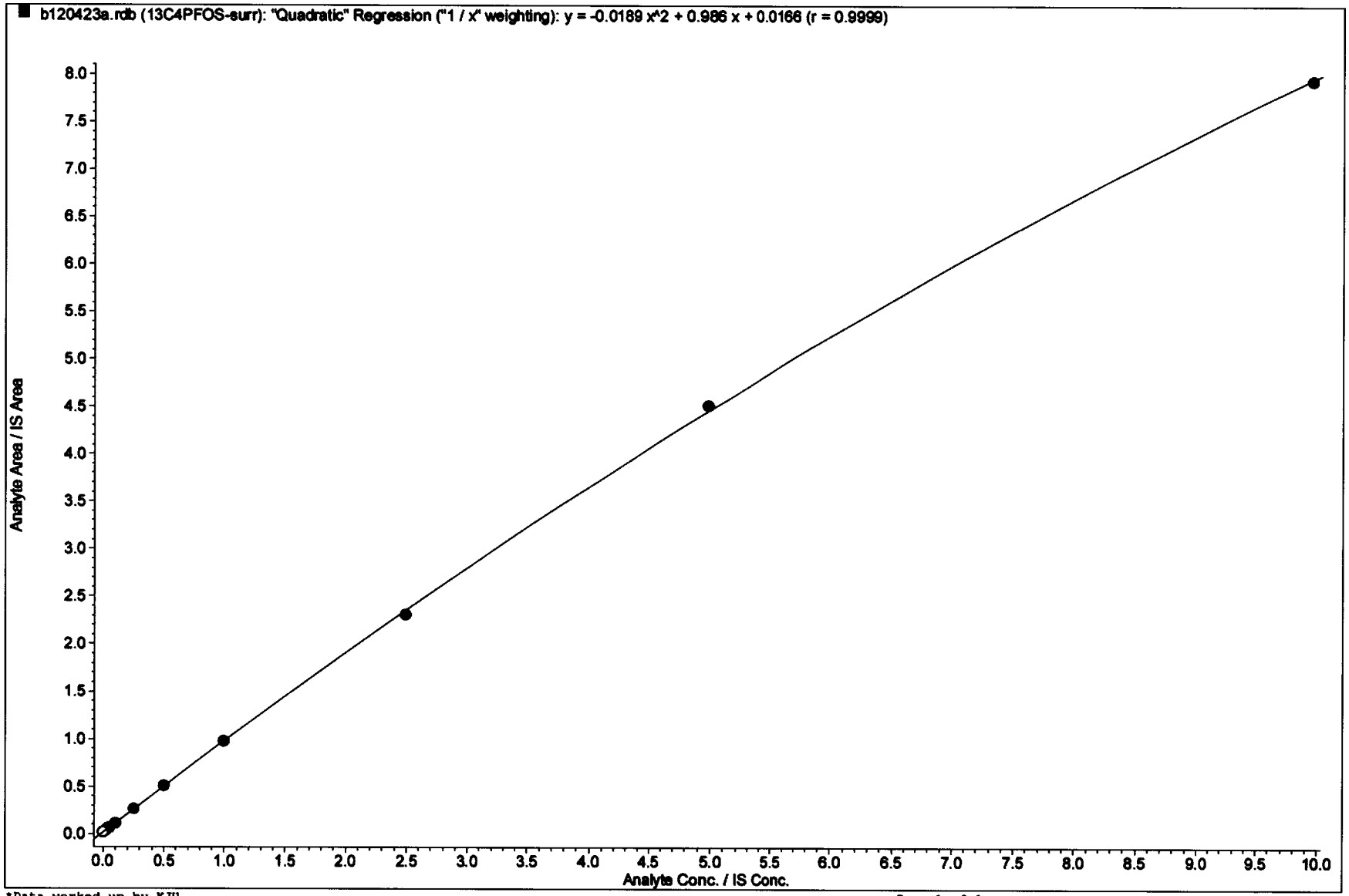
6 Reporting Requirements

For each sampling location, the report will contain the results for the sample, sample duplicate, and field matrix spike. Trip blank and trip blank spike will be reported for the sampling event as will any equipment/rinseate blanks prepared in the field. Laboratory control spikes of reagent water prepared at the time of sample extraction will also be reported and used to evaluate the overall method accuracy and precision. Method blanks of reagent water prepared at the time of sample extraction will be used to determine the method detection limit.

ATTACHMENT B: REPRESENTATIVE SAMPLE CHROMATOGRAMS AND CALIBRATION CURVE(S)

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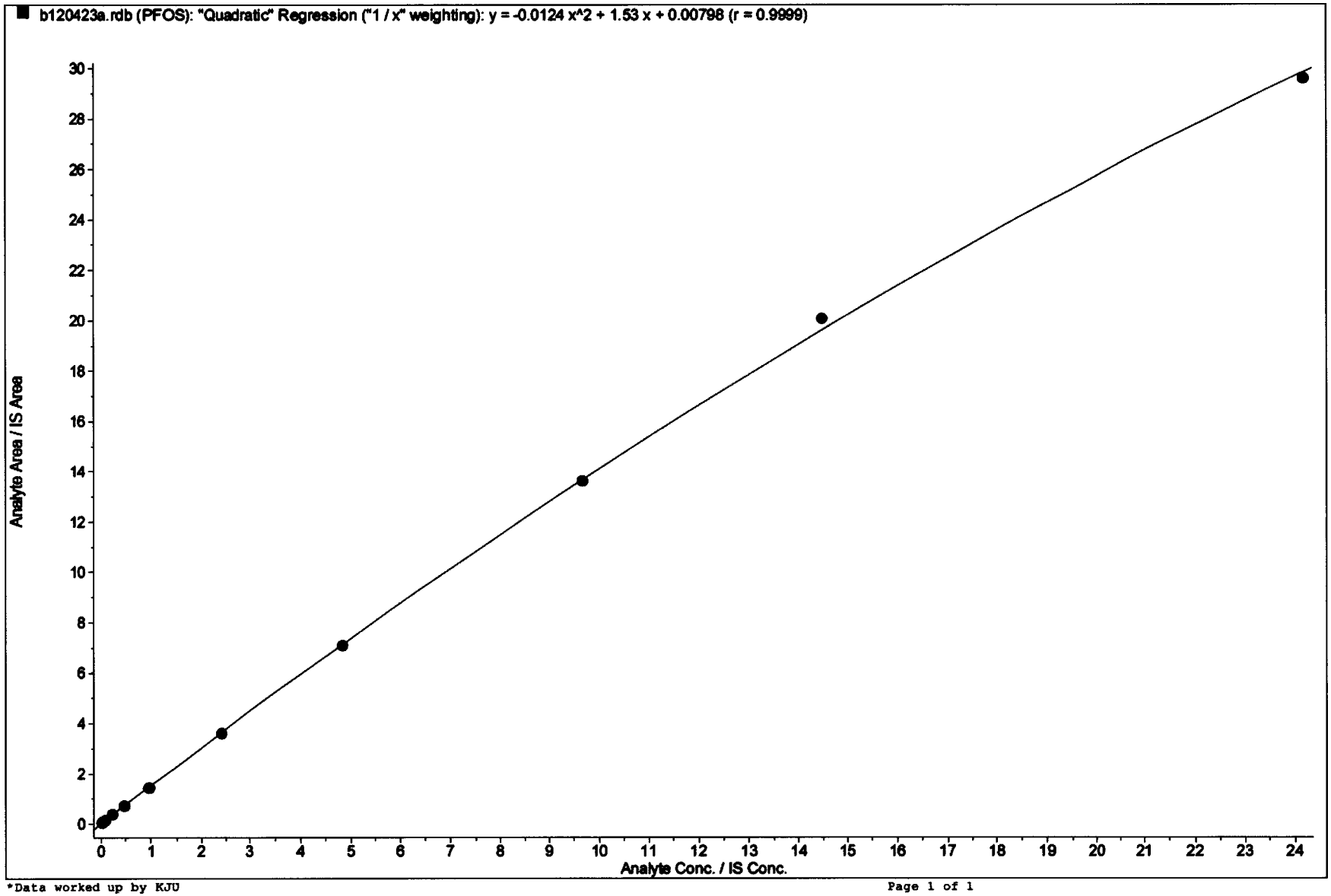


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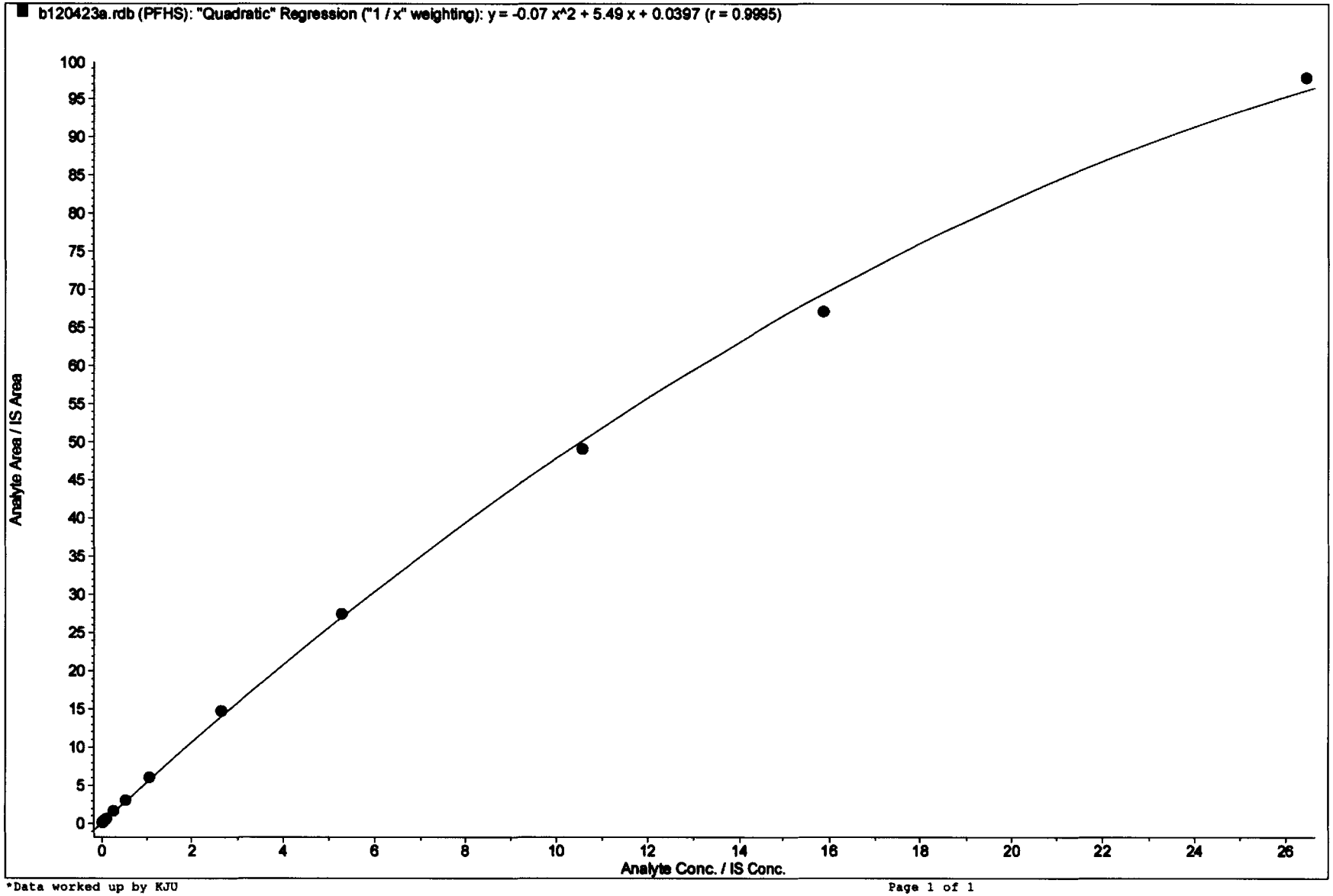
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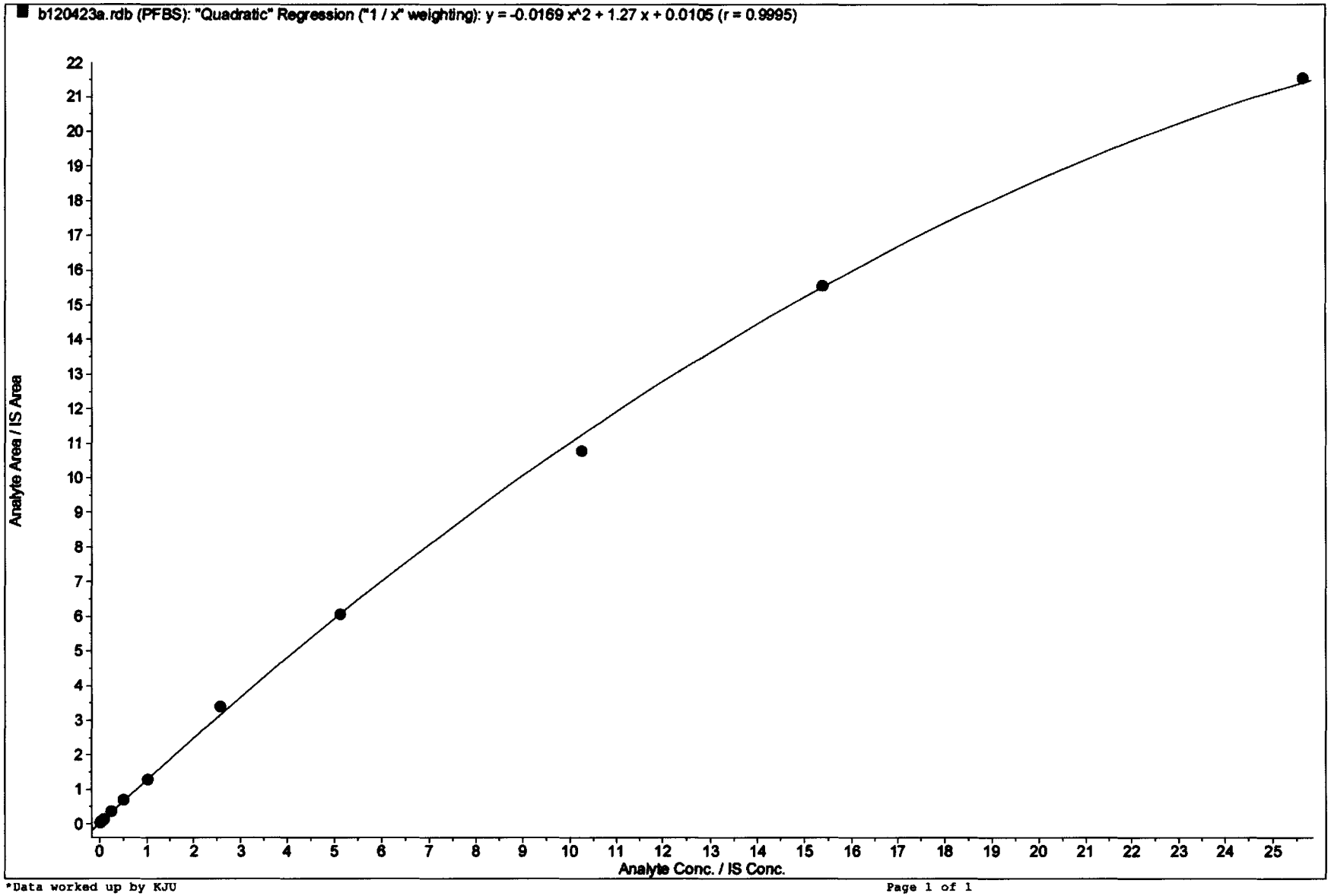
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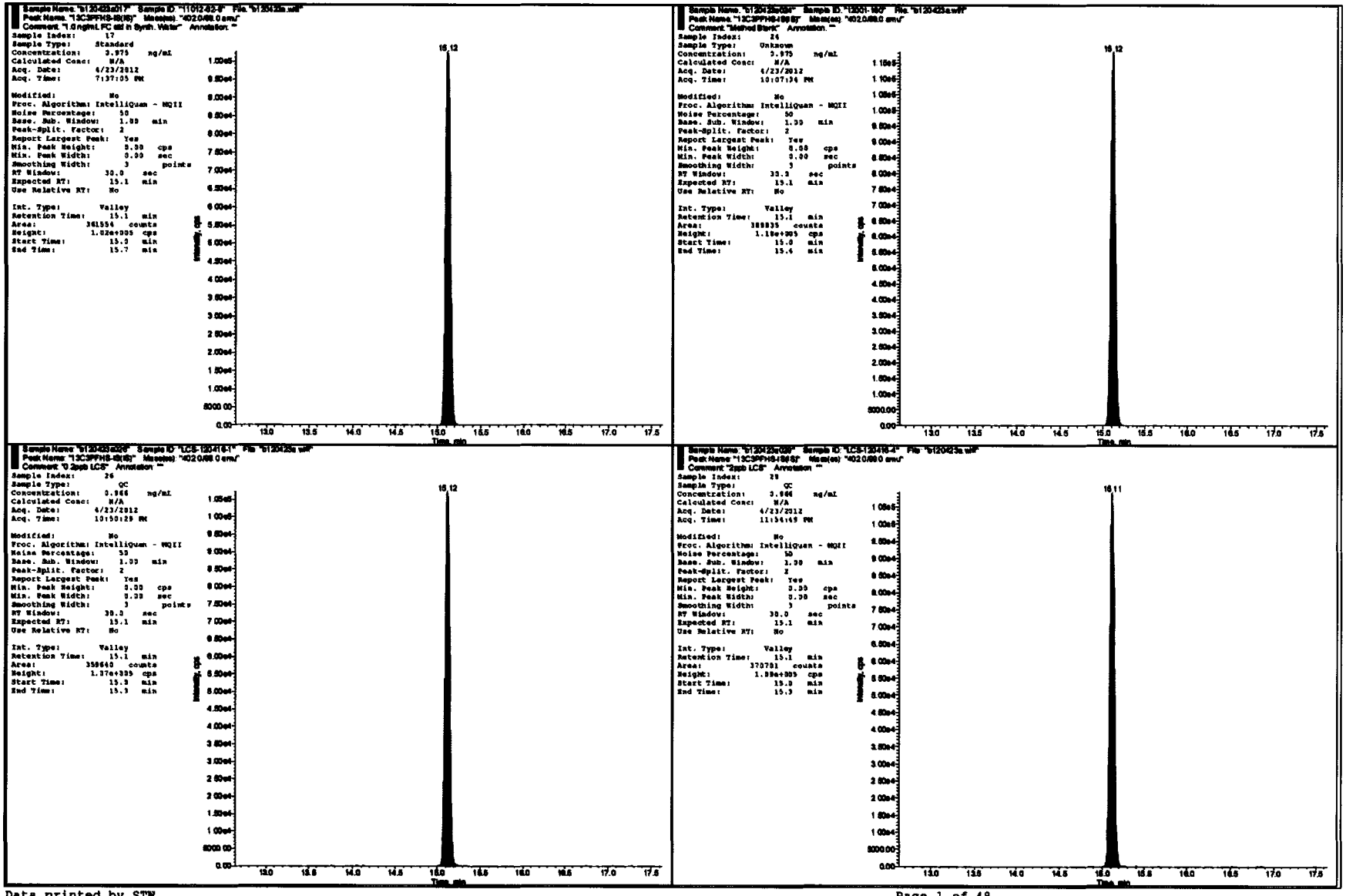
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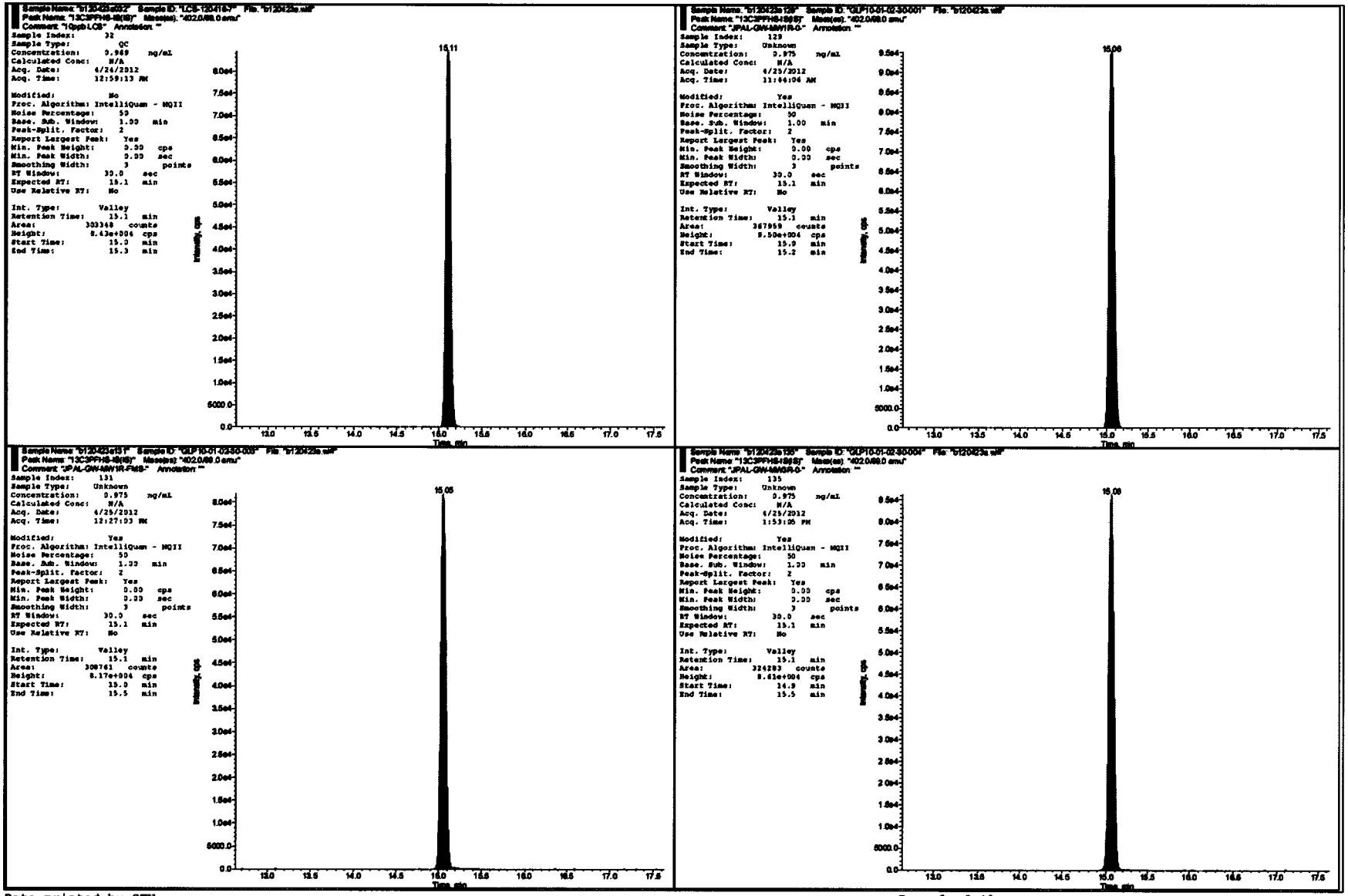
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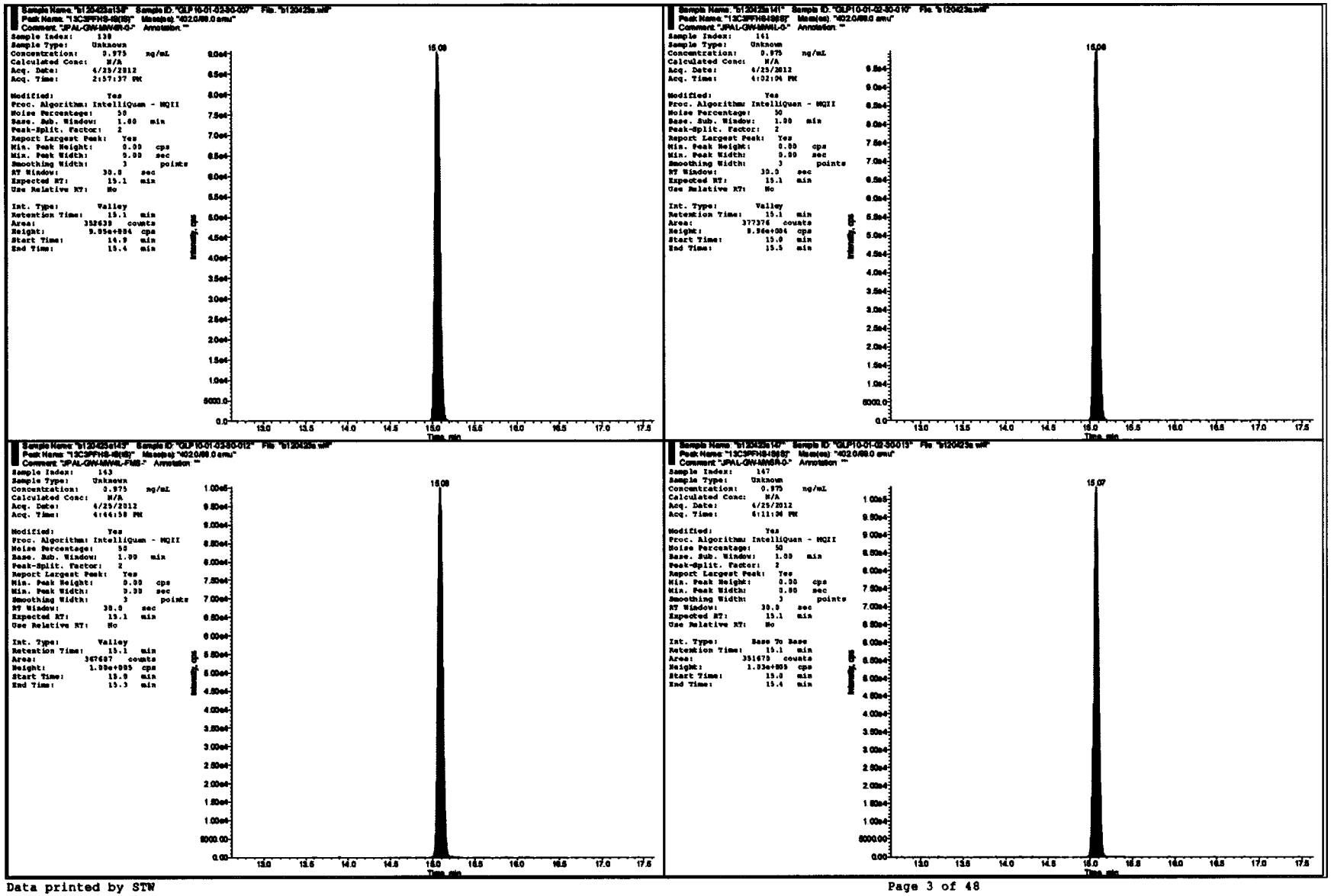
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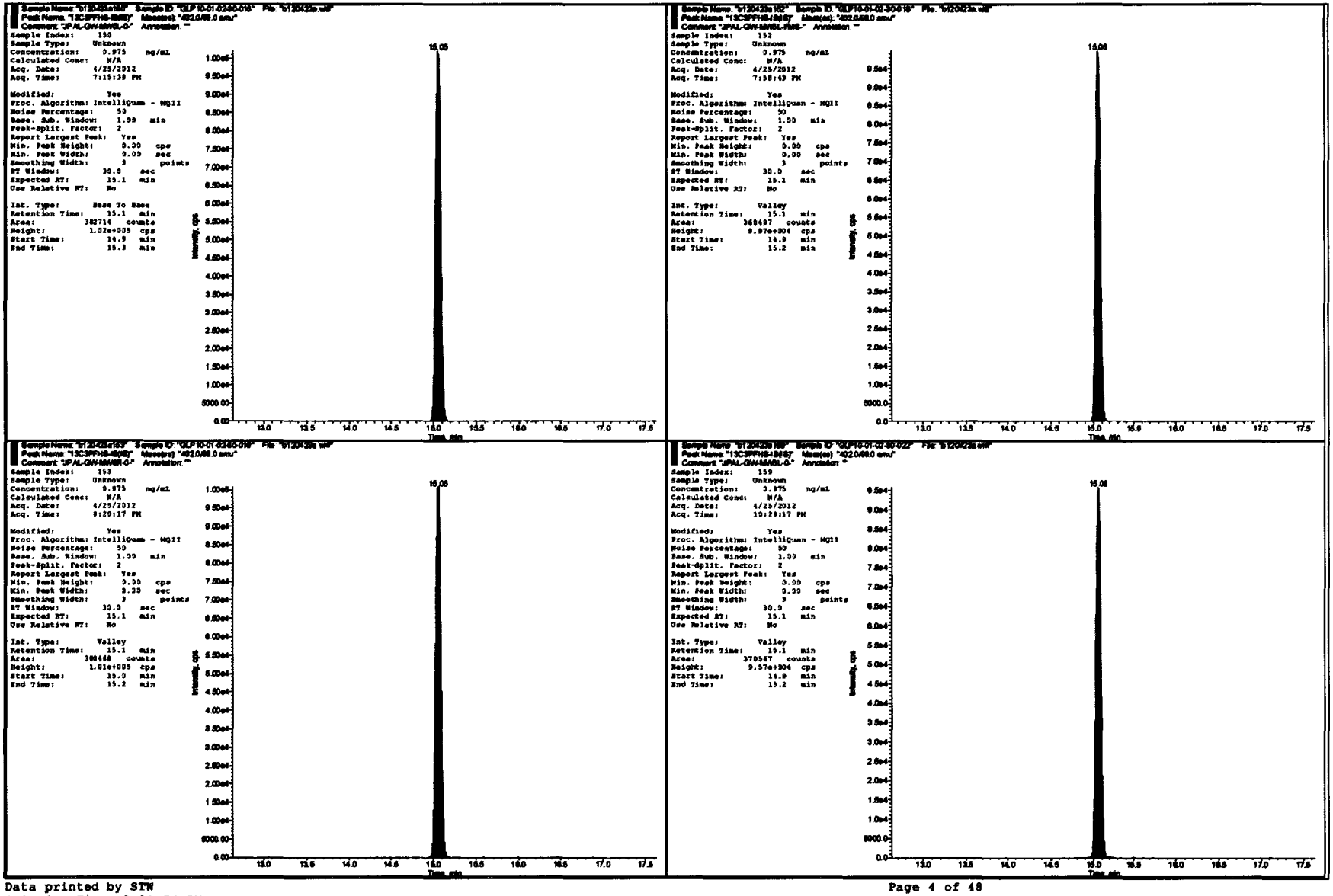
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Printing Time: 2:31:54 PM
Printing Date: Thursday, May 03, 2012

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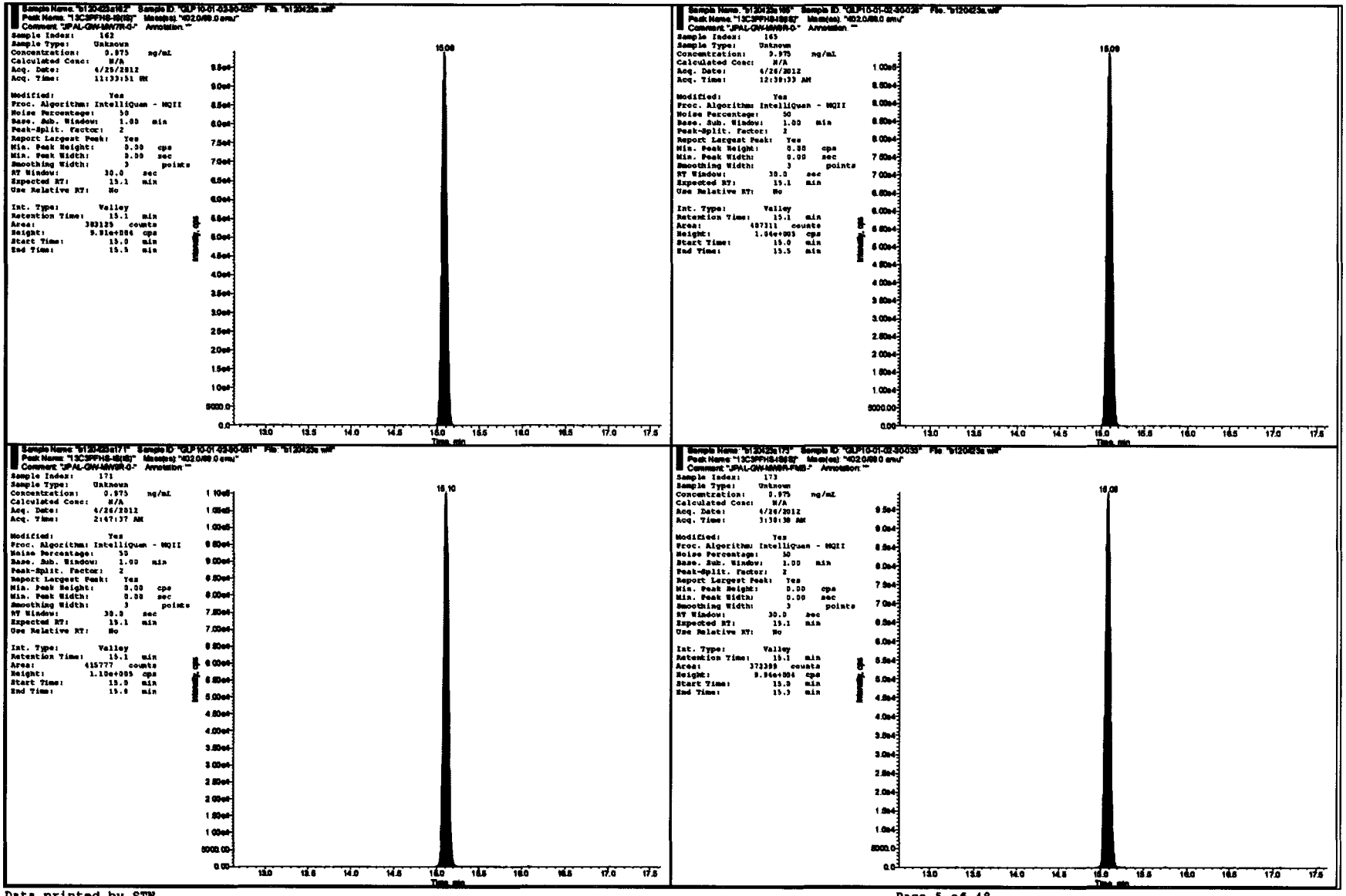


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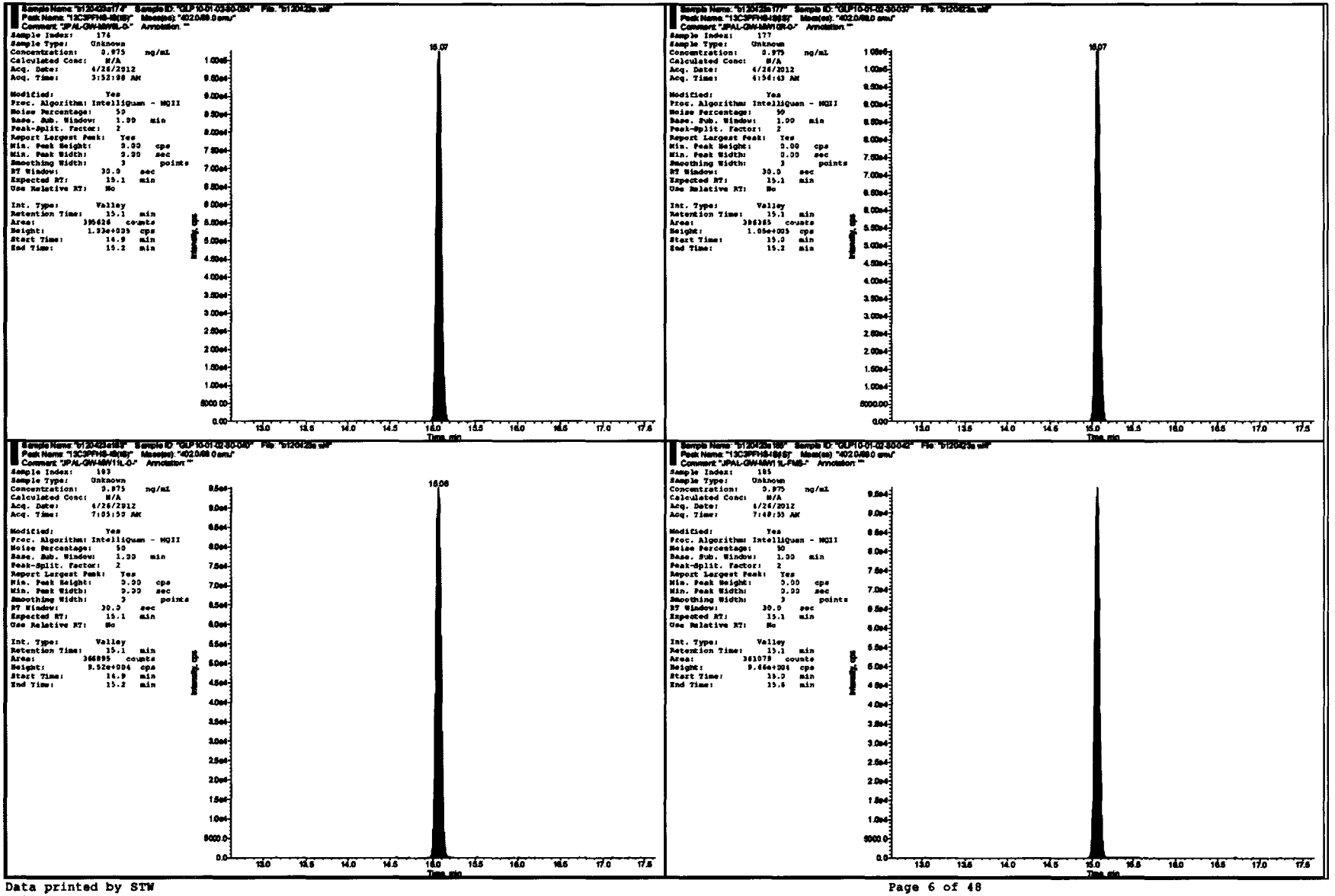


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Printing Date: Thursday, May 03, 2012

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*** Buster J2930203

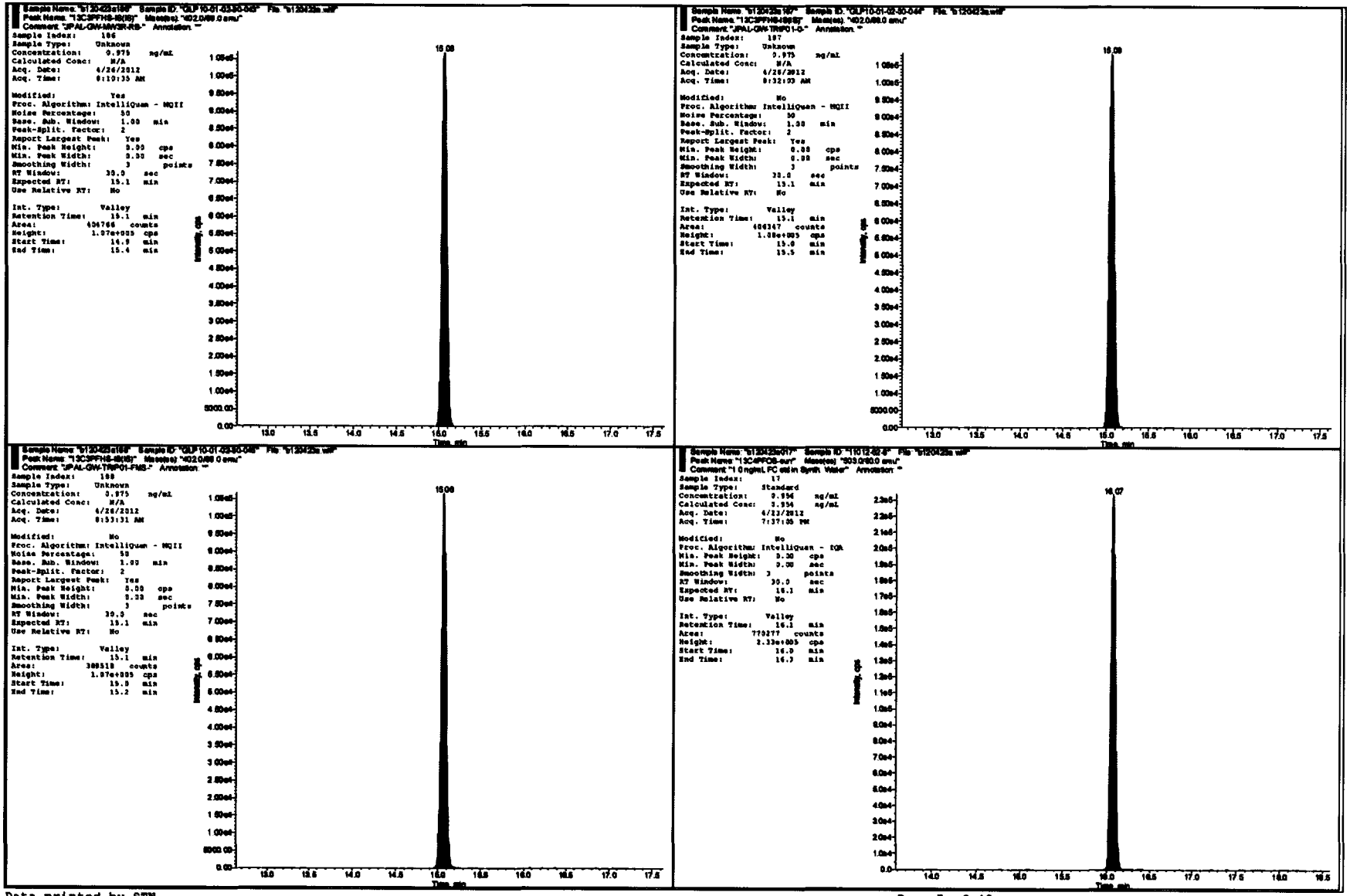
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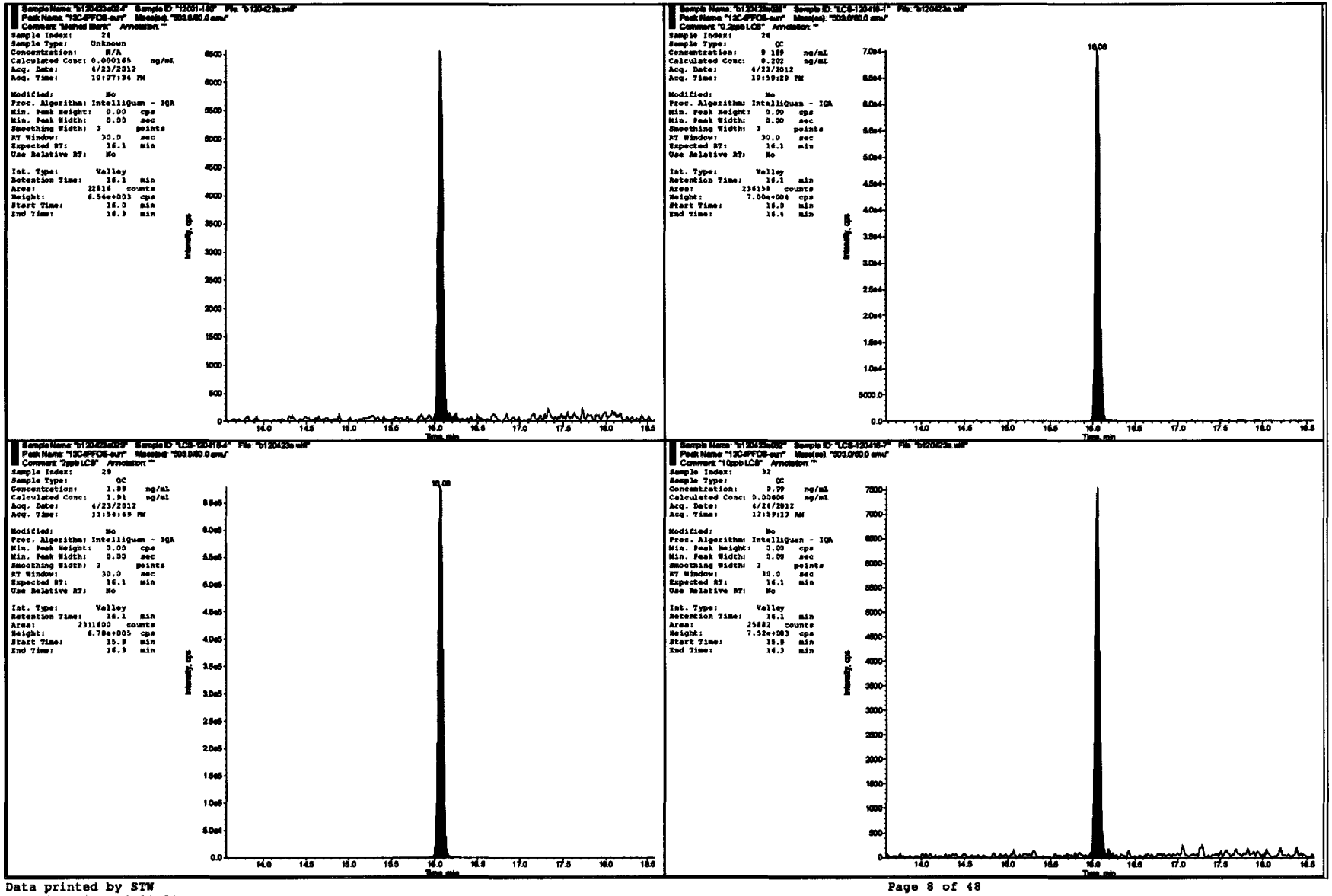
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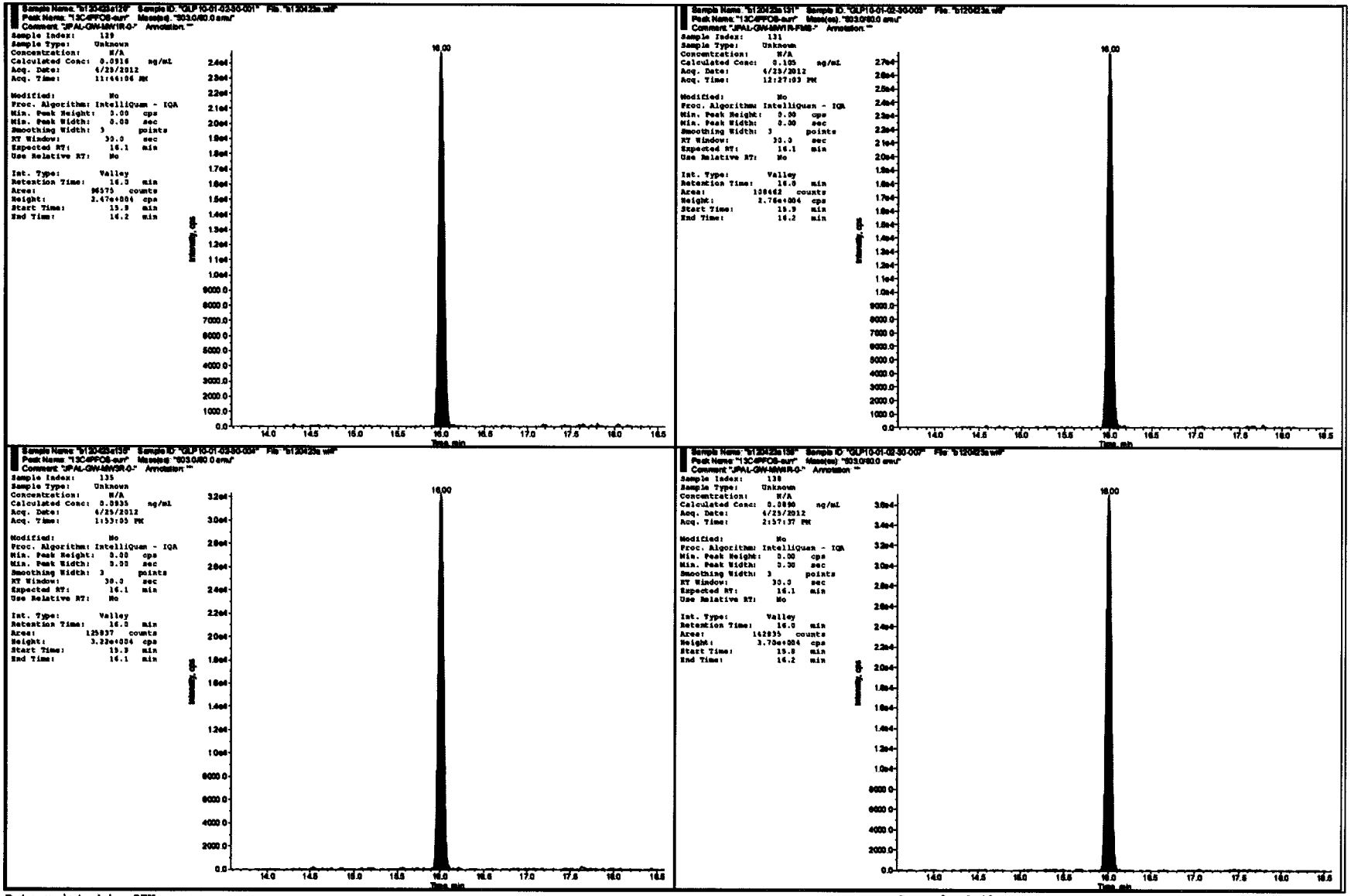


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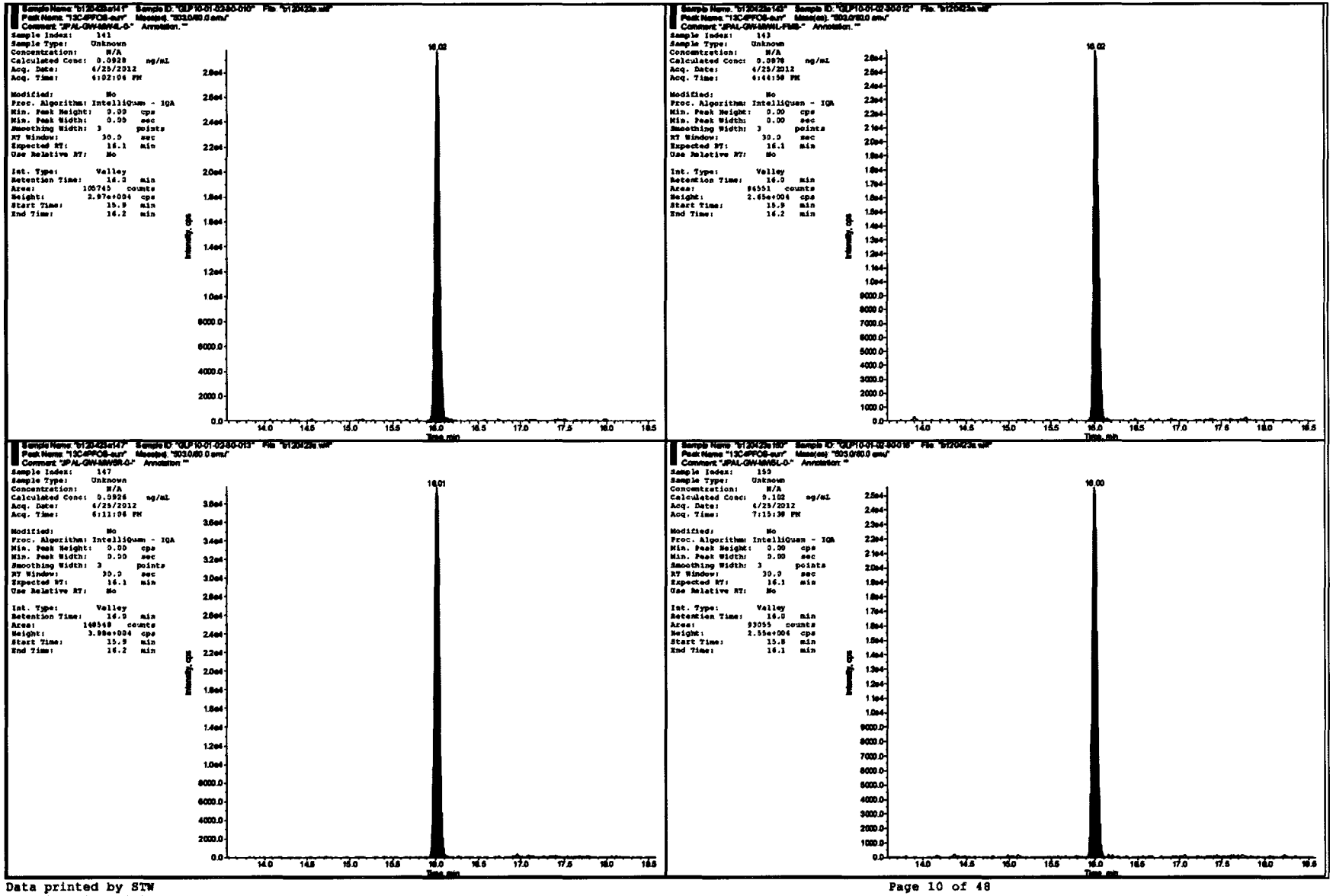
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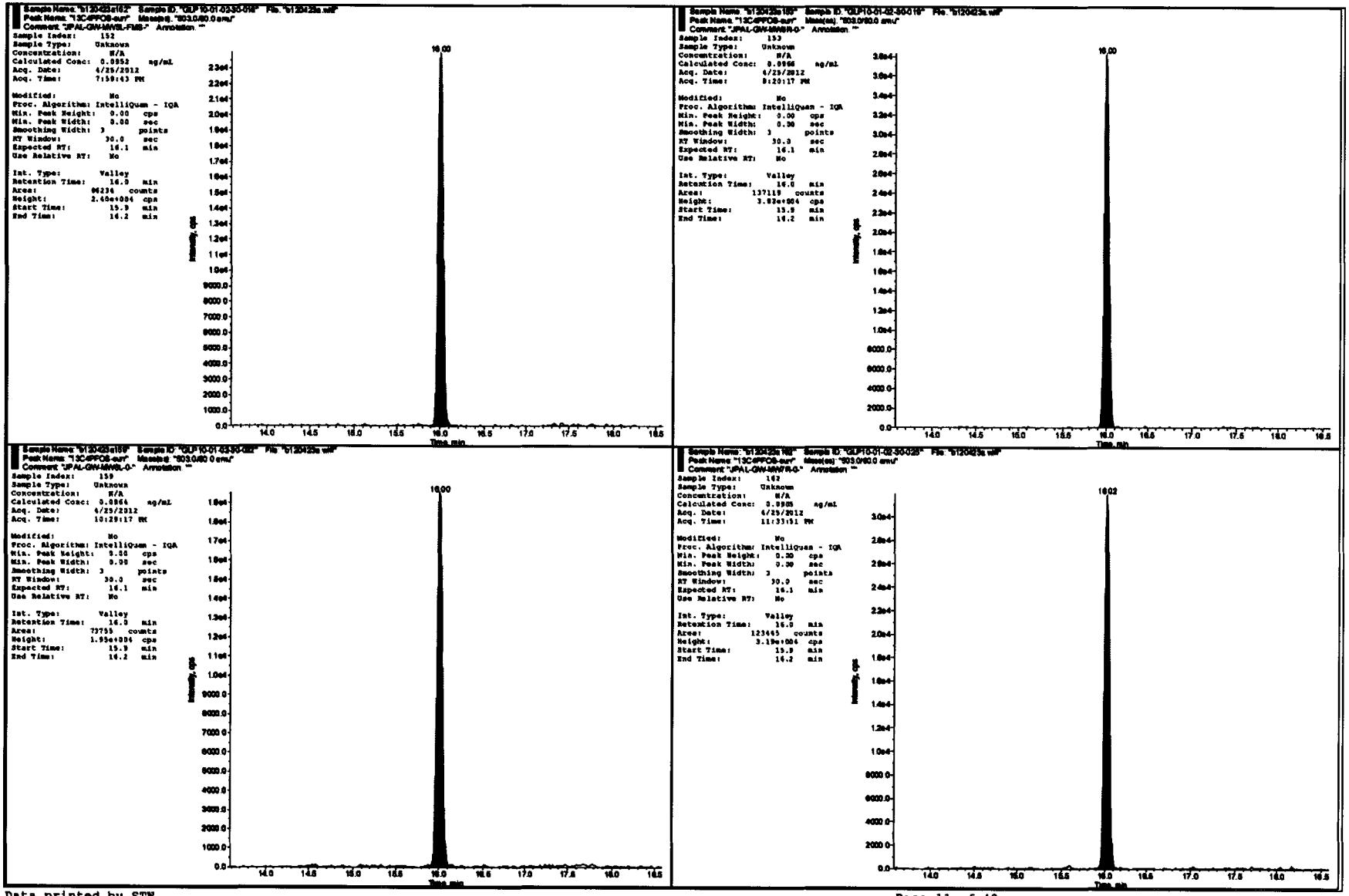


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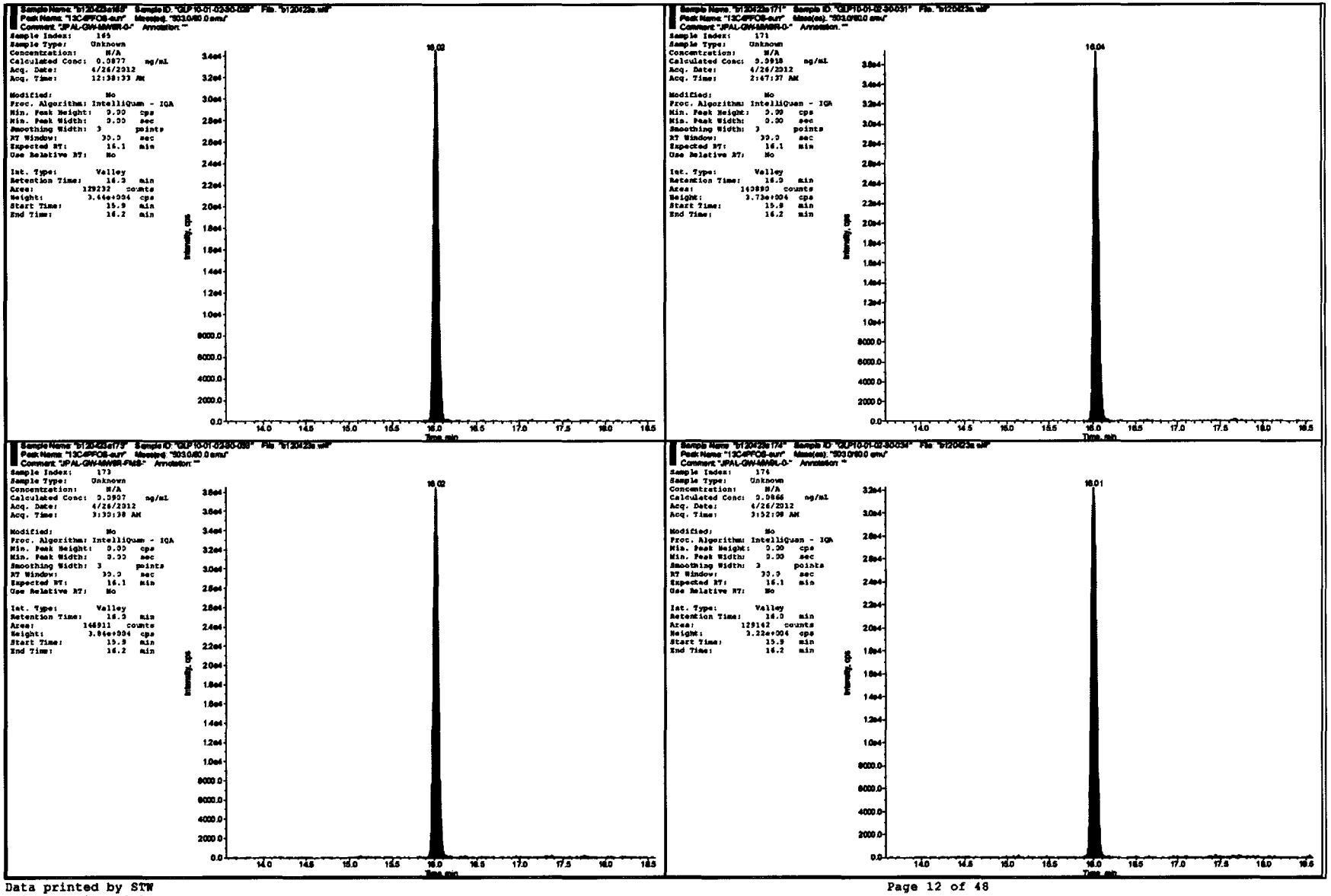
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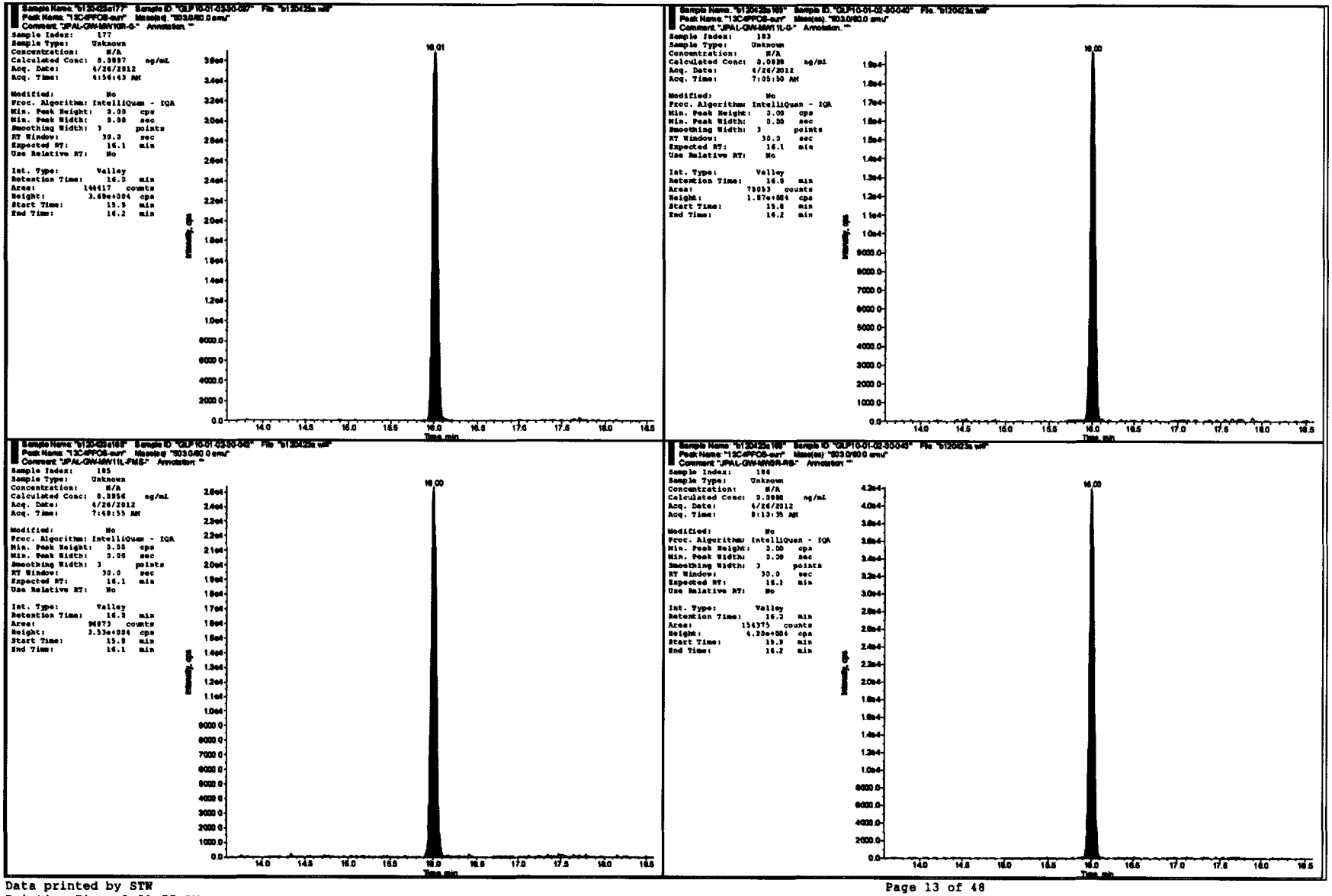


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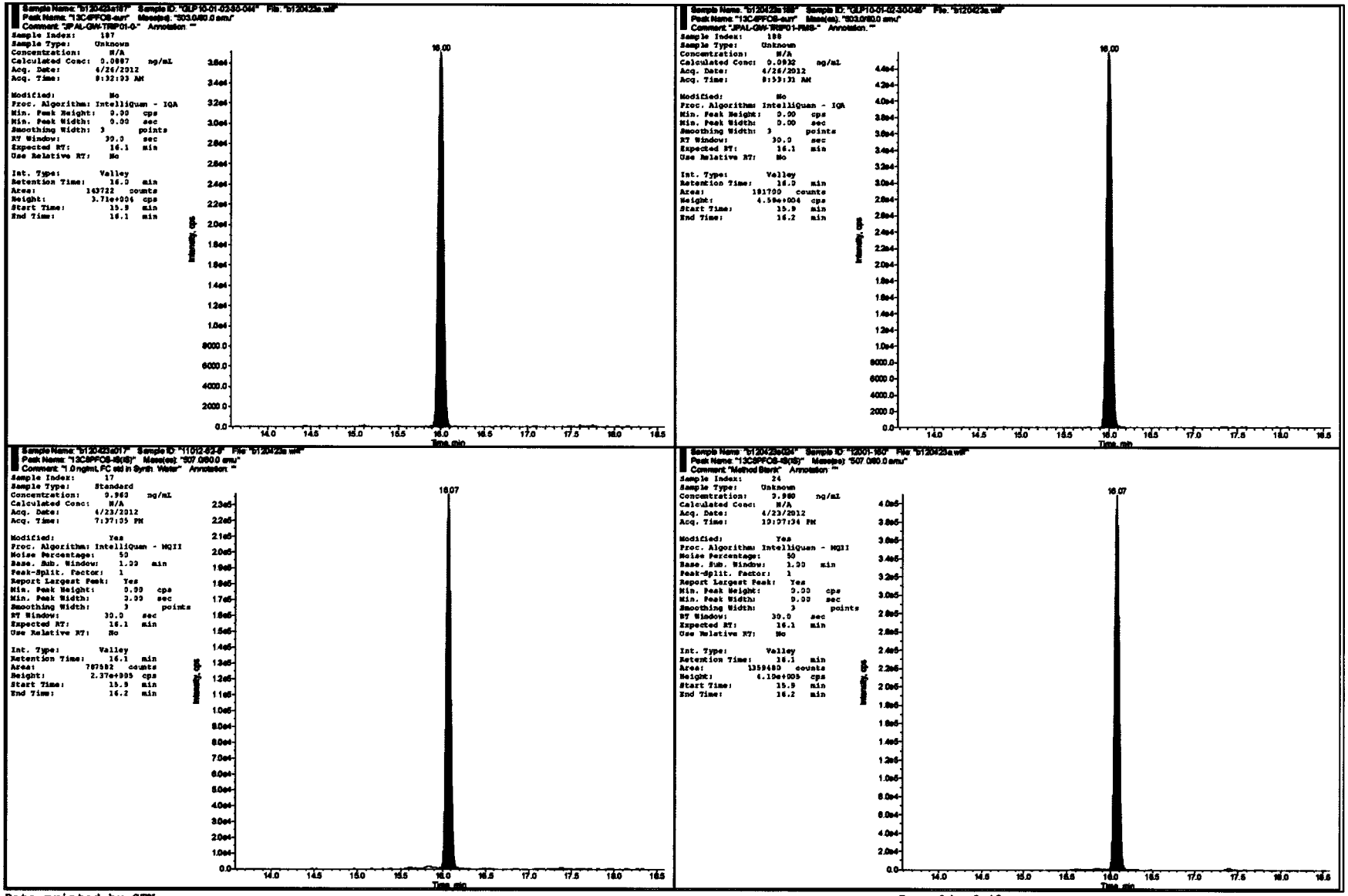
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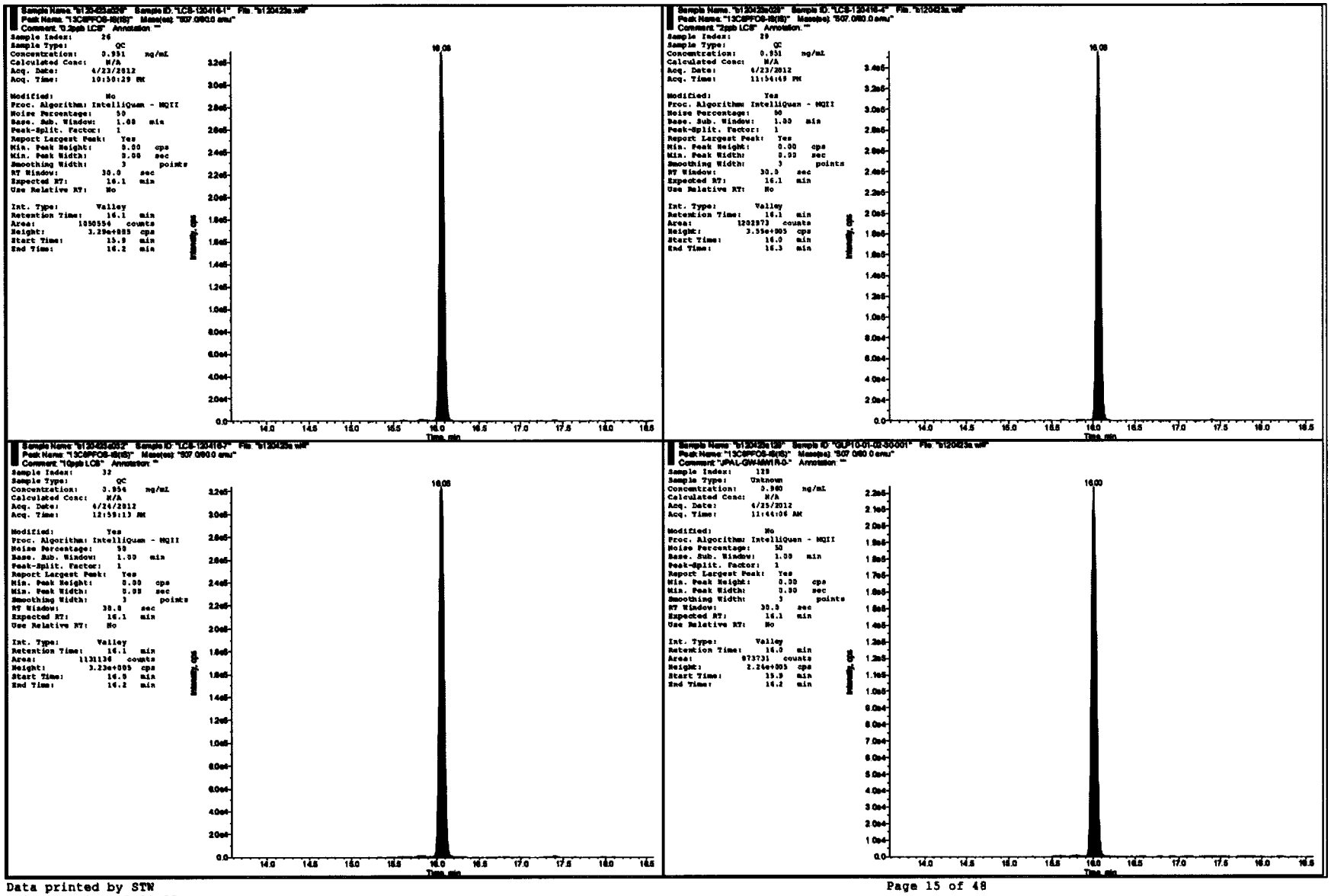
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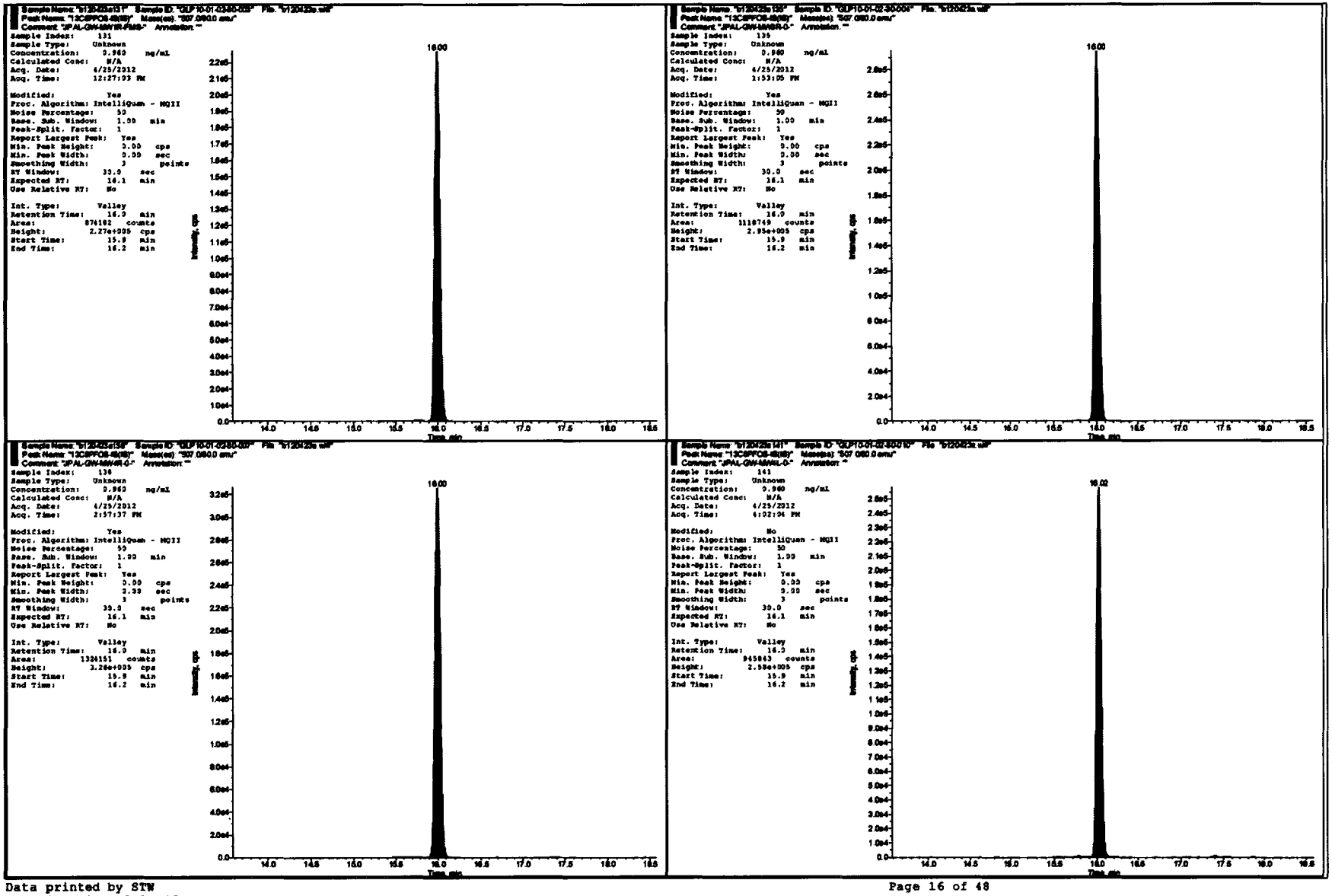
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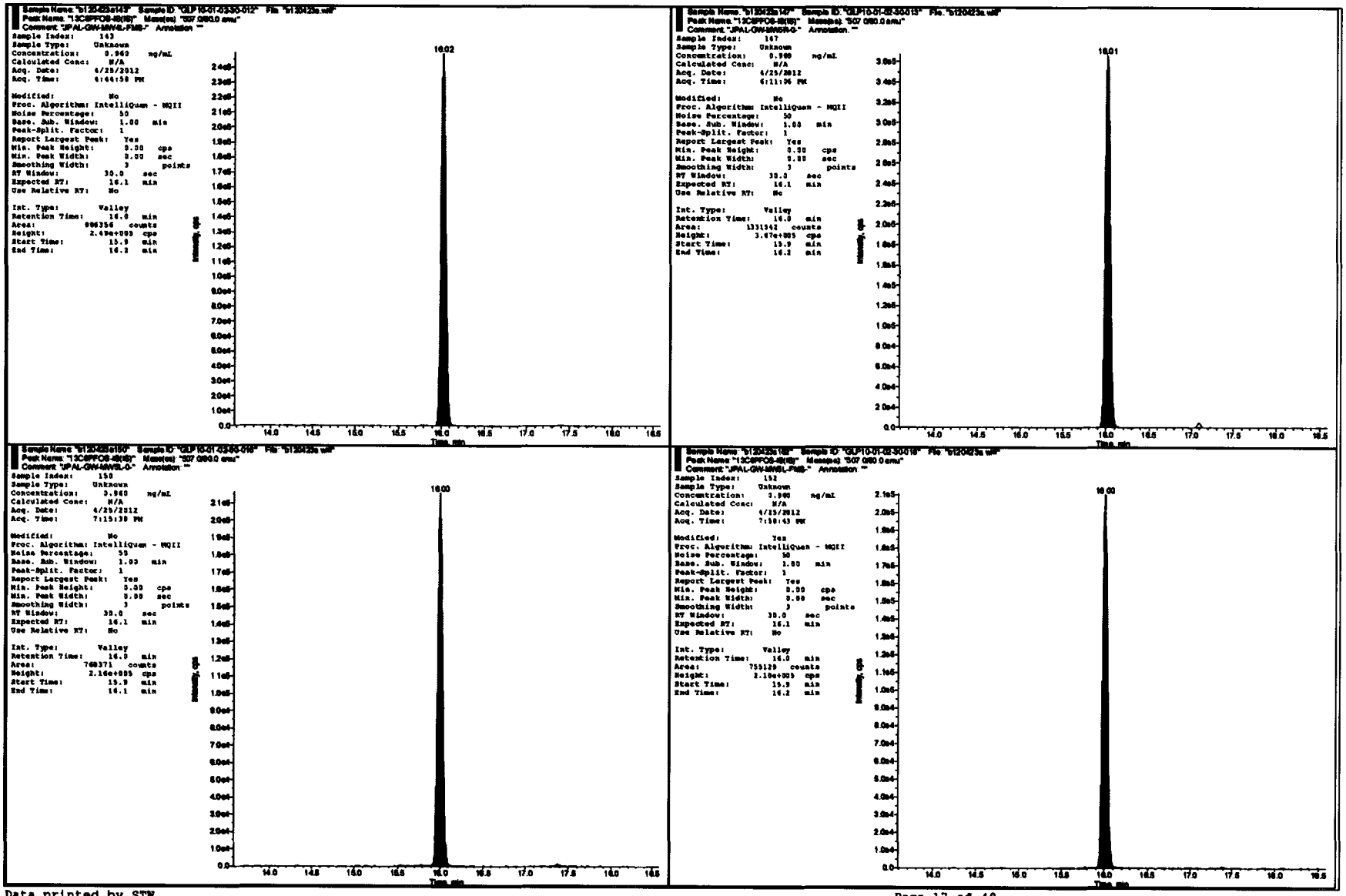


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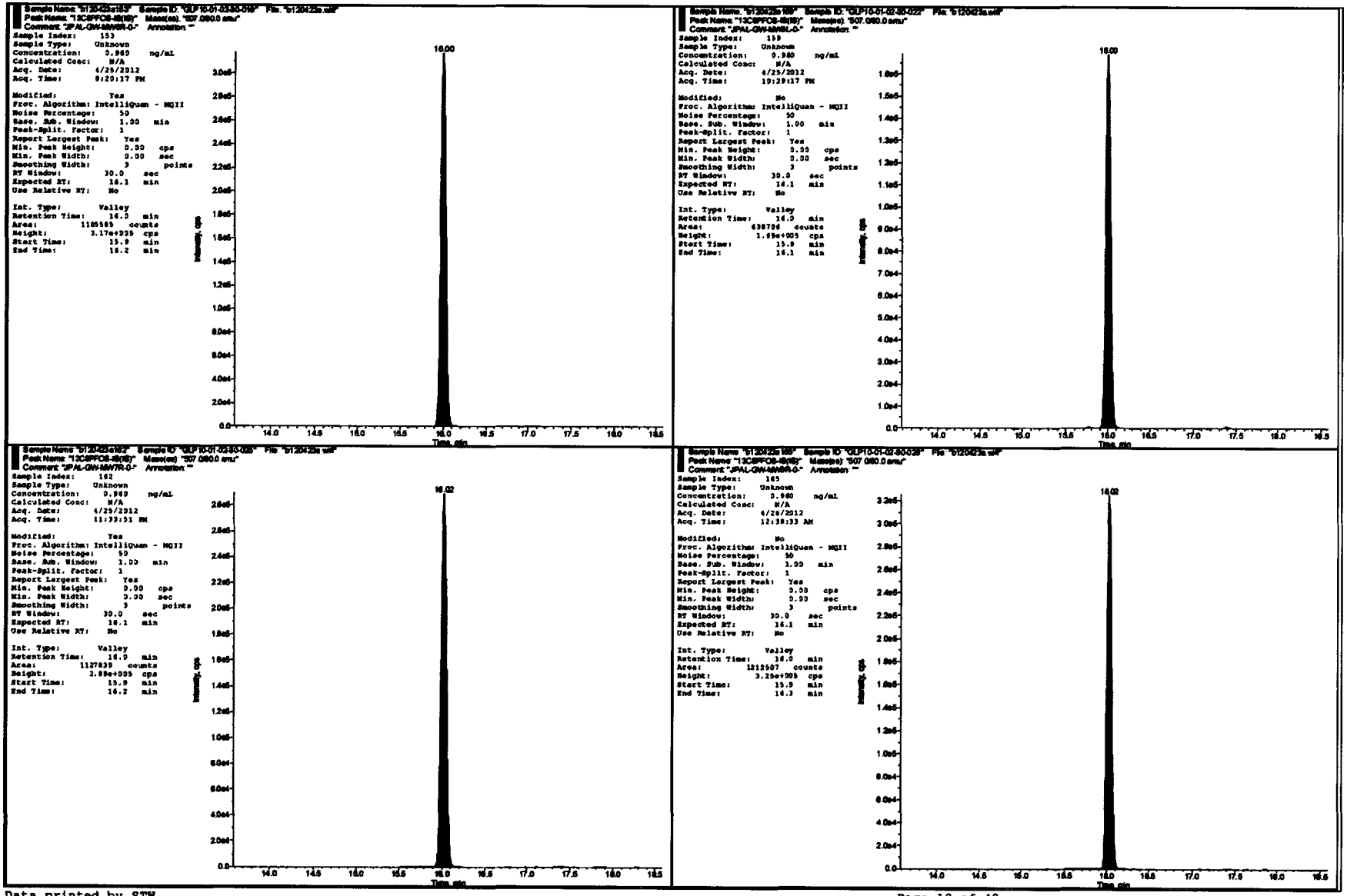
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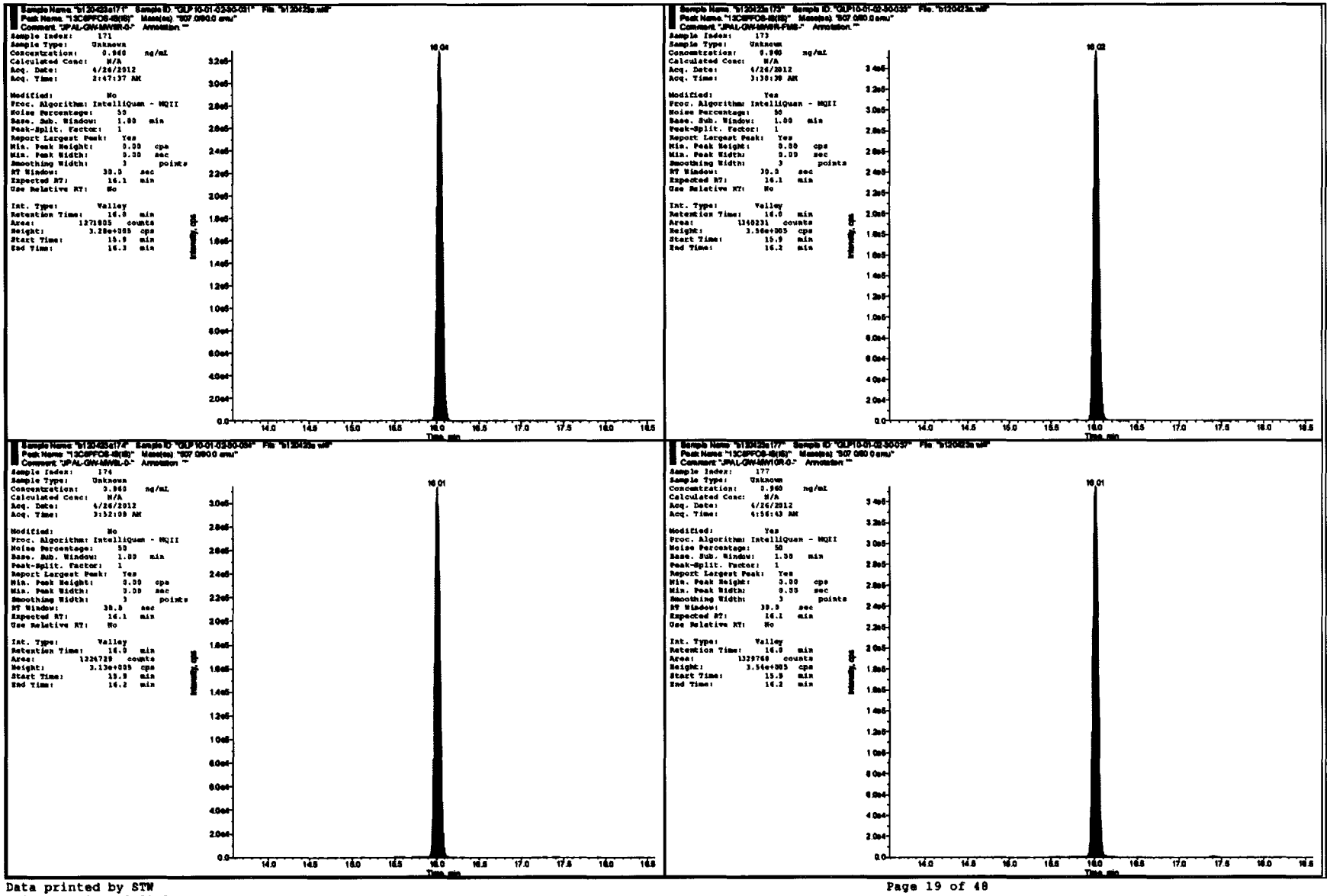
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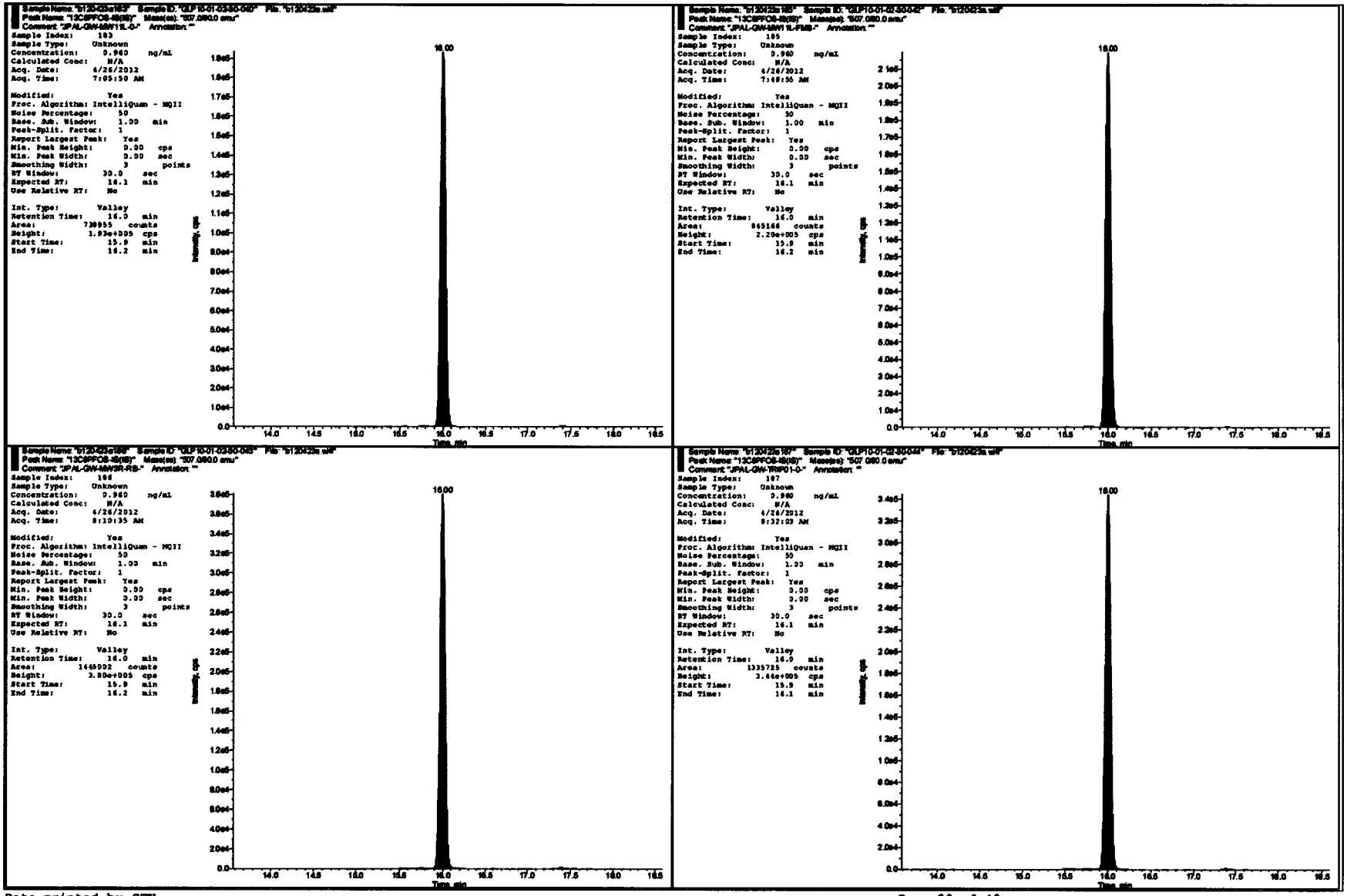


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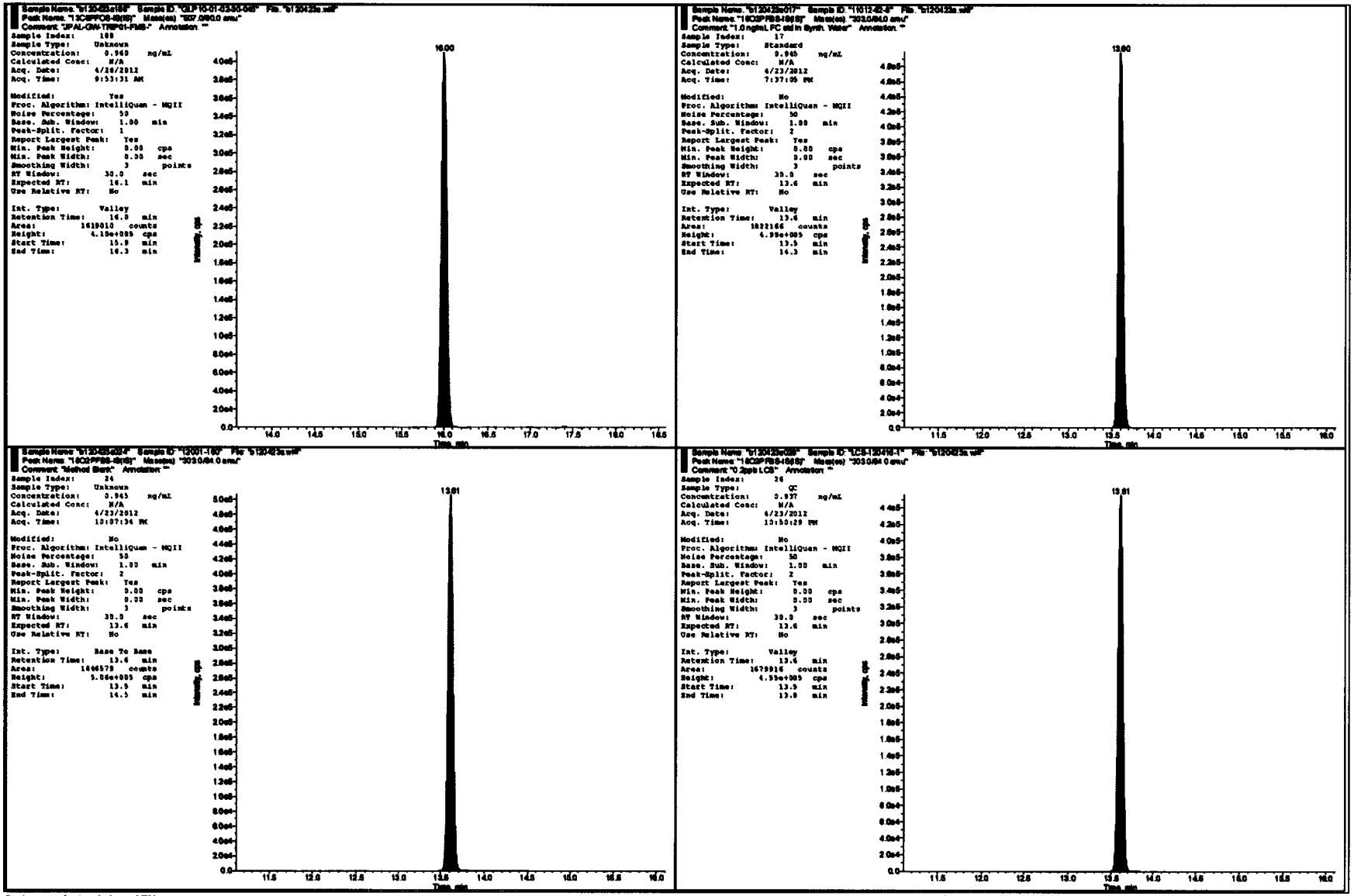
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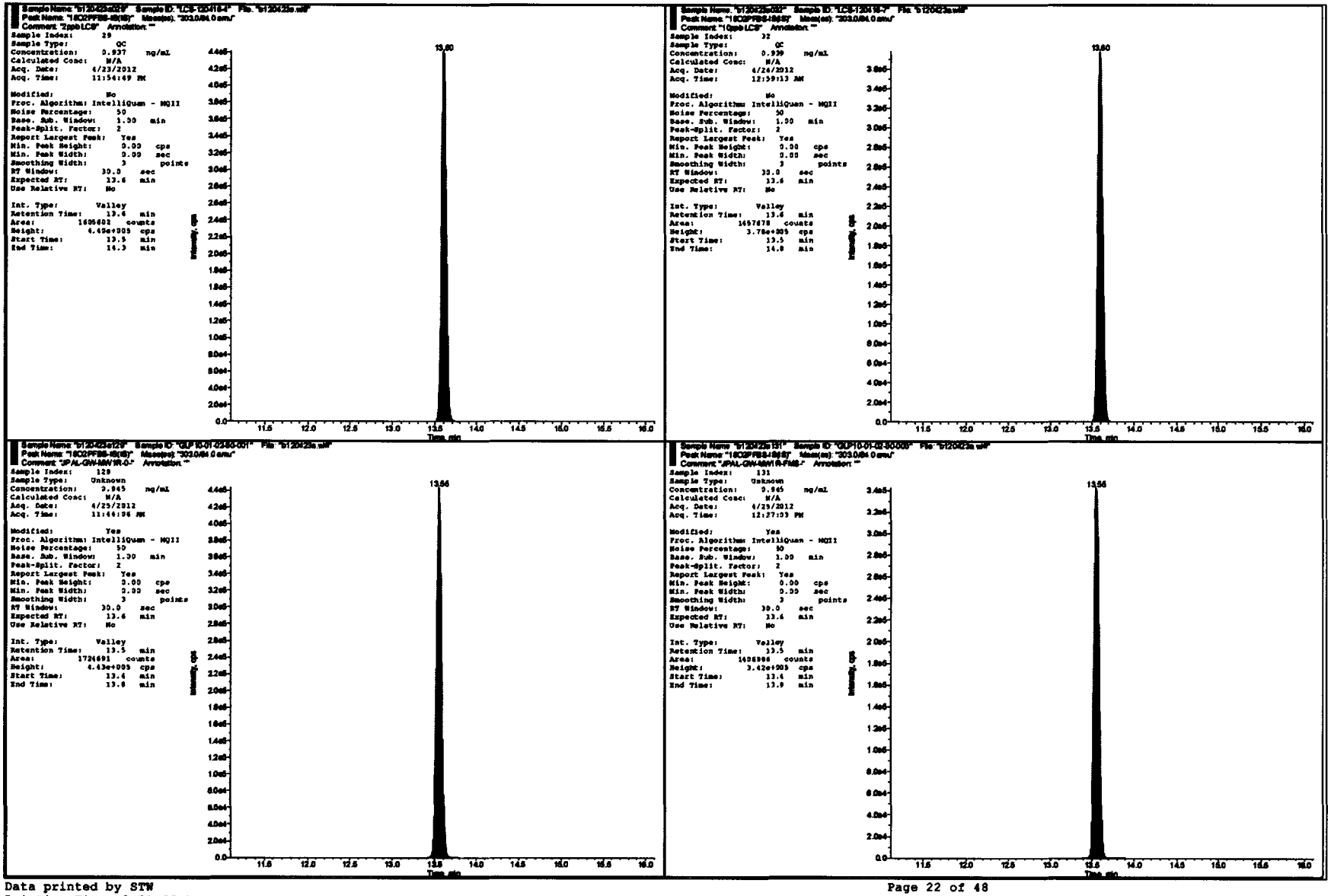
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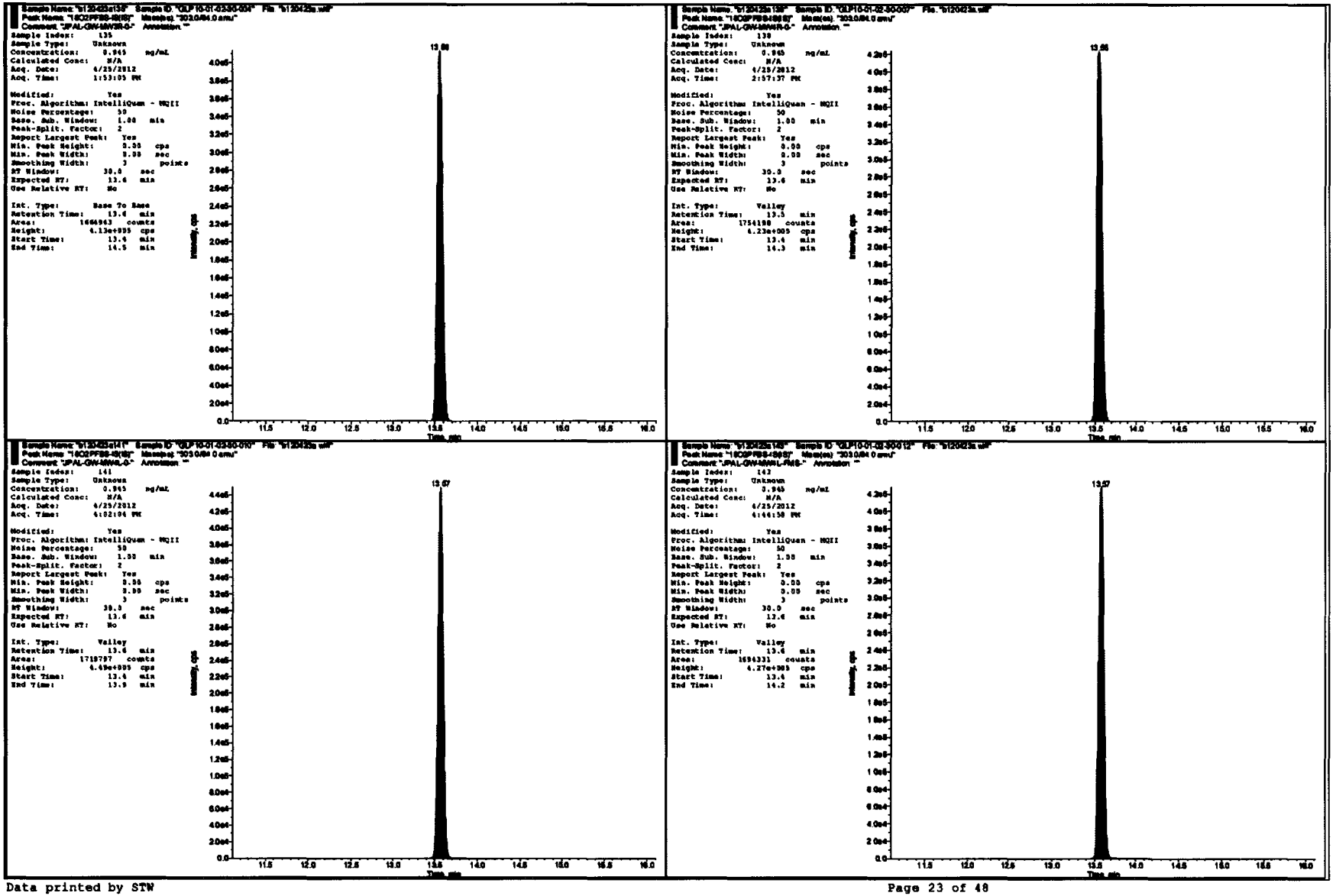
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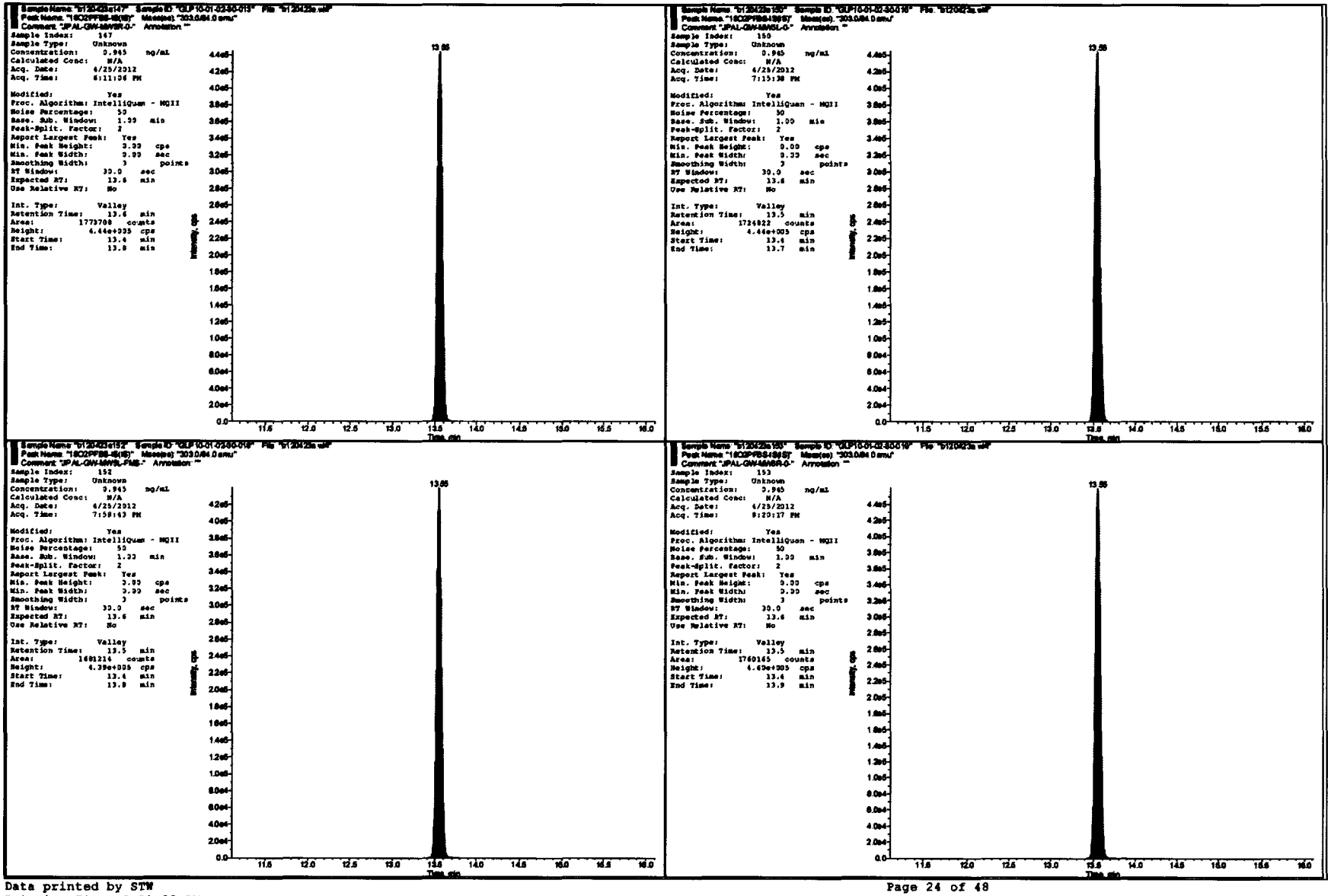
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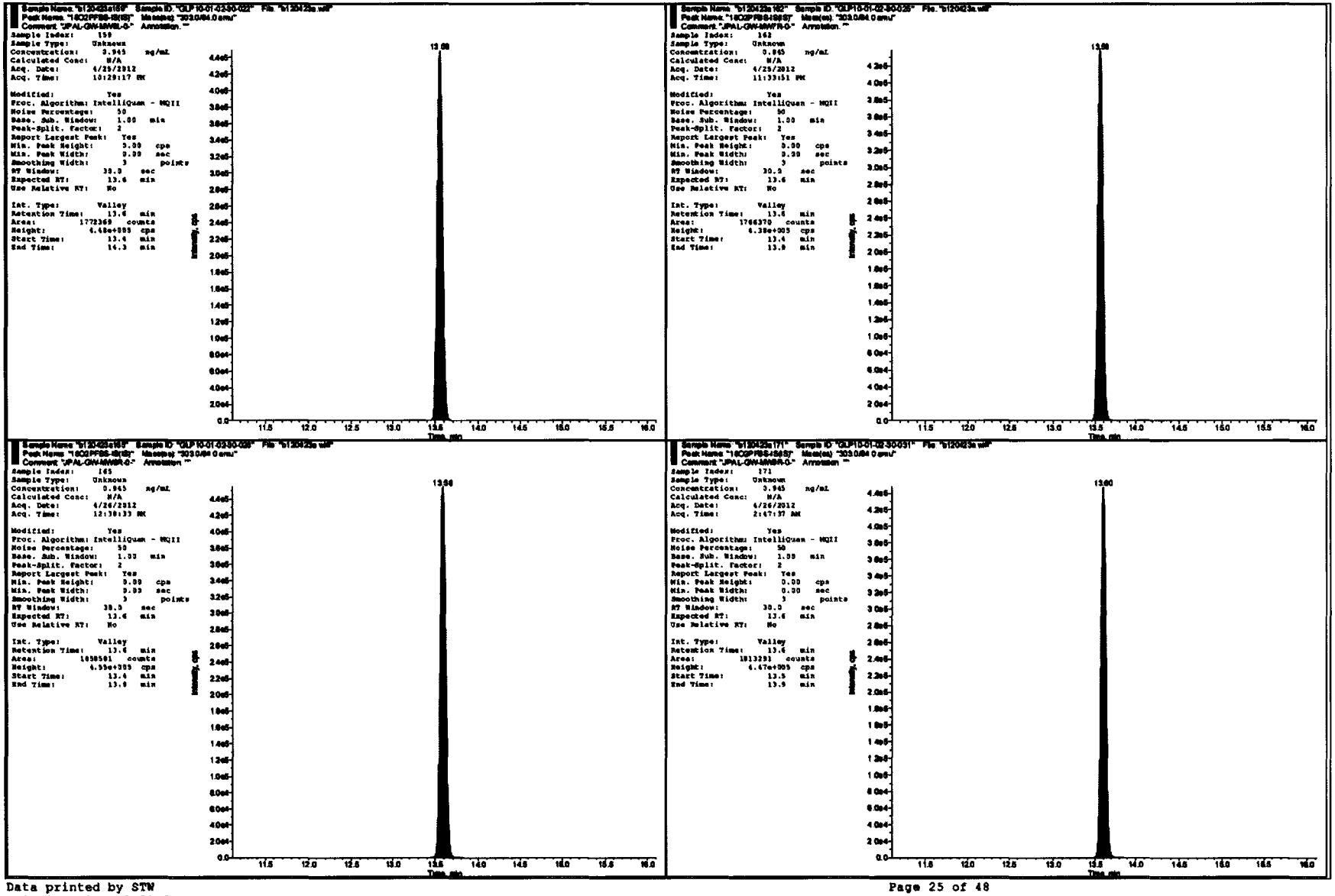


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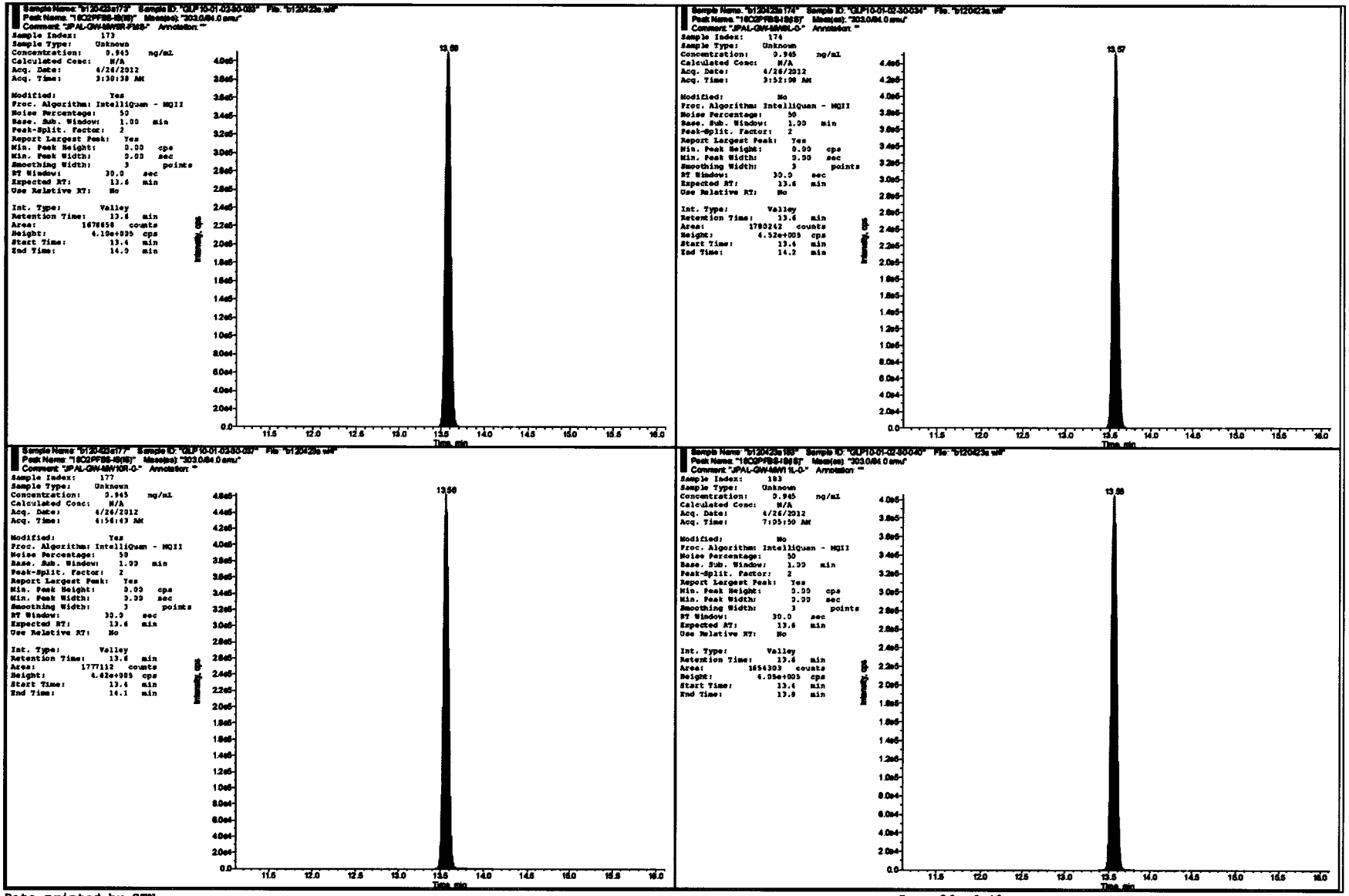


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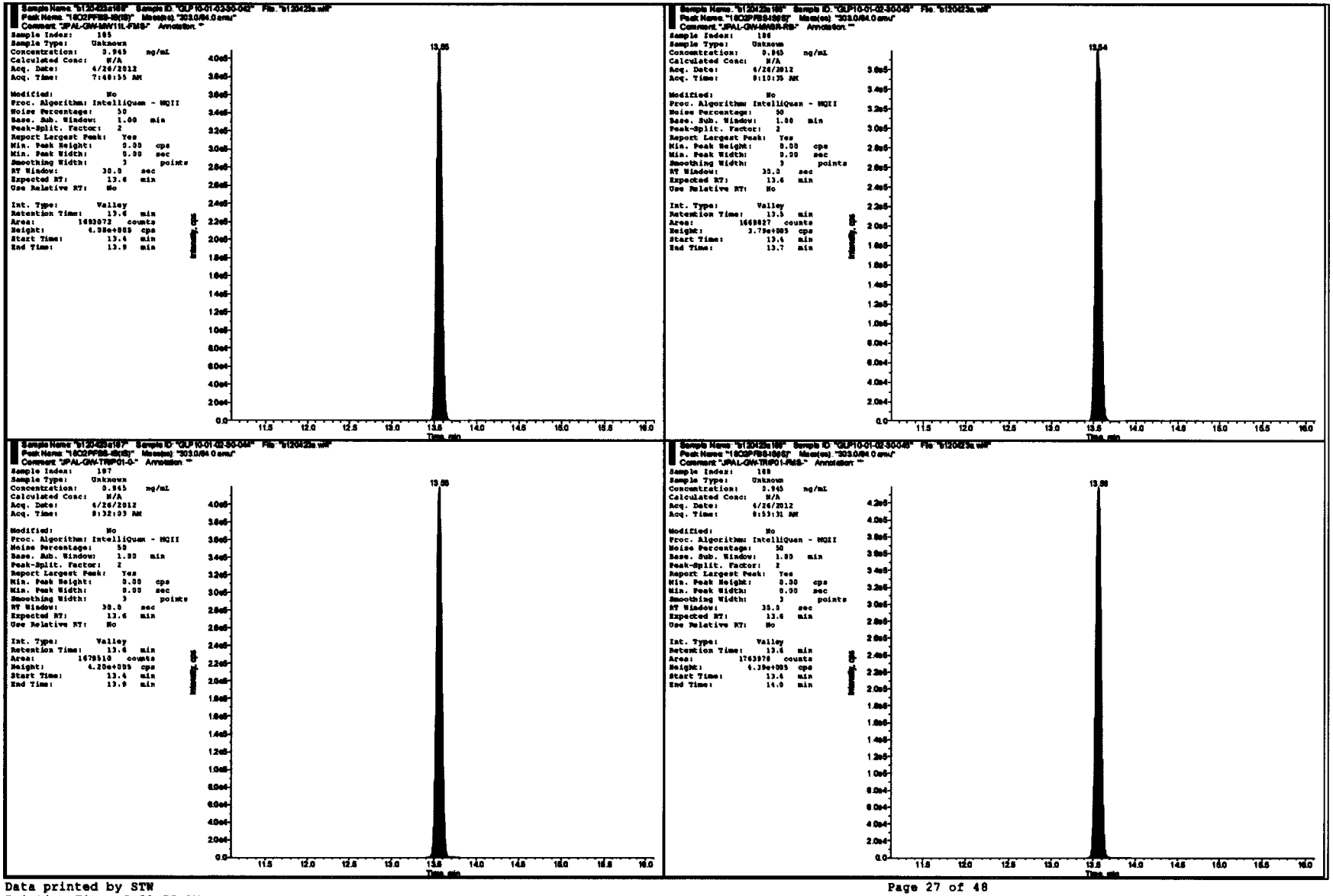
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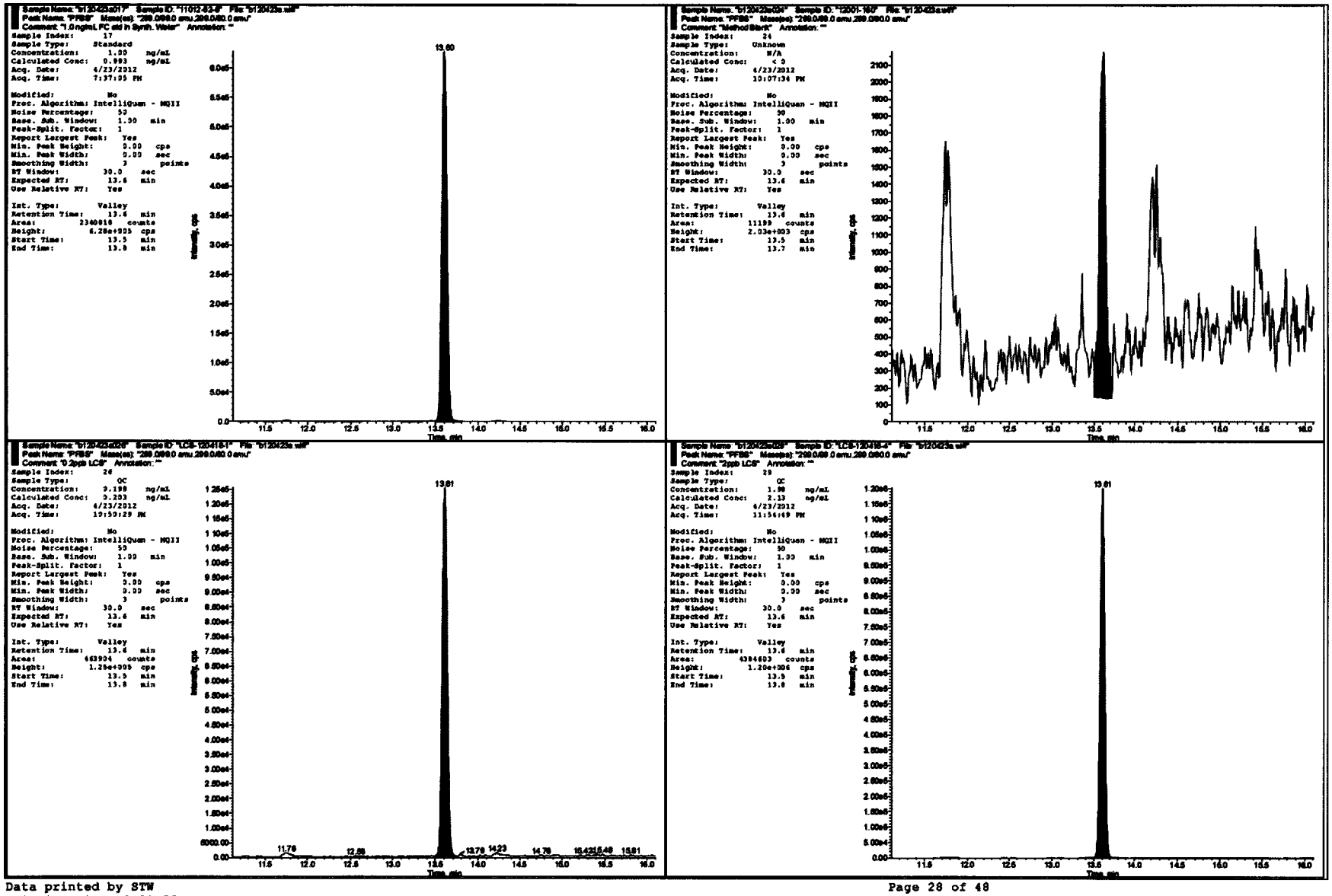
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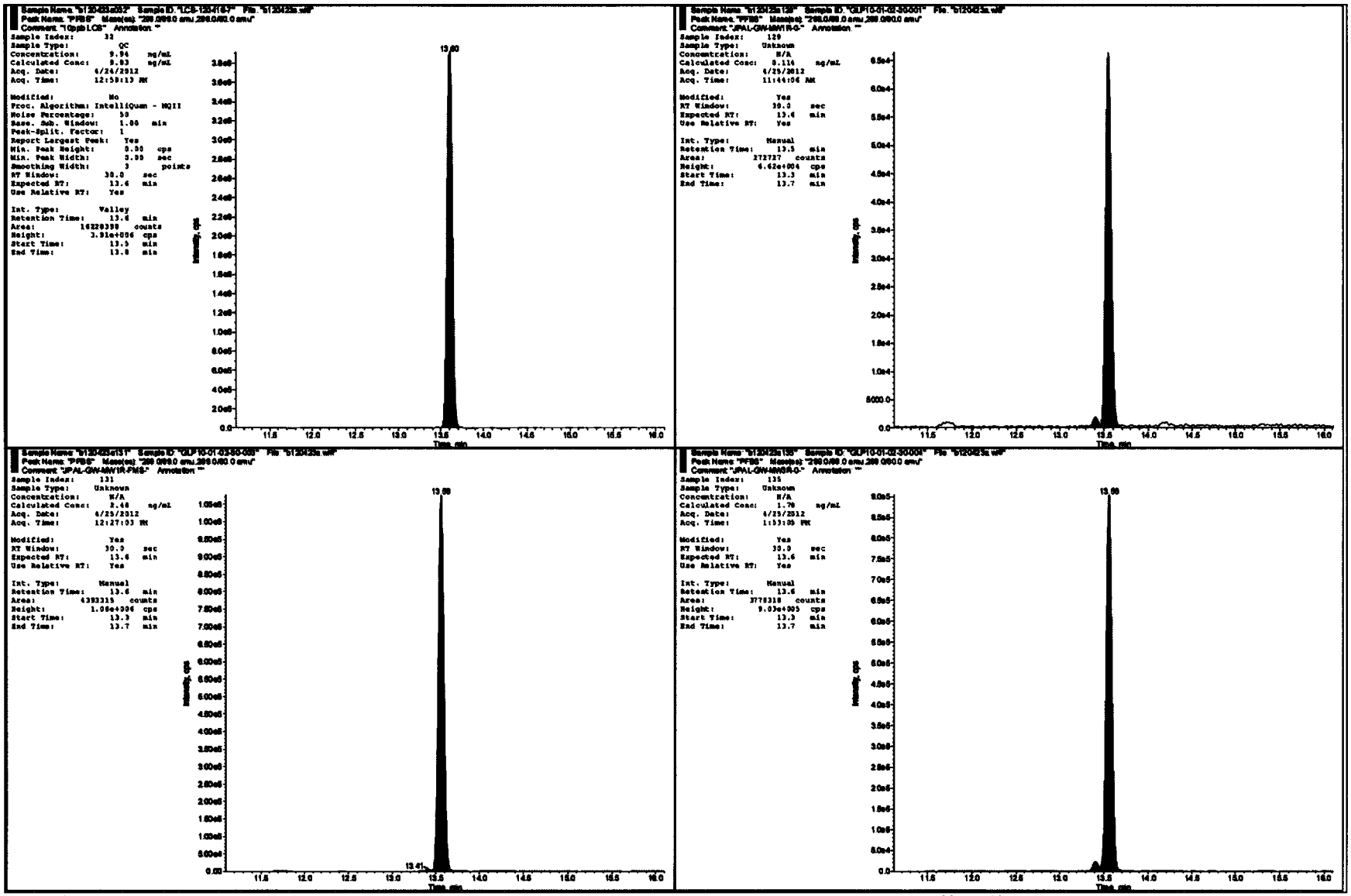


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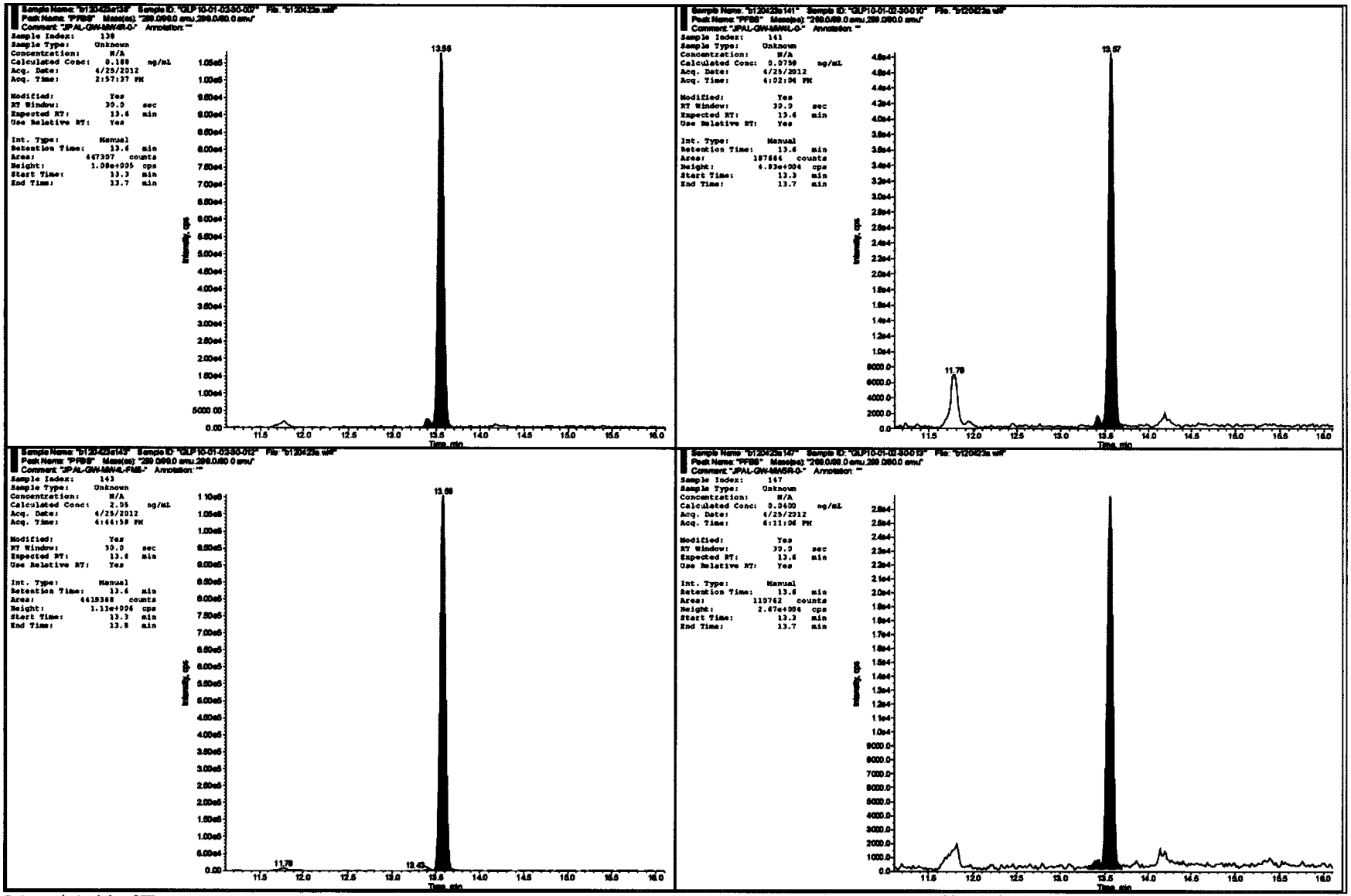
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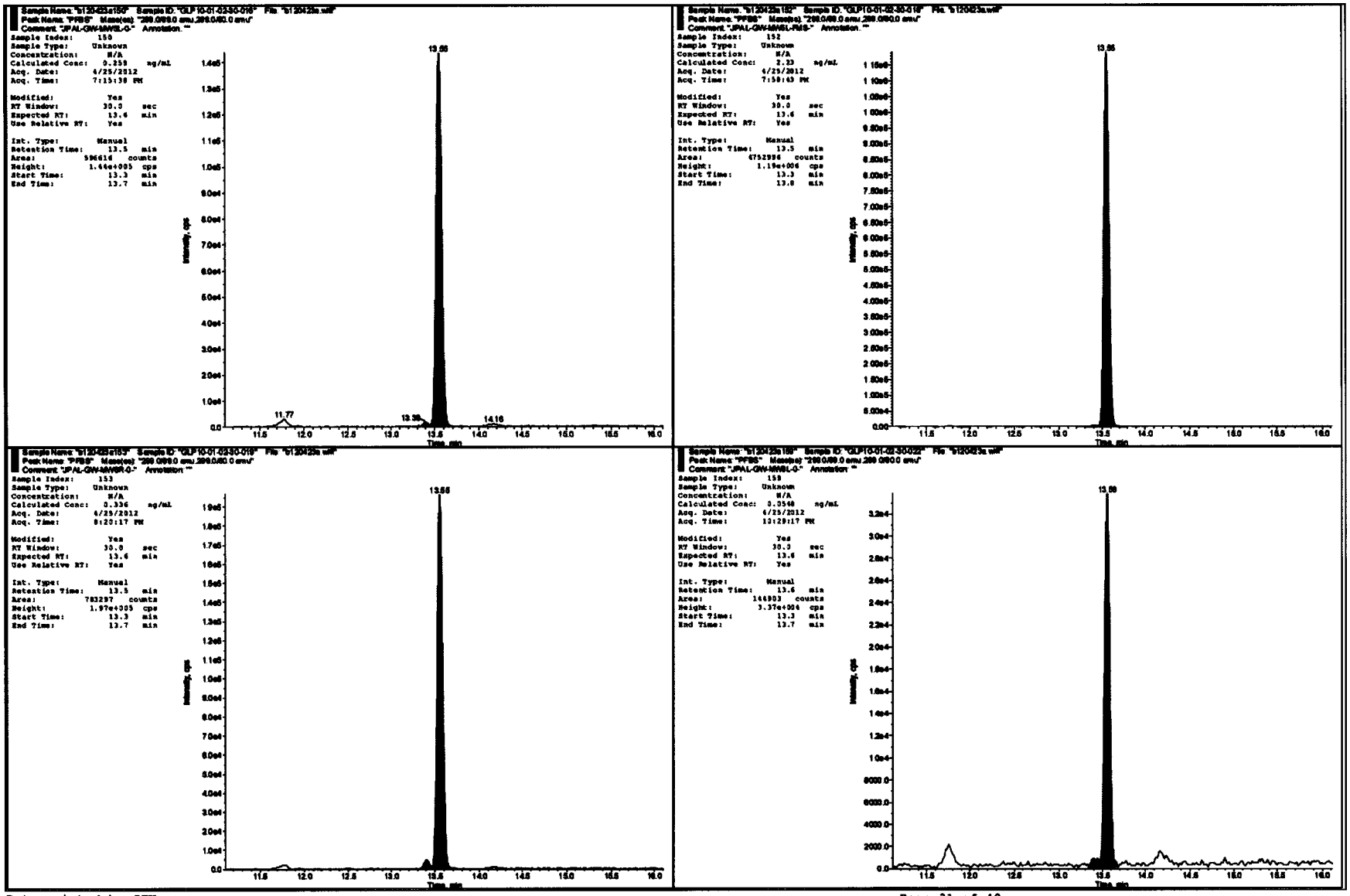
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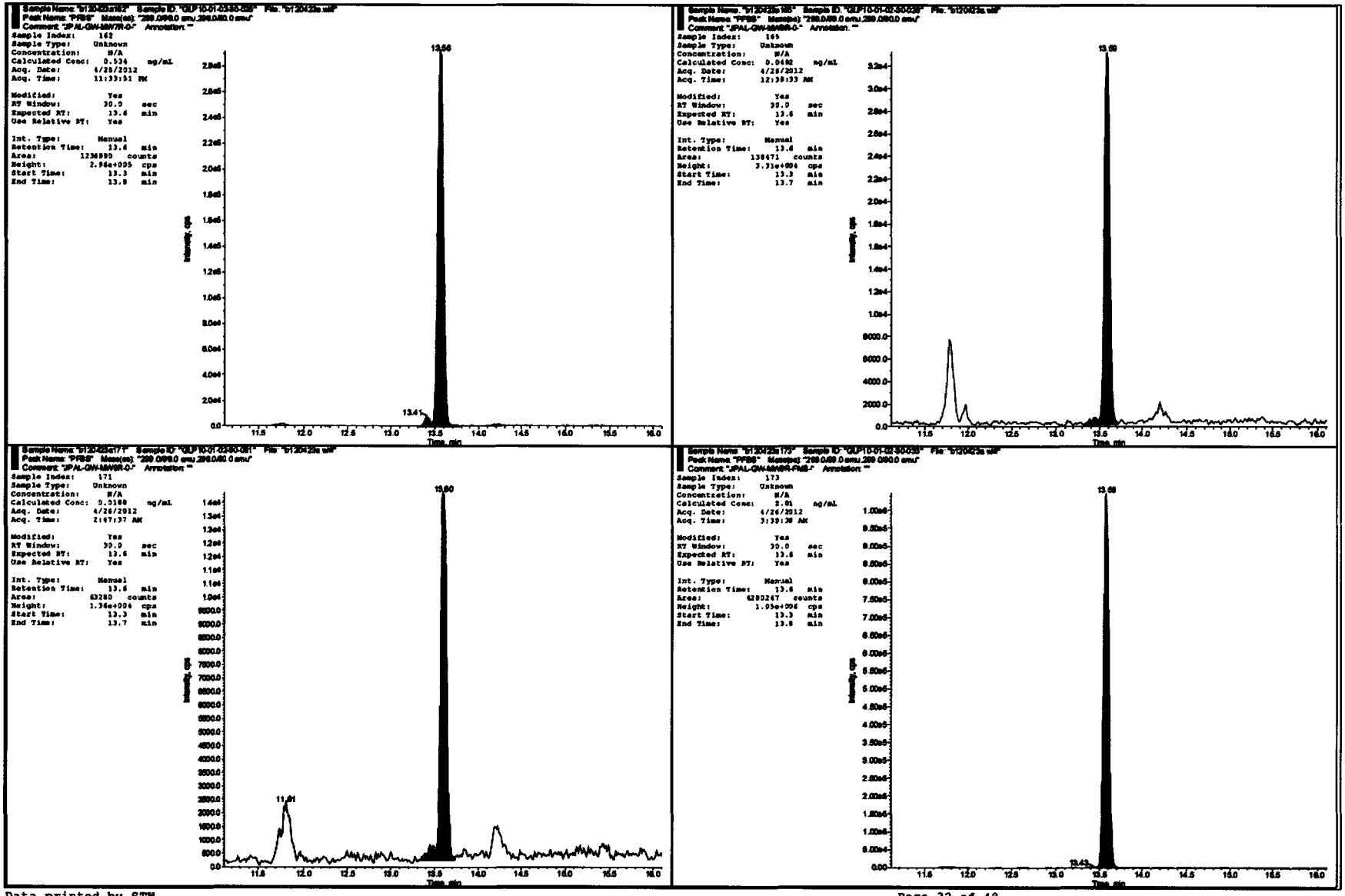
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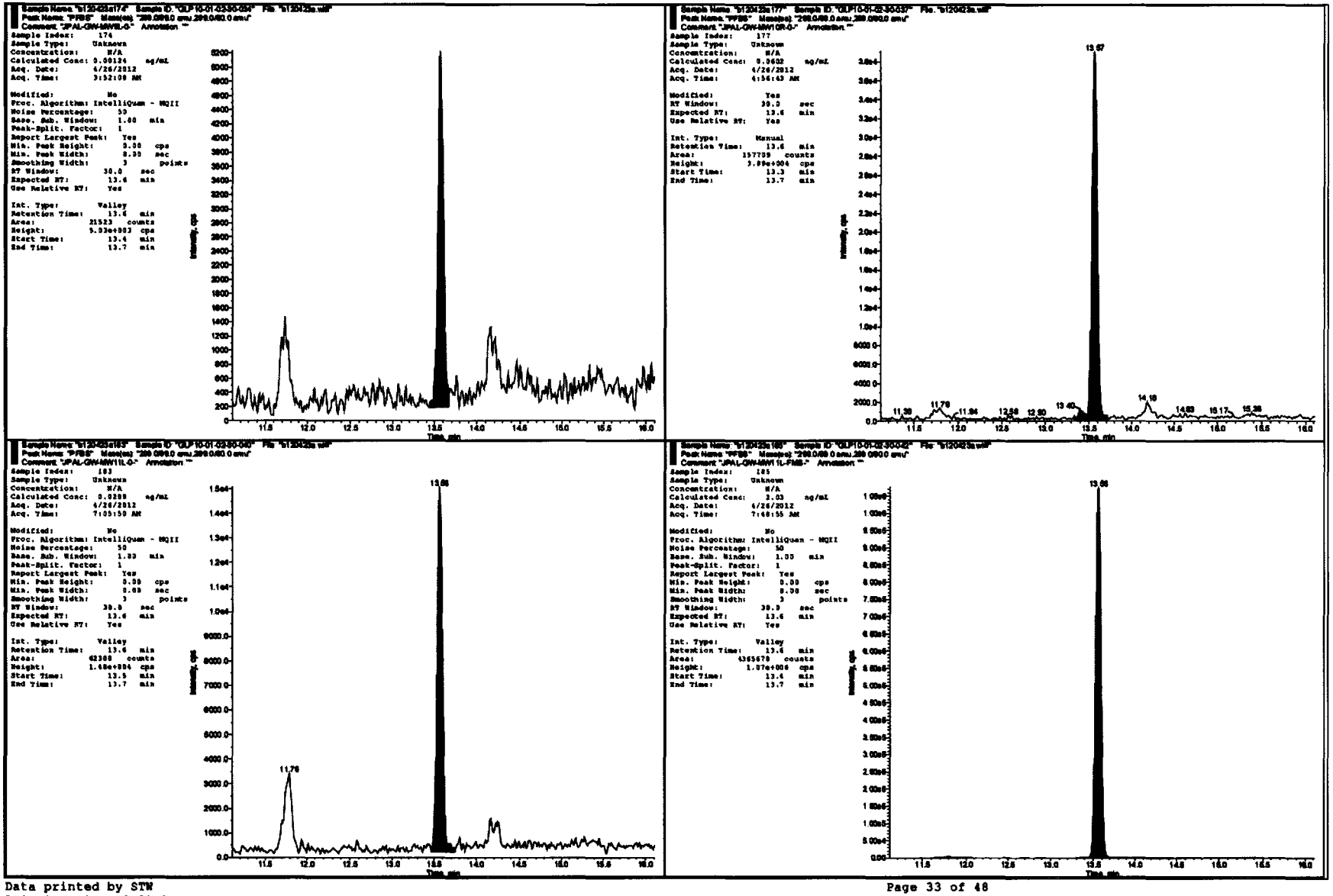
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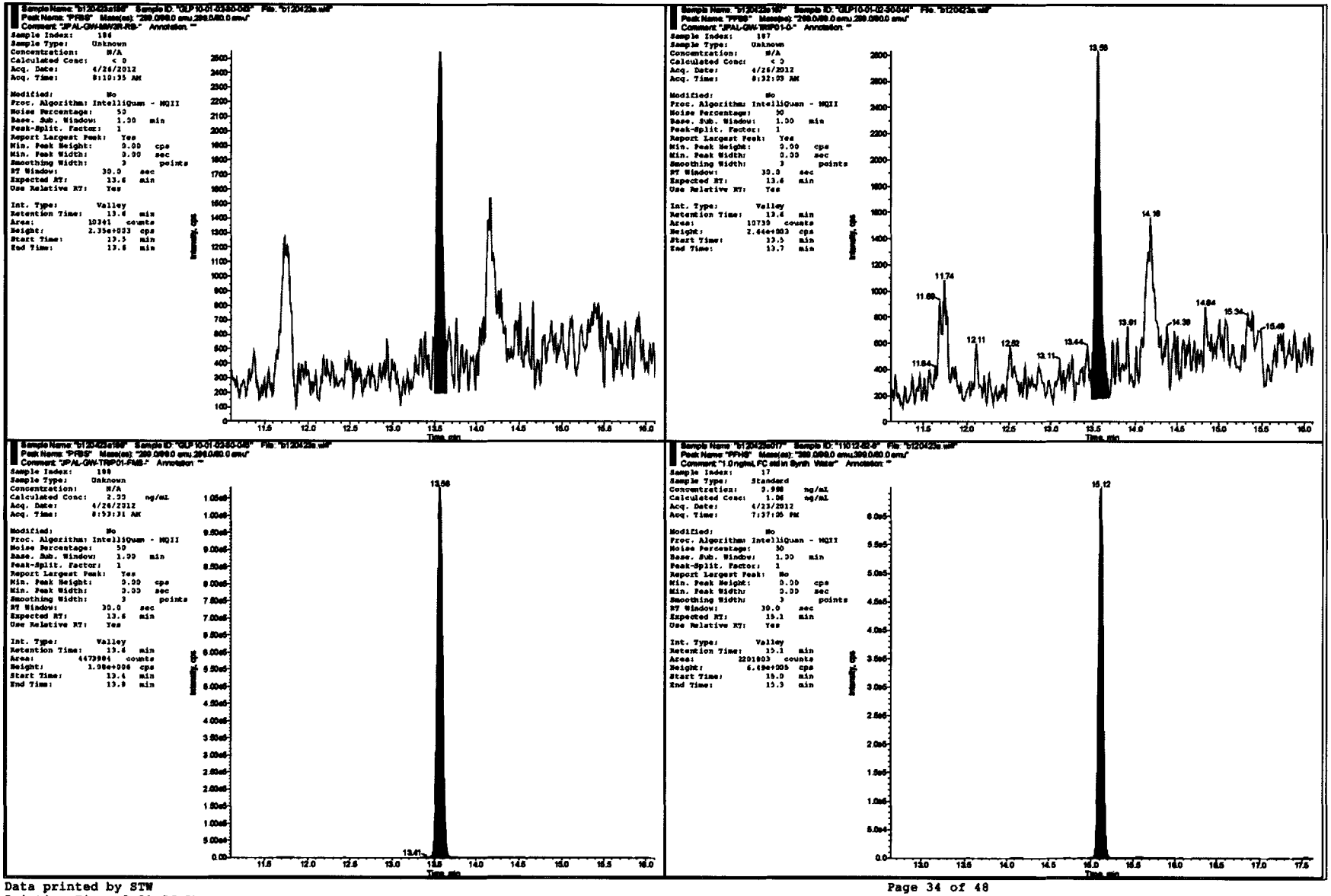
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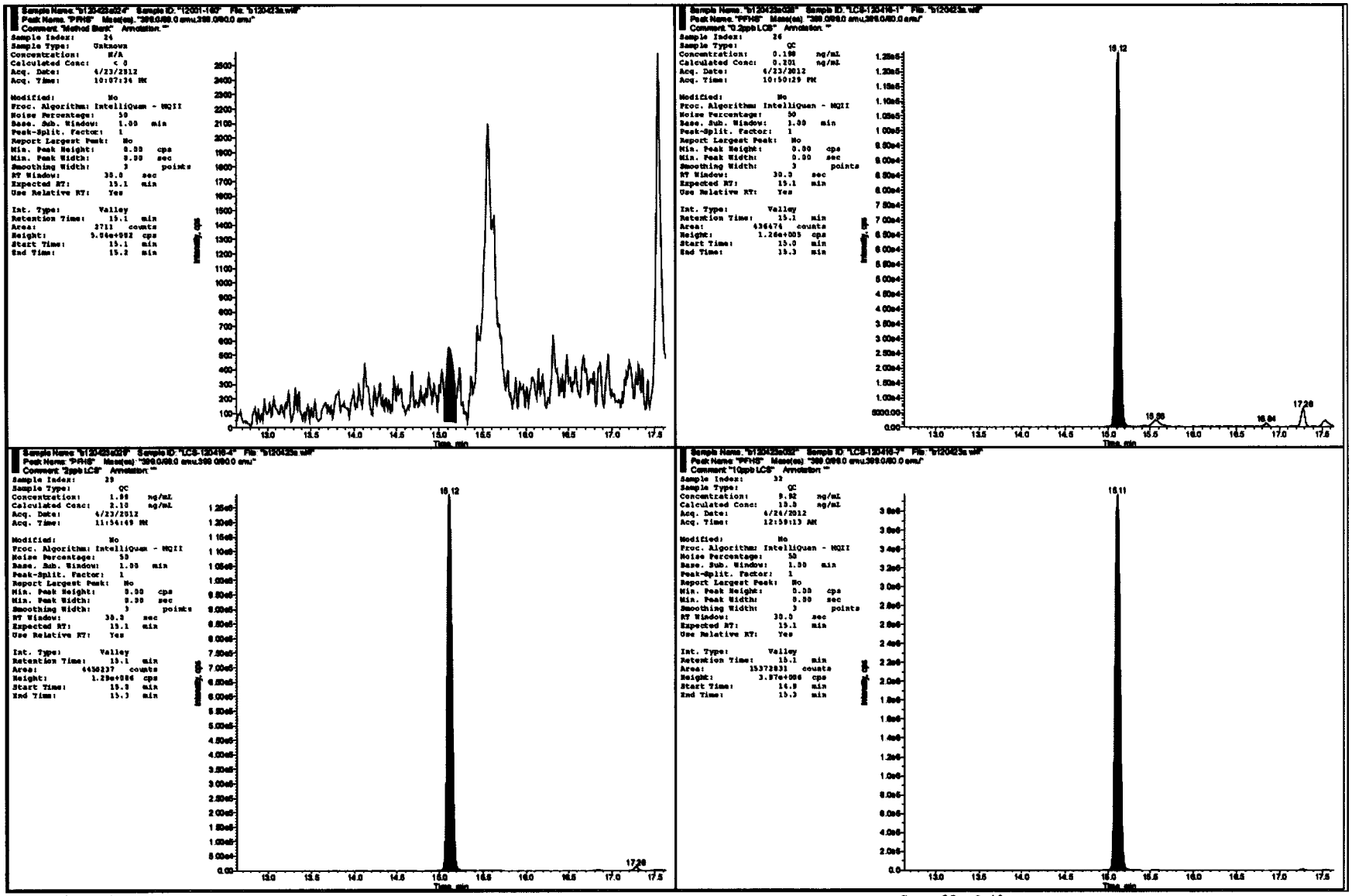


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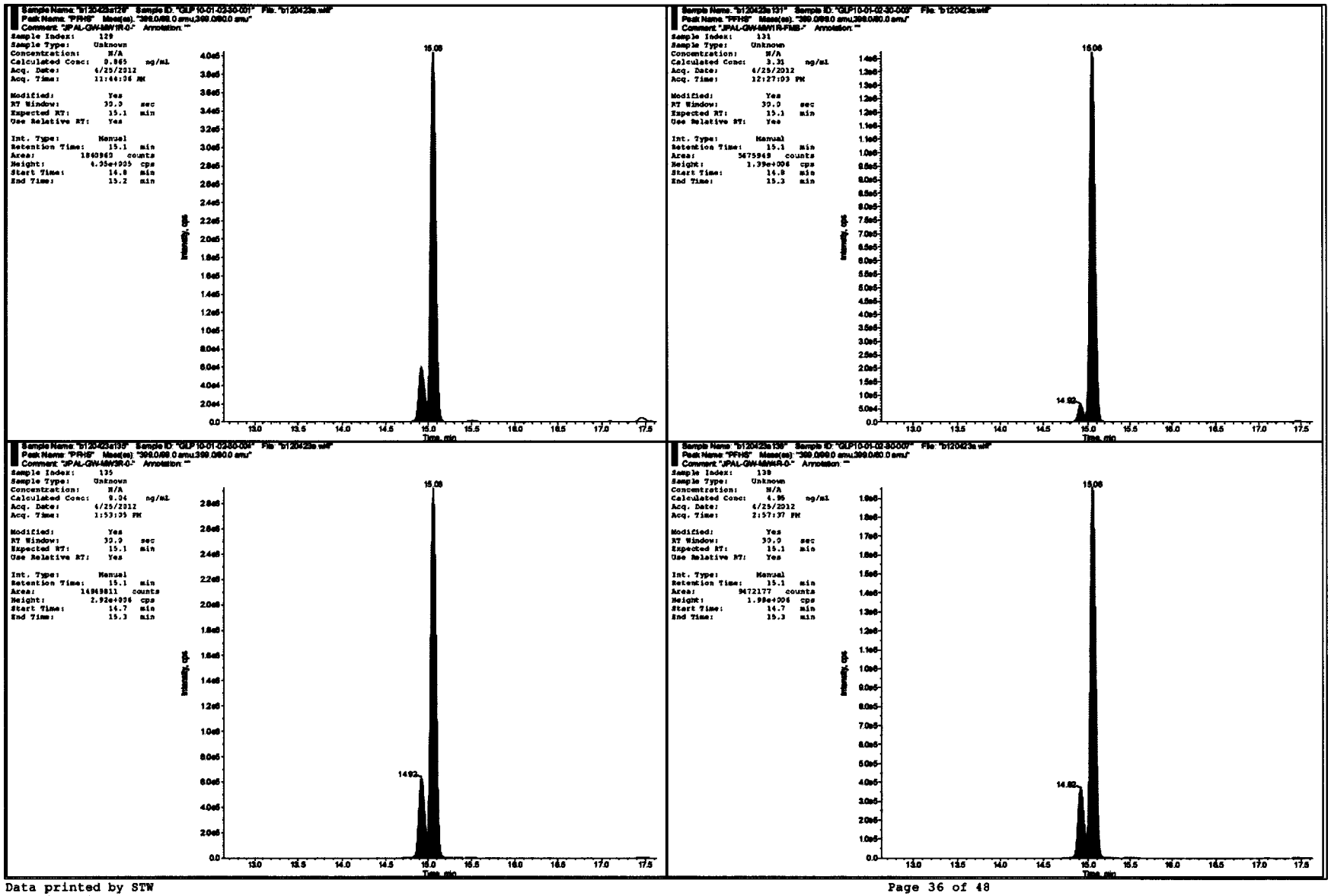


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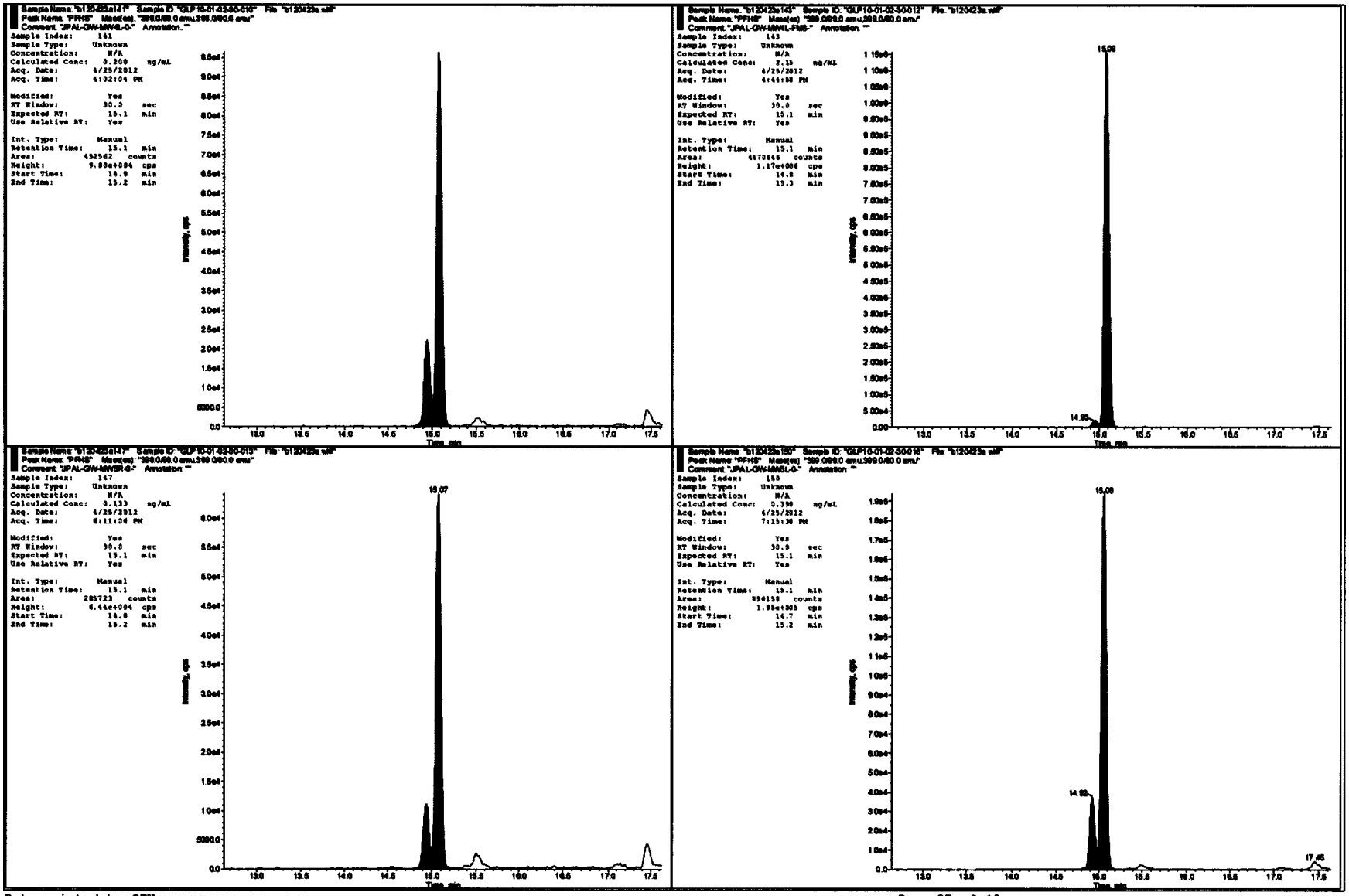


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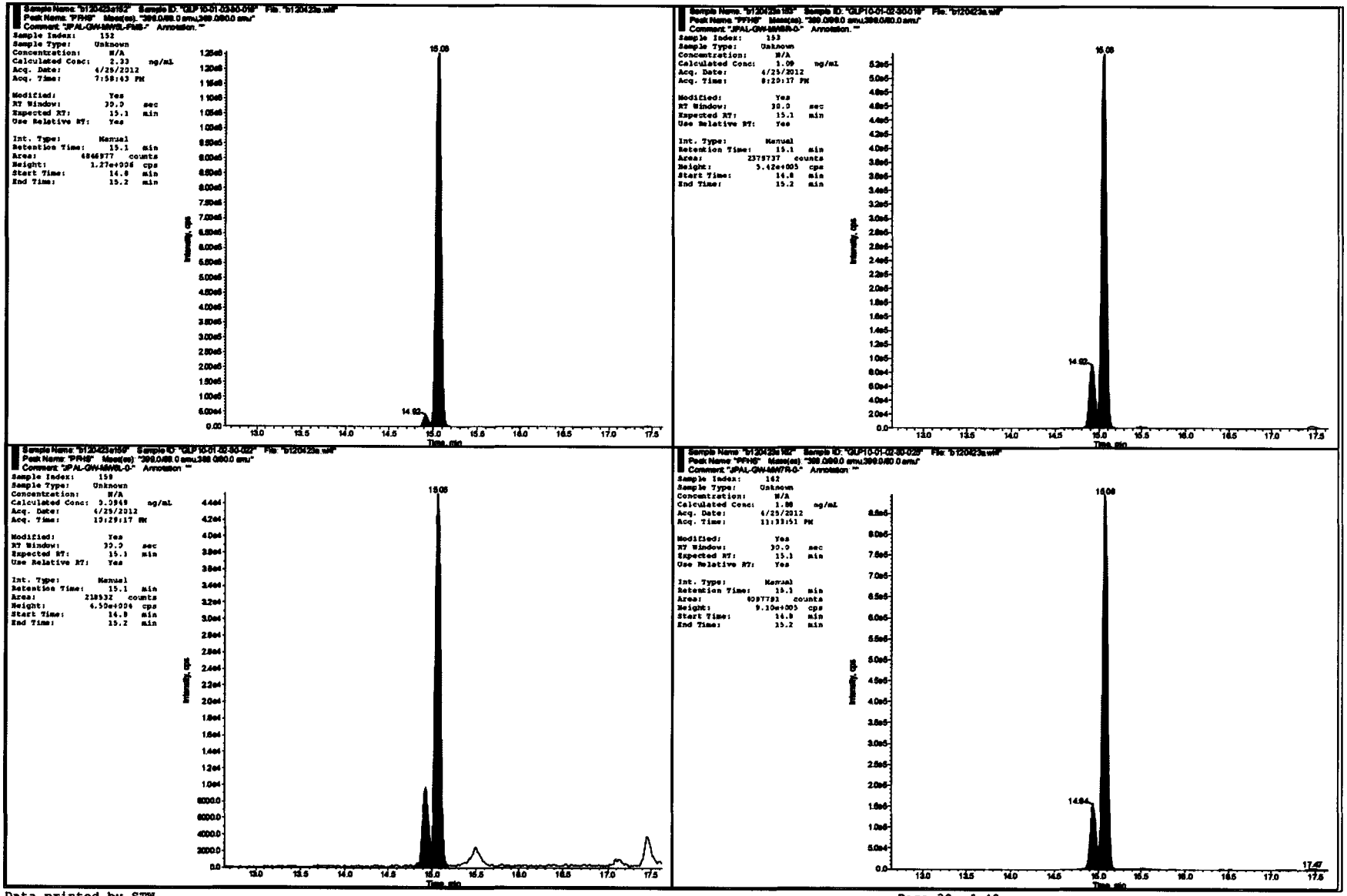
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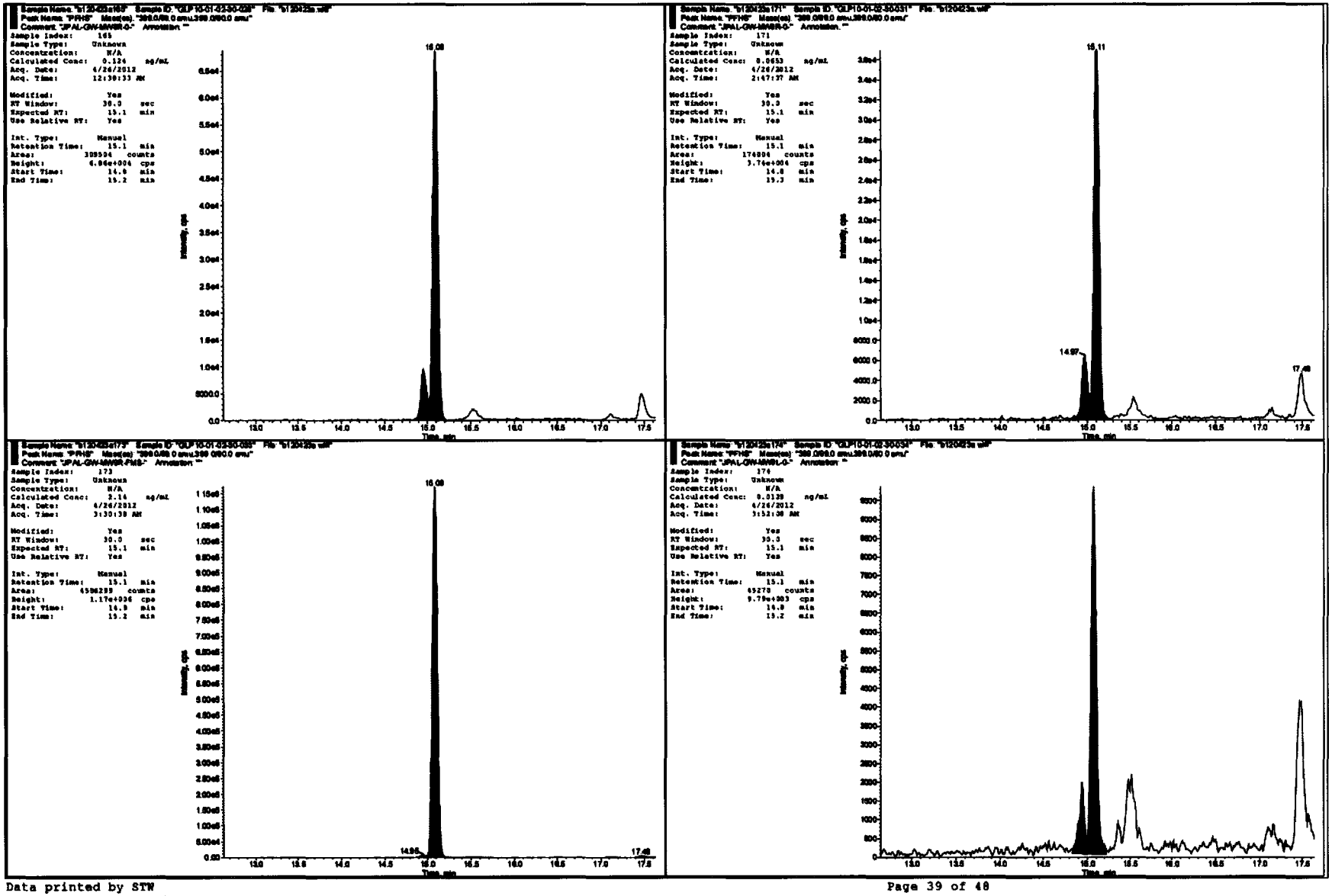


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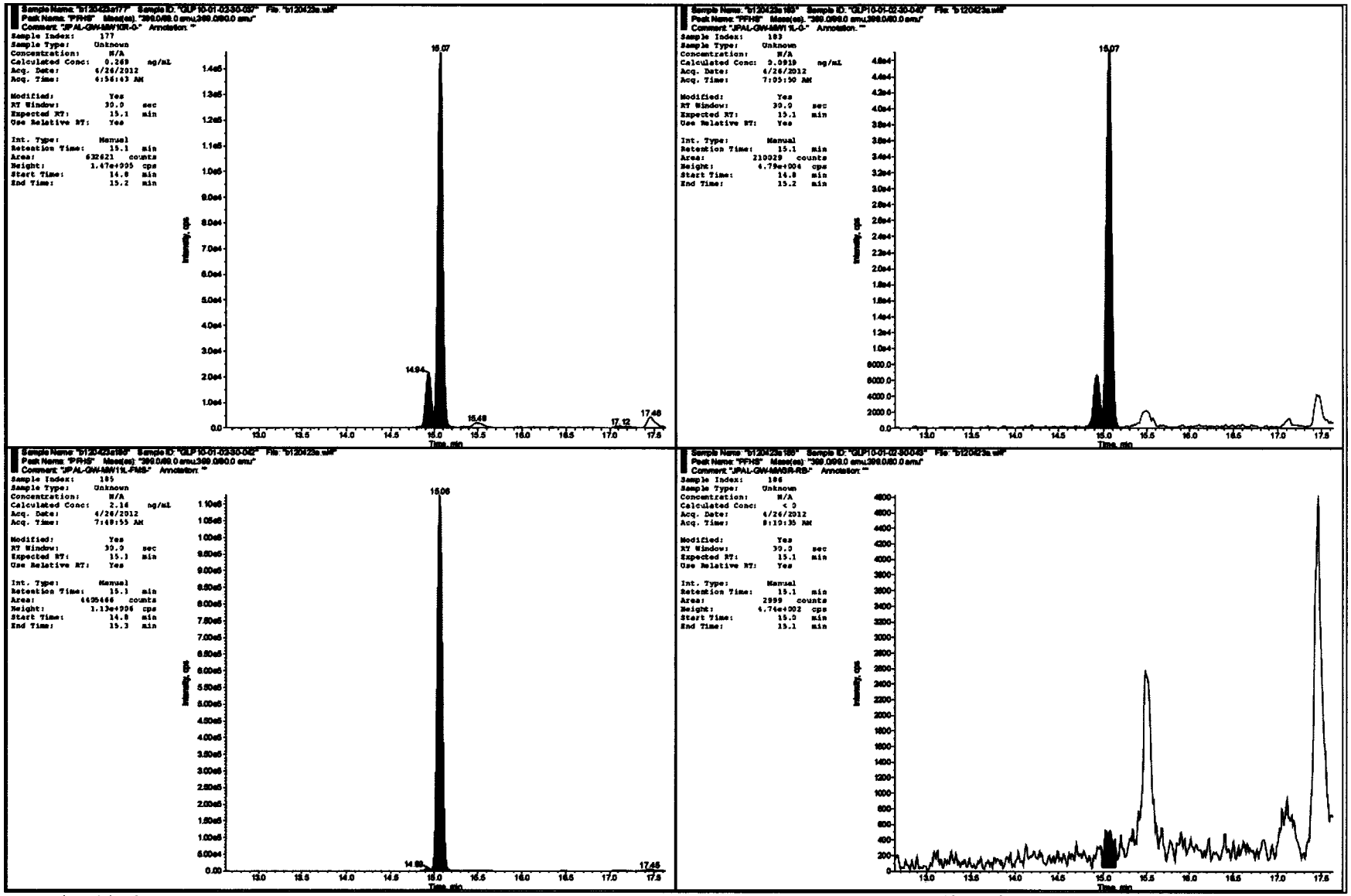
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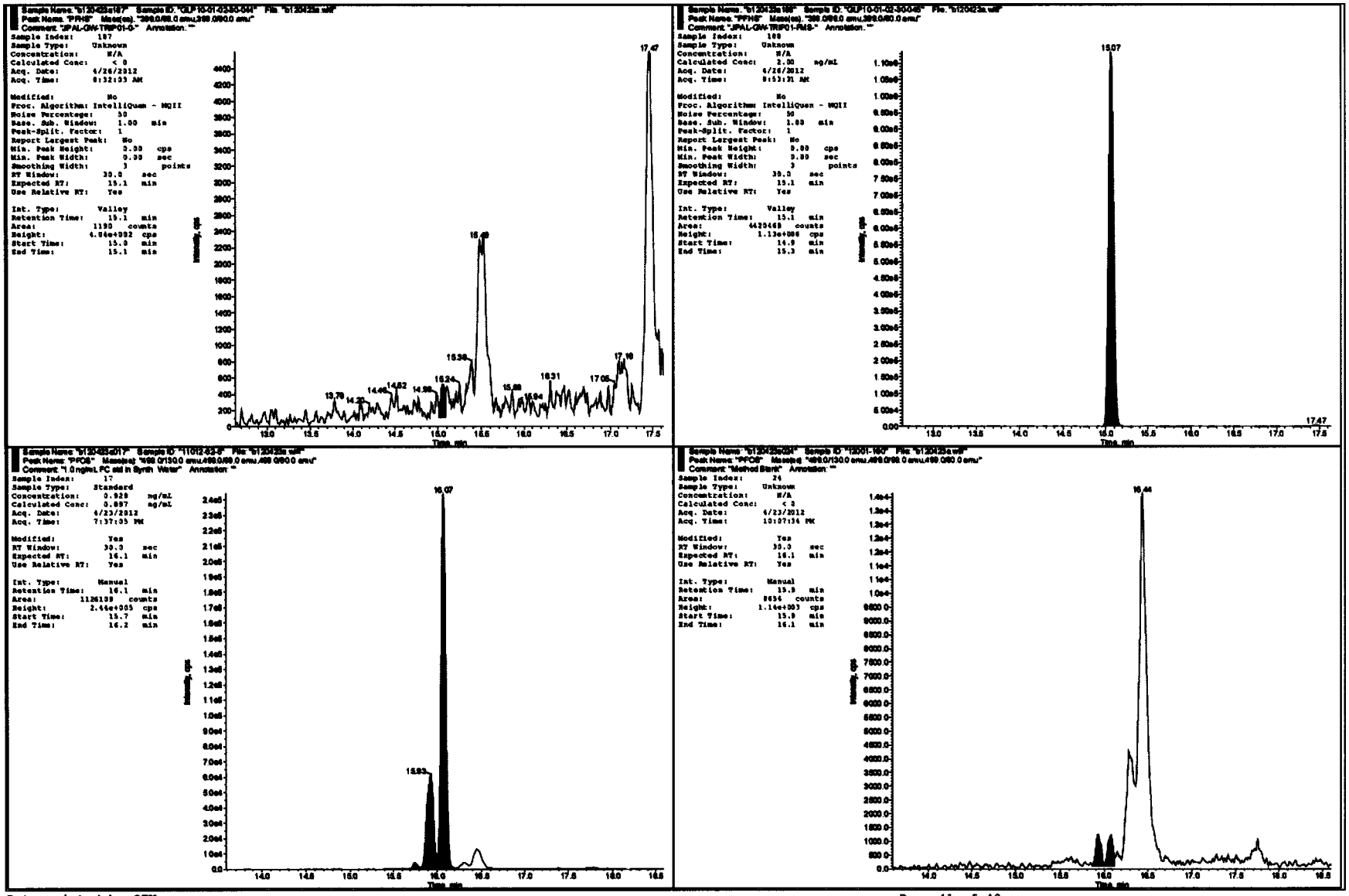
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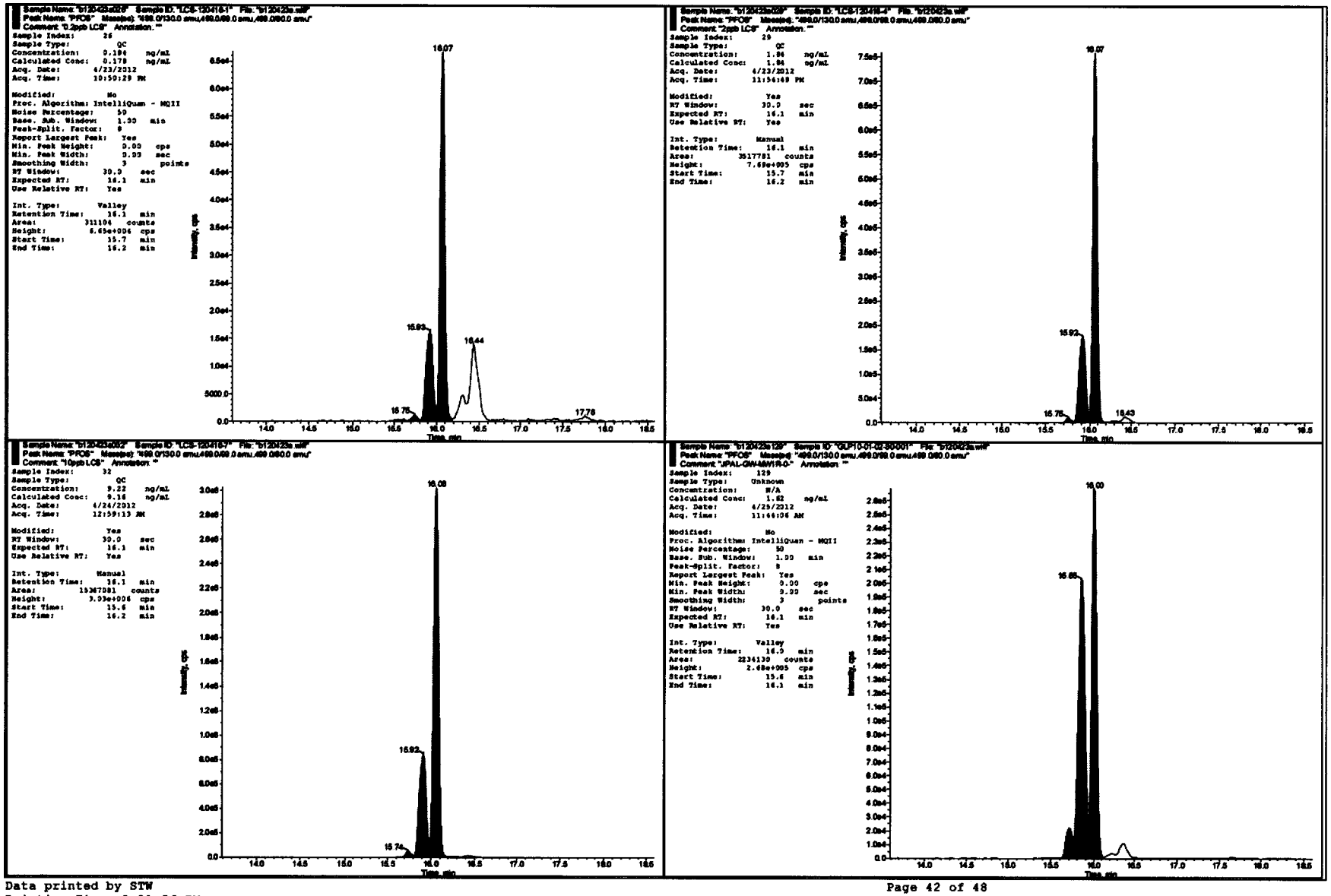
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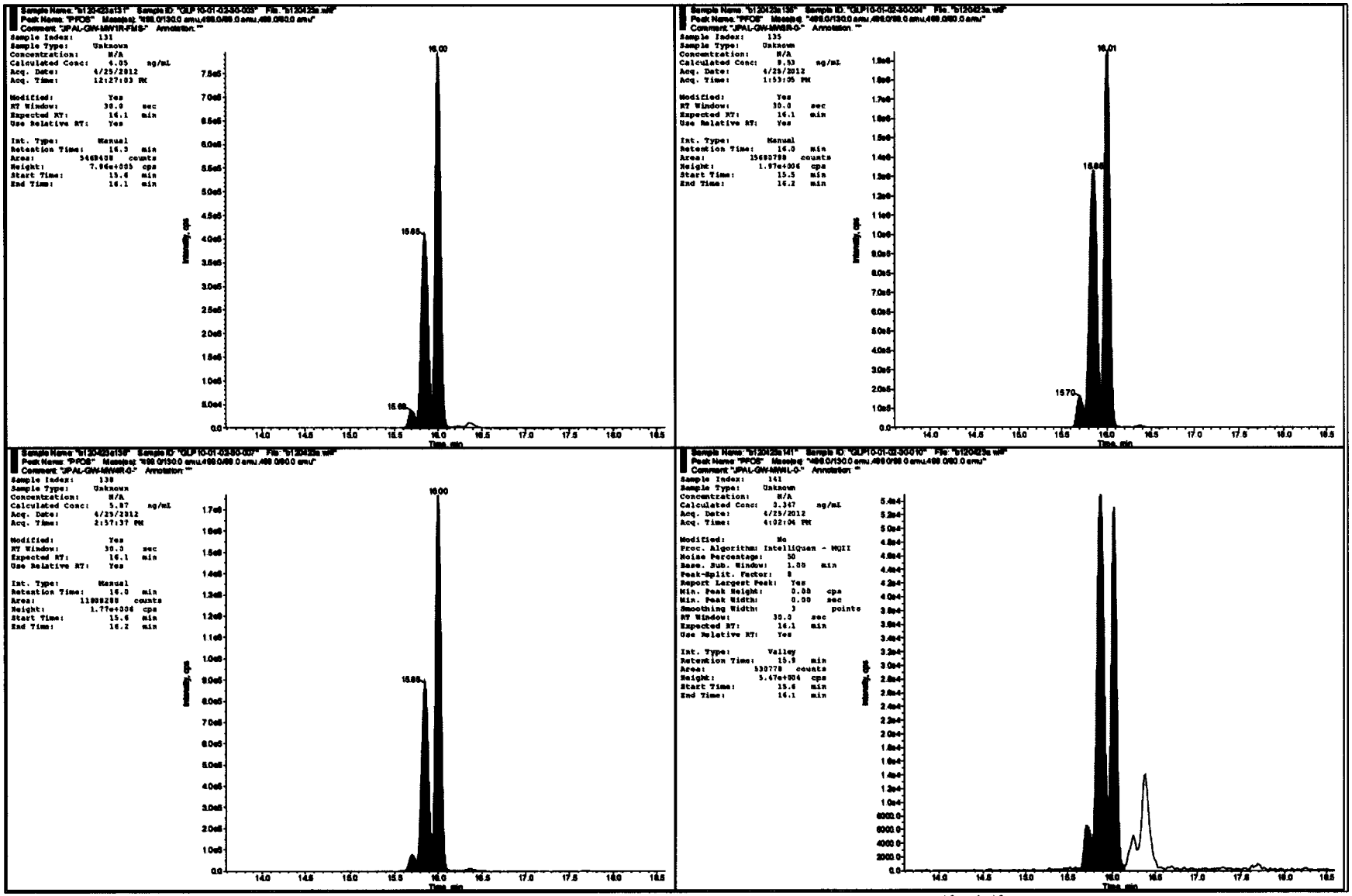


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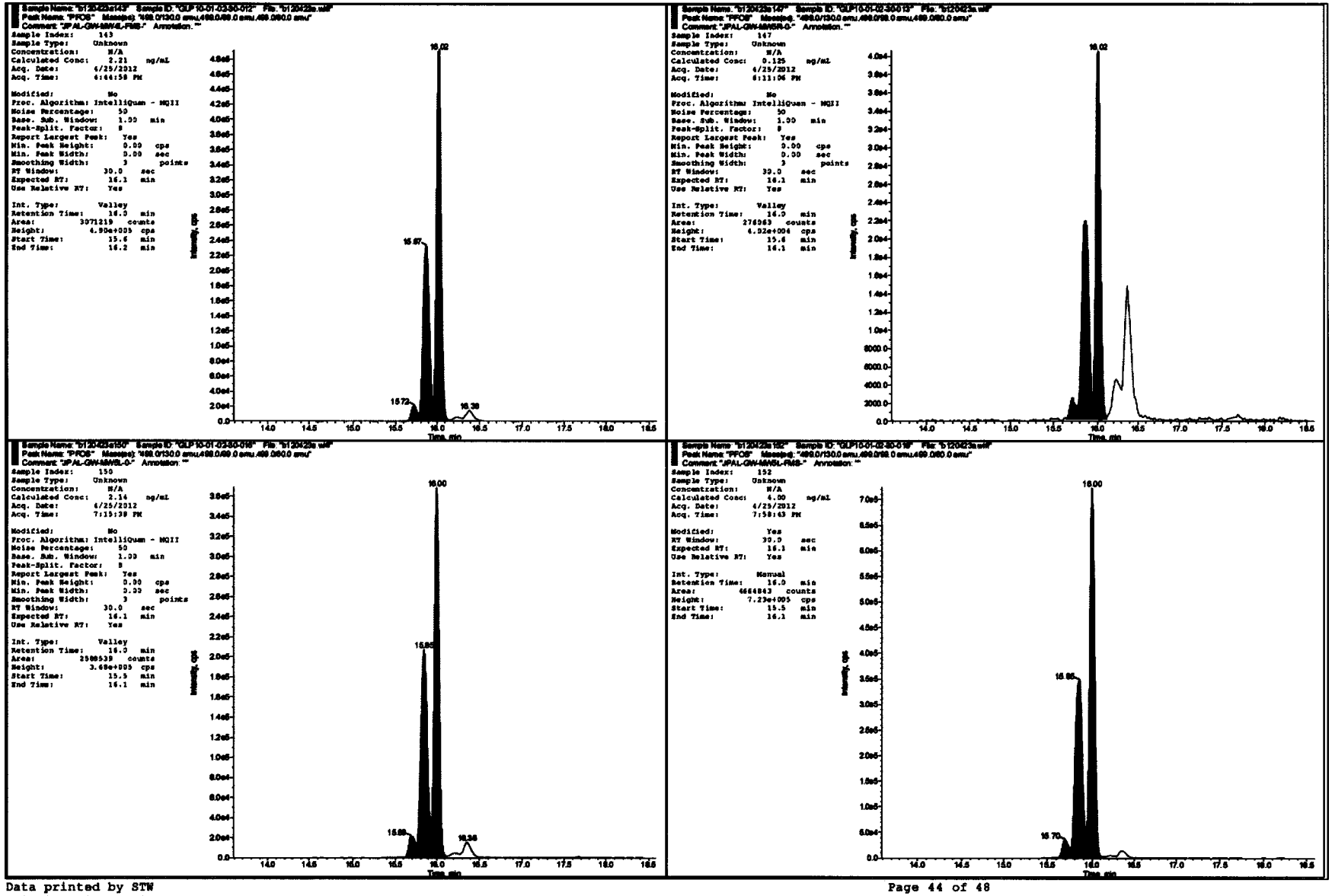
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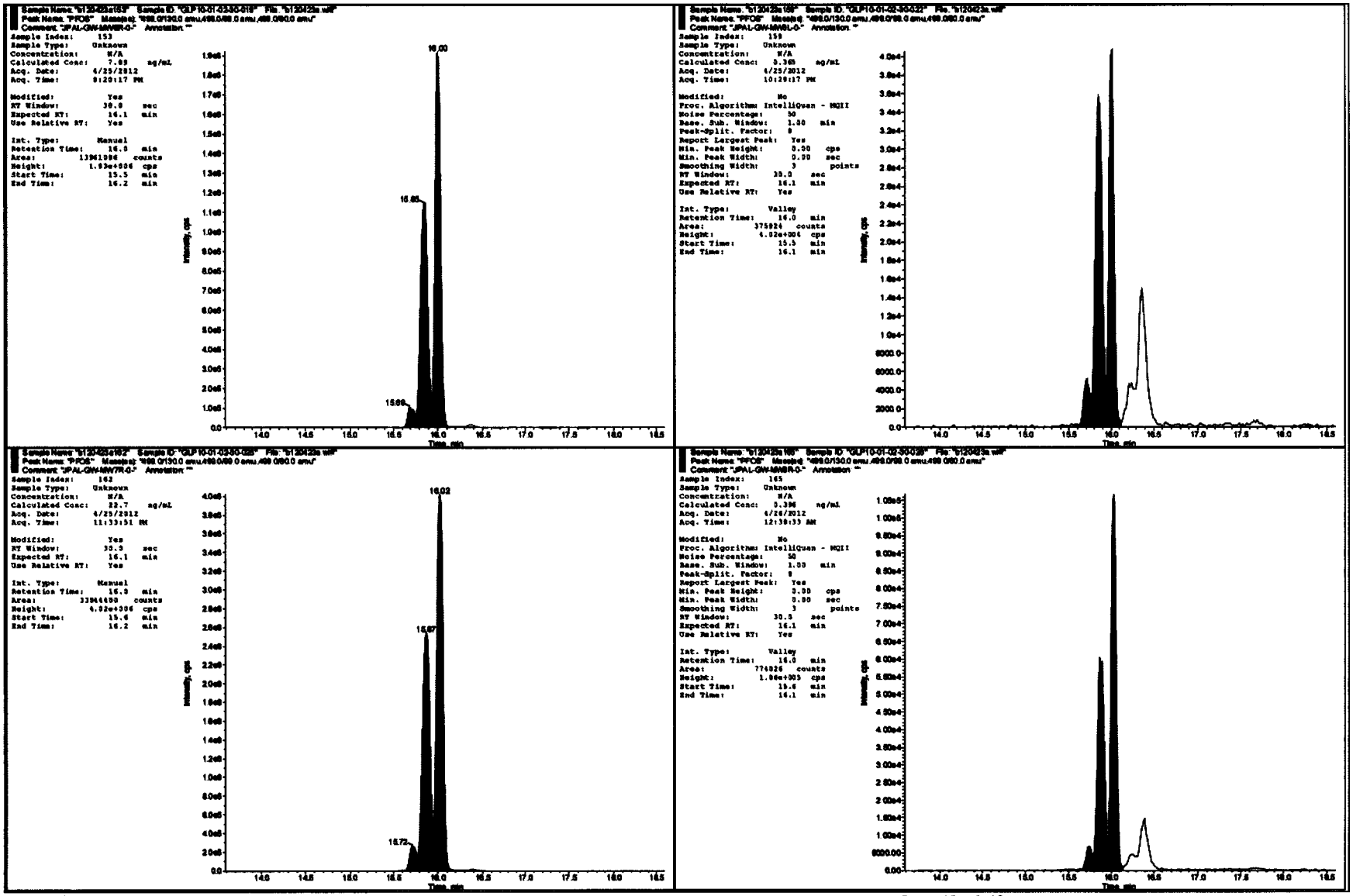


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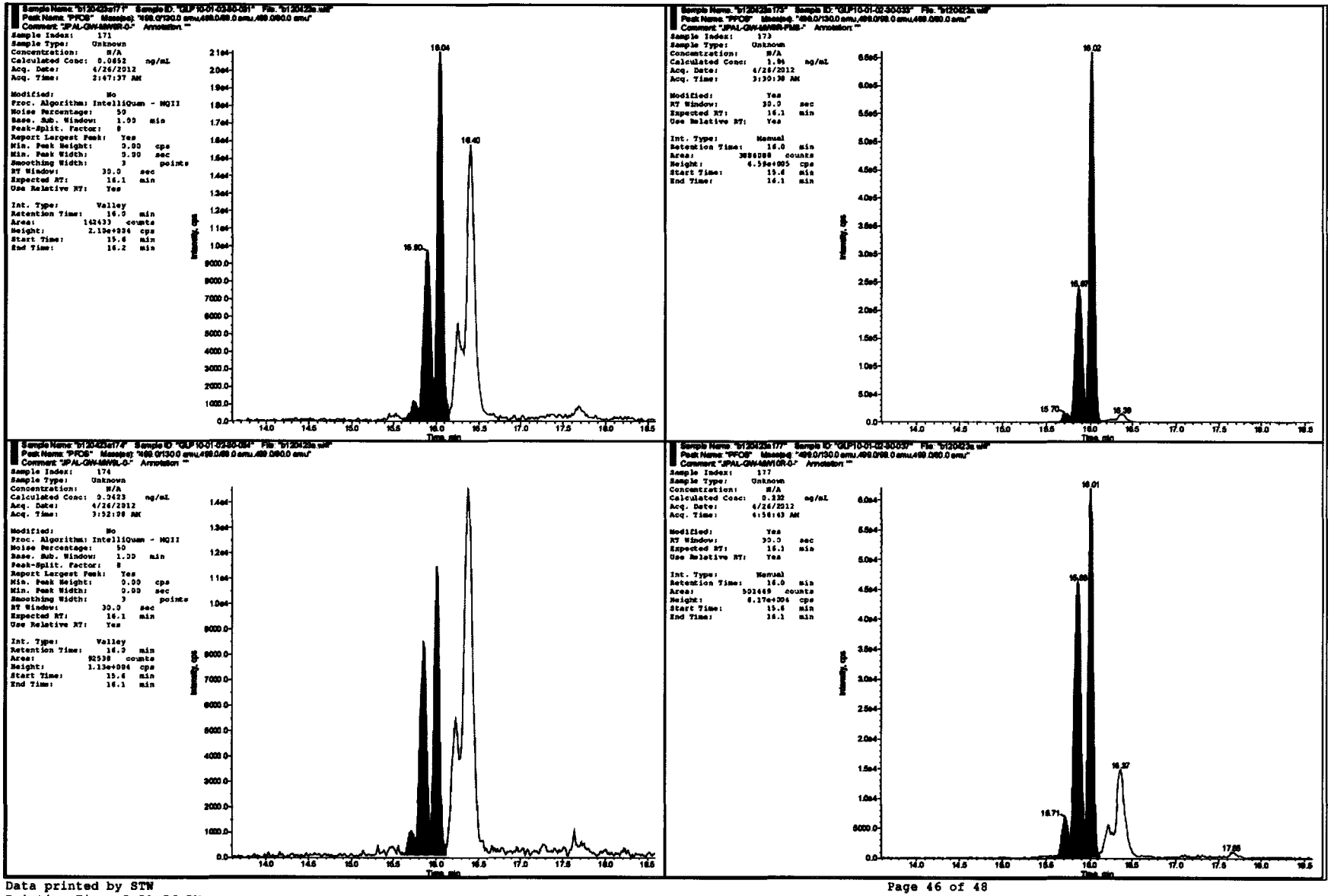
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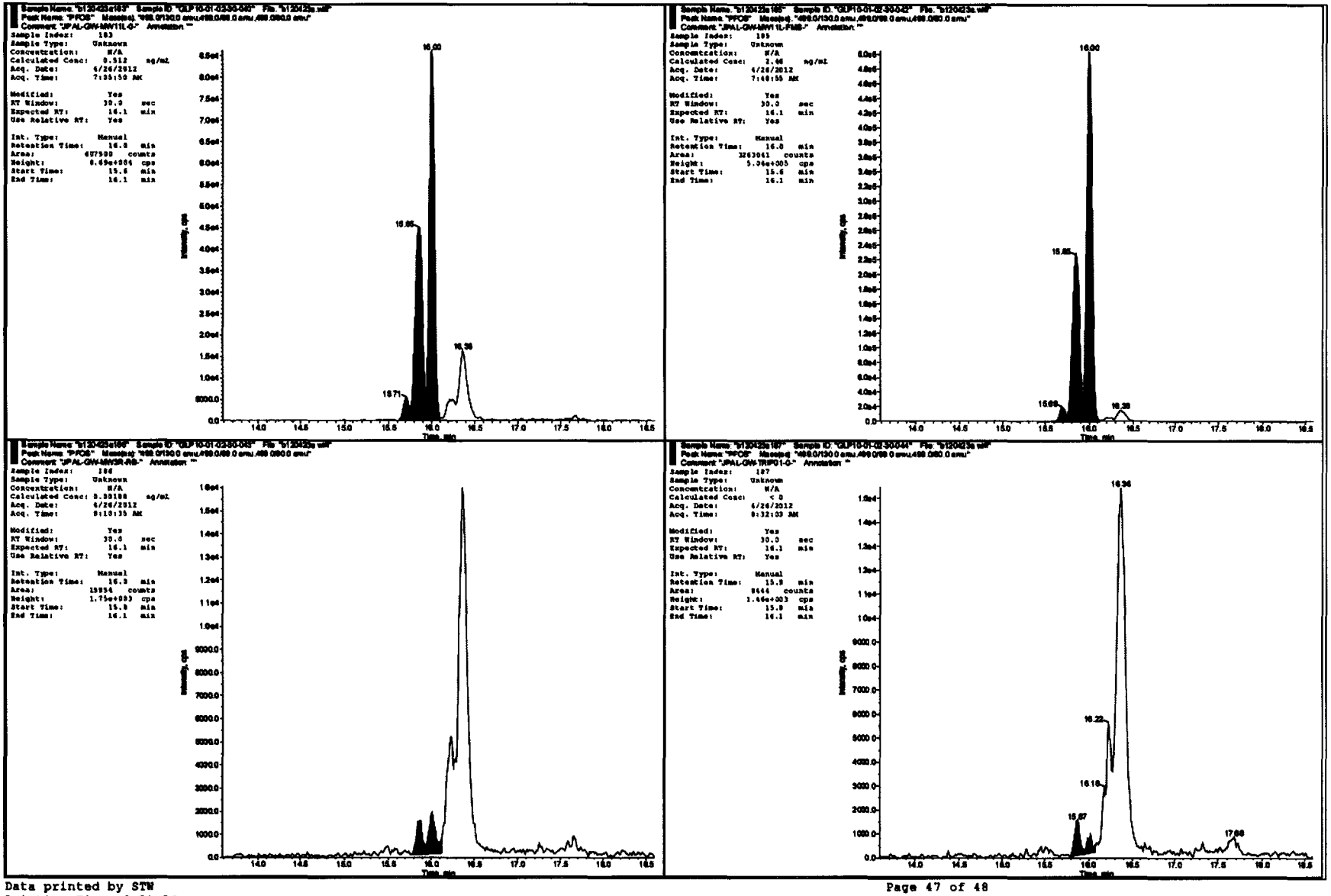
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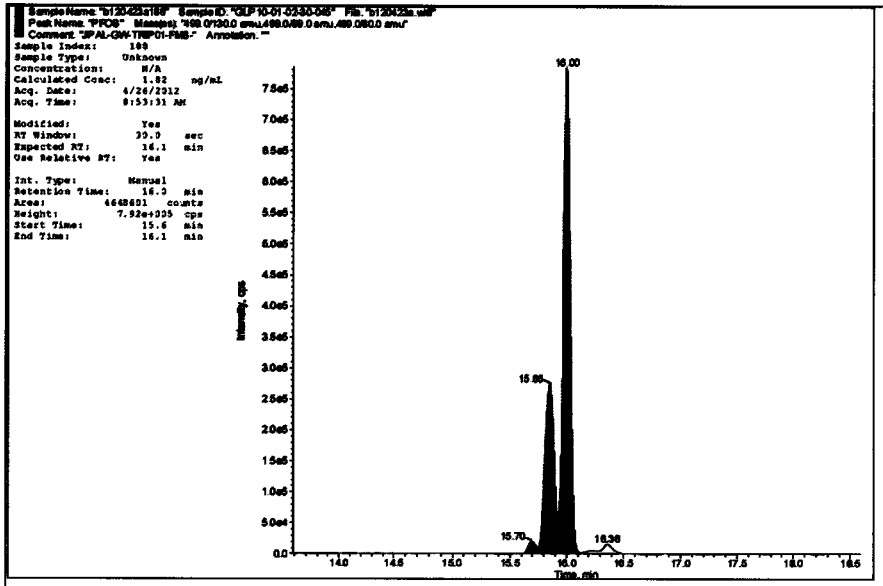
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ATTACHMENT C: ANALYTICAL METHOD(S)

3M Environmental Laboratory

Method

Method of Analysis for the Determination of Perfluorinated Compounds in Water by LC/MS/MS; Direct Injection Analysis

Method Number: ETS-8-044.1

Adoption Date: 4/12/07

Effective Date: 11/7/11

Approved By:

9 NOV 2011

William K. Reagen, Technical Director, Environmental Laboratory — Date

1 Scope and Application

This method describes the direct injection analysis of perfluorinated compounds (PFCs) from water matrices using high-performance liquid chromatography tandem mass spectrometry (HPLC/MS/MS). The method is generally applicable but not limited to the measurement of perfluoroalkyl sulfonamides and perfluorinated alkyl acids (PFAAs) such as perfluorosulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs) (Table 1). Water samples containing heavy particulate may require preparation by an alternate method such as ETS-8-154 "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates In Water By Solid Phase Extraction and High Performance Liquid Chromatography/Mass Spectrometry". The method is applicable to both external standard and internal standard calibration[1].

Table 1. Representative Target Analytes

Acronym	*Analyte*	*Chemical Abstract Services Registry Number (CASRN)*
PFBA (C4 Acid)	Perfluorobutanoic acid	375-22-4
PFPeA (C5 Acid)	Perfluoropentanoic acid	2706-90-3
PFHxA (C6 Acid)	Perfluorohexanoic acid	307-24-4
PFHpA (C7 Acid)	Perfluoroheptanoic acid	375-85-9
PFOA (C8 Acid)	Perfluorooctanoic acid	335-67-1
PFNA (C9 Acid)	Perfluorononanoic acid	375-95-1
PFDA (C10 Acid)	Perfluorodecanoic acid	335-76-2
PFUnA (C11 Acid)	Perfluoroundecanoic acid	2058-94-8
PFDoA (C12 Acid)	Perfluorododecanoic acid	307-55-1
PFTrDA (C13 Acid)	Perfluorotridecanoic acid	72629-94-8
PFBS (C4 Sulfonate)	Perfluorobutanesulfonic acid	375-73-5
PFHS (C6 Sulfonate)	Perfluorohexanesulfonic acid	355-46-4
PFOS (C8 Sulfonate)	Perfluorooctanesulfonic acid	1763-23-1
FBSA (C4 Sulfonamide	Perfluorobutanesulfonamide	30334-69-1
FOSA (C8 Sulfonamide)	Pefluorooctanesulfonamide	754-91-6

The Minimum Reporting Level (MRL) is the Limit of Quantitation (LOQ) that meets Data Quality Objectives (DQOs) that are developed based on the intended use of this method.

Method Flexibility – This is a performance-based method and may be generally applied to the determination of perfluorinated compounds in water matrices when analysis batch quality control (QC) criteria are met[2]. Each set of samples are prepared in an analysis batch with calibration standards, LCSs, blanks, and continuing calibration check standards analyzed on the same instrument during a time period that begins and ends with the analysis of the appropriate continuing calibration check standards. The laboratory is permitted to modify the LC column, mobile phase composition, LC conditions, and MS/MS conditions. Method modifications should be considered to improve method performance or to meet data quality objectives for the study. In all cases where method modifications are implemented, the batch

[1] The method is supported by validation with internal standard calibration for C4-C13 PFCAs, C4, C6, and C8 PFSAs, and C8 perfluoroalkane sulfonamide in laboratory control samples under 3M method validation E11-0667.

[2] Guidance for establishing method QC Criteria based on a.) FDA May 2001, "Guidance for Industry, Bioanalytical Method Validation", b.) EPA Method 537, and c.) European Commission: Guidance for Generating and Reporting Methods of Analysis in Support of Pre-registration Data Requirements for Annex II (Part A, section 4) and Annex III (Part A,section 5) of Directive 91/414, SANCO/3029/99 rev. 4 (11/07/00).

analytical QCs (section 9) must be completed and pass QC acceptance criteria (section 13) if the data from the analytical batch are to be reported.

2 Method Summary

Water samples are analyzed as neat aqueous sample or as solvent diluted aqueous samples by direct injection using LC/MS/MS. Samples containing heavy particulate may not be suitable for analysis by this method. Samples containing suspended particulate should be centrifuged or filtered prior to removing a sample aliquot or diluting with solvent. The water sample is mixed well prior to removing an aliquot or diluting, if necessary, with ASTM Type I water, HPLC water, other suitable water, or solvent (methanol).

Quantitation is by stable isotope internal standard calibration in laboratory reagent water. All perfluorinated compounds (PFCs) target analyte concentrations of perfluorosulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs) are reported as anions and corrected for their salt or free acid forms. Alternatively, quantitation may be performed by external standard calibration.

This is a performance-based method. Method uncertainty for each target analyte is determined for each analytical batch using multiple laboratory control spikes at multiple concentrations. This method also requires that the precision and accuracy for each sample be determined using field matrix spikes to verify that the method is applicable to each sample matrix.

Calibration standards for PFUnA, PFDoA, PFTrDA, and FOSA have been found to be unstable for more than 2 days in 100% water. Samples requiring analysis for these compounds by this method should be diluted 1:1 with methanol and analyzed against a calibration curve prepared in 1:1 synthetic groundwater:MeOH.

3 Definitions

3.1 Analysis Batch

A set of study samples that are prepared with calibration standards, laboratory control samples, and procedural blanks, and analyzed on the same instrument during a time period that begins and ends with the analysis of the appropriate continuing calibration check standards.

3.2 Analytical Sample

A portion of a laboratory sample prepared for analysis.

3.3 Calibration Standard

A solution prepared by spiking a known volume of the Working Standard (WS) into a predetermined amount of ASTM Type I, HPLC grade water, or other suitable water (i.e. matrix water), and analyzed according to this method. Calibration standards are used to calibrate the instrument response with respect to analyte concentration.

3.4 Laboratory Duplicate Sample (LDS, or Lab Dup)

A laboratory duplicate sample is a separate aliquot of a sample taken in the analytical laboratory that is analyzed separately with identical procedures. Analysis of LDSs 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.

3.5 Field Blank (FB)/Trip Blank (TB)

ASTM Type I, HPLC grade water, or other suitable 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 TB is to determine if test substances or other interferences are present in the field environment. This sample is also referred to as a Trip Blank.

3.6 Field Duplicate Sample (FDS, Field Dup)

A sample collected in duplicate at the same time from the same location as the sample. The FDS is handled under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analysis of the FDS 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.

3.7 Field Matrix Spike (FMS)

A sample to which known quantities of the target analytes, ISs and SRSs are added to the sample bottle in the laboratory before the bottles are sent to the field for collection of aqueous samples. A known, specific volume of sample must be added to the 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 is analyzed to ascertain if any matrix effects, interferences, or stability issues may complicate the interpretation of the sample analysis.

3.8 Trip Blank Matrix Spike (TBMS)

An aliquot of ASTM Type I, HPLC grade water, or other suitable water, to which known quantities of the target analytes, ISs and SRSs are added in the laboratory prior to the shipment of the collection bottles. The TBMS is analyzed exactly like a study sample to help determine if the method is in control and whether a loss of analyte or analytical bias could be attributed to sample holding time, sample storage and/or shipment issues. A low and high TBMS are appropriate when expected sample concentrations are not known or may vary.

3.9 Internal Standard (IS)

A compound added to each study sample, calibration standard, laboratory control samples, and procedural blanks at a consistent level (typically around 1 ng/mL). The internal standard(s) are stable isotope labeled versions of the target analytes. The area count ratio of the target analyte to the internal standard is used for calibration. Surrogate ISs are applied when stable isotope ISs of target analytes are unavailable. A surrogate IS is not necessarily a stable isotope labeled version of the target analyte, but is treated as an internal standard for quantitation.

3.10 Laboratory Control Sample (LCS)

An aliquot of control matrix to which known quantities of the target analytes, ISs and SRSs (when applicable) are added in the laboratory at the time when samples are aliquotted. At least three levels (two levels for SRSs) in triplicate are included, one generally at the low end of the calibration curve and one near the mid range and the upper end of the curve. The LCSs are analyzed exactly like a laboratory sample to determine whether the stability of the standards. LCSs should be prepared each day samples are aliquoted.

3.11 Laboratory Matrix Spike (LMS)

A laboratory matrix spike is an aliquot of a sample to which known quantities of target analytes, ISs and SRSs (when applicable) are added in the laboratory. The LMS is analyzed exactly like a laboratory sample to determine whether the sample matrix contributes bias to the analytical results. The endogenous concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LMS corrected for these concentrations. LMSs are optional for analysis of aqueous samples.

3.12 Laboratory Sample

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

3.13 Limit of Quantitation (LOQ)

The lower limit of quantitation (LLOQ) for an analytical batch is the lowest concentration that can be reliably quantitated within the specified limits of precision and accuracy. The LLOQ is generally selected as the lowest non-zero standard in the calibration curve that meets method acceptance criteria. The LLOQ for each target analyte is established for each analysis batch as the lowest calibration standard with area counts at least twice that of the average area counts of the procedural blanks.

The upper limit of quantitation (ULOQ) for an analytical batch is the highest concentration that can be reliably quantitated within the specified limits of precision and accuracy. The highest standard in the calibration curve that meets method acceptance criteria is defined as the ULOQ.

3.14 Method/Procedural Blank

An aliquot of control matrix 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.

3.15 Sample

A sample is an aliquot removed from a larger quantity of material intended to represent the original source material.

3.16 Stock Standard Solution (SSS)

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

3.17 Surrogate Internal Standard

An IS that is not necessarily a stable isotopically labeled target analyte, but is treated as an internal standard for quantitation. Surrogate ISs are used when isotopically labeled counterparts of the target analyte are not commercially or readily available.

3.18 Surrogate Recovery Standard (SRS)

An isotopically labeled standard, not used as an internal standard, that is added to each sample and appropriate QC sample as a means to evaluate the method performance for a chemical class of compounds (e.g., PFSAs, PFCAs).

3.19 Working Standard (WS)

A solution of several analytes prepared in the laboratory from SSSs 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. The analyst should wear gloves, a lab coat, and safety glasses to prevent exposure to chemicals that might be present.

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

The analyst must be familiar with the laboratory equipment and potential hazards including, but not limited to, the use of solvents, pressurized gas and solvent lines, high voltage, and vacuum systems. Refer to the appropriate equipment procedure or operator manual for additional information and cautions.

5 Interferences

During sample preparation and analysis, major potential contaminant sources are reagents and glassware. 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 or minimized 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

6.1 Instrumentation

Analytical balance capable of reading to 0.0001g

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

6.2 Supplies and Materials

Sample collection bottles—HDPE (e.g., Nalgene™) wide-mouth bottles with screw cap.
Note: Do not use fluorinated or Teflon® bottles or lined caps.

Coolers or boxes for sample shipment.

15-mL and 50-mL disposable polypropylene centrifuge tubes.

Class A pipettes and volumetric flasks, various.

2 mL HPLC autovials

Disposable pipettes, polypropylene or glass as appropriate

Centrifuge capable of spinning 15-mL and 50-mL polypropylene tubes at 3000 rpm.

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

Water – Milli-Q, HPLC grade, or other suitably appropriate sources

Calcium Acetate - A.C.S. Reagent Grade

Magnesium Acetate - A.C.S. Reagent Grade

Methanol – HPLC grade

Ammonium Acetate – A.C.S. Reagent Grade

7.2 Representative Target Analytes, ISs, and SRSs

PFBA, Heptafluorobutyric Acid, (C_4 Perfluorinated Acid)

PFPeA, Nonafluoropentanoic Acid (C_5 Perfluorinated Acid)

PFHxA, Perfluorohexanoic Acid (C_6 Perfluorinated Acid)

PFHpA, Tridecafluoroheptanoic Acid, (C_7 Perfluorinated Acid)

PFOA, Ammonium perfluorooctanoate, (C_8 Perfluorinated Acid)

PFNA, Heptadecafluorononanoic Acid, (C_9 Perfluorinated Acid)

PFDA, Nonadecafluorodecanoic Acid (C_{10} Perfluorinated Acid)

PFUnA, Perfluoroundecanoic Acid, (C_{11} Perfluorinated Acid)

PFDoA, Perfluorododecanoic Acid, (C_{12} Perfluorinated Acid)

PFTrDA, Perfluorotridecanoic Acid, (C_{13} Perfluorinated Acid)

FBSA, Perfluorobutanesulfonamide

FOSA, Perfluorooctanesulfonylamide

PFBS, Potassium Perfluorobutanesulfonate

PFHS, Perfluorohexanesulfonate

PFOS, Potassium perfluorooctanesulfonate

PFOA [1,2, 3, 4-^{13}C], $^{13}C_4$-isotopically labeled perfluorooctanoic acid (SRS)

PFOS [1,2, 3, 4-^{13}C], $^{13}C_4$-isotopically labeled Perfluorooctanesulfonate (SRS)

PFUnA [1,2-^{13}C], $^{13}C_2$-isotopically labeled Perfluoroundecanoic acid (SRS)

A custom mix of ISs in a methanolic solution containing ([1,2,3,4-$^{13}C_4$]PFBA, [1,2 - $^{13}C_2$]PFHxA, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA, [1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA, [1,2 - $^{13}C_2$]PFDA, [1,2,3,4,5,6,7 - $^{13}C_7$]PFUnA, [1,2 - $^{13}C_2$]PFDoA, [1,2,3 - $^{13}C_3$]PFHS, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOS, and [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOSA (Wellington Laboratories, Guelph, ON) in combination with added ([1,2,3,4,5-$^{13}C_5$]PFPeA, ([1,2,3,4-$^{13}C_4$]PFHpA, and [$^{18}O_2$]PFBS can be used to prepare a stock IS solution. Alternatively, individual stable isotope ISs can be used to prepare a stock IS mixture.

Other ISs can be applied.

7.3 Reagent Preparation

2 mM Ammonium acetate solution (Analysis)—Weigh 0.3 g of Ammonium acetate and dissolve in 2.0 L of reagent water.

Synthetic Groundwater (containing 25 ppm Ca and Mg) – Weigh 0.61 g of Calcium Acetate and 0.92 g of Magnesium Acetate and dissolve in 6.0 L of reagent water.

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

7.4 Stock Standard Solution (SSS) and Working Standard Solution Preparation

The following standard preparation procedure serves as an example. Weighed amounts and final volumes 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.

100 µg/mL target analyte SSSs—Weigh out 10 mg of analytical standard ***(corrected for percent salt, acid [ETS-4-031] and purity)*** and dilute to 100 mL with methanol or other suitable solvent, in a 100 mL volumetric flask. Transfer to a 125 mL LDPE bottle or other suitable container. Prepare a separate solution for each analyte. Expiration dates and storage conditions of stock solutions should be assigned in accordance with laboratory standard operating procedure. An example of purity and salt correction is given below for PFOS.

$$\text{salt correction factor} = \frac{\text{molecular weight of anion}}{\text{moclecular weight of salt}}$$

$$\text{PFOS } (K^+) \text{salt correction factor} = \frac{499}{538} = 0.9275$$

10 mg $C_8F_{17}SO_3K^+$ with purity 90% = 8.35 mg $C_8F_{17}SO_3^-$ (10 mg*0.90*0.9275=8.35 mg)

10 µg/mL (10,000 ng/mL) mixed working standard—Add 5.0 mL each of the 100 µg/mL SSSs to a 50 mL volumetric flask and bring up to volume with solvent.

1 µg/mL (1,000 ng/mL) mixed working standard—Add 0.5 mL of the 100 µg/mL SSSs to a 50 mL volumetric flask and bring up to volume with solvent.

0.1 µg/mL (100 ng/mL) mixed standard—Add 0.05 mL of the 100 µg/mL SSSs to a 50 mL volumetric flask and bring up to volume with solvent.

Storage Conditions—Store all SSSs and working standards in accordance with laboratory standard operating procedure or in a refrigerator at 4°±2°C for a maximum period of 6 months from the date of preparation.

7.5 Calibration Standards

Calibration can be performed by IS or external calibration. Using the working standards described above, prepare calibration solutions in ASTM Type I water, HPLC water, other suitable water, or a mixture of solvent and water using the information in Table 2 as a guideline. Note: Volumes of water or water/solvent mixtures and working standards may be adjusted to meet the data quality objectives addressed in the general project outline. Calibration levels other than those listed below can be prepared as needed.

For the quantitation of PFOA and PFOS, reference materials of certified mixed linear and branched isomer are preferred. Alternately, reference materials of primarily linear isomers of PFOA and/or PFOS may be used, however, when quantitating with predominantly linear reference standards, additional LCS samples containing both linear and branched isomers of PFOA and PFOS are required[3].

7.5.1 Internal Standard (IS) and Surrogate Recovery Standard (SRS)

For IS calibration, stable isotope internal standards of each target analyte or appropriate surrogate ISs should be spiked at the same level in all calibration standards. Once the calibration standards have been prepared as stated above in Section 7.5, all calibration standards are spiked with a separate internal standard spiking solution. Typically the

[3] A report summarizing an assessment of the use of reference standards containing certified linear and branched isomers of PFOA/PFOS can be found in 3M report E11-0560.

concentration of the internal standard is consistent with the internal standard concentration expected in the samples being prepared, usually 1 ng/mL. The concentration of the internal standard spiking solution is typically 2 µg/mL. A separate zero point or method blank is typically prepared at the same time as the calibration standards, using the same solution used to prepare the standards (ASTM Type I water, HPLC water, other suitable water, or a solvent/water mixture), and is spiked with the internal standard at the same concentration as the calibration curve, typically at 1 ng/mL.

If the samples being analzyed were pre-spiked with SRSs, the calibration curve prepared in Section 7.5 is spiked with a separate SRS spiking solution. Typically, the sample bottles are spiked with a SRS at 0.1 ng/mL. The final calibration curve must consist of at least six calibration points after analysis. The following table provides an example of spike concentrations and volumes used to achieve a multi-point extracted calibration curve with internal standard and surrogate standard.

Table 1 lists recommended stable isotope internal standards for several PFSA and PFCA target compounds. A custom mix of isotopically labeled target analytes in a methanolic solution containing ([1,2,3,4-$^{13}C_4$]PFBA, [1,2-$^{13}C_2$]PFHxA, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA, [1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA, [1,2,3,4,5,6-$^{13}C_6$]PFDA, [1,2,3,4,5,6,7-$^{13}C_7$]PFUnA, [1,2-$^{13}C_2$]PFDoA, [1,2,3-$^{13}C_3$]PFHS, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOS, and [1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA (Wellington Laboratories, Guelph, ON) in combination with added ([1,2,3,4,5-$^{13}C_5$]PFPeA, ([1,2,3,4-$^{13}C_4$]PFHpA, and [$^{18}O_2$]PFBS can be used to prepare a stock IS solution. Alternative sources of certified stable isotope labeled target analytes are applicable. Alternatively, individual stable isotope ISs can be used to prepare a stock IS mixture. The table below lists the recommended stable isotope ISs and SRSs applied in the method. Other stable isotope ISs and SRSs of target analytes not listed in the table may be used if supported by validation and/or analysis batch QCs meeting method acceptance criteria (e.g., [$^{13}C_2$]-PFOA). The same internal standard should be used for a given analyte throughout the entire project/study. Note: some of the compounds listed below are appropriate to use as surrogate ISs when a stable isotope IS of a target analyte is not available. Generally, surrogate isotopically labeled PFCAs are used for PFCAs, and surrogate isotopically labeled PFSAs are used for PFSAs.

Table 2 provides examples of spike concentrations and volumes used to achieve a multi-point calibration curve with ISs and SRSs.

Table 1. Stable Isotope PFCAs and PFSAs used for ISs and SRSs

Compound Name	*Synonym or Acronym*	*Analytical Purpose*	*Reference Standard Source*
$^{13}C_4$-Perfluorobutanoic acid	[1,2,3,4-$^{13}C_4$]PFBA	IS for PFBA	Wellington Labs (Mix or Individual)
$^{13}C_4$-Perfluoropentanoic acid	[1,2,3,4,5-$^{13}C_5$]PFPeA	IS for PFPeA	Wellington Labs (Mix or Individual)
$^{13}C_2$-Perfluorohexanoic acid	[1,2 -$^{13}C_2$]PFHxA	IS for PFHxA	Wellington Labs (Mix or Individual)
$^{13}C_4$-Perfluoroheptanoic acid	[1,2,3,4-$^{13}C_4$]PFHpA	IS for PFHpA	Wellington Labs (Mix or Individual)
$^{13}C_8$-Perfluorooctanoic acid	[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA	IS for PFOA and [1,2,3,4 $^{13}C_4$]PFOA	Wellington Labs (Mix or Individual)
$^{13}C_9$-Perfluorononanoic acid	[1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA	IS for PFNA	Wellington Labs (Mix or Individual)
$^{13}C_6$-Perfluorodecanoic acid	[1,2,3,4,5,6 -$^{13}C_6$]PFDA	IS for PFDA	Wellington Labs (Mix or Individual)
$^{13}C_7$-Perfluoroundecanoic acid	[1,2,3,4,5,6,7 -$^{13}C_7$]PFUnA	IS for PFUnA	Wellington Labs (Mix or Individual)
$^{13}C_2$-Perfluorododecanoic acid	[1,2 -$^{13}C_2$]PFDoA	IS for PFDoA, *PFTA	Wellington Labs (Mix or Individual)
$^{18}O_2$-Ammonium Perfluorobutane sulfonate	[$^{18}O_2$]PFBS	IS for PFBS	RTI International (Individual)
$^{13}C_3$-Ammonium Perfluorohexane sulfonate	[1,2,3-$^{13}C_3$]PFHS	IS for PFHS	Wellington Labs (Mix or Individual)
$^{13}C_8$-Sodium Perfluorooctane sulfonate	[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOS	IS for PFOS and PFOS[1,2,3,4 $^{13}C_4$].	Wellington Labs (Mix or Individual)
$^{13}C_8$-Perfluorooctanesulfonamide	[1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA	IS for FOSA	Wellington Labs (mix) RTI International (Individual)
$^{13}C_4$-Perfluorooctanoic acid	[1,2,3,4-$^{13}C_4$]PFOA	SRS for all PFCAs: C4-C8	Wellington
$^{13}C_2$-Perfluoroundecanoic acid	[1,2 -$^{13}C_2$]PFUnA	SRS for all PFCAs C9-C13	Wellington
$^{13}C_8$-Perfluorooctane sulfonate	[1,2,3,4-$^{13}C_4$]PFOS	SRS for all PFSAs: C4, C6, and C8	Wellington

Table 2. Example Preparation of Calibration Curve with ISs and SRSs

Sample Description	*Concentration of WS, µg/mL*	*Volume of WS, µL*	*Volume of IS (2 µg/mL), µL*	*Concentration of Surrogate, µg/mL*	*Volume of Surrogate, µL*	*Volume of ASTM Type I Water, or other suitable solvent (1), mL*
0.025 ng/mL curve point	0.10	25	50	0.20	12.5	100
0.030 ng/mL curve point	0.10	30	50	0.20	15	100
0.04 ng/mL curve point	0.10	40	50	0.20	20	100
0.05 ng/mL curve point	0.10	50	50	0.20	25	100
0.1 ng/mL curve point	0.10	100	50	0.20	50	100
0.25 ng/mL curve point	0.10	250	50	0.20	125	100
0.5 ng/mL curve point	1.0	50	50	0.20	250	100
1 ng/mL curve point	1.0	100	50	0.20	500	100
2.5 ng/mL curve point	10.0	25	50	10.0	25	100
5.0 ng/mL curve point	10.0	50	50	10.0	50	100
10.0 ng/mL curve point	10.0	100	50	10.0	100	100
25.0 ng/mL curve point	10.0	250	50	10.0	NA	100
50.0 ng/mL curve point	10.0	500	50	10.0	NA	100
75.0 ng/mL curve point	10.0	750	50	10.0	NA	100
100 ng/mL curve point	10.0	1000	50	10.0	NA	100

N/A - Not Applicable
(1) Samples requiring analysis for PFUnA, PFDoA, PFTrDA, and FOSA should be analyzed against a calibration curve prepared in 1:1 synthetic groundwater:MeOH.

8 Sample Collection and Bottle Preparation

Sample collection bottles are prepared by 3M Environmental Laboratory (or subcontract supplier) personnel for shipment at ambient temperature to the collection site. Typically, four separate collection bottles are associated with a single collection site: sample, field duplicate sample, low field matrix spike, and high field matrix spike. Alternatively, the sample and field duplicate sample may contain SRSs in lieu of additional target analyte low field matrix spike and target analyte high field matrix spike samples. Depending on the scope of the project, additional replicates of the field sample and field matrix spikes may be added. Also, it is not uncommon for additional mid-level field matrix spikes to be collected if the expected sample concentrations are truly unknown or could span a large concentration range.

High-density polyethylene (HDPE) wide-mouth Nalgene bottles are used for the sample collection containers. (Volumes of the bottles may vary depending on how much sample is required to meet data quality objectives.) Sample collection volumes are project specific and based on data quality objectives. The Nalgene bottles do not require any pretreatment prior to use. Typically, placement of a sample bottle volumetric "fill to here" line is done by using a sample bottle marker template. Alternatively, bottles may be weighed prior to bottle preparation and weighed again after samples have been collected.

All bottles should be clearly labeled to indicate its intended use as a sample, field sample duplicate, low field matrix spike, high field matrix spike, sample/SRS field matrix spike, field duplicate sample/SRS field matrix spike, trip blank, or trip blank matrix spike. If each location has different designated spike levels, the label should also clearly indicate the sample location designation. Generally, a set of bottles for a given collection site are prepared then grouped together in plastic bags for organizational purposes. For each sample collection event, at least one set of trip blank and trip blank matrix spikes are prepared.

Bottle preparation should be documented in a Note to File or on a sample preparation worksheet and should include the following information: date prepared, total number of bottles prepared, number of sample sites, the standard identification numbers and spike volumes used to prepare spiked bottles, the "fill to here" volume, and any other pertinent information needed for reconstructibility of the data. The Note to File will be included in the final data package for the project.

Samples are collected in the field and shipped to the laboratory at ambient temperature.

8.1 Field Matrix Spike Sample (FMS)

Field matrix spike samples are a requirement of the method. A FMS sample is defined as a QC sample to which known quantities of appropriate target analytes are added to the sample bottle in the field or in the laboratory before the bottles are sent to the field. The sample and field duplicate sample may contain appropriate SRSs in lieu of target analyte FMS samples. Sample quantities are determined volumetrically or gravimetrically. A known, specific volume or weight of sample is added to the sample container without rinsing. Volumetric sample measurements may be acquired by a laboratory applied "fill to this level" line on the outside of the sample container. Target analyte FMS samples should be spiked at approximately 0.5-10 times the expected analyte concentration in the sample. If the expected range of analyte concentrations is unknown, multiple spikes at varying levels may be prepared to increase the likelihood that a spike at an appropriate level is made. Typically a low and a high target analyte spike are prepared for each sampling location. In those instances where SRSs are to be used in lieu of target analyte FMS samples, the sample and field duplicate sample are spiked at approximately 2-5 times the target LOQ. The FMS is analyzed to ascertain if matrix effects or sample holding time contributes bias to the analytical results. For the sample bottles designated for matrix spikes, an appropriate volume of matrix spiking solution is added to the empty bottle prior to sampling. The volume of spike solution added should produce the desired final concentration of target analytes once the bottle is filled with sample to the "fill to here line". The matrix spiking solution(s) should be prepared in a suitable solvent and contain all of the appropriate target analytes, ISs, and SRSs. The target analyte matrix spiking solution is often the same as the working standards used to create the calibration standards. An example of a bottle spike is given below.

"Fill to here" volume = 200 mL (A 250 mL Nalgene bottle is used)

Desired Field Spike Concentration = 0.25 ng/mL

500 µL of a 0.1 µg/mL spiking solution (containing the target analytes) is added to the bottle and the bottle cap promptly sealed.

8.2 Internal Standard and Surrogate Recovery Standard

If analysis of a surrogate recovery standard (SRS) is included in the project objectives, an appropriate volume of a surrogate standard solution is added to all the bottles prior to sampling and SPE. Typically sample bottles are spiked with surrogate recovery standards at a final desired spike concentration of 0.1 ng/mL.

If quantitation by internal standard (IS) is included in the project objective, an appropriate volume of internal standard solution is added to all the bottles prior to sampling and SPE. Typically sample bottles are spiked with internal standard at a final desired spike concentration of 1 ng/mL.

For the trip blank, the SRS spike and IS spike is added to the bottle and then ASTM Type I water (HPLC grade reagent water or other suitable water may used) is added to the "fill to here" line. The bottle is capped and sealing tape may be placed around the outer edge of the cap. Trip blank matrix spikes are prepared by adding the appropriate volume of target analyte spiking solution, IS, and SRS spiking solutions and filling the bottle to the desired volume with the appropriate water and capping and sealing the cap.

9 Quality Control and Data Quality Objectives

9.1 Data Quality Objectives

This method and required quality control samples is designed to generate data accurate to ±30% with a targeted LOQ of 0.025 ng/mL. Any deviations from the quality control measures spelled out below will be documented in the raw data and footnoted in the final report.

9.2 Method/Procedural Blanks

The method/procedural blank is zero point calibration standard (which includes ISs) analyzed in a regular basis with each analysis batch. At a minimum, method blanks are analyzed prior to instrument calibration, prior to the analysis of CCV samples, after every 10 sample injections, and at the end of the analytical run.

The mean area count or area ratios when using internal standard calibration, for each analyte in the method blanks must be less than 50% of the area count counts or area ratios when using internal standard calibration, of the LOQ standard. The standard deviation of the area counts, or area ratios when using internal standard calibration, of these method blanks should be calculated. A specific %RSD acceptance criteria is not specified but is assessed on an analytical batch basis. If the mean area counts or area ratios when using internal standard calibration, of the method blanks exceed 50% of the LOQ standard, then the LOQ must be raised to the first standard level in the curve that meets criteria. Method blanks may be eliminated if technical justification can be provided (e.g. the procedural blank was analyzed after an unexpectedly high level sample). If any procedural blanks are removed from the LOQ determination, document in the raw data and report as appropriate. Laboratory Sample Replicates / Field Duplicate Sample

Typically, samples are collected in duplicates in the field. The relative percent difference (RPD) of duplicate samples should be ≤20% for the precision of sample preparation and analysis to be considered in control. Replicate samples not meeting the ≤20% RPD criteria are flagged and reported as outside of QC acceptance criteria.

9.3 Laboratory Matrix Spikes (LMSs)

LMSs may be performed in lieu of FMSs if FMSs have previously been performed for the sample matrix. Additionally, LMSs may be performed in lieu of FMSs for a sample matrix if the FMS levels were not appropriate for determining spike recoveries relative to endogenous levels of target analytes and appropriate SRSs. Generally, each sample location represents a different sample and sample matrix. LMSs are prepared for each sample and analyzed to determine the matrix effect on spike recovery efficiency of each target analyte and appropriate SRSs. LMSs should be prepared at a minimum of one level and in duplicate. LMS concentrations should be prepared at approximately 0.5-10 times the endogenous concentration or approximately 4-10 times the LOQ concentration of each target analyte.

Lab matrix spike recoveries should fall within ± 30% of expected values. Sample data with LMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria. Data with LMS recovery outside of ±50% of the expected value are reported as NR, where NR is defined as "Not Reportable" data outside of QC acceptance criteria.

9.4 Lab Control Sample

Lab control spikes are prepared for each analysis batch to determine method accuracy and precision. LCSs should be prepared at three levels in triplicate for each target analyte and at a minimum of two levels in triplicate for appropriate SRSs. Low lab control spikes should be prepared at a concentration in the range of approximately four to ten times higher than the targeted lower LOQ, the mid lab control spikes should be prepared at a concentration near the mid-point of the calibration curve and the high lab control spikes at approximately 80% of the upper LOQ. For each target analyte and SRSs, the percent relative standard deviation (method precision) for each control spike level must be less than or equal to 20% and the average recovery (method accuracy) for each control spike level must be 80-120%. Sample data for target analytes outside of the laboratory control spike acceptance criteria will be handled as follows:

If the average recovery of a spiking level falls outside method acceptance, but at least 67% (6 out of 9) of LCS samples are within 20% of their respective nominal value (33% of the QC samples, not all replicates at the same concentration, may be outside 20% of nominal value), the average recovery will be flagged as outside method acceptance criteria. All LCS samples will be control charted as per ETS-4-026. If the average recovery of one of the spiking levels exceeded the analytical method uncertainty as determined by ETS-12-012, that analytical batch uncertainty will be expanded for that particular study.

If more than 67% of the LCS samples fail to meet method acceptance criteria, the data will not be reported.

Calibration standards consisting of mixed branched and linear isomer PFOS/PFOA are preferred. However, for PFOS/PFOA target analytes, if the calibration standards are comprised of predominantly linear isomers only, at least one level of triplicate LCSs should be prepared using PFOS/PFOA which contains a mix of linear and branched isomers. These LCSs will be used to demonstrate quantitative equivalency (or quantitative bias) of the isomeric mix when using a predominantly linear standard for calibration. The mixed linear and branched isomer PFOS/PFOA LCSs recoveries should fall within ± 30% of expected values. Alternatively, in lieu of mixed branched and linear isomer PFOS/PFOA LCSs, mixed branched and linear isomer PFOS/PFOA TBMSs may be applied to demonstrate method accuracy and precision.

9.5 Field Matrix Spikes (FMSs) / Surrogate Recovery Standards (SRSs)

FMSs are prepared for each sampling location and analyzed to determine the matrix effect and sample holding time on the spike recovery of each target analyte and/or appropriate SRS. Generally, each sample location represents a different sample and sample matrix.

FMSs are QC samples to which known quantities of appropriate target analytes are added to the sample bottle in the laboratory before the bottles are sent to the field. Typically a low and a high target analyte FMS are prepared for each sampling location. The sample and field duplicate sample may contain appropriate SRSs in lieu of target analyte low field matrix spike and target analyte high field matrix spike samples.

Field matrix spike method acceptance criteria are recoveries within ±30% of the expected value. If FMS recovery (target analyte or SRS spike) is outside of ±30% of the expected value or could not be assessed because the FMS (target analyte) was spiked at an inappropriate level, the sample result is reported as follows:

1.) If target analyte FMS recovery could not be assessed because the FMS's were at an inappropriate level, then Laboratory Matrix Spikes (LMS) may be substituted. If LMS recoveries are within ±30% the data are reportable and flagged to indicate that the FMS spikes levels were inappropriate.

2.) If multiple target analyte FMS's were prepared on a sample and the closest FMS level to the reported sample meets the ±30% acceptance criteria but additional FMS's are outside the ±30% acceptance range, the data are reportable and flagged to indicate that while there were failing FMS's, the uncertainty will not be expanded since the most appropriate spike level passed.

3.) If the target analyte FMS recoveries are outside of the ±30% acceptance range but at least 30 acceptable historical reportable FMS sample results are available, the data may be reported but flagged with an expanded uncertainty and as not meeting FMS criteria.

4.) Sample data with FMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria with an expanded uncertainty.

5.) If FMS recovery is outside of ±50%, the sample result is reported as NR, where NR is defined as "Not Reportable" due to noncompliant QC results.

The targeted fortification levels should be at least 50% of the endogenous level and less than 10 times the endogenous level to be used without justification to determine the statement of accuracy for analytical results.

Note: It is possible for bottles utilized for Field Matrix Spike samples to be under-filled or over-filled during sample collection. Since this scenario will effect the actual concentration of the FMS sample (surrogate and internal standard concentrations will also be effected, if used), it is important that any obvious under-filling or over-filling of sample bottles be documented in the data package and taken into account in the FMS, ISs, or SRSs recovery calculations. Samples over-filled or under-filled by more than 10% will be require recalculation of the FMS, ISs, and SRS true values.

The average of the sample and the field duplicate should be used to calculate the recovery.

10 Procedures

10.1 Water Sample Preparation

This method is applicable to water samples. Samples containing heavy particulate may not be suitable for analysis by this method. Samples containing suspended particulate should be centrifuge prior to removing a sample aliquot, or filtered.

- Thoroughly mix sample before removing an aliquot and placing in a labeled autovial.
- Dilute sample, if necessary, with ASTM Type I water, HPLC water, other suitable water, or solvent (methanol).
- Lab control spikes are prepared for each analysis batch to determine method accuracy and precision. LCSs should be prepared at three levels in triplicate for each target analyte and at a minimum of two levels in triplicate for appropriate SRSs. Low lab control spikes should be prepared at a concentration in the range of approximately four to ten times higher than the targeted lower LOQ, the mid lab control spikes should be prepared at a concentration near the mid-point of the calibration curve and the high lab control spikes at approximately 80% of the upper LOQ. For IS quantitation, stable isotope internal standards of each target analyte or appropriate surrogate ISs should be spiked at the same level as the samples being analyzed, in all LCSs.
- If LCSs are being prepared using synthetic groundwater, allow the LCSs samples to equilibrate for a minimum of 4 hours before aliquoting for analysis or diluting with solvent (methanol).

11 Sample Analysis - LC/MS/MS

11.1 Instrument Setup

Note: In this example, an Applied Biosystems Sciex API 4000 (API 5000 or API 5500) Tandem Mass Spectrometer (LC/MS/MS) is used. Other brands/models of LC/MS/MS instruments as well as single quadrupole mass spectrometers (LC/MS) may be used as long as the method acceptance 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: Applied Biosystems API 4000, API 5000, or API 5500

Ion Source: Turbo Ion Spray (ABS)

Mode: Electrospray Negative

Scan Type: MRM (Multiple Reaction Monitoring)

Computer: Dell DHM

Software: Windows 2000 or Windows XP, Analyst 1.4.2 or higher versions

HPLC: Agilent Series 1100,1200, or 1290

Agilent Quaternary Pump

Agilent Vacuum Degasser

Agilent Autosampler

Agilent Column Oven

Note: One or more C18 HPLC analytical columns (2.1 mm x 100 mm, 5µm or 2.1 mm x 50 mm, 5µm) may be attached on-line after the purge valve and before the sample injection port to retard and separate any residue contaminants that may be in the mobile phase and/or HPLC system.

HPLC Column: Betasil C18, 4.6mm x 100mm, 5µm (ThermoElectron Corporation)

Column Temperature: 35°C

Injection Volume: 5µL

Mobile Phase (A): 2mM Ammonium Acetate in ASTM Type I water (See 7.3)

Mobile Phase (B): Methanol

Table 3. Liquid Chromatography Gradient Program.

Step Number	*Total Time (min)*	*Flow Rate (µL/min)*	*Percent A (2 mM ammonium acetate)*	*Percent B (Methanol)*
0	0	750	97.0	3.0
1	2.0	750	97.0	3.0
2	14.5	750	5.0	95.0
3	15.5	750	5.0	95.0
4	16.5	750	97.0	3.0
5	20.0	750	97.0	3.0

Note: Other HPLC gradients may be used as long as the method criteria and project data quality objectives 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.

Table 4 Suggested MRM Transitions for Target Analytes, Surrogates, and Internal Standards

Analyte	*Analyte Description*	*Mass Transition Q1 (amu)*	*Mass Transition Q3 (amu)*
PFBA (C4 Acid)	Target	213	169
PFPeA (C5 Acid)	Target	263	219
PFHxA (C6 Acid)	Target	313	269, 119
PFHpA (C7 Acid)	Target	363	319, 169
PFOA (C8 Acid)	Target	413	369, 219, 169
PFNA (C9 Acid)	Target	463	419, 169, 219
PFDA (C10 Acid)	Target	513	469, 269, 219
PFUnA (C11 Acid)	Target	563	519, 269, 219
PFDoA (C12 Acid)	Target	613	569, 169, 319
PFTA (C13 Acid)	Target	663	619, 369, 319
FBSA (C4 Sulfonamide)	Target	298	78
FOSA (C8 Sulfonamide)	Target	498	78
PFBS (C4 Sulfonate)	Target	299	99, 80
PFHS (C6 Sulfonate)	Target	399	99, 80
PFOS (C8 Sulfonate)	Target	499	80, 99, 130
[1,2,3,4 -$^{13}C_4$]PFBA	IS for PFBA	217	172
[1,2,3,4,5 -$^{13}C_5$]PFPeA	IS for PFPeA	268	223
[1,2 -$^{13}C_2$]PFHxA	IS for PFHxA	315	270
[1,2,3,4- $^{13}C_4$]PFHpA	IS for PFHpA	367	322
[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA	IS for PFOA	421	376
[1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA	IS for PFNA	472	427
[1,2,3,4,5,6 -$^{13}C_6$]PFDA	IS for PFDA	519	474
[1,2,3,4,5,6,7 -$^{13}C_7$]PFUnA	IS for PFUnA	570	525
[1,2 -$^{13}C_2$]PFDoA	IS for PFDoA and PFTA	615	570
[$^{18}O_2$]PFBS	IS for PFBS	303	84
[1,2,3-$^{13}C_3$]PFHS	IS for PFHS	402	80
[1,2,3,4- $^{13}C_4$]PFOS	IS for PFOS	503	80
[1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA	IS for FOSA	507	80
[1,2,3,4-$^{13}C_4$]PFOA	Surrogate (C4-C8 Acids)	417	372
[1,2,3,4- $^{13}C_4$]PFOS	Surrogate(Sulfonates, FOSA)	503	80
[1,2 -$^{13}C_2$]PFUnA	Surrogate (C9-C13 Acids)	565	520

Multiple transitions for monitoring the analytes is an option. The use of one daughter ion is acceptable if data sensitivity and selectivity is achieved and provided that retention time criteria are met to assure adequate specificity. While the daughter ions may be chosen at the discretion of the analyst, mass transition 99 is suggested for PFOS. Quantitation may be performed using the total ion chromatogram (TIC, or summed MRMs) for a given analyte. For example, the PFOA TIC would sum all three of the monitored transitions. 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 and the gradient, column, guard column(s) used 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.

11.2 Calibration Curve

Quantitation is by internal standard or external standard calibration. Calibration standards may be prepared in ASTM Type I, HPLC water, other suitable water, or a solvent/water mixture. If internal standard calibration does not meet calibration acceptance criteria, external calibration can be applied. See Table 1 for

recommended application of available internal standards. Quantitation of PFOA and PFOS is by summed analyte-specific mass transitions.

Analyze the standard curve prior to each set of samples. If internal standards were added to the calibration standards area ratios are used to generate the calibration curve. The standard curve may be plotted using a linear regression ($y = mx + b$), weighted 1/x or unweighted, or by quadratic fit ($y = ax^2 + bx + c$), weighted 1/x or unweighted, using suitable software. 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.

High and/or low points may be excluded from the calibration curves to provide a better fit over the 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 (or area ratio if quantitating by IS) are not at least twice that of the average area counts (or area ratio if quantitating by IS) of method and/or solvent blanks. The coefficient of determination (r^2) value for the calibration curve must be greater than or equal to 0.990 (or a correlation coefficient (r) of 0.995). Each point in the curve must be within ±25% of the theoretical concentration with the exception of the LLOQ, which may be within ±30%. 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.

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

11.3 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. Samples must be bracketed by passing CCVs or the calibration curve and a passing CCV to be reportable.

11.4 System Suitability

A minimum of three system suitability samples should be injected at the beginning of each analytical run, prior to the analysis of the calibration curve. Typically these samples are at a concentration near the mid-level of the calibration curve and are repeated injections from one autosampler vial. It is suggested that the system suitability injections have area counts or area ratios when using internal standard calibration, with a target RSD of ≤5% and a target retention time RSD of ≤2%. There is no defined acceptability limit on these results as the %RSD value is dependent on the number of MRM transitions being monitored in the LC/MS/MS run or time period. Ultimately, any effects on these parameters for the System Suitability samples will also be evident on all standards and QC samples analyzed as part of the analysis batch. Any effect of system suitability is incorporated within QC acceptance criteria.[4]

11.5 Sample Analysis and QCs

For each analysis batch, the instrument analysis run sequence should include an initial calibration curve, samples, FDSs, interspersed blanks, interspersed CCVs, appropriate QCs (i.e., LCSs, LMSs, FMSs, TBMSs, and TBs), and a final CCV or calibration curve bracketing samples and appropriate QCs

Inject the same volume (between 5 - 100µL) of each standard, analytical sample and blank into the instrument (unless an on-instrument sample dilution is desired).

Samples containing analytes that are quantitated above the concentration of the highest standard in the curve should be further diluted and reanalyzed.

[4] 3M Environmental Laboratory study E08-0096 evaluated the effect on these results as a function of the number of MRMs being monitored.

12 Data Analysis and Calculations

The chromatography analysis software will typically calculate the amount of target analyte in the sample extracts using the established calibration curve.

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

$$\text{LCS\% recovery} = \frac{\text{LCS Concentration } (\frac{ng}{mL})}{\text{Spike Concentration } (\frac{ng}{mL})} * 100\%$$

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

$$\text{LMS \% recovery} = \frac{\text{LMS Concentration } (\frac{ng}{mL}) - \text{Concentration of Sample } (\frac{ng}{mL})}{\text{Spike Concentration } (\frac{ng}{mL})} * 100\%$$

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

$$\text{Recovery} = \frac{\text{Total analyte found (ng/mL)} - \text{Average analyte found in sample (ng/mL)}}{\text{Analyte added (ng/mL)}} \times 100$$

13 Analysis Batch Method Performance Criteria

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 the final report if the Technical Manager (non-GLP study) or Study Director (GLP study) chooses to report 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 appropriate. 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 – Analysis Batch

A minimum of three system suitability samples should be injected at the beginning of each analytical run. These samples are run prior to the calibration curve. It is suggested that the system suitability injections have area counts with a target RSD of ≤5% and a target retention time RSD of ≤2%. There is no defined acceptability limit on these results as the %RSDs are dependent on the number of MRM transitions being monitored in the LC/MS/MS run or time period. Any effect of system suitability is incorporated in the QC acceptance criteria.

13.2 Calibration and Limit of Quantitation (LOQ) – Analysis Batch

Calibration Curve: The coefficient of determination (r^2) value for the calibration curve must be greater than or equal to 0.990 corresponding to a correlation coefficient (r) = 0.995. Each point in the curve must be within ±25% of the theoretical concentration with the exception of the LLOQ, which may be within ±30%.

CCV Performance: The calibration standards that are interspersed throughout the analytical sequence are evaluated as continuing calibration verifications in addition to being part of the calibration curve. The accuracy

of each curve point must be within 25% of the theoretical value (within 30% for lowest curve point). Samples that are bracketed by CCVs not meeting these criteria must be reanalyzed.

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 average area counts for all prepared procedural blank(s). By definition, the measured value of the LLOQ must be within 30% of the theoretical value.

Demonstration of Specificity: Specificity is demonstrated by chromatographic retention time (within 4% of standard) and the mass spectral response of unique ions.

13.3 Blanks – Method/Procedural Blanks and Trip

Method/Procedural Blanks: Multiple procedural blanks should be interspersed throughout the analysis batch and the analytical sequence. At a minimum, method blanks are analyzed prior to instrument calibration, prior to the analysis of CCV samples, after every 10 sample injections, and at the end of the analytical run.

The mean area counts (or area ratios when using IS calibration) for each analyte must be less than 50% of the area count of the LOQ standard. If the area counts of the procedural blanks exceed 50% of the LOQ standard, then the LOQ must be raised to the first standard level that meets criteria.

Trip Blank: A trip blank of ASTM Type I water (or lab equivalent) is prepared in a sample container in the laboratory and treated as a sample, including exposure to shipping, sampling site conditions, storage, preservation and all analytical procedures. The trip blanks results for each analyte are included with the reported sample results.

13.4 Data Accuracy and Precision – Analysis Batch

Lab Control Spikes: The average recovery at each LCS level for each target analyte and appropriate SRS should be within 80-120% and the percent relative standard deviation of the recoveries must be less than or equal to 20%. If the average recovery of a spiking level falls outside method acceptance, but at least 67% (6 out of 9) of LCS samples are within 20% of their respective nominal value (33% of the QC samples, not all replicates at the same concentration, may be outside 20% of nominal value), the average recovery will be flagged as outside method acceptance criteria. All LCS samples will be control charted as per ETS-12-012. If the average recovery of one of the spiking levels exceeded the analytical method uncertainty as determined by ETS-12-012, that analytical batch uncertainty will be expanded for that particular study. The average recovery at each LCS level for mixed branched/linear isomer PFOA and PFOS should be within 70-130% and the percent relative standard deviation of the recoveries must be less than or equal to 20%.

Field Duplicates: The relative percent difference (RPD) of duplicate samples should be less than 20% for the precision of sample preparation and analysis to be considered in control. Replicate samples not meeting the 20% RPD criteria are flagged and reported as outside of QC acceptance criteria.

Field Matrix Spikes: FMS acceptance criteria are recoveries within ±30% of the expected value for each target analyte and appropriate SRS. Sample data with FMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria. Data with FMS recovery outside of ±50% of the expected value are reported as NR, where NR is defined as "Not Reportable" data outside of QC acceptance criteria. If FMS recovery could not be assessed because FMSs were at an inappropriate level, then Laboratory Matrix Spikes (LMSs) may be substituted. If LMS recoveries are within ±30% for each target analyte and SRSs the data are reportable but flagged as not meeting the FMS method acceptance criteria.

13.5 Analytical Method Uncertainty

Analytical method uncertainty for each target analyte and SRS is determined with control charted historical analysis batch LCS data for the method and reported with each analysis batch.[5] Uncertainty determinations

[5] Method uncertainty based on INTERNATIONAL ANS/ISO/IED STANDARD 17025 reference (GUM, Guide to the Expression of Uncertainty in Measurement). Method application demonstrated in ETS-12-012, citing references: a.) EURACHEM/CITAC Guide, "Quantifying Uncertainty in Analytical Measurement," Second Edition; Editors: S.L.R. Ellison, M. Rosslein, and A. Williams. b.)Georgian, Thomas, "Estimation of Laboratory Analytical Uncertainty Using Laboratory Control Samples," Environmental Testing &

are based on INTERNATIONAL ANS/ISO/IED STANDARD 17025 reference (GUM, Guide to the Expression of Uncertainty in Measurement) and described in ETS-12-012. At least thirty data points are required for determining analytical method uncertainty. The method uncertainty is defined as 2x the standard deviation of the percent recoveries of the pooled lab control spikes. While all LCS data points are control charted, only the most recent fifty data points are used for determining the method uncertainty.

When less than thirty LCS data points have been generated for a given analyte, the analysis batch LCSs are used to determine the data uncertainty. If FMSs meet the ±30% recovery criteria at a level appropriate to the endogenous level, and the LCS meet the ±20% recovery criteria, then the uncertainty of the data is determined as within 100±20%.

Analysis batch sample data with FMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria with expanded uncertainties. Data with FMS recovery outside of ±50% of the expected value are reported as NR, where NR is defined as "Not Reportable" data outside of QC acceptance criteria. If FMS recovery could not be assessed because FMSs were at an inappropriate level, then Laboratory Matrix Spikes (LMSs) may be substituted. If LMS recoveries are within ±30% for each target analyte and appropriate SRSs the data are reportable but flagged as not meeting the FMS method acceptance criteria with uncertainties of ±30%. If FMS do not meet the ±30% recovery criteria, and historical FMS data does not exist, the analytical uncertainty is evaluated on a sample-by-sample basis, the data may be reported with expanded uncertainty and are flagged.

13.6 Quantitation of PFOA/PFOS – Analysis Batch

Calibration standards consisting of mixed branched and linear isomer PFOS/PFOA are preferred. Quantitation is performed by integrating the linear and branched isomers together. Alternately, the linear and branched isomers can be integrated separately, applying the appropriate true value to each calibration curve point for each isomer. The LCS and samples are then quantitated by integrating the linear and branched isomers separately (requires separate analytical results files) and quantitating the resulting peak against the linear or branched calibration curve. The results from both integrations are then summed to produce the final result. Integrating the linear and branched isomers separately may be helpful for those samples where the linear/branched ratios do not closely match those of the reference standards.

However, for PFOS/PFOA target analytes, if the calibration standards are comprised of predominantly linear isomers only the method requires the addition of LCSs of mixed branched/linear isomer PFOS/PFOA. The purpose of including these LCSs is to demonstrate quantitative equivalency (or quantitative bias) of the isomeric mix when using a predominantly linear PFOS or PFOA standard for calibration. Alternatively, in lieu of mixed branched and linear isomer PFOS/PFOA LCSs, mixed branched and linear isomer PFOS/PFOA TBMSs may be applied to demonstrate method accuracy and precision.

An alternate method of quantitation can be performed whereby only the linear isomer of PFOS/PFOA is integrated and used for generating the calibration curve. The LCS and samples are then quantitated by integrating the linear and branched isomers separately (requires separate analytical results files) and quantitating the resulting peak against the linear calibration curve. The results from both integrations are then summed to produce the final result. Integrating the linear and branched isomers separately reduces the on-column concentration for those samples that contain both linear and branched isomers of PFOA/PFOS. This ensures that the concentration detected is within the a range of the calibration curve that is comparable regardless of whether the calibration curve was generated using predominantly linear isomers of PFOS/PFOA or linear plus branched isomers of PFOS/PFOA.

14 Pollution Prevention and Waste Management

Waste generated when performing this method will be disposed of appropriately. The original samples will be archived at the 3M Environmental Laboratory in accordance with internal procedures.

Analysis, November/December 2000. c.)Taylor, B.N. and CE. Kuyatt, NIST Technical Note 1297, 1994 Edition: "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results."d.)Adams, T.M., "A2LA Guide for the Estimation of Measurement Uncertainty in Testing", July 2002.

15 Records

Each data package generated for a study must include all supporting information for reconstruction of the data. Information for the data package must include, but is not limited to the following items: study or project number, sample and standard prep sheets/records, instrument run log (instrument batch records, instrument acquisition method, summary pages), instrument results files, chromatograms, calibration curves, and data calculations.

16 Affected Documents

None.

17 Revisions

Revision Number	Summary of Changes
1	*Section 1. Included the use of internal standard calibration by this method.* *Section 2. Included the use of internal standard calibration by this method. Included the use of a solvent/water mixture when analyzing for PFUnA, PFDoA, PFTrDA, and FOSA.* *Section 3. Added definitions for internal standard, surrogate internal standard, and surrogate recovery standard.* *Section 6.Removed the details regarding the instrument parameters to section 10 of the method.* *Section 7. Updated reference standards to include internal standards and surrogates. Changed concentration levels for working standards and included the use of internal standards and surrogates.* *Section 8. Inserted a new section on sample bottle preparation.* *Section 9 Quality Control. This section was previously section 10 in ETS-8-044.0. Updated QC criteria to be consistent with method ETS-8-154.4.* *Section 10 Procedures. This section was previously section 8 (Sample Handling) in ETS-8-044.0. Added detail regarding the preparation of LCSs. Included the use of methanol as a dilution solvent.* *Section 11 Sample Analysis. This section was previously section 10 in ETS-8-044.0. Included the details regarding the instrument parameters.* *Section 12 Data Analysis and Calculations. This section was previously section 11 in ETS-8-044.0. Removed the equation for calculating the analytes concentration, indicating that this is done by the instrument software.* *Section 13 Method Performance. This section was previously section 12 in ETS-8-044.0. Updated QC criteria to be consistent with ETS-8-154.4. Added information on the determination of analytical method uncertainty and quantitation of PFOA/PFOS.* *Section 14 Pollution Prevention. This section was previously section 13 in ETS-8-044.0.* *Section 15 Records. This section was previously section 14 in ETS-8-044.0.* *Section 16 Affected Documents. This section was previously section 15 in ETS-8-044.0.* *Section 17 Revisions. This section was previously section 16 in ETS-8-044.0.*

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GLP10-01-02. Interim Report 31: Analysis of PFBS, PFHS, and PFOS in Groundwater Samples from New On-Site Wells - Adjacent to the 3M Decatur Wastewater Treatment Plant (WWTP) April 2012

Study Title

Analysis of Perfluorooctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane Sulfonate (PFBS) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program

Data Requirement
EPA TSCA Good Laboratory Practice Standards 40 CFR Part 792

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Interim Report Completion Date
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Project Identification
GLP10-01-02-31

Total Number of Pages
89

The testing reported herein meet the requirements of ANSI/ISO/IEC 17025:2005 "General Requirements for the Competence of Testing and Calibration Laboratories", in accordance with the A2LA Testing Certificate # 2052.01. Testing that complies with this International Standard also meets principles of ISO 9001:2000.

Testing Cert #2052.01

This page has been reserved for specific country requirements.

GLP COMPLIANCE STATEMENT

Report Title: GLP10-01-02, Interim Report 31: Analysis of PFBS, PFHS, and PFOS in Groundwater Samples from New On-Site Wells - Adjacent to the 3M Decatur Wastewater Treatment Plant (WWTP) April 2012.

Study: Analysis of Perfluorooctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane Sulfonate (PFBS) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program.

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

- These are environmental samples where there is no specific test substance, no specific test system and no dosing of a test system.
- The reference substances have not been characterized under the GLPs and the stability under storage conditions at the test site have not been determined under GLPs.

Gary Hohenstein — 5/17/12

Gary Hohenstein, Sponsor Representative — Date

Kesari — 5/25/12

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

QUALITY ASSURANCE STATEMENT

Report Title: GLP10-01-02, Interim Report 31: Analysis of PFBS, PFHS, and PFOS in Groundwater Samples from New On-Site Wells - Adjacent to the 3M Decatur Wastewater Treatment Plant (WWTP) April 2012.

Study: Analysis of Perfluorooctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane Sulfonate (PFBS) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program.

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

Inspection Dates	Phase	Date Reported to	
		Testing Facility Management	Study Director
4/26-27/12, 5/1/12	Data and Report	5/4/12	5/4/12

QAU Representative — Date: 5/9/12

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1 Study Information

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3M Company

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Kelly Ukes, Analyst

Study Dates

Study Initiation: March 8, 2010
Interim 31 Experimental Termination: April 28, 2012
Interim Report Completion: Date of Interim Report Signing

Location of Archives

All original raw data and the analytical report have been archived at the 3M Environmental Laboratory according to 40 CFR Part 792. The test substance and analytical reference standard reserve samples are archived at the 3M Environmental Laboratory according to 40 CFR Part 792

2 Summary

The 3M Environmental Laboratory received groundwater samples from six new on-site temporary residuum monitoring wells in the vicinity of the 3M Decatur facility Wastewater Treatment Plant (WWTP) in Decatur, AL. A total of twenty-eight sample bottles were received at the 3M Environmental Laboratory for perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHS) and perfluorobutane sulfonate (PFBS), and included duplicate groundwater samples and two field matrix spike (FMS) samples from each sampling location. Samples also included one trip blank containing Milli-Q™ water and appropriate trip blank spikes and one equipment rinseate blank. The equipment rinseate blank did not have FMS samples prepared for determination of PFOS, PFHS and PFBS recovery. All samples were logged into the laboratory information management system (LIMS) under project GLP10-01-02-31. The groundwater samples and trip blanks were received from Weston personnel on April 9, 2012. All of the samples were prepared and analyzed for PFBS, PFHS, and PFOS following 3M Environmental Laboratory Method ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds in Water by LC/MS/MS; Direct Injection Analysis".

The average measured PFBS, PFHS, and PFOS concentrations are summarized in **Table 1.** The trip blank sample was below the lower limit of quantitation (LLOQ) for all analytes, indicating adequate control of sample contamination during shipping and sample collections. The analytical method uncertainties associated with the reported results are: PFBS ± 12%, PFHS ± 12% and PFOS ± 35%.

Table 1. Summarized PFBS, PFHS, and PFOS Results (Residuum Monitoring Wells, April 2012).

	PFBS	PFHS	PFOS
Sampling Location	Avg. Conc. (ng/mL) ± RPD	Avg. Conc. (ng/mL) ± RPD	Avg. Conc. (ng/mL) ± RPD
DAL GW TW1R 120405	33.8 ± 0.30%	57.3 ± 2.1%	29.0 ± 9.0%
DAL GW TW2R 120405	117 ± 5.1%	579 ± 5.5%	1090 ± 17%
DAL GW TW3R 120405	304 ± 7.6%	1310 ± 15%	3660 ± 17%
DAL GW TW4R 120405	184 ± 4.9%	19.1 ± 1.0%	247 ± 2.4%
DAL GW TW5R 120405	522 ± 4.4%	43.0 ± 1.6%	696 ± 2.3%
DAL GW TW6R 120405	156 ± 0.64%	46.7 ± 5.6%	281 ± 4.6%
DAL GW TW3R Rinseate Blank	<0.250	<0.250	<0.232
DAL-GW-TRIP01 Blank	<0.250	<0.250	<0.232

The analytical method uncertainties associated with the reported results are: PFBS ± 12%, PFHS ± 12%, and PFOS ± 35%.

3 Introduction

This analytical study was conducted as part of the Phase 3 Environmental Monitoring and Assessment Program for the 3M facility located in Decatur, Alabama. The objective of the overall program is to gain information regarding concentrations of perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHS) and perfluorobutane sulfonate (PFBS), in various environmental media such as groundwater, soils and sediments that are associated with and near the Decatur facility. This analytical study was conducted to analyze groundwater samples collected from six new temporary on-site residuum

monitoring wells located adjacent to the 3M Decatur WWTP for PFOS, PFHS and PFBS in an effort to characterize regional groundwater conditions.

The 3M Environmental Laboratory prepared sample containers (250 mL high-density polyethylene bottles) which were shipped to Decatur, AL Weston personnel prior to field sampling. Sample containers for each sampling location included a field sample, field sample duplicate, and two field matrix spike samples. Each empty container was marked with a "fill to here" line to produce a final sample volume of 200 mL. Containers designated for field matrix samples were fortified with an appropriate matrix spike solution containing PFBS (linear isomer), PFHS (linear isomer), and PFOS (linear and branched isomers) prior to being sent to the field for sample collection. All sample bottles included the addition of $^{18}O_2$-PFBS, $^{13}C_3$-PFHS, and $^{13}C_8$-PFOS (internal standard) at a nominal concentration of 1 ng/mL and $^{13}C_4$-PFOS (surrogate recovery standard) at a nominal concentration of 0.1 ng/mL. Due to the level of PFBS, PFHS, and PFOS detected in the samples, neither the internal standards nor the surrogate recovery standard was utilized during sample analysis. Laboratory matrix spikes were prepared for sampling locations TW2, TW3, TW4, TW5, and TW6 since the field matrix spike levels were not appropriate for these sampling locations for at least one of the target analytes. See section 8.9 of the report for laboratory matrix spike levels. See section 8.8 of the report for field matrix spike levels. See section 8.9 of the report for laboratory matrix spike levels.

Samples were prepared and analyzed according to the procedure defined in 3M Environmental Laboratory method ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds In Water by LC/MS/MS; Direct Injection Analysis".

Table 1 summarizes the average PFBS, PFHS, and PFOS concentrations for the duplicate surface water samples collected and the trip blank sample. Tables 10-17 summarize the individual sample results and the associated field matrix spike recoveries. All results for the quality control samples prepared and analyzed with the samples are reported and discussed elsewhere in this report.

4 *Test & Control Substances*

There was not a test substance or control substances in the classic sense of a GLP study. This study was purely analytical in nature.

5 Reference Substances

Reference Substance	PFBS (Linear)	PFHS (Linear)
Chemical Name	Potassium Perfluorobutane sulfonate	Sodium Perfluorohexane sulfonate
Chemical Formula	$C_4F_9SO_3^-K^+$	$C_6F_{13}SO_3^-Na^+$
Identifier	NA	L-PFHXS
Use	Target Analyte Reference Standard	Target Analyte Reference Standard
Source	3M	Wellington
Expiration Date	01/10/2017	03/25/2018
Storage Conditions	Frozen	Frozen
Chemical Lot Number	41-2600-8442-5	LPFHxSAM08
TCR Number	TCR-121	TCR08-0018
Physical Description	White Powder	Crystalline
Purity	96.7%	100%

Reference Substance	PFOS (Linear + Branched)	PFOS (Linear + Branched)
Chemical Name	Potassium Perfluorooctane sulfonate	Potassium Perfluorooctane sulfonate
Chemical Formula	$C_8F_{17}SO_3^-K^+$	$C_8F_{17}SO_3^-K^+$
Identifier	Br-PFOSK	CAS # 2795-39-3
Use	Target Analyte Reference Standard	FMS Reference Standard
Source	Wellington	Sigma-Aldrich
Expiration Date	03/17/2014; 12/01/2014	02/04/2014
Storage Conditions	Frozen	Ambient
Chemical Lot Number	brPFOSK0708; brPFOSK1111	1424328V
TCR Number	TCR11-0010; TCR11-0041	TCR11-0028
Physical Description	Liquid	White Powder
Purity	99.9%	99.7%

6 Test System

The test systems for this study are groundwater samples collected from wells located in Decatur, AL by Weston Solutions, Inc. personnel. Samples for this study are "real world" samples, not dosed with a specific lot of test substance.

Table 2. Sample Description Key Code.

String Number	String Descriptor	Example
Example	*DAL-GW-TW1R-0-120405*	
1	*Sample Location*	*DAL= Decatur, Alabama*
2	*Sample Type*	*GW = Ground Water*
3	*Well ID*	*Example: TW1R*
4	*Sample Type*	*0=primary sample* *DB=duplicate sample* *LS = low spike* *HS = high spike*
5	*Sampling Date*	*120405- April 5, 2012*

7 Method Summary

7.1 Method

Analysis for all analytes was completed following 3M Environmental Laboratory method ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds In Water by High Performance Liquid Chromatography/Mass Spectrometry Direct Injection Analysis".

7.2 Sample Collection

Samples were collected in 250 mL Nalgene™ (high-density polyethylene) bottles prepared at the 3M Environmental Laboratory. Sample bottles associated with GLP10-01-02-31 were returned to the laboratory at ambient conditions on April 9, 2012. Samples were stored refrigerated at the laboratory after receipt. A set of laboratory prepared Trip Blank and Trip Blank field matrix spikes were sent with the sample collection bottles.

7.3 Sample Preparation

All samples were initially diluted 1:10 by diluting 1 mL of a well mixed sample with 9 mL of Milli Q water and analyzed on 4/13/12.

Sampling locations TW2, TW3, TW4, TW5, and TW6 were re-analyzed and included the preparation of a laboraotry matrix spike with each sample set. Location TW2R was diluted 1:50 by diluting 0.2 mL of the well mixed sample with 9.8 mL of Milli Q water and included a 1000 ppb LMS for PFHS and PFOS. Location TW3R was diluted 1:100 by diluting 0.1 mL of the well mixed sample with 9.9 mL of Milli Q water and included a 2000 ppb LMS and 5000ppb LMS for PFBS, PFHS, and PFOS. Locations TW4R, TW5R and TW6R were diluted 1:10 by diluting 1.0 mL of the well mixed sample with 9.0 mL of Milli Q water. Location TW4R included a 200 ppb LMS for PFOS. Location TW5R included a 500 ppb LMS for PFBS and PFOS. Location TW6R included a 200 ppb LMS for PFOS.

7.4 Analysis

All study samples and quality control samples were analyzed for PFBS, PFHS, and PFOS using high performance liquid chromatography/ tandem mass spectrometry (HPLC/MS/MS). Detailed instrument parameters, the liquid chromatography gradient program, and the specific mass transitions analyzed are described in the raw data hard copies placed in the final data packet, and are briefly described below.

Table 3. Instrument Parameters.

Instrument Name	ETS Ginger	ETS Buster
Analytical Method Followed	ETS-8-044.1	ETS-8-044.1
Analysis Date	4/13/12	4/16/12, 4/27/12
Liquid Chromatograph	Agilent 1100	Agilent 1100
Guard column	Betasil C18 (4.6 mm X 100 mm), 5µ	Betasil C18 (4.6 mm X 100 mm), 5µ
Analytical column	Betasil C18 (4.6 mm X 100 mm), 5µ	Betasil C18 (4.6 mm X 100 mm), 5µ
Injection Volume	2 or 10 µL	2 or 10 µL
Mass Spectrometer	Applied Biosystems API 5000	Applied Biosystems API 4000
Ion Source	Turbo Spray	Turbo Spray
Electrode	Turbo ion electrode	Turbo ion electrode
Polarity	Negative	Negative
Software	Analyst 1.4.2	Analyst 1.4.2

Table 4. Liquid Chromatography Conditions.

Step Number	*Total Time (min)*	*Flow Rate (µL/min)*	*Percent A (2 mM ammonium acetate)*	*Percent B (methanol)*
ETS-8-044.1				
0	0.0	750	97.0	3.0
1	2.0	750	97.0	3.0
2	14.5	750	5.0	95.0
3	15.5	750	5.0	95.0
4	16.5	750	97.0	3.0
5	20.0	750	97.0	3.0

Table 5. Mass Transitions.

Analyte	*Mass Transition Q1/Q3*	*Reference Material Structure*
PFBS	*299/80*	*Linear*
	299/99	
PFHS	*399/80*	*Linear*
	399/99	
PFOS	*499/80*	*Linear + Branched*
	499/99	
	499/130	

Dwell time was 50 or 75 msec for each transition. The individual transitions were summed to produce a "total ion chromatogram" (TIC), which was used for quantitation.

8 Analytical Results

8.1 Calibration

Samples were analyzed against an external standard calibration curve. Calibration standards were prepared by spiking known amounts of the stock solution containing PFBS, PFHS, PFOS (reference standard for PFOS containing both linear and branched isomers) into Milli Q water. Standards ranging from 0.0250 ng/mL to 100 ng/mL (nominal) were analyzed. Low and or high curve points may have been disabled to meet method criteria. A quadratic, 1/x weighted, calibration curve of the peak area counts was used to fit the data for each analyte. The data were not forced through zero during the fitting process. Calculating the standard concentrations using the peak area confirmed accuracy of each curve point. Each curve point was quantitated using the overall calibration curve and reviewed for accuracy. Method calibration accuracy requirements of 100±25% (100±30% for the lowest curve point) were met for all analytes. The correlation coefficient (r) was greater than 0.995 for all analytes. Each curve point was quantitated using the overall calibration curve and reviewed for accuracy. Method calibration accuracy requirements of 100±25% (100±30% for the lowest curve point) were met for all analytes. The correlation coefficient (r) was greater than 0.995 for PFBS, PFHS and PFOS for each analysis.

8.2 System Suitability

A calibration standard was analyzed four times at the beginning of each analytical sequence to demonstrate overall system suitability. The acceptance criteria of less than or equal to 5% relative standard deviation (RSD) for peak area and retention time criteria of less than or equal to 2% RSD was met for PFBS, PFHS and PFOS for each analysis.

8.3 Limit of Quantitation (LOQ)

The LOQ for this analysis is the lowest non-zero calibration standard in the curve that meets linearity and accuracy requirements and for which the area counts or area ratio are at least twice those of the appropriate blanks. The LOQ for all analytes can be found in Table 6.

Table 6. Limit of Quantitation (LOQ).

Analysis Date	*Dilution Factor*	*PFBS LOQ, ng/mL*	*PFHS LOQ, ng/mL*	*PFOS LOQ, ng/mL*
4/13/12	10	0.250	0.250	NA
	50	1.25	1.25	NA
4/16/12	10	0.250	0.250	0.232
	50	1.25	1.25	1.16
	100	2.50	2.50	2.32
4/27/12	10	10.0	9.98	9.28
	50	50.0	49.9	46.4
	100	100	99.8	92.8
	250	250	250	232

NA = Not Applicable

8.4 Continuing Calibration

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

8.5 Blanks

Three types of blanks were prepared and analyzed with the samples: method procedural blanks, a trip blank, and an equipment rinseate blank. Method procedural blank results were reviewed and used to evaluate method performance and to determine the LOQ for PFBS, PFHS and PFOS. The trip blank reflects the shipping and sample collection conditions the sample bottles and samples experience. The equipment rinseate blank is an aqueous sample that reflect the efficiency of equipment cleaning in the field between different sample collections and are proof of no cross contamination of samples from the equipment.

8.6 Lab Control Spikes (LCSs)

Low, mid, and high lab control spikes were prepared for the target analytes and analyzed in triplicate. LCSs were prepared by spiking known amounts of the analyte into Milli-Q water to produce the desired concentration. The spiked water samples were then prepared and analyzed in the same manner as the samples. The method acceptance criteria, average of LCS at each level should be within 100% ± 20% with an RSD ≤20%, was met for all analytes except for the low level LCSs for PFOS analyzed on 4/16/12 which had an average recovery of 75.2%. All LCS samples were used in the determination of the analytical method uncertainty on section 8.7. A method deviation is included in Attachment D.

The following calculations were used to generate data in Table 7 for laboratory control spikes.

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

$$\text{LCS\% RSD} = \frac{\text{standard deviation LCS replicates}}{\text{average LCS recovery}} * 100\%$$

Table 7. Laboratory Control Spike Recovery.

ETS-8-044.1 Analyzed 4/13/12	*PFBS*			*PFHS*		
Lab ID	*Spiked Concentration (ng/mL)*	*Calculated Concentration (ng/mL)*	*%Recovery*	*Spiked Concentration (ng/mL)*	*Calculated Concentration (ng/mL)*	*%Recovery*
LCS-120411-1	0.498	0.479	96.2	0.497	0.472	95.0
LCS-120411-2	0.498	0.466	93.7	0.497	0.464	93.3
LCS-120411-3	0.498	0.476	95.6	0.497	0.469	94.3
Average ± %RSD	**95.2% ± 1.4%**			**94.2% ± 0.91%**		
LCS-120411-4	4.98	4.69	94.1	4.97	4.73	95.2
LCS-120411-5	4.98	4.77	95.8	4.97	4.76	95.7
LCS-120411-6	4.98	4.71	94.5	4.97	4.69	94.4
Average ± %RSD	**94.8% ± 0.94%**			**95.1% ± 0.69%**		
LCS-120411-7	29.9	NA (1)	NA (1)	29.9	NA (1)	NA (1)
LCS-120411-8	29.9	NA (1)	NA (1)	29.9	NA (1)	NA (1)
LCS-120411-9	29.9	NA (1)	NA (1)	29.9	NA (1)	NA (1)
Average ± %RSD	**NA**			**NA**		

NA = Not Applicable
(1) LCS spiked concentration exceeded the calibration range.
(2) LCS did not meet acceptance criteria of 100 ± 20%.

Table 7 continued. Laboratory Control Spike Recovery.

ETS-8-044.1 Analyzed 4/16/12	PFBS			PFHS		
Lab ID	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery
LCS-120411-1	0.498	0.505	101	0.497	0.489	98.3
LCS-120411-2	0.498	0.511	103	0.497	0.491	98.9
LCS-120411-3	0.498	0.500	100	0.497	0.493	99.1
Average ± %RSD	**101% ± 1.5%**			**98.8% ± 0.42%**		
LCS-120411-4	4.98	5.12	103	4.97	4.96	99.7
LCS-120411-5	4.98	5.19	104	4.97	4.79	96.4
LCS-120411-6	4.98	4.95	99.4	4.97	4.95	99.6
Average ± %RSD	**102% ± 2.4%**			**98.6% ± 1.9%**		
LCS-120411-7	29.9	29.3	98.0	29.9	27.0	90.3
LCS-120411-8	29.9	28.8	96.3	29.9	27.7	92.5
LCS-120411-9	29.9	29.0	97.0	29.9	28.3	94.8
Average ± %RSD	**97.1% ± 0.88%**			**92.5% ± 2.4%**		

ETS-8-044.1 Analyzed 4/16/12	PFOS (Linear and Branched)		
Lab ID	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery
LCS-120411-1	0.462	0.348	75.3
LCS-120411-2	0.462	0.351	75.9
LCS-120411-3	0.462	0.344	74.5
Average ± %RSD	**75.2% ± 0.93% (2)**		
LCS-120411-4	4.62	4.20	91.0
LCS-120411-5	4.62	4.17	90.3
LCS-120411-6	4.62	4.26	92.2
Average ± %RSD	**91.2% ± 1.1%**		
LCS-120411-7	27.8	26.5	95.2
LCS-120411-8	27.8	25.8	92.8
LCS-120411-9	27.8	26.8	96.3
Average ± %RSD	**94.8% ± 1.9%**		

NA = Not Applicable
(1) LCS spiked concentration exceeded the calibration range.
(2) LCS did not meet acceptance criteria of 100 ± 20%.

Table 7 continued. Laboratory Control Spike Recovery.

ETS-8-044.1 Analyzed 4/27/12	PFBS			PFHS		
Lab ID	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery
LCS-120426-1	4.98	4.95	99.5	4.97	4.85	97.6
LCS-120426-2	4.98	5.09	102	4.97	5.00	101
LCS-120426-3	4.98	5.30	107	4.97	5.12	103
Average ± %RSD	103% ± 3.7%			101% ± 2.7%		
LCS-120426-4	20.0	18.6	93.0	19.9	17.7	88.8
LCS-120426-5	20.0	18.5	92.6	19.9	18.5	93.1
LCS-120426-6	20.0	18.2	90.8	19.9	18.8	94.6
Average ± %RSD	92.1% ± 1.3%			92.2% ± 3.3%		
LCS-120426-7	49.8	50.4	101	49.7	49.1	98.8
LCS-120426-8	49.8	47.5	95.4	49.7	46.6	93.7
LCS-120426-9	49.8	47.1	94.6	49.7	47.0	94.6
Average ± %RSD	97.0% ± 3.6%			95.7% ± 2.8%		

ETS-8-044.1 Analyzed 4/27/12	PFOS (Linear and Branched)		
Lab ID	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery
LCS-120426-1	4.62	4.26	92.1
LCS-120426-2	4.62	4.02	87.0
LCS-120426-3	4.62	4.21	91.1
Average ± %RSD	90.1% ± 3.0%		
LCS-120426-4	18.5	15.7	85.0
LCS-120426-5	18.5	16.6	89.6
LCS-120426-6	18.5	16.8	90.6
Average ± %RSD	88.4% ± 3.4%		
LCS-120426-7	46.2	46.3	100
LCS-120426-8	46.2	43.8	94.9
LCS-120426-9	46.2	43.5	94.1
Average ± %RSD	96.3% ± 3.3%		

NA = Not Applicable
(1) LCS spiked concentration exceeded the calibration range.
(2) LCS did not meet acceptance criteria of 100 ± 20%.

8.7 Analytical Method Uncertainty

Analytical uncertainty is based on historical QC data that is control charted and used to evaluate method accuracy and precision. The method uncertainty is calculated following ETS-12-012.2. The standard deviation is calculated for the set of accuracy results (in %) obtained for the QC samples. The expanded uncertainty is calculated by multiplying the standard deviation by a factor of 2, which corresponds to a confidence level of 95%.

Table 8. Analytical Uncertainty.

Analyte	Standard Deviation	Method Uncertainty
PFBS	5.91	±12%
PFHS	5.88	±12%
PFOS	17.6	±35%

8.8 Field Matrix Spikes (FMS)

Low, mid, and high field matrix spikes (FMS) were collected at each sampling point to verify that the analytical method is applicable to the collected matrix. Field matrix spikes were generated by adding a measured volume of field sample to a container spiked by the laboratory with PFBS (linear), PFHS (linear), and PFOS (linear and branched) prior to shipping sample containers for sample collection. Field matrix spike recoveries within method acceptance criteria of 100±30% confirm that "unknown" components in the sample matrix do not significantly interfere with the extraction and analysis of the analytes of interest. Field matrix spike concentrations must be 50% of the sample concentration to be considered an appropriate field spike. Field matrix spikes are presented in section 9 of this report.

Table 9. Field Matrix Spike Levels.

Sampling Location	Spike Level	PFBS, ng/mL	PFHS, ng/mL	PFOS, ng/mL
All locations and Trip Blank	Low	10	9.98	9.98
	High	100	99.8	99.8

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

8.9 Lab Matrix Spikes (LMS)

Due to the high levels of PFBS, PFHS, and/or PFOS detected in sampling locations TW2, TW3, TW4, TW5, and TW6, the FMS spike levels were not appropriate for at least one of the analytes. Therefore, laboratory matrix spikes (LMS) samples were prepared to verify that the analytical method is applicable to the collected matrix. Laboratory matrix spikes were generated by adding a measured volume of PFBS, PFHS, and PFOS (reference standard containing both linear and branched isomers) to an aliquot of the primary sample. Since all samples required dilution prior to sample analysis, the laboratory matrix spike added was based on the on-column instrument concentration.

Sampling locationTW2; the primary sample (GLP10-01-02-31-005) was diluted 1:50, to which 20 ng/mL (nominal) of target analytes were added for a LMS concentration of approximately 1000 ng/mL.

Sampling location TW3; the primary sample (GLP10-01-02-31-009) was diluted 1:100, to which the low LMS had 20 ng/mL (nominal) of target analytes added for a LMS concentration of approximately 2000 ng/mL, and the high LMS had 50 ng/mL (nominal) of target analytes added for a LMS concentration of approximately 5000 ng/mL.

Sampling location TW4; the primary sample (GLP10-01-02-31-013) was diluted 1:10, to which 20 ng/mL (nominal) of target analytes were added for a LMS concentration of approximately 200 ng/mL.

Sampling location TW5; the primary sample (GLP10-01-02-31-017) was diluted 1:50, to which 10 ng/mL (nominal) of target analytes were added for a LMS concentration of approximately 500 ng/mL.

Sampling location TW6; the primary sample (GLP10-01-01-32-017) was diluted 1:10, to which 20 ng/mL (nominal) of target analytes were added for a LMS concentration of approximately 200 ng/mL.

Lab matrix spike recoveries within method acceptance criteria of 100±30% confirm that "unknown" components in the sample matrix do not significantly interfere with the extraction and analysis of the analytes of interest. Lab matrix spike concentrations must be 50% of the sample concentration to be considered an appropriate field spike. Lab matrix spikes are presented in section 9 of this report.

The following calculation was used to calculate the lab matrix spike recovery in Section 9 of the report:

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

9 *Data Summary and Discussion*

The tables below summarize the sample results and field or lab matrix spike recoveries for the sampling locations as well as the Trip Blank. Results and average values are rounded to three significant figures according to EPA rounding rules. Because of rounding, values may vary slightly from those listed in the raw data. Field matrix spike and lab matrix spike recoveries meeting the method acceptance criteria of ± 30%, demonstrate that the method was appropriate for the given matrix and their respective quantitative ranges.

DAL GW TW1R 120405; The recovery of the high field matix spike for PFOS was 65.8%. Since the analytical method uncertainty was calculated at ± 35% for PFOS, no further adjustment to the analytical uncertainty is needed for DAL GW TW1R.

Table 10. DAL GW TW1R 120405

		PFBS		PFHS		PFOS	
3M LIMS ID	*Description*	*Concentration (ng/mL)*	*%Recovery*	*Concentration (ng/mL)*	*%Recovery*	*Concentration (ng/mL)*	*%Recovery*
GLP10-01-02-31-001	DAL-GW-TW1R-0-120405	33.8	NA	56.7	NA	27.7	NA
GLP10-01-02-31-002	DAL-GW-TW1R-DB-120405	33.7	NA	57.9	NA	30.3	NA
GLP10-01-02-31-003	DAL-GW-TW1R-LS-120405	42.8	NC	63.3	NC	35.4	NC
GLP10-01-02-31-004	DAL-GW-TW1R-HS-120405	120	86.3	147	89.9	94.7	65.8 (1)
Average Concentration (ng/mL) ± %RPD		*33.8 ng/mL ± 0.30%*		*57.3 ng/mL ± 2.1*		*29.0 ng/mL ± 9.0%*	

NA = Not Applicable
NC = Not Calculated; the sample concentration is greater than 2x the spike level.
Samples analyzed using a 1:10 dilution factor
PFBS and PFHS reported from 4/13/12 analysis. PFOS results reported from 4/16/12 analysis.
(1) FMS recovery did not meet acceptance criteria.

Table 11. DAL GW TW2R 120405

		PFBS		PFHS		PFOS	
3M LIMS ID	*Description*	*Concentration (ng/mL)*	*%Recovery*	*Concentration (ng/mL)*	*%Recovery*	*Concentration (ng/mL)*	*%Recovery*
GLP10-01-02-31-005	DAL-GW-TW2R-0-120405	120	NA	563	NA	995	NA
GLP10-01-02-31-006	DAL-GW-TW2R-DB-120405	114	NA	595	NA	1180	NA
GLP10-01-02-31-007	DAL-GW-TW2R-LS-120405	125	NC	NA (1)	NA (1)	NA (1)	NA (1)
GLP10-01-02-31-008	DAL-GW-TW2R-HS-120405	217	100	NA (1)	NA (1)	NA (1)	NA (1)
GLP10-01-02-31-005; 1000ppb LMS	DAL-GW-TW2R-0-LMS	NA (1)	NA (1)	1520	94.5	2020	101
Average Concentration (ng/mL) ± %RPD		*117 ng/mL ± 5.1%*		*579 ng/mL ± 5.5%*		*1090 ng/mL ± 17%*	

NA = Not Applicable
NC = Not Calculated; the sample concentration is greater than 2x the spike level.
Samples analyzed on 4/13/12 for PFBS using a 1:10 dilution factor), and on 4/27/12 for PFHS and PFOS using a 1:50 dilution factor.
(1) Sample not analyzed for this analyte due to inappropriate spike level.

Table 12. DAL GW TW3R 120405

		PFBS		PFHS		PFOS	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
GLP10-01-02-31-009	DAL-GW-TW3R-0-120405	292	NA	1210	NA	3340	NA
GLP10-01-02-31-010	DAL-GW-TW3R-DB-120405	315	NA	1410	NA	3970	NA
GLP10-01-02-31-011	DAL-GW-TW3R-LS-120405	NA (1)	NA (1)	NA (1)	NA (1)	NA (1)	NA (1)
GLP10-01-02-31-012	DAL-GW-TW3R-HS-120405	NA (1)	NA (1)	NA (1)	NA (1)	NA (1)	NA (1)
GLP10-01-02-31-009; 2000ppb LMS	DAL-GW-TW3R-0-LMS	2280	98.8	3160	93.0	5240	85.7
GLP10-01-02-31-009; 5000ppb LMS	DAL-GW-TW3R-0-LMS	4960	93.5	5940	93.2	8480	104
Average Concentration (ng/mL) ± %RPD		*304 ng/mL ± 7.6%*		*1310 ng/mL ± 15%*		*3660 ng/mL ± 17%*	

NA = Not Applicable
Samples analyzed on 4/27/12 using a 1:100 dilution factor; 5000ppb LMS analyzed using a 1:250 dilution factor.
(1) Sample not analyzed for this analyte due to inappropriate spike level.

Table 13. DAL GW TW4R 120405

		PFBS		PFHS		PFOS	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
GLP10-01-02-31-013	DAL-GW-TW4R-0-120405	179	NA	19.0	NA	244	NA
GLP10-01-02-31-014	DAL-GW-TW4R-DB-120405	188	NA	19.2	NA	250	NA
GLP10-01-02-31-015	DAL-GW-TW4R-LS-120405	NA (1)	NA (1)	28.2	91.2	NA (1)	NA (1)
GLP10-01-02-31-016	DAL-GW-TW4R-HS-120405	278	94.5	102	83.1	NA (1)	NA (1)
GLP10-01-02-31-013; 200ppb LMS	DAL-GW-TW4R-0-LMS	NA (1)	NA (1)	NA (1)	NA (1)	450	110
Average Concentration (ng/mL) ± %RPD		*184 ng/mL ± 4.9%*		*19.1 ng/mL ± 1.0%*		*247 ng/mL ± 2.4%*	

NA = Not Applicable
Samples analyzed on 4/16/12 for PFBS using a 1:50 dilution factor and on 4/27/12 for PFHS and PFOS using a 1:10 dilution factor.
(1) Sample not analyzed for this analyte due to inappropriate spike level.

Table 14. DAL GW TW5R 120405

		PFBS		PFHS		PFOS	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
GLP10-01-02-31-017	DAL-GW-TW5R-0-120405	533	NA	43.3	NA	704	NA
GLP10-01-02-31-018	DAL-GW-TW5R-DB-120405	510	NA	42.6	NA	688	NA
GLP10-01-02-31-019	DAL-GW-TW5R-LS-120405	NA (1)	NA (1)	51.1	NC	NA (1)	NA (1)
GLP10-01-02-31-020	DAL-GW-TW5R-HS-120405	NA (1)	NA (1)	136	93.2	NA (1)	NA (1)
GLP10-01-02-31-017; 500ppb LMS	DAL-GW-TW5R-0-LMS	988	93.3	NA (1)	NA (1)	696	91.4
Average Concentration (ng/mL) ± %RPD		522 ng/mL ± 4.4%		43.0 ng/mL ± 1.6%		696 ng/mL ± 2.3%	

NA = Not Applicable
NC = Not Calculated; the sample concentration is greater than 2x the spike level.
Samples analyzed on 4/27/12 for PFBS and PFOS using a 1:50 dilution factor and on 4/13/12 for PFHS using a 1:10 dilution factor.
(1) Sample not analyzed for this analyte due to inappropriate spike level.

Table 15. DAL GW TW6R 120405

		PFBS (1)		PFHS (2)		PFOS (1)	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
GLP10-01-02-31-021	DAL-GW-TW6R-0-120405	156	NA	48.0	NA	287	NA
GLP10-01-02-31-022	DAL-GW-TW6R-DB-120405	155	NA	45.4	NA	274	NA
GLP10-01-02-31-023	DAL-GW-TW6R-LS-120405	NA (1)	NA (1)	54.6	NC	NA (1)	NA (1)
GLP10-01-02-31-024	DAL-GW-TW6R-HS-120405	238	82.5	131	84.5	NA (1)	NA (1)
GLP10-01-02-31-021; 200ppb LMS	DAL-GW-TW6R-0-LMS	NA (1)	NA (1)	NA (1)	NA (1)	456	94.9
Average Concentration (ng/mL) ± %RPD		156 ng/mL ± 0.64%		46.7 ng/mL ± 5.6%		281 ng/mL ± 4.6%	

NA = Not Applicable
NC = Not Calculated; the sample concentration is greater than 2x the spike level.
Samples analyzed on 4/27/12 for PFBS and PFOS using a 1:50 dilution factor and on 4/13/12 for PFHS using a 1:10 dilution factor.
(1) Sample not analyzed for this analyte due to inappropriate spike level.

Table 16. DAL GW TRIP01 120405

		PFBS		PFHS		PFOS	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
GLP10-01-02-31-026	DAL-GW-TRIP01-0-120405	<0.250	NA	<0.250	NA	<0.232	NA
GLP10-01-02-31-027	DAL-GW-TRIP01-LS-120405	8.51	85.1	8.60	86.2	6.96	69.7
GLP10-01-02-31-028	DAL-GW-TRIP01-HS-120405	92.0	92.0	88.4	88.6	70.1	70.2

NA = Not Applicable
Samples analyzed for PFBS and PFHS on 4/13/12 and on 4/16/12 for PFOS using a 1:10 dilution factor.

Table 17. Rinseate Blank

		PFBS	PFHS	PFOS
3M LIMS ID	Description	Concentration (ng/mL)	Concentration (ng/mL)	Concentration (ng/mL)
GLP10-01-02-31-028	DAL-GW-TW3R-RB-120405	<0.250	<0.250	<0.232

Samples analyzed for PFBS and PFHS on 4/13/12 and on 4/16/12 for PFOS using a 1:10 dilution factor.

10 Conclusion

Laboratory control spikes, field matrix spikes, and lab matrix spikes were used to determine the analytical method accuracy and precision for PFBS, PFHS, and PFOS. Analysis was successfully completed following 3M Environmental Laboratory method ETS-8-044.1 described herein.

11 Data/Sample Retention

All remaining samples and associated project data (hardcopy and electronic) will be archived according to 3M Environmental Laboratory standard operating procedures.

12 Attachments

Attachment A: Protocol Amendment 31 (General Project Outline)
Attachment B: Representative Chromatograms and Calibration Curves
Attachment C: Analytical Method-ETS-8-044.1
Attachment D: Method Deviation

13 Signatures

5/10/2012

Cleston Lange, Ph.D., 3M Principal Analytical Investigator — Date

11 MAY 2012

William K. Reagen, Ph.D., 3M Environmental Laboratory Department Manager — Date

5/17/12

Gary Hohenstein, Sponsor Representative — Date

5/25/12

Jaisimha Kesari, Study Director — Date

ATTACHMENT A: PROTOCOL AMENDMENT

Study Title

Analysis of Perfluorooctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane sulfonate (PFBS) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program

PROTOCOL AMENDMENT NO. 31

Amendment Date:
March 28, 2012

Performing Laboratory
3M Environmental, Health, and Safety Operations
3M Environmental Laboratory
Building 260-5N-17
Maplewood, MN 55144-1000

Laboratory Project Identification
GLP10-01-02

Sampling Event

New On-Site Wells - Adjacent to 3M Decatur WWTP

This amendment modifies the following portion of protocol:

"Analysis of PFOS, PFHS and PFBS in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program"

PROTOCOL READS:

No changes to the wording of the protocol are required.

AMEND TO READ:

No changes to the wording of the protocol are required. This amendment only addresses and documents the addition of the General Project Outline (GPO) for the collection and analysis of groundwater samples as part of the 3M Decatur Phase 3 Program for PFOS, PFHS and PFBS (GLP10-01-02). The anticipated sample collection will occur around the timeframe of the week of April 2, 2012. The groundwater samples for this sampling event will be entered into the 3M Environmental Laboratory LIMS as project GLP10-01-02-31 and reported as interim report GLP10-01-02-31, (reflecting study GLP10-01-02 and amendment - 31).

Reason:

The reason for this amendment is to document the General Project Outline (GPO) which describes the anticipate groundwater sample collection event for six new on-site temporary residuum monitoring wells in the vicinity of the Wastewater Treatment Plant (WWTP) at the 3M Decatur facility.

The GPO is three pages in length and included as attached to this amendment form.

Amendment Approval

Gary Hohenstein, Sponsor Representative — Date: 4/5/12

Cleston C. Lange, Principal Analytical Investigator — Date: 3/29/2012

William Reagen, EHS Opns Environmental Lab Management — Date: 2 APRIL 2012

Jaisimha Kesari P.E., DEE, Study Director — Date: 4/12/12

3M Environmental Health & Safety Operations, Environmental Laboratory

General Project Outline

To: Gary Hohenstein, 3M EHS&Opns

From: Susan Wolf, 3M EHS&Opns; Environmental Lab

cc: William Reagen, 3M EHS&Opns; Environmental Lab

Cleston Lange, 3M EHS&Opns; Environmental Lab

Jai Kesari, Weston Solutions

Date: March 22, 2012

Subject: Analysis of Perfluorooctane Sulfonate (PFOS), Perfluorohexane Sulfonate (PFHS) and Perfluorobutane sulfonate (PFBS) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program; GLP Interim Report 31; New On-Site Wells – Adjacent to the 3M Decatur Wastewater Treatment Plant (WWTP)

1 General Project Information

Contacts	**3M Sponsor Representative** Gary Hohenstein 3M EHS Operations 3M Building 224-5W-03 Saint Paul, MN 55144-1000 Phone: (651) 737-3570 gahohenstein@mmm.com **3M Environmental Laboratory Management** William K. Reagen 3M EHS Opns, Environmental Laboratory 260-5N-17 651 733-9739 wkreagen@mmm.com **Principal Analytical Investigator** Cleston Lange 3M EHS Opns, Environmental Laboratory 260-5N-17 651 733-9860 cclange@mmm.com **Sampling Coordinator** Timothy Frinak Weston Solutions Timothy.frinak@westonsolutions.com Phone: (334)-332-9123
Lab Request Number	**GLP10-01-02-31**
Six Digit Department Number	Dept #530711, Project #0022674449
Project Schedule/Test Dates	Sampling scheduled for the week of April 2, 2012

All verbal and written correspondence will be directed to Gary Hohenstein.

2 Background Information and Project Objective(s)

The 3M EHS Operations Laboratory (3M Environmental Lab) will receive and analyze groundwater samples collected from six new temporary on-site residuum monitoring wells located adjacent to the 3M Decatur WWTP for Perfluorobutanesulfonate (PFBS), Perfluorohexanesulfonate (PFHS), and Perfluorooctanesulfonate (PFOS). Analyses will be conducted under the GLP requirements of EPA TSCA Good Laboratory Practice Standards 40 CFR 792.

Groundwater samples will be collected by Weston Solutions personnel the week of April 2, 2012. The 3M Environmental Laboratory will prepare the sample bottles with all required spikes to ensure that results for PFBS, PFHS, and PFOS are of a known precision and accuracy. The final report will be submitted to Gary Hohenstein and Jai Kesari upon completion under interim report GLP10-01-02-31.

3 Project Schedule

Sample collection bottles will be prepared by 3M Environmental Laboratory for sampling the week of April 2, 2012. Sample bottles will be shipped in coolers overnight to 3M Decatur for arrival on Friday, March 30, 2012. Sample bottles should be stored refrigerated on-site until sample collection.

Martin Smith \ Weston Trailer
3M Decatur Plant
1400 State Docks Road
Decatur, Alabama 35601

4 Test Parameters

The targeted limit of quantitation will be **0.025 ng/mL** (ppb) for PFBS, PFHS, and PFOS.

Six sampling locations have been specified; TW1R, TW2R, TW3R, TW4R, TW5R, and TW6R. These are new wells with no historical sampling values for estimating field matrix spike levels, however, information received from Weston indicates that locations TW3R, TW4R and potentially TW5R, are expected to have higher concentrations based on the expected groundwater gradients in the area of these wells and field observations. Given the limited information on expected levels, at each sampling location, a total of four sample bottles will be collected (sample, sample duplicate low field matrix spike and high field matrix spike). The low field matrix spike will be prepared at 10 ng/mL and the high field matrix spike will be prepared at 100 ng/mL. The "fill to here" line on each 250 mL Nalgene bottle will be 200 mL. One set of trip blanks consisting of reagent-grade water as well as a low and high trip blank spike will be prepared at the 3M Environmental Laboratory and sent to the sampling location with the other bottles. All sample bottles will include the addition of $^{18}O_2$-PFBS, $^{18}O_2$-PFHS, and $^{13}C_8$-PFOS (internal standard) at a nominal concentration of 1 ng/mL. All sample bottles will also include the addition of $^{13}C_4$-PFOS (surrogate spike) at a nominal concentration of 0.1 ng/mL. One additional bottle will be prepared to be used for the preparation of the equipment rinseate blank. A 500-mL bottle of laboratory reagent water will be sent with the sample bottles to be used to generate the rinseate blank sample.

5 Test Methods

Samples will be prepared and analyzed by LC/MS/MS following ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds In Water by LC/MS/MS; Direct Injection Analysis".

The data quality objectives for these studies are quantitative results for the target analytes with an analytical accuracy of 100±30%. Field matrix spikes not yielding recoveries within 100±30% will be addressed in the report and the final accuracy statement may be adjusted accordingly.

Where applicable, samples will be analyzed against an internal standard calibration curve. Each curve point will contain isotopically-labeled perfluorocarboxylic acids and perfluorosulfonic acids at a nominal concentration of 1

ng/mL. The calibration curve will be generated by taking the ratio of the standard peak area counts over the internal standard peak area counts to fit the data for each analyte.

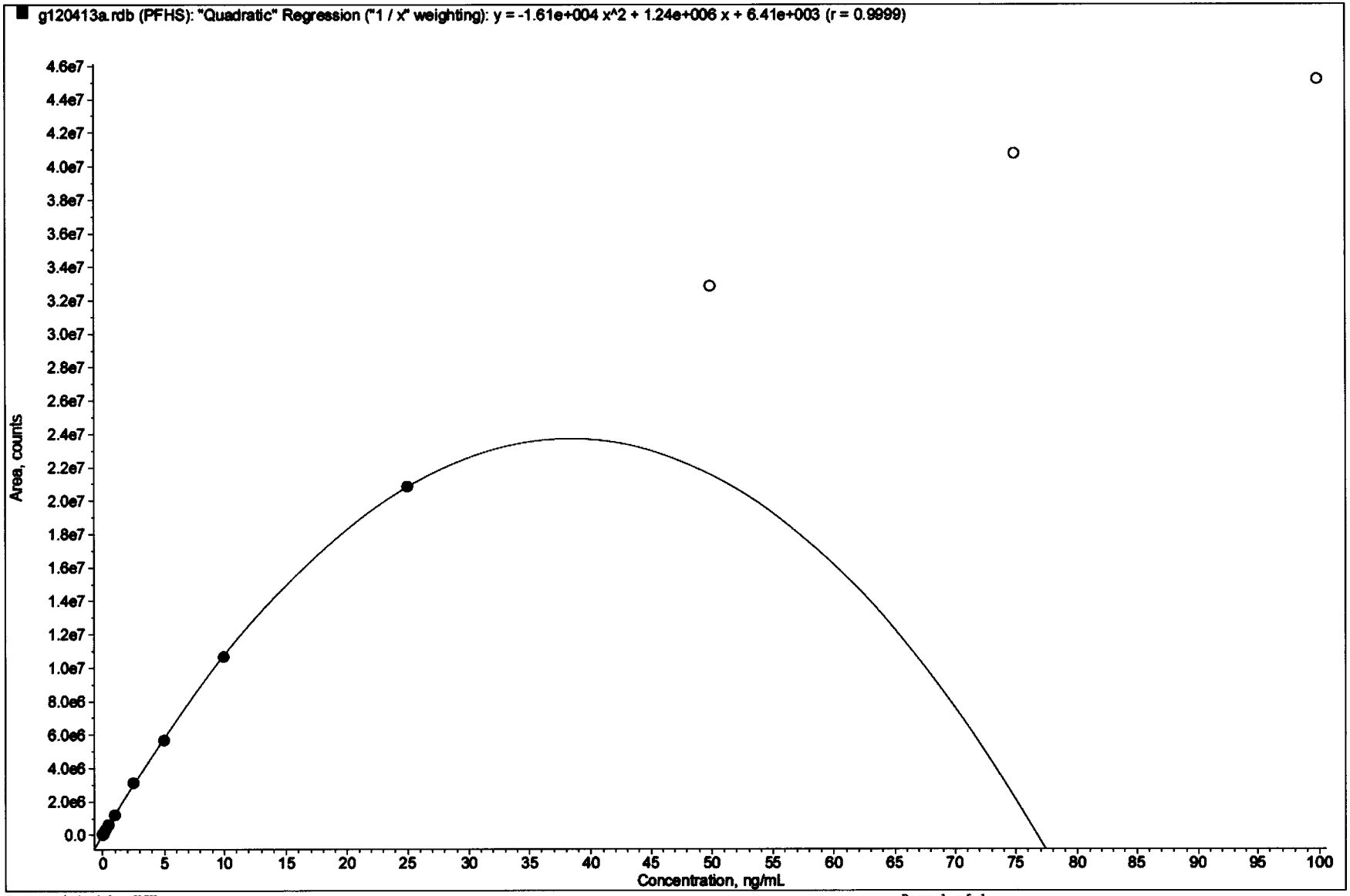
6 Reporting Requirements

For each sampling location, the report will contain the results for the sample, sample duplicate, and field matrix spike. Trip blank and trip blank spike will be reported for the sampling event as will any equipment/rinseate blanks prepared in the field. Laboratory control spikes of reagent water prepared at the time of sample extraction will also be reported and used to evaluate the overall method accuracy and precision. Method blanks of reagent water prepared at the time of sample extraction will be used to determine the method detection limit.

ATTACHMENT B: REPRESENTATIVE SAMPLE CHROMATOGRAMS AND CALIBRATION CURVE(S)

*** Ginger AG01330509

Results Name: g120413a.rdb

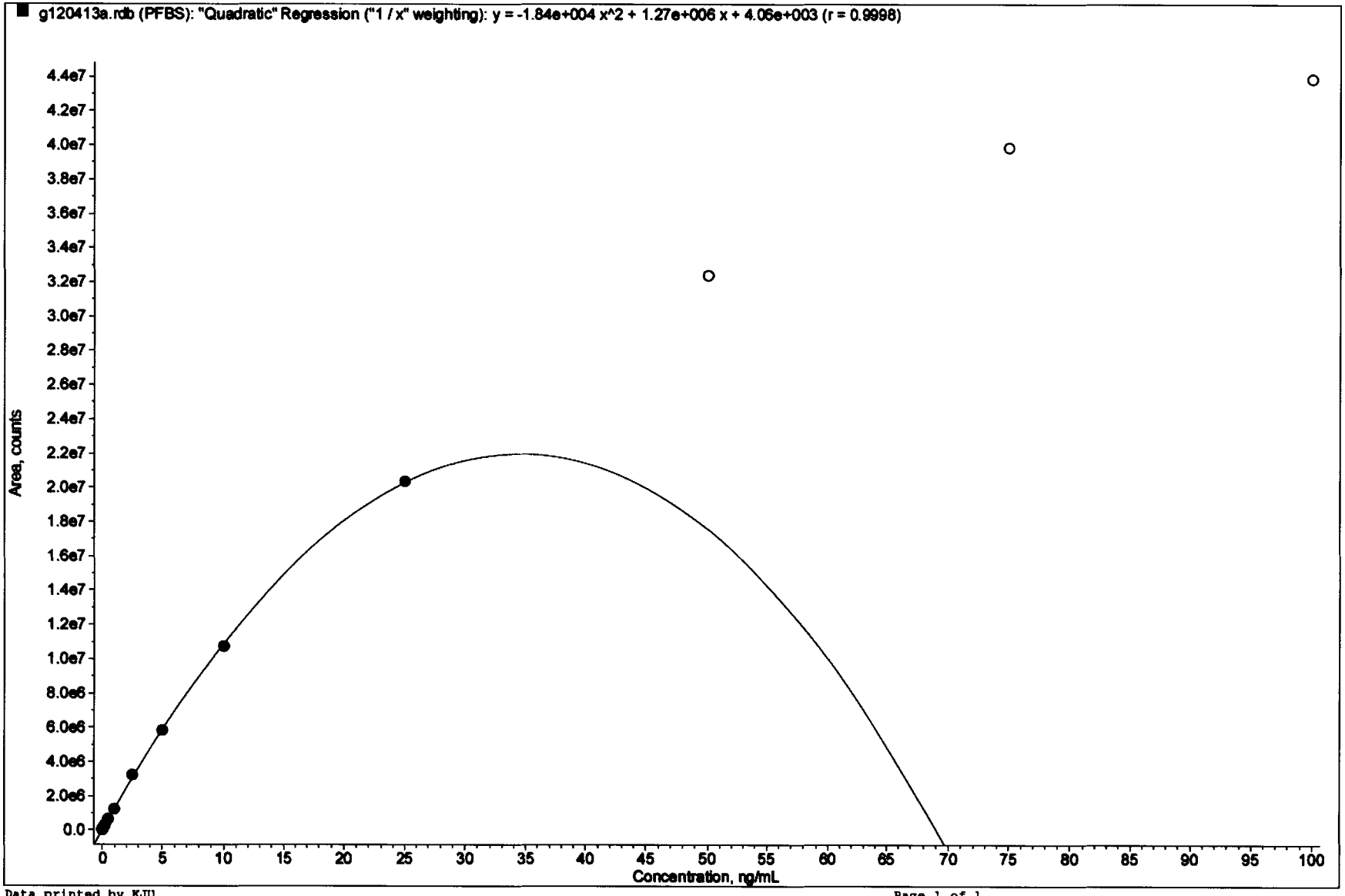


Data printed by KJU
Printing Time: 4:46:58 PM
Printing Date: Monday, April 16, 2012

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*** Ginger AG01330509

Results Name: g120413a.rdb

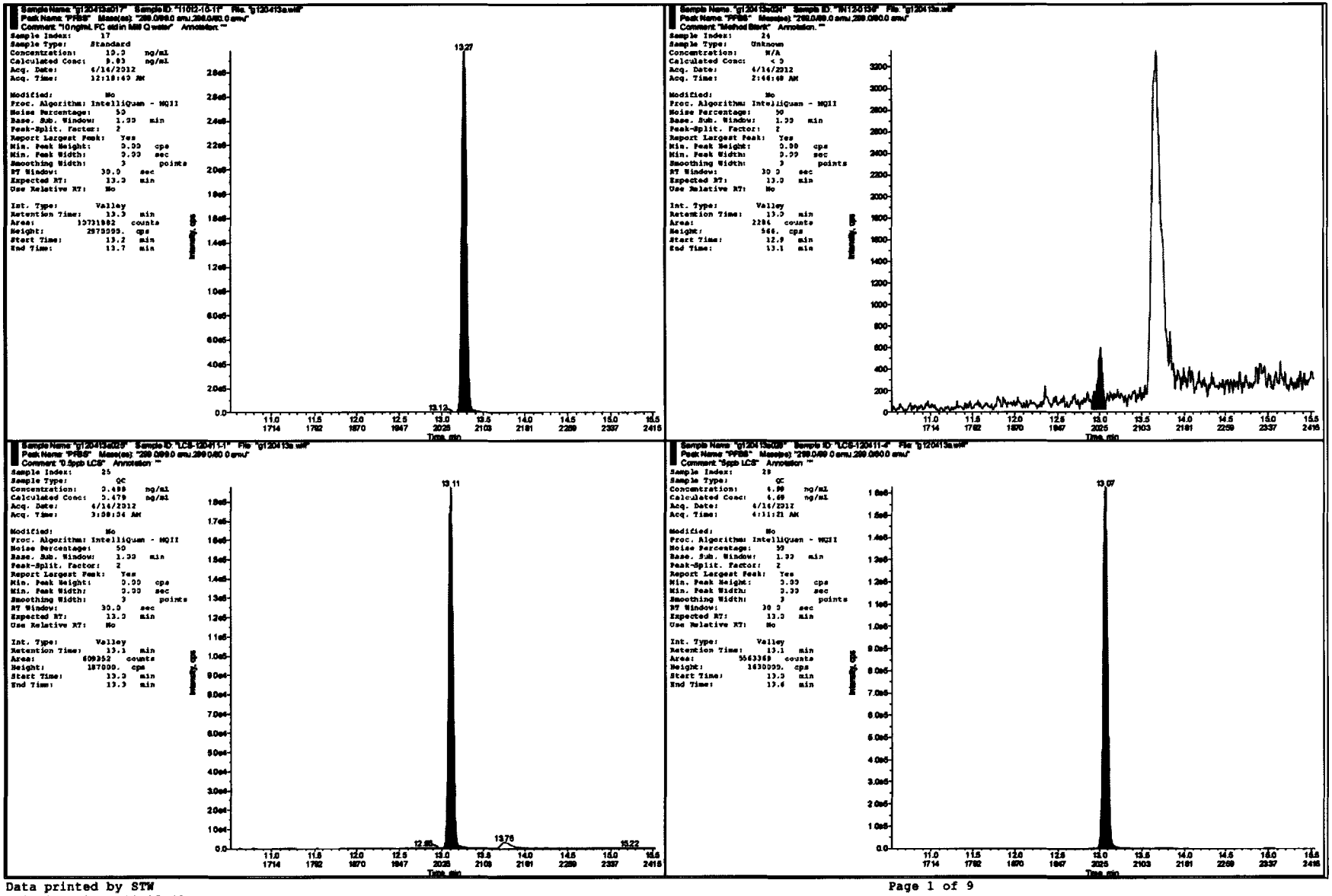


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Page 1 of 1

*** Ginger AG01330509

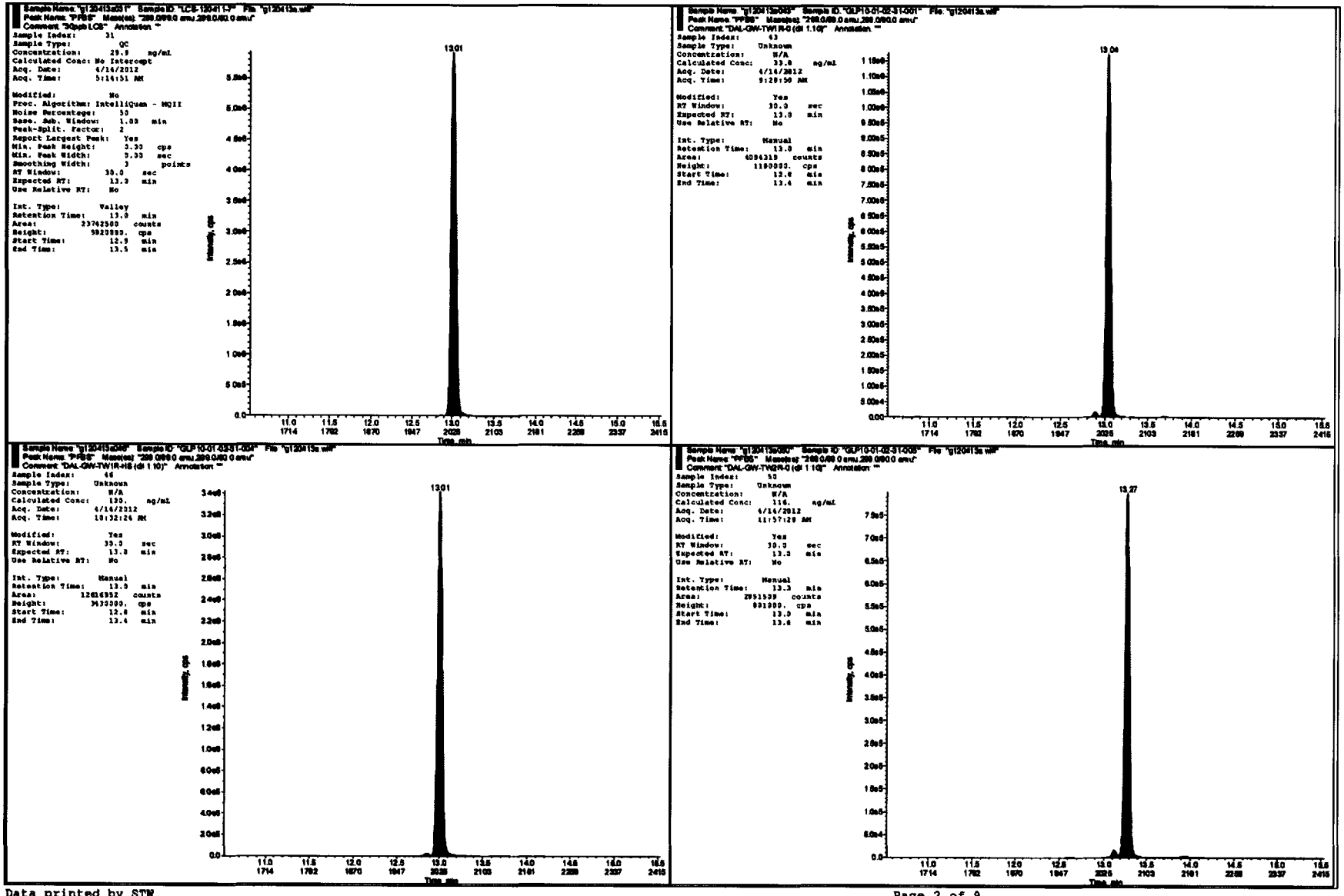
Results Name: g120413a.rdb



Data printed by STW
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Printing Date: Wednesday, May 09, 2012

*** Ginger AG01330509

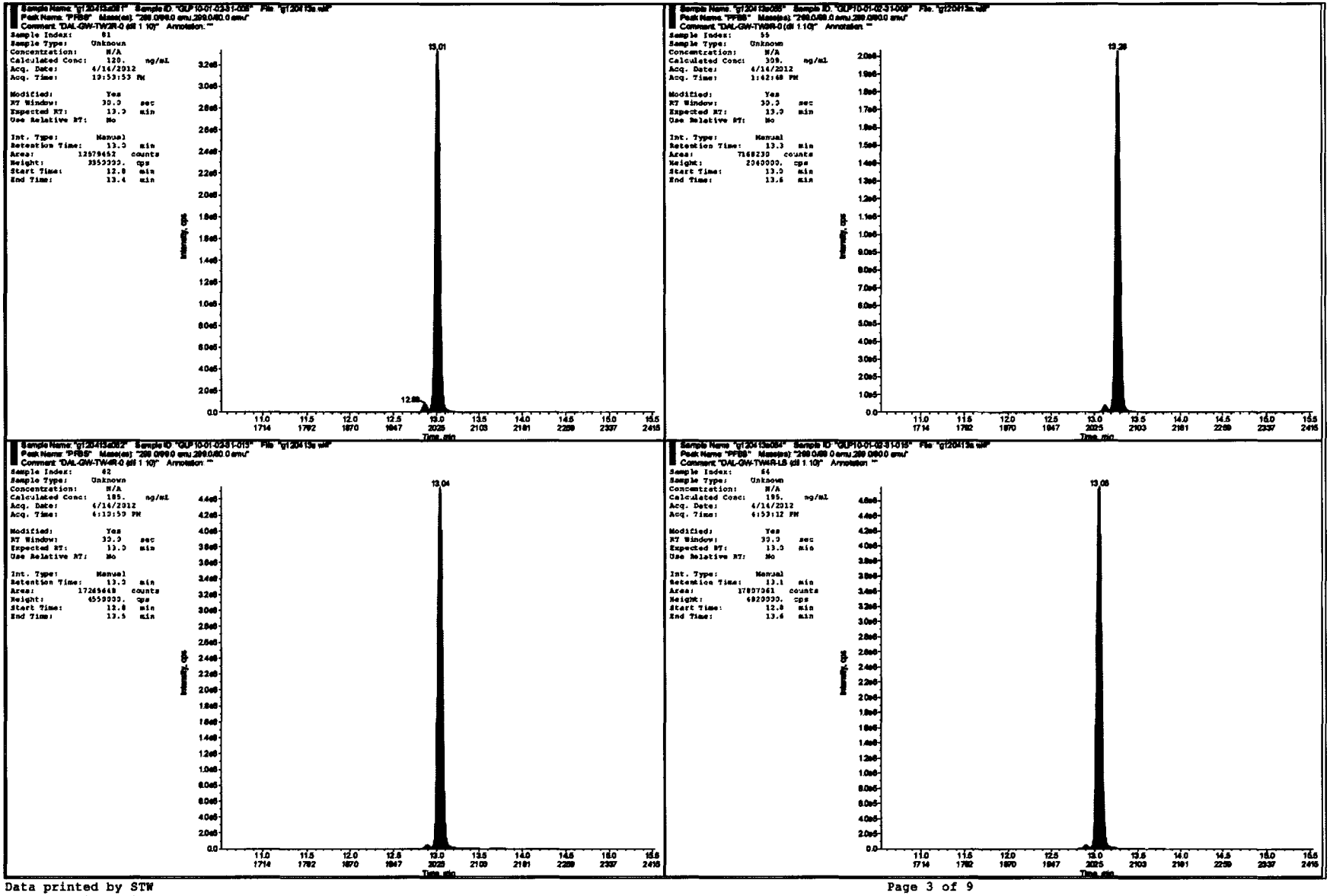
Results Name: g120413a.rdb



Data printed by STW
Printing Time: 11:15:42 AM
Printing Date: Wednesday, May 09, 2012

*** Ginger AG01330509

Results Name: g120413a.rdb

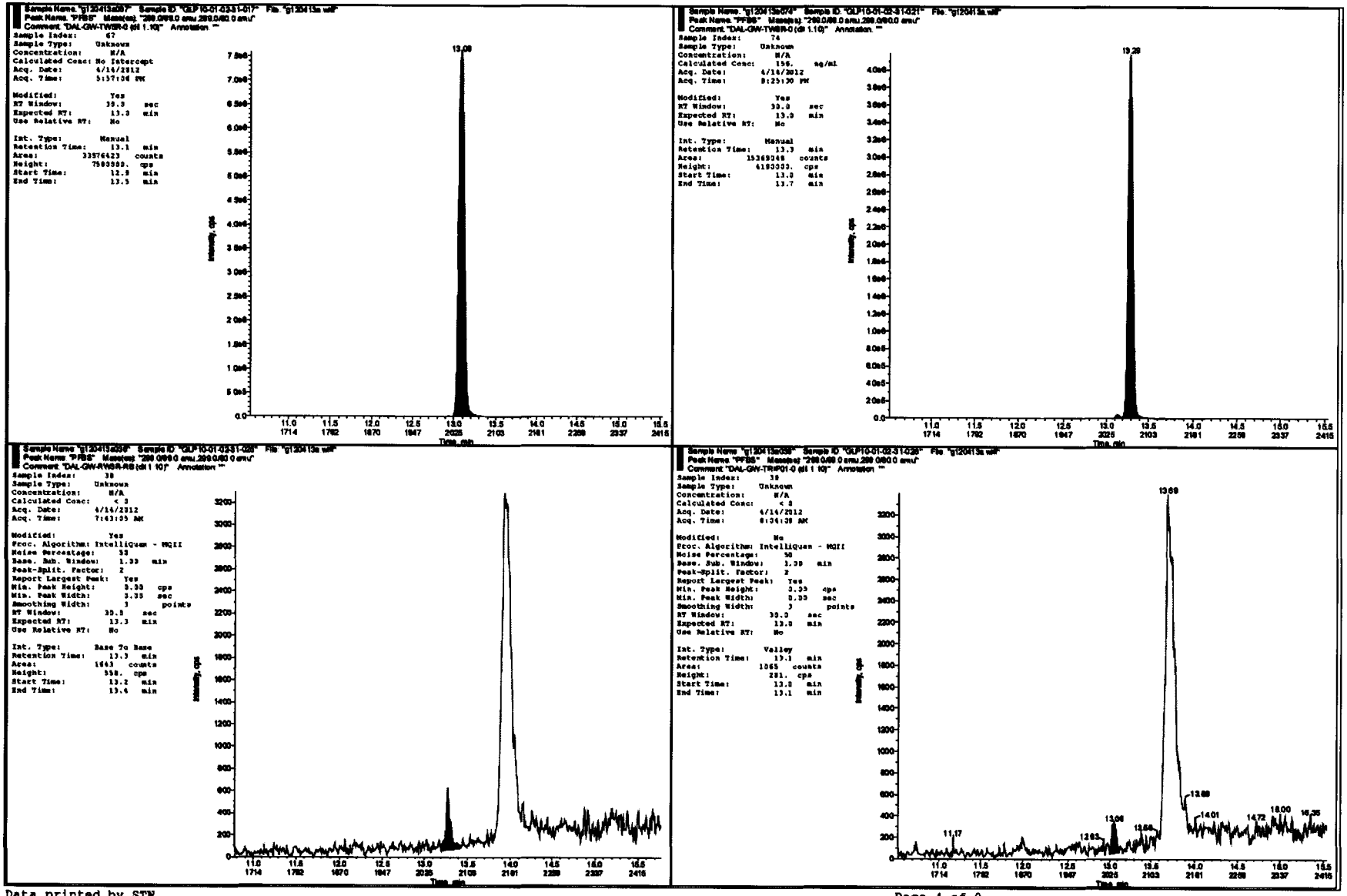


Data printed by STW
Printing Time: 11:15:43 AM
Printing Date: Wednesday, May 09, 2012

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*** Ginger AG01330509

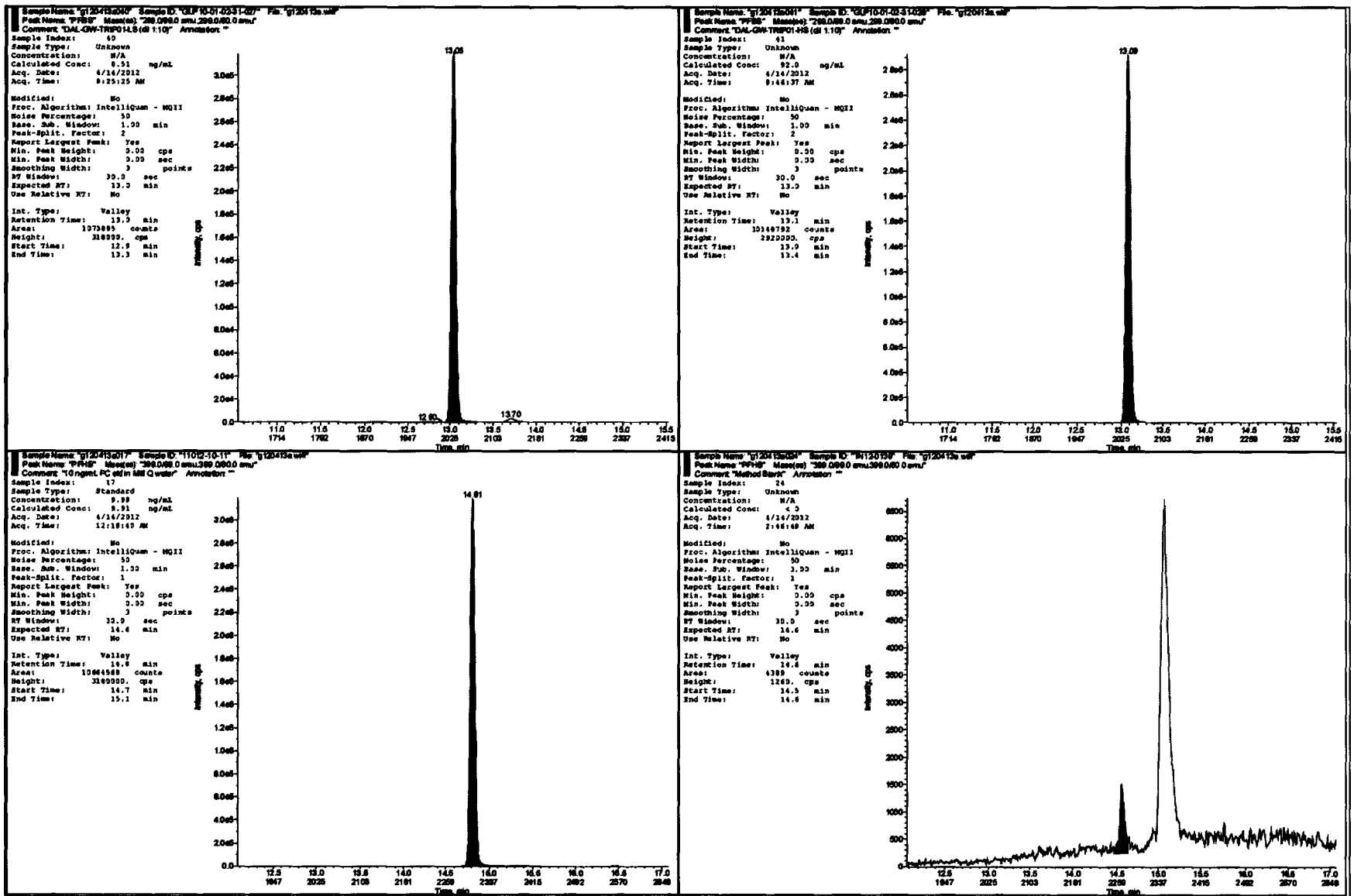
Results Name: g120413a.rdb



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Printing Date: Wednesday, May 09, 2012

*** Ginger AG01330509

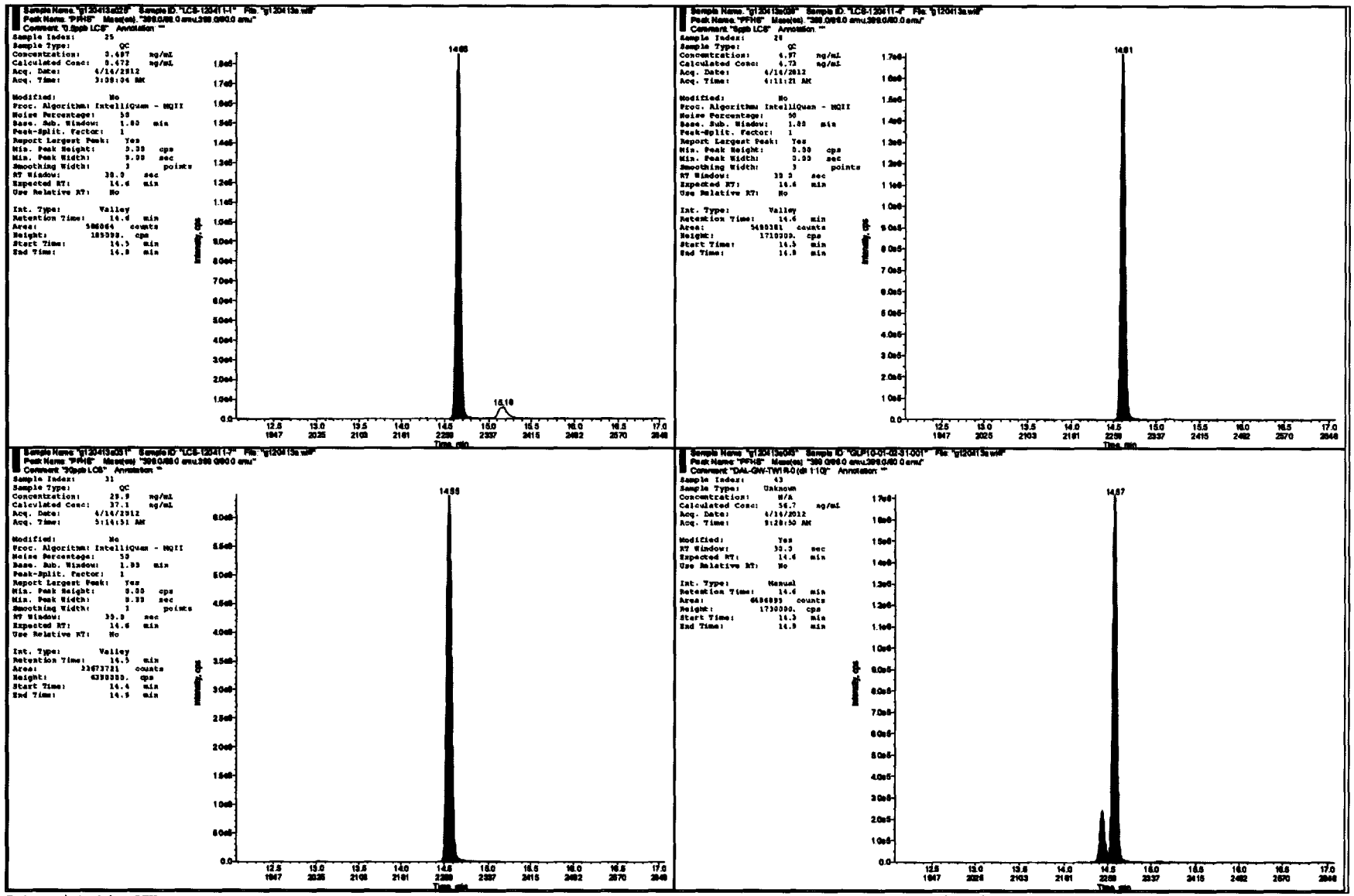
Results Name: g120413a.rdb



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Printing Date: Wednesday, May 09, 2012

*** Ginger AG01330509

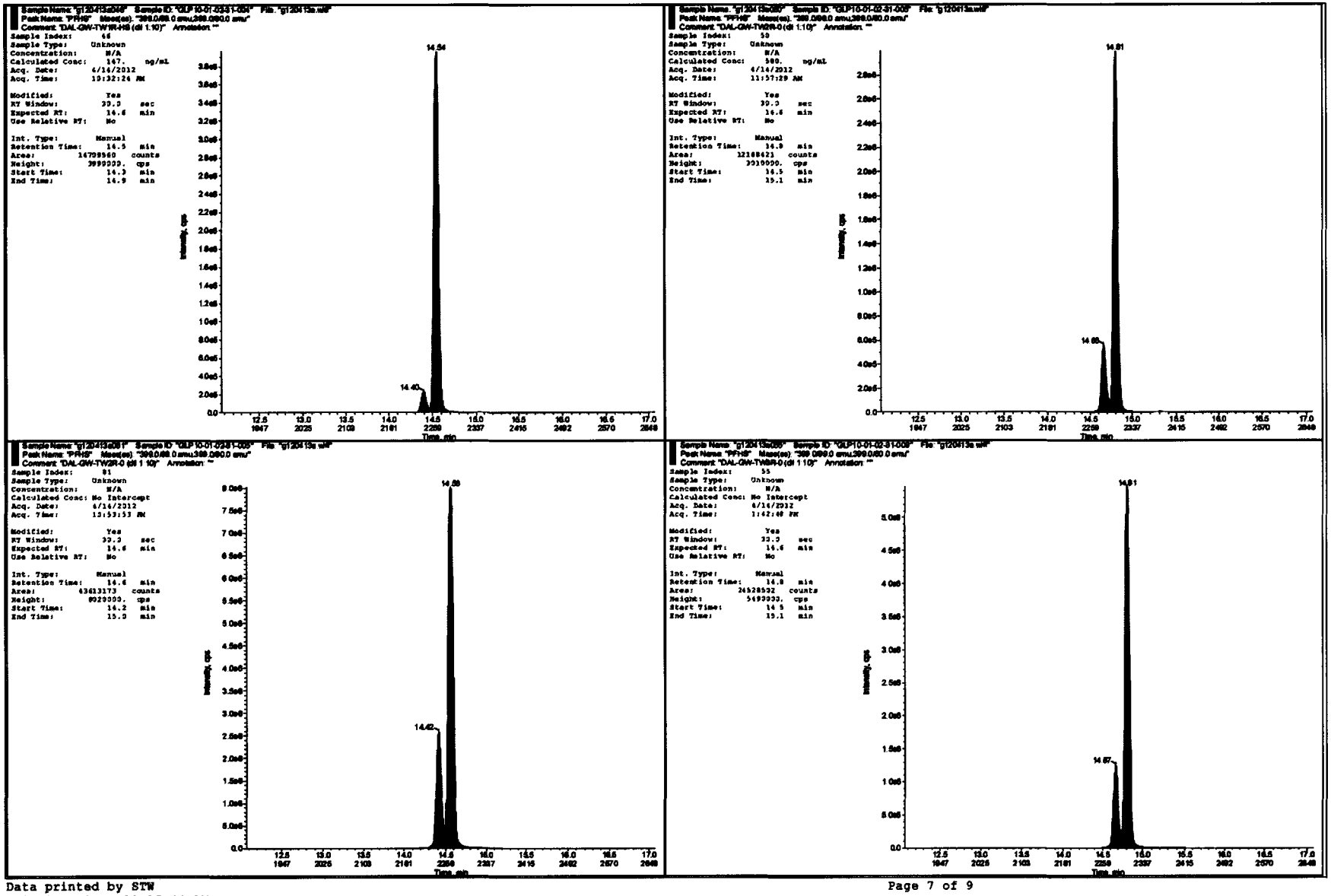
Results Name: g120413a.rdb



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Printing Time: 11:15:43 AM
Printing Date: Wednesday, May 09, 2012

*** Ginger AG01330509

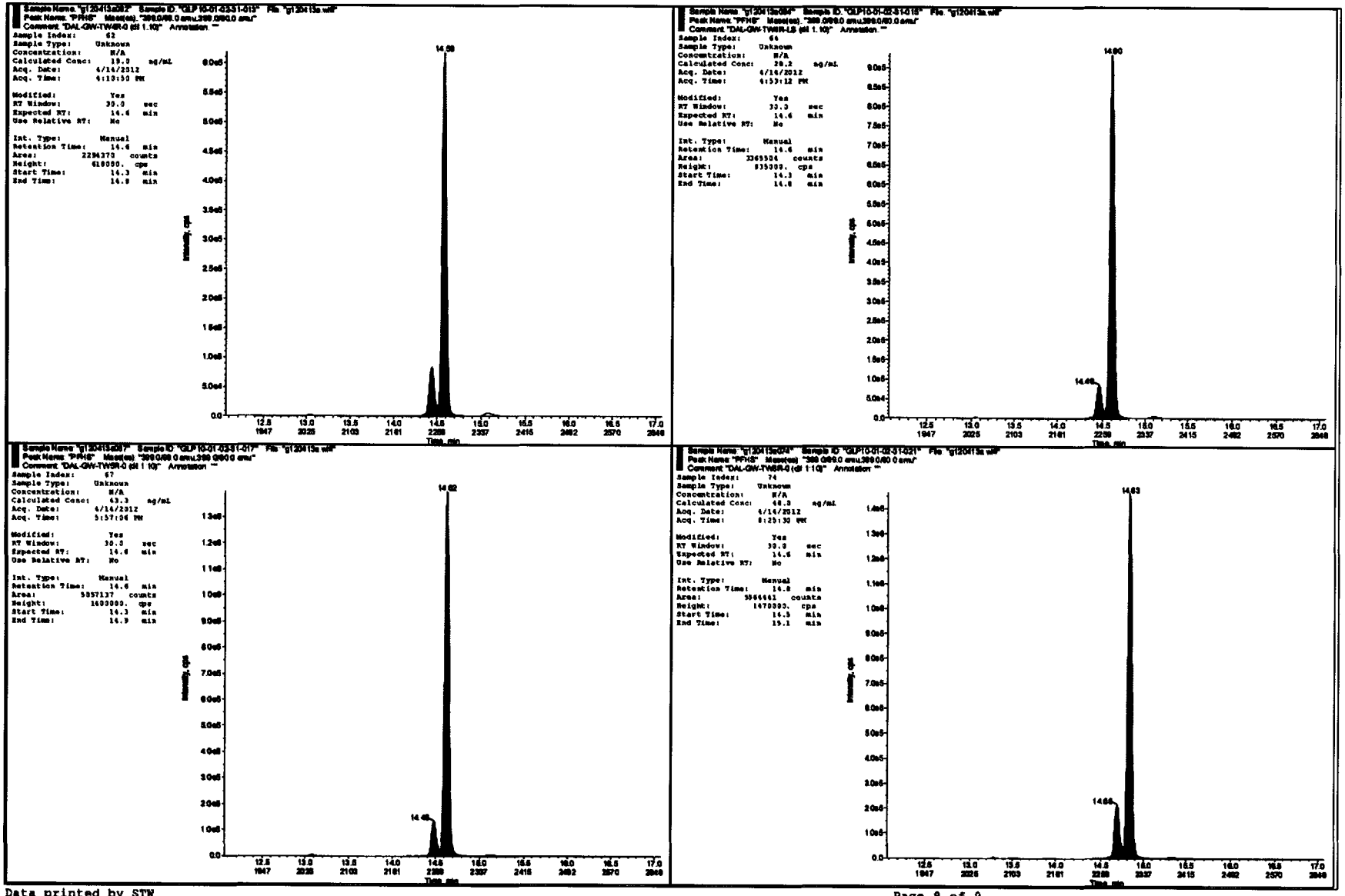
Results Name: g120413a.rdb



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*** Ginger AG01330509

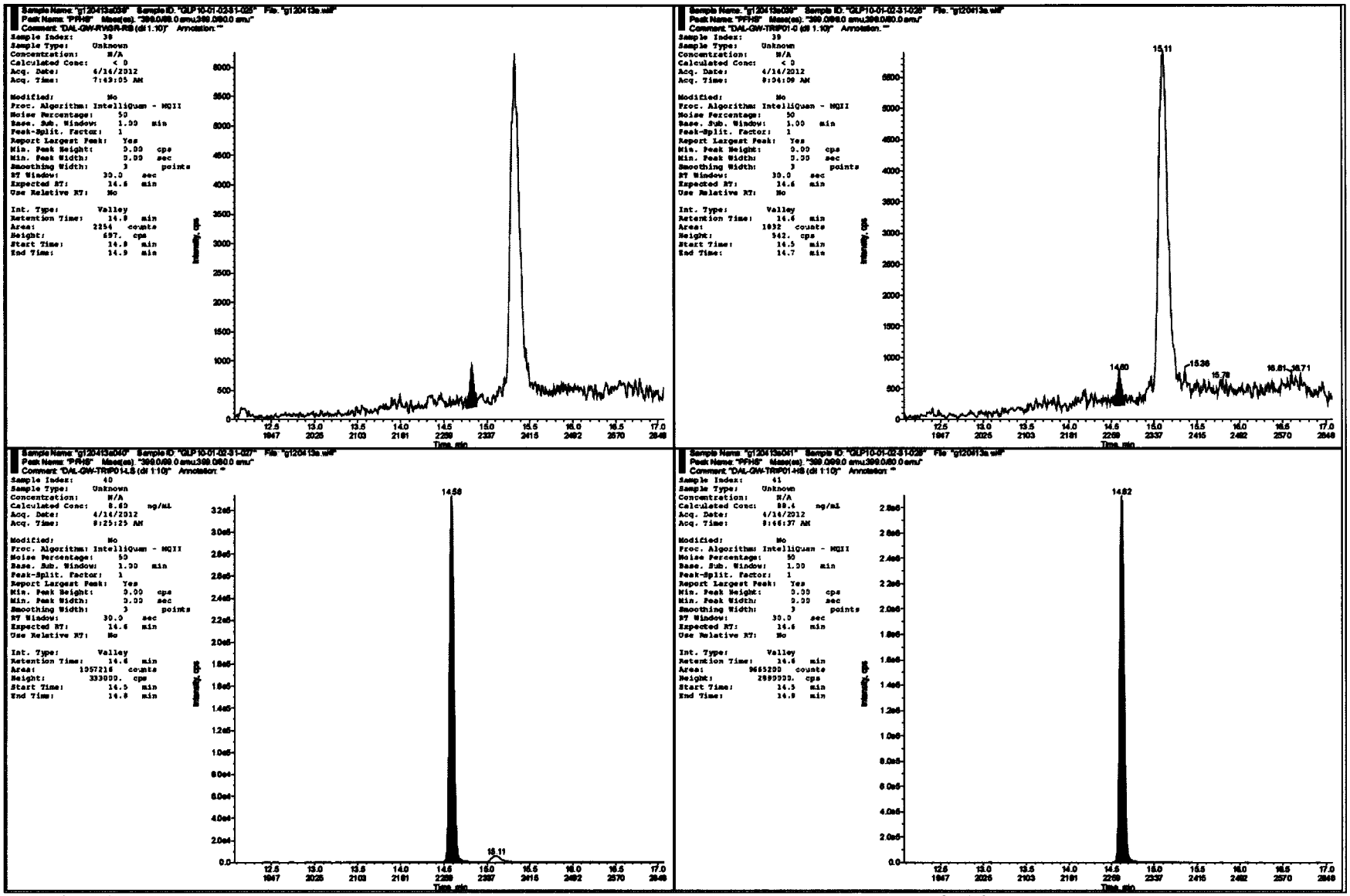
Results Name: g120413a.rdb



Data printed by STW
Printing Time: 11:15:44 AM
Printing Date: Wednesday, May 09, 2012

*** Ginger AG01330509

Results Name: g120413a.rdb

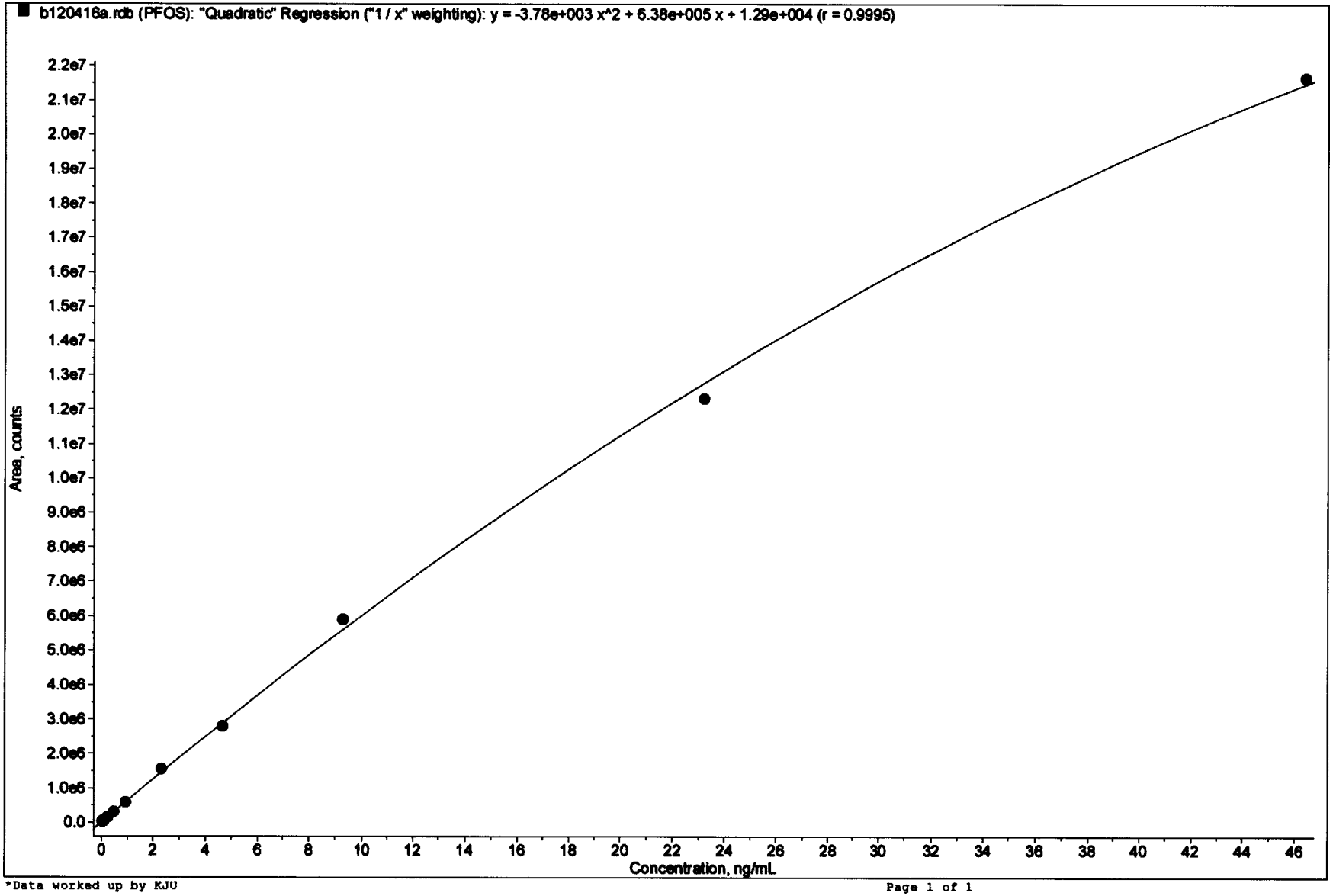


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Printing Time: 11:15:44 AM
Printing Date: Wednesday, May 09, 2012

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Workstation: ETSBUSTER

Batch Name: b120416a.dab



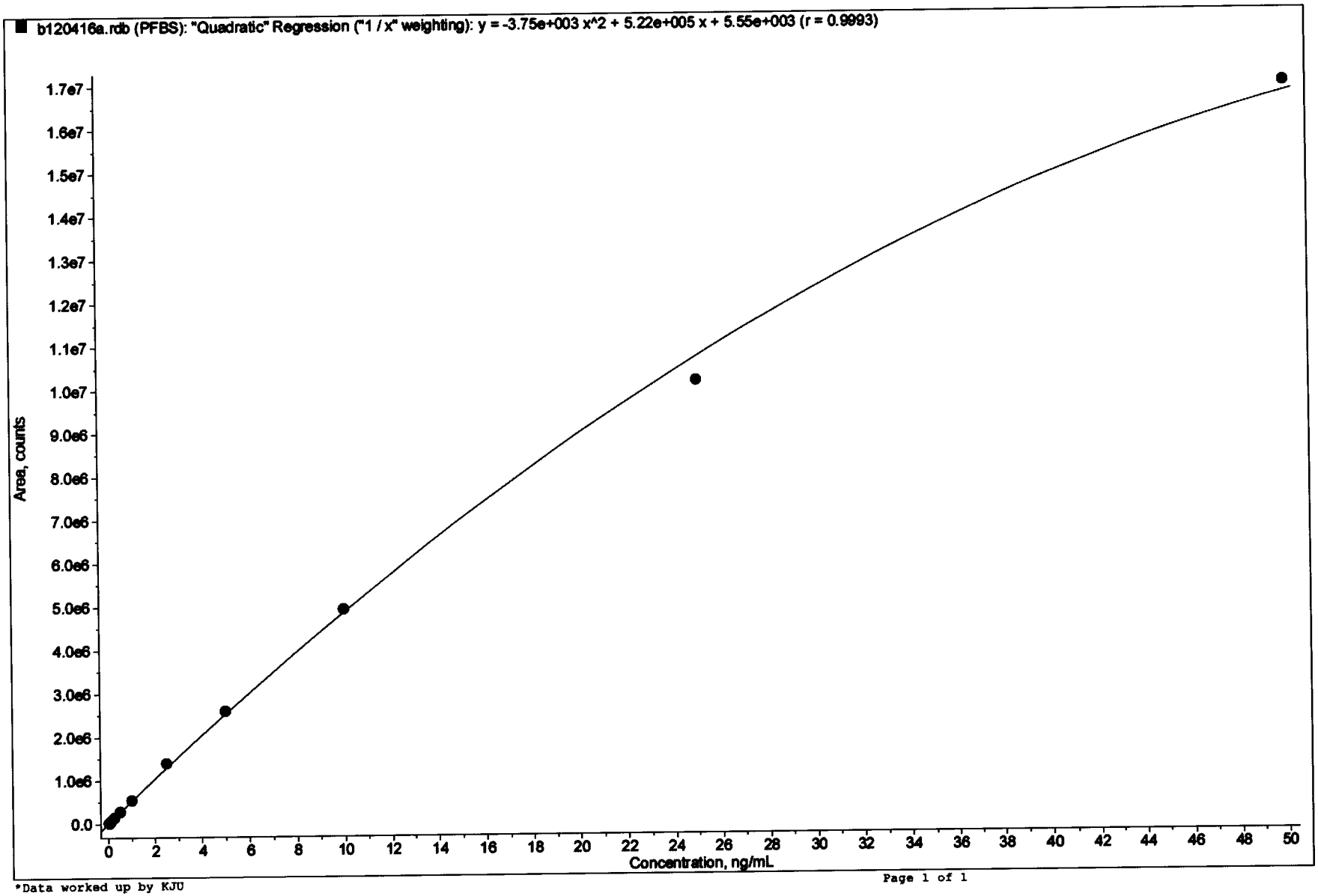
*Data worked up by KJU

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Printing Time: 2:17:59 PM
Printing Date: Wednesday, April 18, 2012

Workstation: ETSBUSTER

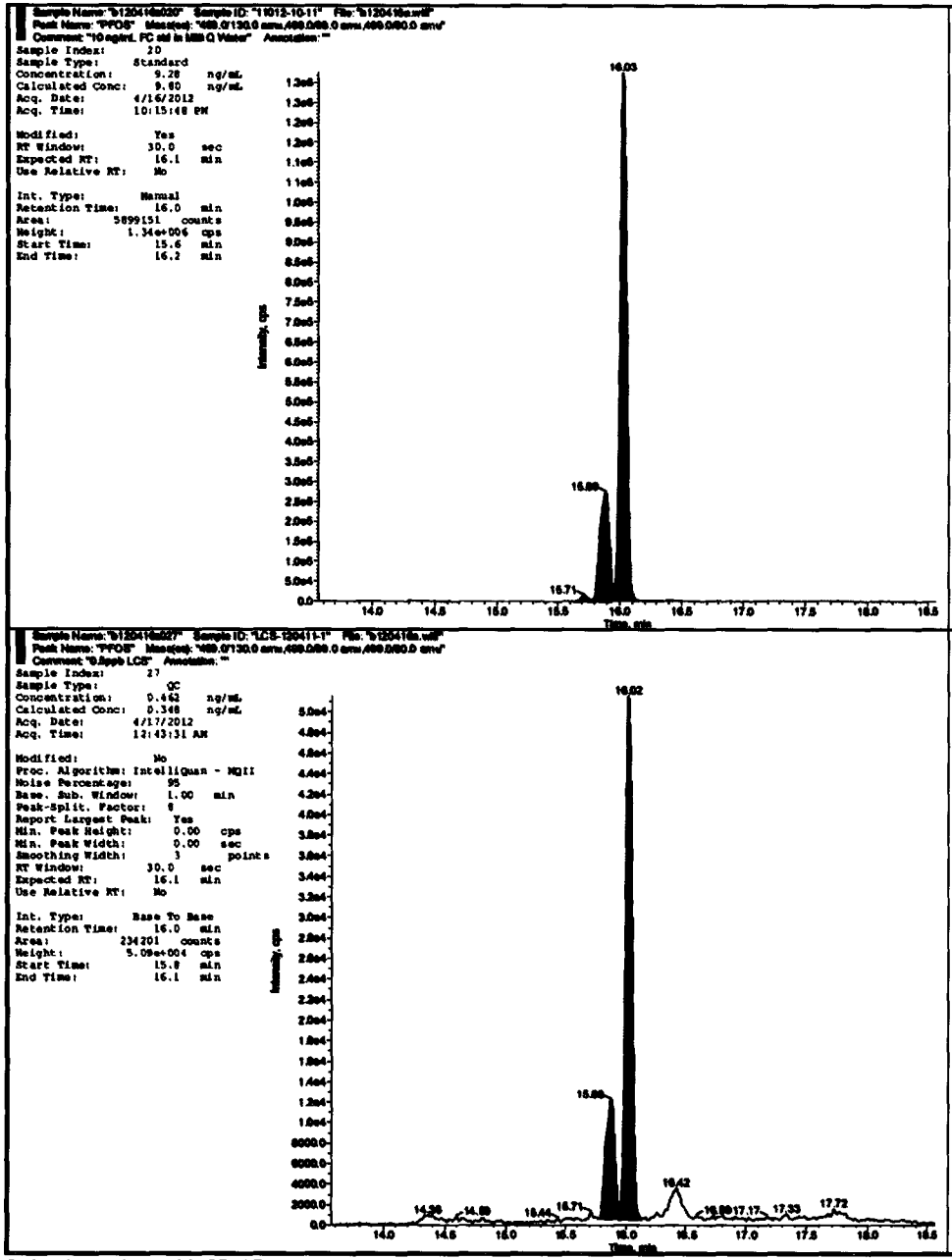
Batch Name: b120416a.dab

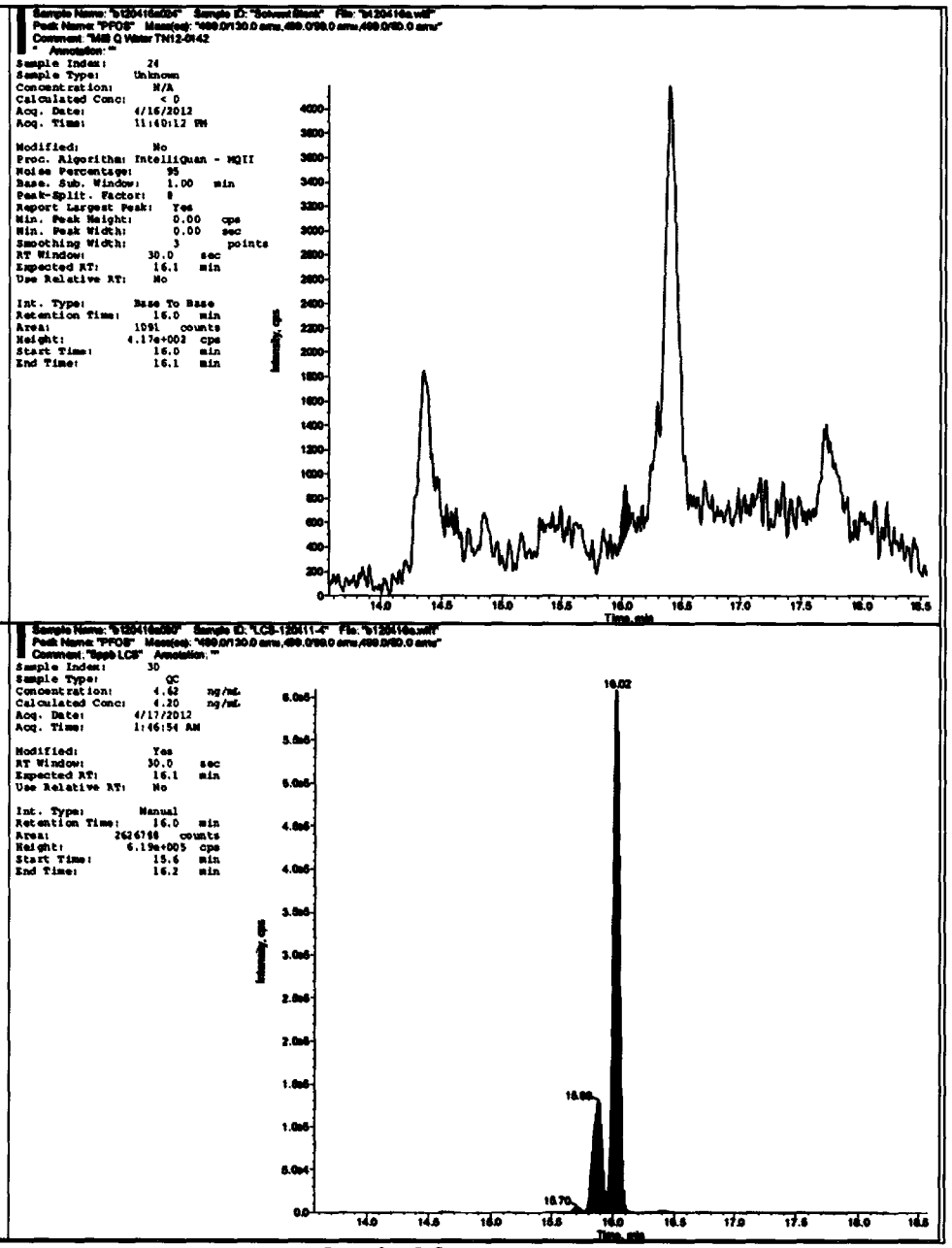


*Data worked up by KJU

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Printing Time: 2:17:43 PM
Printing Date: Wednesday, April 18, 2012

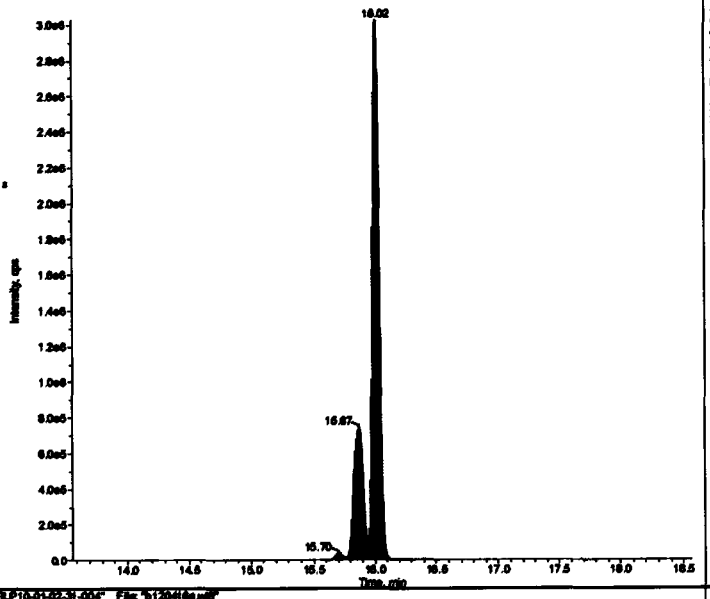




Printing Time: 11:27:17 AM
Printing Date: Wednesday, May 09, 2012

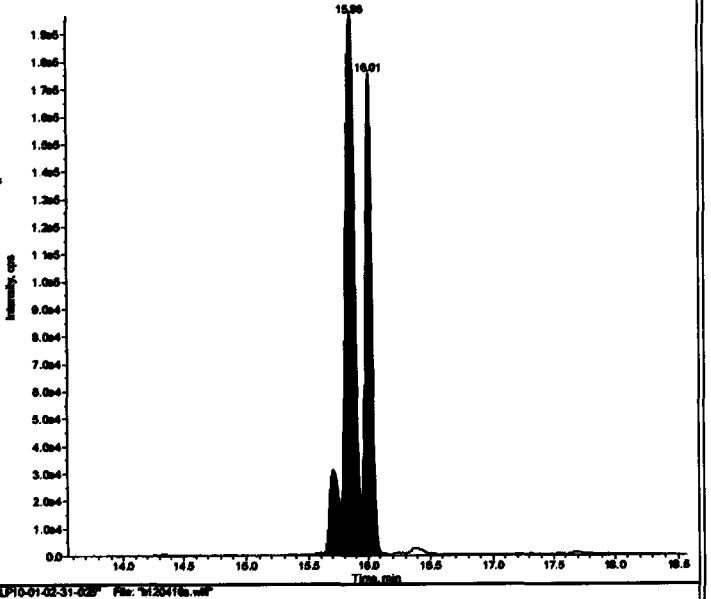
Sample Name: "b120418s033" Sample ID: "LCS-120411-7" File: "b120418s.wiff"
Peak Name: "PFOS" Mass(es): "499.0/130.0 amu,499.0/99.0 amu,499.0/80.0 amu"
Comment: "30ppb LCS" Annotation: ""

Sample Index:	33	
Sample Type:	QC	
Concentration:	27.8	ng/mL
Calculated Conc:	26.5	ng/mL
Acq. Date:	4/17/2012	
Acq. Time:	2:50:10 AM	
Modified:	No	
Proc. Algorithm:	IntelliQuan - MQII	
Noise Percentage:	95	
Base. Sub. Window:	1.00	min
Peak-Split. Factor:	8	
Report Largest Peak:	Yes	
Min. Peak Height:	0.00	cps
Min. Peak Width:	0.00	sec
Smoothing Width:	3	points
RT Window:	30.0	sec
Expected RT:	16.1	min
Use Relative RT:	No	
Int. Type:	Valley	
Retention Time:	16.0	min
Area:	14250414	counts
Height:	3.03e+006	cps
Start Time:	15.6	min
End Time:	16.3	min



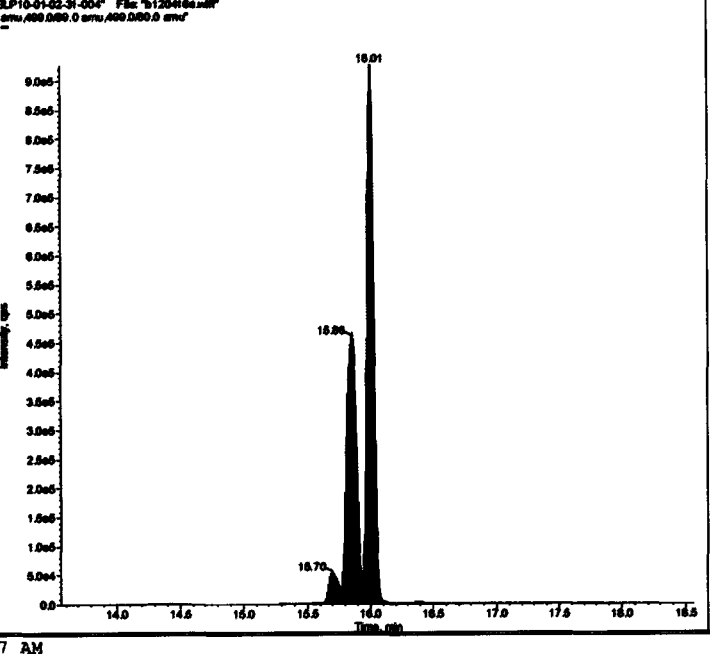
Sample Name: "b120418s044" Sample ID: "GLP10-01-02-31-001" File: "b120418s.wiff"
Peak Name: "PFOS" Mass(es): "499.0/130.0 amu,499.0/99.0 amu,499.0/80.0 amu"
Comment: "DAL-GW-TW1R-0" Annotation: ""

Sample Index:	44	
Sample Type:	Unknown	
Concentration:	N/A	
Calculated Conc:	27.7	ng/mL
Acq. Date:	4/17/2012	
Acq. Time:	6:42:17 AM	
Modified:	No	
Proc. Algorithm:	IntelliQuan - MQII	
Noise Percentage:	95	
Base. Sub. Window:	1.00	min
Peak-Split. Factor:	8	
Report Largest Peak:	Yes	
Min. Peak Height:	0.00	cps
Min. Peak Width:	0.00	sec
Smoothing Width:	3	points
RT Window:	30.0	sec
Expected RT:	16.1	min
Use Relative RT:	No	
Int. Type:	Base To Base	
Retention Time:	15.9	min
Area:	1747791	counts
Height:	1.96e+005	cps
Start Time:	15.5	min
End Time:	16.2	min



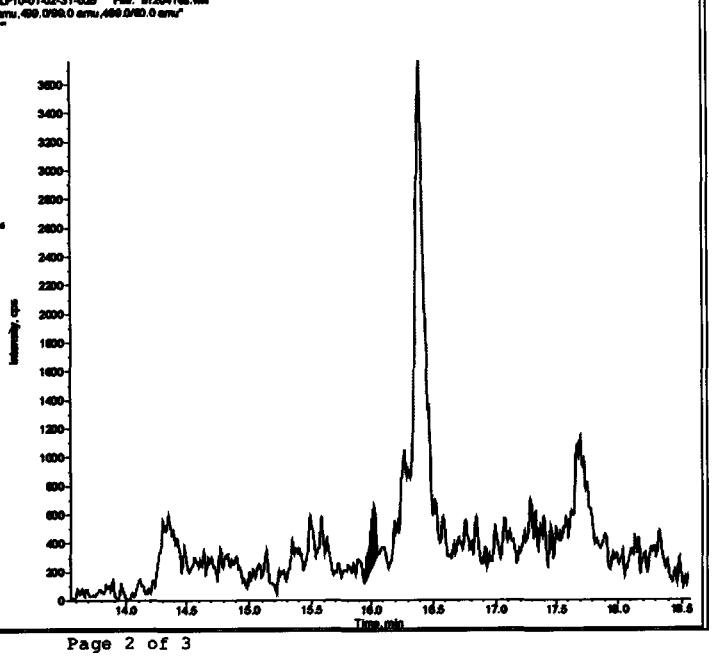
Sample Name: "b120418s047" Sample ID: "GLP10-01-02-31-004" File: "b120418s.wiff"
Peak Name: "PFOS" Mass(es): "499.0/130.0 amu,499.0/99.0 amu,499.0/80.0 amu"
Comment: "DAL-GW-TW1R-HB" Annotation: ""

Sample Index:	47	
Sample Type:	Unknown	
Concentration:	N/A	
Calculated Conc:	94.7	ng/mL
Acq. Date:	4/17/2012	
Acq. Time:	7:45:24 AM	
Modified:	Yes	
RT Window:	30.0	sec
Expected RT:	16.1	min
Use Relative RT:	No	
Int. Type:	Manual	
Retention Time:	16.0	min
Area:	5713870	counts
Height:	9.27e+005	cps
Start Time:	15.5	min
End Time:	16.2	min

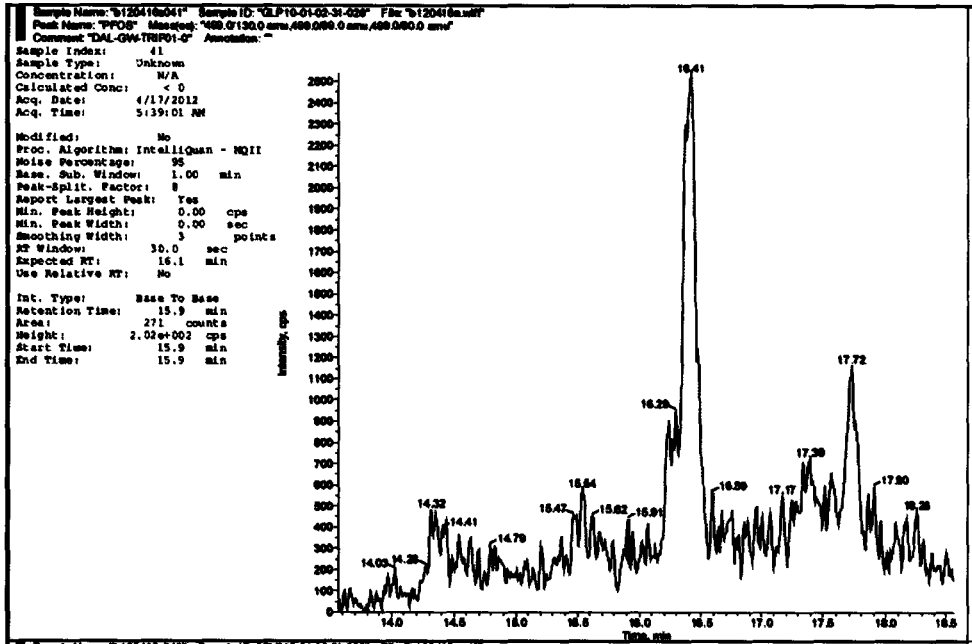


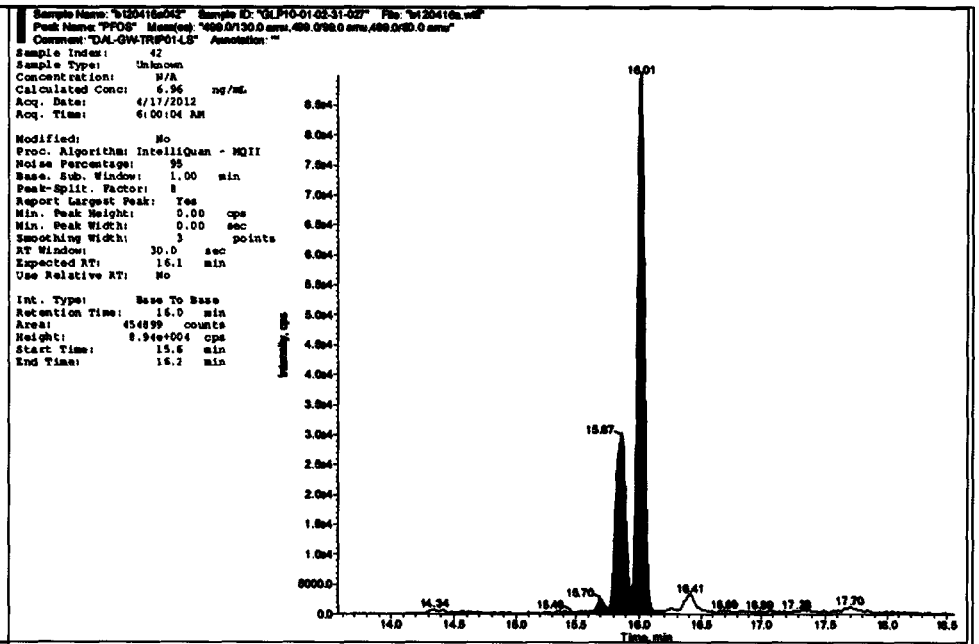
Sample Name: "b120418s048" Sample ID: "GLP10-01-02-31-025" File: "b120418s.wiff"
Peak Name: "PFOS" Mass(es): "499.0/130.0 amu,499.0/99.0 amu,499.0/80.0 amu"
Comment: "DAL-GW-RW3R-RB" Annotation: ""

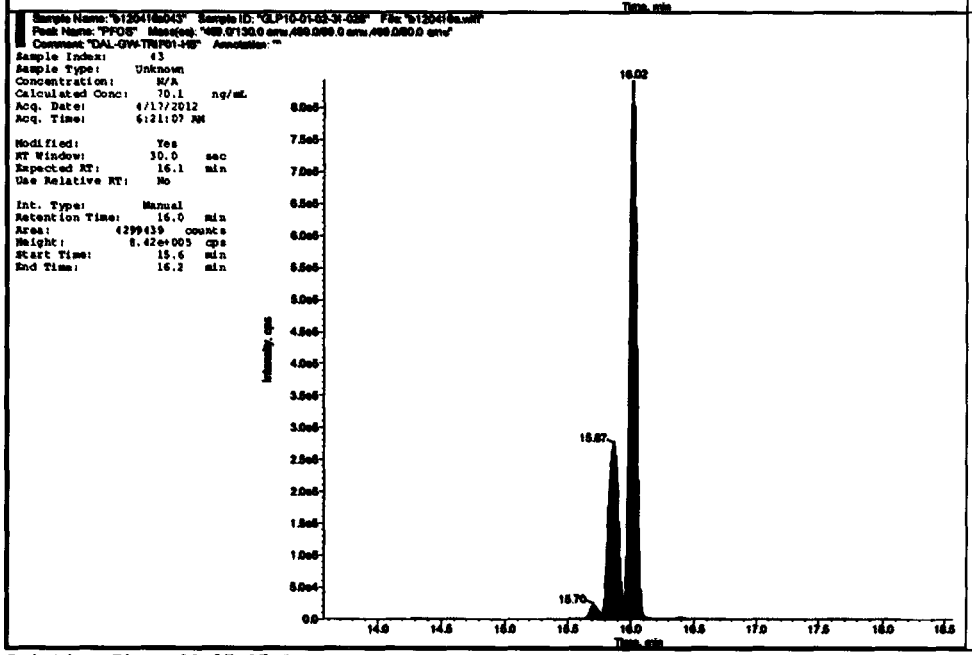
Sample Index:	40	
Sample Type:	Unknown	
Concentration:	N/A	
Calculated Conc:	< 0	
Acq. Date:	4/17/2012	
Acq. Time:	5:17:54 AM	
Modified:	No	
Proc. Algorithm:	IntelliQuan - MQII	
Noise Percentage:	95	
Base. Sub. Window:	1.00	min
Peak-Split. Factor:	8	
Report Largest Peak:	Yes	
Min. Peak Height:	0.00	cps
Min. Peak Width:	0.00	sec
Smoothing Width:	3	points
RT Window:	30.0	sec
Expected RT:	16.1	min
Use Relative RT:	No	
Int. Type:	Base To Base	
Retention Time:	16.0	min
Area:	1220	counts
Height:	3.96e+002	cps
Start Time:	15.9	min
End Time:	16.1	min



Printing Time: 11:27:17 AM
Printing Date: Wednesday, May 09, 2012







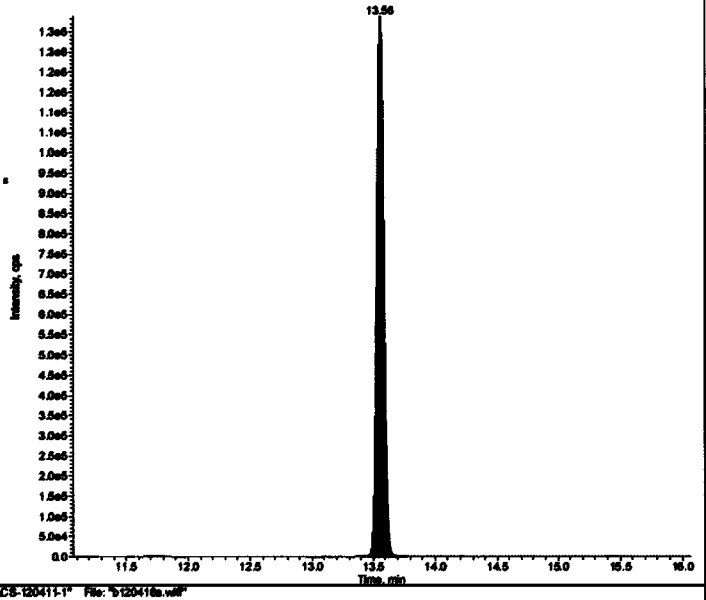
Printing Time: 11:27:17 AM
Printing Date: Wednesday, May 09, 2012

Sample Name: "b120416a027" Sample ID: "11012-10-11" File: "b120416a.wiff"
Peak Name: "PFBS" Mass(es): "299.0/80.0 amu,299.0/80.0 amu"
Comment: "10 ng/mL FC std in Milli Q Water" Annotation: ""

Sample Index: 20
Sample Type: Standard
Concentration: 10.0 ng/mL
Calculated Conc: 10.2 ng/mL
Acq. Date: 4/16/2012
Acq. Time: 10:15:48 PM

Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 1
Report Largest Peak: Yes
Min. Peak Height: 0.00 cps
Min. Peak Width: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 13.6 min
Use Relative RT: No

Int. Type: Valley
Retention Time: 13.6 min
Area: 4930110 counts
Height: 1.34e+006 cps
Start Time: 13.5 min
End Time: 13.8 min

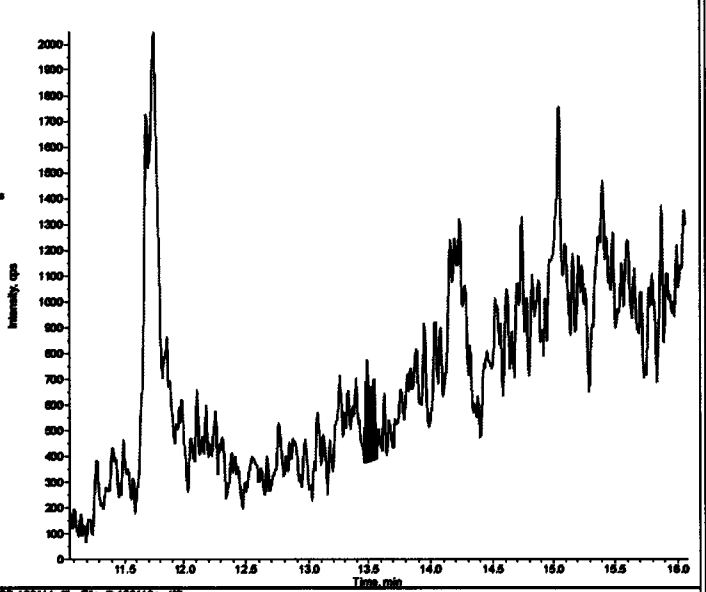


Sample Name: "b120416a054" Sample ID: "Solvent Blank" File: "b120416a.wiff"
Peak Name: "PFBS" Mass(es): "299.0/80.0 amu,299.0/80.0 amu"
Comment: "Milli Q Water TM12-0142
" Annotation: ""

Sample Index: 24
Sample Type: Unknown
Concentration: N/A
Calculated Conc: < 0
Acq. Date: 4/16/2012
Acq. Time: 11:40:12 PM

Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 1
Report Largest Peak: Yes
Min. Peak Height: 0.00 cps
Min. Peak Width: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 13.6 min
Use Relative RT: No

Int. Type: Valley
Retention Time: 13.5 min
Area: 1362 counts
Height: 3.91e+002 cps
Start Time: 13.5 min
End Time: 13.6 min

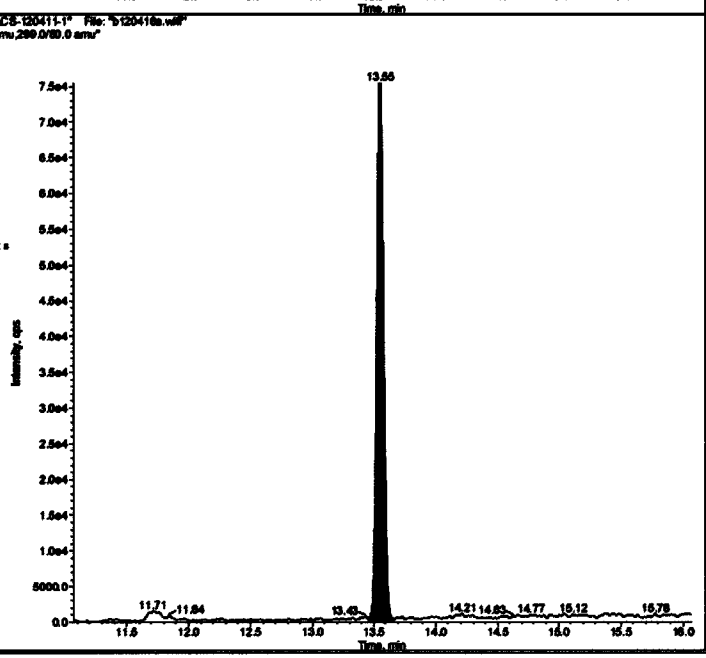


Sample Name: "b120416a027" Sample ID: "LCS-120411-1" File: "b120416a.wiff"
Peak Name: "PFBS" Mass(es): "299.0/80.0 amu,299.0/80.0 amu"
Comment: "0.5ppb LCS" Annotation: ""

Sample Index: 27
Sample Type: QC
Concentration: 0.498 ng/mL
Calculated Conc: 0.505 ng/mL
Acq. Date: 4/17/2012
Acq. Time: 12:43:31 AM

Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 1
Report Largest Peak: Yes
Min. Peak Height: 0.00 cps
Min. Peak Width: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 13.6 min
Use Relative RT: No

Int. Type: Valley
Retention Time: 13.6 min
Area: 268240 counts
Height: 7.52e+004 cps
Start Time: 13.5 min
End Time: 13.7 min

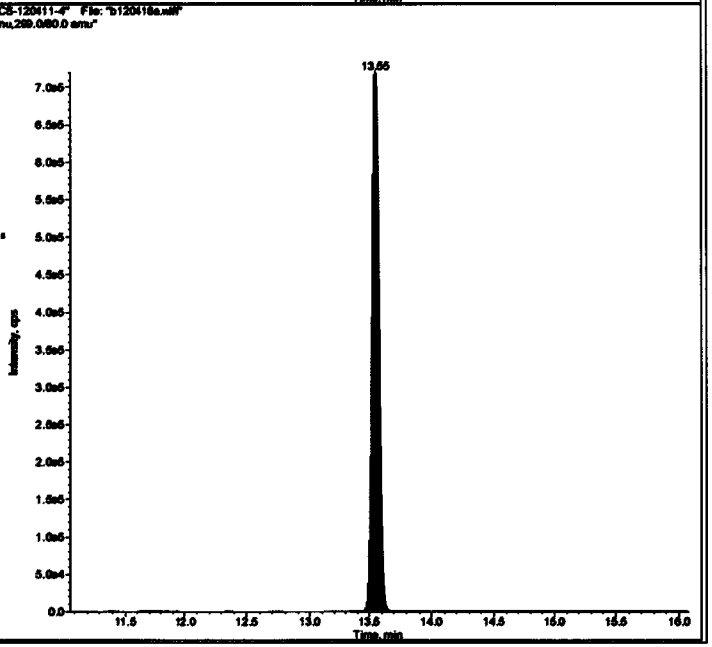


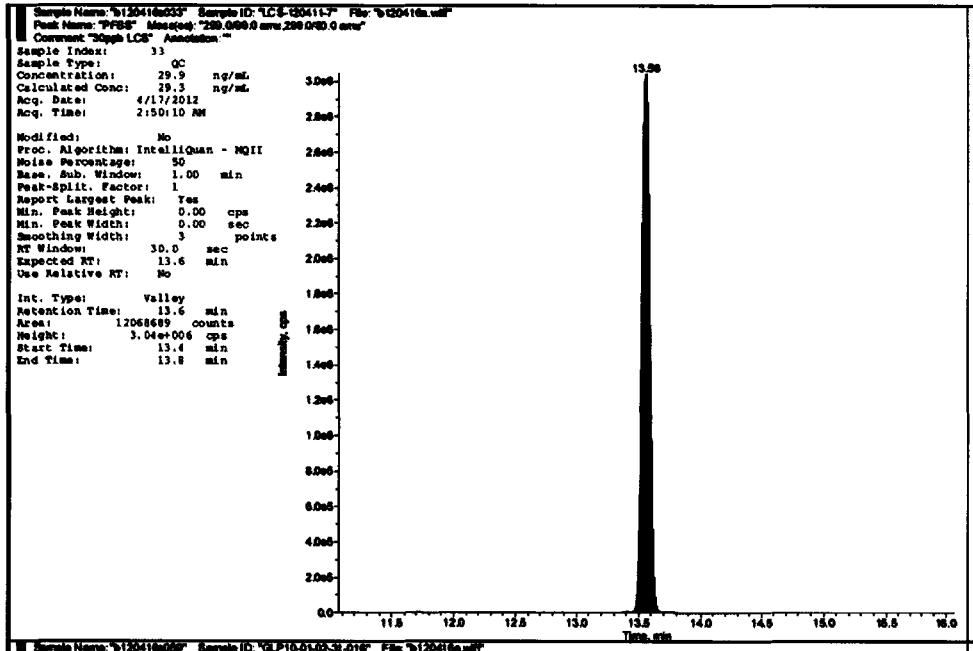
Sample Name: "b120416a050" Sample ID: "LCS-120411-4" File: "b120416a.wiff"
Peak Name: "PFBS" Mass(es): "299.0/80.0 amu,299.0/80.0 amu"
Comment: "5ppb LCS" Annotation: ""

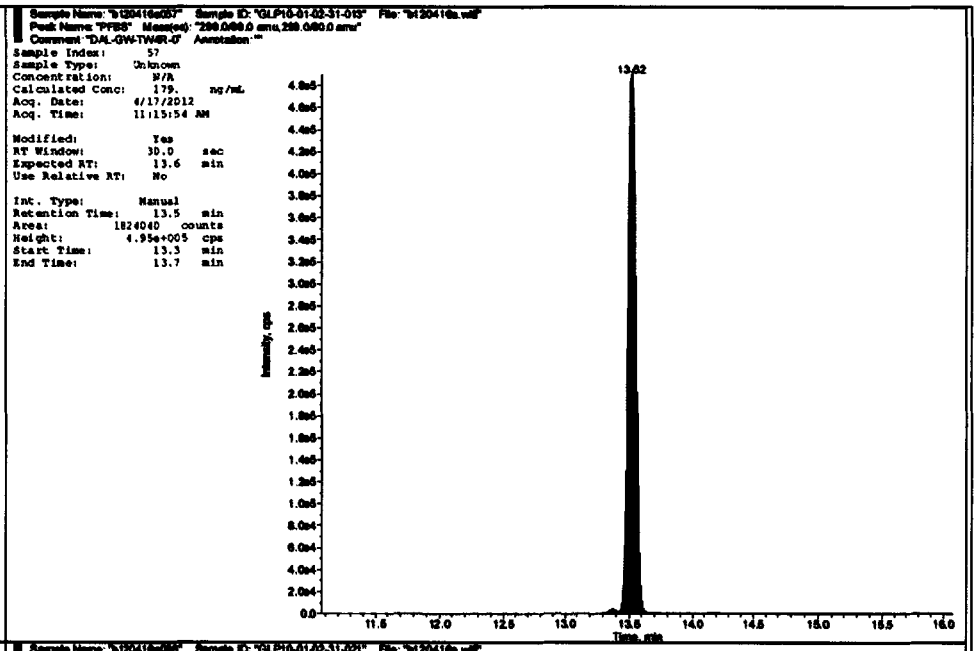
Sample Index: 30
Sample Type: QC
Concentration: 4.96 ng/mL
Calculated Conc: 5.12 ng/mL
Acq. Date: 4/17/2012
Acq. Time: 1:46:54 AM

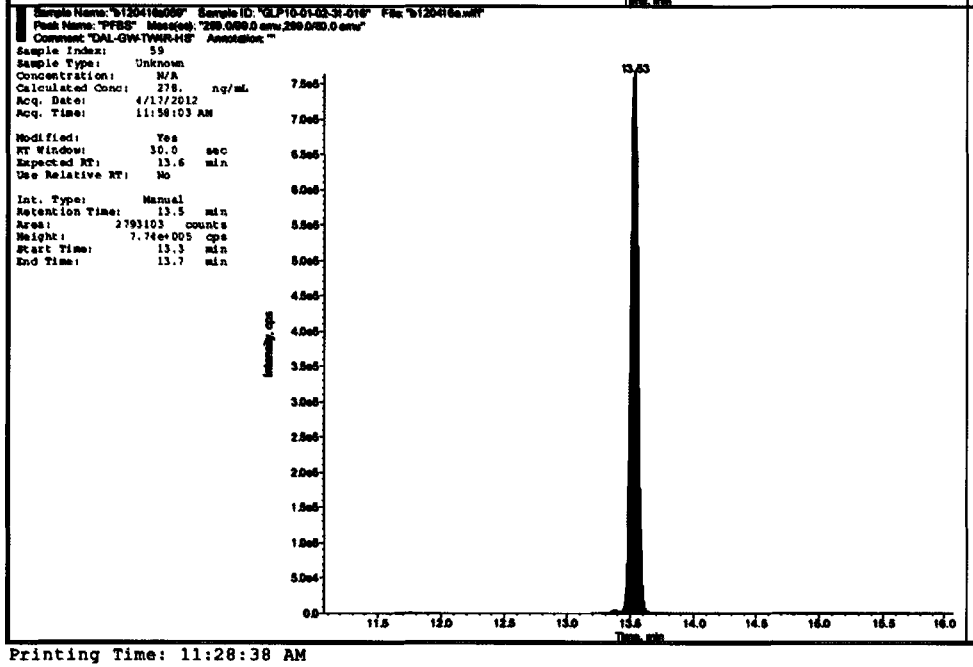
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 1
Report Largest Peak: Yes
Min. Peak Height: 0.00 cps
Min. Peak Width: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 13.6 min
Use Relative RT: No

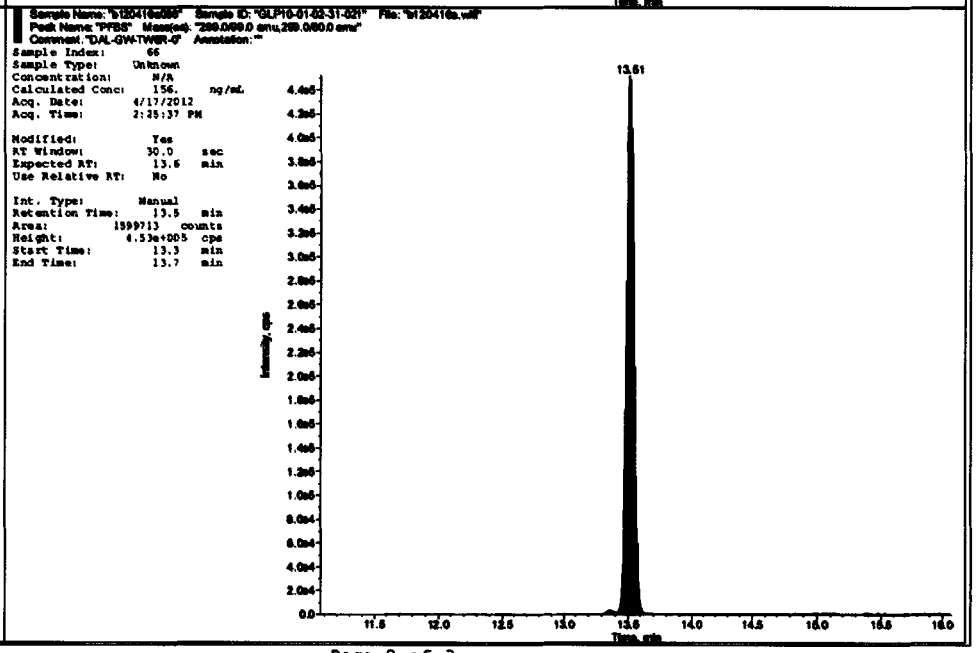
Int. Type: Valley
Retention Time: 13.5 min
Area: 2576292 counts
Height: 7.20e+005 cps
Start Time: 13.4 min
End Time: 13.7 min



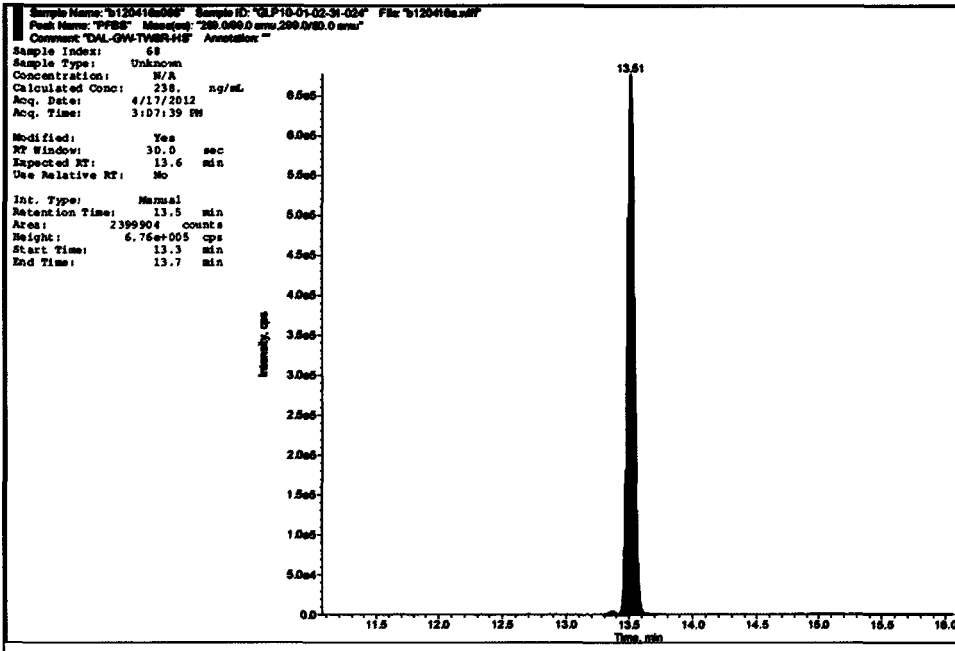

Sample Name: "b120416s033" Sample ID: "LCS-120411-7" File: "b120416s.wiff"
Peak Name: "PFBS" Mass(es): "299.0/80.0 amu,299.0/80.0 amu"
Comment: "30ppb LCS" Annotation: ""
Sample Index: 33
Sample Type: QC
Concentration: 29.9 ng/mL
Calculated Conc: 29.3 ng/mL
Acq. Date: 4/17/2012
Acq. Time: 2:50:10 AM
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 1
Report Largest Peak: Yes
Min. Peak Height: 0.00 cps
Min. Peak Width: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 13.6 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 13.6 min
Area: 12068689 counts
Height: 3.04e+006 cps
Start Time: 13.4 min
End Time: 13.8 min
13.58
Intensity, cps
Time, min


Sample Name: "b120416s057" Sample ID: "GLP10-01-02-31-013" File: "b120416s.wiff"
Peak Name: "PFBS" Mass(es): "299.0/80.0 amu,299.0/80.0 amu"
Comment: "DAL-GW-TWWR-0" Annotation: ""
Sample Index: 57
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 179. ng/mL
Acq. Date: 4/17/2012
Acq. Time: 11:15:54 AM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 13.6 min
Use Relative RT: No
Int. Type: Manual
Retention Time: 13.5 min
Area: 1824040 counts
Height: 4.95e+005 cps
Start Time: 13.3 min
End Time: 13.7 min
13.62
Intensity, cps
Time, min


Sample Name: "b120416s069" Sample ID: "GLP10-01-02-31-016" File: "b120416s.wiff"
Peak Name: "PFBS" Mass(es): "299.0/80.0 amu,299.0/80.0 amu"
Comment: "DAL-GW-TWWR-HIT" Annotation: ""
Sample Index: 59
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 278. ng/mL
Acq. Date: 4/17/2012
Acq. Time: 11:50:03 AM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 13.6 min
Use Relative RT: No
Int. Type: Manual
Retention Time: 13.5 min
Area: 2793103 counts
Height: 7.74e+005 cps
Start Time: 13.3 min
End Time: 13.7 min
13.63
Intensity, cps
Time, min


Sample Name: "b120416s065" Sample ID: "GLP10-01-02-31-021" File: "b120416s.wiff"
Peak Name: "PFBS" Mass(es): "299.0/80.0 amu,299.0/80.0 amu"
Comment: "DAL-GW-TWWR-0" Annotation: ""
Sample Index: 65
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 156. ng/mL
Acq. Date: 4/17/2012
Acq. Time: 2:35:37 PM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 13.6 min
Use Relative RT: No
Int. Type: Manual
Retention Time: 13.5 min
Area: 1599713 counts
Height: 6.53e+005 cps
Start Time: 13.3 min
End Time: 13.7 min
13.61
Intensity, cps
Time, min

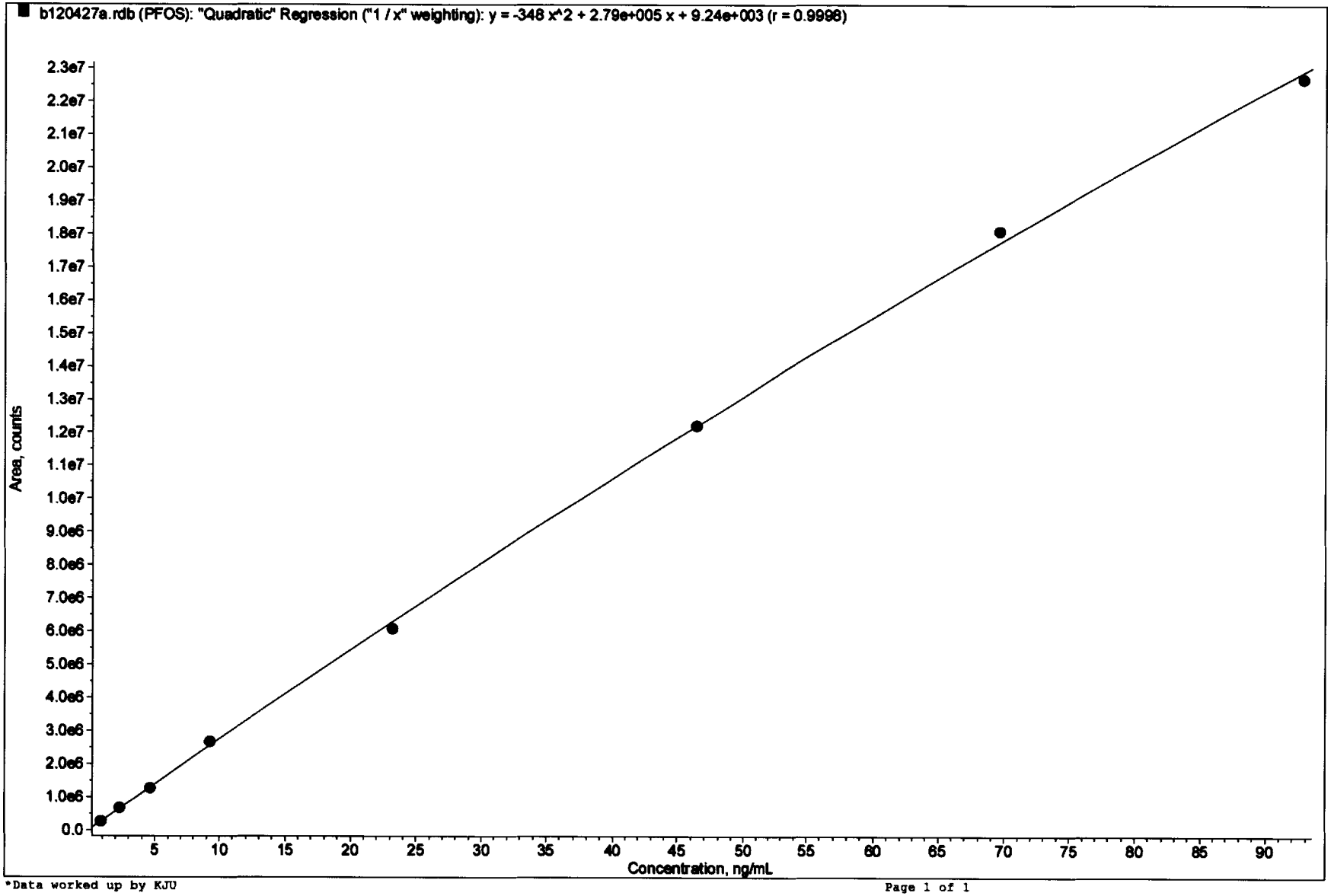
*** Buster J2930203



Printing Time: 11:28:38 AM
Printing Date: Wednesday, May 09, 2012

Workstation: ETSBUSTER

Batch Name: b120427a.dab



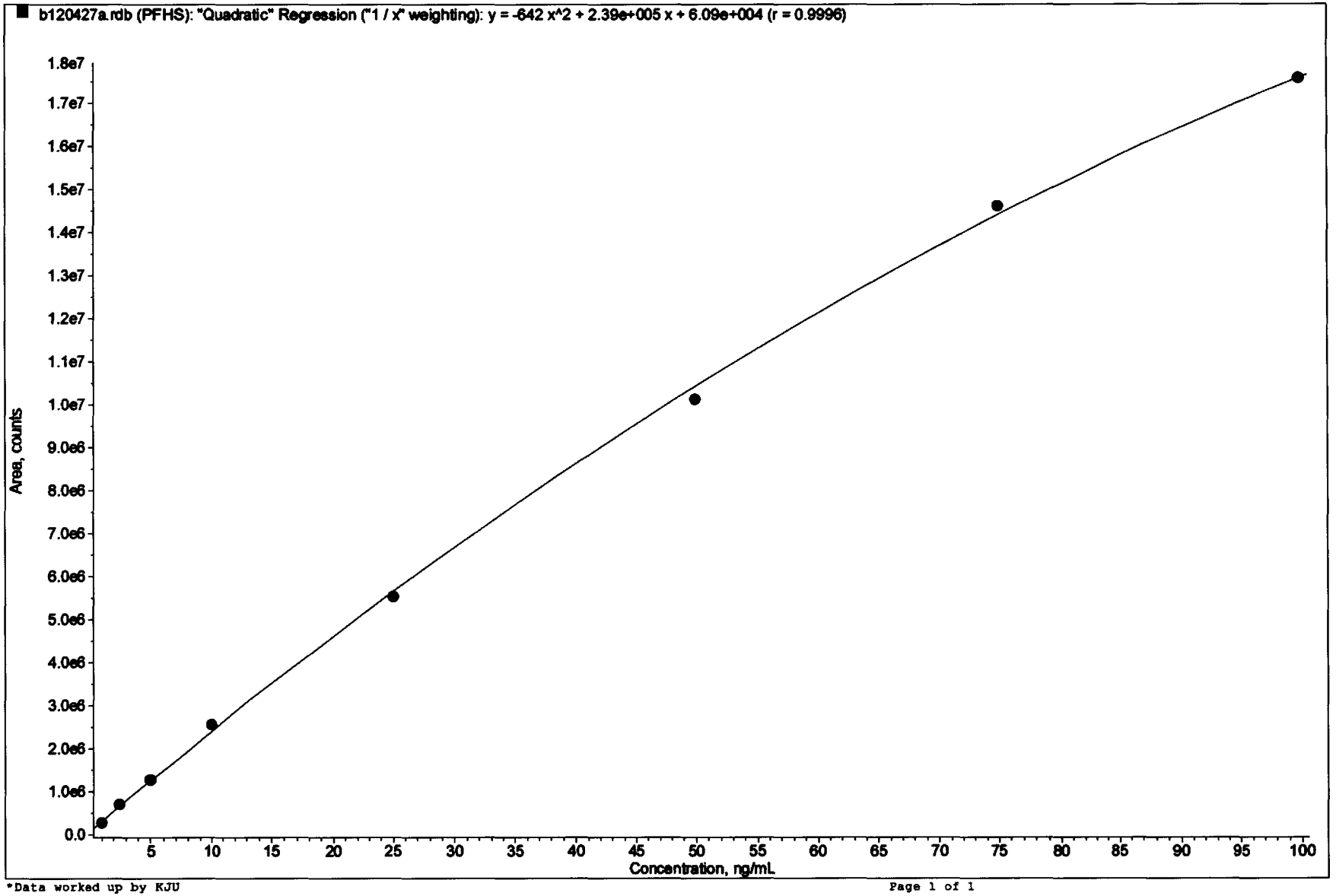
*Data worked up by KJU

Page 1 of 1

Printing Time: 2:04:20 PM
Printing Date: Monday, April 30, 2012

Workstation: ETSBUSTER

Batch Name: b120427a.dab



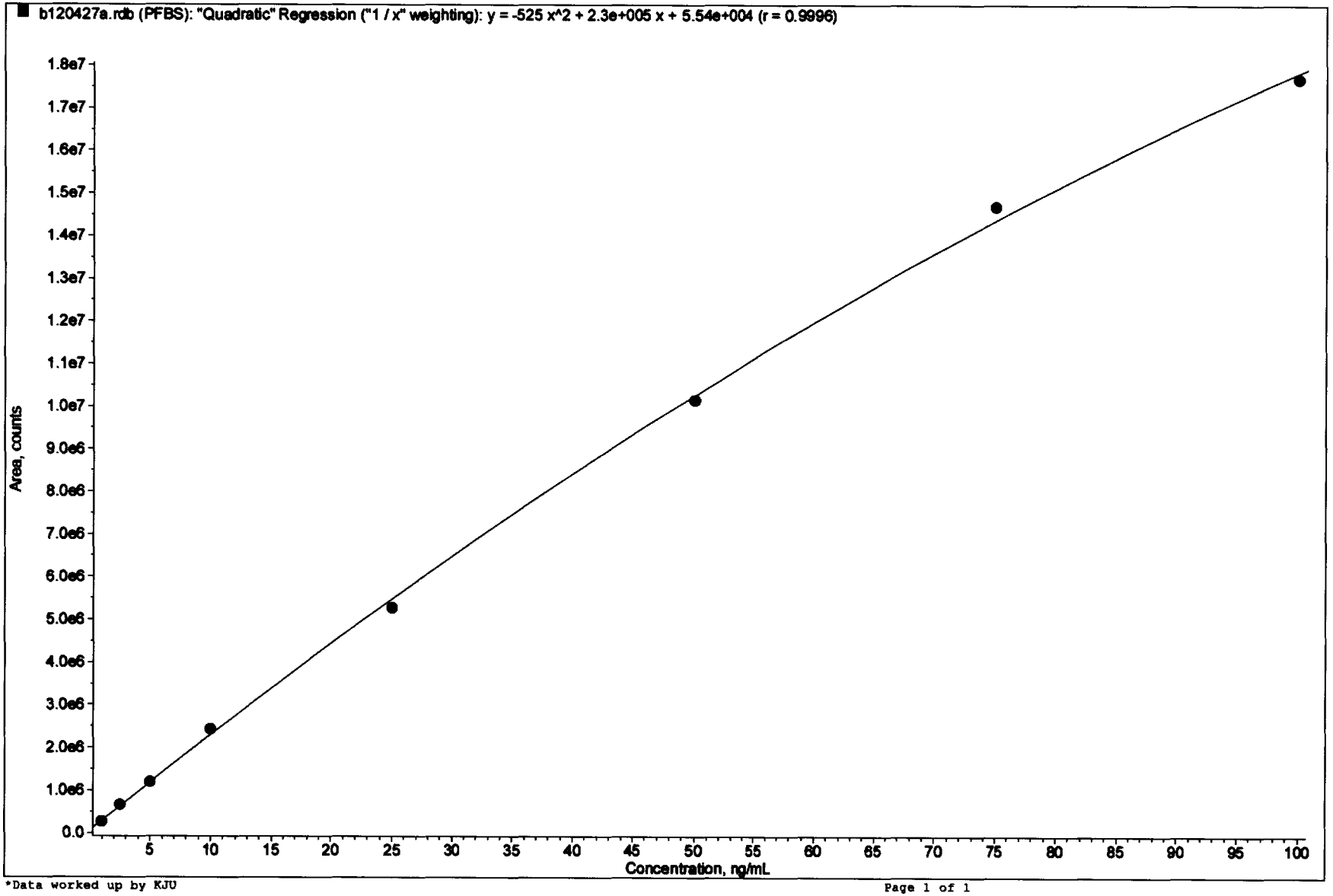
*Data worked up by KJU

Page 1 of 1

Printing Time: 2:03:53 PM
Printing Date: Monday, April 30, 2012

Workstation: ETSBUSTER

Batch Name: b120427a.dab



*Data worked up by KJU

Page 1 of 1

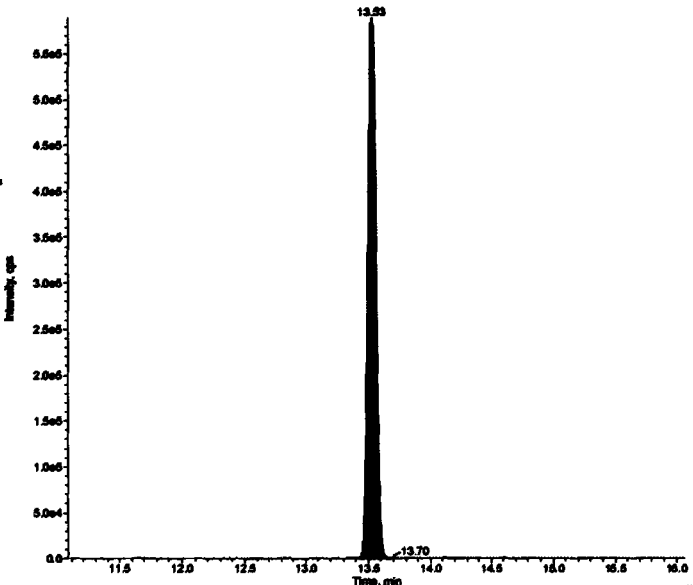
Printing Time: 2:04:06 PM
Printing Date: Monday, April 30, 2012

Sample Name: "b120427s012" Sample ID: "11012-10-11" File: "b120427a.wiff"
Peak Name: "PFBS" Mass(es): "299.0/80.0 amu,299.0/80.0 amu"
Comment: "10 ng/mL FC std in Milli Q Water" Annotation: ""

Sample Index: 12
Sample Type: Standard
Concentration: 10.0 ng/mL
Calculated Conc: 10.6 ng/mL
Acq. Date: 4/27/2012
Acq. Time: 5:30:22 PM

Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 1
Report Largest Peak: Yes
Min. Peak Height: 0.00 cps
Min. Peak Width: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 13.6 min
Use Relative RT: No

Int. Type: Valley
Retention Time: 13.5 min
Area: 2433672 counts
Height: 5.89e+005 cps
Start Time: 13.4 min
End Time: 13.7 min

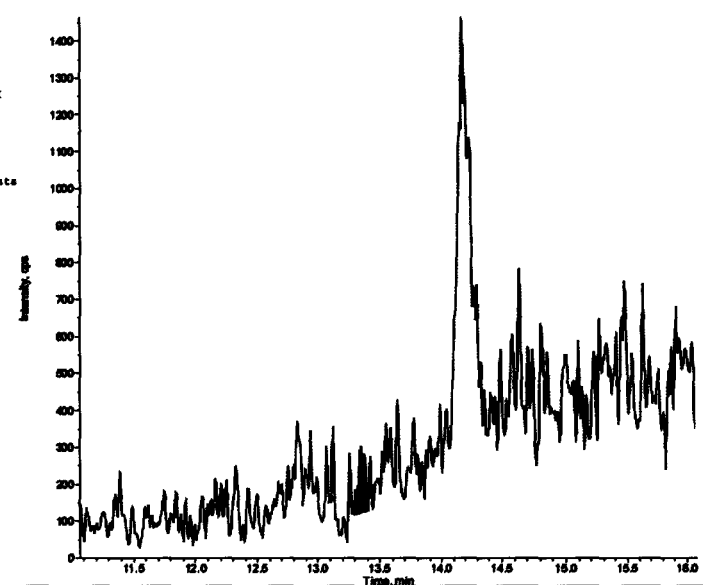


Sample Name: "b120427s007" Sample ID: "Solvent Blank" File: "b120427a.wiff"
Peak Name: "PFBS" Mass(es): "299.0/80.0 amu,299.0/80.0 amu"
Comment: "Milli Q Water TN12-0156" Annotation: ""

Sample Index: 20
Sample Type: Unknown
Concentration: N/A
Calculated Conc: < 0
Acq. Date: 4/27/2012
Acq. Time: 8:18:29 PM

Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 1
Report Largest Peak: Yes
Min. Peak Height: 0.00 cps
Min. Peak Width: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 13.6 min
Use Relative RT: No

Int. Type: Valley
Retention Time: 13.4 min
Area: 611 counts
Height: 1.77e+002 cps
Start Time: 13.3 min
End Time: 13.4 min

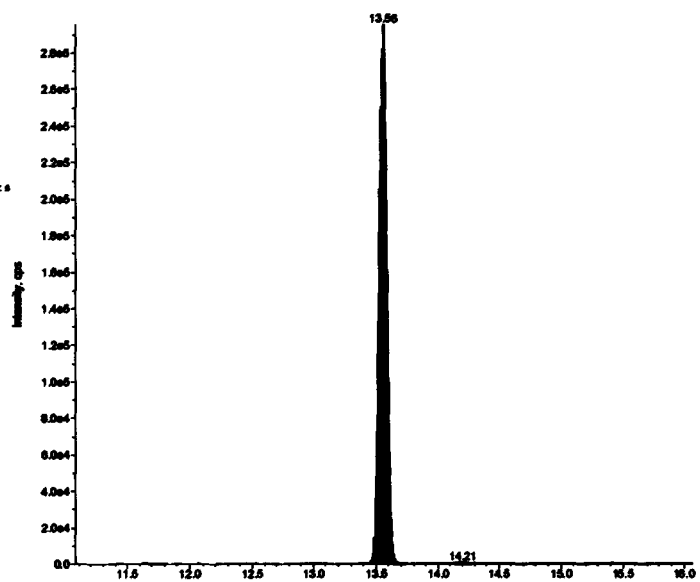


Sample Name: "b120427s021" Sample ID: "LCS-120426-1" File: "b120427a.wiff"
Peak Name: "PFBS" Mass(es): "299.0/80.0 amu,299.0/80.0 amu"
Comment: "5ppb LCS" Annotation: ""

Sample Index: 21
Sample Type: QC
Concentration: 4.98 ng/mL
Calculated Conc: 4.95 ng/mL
Acq. Date: 4/27/2012
Acq. Time: 8:39:30 PM

Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 1
Report Largest Peak: Yes
Min. Peak Height: 0.00 cps
Min. Peak Width: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 13.6 min
Use Relative RT: No

Int. Type: Valley
Retention Time: 13.6 min
Area: 1183526 counts
Height: 2.96e+005 cps
Start Time: 13.4 min
End Time: 13.7 min

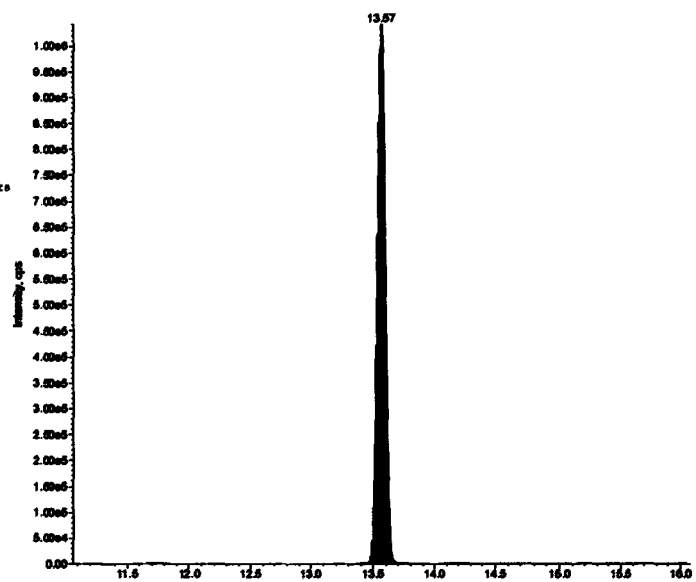


Sample Name: "b120427s024" Sample ID: "LCS-120426-4" File: "b120427a.wiff"
Peak Name: "PFBS" Mass(es): "299.0/80.0 amu,299.0/80.0 amu"
Comment: "20ppb LCS" Annotation: ""

Sample Index: 24
Sample Type: QC
Concentration: 20.0 ng/mL
Calculated Conc: 18.6 ng/mL
Acq. Date: 4/27/2012
Acq. Time: 9:42:39 PM

Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 1
Report Largest Peak: Yes
Min. Peak Height: 0.00 cps
Min. Peak Width: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 13.6 min
Use Relative RT: No

Int. Type: Valley
Retention Time: 13.6 min
Area: 4157125 counts
Height: 1.04e+006 cps
Start Time: 13.4 min
End Time: 13.7 min



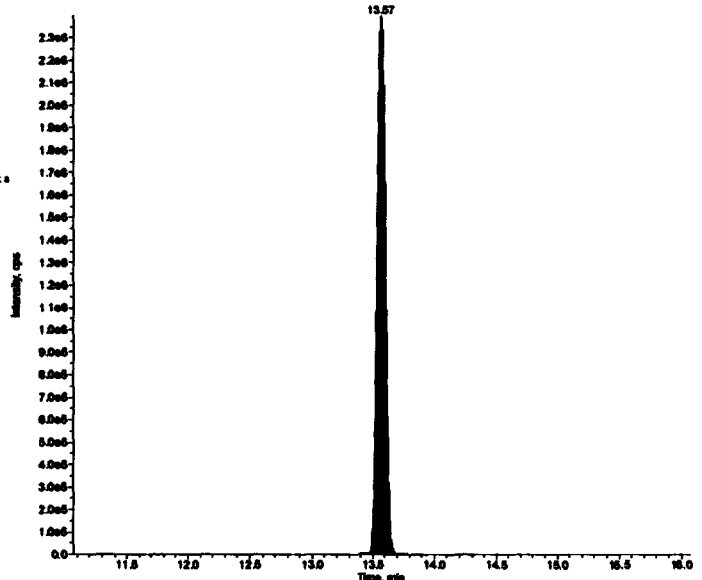
Printing Time: 11:31:04 AM
Printing Date: Wednesday, May 09, 2012

Sample Name: "b120427d027" Sample ID: "LCS-120426-7" File: "b120427a.wiff"
Peak Name: "PFBS" Mass(es): "299.0/80.0 amu,299.0/80.0 amu"
Comment: "50ppb LCS" Annotation: ""

Sample Index: 27
Sample Type: QC
Concentration: 49.8 ng/mL
Calculated Conc: 50.4 ng/mL
Acq. Date: 4/27/2012
Acq. Time: 10:45:36 PM

Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 50
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 1
Report Largest Peak: Yes
Min. Peak Height: 0.00 cps
Min. Peak Width: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 13.6 min
Use Relative RT: No

Int. Type: Valley
Retention Time: 13.6 min
Area: 10333827 counts
Height: 2.40e+006 cps
Start Time: 13.5 min
End Time: 13.8 min

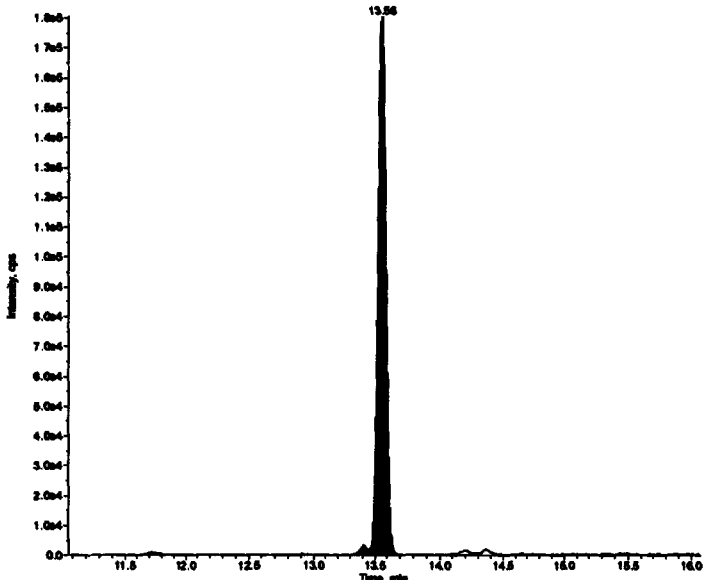


Sample Name: "b120427d028" Sample ID: "GLP10-01-02-31-008" File: "b120427a.wiff"
Peak Name: "PFBS" Mass(es): "299.0/80.0 amu,299.0/80.0 amu"
Comment: "DAL-GW-TWSR-0 (dil 1:100)" Annotation: ""

Sample Index: 38
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 292. ng/mL
Acq. Date: 4/28/2012
Acq. Time: 2:36:55 AM

Modified: Yes
RT Window: 30.0 sec
Expected RT: 13.6 min
Use Relative RT: No

Int. Type: Manual
Retention Time: 13.6 min
Area: 723278 counts
Height: 1.81e+005 cps
Start Time: 13.3 min
End Time: 13.7 min

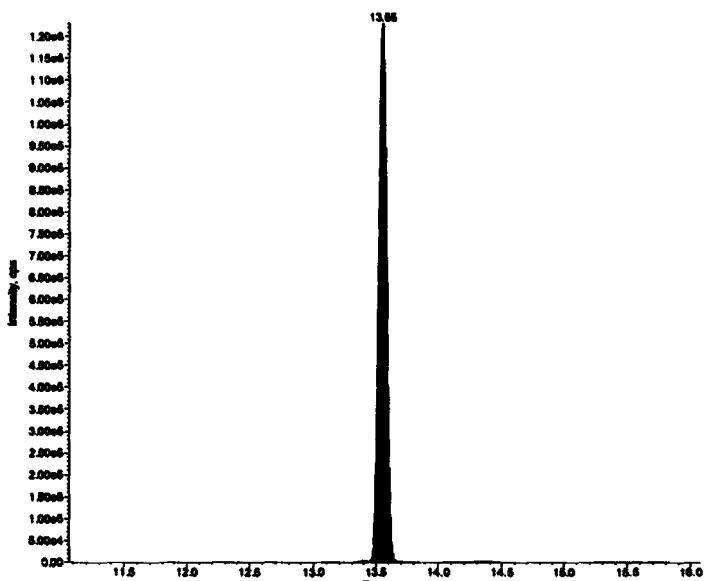


Sample Name: "b120427d040" Sample ID: "GLP10-01-02-31-005; LMS" File: "b120427a.wiff"
Peak Name: "PFBS" Mass(es): "299.0/80.0 amu,299.0/80.0 amu"
Comment: "DAL-GW-TWSR-0 2000ppb LMS (dil 1:100)" Annotation: ""

Sample Index: 40
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 2280. ng/mL
Acq. Date: 4/28/2012
Acq. Time: 3:18:57 AM

Modified: Yes
RT Window: 30.0 sec
Expected RT: 13.6 min
Use Relative RT: No

Int. Type: Manual
Retention Time: 13.5 min
Area: 5024434 counts
Height: 1.23e+006 cps
Start Time: 13.3 min
End Time: 13.7 min

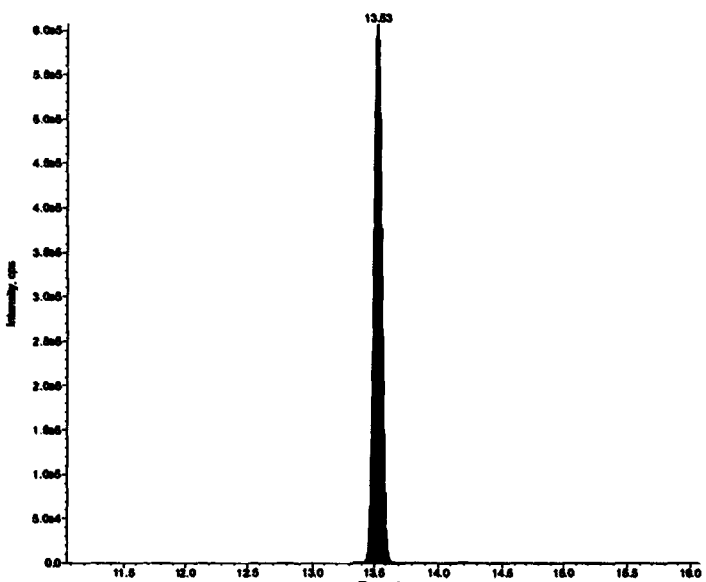


Sample Name: "b120427d041" Sample ID: "GLP10-01-02-31-017" File: "b120427a.wiff"
Peak Name: "PFBS" Mass(es): "299.0/80.0 amu,299.0/80.0 amu"
Comment: "DAL-GW-TWSR-0 (dil 1:20)" Annotation: ""

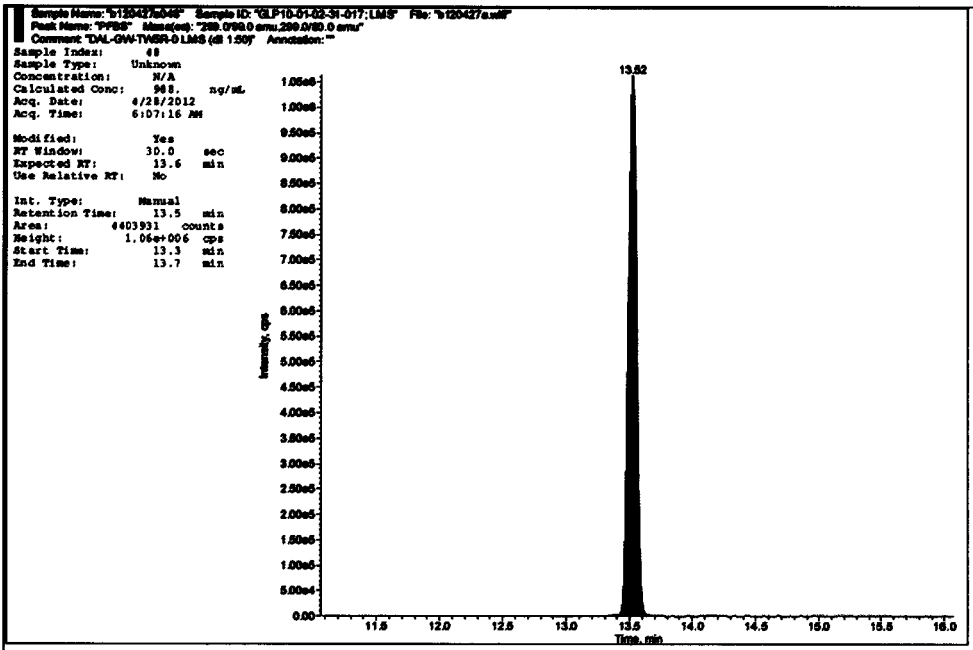
Sample Index: 46
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 533. ng/mL
Acq. Date: 4/28/2012
Acq. Time: 5:25:16 AM

Modified: Yes
RT Window: 30.0 sec
Expected RT: 13.6 min
Use Relative RT: No

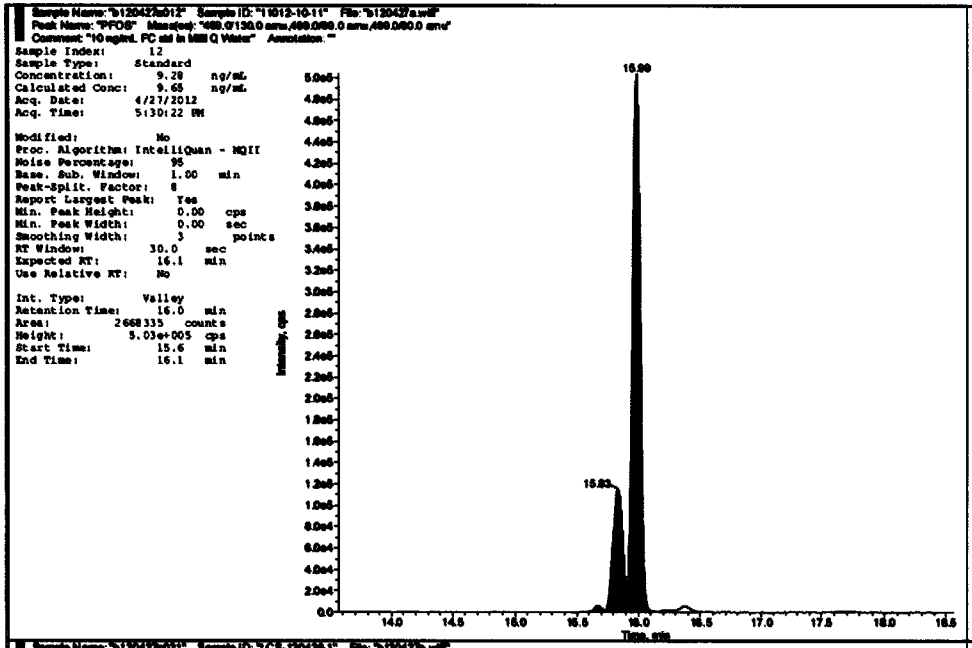
Int. Type: Manual
Retention Time: 13.5 min
Area: 1453239 counts
Height: 6.10e+005 cps
Start Time: 13.3 min
End Time: 13.7 min

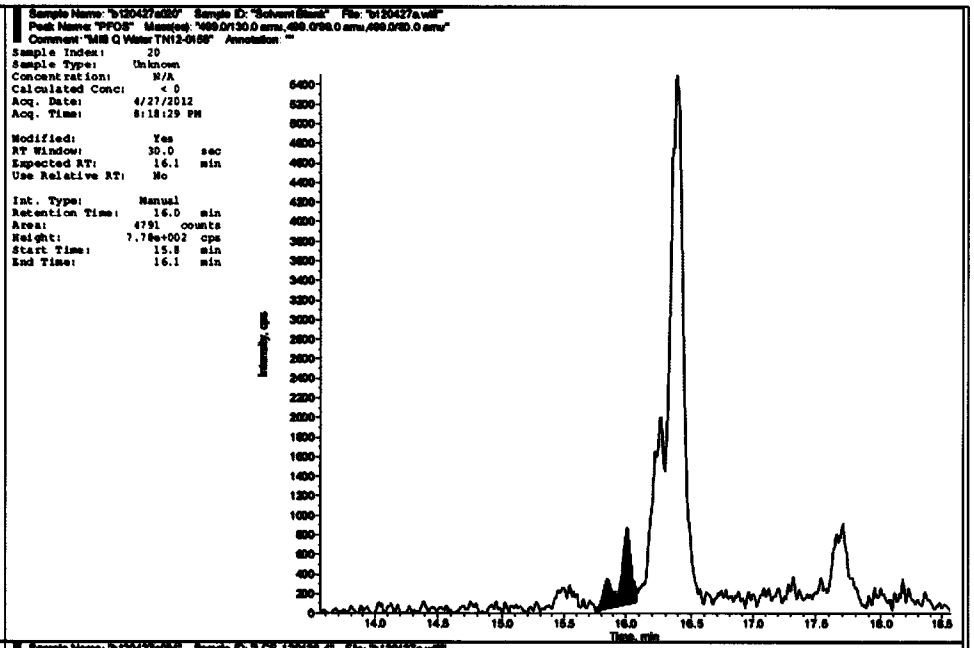


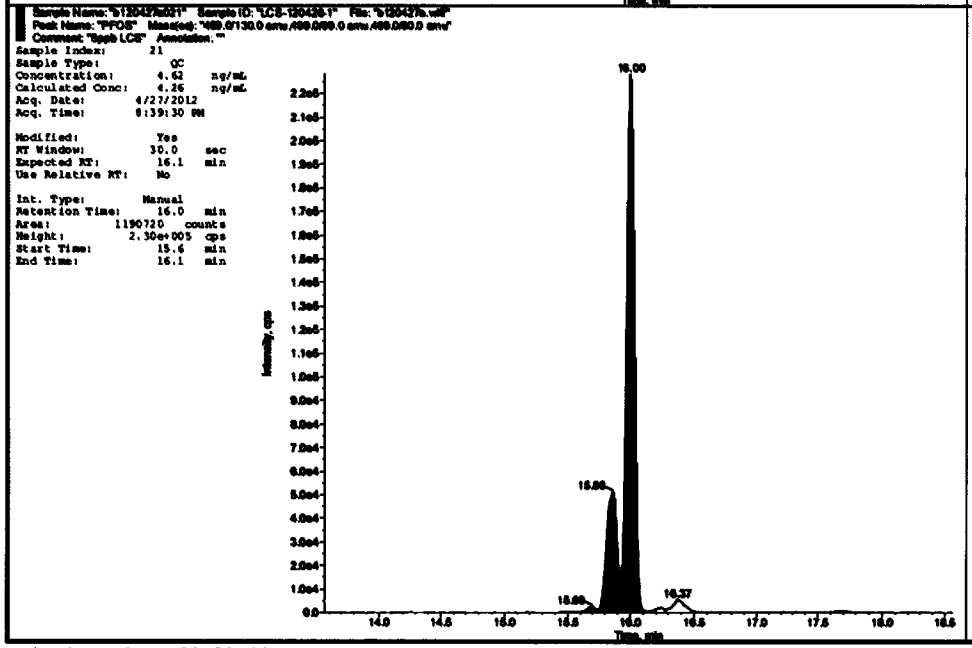
*** Buster J2930203

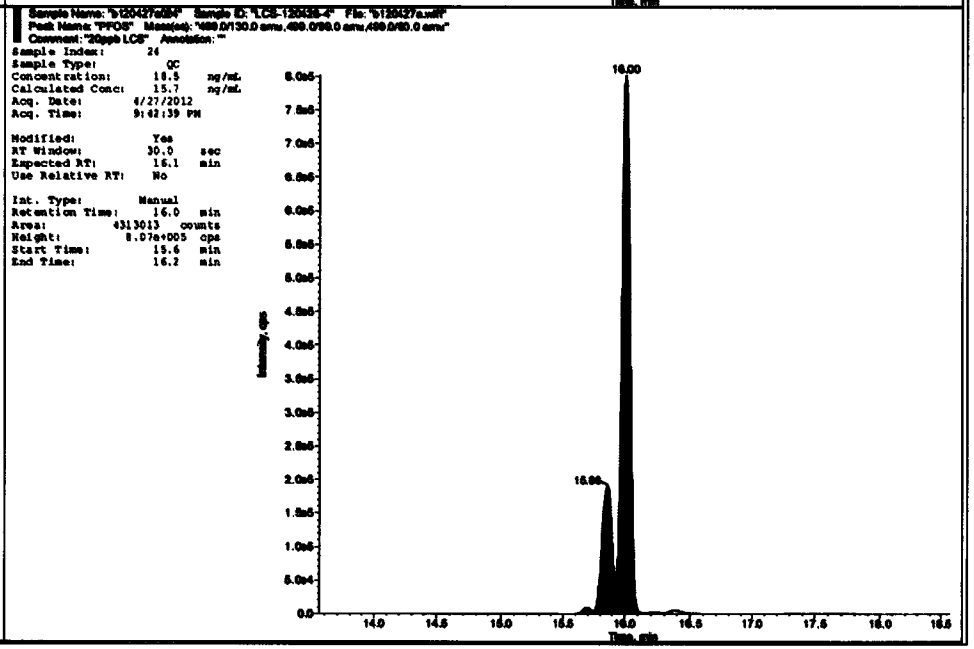


Printing Time: 11:31:04 AM
Printing Date: Wednesday, May 09, 2012


Sample Index: 12
Sample Type: Standard
Concentration: 9.28 ng/mL
Calculated Conc: 9.65 ng/mL
Acq. Date: 4/27/2012
Acq. Time: 5:30:22 PM
Modified: No
Proc. Algorithm: IntelliQuan - MQII
Noise Percentage: 95
Base. Sub. Window: 1.00 min
Peak-Split. Factor: 6
Report Largest Peak: Yes
Min. Peak Height: 0.00 cps
Min. Peak Width: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 16.1 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 16.0 min
Area: 2668335 counts
Height: 5.03e+005 cps
Start Time: 15.6 min
End Time: 16.1 min
16.00
15.83
Intensity, cps
Time, min


Sample Index: 20
Sample Type: Unknown
Concentration: N/A
Calculated Conc: < 0
Acq. Date: 4/27/2012
Acq. Time: 8:18:29 PM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 16.1 min
Use Relative RT: No
Int. Type: Manual
Retention Time: 16.0 min
Area: 4791 counts
Height: 7.78e+002 cps
Start Time: 15.8 min
End Time: 16.1 min
Intensity, cps
Time, min


Sample Index: 21
Sample Type: QC
Concentration: 4.62 ng/mL
Calculated Conc: 4.26 ng/mL
Acq. Date: 4/27/2012
Acq. Time: 8:39:30 PM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 16.1 min
Use Relative RT: No
Int. Type: Manual
Retention Time: 16.0 min
Area: 1190720 counts
Height: 2.30e+005 cps
Start Time: 15.6 min
End Time: 16.1 min
16.00
15.86
15.69
16.37
Intensity, cps
Time, min

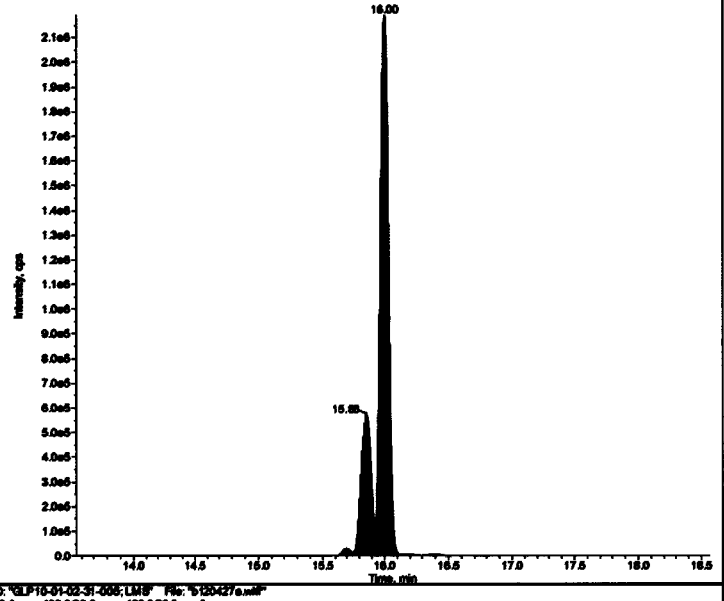

Sample Index: 24
Sample Type: QC
Concentration: 18.5 ng/mL
Calculated Conc: 15.7 ng/mL
Acq. Date: 4/27/2012
Acq. Time: 9:42:39 PM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 16.1 min
Use Relative RT: No
Int. Type: Manual
Retention Time: 16.0 min
Area: 4313013 counts
Height: 8.07e+005 cps
Start Time: 15.6 min
End Time: 16.2 min
16.00
15.86
Intensity, cps
Time, min

Sample Name: "b120427b027" Sample ID: "LCS-120430-7" File: "b120427a.wiff"
Peak Name: "PFOS" Mass(es): "499.0/130.0 amu,499.0/99.0 amu,499.0/80.0 amu"
Comment: "50ppb LCS" Annotation: ""

Sample Index: 27
Sample Type: QC
Concentration: 46.2 ng/mL
Calculated Conc: 46.3 ng/mL
Acq. Date: 4/27/2012
Acq. Time: 10:45:36 PM

Modified: Yes
RT Window: 30.0 sec
Expected RT: 16.1 min
Use Relative RT: No

Int. Type: Manual
Retention Time: 16.0 min
Area: 12177430 counts
Height: 2.20e+006 cps
Start Time: 15.6 min
End Time: 16.2 min

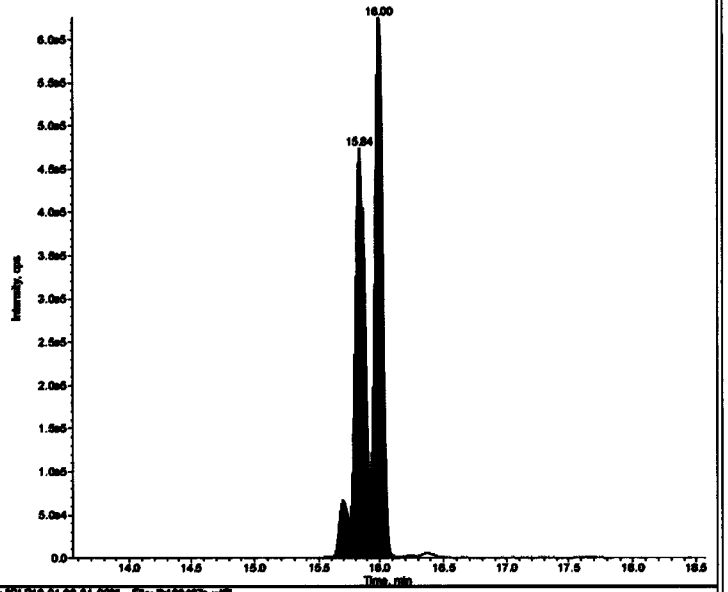


Sample Name: "b120427a034" Sample ID: "GLP10-01-02-31-005" File: "b120427a.wiff"
Peak Name: "PFOS" Mass(es): "499.0/130.0 amu,499.0/99.0 amu,499.0/80.0 amu"
Comment: "DAL-GW-TW2R-0 (dil 1:50)" Annotation: ""

Sample Index: 34
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 995. ng/mL
Acq. Date: 4/28/2012
Acq. Time: 1:12:43 AM

Modified: Yes
RT Window: 30.0 sec
Expected RT: 16.1 min
Use Relative RT: No

Int. Type: Manual
Retention Time: 16.0 min
Area: 5421689 counts
Height: 6.29e+005 cps
Start Time: 15.5 min
End Time: 16.2 min

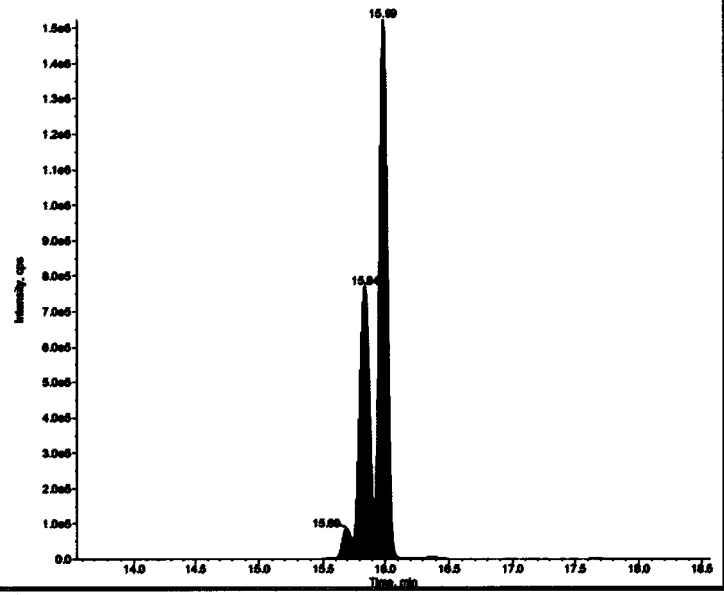


Sample Name: "b120427b039" Sample ID: "GLP10-01-02-31-006;LMS" File: "b120427a.wiff"
Peak Name: "PFOS" Mass(es): "499.0/130.0 amu,499.0/99.0 amu,499.0/80.0 amu"
Comment: "DAL-GW-TW2R-0 LMS (dil 1:50)" Annotation: ""

Sample Index: 36
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 2020. ng/mL
Acq. Date: 4/28/2012
Acq. Time: 1:54:50 AM

Modified: Yes
RT Window: 30.0 sec
Expected RT: 16.1 min
Use Relative RT: No

Int. Type: Manual
Retention Time: 16.0 min
Area: 10706006 counts
Height: 1.53e+006 cps
Start Time: 15.5 min
End Time: 16.1 min

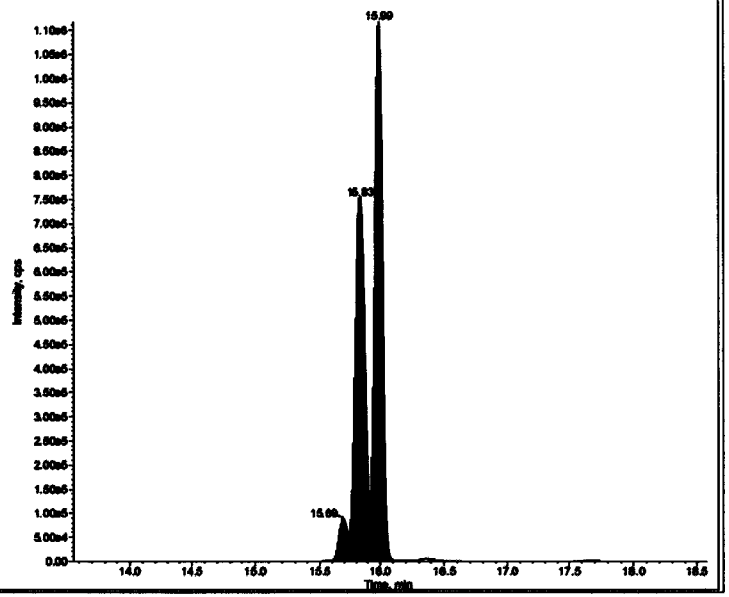


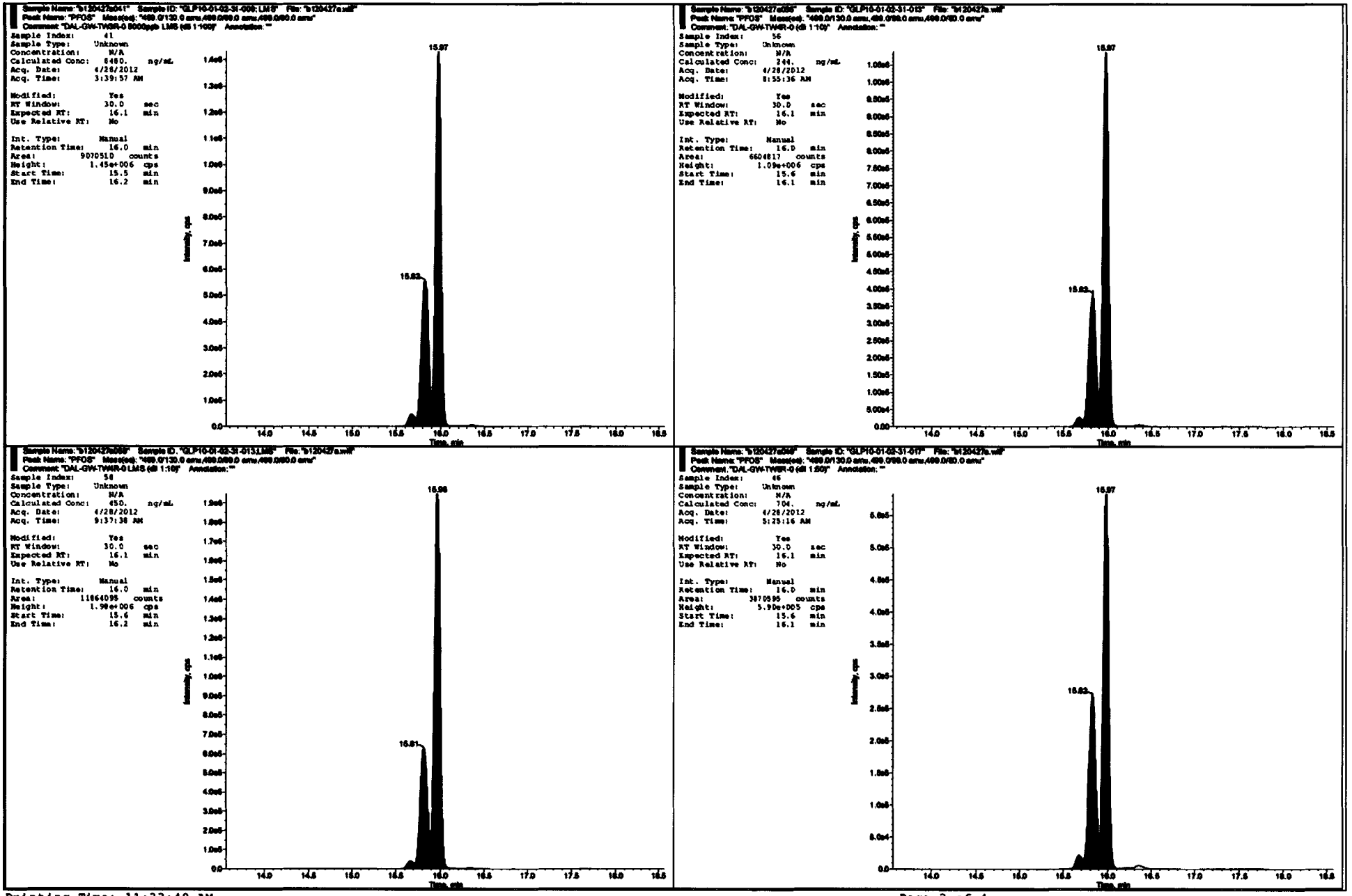
Sample Name: "b120427a035" Sample ID: "GLP10-01-02-31-009" File: "b120427a.wiff"
Peak Name: "PFOS" Mass(es): "499.0/130.0 amu,499.0/99.0 amu,499.0/80.0 amu"
Comment: "DAL-GW-TW3R-0 (dil 1:100)" Annotation: ""

Sample Index: 38
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 3340. ng/mL
Acq. Date: 4/28/2012
Acq. Time: 2:36:55 AM

Modified: Yes
RT Window: 30.0 sec
Expected RT: 16.1 min
Use Relative RT: No

Int. Type: Manual
Retention Time: 16.0 min
Area: 8941101 counts
Height: 1.12e+006 cps
Start Time: 15.5 min
End Time: 16.1 min



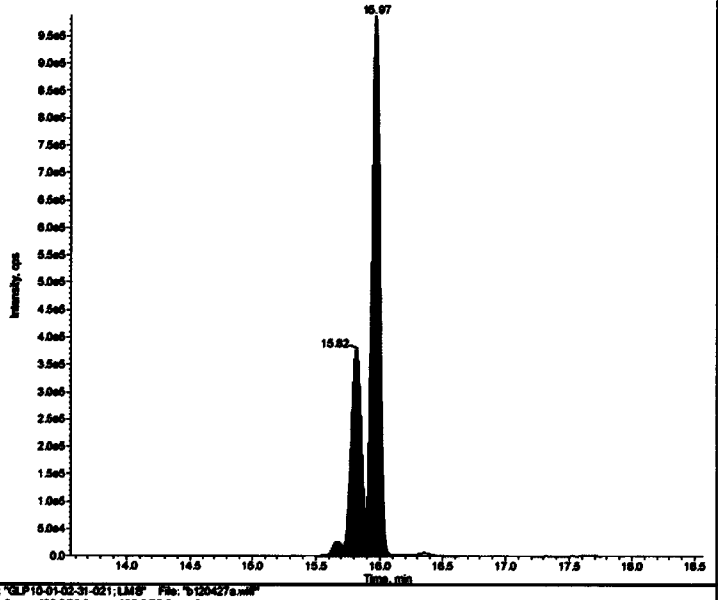

Sample Index: 41
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 5480. ng/mL
Acq. Date: 4/26/2012
Acq. Time: 3:39:57 AM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 16.1 min
Use Relative RT: No
Int. Type: Manual
Retention Time: 16.0 min
Area: 9070510 counts
Height: 1.45e+006 cps
Start Time: 15.5 min
End Time: 16.2 min
15.97
15.83
Intensity, cps
Time, min
Sample Index: 56
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 244. ng/mL
Acq. Date: 4/26/2012
Acq. Time: 8:55:36 AM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 16.1 min
Use Relative RT: No
Int. Type: Manual
Retention Time: 16.0 min
Area: 6604817 counts
Height: 1.09e+006 cps
Start Time: 15.6 min
End Time: 16.1 min
15.97
15.83
Intensity, cps
Time, min
Sample Index: 58
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 450. ng/mL
Acq. Date: 4/26/2012
Acq. Time: 9:37:38 AM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 16.1 min
Use Relative RT: No
Int. Type: Manual
Retention Time: 16.0 min
Area: 11664095 counts
Height: 1.98e+006 cps
Start Time: 15.6 min
End Time: 16.2 min
15.98
16.81
Intensity, cps
Time, min
Sample Index: 66
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 704. ng/mL
Acq. Date: 4/26/2012
Acq. Time: 5:25:16 AM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 16.1 min
Use Relative RT: No
Int. Type: Manual
Retention Time: 16.0 min
Area: 3870895 counts
Height: 5.90e+005 cps
Start Time: 15.6 min
End Time: 16.1 min
15.97
15.83
Intensity, cps
Time, min

Sample Name: "b120427s046" Sample ID: "GLP10-01-02-31-017; LMS" File: "b120427a.wiff"
Peak Name: "PFOS" Mass(es): "499.0/130.0 amu,499.0/99.0 amu,499.0/80.0 amu"
Comment: "DAL-GW-TWER-0 LMS (dil 1:50)" Annotation: ""

Sample Index: 48
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 1120. ng/mL
Acq. Date: 4/28/2012
Acq. Time: 6:07:16 AM

Modified: Yes
RT Window: 30.0 sec
Expected RT: 16.1 min
Use Relative RT: No

Int. Type: Manual
Retention Time: 16.0 min
Area: 6078162 counts
Height: 9.88e+005 cps
Start Time: 15.5 min
End Time: 16.1 min

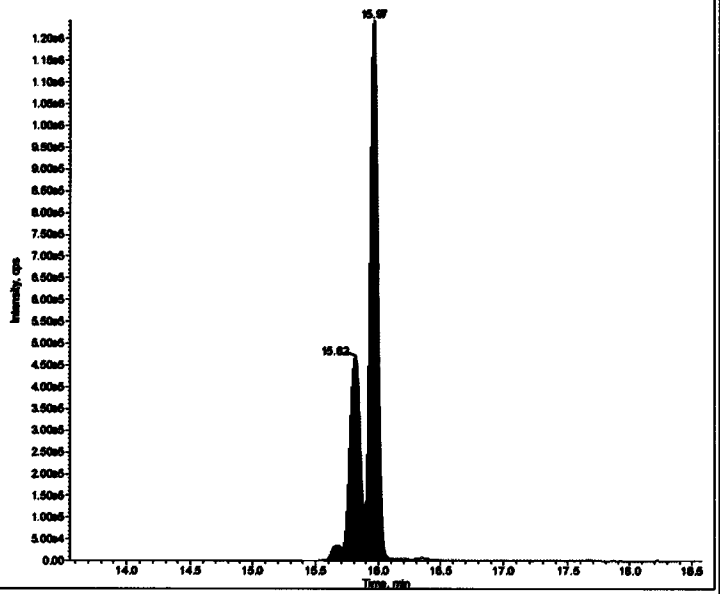


Sample Name: "b120427s050" Sample ID: "GLP10-01-02-31-021" File: "b120427a.wiff"
Peak Name: "PFOS" Mass(es): "499.0/130.0 amu,499.0/99.0 amu,499.0/80.0 amu"
Comment: "DAL-GW-TWER-0 (dil 1:10)" Annotation: ""

Sample Index: 50
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 287. ng/mL
Acq. Date: 4/28/2012
Acq. Time: 6:49:24 AM

Modified: Yes
RT Window: 30.0 sec
Expected RT: 16.1 min
Use Relative RT: No

Int. Type: Manual
Retention Time: 16.0 min
Area: 7742598 counts
Height: 1.25e+006 cps
Start Time: 15.6 min
End Time: 16.1 min

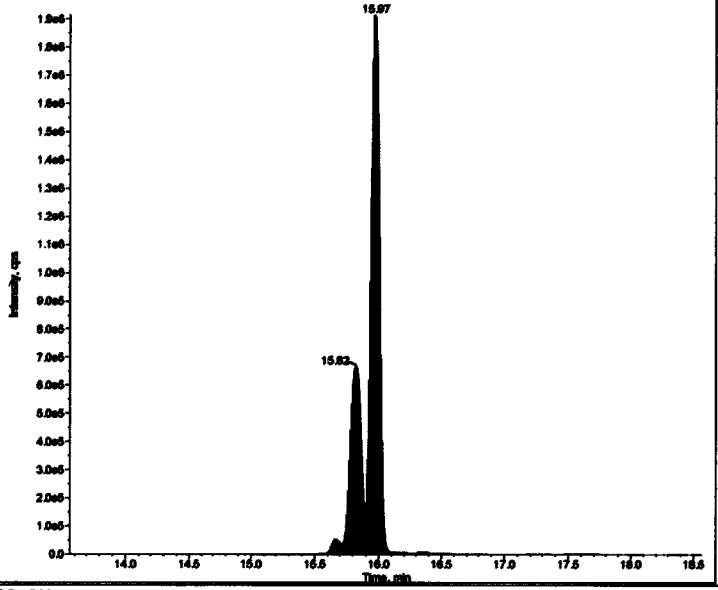


Sample Name: "b120427s052" Sample ID: "GLP10-01-02-31-021; LMS" File: "b120427a.wiff"
Peak Name: "PFOS" Mass(es): "499.0/130.0 amu,499.0/99.0 amu,499.0/80.0 amu"
Comment: "DAL-GW-TWER-0 LMS (dil 1:10)" Annotation: ""

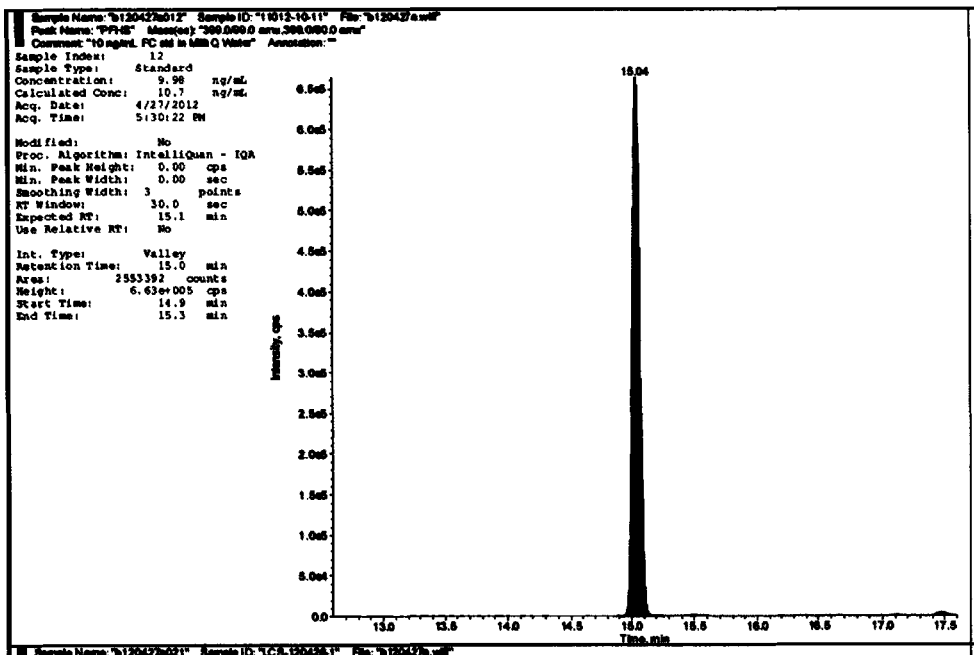
Sample Index: 52
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 456. ng/mL
Acq. Date: 4/28/2012
Acq. Time: 7:31:25 AM

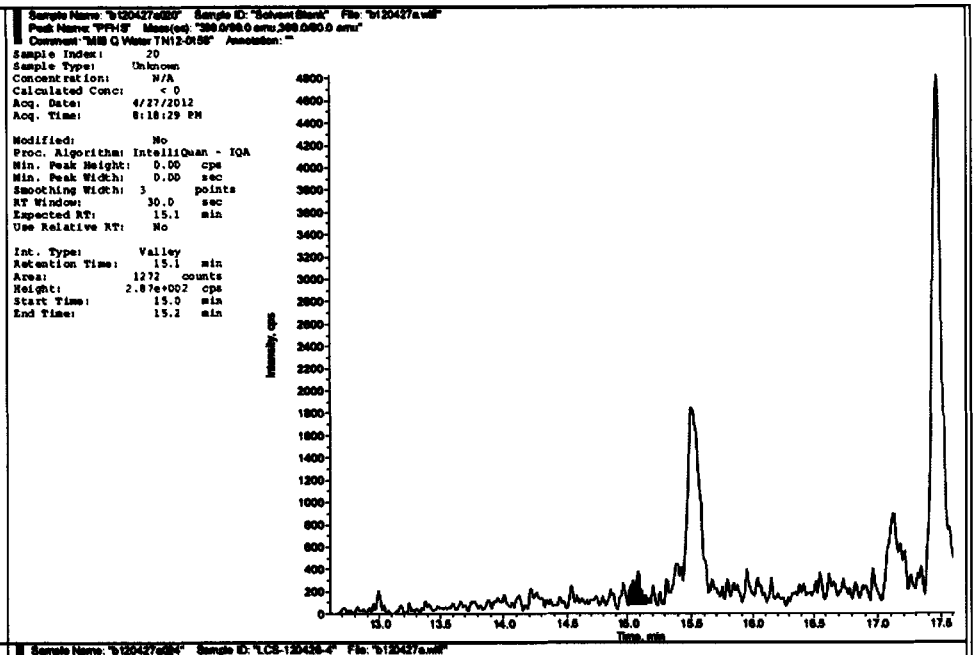
Modified: Yes
RT Window: 30.0 sec
Expected RT: 16.1 min
Use Relative RT: No

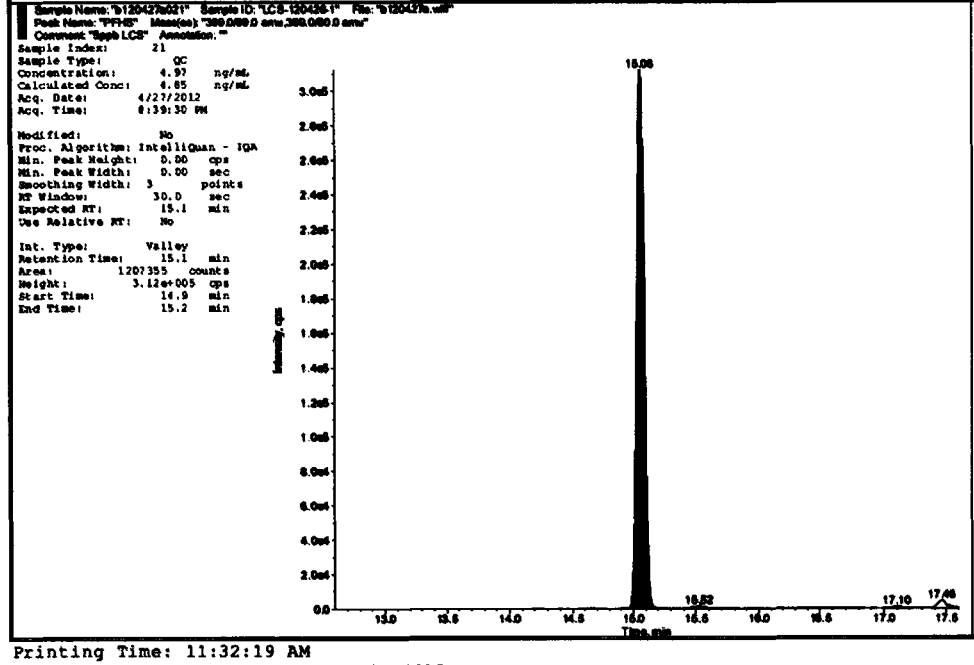
Int. Type: Manual
Retention Time: 16.0 min
Area: 12003443 counts
Height: 1.93e+006 cps
Start Time: 15.5 min
End Time: 16.1 min

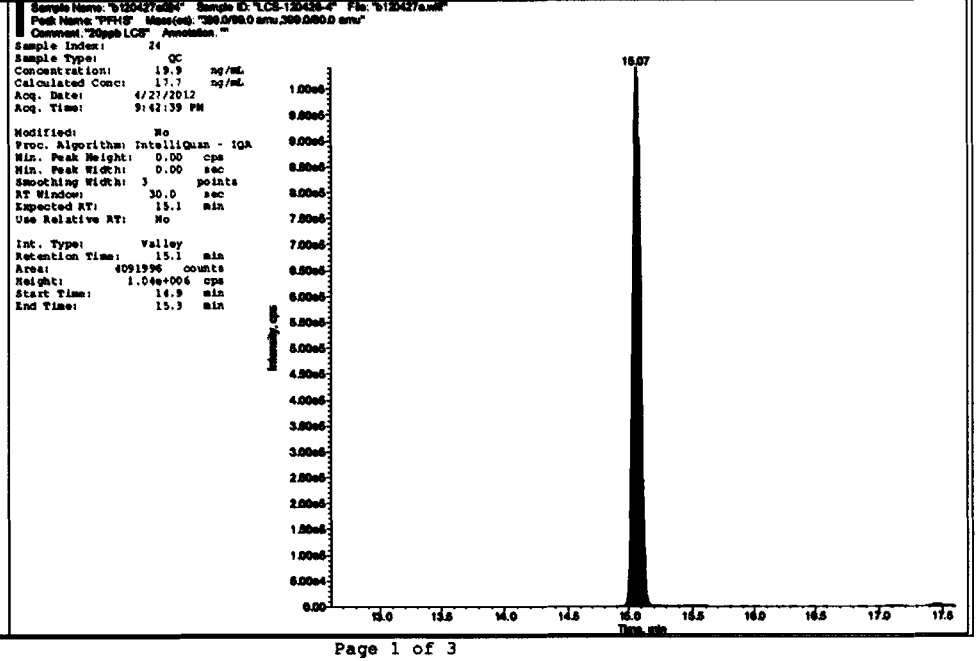


Printing Time: 11:33:49 AM
Printing Date: Wednesday, May 09, 2012


Sample Name: "b120427b012" Sample ID: "1012-10-11" File: "b120427a.wiff"
Peak Name: "PFHS" Mass(es): "399.0/99.0 amu,399.0/80.0 amu"
Comment: "10 ng/mL FC std in Milli Q Water" Annotation: ""
Sample Index: 12
Sample Type: Standard
Concentration: 9.98 ng/mL
Calculated Conc: 10.7 ng/mL
Acq. Date: 4/27/2012
Acq. Time: 5:30:22 PM
Modified: No
Proc. Algorithm: IntelliQuan - IQA
Min. Peak Height: 0.00 cps
Min. Peak Width: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 15.1 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 15.0 min
Area: 2553392 counts
Height: 6.63e+005 cps
Start Time: 14.9 min
End Time: 15.3 min
15.04
Intensity, cps
Time, min


Sample Name: "b120427a020" Sample ID: "Solvent Blank" File: "b120427a.wiff"
Peak Name: "PFHS" Mass(es): "399.0/99.0 amu,399.0/80.0 amu"
Comment: "Milli Q Water TN12-0156" Annotation: ""
Sample Index: 20
Sample Type: Unknown
Concentration: N/A
Calculated Conc: < 0
Acq. Date: 4/27/2012
Acq. Time: 8:18:29 PM
Modified: No
Proc. Algorithm: IntelliQuan - IQA
Min. Peak Height: 0.00 cps
Min. Peak Width: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 15.1 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 15.1 min
Area: 1272 counts
Height: 2.87e+002 cps
Start Time: 15.0 min
End Time: 15.2 min
Intensity, cps
Time, min

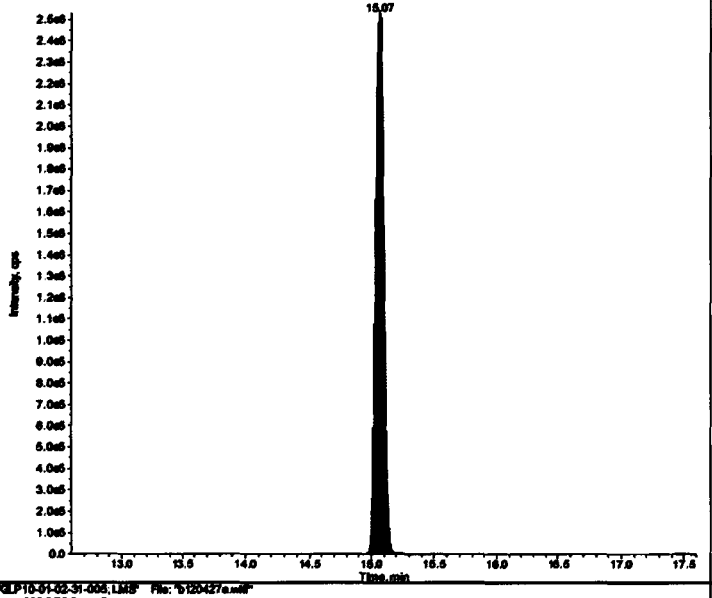

Sample Name: "b120427b021" Sample ID: "LCS-120426-1" File: "b120427b.wiff"
Peak Name: "PFHS" Mass(es): "399.0/99.0 amu,399.0/80.0 amu"
Comment: "5ppb LCS" Annotation: ""
Sample Index: 21
Sample Type: QC
Concentration: 4.97 ng/mL
Calculated Conc: 4.85 ng/mL
Acq. Date: 4/27/2012
Acq. Time: 8:39:30 PM
Modified: No
Proc. Algorithm: IntelliQuan - IQA
Min. Peak Height: 0.00 cps
Min. Peak Width: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 15.1 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 15.1 min
Area: 1207355 counts
Height: 3.12e+005 cps
Start Time: 14.9 min
End Time: 15.2 min
15.06
16.82
17.10
17.46
Intensity, cps
Time, min


Sample Name: "b120427a024" Sample ID: "LCS-120426-4" File: "b120427a.wiff"
Peak Name: "PFHS" Mass(es): "399.0/99.0 amu,399.0/80.0 amu"
Comment: "20ppb LCS" Annotation: ""
Sample Index: 24
Sample Type: QC
Concentration: 19.9 ng/mL
Calculated Conc: 17.7 ng/mL
Acq. Date: 4/27/2012
Acq. Time: 9:42:39 PM
Modified: No
Proc. Algorithm: IntelliQuan - IQA
Min. Peak Height: 0.00 cps
Min. Peak Width: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 15.1 min
Use Relative RT: No
Int. Type: Valley
Retention Time: 15.1 min
Area: 4091996 counts
Height: 1.04e+006 cps
Start Time: 14.9 min
End Time: 15.3 min
15.07
Intensity, cps
Time, min

Peak Name: "PFHS" Mass(es): "399.0/80.0 amu,399.0/80.0 amu"
Comment: "50ppb LCS" Annotation: ""
Sample Index: 27
Sample Type: QC
Concentration: 49.7 ng/mL
Calculated Conc: 49.1 ng/mL
Acq. Date: 4/27/2012
Acq. Time: 10:45:36 PM

Modified: No
Proc. Algorithm: IntelliQuan - IQA
Min. Peak Height: 0.00 cps
Min. Peak Width: 0.00 sec
Smoothing Width: 3 points
RT Window: 30.0 sec
Expected RT: 15.1 min
Use Relative RT: No

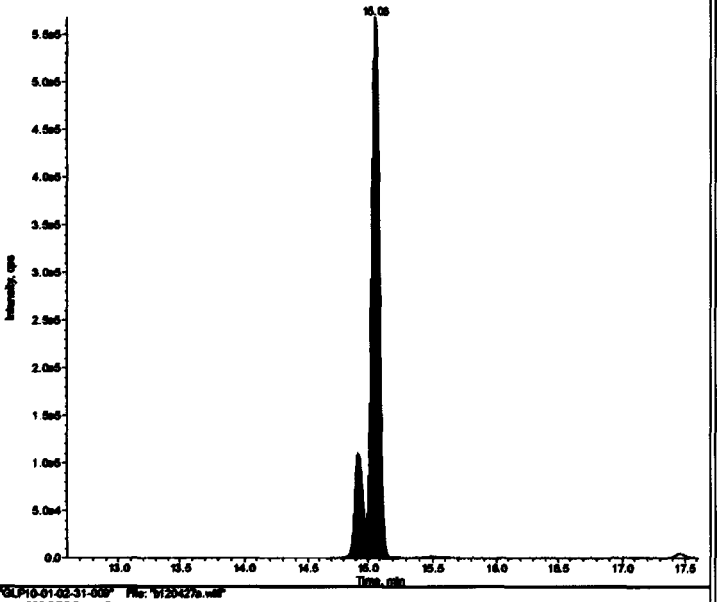
Int. Type: Valley
Retention Time: 15.1 min
Area: 10271750 counts
Height: 2.53e+006 cps
Start Time: 14.9 min
End Time: 15.3 min



Peak Name: "PFHS" Mass(es): "399.0/80.0 amu,399.0/80.0 amu"
Comment: "DAL-GW-TW2R-0 (dil 1:50)" Annotation: ""
Sample Index: 34
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 563. ng/mL
Acq. Date: 4/28/2012
Acq. Time: 1:12:43 AM

Modified: Yes
RT Window: 30.0 sec
Expected RT: 15.1 min
Use Relative RT: No

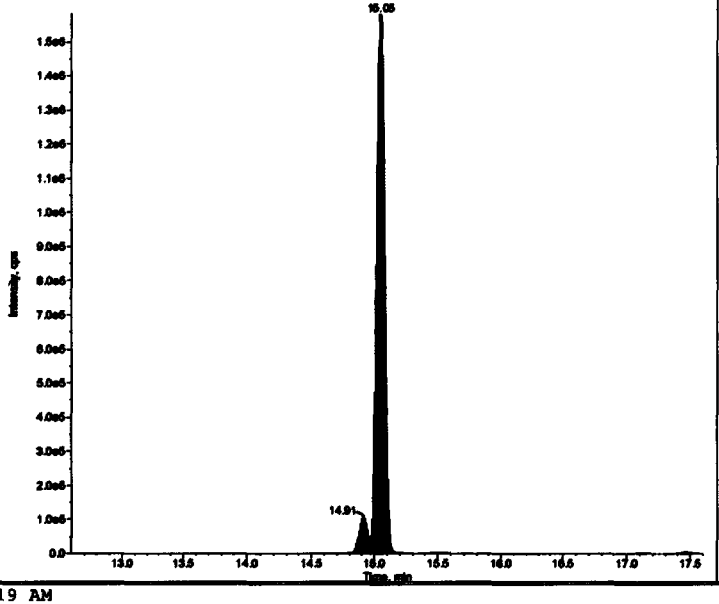
Int. Type: Manual
Retention Time: 15.1 min
Area: 2678296 counts
Height: 5.68e+005 cps
Start Time: 14.8 min
End Time: 15.2 min



Peak Name: "PFHS" Mass(es): "399.0/80.0 amu,399.0/80.0 amu"
Comment: "DAL-GW-TW2R-0 LMS (dil 1:50)" Annotation: ""
Sample Index: 36
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 1520. ng/mL
Acq. Date: 4/28/2012
Acq. Time: 1:54:50 AM

Modified: Yes
RT Window: 30.0 sec
Expected RT: 15.1 min
Use Relative RT: No

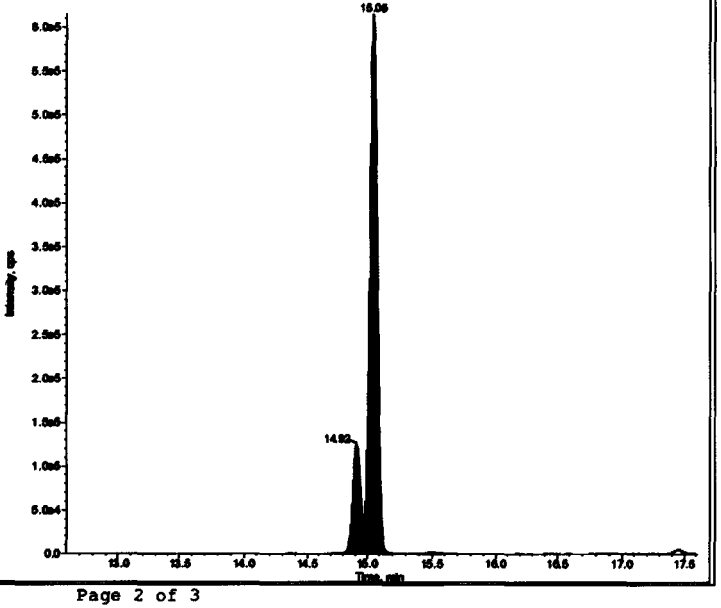
Int. Type: Manual
Retention Time: 15.0 min
Area: 6734170 counts
Height: 1.60e+006 cps
Start Time: 14.8 min
End Time: 15.2 min



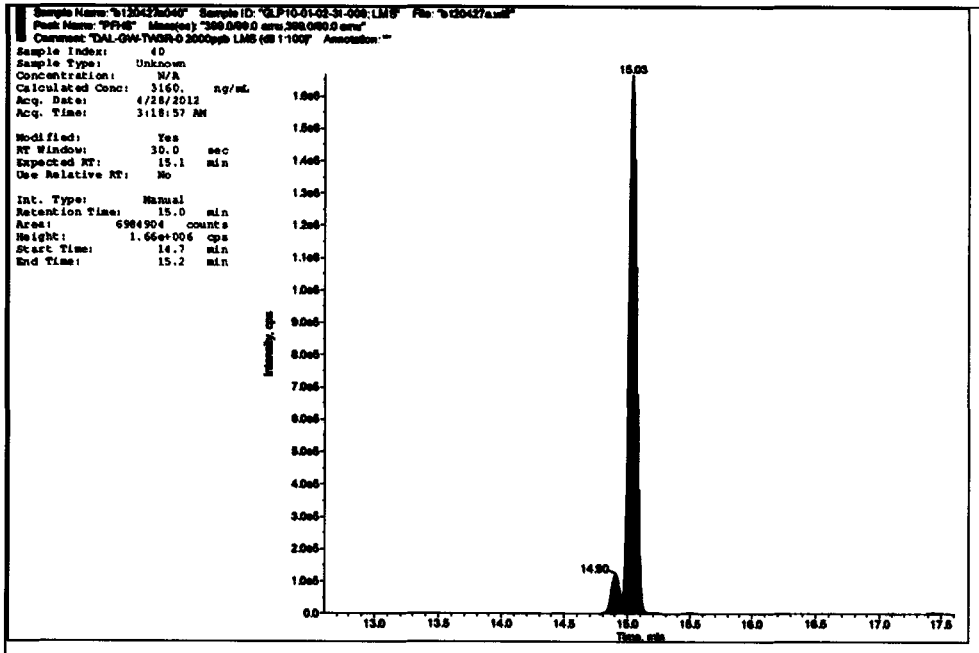
Peak Name: "PFHS" Mass(es): "399.0/80.0 amu,399.0/80.0 amu"
Comment: "DAL-GW-TW3R-0 (dil 1:100)" Annotation: ""
Sample Index: 38
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 1210. ng/mL
Acq. Date: 4/28/2012
Acq. Time: 2:36:55 AM

Modified: Yes
RT Window: 30.0 sec
Expected RT: 15.1 min
Use Relative RT: No

Int. Type: Manual
Retention Time: 15.1 min
Area: 2858749 counts
Height: 6.16e+005 cps
Start Time: 14.8 min
End Time: 15.2 min



Printing Time: 11:32:19 AM
Printing Date: Wednesday, May 09, 2012


Sample Index: 40
Sample Type: Unknown
Concentration: N/A
Calculated Conc: 3160. ng/mL
Acq. Date: 4/28/2012
Acq. Time: 3:18:57 AM
Modified: Yes
RT Window: 30.0 sec
Expected RT: 15.1 min
Use Relative RT: No
Int. Type: Manual
Retention Time: 15.0 min
Area: 6904904 counts
Height: 1.66e+006 cps
Start Time: 14.7 min
End Time: 15.2 min
15.03
14.90
Time, min

ATTACHMENT C: ANALYTICAL METHOD(S)

3M Environmental Laboratory

Method

Method of Analysis for the Determination of Perfluorinated Compounds in Water by LC/MS/MS; Direct Injection Analysis

Method Number: ETS-8-044.1

Adoption Date: 4/12/07

Effective Date: 11/9/11

Approved By:

9 NOV 2011

William K. Reagen, Technical Director, Environmental Laboratory — Date

1 Scope and Application

This method describes the direct injection analysis of perfluorinated compounds (PFCs) from water matrices using high-performance liquid chromatography tandem mass spectrometry (HPLC/MS/MS). The method is generally applicable but not limited to the measurement of perfluoroalkyl sulfonamides and perfluorinated alkyl acids (PFAAs) such as perfluorosulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs) (Table 1). Water samples containing heavy particulate may require preparation by an alternate method such as ETS-8-154 "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates In Water By Solid Phase Extraction and High Performance Liquid Chromatography/Mass Spectrometry". The method is applicable to both external standard and internal standard calibration[1].

Table 1. Representative Target Analytes

Acronym	*Analyte*	*Chemical Abstract Services Registry Number (CASRN)*
PFBA (C4 Acid)	Perfluorobutanoic acid	375-22-4
PFPeA (C5 Acid)	Perfluoropentanoic acid	2706-90-3
PFHxA (C6 Acid)	Perfluorohexanoic acid	307-24-4
PFHpA (C7 Acid)	Perfluoroheptanoic acid	375-85-9
PFOA (C8 Acid)	Perfluorooctanoic acid	335-67-1
PFNA (C9 Acid)	Perfluorononanoic acid	375-95-1
PFDA (C10 Acid)	Perfluorodecanoic acid	335-76-2
PFUnA (C11 Acid)	Perfluoroundecanoic acid	2058-94-8
PFDoA (C12 Acid)	Perfluorododecanoic acid	307-55-1
PFTrDA (C13 Acid)	Perfluorotridecanoic acid	72629-94-8
PFBS (C4 Sulfonate)	Perfluorobutanesulfonic acid	375-73-5
PFHS (C6 Sulfonate)	Perfluorohexanesulfonic acid	355-46-4
PFOS (C8 Sulfonate)	Perfluorooctanesulfonic acid	1763-23-1
FBSA (C4 Sulfonamide	Perfluorobutanesulfonamide	30334-69-1
FOSA (C8 Sulfonamide)	Pefluorooctanesulfonamide	754-91-6

The Minimum Reporting Level (MRL) is the Limit of Quantitation (LOQ) that meets Data Quality Objectives (DQOs) that are developed based on the intended use of this method.

Method Flexibility – This is a performance-based method and may be generally applied to the determination of perfluorinated compounds in water matrices when analysis batch quality control (QC) criteria are met[2]. Each set of samples are prepared in an analysis batch with calibration standards, LCSs, blanks, and continuing calibration check standards analyzed on the same instrument during a time period that begins and ends with the analysis of the appropriate continuing calibration check standards. The laboratory is permitted to modify the LC column, mobile phase composition, LC conditions, and MS/MS conditions. Method modifications should be considered to improve method performance or to meet data quality objectives for the study. In all cases where method modifications are implemented, the batch

[1] The method is supported by validation with internal standard calibration for C4-C13 PFCAs, C4, C6, and C8 PFSAs, and C8 perfluoroalkane sulfonamide in laboratory control samples under 3M method validation E11-0667.

[2] Guidance for establishing method QC Criteria based on a.) FDA May 2001, "Guidance for Industry, Bioanalytical Method Validation", b.) EPA Method 537, and c.) European Commission: Guidance for Generating and Reporting Methods of Analysis in Support of Pre-registration Data Requirements for Annex II (Part A, section 4) and Annex III (Part A,section 5) of Directive 91/414, SANCO/3029/99 rev. 4 (11/07/00).

analytical QCs (section 9) must be completed and pass QC acceptance criteria (section 13) if the data from the analytical batch are to be reported.

2 Method Summary

Water samples are analyzed as neat aqueous sample or as solvent diluted aqueous samples by direct injection using LC/MS/MS. Samples containing heavy particulate may not be suitable for analysis by this method. Samples containing suspended particulate should be centrifuged or filtered prior to removing a sample aliquot or diluting with solvent. The water sample is mixed well prior to removing an aliquot or diluting, if necessary, with ASTM Type I water, HPLC water, other suitable water, or solvent (methanol).

Quantitation is by stable isotope internal standard calibration in laboratory reagent water. All perfluorinated compounds (PFCs) target analyte concentrations of perfluorosulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs) are reported as anions and corrected for their salt or free acid forms. Alternatively, quantitation may be performed by external standard calibration.

This is a performance-based method. Method uncertainty for each target analyte is determined for each analytical batch using multiple laboratory control spikes at multiple concentrations. This method also requires that the precision and accuracy for each sample be determined using field matrix spikes to verify that the method is applicable to each sample matrix.

Calibration standards for PFUnA, PFDoA, PFTrDA, and FOSA have been found to be unstable for more than 2 days in 100% water. Samples requiring analysis for these compounds by this method should be diluted 1:1 with methanol and analyzed against a calibration curve prepared in 1:1 synthetic groundwater:MeOH.

3 Definitions

3.1 Analysis Batch

A set of study samples that are prepared with calibration standards, laboratory control samples, and procedural blanks, and analyzed on the same instrument during a time period that begins and ends with the analysis of the appropriate continuing calibration check standards.

3.2 Analytical Sample

A portion of a laboratory sample prepared for analysis.

3.3 Calibration Standard

A solution prepared by spiking a known volume of the Working Standard (WS) into a predetermined amount of ASTM Type I, HPLC grade water, or other suitable water (i.e. matrix water), and analyzed according to this method. Calibration standards are used to calibrate the instrument response with respect to analyte concentration.

3.4 Laboratory Duplicate Sample (LDS, or Lab Dup)

A laboratory duplicate sample is a separate aliquot of a sample taken in the analytical laboratory that is analyzed separately with identical procedures. Analysis of LDSs 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.

3.5 Field Blank (FB)/Trip Blank (TB)

ASTM Type I, HPLC grade water, or other suitable 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 TB is to determine if test substances or other interferences are present in the field environment. This sample is also referred to as a Trip Blank.

3.6 Field Duplicate Sample (FDS, Field Dup)

A sample collected in duplicate at the same time from the same location as the sample. The FDS is handled under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analysis of the FDS 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.

3.7 Field Matrix Spike (FMS)

A sample to which known quantities of the target analytes, ISs and SRSs are added to the sample bottle in the laboratory before the bottles are sent to the field for collection of aqueous samples. A known, specific volume of sample must be added to the 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 is analyzed to ascertain if any matrix effects, interferences, or stability issues may complicate the interpretation of the sample analysis.

3.8 Trip Blank Matrix Spike (TBMS)

An aliquot of ASTM Type I, HPLC grade water, or other suitable water, to which known quantities of the target analytes, ISs and SRSs are added in the laboratory prior to the shipment of the collection bottles. The TBMS is analyzed exactly like a study sample to help determine if the method is in control and whether a loss of analyte or analytical bias could be attributed to sample holding time, sample storage and/or shipment issues. A low and high TBMS are appropriate when expected sample concentrations are not known or may vary.

3.9 Internal Standard (IS)

A compound added to each study sample, calibration standard, laboratory control samples, and procedural blanks at a consistent level (typically around 1 ng/mL). The internal standard(s) are stable isotope labeled versions of the target analytes. The area count ratio of the target analyte to the internal standard is used for calibration. Surrogate ISs are applied when stable isotope ISs of target analytes are unavailable. A surrogate IS is not necessarily a stable isotope labeled version of the target analyte, but is treated as an internal standard for quantitation.

3.10 Laboratory Control Sample (LCS)

An aliquot of control matrix to which known quantities of the target analytes, ISs and SRSs (when applicable) are added in the laboratory at the time when samples are aliquotted. At least three levels (two levels for SRSs) in triplicate are included, one generally at the low end of the calibration curve and one near the mid range and the upper end of the curve. The LCSs are analyzed exactly like a laboratory sample to determine whether the stability of the standards. LCSs should be prepared each day samples are aliquoted.

3.11 Laboratory Matrix Spike (LMS)

A laboratory matrix spike is an aliquot of a sample to which known quantities of target analytes, ISs and SRSs (when applicable) are added in the laboratory. The LMS is analyzed exactly like a laboratory sample to determine whether the sample matrix contributes bias to the analytical results. The endogenous concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LMS corrected for these concentrations. LMSs are optional for analysis of aqueous samples.

3.12 Laboratory Sample

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

3.13 Limit of Quantitation (LOQ)

The lower limit of quantitation (LLOQ) for an analytical batch is the lowest concentration that can be reliably quantitated within the specified limits of precision and accuracy. The LLOQ is generally selected as the lowest non-zero standard in the calibration curve that meets method acceptance criteria. The LLOQ for each target analyte is established for each analysis batch as the lowest calibration standard with area counts at least twice that of the average area counts of the procedural blanks.

The upper limit of quantitation (ULOQ) for an analytical batch is the highest concentration that can be reliably quantitated within the specified limits of precision and accuracy. The highest standard in the calibration curve that meets method acceptance criteria is defined as the ULOQ.

3.14 Method/Procedural Blank

An aliquot of control matrix 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.

3.15 Sample

A sample is an aliquot removed from a larger quantity of material intended to represent the original source material.

3.16 Stock Standard Solution (SSS)

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

3.17 Surrogate Internal Standard

An IS that is not necessarily a stable isotopically labeled target analyte, but is treated as an internal standard for quantitation. Surrogate ISs are used when isotopically labeled counterparts of the target analyte are not commercially or readily available.

3.18 Surrogate Recovery Standard (SRS)

An isotopically labeled standard, not used as an internal standard, that is added to each sample and appropriate QC sample as a means to evaluate the method performance for a chemical class of compounds (e.g., PFSAs, PFCAs).

3.19 Working Standard (WS)

A solution of several analytes prepared in the laboratory from SSSs 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. The analyst should wear gloves, a lab coat, and safety glasses to prevent exposure to chemicals that might be present.

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

The analyst must be familiar with the laboratory equipment and potential hazards including, but not limited to, the use of solvents, pressurized gas and solvent lines, high voltage, and vacuum systems. Refer to the appropriate equipment procedure or operator manual for additional information and cautions.

5 Interferences

During sample preparation and analysis, major potential contaminant sources are reagents and glassware. 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 or minimized 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

6.1 Instrumentation

Analytical balance capable of reading to 0.0001g

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

6.2 Supplies and Materials

Sample collection bottles—HDPE (e.g., Nalgene™) wide-mouth bottles with screw cap.
Note: Do not use fluorinated or Teflon® bottles or lined caps.

Coolers or boxes for sample shipment.

15-mL and 50-mL disposable polypropylene centrifuge tubes.

Class A pipettes and volumetric flasks, various.

2 mL HPLC autovials

Disposable pipettes, polypropylene or glass as appropriate

Centrifuge capable of spinning 15-mL and 50-mL polypropylene tubes at 3000 rpm.

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

Water – Milli-Q, HPLC grade, or other suitably appropriate sources

Calcium Acetate - A.C.S. Reagent Grade

Magnesium Acetate - A.C.S. Reagent Grade

Methanol – HPLC grade

Ammonium Acetate – A.C.S. Reagent Grade

7.2 Representative Target Analytes, ISs, and SRSs

PFBA, Heptafluorobutyric Acid, (C_4 Perfluorinated Acid)

PFPeA, Nonafluoropentanoic Acid (C_5 Perfluorinated Acid)

PFHxA, Perfluorohexanoic Acid (C_6 Perfluorinated Acid)

PFHpA, Tridecafluoroheptanoic Acid, (C_7 Perfluorinated Acid)

PFOA, Ammonium perfluorooctanoate, (C_8 Perfluorinated Acid)

PFNA, Heptadecafluorononanoic Acid, (C_9 Perfluorinated Acid)

PFDA, Nonadecafluorodecanoic Acid (C_{10} Perfluorinated Acid)

PFUnA, Perfluoroundecanoic Acid, (C_{11} Perfluorinated Acid)

PFDoA, Perfluorododecanoic Acid, (C_{12} Perfluorinated Acid)

PFTrDA, Perfluorotridecanoic Acid, (C_{13} Perfluorinated Acid)

FBSA, Perfluorobutanesulfonamide

FOSA, Perfluorooctanesulfonylamide

PFBS, Potassium Perfluorobutanesulfonate

PFHS, Perfluorohexanesulfonate

PFOS, Potassium perfluorooctanesulfonate

PFOA [1,2, 3, 4-^{13}C], $^{13}C_4$-isotopically labeled perfluorooctanoic acid (SRS)

PFOS [1,2, 3, 4-^{13}C], $^{13}C_4$-isotopically labeled Perfluorooctanesulfonate (SRS)

PFUnA [1,2-^{13}C], $^{13}C_2$-isotopically labeled Perfluoroundecanoic acid (SRS)

A custom mix of ISs in a methanolic solution containing ([1,2,3,4-$^{13}C_4$]PFBA, [1,2-$^{13}C_2$]PFHxA, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA, [1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA, [1,2-$^{13}C_2$]PFDA, [1,2,3,4,5,6,7-$^{13}C_7$]PFUnA, [1,2-$^{13}C_2$]PFDoA, [1,2,3-$^{13}C_3$]PFHS, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOS, and [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOSA (Wellington Laboratories, Guelph, ON) in combination with added ([1,2,3,4,5-$^{13}C_5$]PFPeA, ([1,2,3,4-$^{13}C_4$]PFHpA, and [$^{18}O_2$]PFBS can be used to prepare a stock IS solution. Alternatively, individual stable isotope ISs can be used to prepare a stock IS mixture.

Other ISs can be applied.

7.3 Reagent Preparation

2 mM Ammonium acetate solution (Analysis)—Weigh 0.3 g of Ammonium acetate and dissolve in 2.0 L of reagent water.

Synthetic Groundwater (containing 25 ppm Ca and Mg) – Weigh 0.61 g of Calcium Acetate and 0.92 g of Magnesium Acetate and dissolve in 6.0 L of reagent water.

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

7.4 Stock Standard Solution (SSS) and Working Standard Solution Preparation

The following standard preparation procedure serves as an example. Weighed amounts and final volumes 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.

100 µg/mL target analyte SSSs—Weigh out 10 mg of analytical standard ***(corrected for percent salt, acid [ETS-4-031] and purity)*** and dilute to 100 mL with methanol or other suitable solvent, in a 100 mL volumetric flask. Transfer to a 125 mL LDPE bottle or other suitable container. Prepare a separate solution for each analyte. Expiration dates and storage conditions of stock solutions should be assigned in accordance with laboratory standard operating procedure. An example of purity and salt correction is given below for PFOS.

$$\text{salt correction factor} = \frac{\text{molecular weight of anion}}{\text{moclecular weight of salt}}$$

$$\text{PFOS } (K^+)\text{salt correction factor} = \frac{499}{538} = 0.9275$$

10 mg $C_8F_{17}SO_3^-K^+$ with purity 90% = 8.35 mg $C_8F_{17}SO_3^-$ (10 mg*0.90*0.9275=8.35 mg)

10 µg/mL (10,000 ng/mL) mixed working standard—Add 5.0 mL each of the 100 µg/mL SSSs to a 50 mL volumetric flask and bring up to volume with solvent.

1 µg/mL (1,000 ng/mL) mixed working standard—Add 0.5 mL of the 100 µg/mL SSSs to a 50 mL volumetric flask and bring up to volume with solvent.

0.1 µg/mL (100 ng/mL) mixed standard—Add 0.05 mL of the 100 µg/mL SSSs to a 50 mL volumetric flask and bring up to volume with solvent.

Storage Conditions—Store all SSSs and working standards in accordance with laboratory standard operating procedure or in a refrigerator at 4°±2°C for a maximum period of 6 months from the date of preparation.

7.5 Calibration Standards

Calibration can be performed by IS or external calibration. Using the working standards described above, prepare calibration solutions in ASTM Type I water, HPLC water, other suitable water, or a mixture of solvent and water using the information in Table 2 as a guideline. Note: Volumes of water or water/solvent mixtures and working standards may be adjusted to meet the data quality objectives addressed in the general project outline. Calibration levels other than those listed below can be prepared as needed.

For the quantitation of PFOA and PFOS, reference materials of certified mixed linear and branched isomer are preferred. Alternately, reference materials of primarily linear isomers of PFOA and/or PFOS may be used, however, when quantitating with predominantly linear reference standards, additional LCS samples containing both linear and branched isomers of PFOA and PFOS are required[3].

7.5.1 Internal Standard (IS) and Surrogate Recovery Standard (SRS)

For IS calibration, stable isotope internal standards of each target analyte or appropriate surrogate ISs should be spiked at the same level in all calibration standards. Once the calibration standards have been prepared as stated above in Section 7.5, all calibration standards are spiked with a separate internal standard spiking solution. Typically the

[3] A report summarizing an assessment of the use of reference standards containing certified linear and branched isomers of PFOA/PFOS can be found in 3M report E11-0560.

concentration of the internal standard is consistent with the internal standard concentration expected in the samples being prepared, usually 1 ng/mL. The concentration of the internal standard spiking solution is typically 2 µg/mL. A separate zero point or method blank is typically prepared at the same time as the calibration standards, using the same solution used to prepare the standards (ASTM Type I water, HPLC water, other suitable water, or a solvent/water mixture), and is spiked with the internal standard at the same concentration as the calibration curve, typically at 1 ng/mL.

If the samples being analzyed were pre-spiked with SRSs, the calibration curve prepared in Section 7.5 is spiked with a separate SRS spiking solution. Typically, the sample bottles are spiked with a SRS at 0.1 ng/mL. The final calibration curve must consist of at least six calibration points after analysis. The following table provides an example of spike concentrations and volumes used to achieve a multi-point extracted calibration curve with internal standard and surrogate standard.

Table 1 lists recommended stable isotope internal standards for several PFSA and PFCA target compounds. A custom mix of isotopically labeled target analytes in a methanolic solution containing ([1,2,3,4-$^{13}C_4$]PFBA, [1,2 -$^{13}C_2$]PFHxA, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA, [1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA, [1,2,3,4,5,6 -$^{13}C_6$]PFDA, [1,2,3,4,5,6,7 -$^{13}C_7$]PFUnA, [1,2 -$^{13}C_2$]PFDoA, [1,2,3-$^{13}C_3$]PFHS, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOS, and [1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA (Wellington Laboratories, Guelph, ON) in combination with added ([1,2,3,4,5-$^{13}C_5$]PFPeA, ([1,2,3,4-$^{13}C_4$]PFHpA, and [$^{18}O_2$]PFBS can be used to prepare a stock IS solution. Alternative sources of certified stable isotope labeled target analytes are applicable. Alternatively, individual stable isotope ISs can be used to prepare a stock IS mixture. The table below lists the recommended stable isotope ISs and SRSs applied in the method. Other stable isotope ISs and SRSs of target analytes not listed in the table may be used if supported by validation and/or analysis batch QCs meeting method acceptance criteria (e.g., [$^{13}C_2$]-PFOA). The same internal standard should be used for a given analyte throughout the entire project/study. Note: some of the compounds listed below are appropriate to use as surrogate ISs when a stable isotope IS of a target analyte is not available. Generally, surrogate isotopically labeled PFCAs are used for PFCAs, and surrogate isotopically labeled PFSAs are used for PFSAs.

Table 2 provides examples of spike concentrations and volumes used to achieve a multi-point calibration curve with ISs and SRSs.

Table 1. Stable Isotope PFCAs and PFSAs used for ISs and SRSs

Compound Name	*Synonym or Acronym*	*Analytical Purpose*	*Reference Standard Source*
$^{13}C_4$-Perfluorobutanoic acid	[1,2,3,4-$^{13}C_4$]PFBA	IS for PFBA	Wellington Labs (Mix or Individual)
$^{13}C_4$-Perfluoropentanoic acid	[1,2,3,4,5-$^{13}C_5$]PFPeA	IS for PFPeA	Wellington Labs (Mix or Individual)
$^{13}C_2$-Perfluorohexanoic acid	[1,2 -$^{13}C_2$]PFHxA	IS for PFHxA	Wellington Labs (Mix or Individual)
$^{13}C_4$-Perfluoroheptanoic acid	[1,2,3,4-$^{13}C_4$]PFHpA	IS for PFHpA	Wellington Labs (Mix or Individual)
$^{13}C_8$-Perfluorooctanoic acid	[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA	IS for PFOA and [1,2,3,4 $^{13}C_4$]PFOA	Wellington Labs (Mix or Individual)
$^{13}C_9$-Perfluorononanoic acid	[1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA	IS for PFNA	Wellington Labs (Mix or Individual)
$^{13}C_6$-Perfluorodecanoic acid	[1,2,3,4,5,6 -$^{13}C_6$]PFDA	IS for PFDA	Wellington Labs (Mix or Individual)
$^{13}C_7$-Perfluoroundecanoic acid	[1,2,3,4,5,6,7 -$^{13}C_7$]PFUnA	IS for PFUnA	Wellington Labs (Mix or Individual)
$^{13}C_2$-Perfluorododecanoic acid	[1,2 -$^{13}C_2$]PFDoA	IS for PFDoA, *PFTA	Wellington Labs (Mix or Individual)
$^{18}O_2$-Ammonium Perfluorobutane sulfonate	[$^{18}O_2$]PFBS	IS for PFBS	RTI International (Individual)
$^{13}C_3$-Ammonium Perfluorohexane sulfonate	[1,2,3-$^{13}C_3$]PFHS	IS for PFHS	Wellington Labs (Mix or Individual)
$^{13}C_8$-Sodium Perfluorooctane sulfonate	[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOS	IS for PFOS and PFOS[1,2,3,4 $^{13}C_4$].	Wellington Labs (Mix or Individual)
$^{13}C_8$-Perfluorooctanesulfonamide	[1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA	IS for FOSA	Wellington Labs (mix) RTI International (Individual)
$^{13}C_4$-Perfluorooctanoic acid	[1,2,3,4-$^{13}C_4$]PFOA	SRS for all PFCAs: C4-C8	Wellington
$^{13}C_2$-Perfluoroundecanoic acid	[1,2 -$^{13}C_2$]PFUnA	SRS for all PFCAs C9-C13	Wellington
$^{13}C_8$-Perfluorooctane sulfonate	[1,2,3,4-$^{13}C_4$]PFOS	SRS for all PFSAs: C4, C6, and C8	Wellington

Table 2. Example Preparation of Calibration Curve with ISs and SRSs

Sample Description	*Concentration of WS, µg/mL*	*Volume of WS, µL*	*Volume of IS (2 µg/mL), µL*	*Concentration of Surrogate, µg/mL*	*Volume of Surrogate, µL*	*Volume of ASTM Type I Water, or other suitable solvent (1), mL*
0.025 ng/mL curve point	0.10	25	50	0.20	12.5	100
0.030 ng/mL curve point	0.10	30	50	0.20	15	100
0.04 ng/mL curve point	0.10	40	50	0.20	20	100
0.05 ng/mL curve point	0.10	50	50	0.20	25	100
0.1 ng/mL curve point	0.10	100	50	0.20	50	100
0.25 ng/mL curve point	0.10	250	50	0.20	125	100
0.5 ng/mL curve point	1.0	50	50	0.20	250	100
1 ng/mL curve point	1.0	100	50	0.20	500	100
2.5 ng/mL curve point	10.0	25	50	10.0	25	100
5.0 ng/mL curve point	10.0	50	50	10.0	50	100
10.0 ng/mL curve point	10.0	100	50	10.0	100	100
25.0 ng/mL curve point	10.0	250	50	10.0	NA	100
50.0 ng/mL curve point	10.0	500	50	10.0	NA	100
75.0 ng/mL curve point	10.0	750	50	10.0	NA	100
100 ng/mL curve point	10.0	1000	50	10.0	NA	100

N/A - Not Applicable
(1) Samples requiring analysis for PFUnA, PFDoA, PFTrDA, and FOSA should be analyzed against a calibration curve prepared in 1:1 synthetic groundwater:MeOH.

8 Sample Collection and Bottle Preparation

Sample collection bottles are prepared by 3M Environmental Laboratory (or subcontract supplier) personnel for shipment at ambient temperature to the collection site. Typically, four separate collection bottles are associated with a single collection site: sample, field duplicate sample, low field matrix spike, and high field matrix spike. Alternatively, the sample and field duplicate sample may contain SRSs in lieu of additional target analyte low field matrix spike and target analyte high field matrix spike samples. Depending on the scope of the project, additional replicates of the field sample and field matrix spikes may be added. Also, it is not uncommon for additional mid-level field matrix spikes to be collected if the expected sample concentrations are truly unknown or could span a large concentration range.

High-density polyethylene (HDPE) wide-mouth Nalgene bottles are used for the sample collection containers. (Volumes of the bottles may vary depending on how much sample is required to meet data quality objectives.) Sample collection volumes are project specific and based on data quality objectives. The Nalgene bottles do not require any pretreatment prior to use. Typically, placement of a sample bottle volumetric "fill to here" line is done by using a sample bottle marker template. Alternatively, bottles may be weighed prior to bottle preparation and weighed again after samples have been collected.

All bottles should be clearly labeled to indicate its intended use as a sample, field sample duplicate, low field matrix spike, high field matrix spike, sample/SRS field matrix spike, field duplicate sample/SRS field matrix spike, trip blank, or trip blank matrix spike. If each location has different designated spike levels, the label should also clearly indicate the sample location designation. Generally, a set of bottles for a given collection site are prepared then grouped together in plastic bags for organizational purposes. For each sample collection event, at least one set of trip blank and trip blank matrix spikes are prepared.

Bottle preparation should be documented in a Note to File or on a sample preparation worksheet and should include the following information: date prepared, total number of bottles prepared, number of sample sites, the standard identification numbers and spike volumes used to prepare spiked bottles, the "fill to here" volume, and any other pertinent information needed for reconstructibility of the data. The Note to File will be included in the final data package for the project.

Samples are collected in the field and shipped to the laboratory at ambient temperature.

8.1 Field Matrix Spike Sample (FMS)

Field matrix spike samples are a requirement of the method. A FMS sample is defined as a QC sample to which known quantities of appropriate target analytes are added to the sample bottle in the field or in the laboratory before the bottles are sent to the field. The sample and field duplicate sample may contain appropriate SRSs in lieu of target analyte FMS samples. Sample quantities are determined volumetrically or gravimetrically. A known, specific volume or weight of sample is added to the sample container without rinsing. Volumetric sample measurements may be acquired by a laboratory applied "fill to this level" line on the outside of the sample container. Target analyte FMS samples should be spiked at approximately 0.5-10 times the expected analyte concentration in the sample. If the expected range of analyte concentrations is unknown, multiple spikes at varying levels may be prepared to increase the likelihood that a spike at an appropriate level is made. Typically a low and a high target analyte spike are prepared for each sampling location. In those instances where SRSs are to be used in lieu of target analyte FMS samples, the sample and field duplicate sample are spiked at approximately 2-5 times the target LOQ. The FMS is analyzed to ascertain if matrix effects or sample holding time contributes bias to the analytical results. For the sample bottles designated for matrix spikes, an appropriate volume of matrix spiking solution is added to the empty bottle prior to sampling. The volume of spike solution added should produce the desired final concentration of target analytes once the bottle is filled with sample to the "fill to here line". The matrix spiking solution(s) should be prepared in a suitable solvent and contain all of the appropriate target analytes, ISs, and SRSs. The target analyte matrix spiking solution is often the same as the working standards used to create the calibration standards. An example of a bottle spike is given below.

"Fill to here" volume = 200 mL (A 250 mL Nalgene bottle is used)

Desired Field Spike Concentration = 0.25 ng/mL

500 µL of a 0.1 µg/mL spiking solution (containing the target analytes) is added to the bottle and the bottle cap promptly sealed.

8.2 Internal Standard and Surrogate Recovery Standard

If analysis of a surrogate recovery standard (SRS) is included in the project objectives, an appropriate volume of a surrogate standard solution is added to all the bottles prior to sampling and SPE. Typically sample bottles are spiked with surrogate recovery standards at a final desired spike concentration of 0.1 ng/mL.

If quantitation by internal standard (IS) is included in the project objective, an appropriate volume of internal standard solution is added to all the bottles prior to sampling and SPE. Typically sample bottles are spiked with internal standard at a final desired spike concentration of 1 ng/mL.

For the trip blank, the SRS spike and IS spike is added to the bottle and then ASTM Type I water (HPLC grade reagent water or other suitable water may used) is added to the "fill to here" line. The bottle is capped and sealing tape may be placed around the outer edge of the cap. Trip blank matrix spikes are prepared by adding the appropriate volume of target analyte spiking solution, IS, and SRS spiking solutions and filling the bottle to the desired volume with the appropriate water and capping and sealing the cap.

9 Quality Control and Data Quality Objectives

9.1 Data Quality Objectives

This method and required quality control samples is designed to generate data accurate to ±30% with a targeted LOQ of 0.025 ng/mL. Any deviations from the quality control measures spelled out below will be documented in the raw data and footnoted in the final report.

9.2 Method/Procedural Blanks

The method/procedural blank is zero point calibration standard (which includes ISs) analyzed in a regular basis with each analysis batch. At a minimum, method blanks are analyzed prior to instrument calibration, prior to the analysis of CCV samples, after every 10 sample injections, and at the end of the analytical run.

The mean area count or area ratios when using internal standard calibration, for each analyte in the method blanks must be less than 50% of the area count counts or area ratios when using internal standard calibration, of the LOQ standard. The standard deviation of the area counts, or area ratios when using internal standard calibration, of these method blanks should be calculated. A specific %RSD acceptance criteria is not specified but is assessed on an analytical batch basis. If the mean area counts or area ratios when using internal standard calibration, of the method blanks exceed 50% of the LOQ standard, then the LOQ must be raised to the first standard level in the curve that meets criteria. Method blanks may be eliminated if technical justification can be provided (e.g. the procedural blank was analyzed after an unexpectedly high level sample). If any procedural blanks are removed from the LOQ determination, document in the raw data and report as appropriate. Laboratory Sample Replicates / Field Duplicate Sample

Typically, samples are collected in duplicates in the field. The relative percent difference (RPD) of duplicate samples should be ≤20% for the precision of sample preparation and analysis to be considered in control. Replicate samples not meeting the ≤20% RPD criteria are flagged and reported as outside of QC acceptance criteria.

9.3 Laboratory Matrix Spikes (LMSs)

LMSs may be performed in lieu of FMSs if FMSs have previously been performed for the sample matrix. Additionally, LMSs may be performed in lieu of FMSs for a sample matrix if the FMS levels were not appropriate for determining spike recoveries relative to endogenous levels of target analytes and appropriate SRSs. Generally, each sample location represents a different sample and sample matrix. LMSs are prepared for each sample and analyzed to determine the matrix effect on spike recovery efficiency of each target analyte and appropriate SRSs. LMSs should be prepared at a minimum of one level and in duplicate. LMS concentrations should be prepared at approximately 0.5-10 times the endogenous concentration or approximately 4-10 times the LOQ concentration of each target analyte.

Lab matrix spike recoveries should fall within ± 30% of expected values. Sample data with LMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria. Data with LMS recovery outside of ±50% of the expected value are reported as NR, where NR is defined as "Not Reportable" data outside of QC acceptance criteria.

9.4 Lab Control Sample

Lab control spikes are prepared for each analysis batch to determine method accuracy and precision. LCSs should be prepared at three levels in triplicate for each target analyte and at a minimum of two levels in triplicate for appropriate SRSs. Low lab control spikes should be prepared at a concentration in the range of approximately four to ten times higher than the targeted lower LOQ, the mid lab control spikes should be prepared at a concentration near the mid-point of the calibration curve and the high lab control spikes at approximately 80% of the upper LOQ. For each target analyte and SRSs, the percent relative standard deviation (method precision) for each control spike level must be less than or equal to 20% and the average recovery (method accuracy) for each control spike level must be 80-120%. Sample data for target analytes outside of the laboratory control spike acceptance criteria will be handled as follows:

If the average recovery of a spiking level falls outside method acceptance, but at least 67% (6 out of 9) of LCS samples are within 20% of their respective nominal value (33% of the QC samples, not all replicates at the same concentration, may be outside 20% of nominal value), the average recovery will be flagged as outside method acceptance criteria. All LCS samples will be control charted as per ETS-4-026. If the average recovery of one of the spiking levels exceeded the analytical method uncertainty as determined by ETS-12-012, that analytical batch uncertainty will be expanded for that particular study.

If more than 67% of the LCS samples fail to meet method acceptance criteria, the data will not be reported.

Calibration standards consisting of mixed branched and linear isomer PFOS/PFOA are preferred. However, for PFOS/PFOA target analytes, if the calibration standards are comprised of predominantly linear isomers only, at least one level of triplicate LCSs should be prepared using PFOS/PFOA which contains a mix of linear and branched isomers. These LCSs will be used to demonstrate quantitative equivalency (or quantitative bias) of the isomeric mix when using a predominantly linear standard for calibration. The mixed linear and branched isomer PFOS/PFOA LCSs recoveries should fall within ± 30% of expected values. Alternatively, in lieu of mixed branched and linear isomer PFOS/PFOA LCSs, mixed branched and linear isomer PFOS/PFOA TBMSs may be applied to demonstrate method accuracy and precision.

9.5 Field Matrix Spikes (FMSs) / Surrogate Recovery Standards (SRSs)

FMSs are prepared for each sampling location and analyzed to determine the matrix effect and sample holding time on the spike recovery of each target analyte and/or appropriate SRS. Generally, each sample location represents a different sample and sample matrix.

FMSs are QC samples to which known quantities of appropriate target analytes are added to the sample bottle in the laboratory before the bottles are sent to the field. Typically a low and a high target analyte FMS are prepared for each sampling location. The sample and field duplicate sample may contain appropriate SRSs in lieu of target analyte low field matrix spike and target analyte high field matrix spike samples.

Field matrix spike method acceptance criteria are recoveries within ±30% of the expected value. If FMS recovery (target analyte or SRS spike) is outside of ±30% of the expected value or could not be assessed because the FMS (target analyte) was spiked at an inappropriate level, the sample result is reported as follows:

1.) If target analyte FMS recovery could not be assessed because the FMS's were at an inappropriate level, then Laboratory Matrix Spikes (LMS) may be substituted. If LMS recoveries are within ±30% the data are reportable and flagged to indicate that the FMS spikes levels were inappropriate.

2.) If multiple target analyte FMS's were prepared on a sample and the closest FMS level to the reported sample meets the ±30% acceptance criteria but additional FMS's are outside the ±30% acceptance range, the data are reportable and flagged to indicate that while there were failing FMS's, the uncertainty will not be expanded since the most appropriate spike level passed.

3.) If the target analyte FMS recoveries are outside of the ±30% acceptance range but at least 30 acceptable historical reportable FMS sample results are available, the data may be reported but flagged with an expanded uncertainty and as not meeting FMS criteria.

4.) Sample data with FMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria with an expanded uncertainty.

5.) If FMS recovery is outside of ±50%, the sample result is reported as NR, where NR is defined as "Not Reportable" due to noncompliant QC results.

The targeted fortification levels should be at least 50% of the endogenous level and less than 10 times the endogenous level to be used without justification to determine the statement of accuracy for analytical results.

Note: It is possible for bottles utilized for Field Matrix Spike samples to be under-filled or over-filled during sample collection. Since this scenario will effect the actual concentration of the FMS sample (surrogate and internal standard concentrations will also be effected, if used), it is important that any obvious under-filling or over-filling of sample bottles be documented in the data package and taken into account in the FMS, ISs, or SRSs recovery calculations. Samples over-filled or under-filled by more than 10% will be require recalculation of the FMS, ISs, and SRS true values.

The average of the sample and the field duplicate should be used to calculate the recovery.

10 Procedures

10.1 Water Sample Preparation

This method is applicable to water samples. Samples containing heavy particulate may not be suitable for analysis by this method. Samples containing suspended particulate should be centrifuge prior to removing a sample aliquot, or filtered.

- Thoroughly mix sample before removing an aliquot and placing in a labeled autovial.
- Dilute sample, if necessary, with ASTM Type I water, HPLC water, other suitable water, or solvent (methanol).
- Lab control spikes are prepared for each analysis batch to determine method accuracy and precision. LCSs should be prepared at three levels in triplicate for each target analyte and at a minimum of two levels in triplicate for appropriate SRSs. Low lab control spikes should be prepared at a concentration in the range of approximately four to ten times higher than the targeted lower LOQ, the mid lab control spikes should be prepared at a concentration near the mid-point of the calibration curve and the high lab control spikes at approximately 80% of the upper LOQ. For IS quantitation, stable isotope internal standards of each target analyte or appropriate surrogate ISs should be spiked at the same level as the samples being analyzed, in all LCSs.
- If LCSs are being prepared using synthetic groundwater, allow the LCSs samples to equilibrate for a minimum of 4 hours before aliquoting for analysis or diluting with solvent (methanol).

11 Sample Analysis - LC/MS/MS

11.1 Instrument Setup

Note: In this example, an Applied Biosystems Sciex API 4000 (API 5000 or API 5500) Tandem Mass Spectrometer (LC/MS/MS) is used. Other brands/models of LC/MS/MS instruments as well as single quadrupole mass spectrometers (LC/MS) may be used as long as the method acceptance 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: Applied Biosystems API 4000, API 5000, or API 5500

Ion Source: Turbo Ion Spray (ABS)

Mode: Electrospray Negative

Scan Type: MRM (Multiple Reaction Monitoring)

Computer: Dell DHM

Software: Windows 2000 or Windows XP, Analyst 1.4.2 or higher versions

HPLC: Agilent Series 1100,1200, or 1290

Agilent Quaternary Pump

Agilent Vacuum Degasser

Agilent Autosampler

Agilent Column Oven

Note: One or more C18 HPLC analytical columns (2.1 mm x 100 mm, 5µm or 2.1 mm x 50 mm, 5µm) may be attached on-line after the purge valve and before the sample injection port to retard and separate any residue contaminants that may be in the mobile phase and/or HPLC system.

HPLC Column: Betasil C18, 4.6mm x 100mm, 5µm (ThermoElectron Corporation)

Column Temperature: 35°C

Injection Volume: 5µL

Mobile Phase (A): 2mM Ammonium Acetate in ASTM Type I water (See 7.3)

Mobile Phase (B): Methanol

Table 3. Liquid Chromatography Gradient Program.

Step Number	*Total Time (min)*	*Flow Rate (µL/min)*	*Percent A (2 mM ammonium acetate)*	*Percent B (Methanol)*
0	0	750	97.0	3.0
1	2.0	750	97.0	3.0
2	14.5	750	5.0	95.0
3	15.5	750	5.0	95.0
4	16.5	750	97.0	3.0
5	20.0	750	97.0	3.0

Note: Other HPLC gradients may be used as long as the method criteria and project data quality objectives 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.

Table 4 Suggested MRM Transitions for Target Analytes, Surrogates, and Internal Standards

Analyte	*Analyte Description*	*Mass Transition Q1 (amu)*	*Mass Transition Q3 (amu)*
PFBA (C4 Acid)	Target	213	169
PFPeA (C5 Acid)	Target	263	219
PFHxA (C6 Acid)	Target	313	269, 119
PFHpA (C7 Acid)	Target	363	319, 169
PFOA (C8 Acid)	Target	413	369, 219, 169
PFNA (C9 Acid)	Target	463	419, 169, 219
PFDA (C10 Acid)	Target	513	469, 269, 219
PFUnA (C11 Acid)	Target	563	519, 269, 219
PFDoA (C12 Acid)	Target	613	569, 169, 319
PFTA (C13 Acid)	Target	663	619, 369, 319
FBSA (C4 Sulfonamide)	Target	298	78
FOSA (C8 Sulfonamide)	Target	498	78
PFBS (C4 Sulfonate)	Target	299	99, 80
PFHS (C6 Sulfonate)	Target	399	99, 80
PFOS (C8 Sulfonate)	Target	499	80, 99, 130
[1,2,3,4 -$^{13}C_4$]PFBA	IS for PFBA	217	172
[1,2,3,4,5 -$^{13}C_5$]PFPeA	IS for PFPeA	268	223
[1,2 -$^{13}C_2$]PFHxA	IS for PFHxA	315	270
[1,2,3,4- $^{13}C_4$]PFHpA	IS for PFHpA	367	322
[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA	IS for PFOA	421	376
[1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA	IS for PFNA	472	427
[1,2,3,4,5,6 -$^{13}C_6$]PFDA	IS for PFDA	519	474
[1,2,3,4,5,6,7 -$^{13}C_7$]PFUnA	IS for PFUnA	570	525
[1,2 -$^{13}C_2$]PFDoA	IS for PFDoA and PFTA	615	570
[$^{18}O_2$]PFBS	IS for PFBS	303	84
[1,2,3-$^{13}C_3$]PFHS	IS for PFHS	402	80
[1,2,3,4- $^{13}C_4$]PFOS	IS for PFOS	503	80
[1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA	IS for FOSA	507	80
[1,2,3,4-$^{13}C_4$]PFOA	Surrogate (C4-C8 Acids)	417	372
[1,2,3,4- $^{13}C_4$]PFOS	Surrogate(Sulfonates, FOSA)	503	80
[1,2 -$^{13}C_2$]PFUnA	Surrogate (C9-C13 Acids)	565	520

Multiple transitions for monitoring the analytes is an option. The use of one daughter ion is acceptable if data sensitivity and selectivity is achieved and provided that retention time criteria are met to assure adequate specificity. While the daughter ions may be chosen at the discretion of the analyst, mass transition 99 is suggested for PFOS. Quantitation may be performed using the total ion chromatogram (TIC, or summed MRMs) for a given analyte. For example, the PFOA TIC would sum all three of the monitored transitions. 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 and the gradient, column, guard column(s) used 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.

11.2 Calibration Curve

Quantitation is by internal standard or external standard calibration. Calibration standards may be prepared in ASTM Type I, HPLC water, other suitable water, or a solvent/water mixture. If internal standard calibration does not meet calibration acceptance criteria, external calibration can be applied. See Table 1 for

recommended application of available internal standards. Quantitation of PFOA and PFOS is by summed analyte-specific mass transitions.

Analyze the standard curve prior to each set of samples. If internal standards were added to the calibration standards area ratios are used to generate the calibration curve. The standard curve may be plotted using a linear regression ($y = mx + b$), weighted 1/x or unweighted, or by quadratic fit ($y = ax^2 + bx + c$), weighted 1/x or unweighted, using suitable software. 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.

High and/or low points may be excluded from the calibration curves to provide a better fit over the 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 (or area ratio if quantitating by IS) are not at least twice that of the average area counts (or area ratio if quantitating by IS) of method and/or solvent blanks. The coefficient of determination (r^2) value for the calibration curve must be greater than or equal to 0.990 (or a correlation coefficient (r) of 0.995). Each point in the curve must be within ±25% of the theoretical concentration with the exception of the LLOQ, which may be within ±30%. 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.

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

11.3 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. Samples must be bracketed by passing CCVs or the calibration curve and a passing CCV to be reportable.

11.4 System Suitability

A minimum of three system suitability samples should be injected at the beginning of each analytical run, prior to the analysis of the calibration curve. Typically these samples are at a concentration near the mid-level of the calibration curve and are repeated injections from one autosampler vial. It is suggested that the system suitability injections have area counts or area ratios when using internal standard calibration, with a target RSD of ≤5% and a target retention time RSD of ≤2%. There is no defined acceptability limit on these results as the %RSD value is dependent on the number of MRM transitions being monitored in the LC/MS/MS run or time period. Ultimately, any effects on these parameters for the System Suitability samples will also be evident on all standards and QC samples analyzed as part of the analysis batch. Any effect of system suitability is incorporated within QC acceptance criteria.[4]

11.5 Sample Analysis and QCs

For each analysis batch, the instrument analysis run sequence should include an initial calibration curve, samples, FDSs, interspersed blanks, interspersed CCVs, appropriate QCs (i.e., LCSs, LMSs, FMSs, TBMSs, and TBs), and a final CCV or calibration curve bracketing samples and appropriate QCs

Inject the same volume (between 5 - 100µL) of each standard, analytical sample and blank into the instrument (unless an on-instrument sample dilution is desired).

Samples containing analytes that are quantitated above the concentration of the highest standard in the curve should be further diluted and reanalyzed.

[4] 3M Environmental Laboratory study E08-0096 evaluated the effect on these results as a function of the number of MRMs being monitored.

12 Data Analysis and Calculations

The chromatography analysis software will typically calculate the amount of target analyte in the sample extracts using the established calibration curve.

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

$$\text{LCS\% recovery} = \frac{\text{LCS Concentration } (\frac{ng}{mL})}{\text{Spike Concentration } (\frac{ng}{mL})} * 100\%$$

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

$$\text{LMS \% recovery} = \frac{\text{LMS Concentration } (\frac{ng}{mL}) - \text{Concentration of Sample } (\frac{ng}{mL})}{\text{Spike Concentration } (\frac{ng}{mL})} * 100\%$$

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

$$\text{Recovery} = \frac{\text{Total analyte found (ng/mL)} - \text{Average analyte found in sample (ng/mL)}}{\text{Analyte added (ng/mL)}} \times 100$$

13 Analysis Batch Method Performance Criteria

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 the final report if the Technical Manager (non-GLP study) or Study Director (GLP study) chooses to report 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 appropriate. 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 – Analysis Batch

A minimum of three system suitability samples should be injected at the beginning of each analytical run. These samples are run prior to the calibration curve. It is suggested that the system suitability injections have area counts with a target RSD of ≤5% and a target retention time RSD of ≤2%. There is no defined acceptability limit on these results as the %RSDs are dependent on the number of MRM transitions being monitored in the LC/MS/MS run or time period. Any effect of system suitability is incorporated in the QC acceptance criteria.

13.2 Calibration and Limit of Quantitation (LOQ) – Analysis Batch

Calibration Curve: The coefficient of determination (r^2) value for the calibration curve must be greater than or equal to 0.990 corresponding to a correlation coefficient (r) = 0.995. Each point in the curve must be within ±25% of the theoretical concentration with the exception of the LLOQ, which may be within ±30%.

CCV Performance: The calibration standards that are interspersed throughout the analytical sequence are evaluated as continuing calibration verifications in addition to being part of the calibration curve. The accuracy

of each curve point must be within 25% of the theoretical value (within 30% for lowest curve point). Samples that are bracketed by CCVs not meeting these criteria must be reanalyzed.

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 average area counts for all prepared procedural blank(s). By definition, the measured value of the LLOQ must be within 30% of the theoretical value.

Demonstration of Specificity: Specificity is demonstrated by chromatographic retention time (within 4% of standard) and the mass spectral response of unique ions.

13.3 Blanks – Method/Procedural Blanks and Trip

Method/Procedural Blanks: Multiple procedural blanks should be interspersed throughout the analysis batch and the analytical sequence. At a minimum, method blanks are analyzed prior to instrument calibration, prior to the analysis of CCV samples, after every 10 sample injections, and at the end of the analytical run.

The mean area counts (or area ratios when using IS calibration) for each analyte must be less than 50% of the area count of the LOQ standard. If the area counts of the procedural blanks exceed 50% of the LOQ standard, then the LOQ must be raised to the first standard level that meets criteria.

Trip Blank: A trip blank of ASTM Type I water (or lab equivalent) is prepared in a sample container in the laboratory and treated as a sample, including exposure to shipping, sampling site conditions, storage, preservation and all analytical procedures. The trip blanks results for each analyte are included with the reported sample results.

13.4 Data Accuracy and Precision – Analysis Batch

Lab Control Spikes: The average recovery at each LCS level for each target analyte and appropriate SRS should be within 80-120% and the percent relative standard deviation of the recoveries must be less than or equal to 20%. If the average recovery of a spiking level falls outside method acceptance, but at least 67% (6 out of 9) of LCS samples are within 20% of their respective nominal value (33% of the QC samples, not all replicates at the same concentration, may be outside 20% of nominal value), the average recovery will be flagged as outside method acceptance criteria. All LCS samples will be control charted as per ETS-12-012. If the average recovery of one of the spiking levels exceeded the analytical method uncertainty as determined by ETS-12-012, that analytical batch uncertainty will be expanded for that particular study. The average recovery at each LCS level for mixed branched/linear isomer PFOA and PFOS should be within 70-130% and the percent relative standard deviation of the recoveries must be less than or equal to 20%.

Field Duplicates: The relative percent difference (RPD) of duplicate samples should be less than 20% for the precision of sample preparation and analysis to be considered in control. Replicate samples not meeting the 20% RPD criteria are flagged and reported as outside of QC acceptance criteria.

Field Matrix Spikes: FMS acceptance criteria are recoveries within ±30% of the expected value for each target analyte and appropriate SRS. Sample data with FMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria. Data with FMS recovery outside of ±50% of the expected value are reported as NR, where NR is defined as "Not Reportable" data outside of QC acceptance criteria. If FMS recovery could not be assessed because FMSs were at an inappropriate level, then Laboratory Matrix Spikes (LMSs) may be substituted. If LMS recoveries are within ±30% for each target analyte and SRSs the data are reportable but flagged as not meeting the FMS method acceptance criteria.

13.5 Analytical Method Uncertainty

Analytical method uncertainty for each target analyte and SRS is determined with control charted historical analysis batch LCS data for the method and reported with each analysis batch.[5] Uncertainty determinations

[5] Method uncertainty based on INTERNATIONAL ANS/ISO/IED STANDARD 17025 reference (GUM, Guide to the Expression of Uncertainty in Measurement). Method application demonstrated in ETS-12-012, citing references: a.) EURACHEM/CITAC Guide, "Quantifying Uncertainty in Analytical Measurement," Second Edition; Editors: S.L.R. Ellison, M. Rosslein, and A. Williams. b.)Georgian, Thomas, "Estimation of Laboratory Analytical Uncertainty Using Laboratory Control Samples," Environmental Testing &

are based on INTERNATIONAL ANS/ISO/IED STANDARD 17025 reference (GUM, Guide to the Expression of Uncertainty in Measurement) and described in ETS-12-012. At least thirty data points are required for determining analytical method uncertainty. The method uncertainty is defined as 2x the standard deviation of the percent recoveries of the pooled lab control spikes. While all LCS data points are control charted, only the most recent fifty data points are used for determining the method uncertainty.

When less than thirty LCS data points have been generated for a given analyte, the analysis batch LCSs are used to determine the data uncertainty. If FMSs meet the ±30% recovery criteria at a level appropriate to the endogenous level, and the LCS meet the ±20% recovery criteria, then the uncertainty of the data is determined as within 100±20%.

Analysis batch sample data with FMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria with expanded uncertainties. Data with FMS recovery outside of ±50% of the expected value are reported as NR, where NR is defined as "Not Reportable" data outside of QC acceptance criteria. If FMS recovery could not be assessed because FMSs were at an inappropriate level, then Laboratory Matrix Spikes (LMSs) may be substituted. If LMS recoveries are within ±30% for each target analyte and appropriate SRSs the data are reportable but flagged as not meeting the FMS method acceptance criteria with uncertainties of ±30%. If FMS do not meet the ±30% recovery criteria, and historical FMS data does not exist, the analytical uncertainty is evaluated on a sample-by-sample basis, the data may be reported with expanded uncertainty and are flagged.

13.6 Quantitation of PFOA/PFOS – Analysis Batch

Calibration standards consisting of mixed branched and linear isomer PFOS/PFOA are preferred. Quantitation is performed by integrating the linear and branched isomers together. Alternately, the linear and branched isomers can be integrated separately, applying the appropriate true value to each calibration curve point for each isomer. The LCS and samples are then quantitated by integrating the linear and branched isomers separately (requires separate analytical results files) and quantitating the resulting peak against the linear or branched calibration curve. The results from both integrations are then summed to produce the final result. Integrating the linear and branched isomers separately may be helpful for those samples where the linear/branched ratios do not closely match those of the reference standards.

However, for PFOS/PFOA target analytes, if the calibration standards are comprised of predominantly linear isomers only the method requires the addition of LCSs of mixed branched/linear isomer PFOS/PFOA. The purpose of including these LCSs is to demonstrate quantitative equivalency (or quantitative bias) of the isomeric mix when using a predominantly linear PFOS or PFOA standard for calibration. Alternatively, in lieu of mixed branched and linear isomer PFOS/PFOA LCSs, mixed branched and linear isomer PFOS/PFOA TBMSs may be applied to demonstrate method accuracy and precision.

An alternate method of quantitation can be performed whereby only the linear isomer of PFOS/PFOA is integrated and used for generating the calibration curve. The LCS and samples are then quantitated by integrating the linear and branched isomers separately (requires separate analytical results files) and quantitating the resulting peak against the linear calibration curve. The results from both integrations are then summed to produce the final result. Integrating the linear and branched isomers separately reduces the on-column concentration for those samples that contain both linear and branched isomers of PFOA/PFOS. This ensures that the concentration detected is within the a range of the calibration curve that is comparable regardless of whether the calibration curve was generated using predominantly linear isomers of PFOS/PFOA or linear plus branched isomers of PFOS/PFOA.

14 Pollution Prevention and Waste Management

Waste generated when performing this method will be disposed of appropriately. The original samples will be archived at the 3M Environmental Laboratory in accordance with internal procedures.

Analysis, November/December 2000. c.)Taylor, B.N. and CE. Kuyatt, NIST Technical Note 1297, 1994 Edition: "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results."d.)Adams, T.M., "A2LA Guide for the Estimation of Measurement Uncertainty in Testing", July 2002.

15 Records

Each data package generated for a study must include all supporting information for reconstruction of the data. Information for the data package must include, but is not limited to the following items: study or project number, sample and standard prep sheets/records, instrument run log (instrument batch records, instrument acquisition method, summary pages), instrument results files, chromatograms, calibration curves, and data calculations.

16 Affected Documents

None.

17 Revisions

Revision Number	Summary of Changes
1	*Section 1. Included the use of internal standard calibration by this method.* *Section 2. Included the use of internal standard calibration by this method. Included the use of a solvent/water mixture when analyzing for PFUnA, PFDoA, PFTrDA, and FOSA.* *Section 3. Added definitions for internal standard, surrogate internal standard, and surrogate recovery standard.* *Section 6.Removed the details regarding the instrument parameters to section 10 of the method.* *Section 7. Updated reference standards to include internal standards and surrogates. Changed concentration levels for working standards and included the use of internal standards and surrogates.* *Section 8. Inserted a new section on sample bottle preparation.* *Section 9 Quality Control. This section was previously section 10 in ETS-8-044.0. Updated QC criteria to be consistent with method ETS-8-154.4.* *Section 10 Procedures. This section was previously section 8 (Sample Handling) in ETS-8-044.0. Added detail regarding the preparation of LCSs. Included the use of methanol as a dilution solvent.* *Section 11 Sample Analysis. This section was previously section 10 in ETS-8-044.0. Included the details regarding the instrument parameters.* *Section 12 Data Analysis and Calculations. This section was previously section 11 in ETS-8-044.0. Removed the equation for calculating the analytes concentration, indicating that this is done by the instrument software.* *Section 13 Method Performance. This section was previously section 12 in ETS-8-044.0. Updated QC criteria to be consistent with ETS-8-154.4. Added information on the determination of analytical method uncertainty and quantitation of PFOA/PFOS.* *Section 14 Pollution Prevention. This section was previously section 13 in ETS-8-044.0.* *Section 15 Records. This section was previously section 14 in ETS-8-044.0.* *Section 16 Affected Documents. This section was previously section 15 in ETS-8-044.0.* *Section 17 Revisions. This section was previously section 16 in ETS-8-044.0.*

ATTACHMENT D: DEVIATION(S)

RECORD OF DEVIATION/NONCONFORMANCE

I. Identification

Study / Project No.	Date(s) of Occurrence:	Document Number:
GLP10-01-02-31	4/16/12	ETS-8-044.1

Deviation type (Check one): ☐ SOP ☐ Protocol ☐ Equipment Procedure ☐ GPO ☑ Method ☐ Other:

II. Description (attach extra pages as needed)

Method Requirements:

1. LCS recovery within ±20% (section 13.4).
2. FMS recovery within ±30% (section 13.4).

Actual procedure/process:

1. The low set of LCSs had an average recovery of 75.2% for PFOS.
2. The sampling location DAL GW TW1R HS had a PFOS FMS recovery of 65.8%.

III. Actions Taken

(such as amendment issued, SOP revision, etc.)

Corrective Action (☐ Yes ☑ No) Reference:

Acceptability of the nonconforming work:

1. The non-compliant LCSs will be flagged in the final report. All LCSs were used in the determination of the analytical method uncertainty. Since the %bias was less than the calculated method uncertainty for PFOS of ±35%, the method uncertainty does not need to be expanded further.
2. The sampling location with a FMS recovery outside method acceptance criteria will be flagged in the report. Since the analytical method uncertainty was calculated at 35%, the uncertainty for DAL GW TW1R does not need to be expanded further.

Actions: ☐ Halting of Work ☐ Client Notification ☐ Work Recall ☐ Withholding of Report
☑ Other: Deviations will be noted in final report.

Project Lead/PAI Approval:	Date:
Study Director (if GLP):	Date:
Sponsor Approval (for GLP protocol deviations): NA	Date: NA
Technical Reviewer (optional): NA	Date: NA
Laboratory Department Manager Approval:	Date:

IV. Authorization to Resume Work

Where halting of work occurred, resumption of work must first be approved by Laboratory Management

Laboratory Department Manager Approval: NA	Date: NA

Deviation No. _____

(assigned by Study Director or Team Leader at the end of study or project)

346792

3M

2012 JUL 10 AM 8:08

GLP10-01-01, Interim Report 31: Analysis of PFOA in Groundwater Samples Collected at Off-Site Wells on Bert Jeffries Property in Decatur, AL in April 2012

Study Title

Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program

Data Requirement

EPA TSCA Good Laboratory Practice Standards 40 CFR Part 792

Study Director

Jaisimha Kesari P.E., DEE
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1400 Weston Way
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Author

Susan Wolf
3M Environmental Laboratory

Interim Report Completion Date

Date of signing

Performing Laboratory

3M Environmental Health and Safety Operations
Environmental Laboratory
3M Center, Bldg 260-05-N-17
St. Paul, MN 55144

Project Identification

GLP10-01-01-31

Total Number of Pages

75

A2LA ACCREDITED

The testing reported herein meet the requirements of ANSI/ISO/IEC 17025:2005 "General Requirements for the Competence of Testing and Calibration Laboratories", in accordance with the A2LA Testing Certificate # 2052.01. Testing that complies with this International Standard also meets principles of ISO 9001:2000.

Testing Cert #2052.01

This page has been reserved for specific country requirements.

GLP COMPLIANCE STATEMENT

Report Title: GLP10-01-01, Interim Report 31. Analysis of PFOA in Groundwater Samples Collected at the Off-Site Wells on Bert Jefferies property in Decatur, AL in April 2012.

Study: Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program.

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

- These are environmental samples where there is no specific test substance, no specific test system and no dosing of a test system.
- The reference substances have not been characterized under the GLPs and the stability under storage conditions at the test site have not been determined under GLPs.

Gary Hohenstein 5/8/12

Gary Hohenstein, Sponsor Representative — Date

5/14/12

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

QUALITY ASSURANCE STATEMENT

Report Title: GLP10-01-01, Interim Report 31. Analysis of PFOA in Groundwater Samples Collected at the Off-Site Wells on Bert Jeffries property in Decatur, AL in April 2012.

Study: Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program.

This report and the accompanying data were audited by the 3M Environmental Laboratory Quality Assurance Unit (QAU), as indicated below. The findings were reported to the principal analytical investigator (P.A.I.), laboratory management and study director.

Inspection Dates	Phase	Date Reported to	
		Testing Facility Management	Study Director
4/25/12 – 4/26/12	Data and Report	5/1/12	5/1/12

Megan Carlson 5/4/12

QAU Representative Date

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Table 20. JPAL GW MW9R 120405 20

Table 21. JPAL GW MW9L 120405 20

Table 22. JPAL GW MW10R 120405 21

Table 23. JPAL GW MW11L 120405 21

Table 24. JPAL GW MW3R RB 120405 21

Table 25. JPAL GW TRIP 120316 21

1 Study Information

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Study Dates

Study Initiation: March 8, 2010
Interim Report 31 Experimental Termination: April 21, 2012
Interim Report Completion: Date of Interim Report Signing

Location of Archives

All original raw data and the analytical report have been archived at the 3M Environmental Laboratory according to 40 CFR Part 792. The test substance and analytical reference standard reserve samples are archived at the 3M Environmental Laboratory according to 40 CFR Part 792

2 Summary

The 3M Environmental Laboratory prepared sample containers for fourteen locations on the Bert Jeffries property. A total of forty-five sample bottles were received at the 3M Environmental Laboratory for perfluorooctanoate (PFOA) analysis from Weston personnel on April 9, 2012. All samples were logged into the laboratory information management system (LIMS) under project GLP10-01-01-31.

For each sampling location, a field sample, field duplicate sample and field matrix spike (FMS) sample were collected. Samples also included a trip blank containing Milli-Q™ water and an appropriate trip blank spike. A single equipment rinseate blank was also collected. The equipment rinseate blank did not have FMS samples prepared for determination of PFOA recovery. All sample bottles were fortified with internal standard $^{13}C_8$-PFOA and surrogate recovery standard $^{13}C_4$-PFOA prior to sample collection. All of the samples were prepared and analyzed for PFOA and the surrogate recovery standard $^{13}C_4$-PFOA, following 3M Environmental Laboratory Method ETS-8-044.1. Where applicable, samples were analyzed against an internal standard calibration curve.

The average measured PFOA concentrations are summarized in Table 1. The trip blank and equipment blank samples were below the lower limit of quantitation (LLOQ) of 0.0240 ng/mL, indicating adequate control of sample contamination during shipping and sample collection. The analytical uncertainty for PFOA was estimated at ±17%.

Table 1. Summarized PFOA Results (Bert Jeffries Property, April 2012)

Sample ID	Avg. PFOA Concentration (ng/mL) (1)	Relative Percent Difference
JPAL GW MW1R 120405	1.61	5.6%
JPAL GW MW3R 120405	7.88	0.63%
JPAL GW MW4R 120405	2.24	1.3%
JPAL GW MW4L 120405	0.162	2.5%
JPAL GW MW5R 120405	0.174	3.4%
JPAL GW MW5L 120405	0.862	4.8%
JPAL GW MW6R 120405	2.86	0.70%
JPAL GW MW6L 120405	0.203	3.5%
JPAL GW MW7R 120405	8.26	2.7%
JPAL GW MW8R 120405	0.307	1.6%
JPAL GW MW9R 120405	0.124	0.81%
JPAL GW MW9L 120405	0.0248	NA (1)
JPAL GW MW10R 120405	0.507	2.6%
JPAL GW MW11L 120405	0.290	8.3%
Trip Blanks (Milli-Q™ Water)	<0.0240	NA
GLP10-01-01-31 Equipment rinseate blank: JPAL GW MW3R	<0.0240	NA

NA: not applicable
The analytical method uncertainty analyzed by internal calibration for PFOA is ±17%.
(1) A RPD value could not be calculated due to one of the sample replicates having a PFOA result BLOQ.

3 Introduction

This analytical study was conducted as part of the Phase 3 Environmental Monitoring and Assessment Program for the 3M facility located in Decatur, Alabama. The objective of the overall program is to gain information regarding concentrations of perfluorooctanoate (PFOA) in various environmental media such as groundwater, soils and sediments that are associated with and near the Decatur facility. This analytical study was conducted to analyze ground water samples collected from fourteen locations from Off-Site Wells on the Bert Jefferies property in Decatur, AL for PFOA.

The 3M Environmental Laboratory prepared sample bottles (250 mL high-density polyethylene) which were shipped to Decatur, AL Weston personnel prior to field sampling. Sample bottle sets for each sampling location included a field sample, field sample duplicate, and one field spike sample. Each empty container for sampling was marked with a "fill to here" line to produce a final sample volume of 200 mL. Containers designated for field matrix samples were fortified with an appropriate matrix spike solution containing PFOA prior to being sent to the field for sample collection. All sample bottles included the addition of $^{13}C_8$-PFOA (internal standard) at a nominal concentration of 1 ng/mL and $^{13}C_4$-PFOA (surrogate recovery standard) at a nominal concentration of 0.1 ng/mL. See section 8.8 of the report for field matrix spike levels.

Samples were prepared and analyzed according to the procedure defined in 3M Environmental Laboratory method ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds in Water by LC/MS/MS; Direct Injection Analysis". The use of an internal standard was used to aid in the data quality objectives.

Table 1 summarizes the average PFOA concentration for the duplicate surface water samples collected and the trip blank sample. Tables 10-25 summarize the individual sample results and the associated FMS recoveries. All results for the quality control samples prepared and analyzed with the samples are reported and discussed elsewhere in this report.

4 Test & Control Substances

There was not a test substance or control substances in the classic sense of a GLP study. This study was purely analytical in nature.

5 Reference Substances

The analytical reference substances used for this study are listed below.

Reference Substance	PFOA (Linear + Branched)	PFOA (Linear + Branched	$^{13}C_4$-PFOA	$^{13}C_8$-PFOA
Chemical Name	Perfluorooctanoate	Perfluorooctanoate	Perfluorooctanoate	Perfluorooctanoate
Chemical Formula	$C_7F_{15}COOH$	$C_7F_{15}COO^-$	$^{13}C_4HF_{15}O_2$	$^{13}C_8HF_{15}O_2$
Identifier	CAS # 95328-99-7	CAS # 335-67-1	MPFOA	MPFC-C-0112
Use	Target Analyte Reference Standard	FMS Reference Standard	Surrogate	Internal Standard
Source	Wellington	Sigma Aldrich	Wellington	Wellington
Expiration Date	03/17/2014	07/27/2016	12/07/2013	01/24/2015
Storage Conditions	Frozen	Ambient	Frozen	Frozen
Chemical Lot Number	TPFOA0311	MKBD4574V	MPFOA1210	012312
TCR Number	TCR11-0009, TCR11-0042	TCR11-0029	TCR11-0001	TCR12-0004
Physical Description	Liquid	Powder	Liquid	Liquid
Purity	98.3%	96.8%	>98%	NA (1)

(1) Compound is part of a custom mixture of mass-labeled perfluorinated compounds at a concentration of 5.0 µg/mL.

6 Test System

There was not a test system for this study in the classic sense of a GLP study. This study was conducted for analysis of surface water samples collected from the Jeffries property located near Decatur, AL by Weston Solutions, Inc. personnel. Samples for this study are "real world" environmental samples.

Table 2. Sample Description Key Code.

String Number	String Descriptor	Example
Example	*JPAL-GW-MW1R-0-120405*	
1	*Sample Location*	*JPAL= Jeffries Property, Alabama*
2	*Sample Type*	*GW= Ground Water*
3	*Well Identifier*	*Example: MW1R*
4	*Well Level*	*R = Residuum shallow water-bearing zone* *L = Bedrock water-bearing zone* *S = Epikarst middle water-bearing zone*
5	*Sampling Date*	*120405- April 5, 2012*
6	*Sample Type*	*0=primary sample* *DB=duplicate sample* *FMS = Field Matrix Spike*

7 Method Summary

7.1 Method

Analysis for all analytes was completed following 3M Environmental Laboratory method ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds In Water by High Performance Liquid Chromatography/Mass Spectrometry Direct Injection Analysis".

7.2 Sample Collection

Samples were collected in 250 mL Nalgene™ (high-density polyethylene) bottles prepared at the 3M Environmental Laboratory. Sample bottles associated with GLP10-01-01-31 were returned to the laboratory at ambient conditions on April 9, 2012. Samples were stored refrigerated at the laboratory after receipt. A set of laboratory prepared Trip Blank and Trip Blank field matrix spikes were sent with the set of sample collection bottles.

7.3 Sample Preparation

Samples were prepared by removing an aliquot of the well mixed sample and placing it in an autovial for analysis.

During the preparation of the laboratory control samples, an aliquot of a separate internal standard spiking solution was added to the laboratory control samples (nominal concentration of 1 ng/mL). The samples bottles were spiked with an internal standard mix at a nominal concentration of 1 ng/mL prior to being sent to the field for sample collection.

7.4 Analysis

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

raw data hard copies placed in the final data packet, and are briefly described below in **Table 3, Table 4** and **Table 5.**

Table 3. Instrument Parameters.

Instrument Name	**ETS Buster**
Analytical Method Followed	ETS-8-044.1
Analysis Date	4/18/12
Liquid Chromatograph	Agilent 1100
Guard column	Betasil C18 (4.6 mm X 100 mm), 5µ
Analytical column	Betasil C18 (4.6 mm X 100 mm), 5µ
Injection Volume	50 µL
Mass Spectrometer	Applied Biosystems API 4000
Ion Source	Turbo Spray
Electrode	Turbo ion electrode
Polarity	Negative
Software	Analyst 1.4.2

Table 4. Liquid Chromatography Conditions.

Step Number	*Total Time (min)*	*Flow Rate (µL/min)*	*Percent A (2 mM ammonium acetate)*	*Percent B (Methanol)*
ETS-8-044.1 Analysis				
0	0.0	750	97.0	3.0
1	2.0	750	97.0	3.0
2	14.5	750	5.0	95.0
3	15.5	750	5.0	95.0
4	16.5	750	97.0	3.0
5	20.0	750	97.0	3.0

Table 5. Mass Transitions.

Analyte	*Mass Transition Q1/Q3*	*Internal Standard*	*Mass Transition Q1/Q3*
PFOA	*413/369*	*[$^{13}C_8$]-PFOA*	*421/376*
	413/219		
	413/169		
[$^{13}C_4$]-PFOA	*417/372*	*[$^{13}C_8$]-PFOA*	*421/376*
Dwell time was 50 msec for each transition. The individual transitions were summed to produce a "total ion chromatogram" (TIC), which was used for quantitation.			

8 Analytical Results

8.1 Calibration

Samples were analyzed using a stable isotope internal standard calibration curve. Calibration standards were prepared by spiking known amounts of the stock solution containing PFOA (reference standard containing both linear and branched isomers) into a laboratory-prepared synthetic groundwater containing calcium and magnesium. A separate internal standard spiking solution was prepared and an aliquot was added at the same level to all calibration standards and laboratory control samples at a nominal concentration of 1 ng/mL. A calibration curve ranging from approximately 0.025 ng/mL to 25 ng/mL (0.025 ng/mL to 10 ng/mL for $^{13}C_4$-PFOA surrogate) was prepared. A quadratic, 1/x weighted, calibration curve of the standard peak area ratios was used to fit the data for each analyte. The data were not forced through zero during the fitting process. Calculating the standard concentrations using the peak area/ peak area ratios and the resultant calibration curve confirmed accuracy of each curve point.

Each curve point was quantitated using the overall calibration curve and reviewed for accuracy. Method calibration accuracy requirements of 100 ± 25% (100 ± 31% for the lowest curve point) were met for PFOA and $^{13}C_4$-PFOA surrogate. The correlation coefficient (r) was greater than 0.995 for both analytes.

8.2 System Suitability

A calibration standard was analyzed four times at the beginning of the analytical sequence to demonstrate overall system suitability. The acceptance criteria of less than or equal to 5% relative standard deviation (RSD) for peak area and retention time criteria of less than or equal to 2% RSD was met for PFOA and $^{13}C_4$-PFOA surrogate.

8.3 Limit of Quantitation (LOQ)

The LOQ for this analysis is the lowest non-zero calibration standard in the curve that meets linearity and accuracy requirements and for which the area counts are at least twice those of the appropriate blanks. The nominal LOQ for PFOA can be found in Table 6.

Table 6. Limit of Quantitation (LOQ).

Analysis Date	*PFOA ng/mL*
4/16/12	0.0240

8.4 Continuing Calibration

During the course of each analytical sequence, continuing calibration verification samples (CCVs) were analyzed to confirm that the instrument response and the initial calibration curve were still in control. All CCVs met method criteria of 100% ± 25% for PFOA and $^{13}C_4$-PFOA surrogate.

8.5 Blanks

Three types of blanks were prepared and analyzed with the samples: procedural blanks, trip blanks, and equipment rinseate blanks. Procedural blank results were reviewed and used to evaluate method performance and to determine the LOQ for PFOA. Trip blanks reflect the shipping and sample collection conditons the sample bottles and samples experience. Equipment rinseate blanks are aqueous samples that reflect the efficiency of equipment cleaning in the field between different sample collections to ensure no cross contamination of samples from the equipment.

8.6 Lab Control Spikes (LCSs)

Low, mid, and high lab control spikes were prepared for the target analytes and analyzed in triplicate, while only low and high lab control spikes were prepared for the $^{13}C_4$-PFOA surrogate. LCSs were prepared by spiking known amounts of the analyte into 10 mL of synthetic groundwater to produce the desired concentration. The spiked water samples were then analyzed in the same manner as the samples. The method acceptance criteria, average of LCS at each level should be within 100% ± 20% with an RSD ≤20%, were met for both PFOA and $^{13}C_4$-PFOA surrogate.

The following calculations were used to generate data in Table 7 for laboratory control spikes:

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

$$\text{LCS\% RSD} = \frac{\text{standard deviation LCS replicates}}{\text{average LCS recovery}} * 100\%$$

Table 7. Laboratory Control Spike Recovery.

ETS-8-044.1 Analyzed 4/16/12	*PFOA (Linear + Branched)*			*$^{13}C_4$-PFOA surrogate*		
Lab ID	*Spiked Concentration (ng/mL)*	*Calculated Concentration (ng/mL)*	*%Recovery*	*Spiked Concentration (ng/mL)*	*Calculated Concentration (ng/mL)*	*%Recovery*
LCS-120416-1	0.190	0.186	97.7	0.198	0.207	104
LCS-120416-2	0.190	0.195	103	0.198	0.212	107
LCS-120416-3	0.190	0.197	104	0.198	0.216	109
Average ± %RSD	**102% ± 3.3%**			**107% ± 2.4%**		
LCS-120416-4	1.90	1.94	102	1.98	2.06	104
LCS-120416-5	1.90	1.97	104	1.98	2.10	106
LCS-120416-6	1.90	2.00	105	1.98	2.12	107
Average ± %RSD	**104% ± 1.5%**			**106% ± 1.4%**		
LCS-120416-7	9.52	8.85	93.0	NA	NA	NA
LCS-120416-8	9.52	8.62	90.5	NA	NA	NA
LCS-120416-9	9.52	8.80	92.4	NA	NA	NA
Average ± %RSD	**92.0% ± 1.4%**			**NA**		

NA = Not applicable

8.7 Analytical Method Uncertainty

Analytical uncertainty is based on historical QC data that is control charted and used to evaluate method accuracy and precision. The method uncertainty is calculated following ETS-12-012.2. The standard deviation is calculated for the set of accuracy results (in %) obtained for the QC samples. The expanded uncertainty is calculated by multiplying the standard deviation by a factor of 2, which corresponds to a confidence level of 95%.

Table 8. Analytical Method Uncertainty.

Analyte	Method	Standard Deviation	Method Uncertainty
PFOA	ETS-8-044.1	8.47	±17%

8.8 Field Matrix Spikes (FMS)

A single field matrix spike was collected at each sampling point to verify that the analytical method is applicable to the collected matrix. The field matrix spike was generated by adding a measured volume of field sample to a container spiked by the laboratory with PFOA (reference standard containing both linear and branched isomers) prior to shipping sample containers for sample collection. Field matrix spike recoveries within method acceptance criteria of 100±30% confirm that "unknown" components in the sample matrix do not significantly interfere with the extraction and analysis of the analytes of interest. Field matrix spike concentrations must be 50% of the sample concentration to be considered an appropriate field spike. Field matrix spikes are presented in section 9 of this report.

Table 9. Field Matrix Spike Levels.

Sampling Location	PFOA, ng/mL
All Locations and Trip Blank	2.00

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

8.9 Data Summary and Discussion

The tables below summarize the sample results and field matrix spike recoveries for the sampling locations as well as the equipment rinseate and trip blank samples. Results and average values are rounded to three significant figures according to EPA rounding rules. Because of rounding, values may vary slightly from those listed in the raw data. Field matrix spike recoveries meeting the method acceptance criteria of ± 30%, demonstrate that the method was appropriate for the given matrix and their respective quantitative ranges.

JPAL GW MW3R 120405; The field matrix spike level was not appropriate as compared to the PFOA concentration in the sample. However, the $^{13}C_4$-PFOA surrogate recovery added to all sample bottles met method acceptance criteria.

JPAL GW MW7R 120405; The field matrix spike level was not appropriate as compared to the PFOA concentration in the sample. However, the $^{13}C_4$-PFOA surrogate recovery added to all sample bottles met method acceptance criteria.

Table 10. JPAL GW MW1R 120405

		PFOA		$^{13}C_4$-PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-31-001	JPAL-GW-MW1R-0-120405	1.56	NA	96.1
GLP10-01-01-31-002	JPAL-GW-MW1R-DB-120405	1.65	NA	101
GLP10-01-01-31-003	JPAL-GW-MW1R-FMS-120405	4.09	124	110
Average Concentration (ng/mL) ± %RPD/RSD		1.61 ng/mL ± 5.6 %		103% ± 7.0%

NA = Not Applicable

Table 11. JPAL GW MW3R 120405

		PFOA		$^{13}C_4$-PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-31-004	JPAL-GW-MW3R-0-120405	7.90	NA	98.6
GLP10-01-01-31-005	JPAL-GW-MW3R-DB-120405	7.85	NA	94.1
GLP10-01-01-31-006	JPAL-GW-MW3R-FMS-120405	9.23	NC	96.8
Average Concentration (ng/mL) ± %RPD/RSD		7.88 ng/mL ± 0.63%		96.5% ± 2.4%

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

Table 12. JPAL GW MW4R 120405

		PFOA		$^{13}C_4$-PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-31-007	JPAL-GW-MW4R-0-120405	2.22	NA	97.2
GLP10-01-01-31-008	JPAL-GW-MW4R-DB-120405	2.25	NA	98.7
GLP10-01-01-31-009	JPAL-GW-MW4R-FMS-120405	4.21	98.8	104
Average Concentration (ng/mL) ± %RPD/RSD		2.24 ng/mL ± 1.3%		100% ± 3.7%

NA = Not Applicable

Table 13. JPAL GW MW4L 120405

		PFOA		$^{13}C_4$-PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-31-010	JPAL-GW-MW4L-0-120405	0.164	NA	104
GLP10-01-01-31-011	JPAL-GW-MW4L-DB-120405	0.160	NA	100
GLP10-01-01-31-012	JPAL-GW-MW4L-FMS-120405	2.11	97.4	100
Average Concentration (ng/mL) ± %RPD/RSD		0.162 ng/mL ± 2.5%		101% ± 2.4%

NA = Not Applicable

Table 14. JPAL GW MW5R 120405

		PFOA		$^{13}C_4$-PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-31-013	JPAL-GW-MW5R-0-120405	0.171	NA	98.7
GLP10-01-01-31-014	JPAL-GW-MW5R-DB-120405	0.177	NA	101
GLP10-01-01-31-015	JPAL-GW-MW5R-FMS-120405	2.08	95.3	99.6
Average Concentration (ng/mL) ± %RPD/RSD		0.174 ng/mL ± 3.4%		99.8% ± 1.3%

NA = Not Applicable

Table 15. JPAL GW MW5L 120405

		PFOA		$^{13}C_4$-PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-31-016	JPAL-GW-MW5L-0-120405	0.882	NA	98.4
GLP10-01-01-31-017	JPAL-GW-MW5L-DB-120405	0.841	NA	95.1
GLP10-01-01-31-018	JPAL-GW-MW5L-FMS-120405	2.71	92.4	97.2
Average Concentration (ng/mL) ± %RPD/RSD		0.862 ng/mL ± 4.8%		96.9% ± 1.7%

NA = Not Applicable

Table 16. JPAL GW MW6R 120405

		PFOA		$^{13}C_4$-PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-31-019	JPAL-GW-MW6R-0-120405	2.87	NA	96.1
GLP10-01-01-31-020	JPAL-GW-MW6R-DB-120405	2.85	NA	97.6
GLP10-01-01-31-021	JPAL-GW-MW6R-FMS-120405	4.62	88.0	97.3
Average Concentration (ng/mL) ± %RPD/RSD		*2.86 ng/mL ± 0.70%*		*97.0% ± 0.82%*

NA = Not Applicable

Table 17. JPAL GW MW6L 120405

		PFOA		$^{13}C_4$-PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-31-022	JPAL-GW-MW6L-0-120405	0.206	NA	97.4
GLP10-01-01-31-023	JPAL-GW-MW6L-DB-120405	0.199	NA	94.0
GLP10-01-01-31-024	JPAL-GW-MW6L-FMS-120405	2.14	96.9	100
Average Concentration (ng/mL) ± %RPD/RSD		*0.203 ng/mL ± 3.5%*		*97.2% ± 3.2%*

NA = Not Applicable

Table 18. JPAL GW MW7R 120405

		PFOA		$^{13}C_4$-PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-31-025	JPAL-GW-MW7R-0-120405	8.37	NA	102
GLP10-01-01-31-026	JPAL-GW-MW7R-DB-120405	8.15	NA	95.9
GLP10-01-01-31-027	JPAL-GW-MW7R-FMS-120405	9.85	NC	95.8
Average Concentration (ng/mL) ± %RPD/RSD		*8.26 ng/mL ± 2.7%*		*98.0% ± 3.8%*

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

Table 19. JPAL GW MW8R 120405

		PFOA		$^{13}C_4$-PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-31-028	JPAL-GW-MW8R-0-120405	0.304	NA	94.1
GLP10-01-01-31-029	JPAL-GW-MW8R-DB-120405	0.309	NA	98.7
GLP10-01-01-31-030	JPAL-GW-MW8R-FMS-120405	2.22	95.7	98.4
Average Concentration (ng/mL) ± %RPD/RSD		0.307 ng/mL ± 1.6%		97.1% ± 2.7%

NA = Not Applicable

Table 20. JPAL GW MW9R 120405

		PFOA		$^{13}C_4$-PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-31-031	JPAL-GW-MW9R-0-120405	0.123	NA	94.6
GLP10-01-01-31-032	JPAL-GW-MW9R-DB-120405	0.124	NA	96.5
GLP10-01-01-31-033	JPAL-GW-MW9R-FMS-120405	2.01	94.3	94.6
Average Concentration (ng/mL) ± %RPD/RSD		0.124 ng/mL ± 0.81%		95.2% ± 1.2%

NA = Not Applicable

Table 21. JPAL GW MW9L 120405

		PFOA		$^{13}C_4$-PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-31-034	JPAL-GW-MW9L-0-120405	0.0248	NA	97.8
GLP10-01-01-31-035	JPAL-GW-MW9L-DB-120405	<0.0240	NA	98.8
GLP10-01-01-31-036	JPAL-GW-MW9L-FMS-120405	1.87	92.3	97.1
Average Concentration (ng/mL) ± %RPD/RSD		0.0248 ng/mL		97.9% ± 0.87%

NA = Not Applicable

Table 22. JPAL GW MW10R 120405

		PFOA		$^{13}C_4$-PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-31-037	JPAL-GW-MW10R-0-120405	0.513	NA	98.2
GLP10-01-01-31-038	JPAL-GW-MW10R-DB-120405	0.500	NA	92.4
GLP10-01-01-31-039	JPAL-GW-MW10R-FMS-120405	2.37	93.2	93.3
Average Concentration (ng/mL) ± %RPD/RSD		*0.507 ng/mL ± 2.6%*		*94.6% ± 3.3%*

NA = Not Applicable

Table 23. JPAL GW MW11L 120405

		PFOA		$^{13}C_4$-PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-31-040	JPAL-GW-MW11L-0-120405	0.302	NA	98.8
GLP10-01-01-31-041	JPAL-GW-MW11L-DB-120405	0.278	NA	97.5
GLP10-01-01-31-042	JPAL-GW-MW11L-FMS-120405	2.19	95.0	99.0
Average Concentration (ng/mL) ± %RPD/RSD		*0.290 ng/mL ± 8.3%*		*98.4% ± 0.83%*

NA = Not Applicable

Table 24. JPAL GW MW3R RB 120405

		PFOA	$^{13}C_4$-PFOA
3M LIMS ID	Description	Concentration (ng/mL)	Recovery
GLP10-01-01-31-043	JPAL-GW-MW3R-RB-120405	<0.0240	97.8

Table 25. JPAL GW TRIP 120316

		PFOA		$^{13}C_4$-PFOA
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	%Recovery
GLP10-01-01-31-044	JPAL-GW-TRIP01-0-120316	<0.0240	NA	98.0
GLP10-01-01-31-045	JPAL-GW-TRIP01-FMS-120316	1.92	96.0	94.9

NA = Not Applicable

9 Conclusion

Laboratory control spikes and field matrix spikes were used to determine the analytical method accuracy and precision for PFOA. Analysis was successfully completed following 3M Environmental Laboratory method ETS-8-044.1 described herein.

10 Data/Sample Retention

All remaining samples and associated project data (hardcopy and electronic) will be archived according to 3M Environmental Laboratory standard operating procedures.

11 Attachments

Attachment A: Protocol Amendment 31 (General Project Outline)

Attachment B: Representative Chromatograms and Calibration Curves

Attachment C: Analytical Method – ETS-8-044.1

12 Signatures

5/4/2012
Cleston Lange, Ph.D., 3M Principal Analytical Investigator — Date

4 MAY 2012
William K. Reagen, Ph.D., 3M Environmental Laboratory Manager — Date

5/8/12
Gary Hohenstein, 3M Sponsor Representative — Date

5/14/12
Jaisimha Kesari, Study Director — Date

ATTACHMENT A: PROTOCOL AMENDMENT

Study Title

Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program

PROTOCOL AMENDMENT NO. 31

Amendment Date:
March 22, 2012

Performing Laboratory
3M Environmental, Health, and Safety Operations
3M Environmental Laboratory
Building 260-5N-17
Maplewood, MN 55144-1000

Laboratory Project Identification
GLP10-01-01

Sampling Event

Off-Site Wells - Bert Jeffries Property

Analytical Protocol: GLP10-01-01
Amendment 31

This amendment modifies the following portion of protocol:

"Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program"

PROTOCOL READS:

No changes to the wording of the protocol are required.

AMEND TO READ:

No changes to the wording of the protocol are required. This amendment only addresses and documents the addition of the General Project Outline (GPO) for the collection and analysis of groundwater samples as part of the 3M Decatur Phase 3 Program for PFOA (GLP10-01-01). The anticipated sample collection will occur around the timeframe of the week of March 26, 2012. The groundwater samples for this sampling event will be entered into the 3M Environmental Laboratory LIMS as project GLP10-01-01-31 and reported as interim report GLP10-01-01-31, (reflecting study GLP10-01-01 and amendment -31).

Reason:

The reason for this amendment is to document the General Project Outline (GPO) which describes the anticipate groundwater sample collection event for fourteen off-site wells at the Bert Jeffries Property.

The GPO is three pages in length and included as attached to this amendment form.

Amendment Approval

Gary Hohenstein, Sponsor Representative — Date: 3/26/12

Cleston C. Lange, Principal Analytical Investigator — Date: 3/22/2012

William Reagen, EHS Opns Environmental Lab Management — Date: 23 MARCH 2012

Jaisimha Kesari P.E., DEE, Study Director — Date: 3/30/12

3M Environmental Health & Safety Operations, Environmental Laboratory

General Project Outline

To: Gary Hohenstein, 3M EHS&Opns

From: Susan Wolf, 3M EHS&Opns; Environmental Lab

cc: William Reagen, 3M EHS&Opns; Environmental Lab

Cleston Lange, 3M EHS&Opns; Environmental Lab

Jai Kesari, Weston Solutions

Date: March 22, 2012

Subject: Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program; GLP Interim Report 31; Off-Site Wells Bert Jeffries Property

1 General Project Information

Contacts	**3M Sponsor Representative** Gary Hohenstein 3M EHS Operations 3M Building 224-5W-03 Saint Paul, MN 55144-1000 Phone: (651) 737-3570 gahohenstein@mmm.com **3M Environmental Laboratory Management** William K. Reagen 3M EHS Opns, Environmental Laboratory 260-5N-17 651 733-9739 wkreagen@mmm.com **Principal Analytical Investigator** Cleston Lange 3M EHS Opns, Environmental Laboratory 260-5N-17 651 733-9860 cclange@mmm.com **Sampling Coordinator** Timothy Frinak Weston Solutions Timothy.frinak@westonsolutions.com Phone: (334)-332-9123
Lab Request Number	**GLP10-01-01-31**
Six Digit Department Number	Dept #530711, Project #0022674449
Project Schedule/Test Dates	Sampling scheduled for the week of March 26, 2012

All verbal and written correspondence will be directed to Gary Hohenstein and Jai Kesari.

2 Background Information and Project Objective(s)

The 3M EHS Operations Laboratory (3M Environmental Lab) will receive and analyze groundwater samples collected from fourteen sampling locations for Perfluorooctanoic Acid (PFOA) from wells located on the Bert Jeffries property. Analyses will be conducted under the GLP requirements of EPA TSCA Good Laboratory Practice Standards 40 CFR 792.

Groundwater samples will be collected by Weston Solutions personnel the week of March 26, 2012. The 3M Environmental Laboratory will prepare the sample bottles with all required spikes to ensure that results for PFOA are of a known precision and accuracy. The final report will be submitted to Gary Hohenstein and Jai Kesari upon completion under interim report GLP10-01-01-31.

3 Project Schedule

Sample collection bottles will be prepared by 3M Environmental Laboratory for sampling the week of March 26, 2012. Sample bottles will be shipped in coolers overnight to 3M Decatur for arrival on Friday, March 23, 2012. Sample bottles should be stored refrigerated on-site until sample collection.

Martin Smith \ Weston Trailer
3M Decatur Plant
1400 State Docks Road
Decatur, Alabama 35601

4 Test Parameters

The targeted limit of quantitation will be **0.025 ng/mL** (ppb) for PFOA.

Fourteen sampling locations have been specified. For each sampling location, a total of three sample bottles will be collected (sample, sample duplicate and 2 ng/mL field matrix spike). The "fill to here" line on each 250 mL Nalgene bottle will be 200 mL. One set of trip blanks consisting of reagent-grade water as well as a trip blank spike at 2 ng/mL will be prepared at the 3M Environmental Laboratory and sent to the sampling location with the other bottles. All sample bottles will include the addition of $^{13}C_8$-PFOA (internal standard) at a nominal concentration of 1 ng/mL. All sample bottles will also include the addition of $^{13}C_4$-PFOA (surrogate spike) at a nominal concentration of 0.1 ng/mL. One additional bottle will be prepared to be used for the preparation of the equipment rinseate blank. A 500-mL bottle of laboratory reagent water will be sent with the sample bottles to be used to generate the rinseate blank sample.

5 Test Methods

Samples will be prepared and analyzed by LC/MS/MS following ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds In Water by LC/MS/MS; Direct Injection Analysis".

The data quality objectives for these studies are quantitative results for the target analytes with an analytical accuracy of 100±30%. Field matrix spikes not yielding recoveries within 100±30% will be addressed in the report and the final accuracy statement may be adjusted accordingly.

Where applicable, samples will be analyzed against an internal standard calibration curve. Each curve point will contain isotopically-labeled perfluorocarboxylic acids and perfluorosulfonic acids at a nominal concentration of 1 ng/mL. The calibration curve will be generated by taking the ratio of the standard peak area counts over the internal standard peak area counts to fit the data for each analyte.

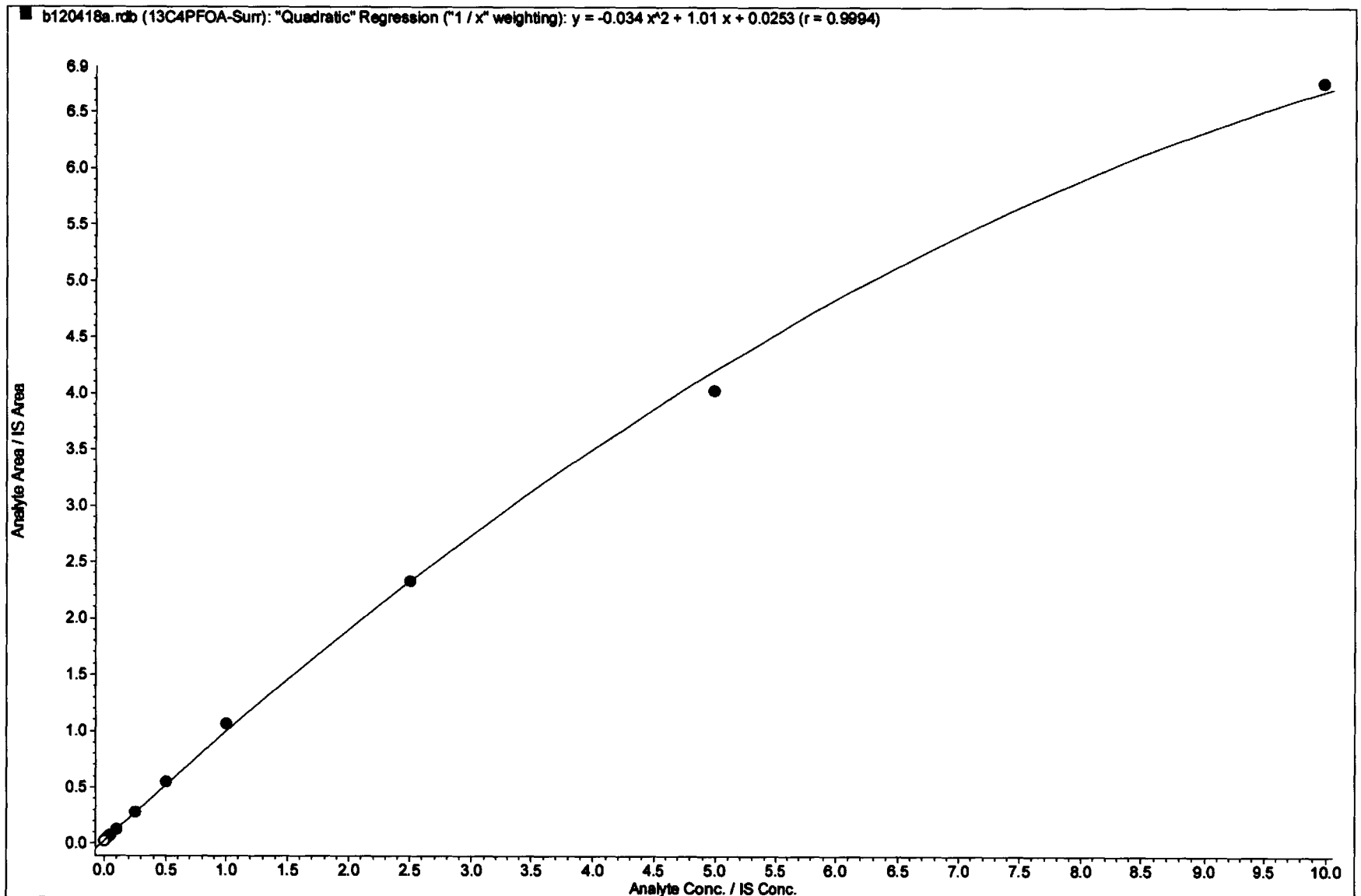
6 Reporting Requirements

For each sampling location, the report will contain the results for the sample, sample duplicate, and field matrix spike. Trip blank and trip blank spike will be reported for the sampling event as will any equipment/rinseate blanks prepared in the field. Laboratory control spikes of reagent water prepared at the time of sample extraction will also be reported and used to evaluate the overall method accuracy and precision. Method blanks of reagent water prepared at the time of sample extraction will be used to determine the method detection limit.

ATTACHMENT B: REPRESENTATIVE SAMPLE CHROMATOGRAMS AND CALIBRATION CURVE(S)

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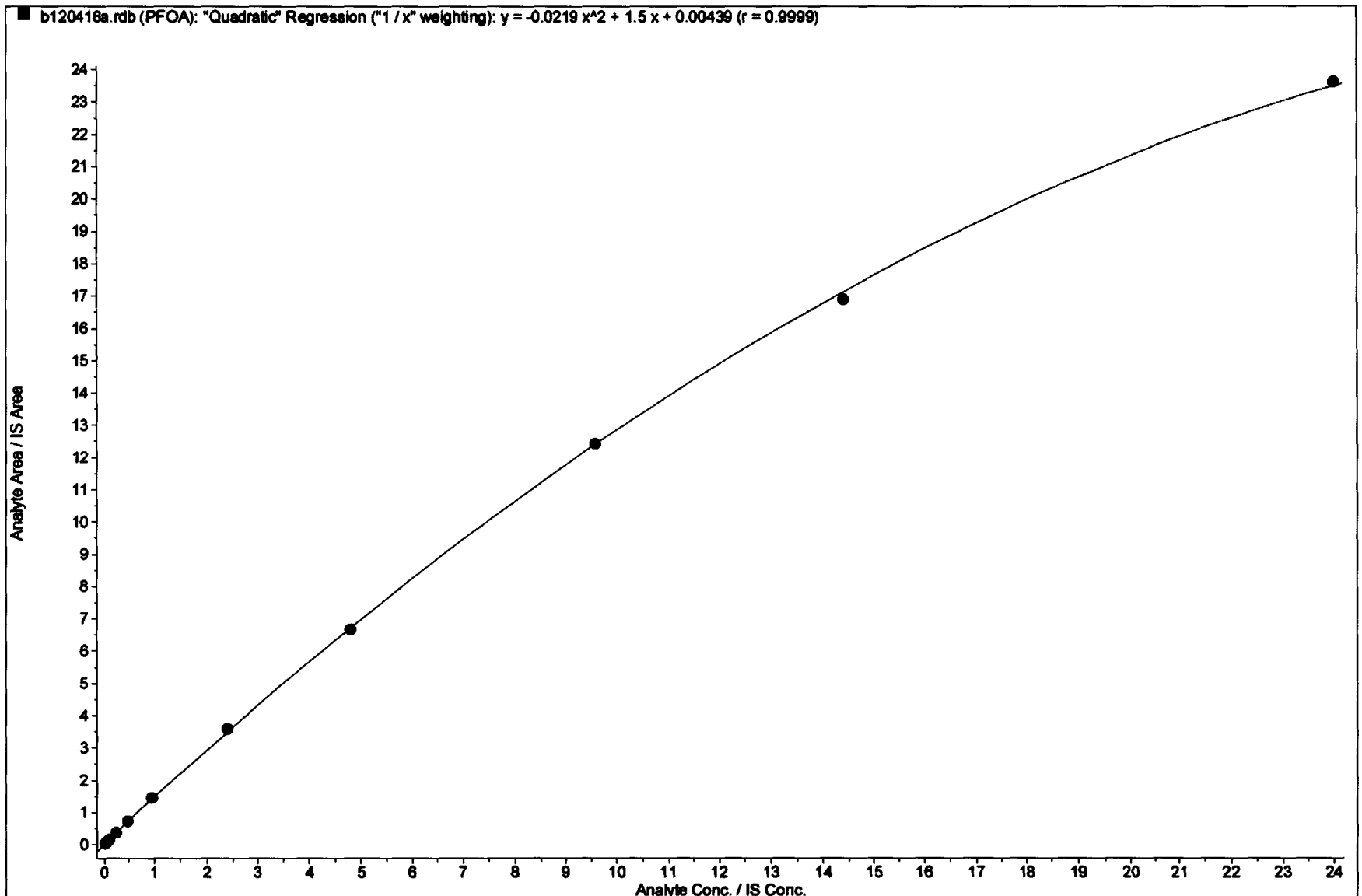
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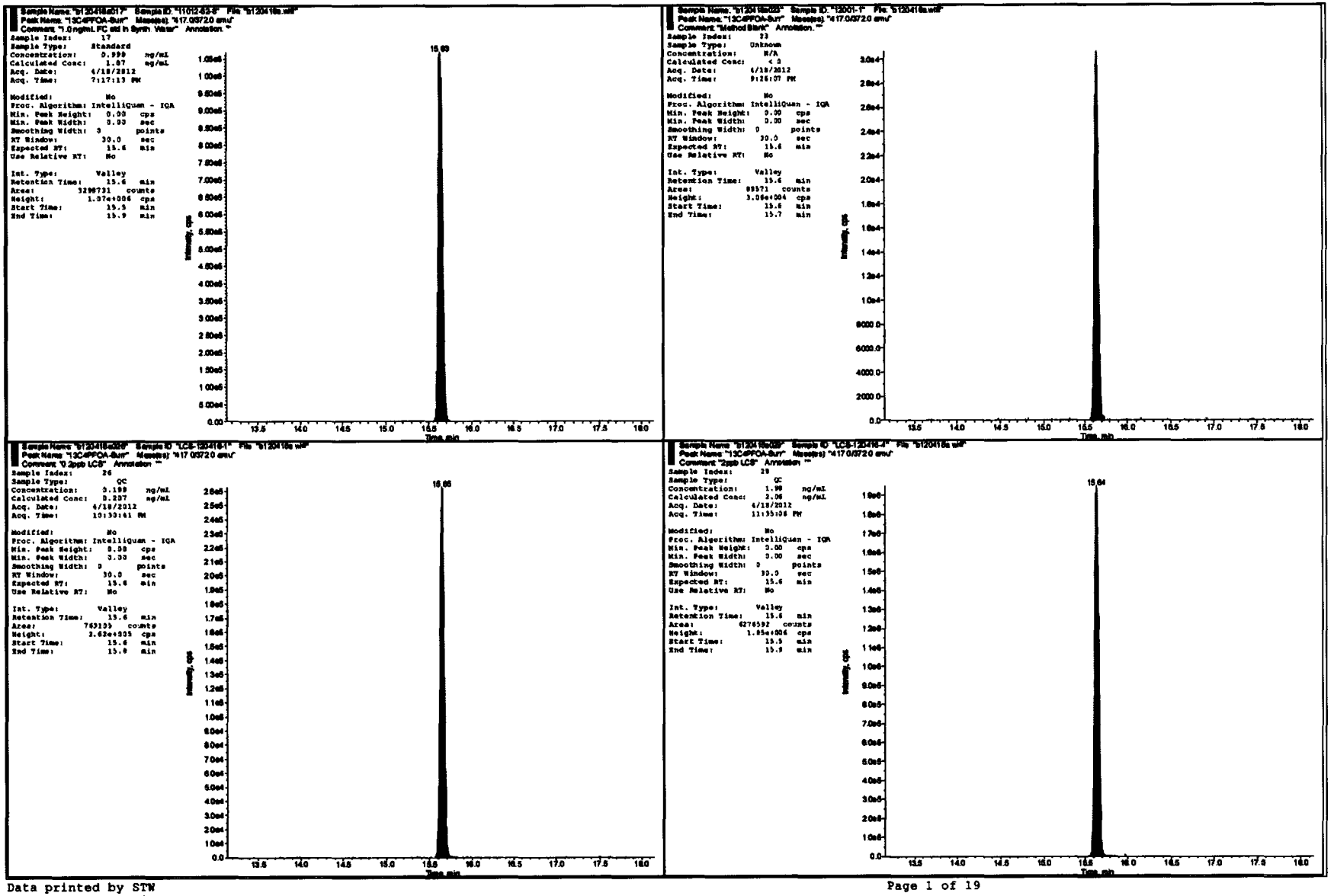
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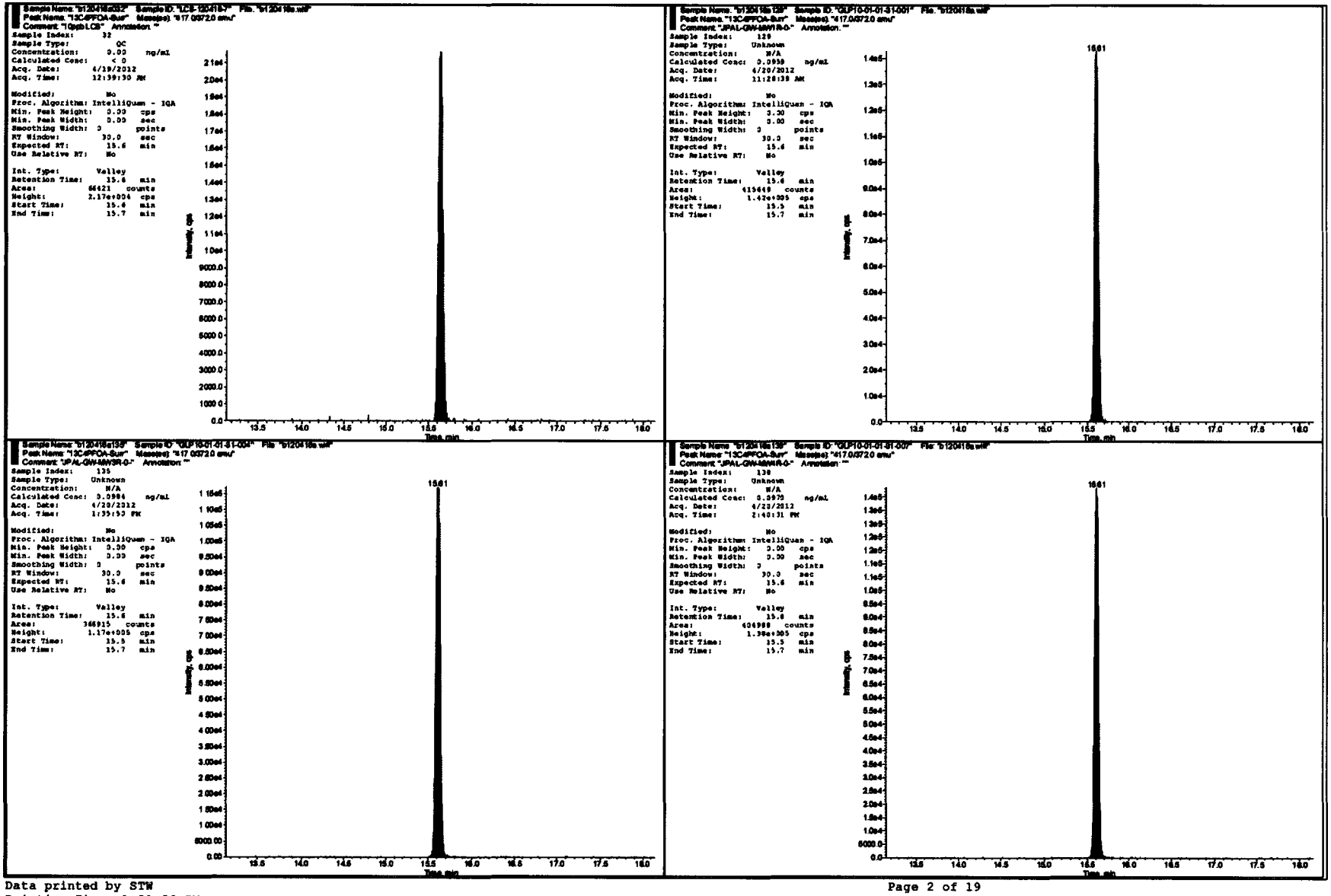
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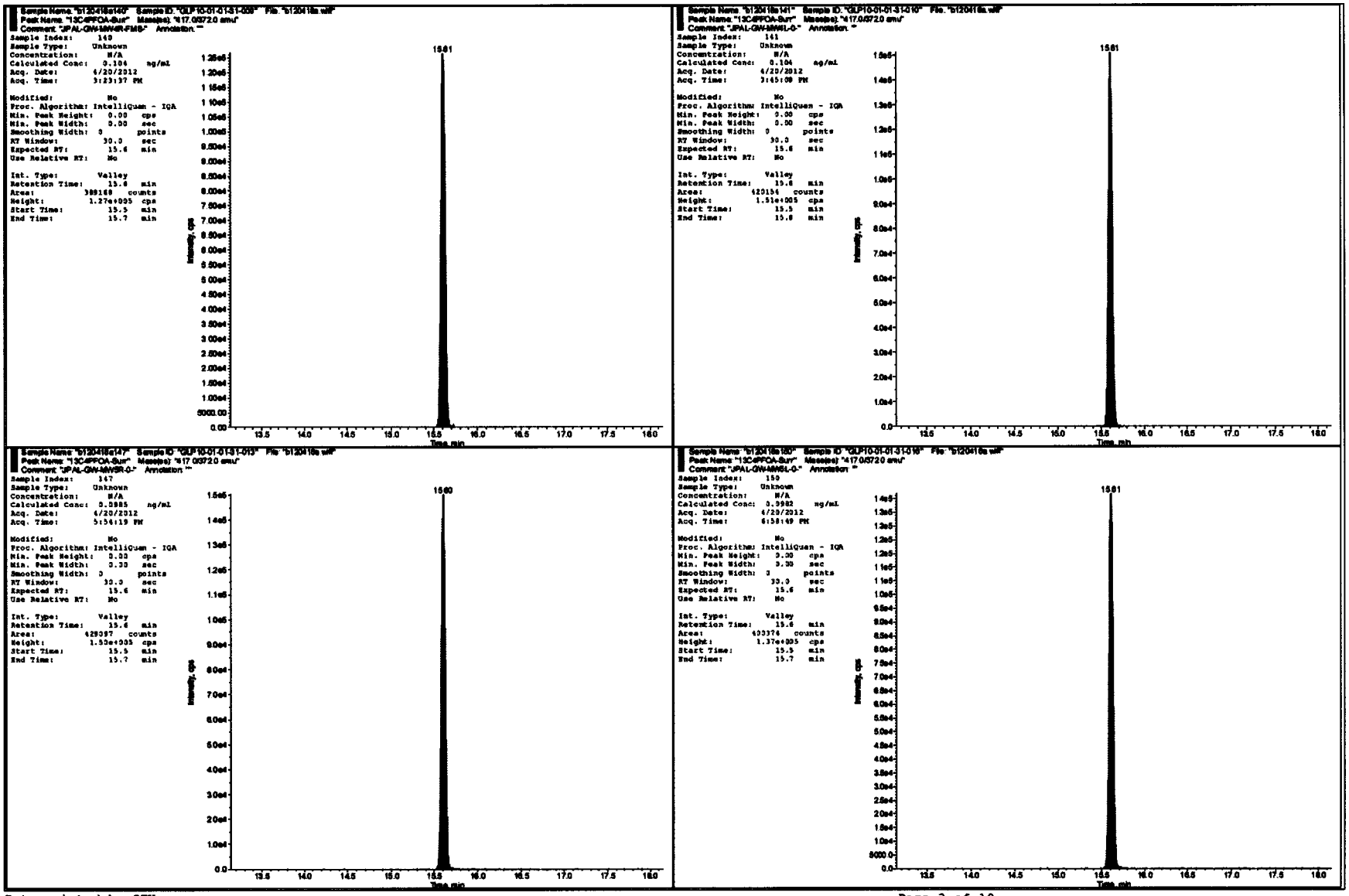
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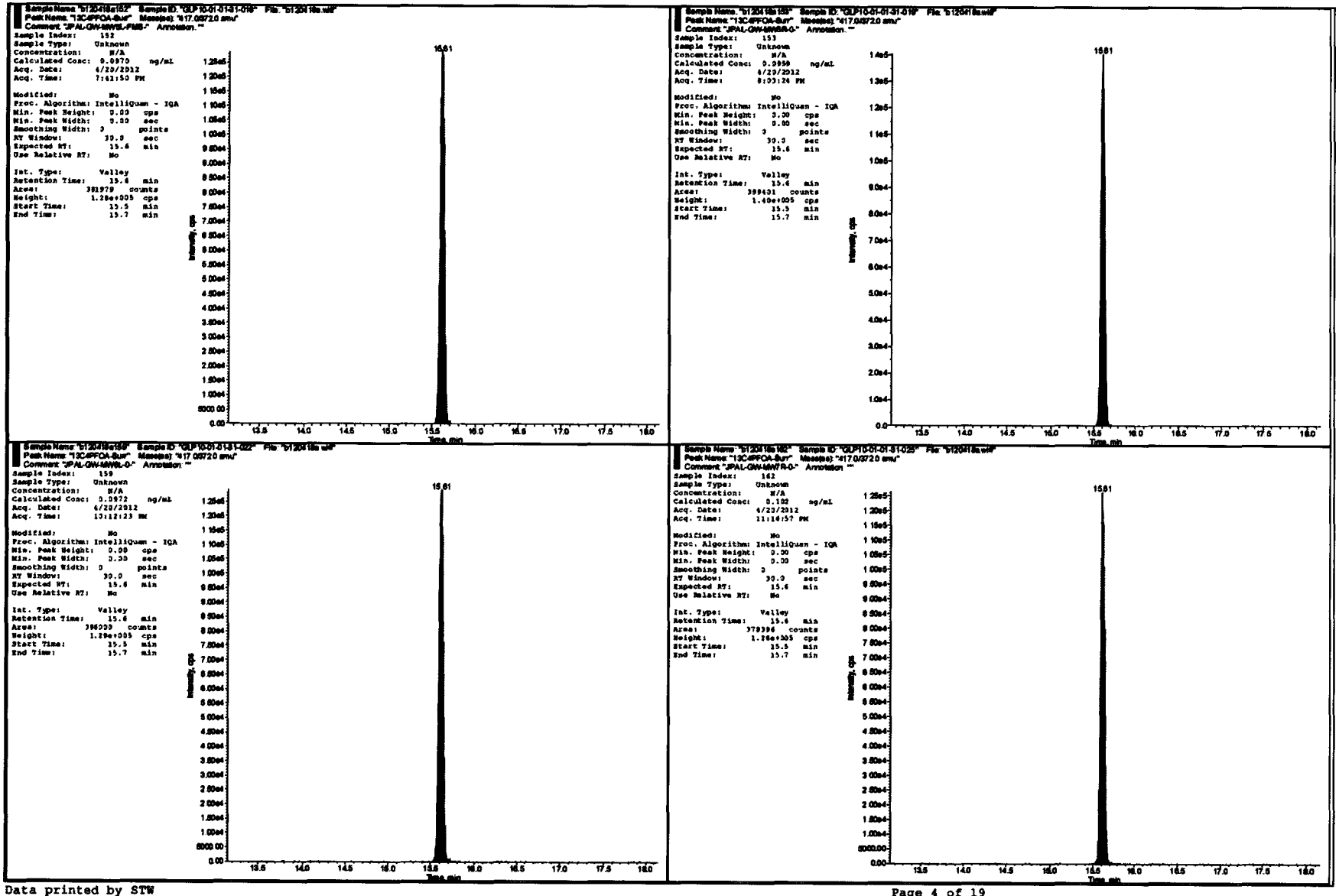
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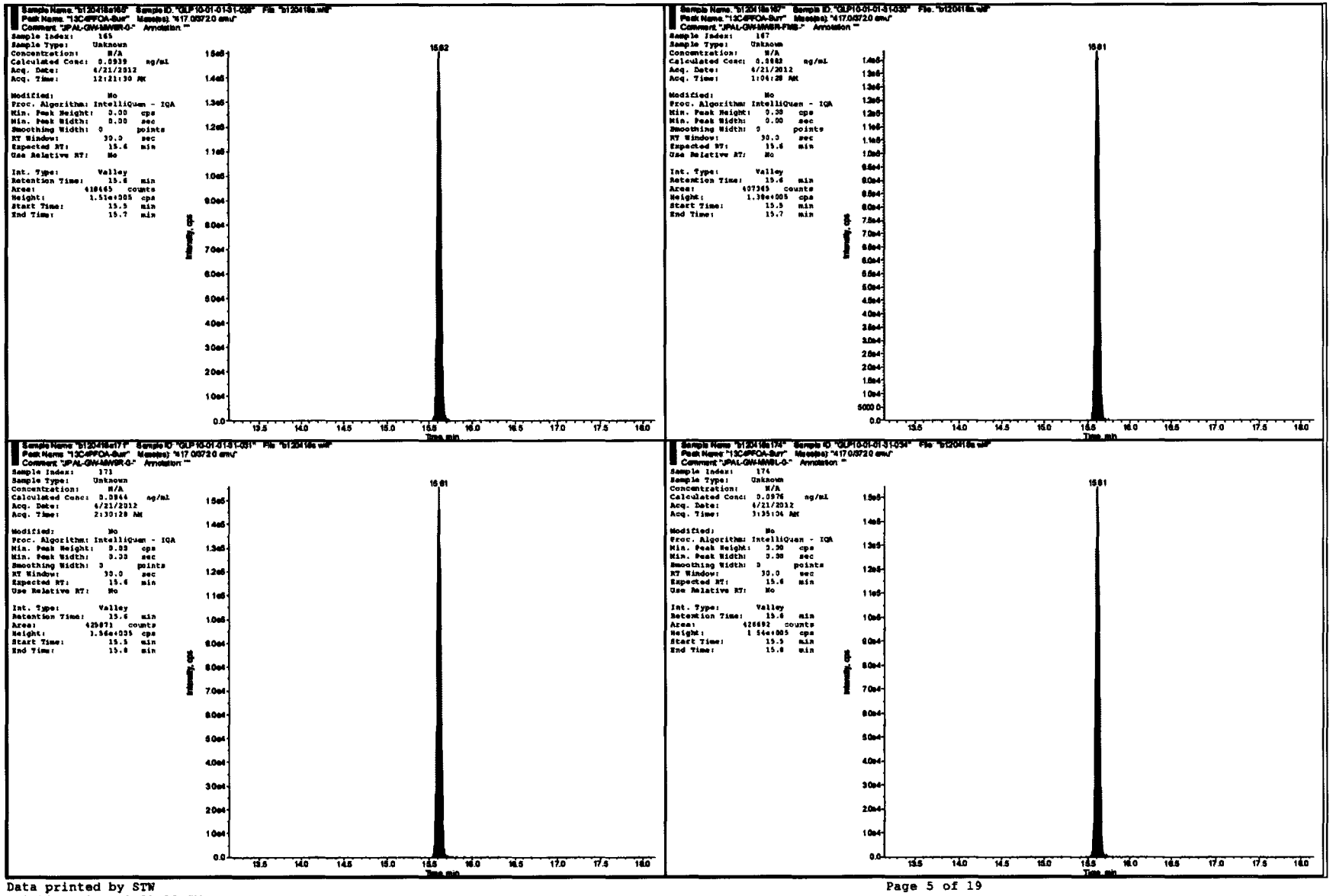
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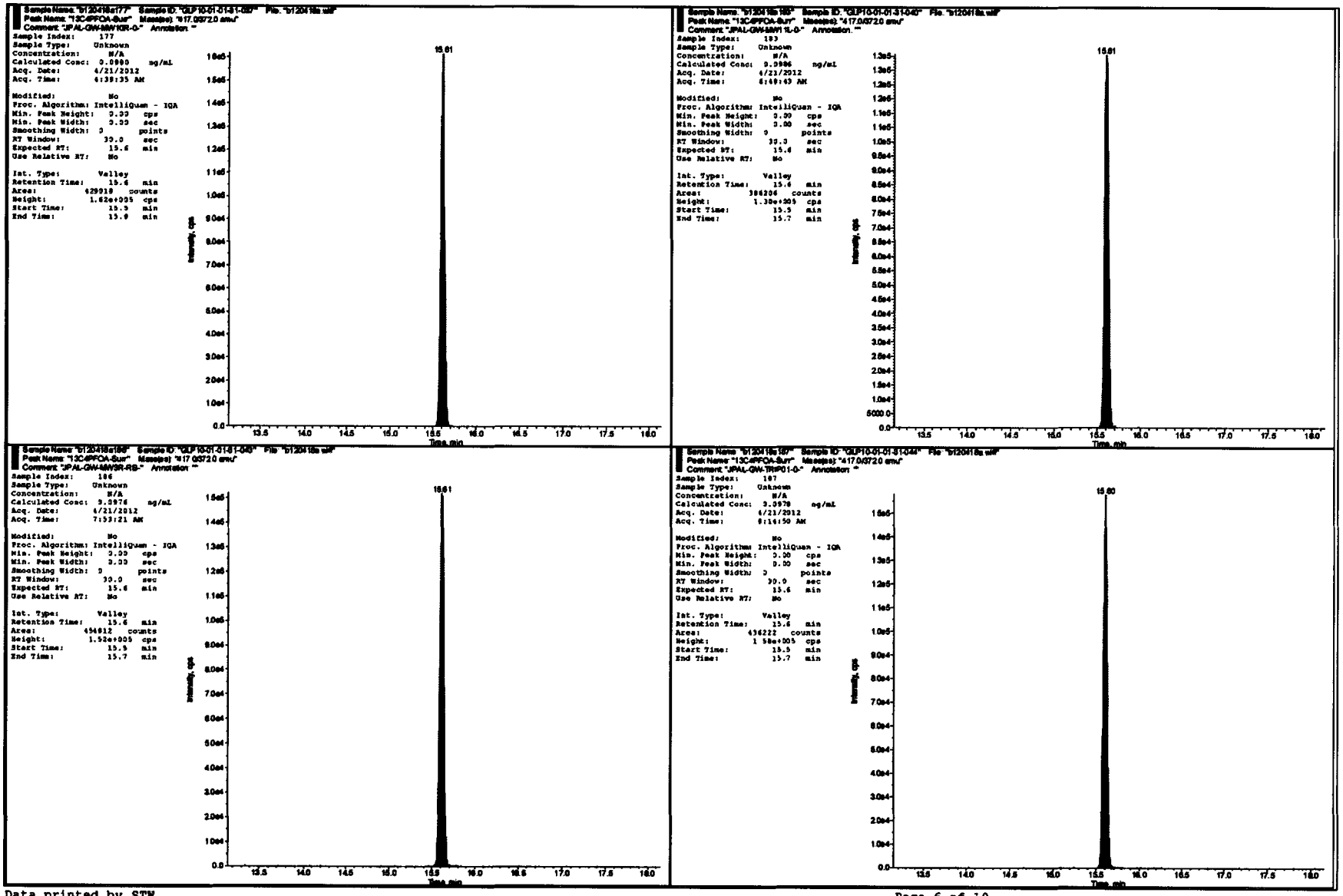
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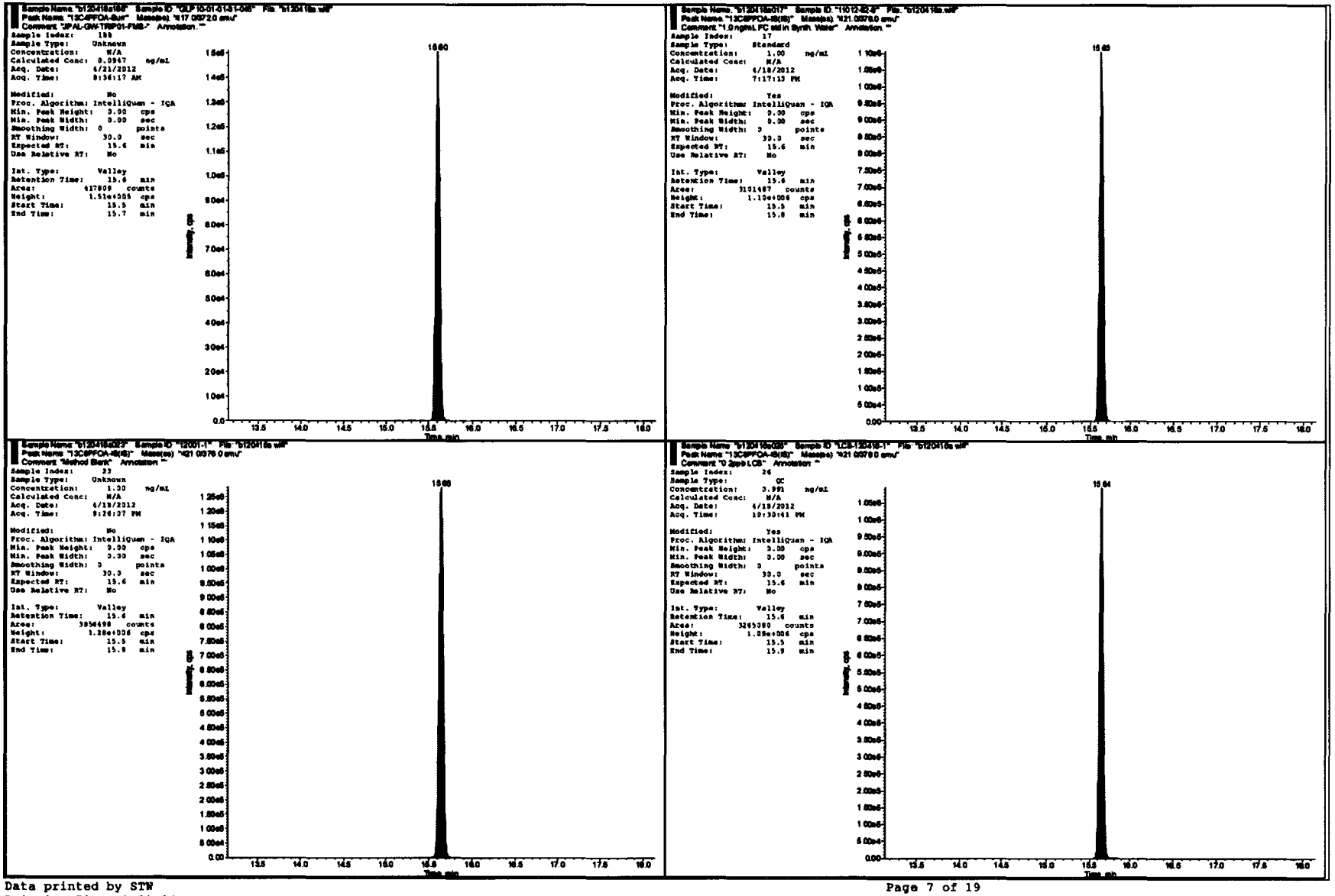


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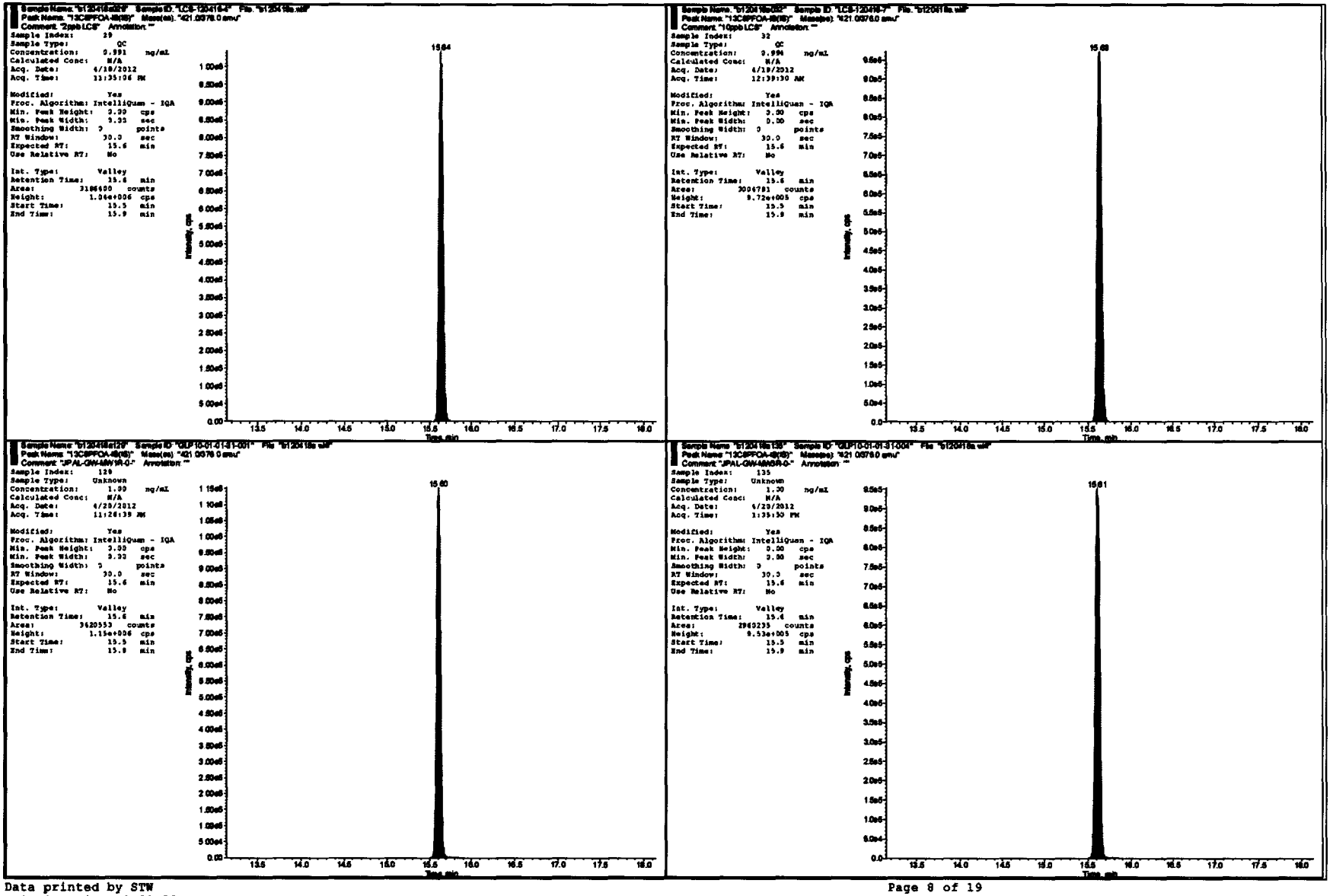
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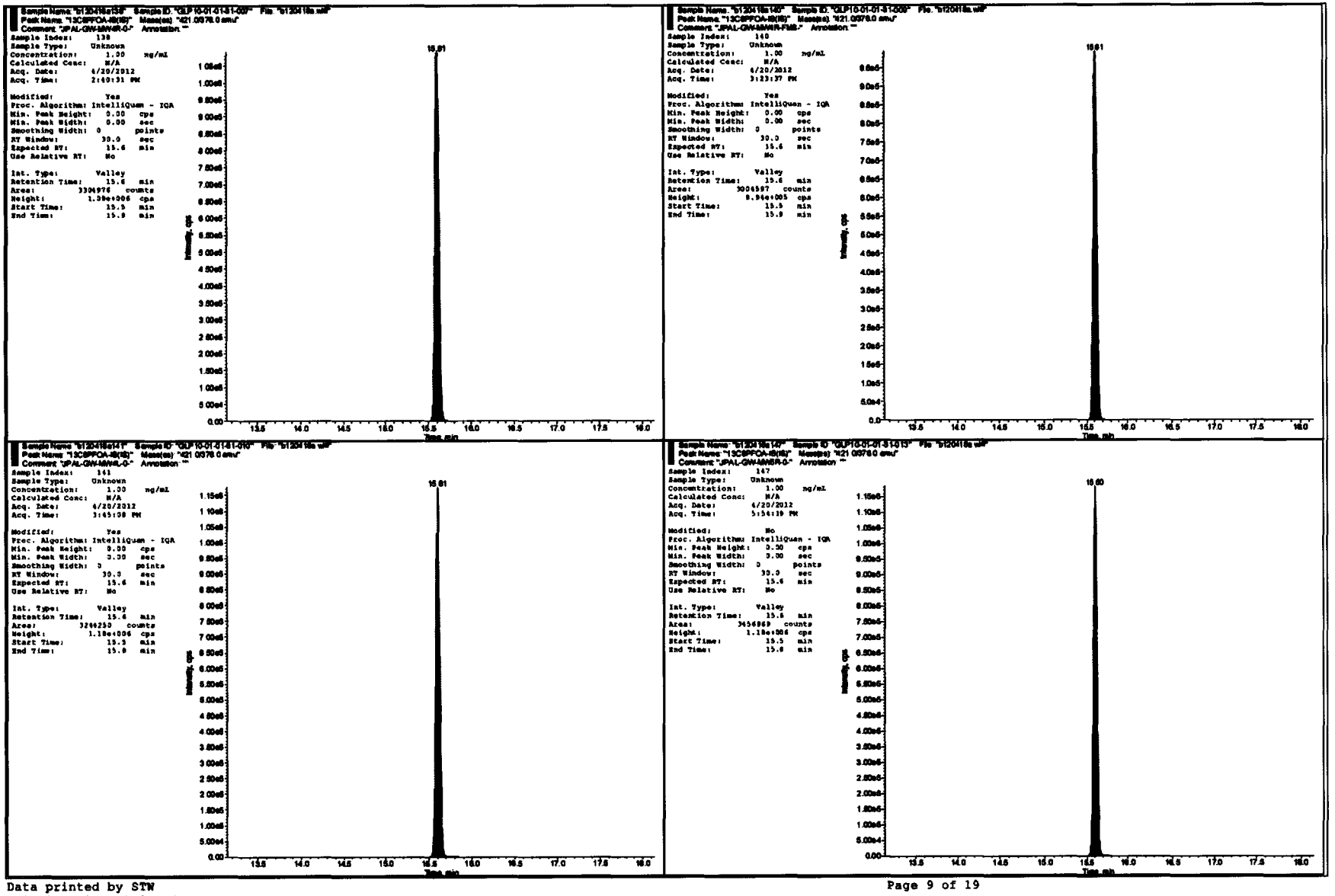


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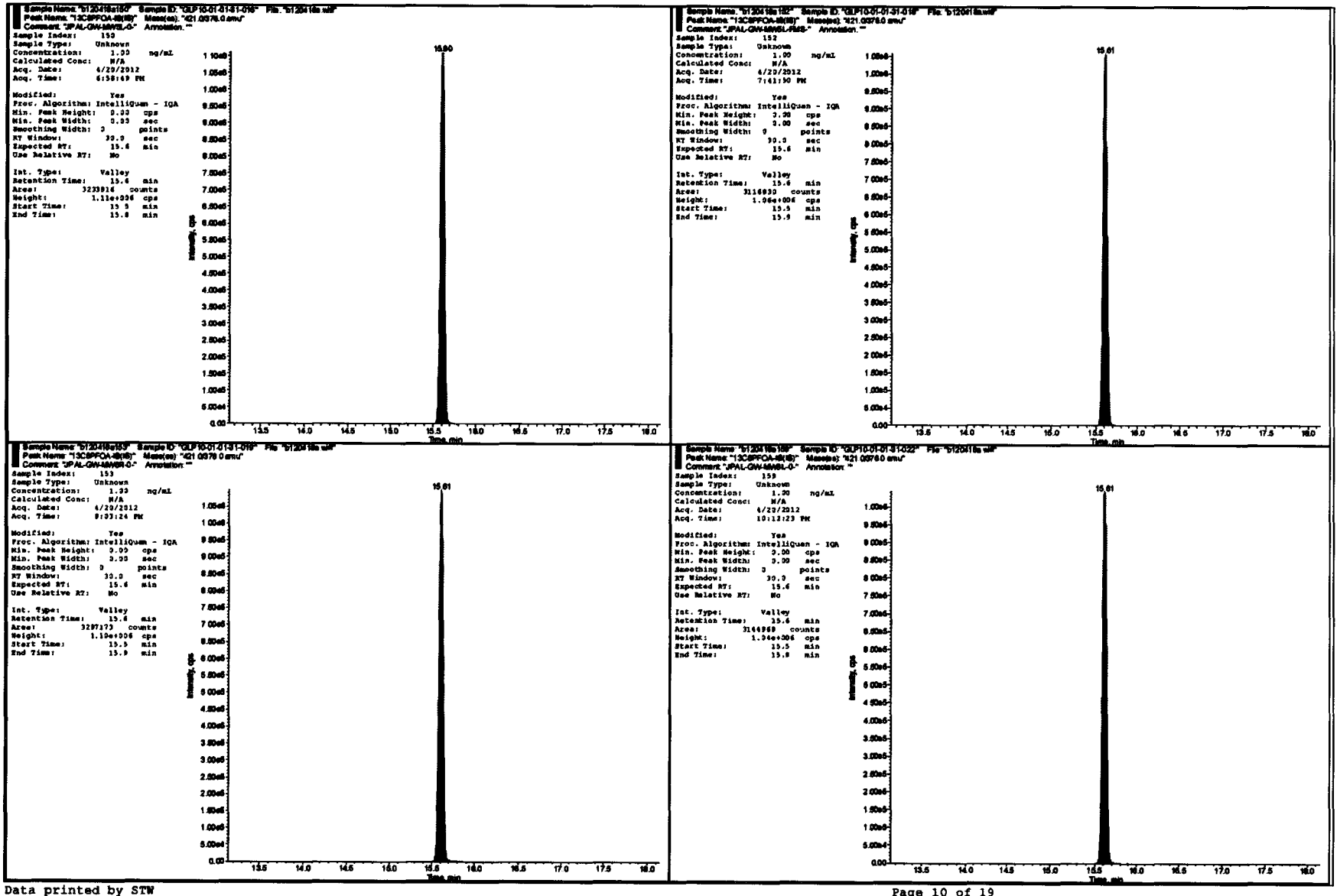
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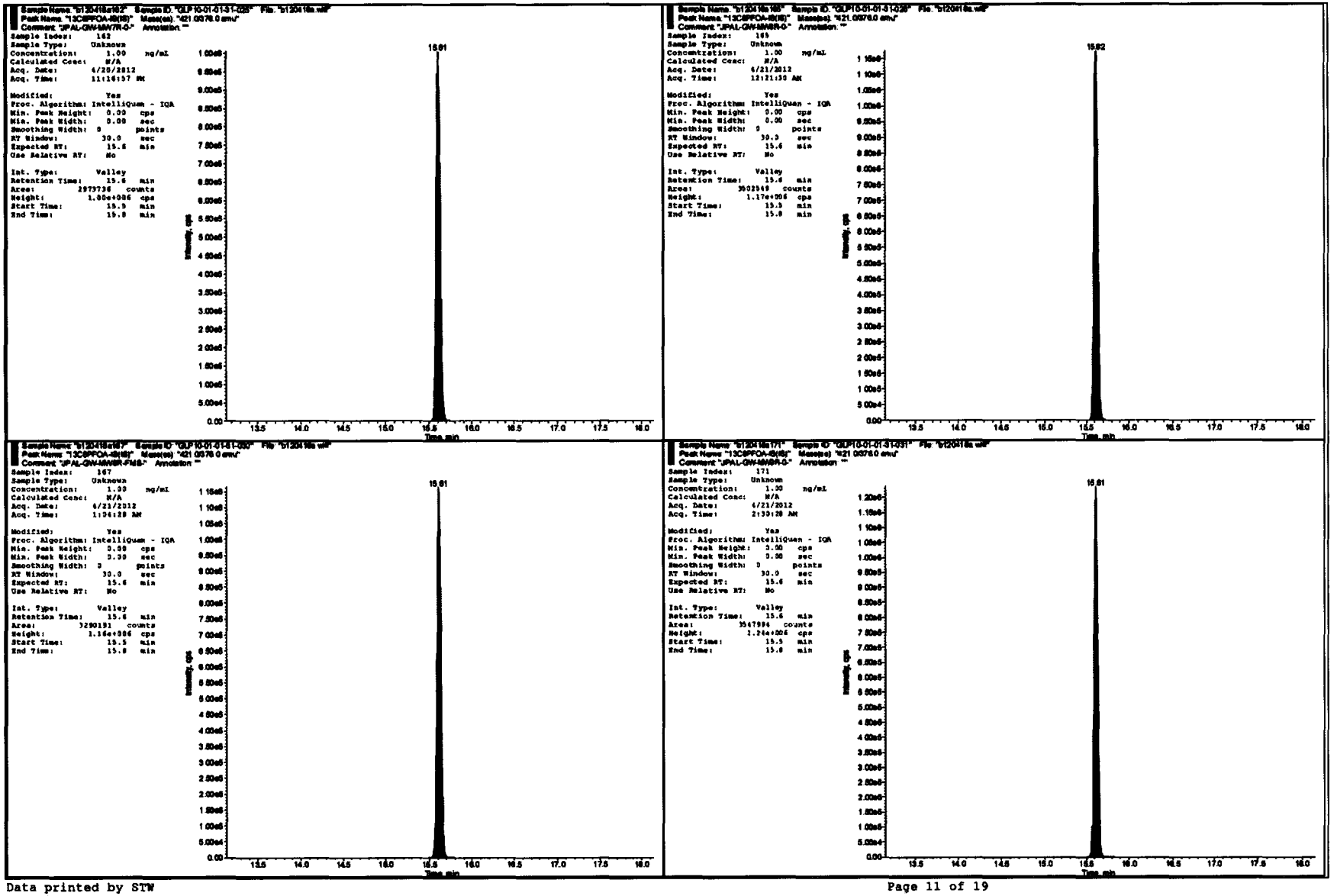
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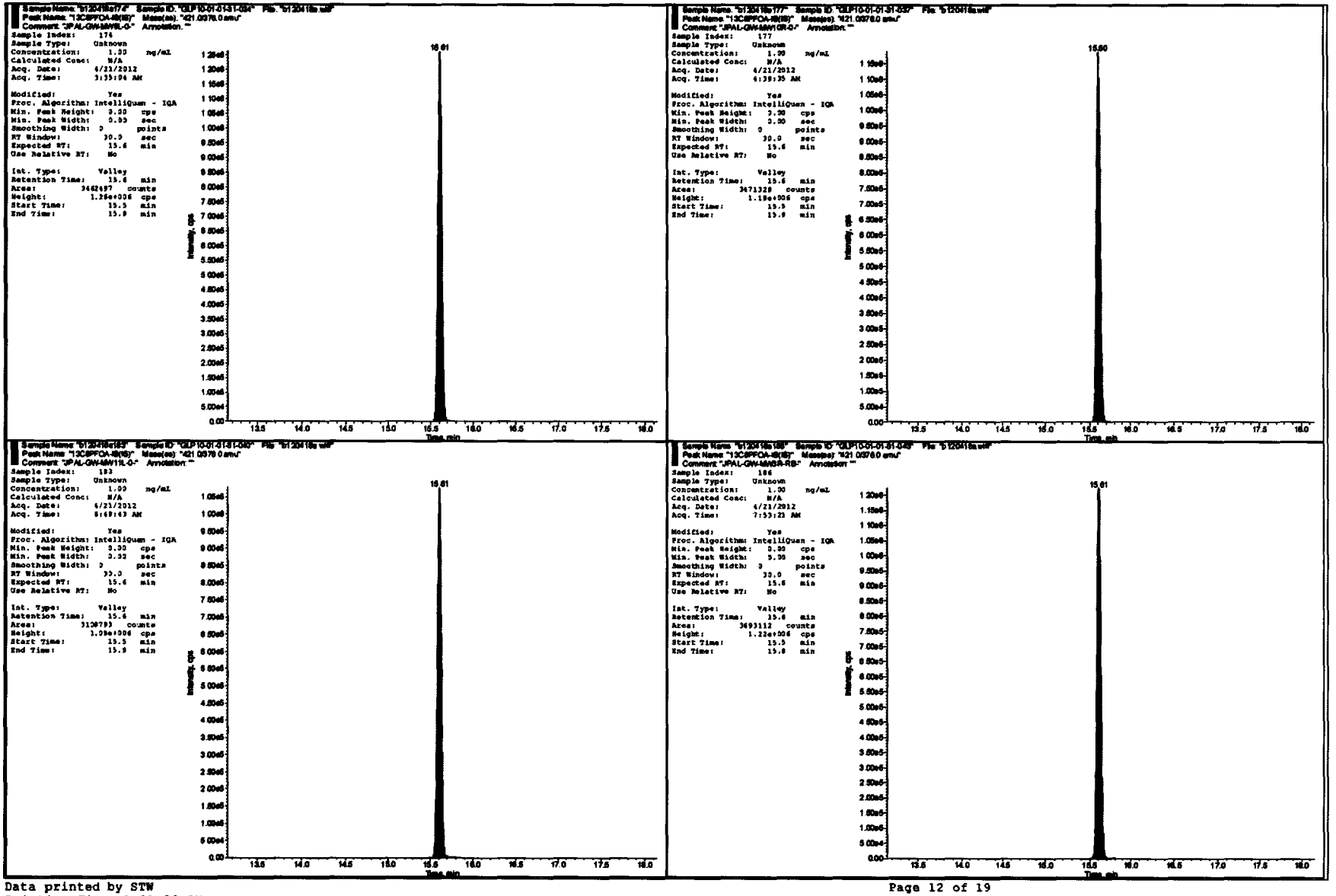
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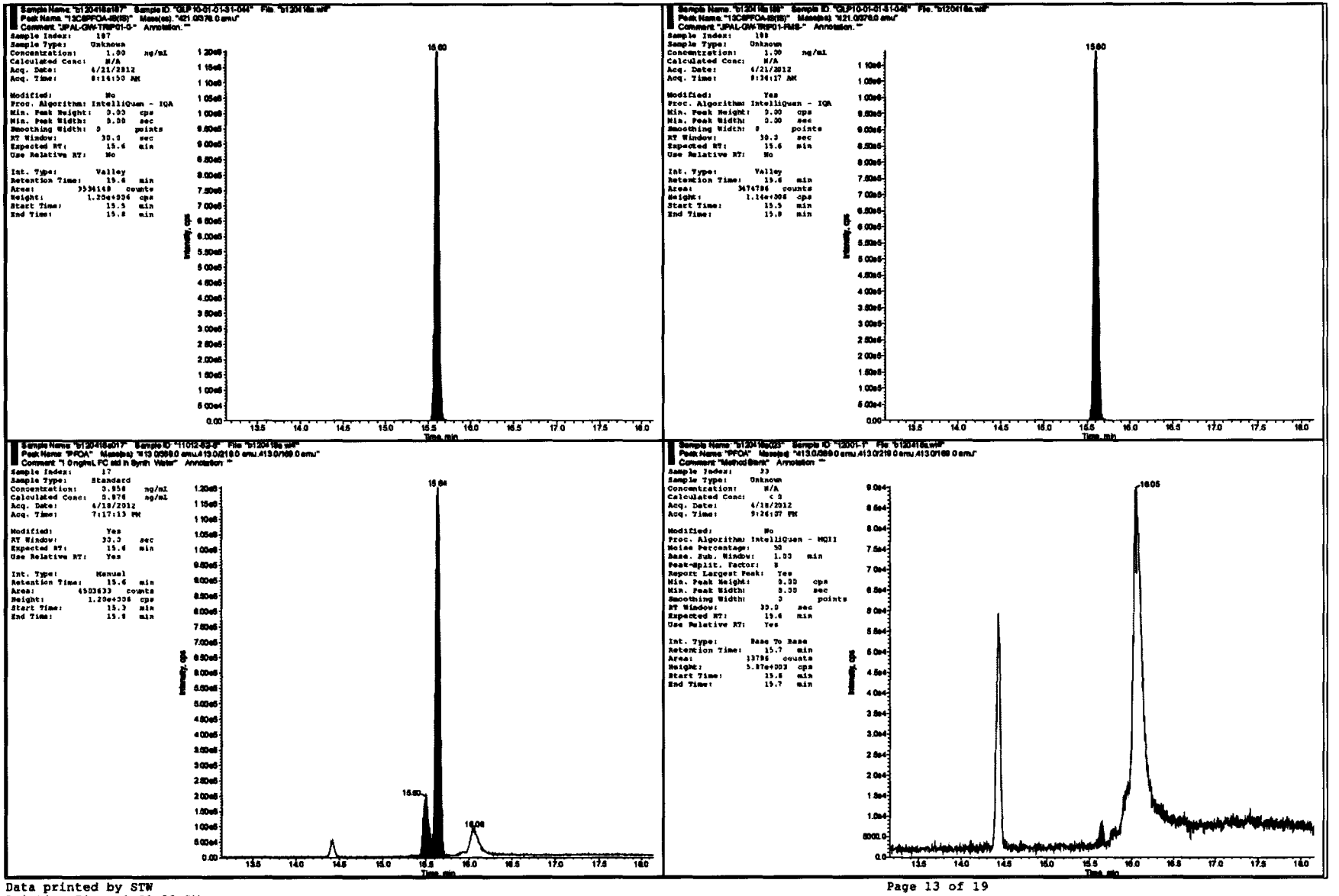
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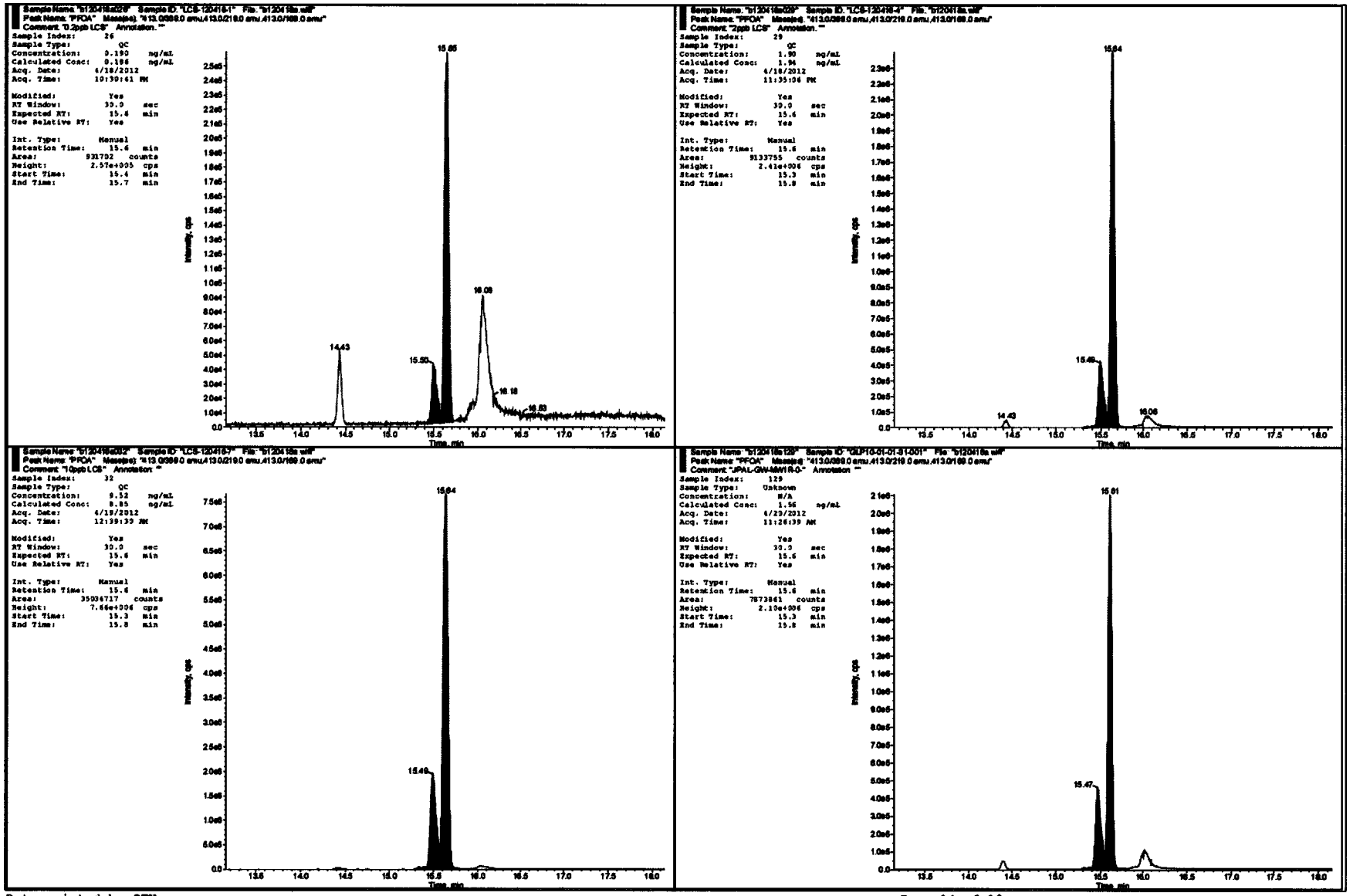
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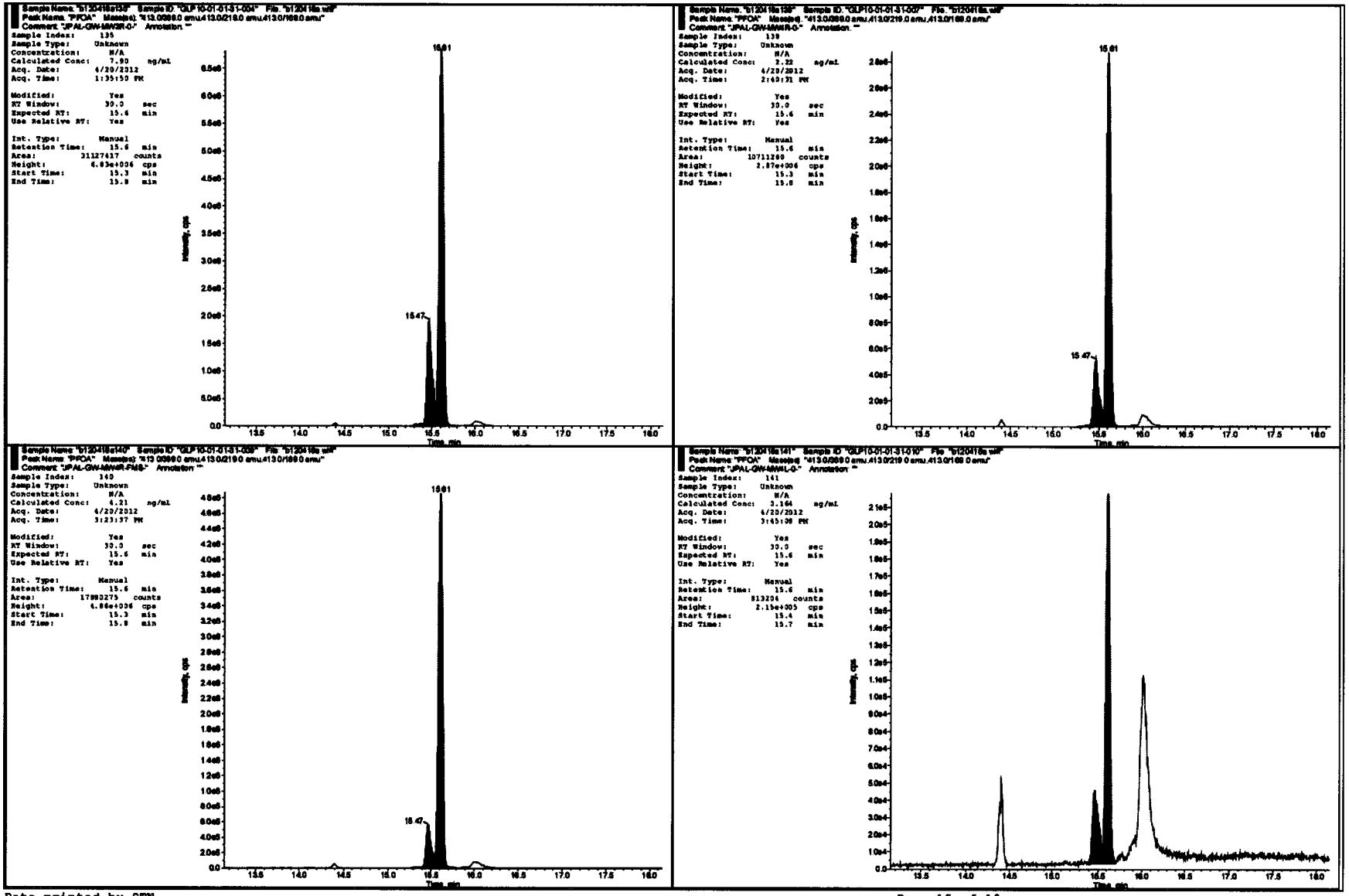


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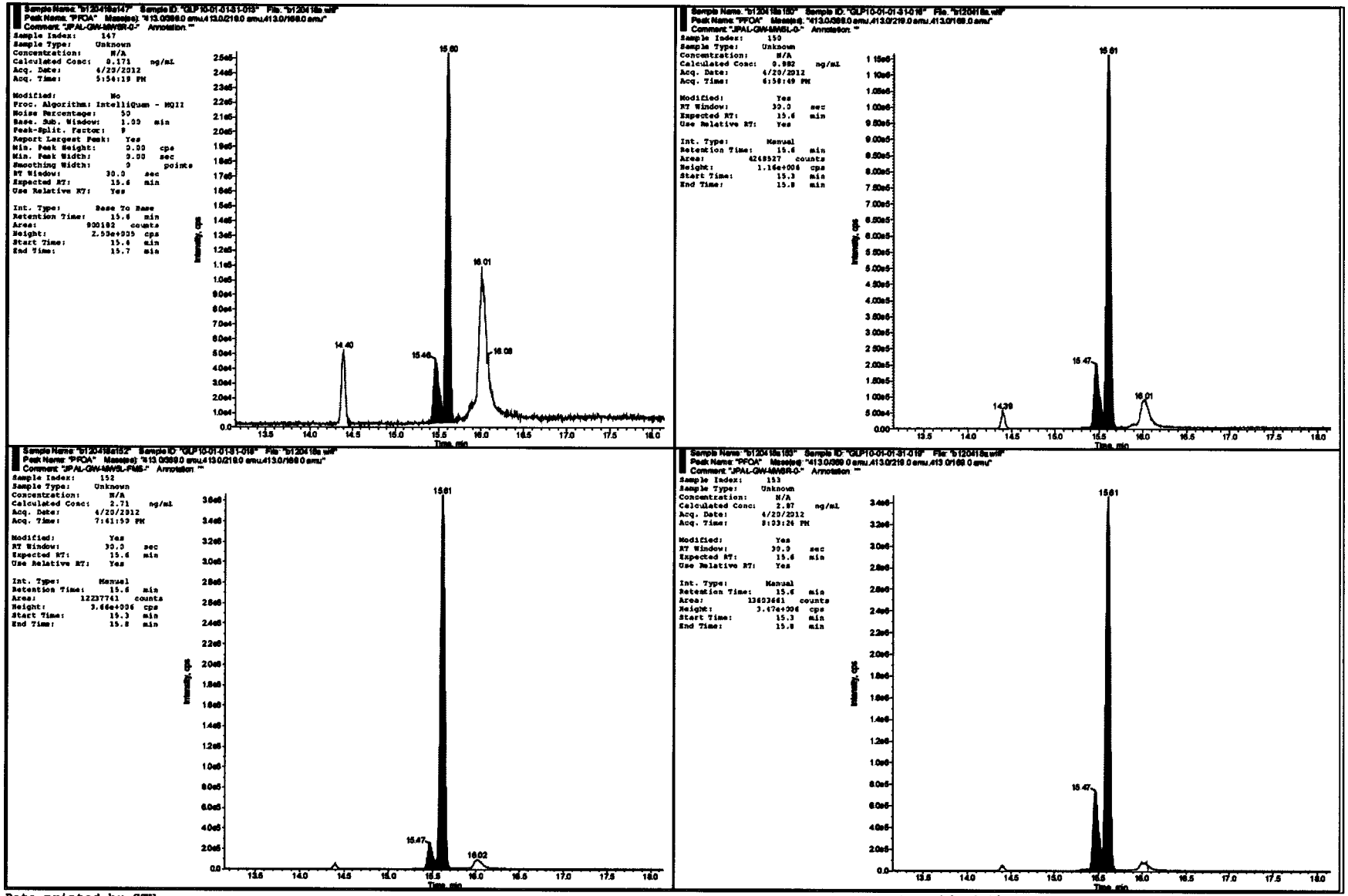
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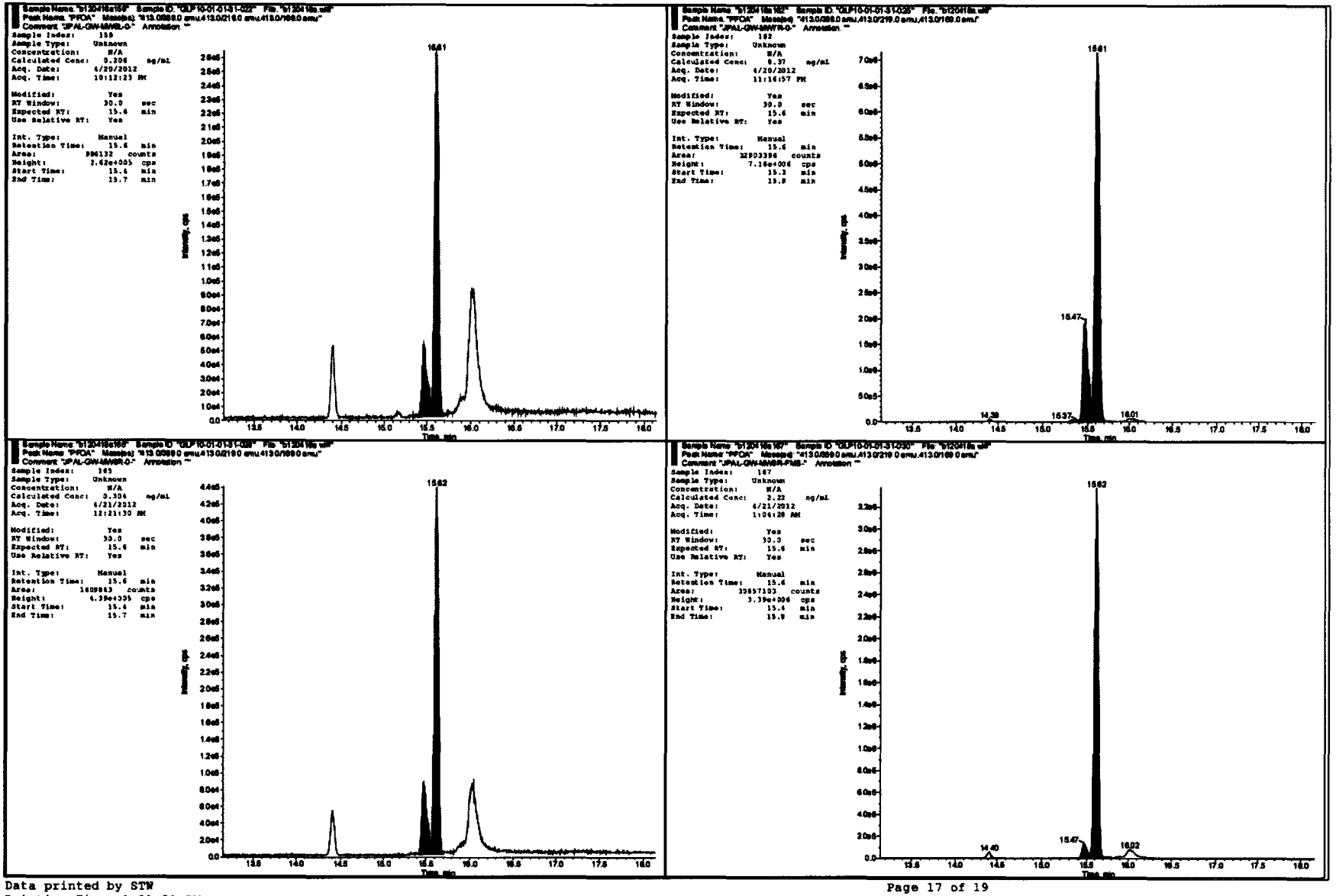
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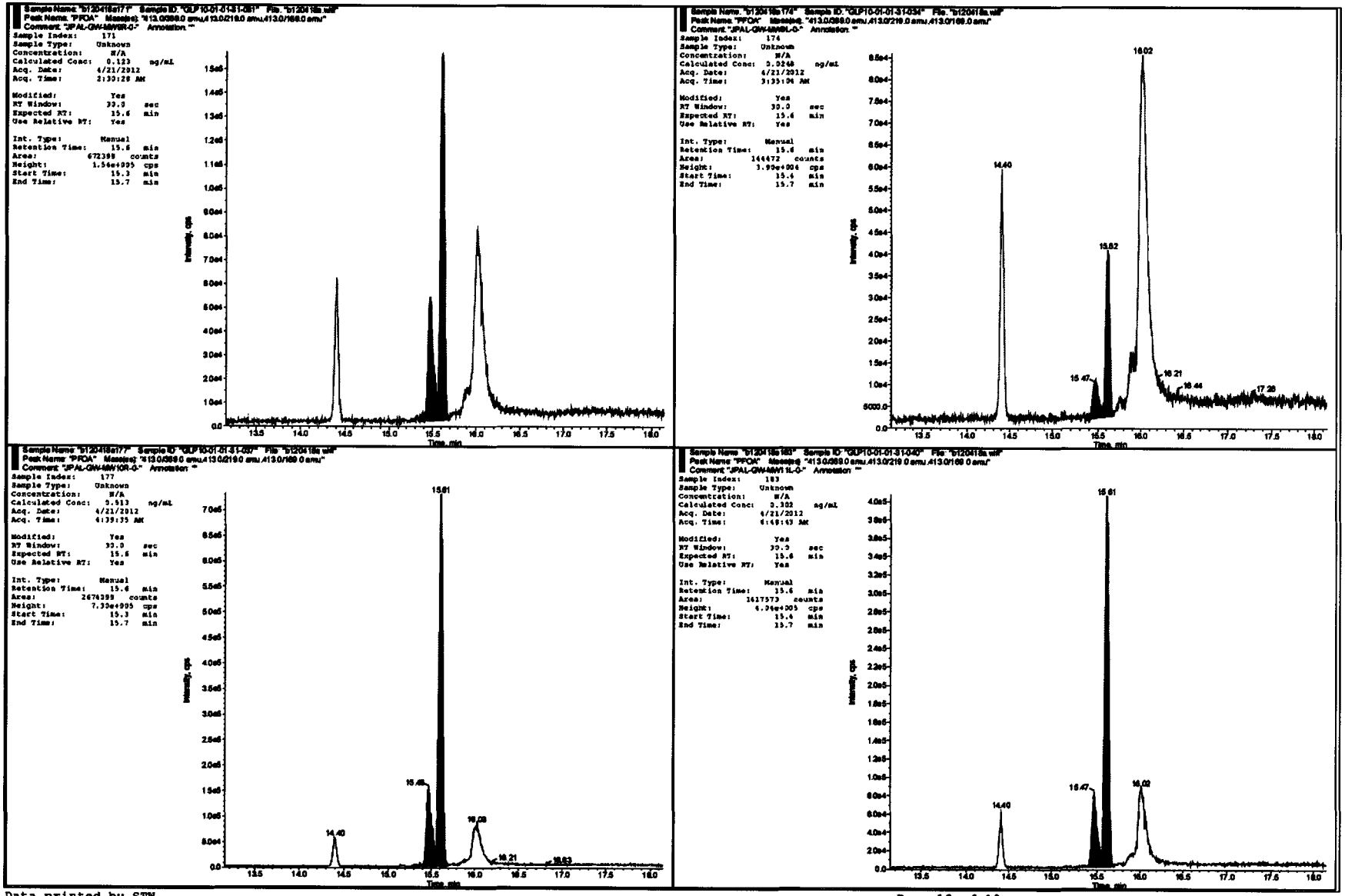
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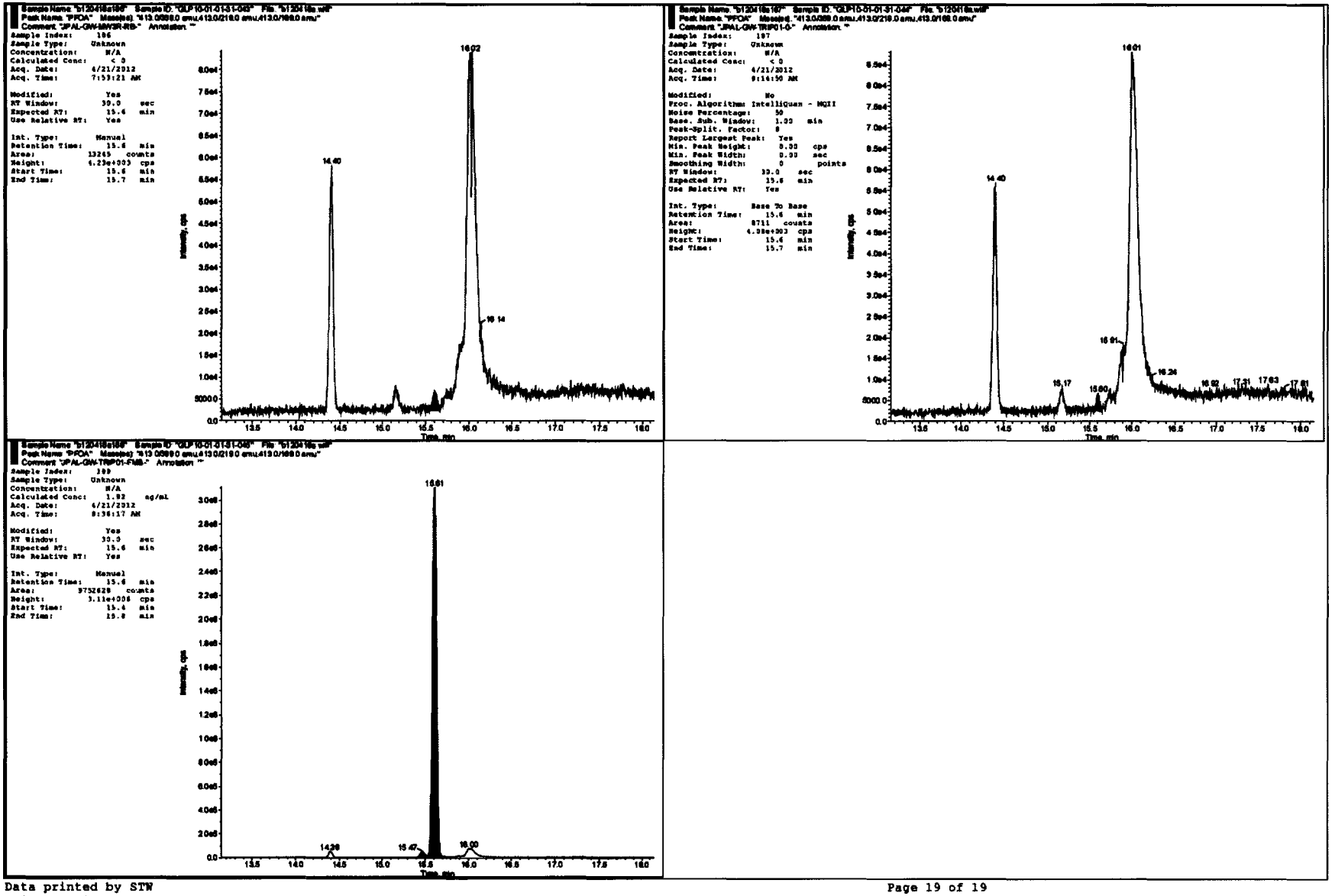


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ATTACHMENT C: ANALYTICAL METHOD(S)

3M Environmental Laboratory

Method

Method of Analysis for the Determination of Perfluorinated Compounds in Water by LC/MS/MS; Direct Injection Analysis

Method Number: ETS-8-044.1

Adoption Date: 4/12/07

Effective Date: 11/9/11

Approved By:

9 NOV 2011

William K. Reagen, Technical Director, Environmental Laboratory — Date

1 Scope and Application

This method describes the direct injection analysis of perfluorinated compounds (PFCs) from water matrices using high-performance liquid chromatography tandem mass spectrometry (HPLC/MS/MS). The method is generally applicable but not limited to the measurement of perfluoroalkyl sulfonamides and perfluorinated alkyl acids (PFAAs) such as perfluorosulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs) (Table 1). Water samples containing heavy particulate may require preparation by an alternate method such as ETS-8-154 "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates In Water By Solid Phase Extraction and High Performance Liquid Chromatography/Mass Spectrometry". The method is applicable to both external standard and internal standard calibration[1].

Table 1. Representative Target Analytes

Acronym	*Analyte*	*Chemical Abstract Services Registry Number (CASRN)*
PFBA (C4 Acid)	Perfluorobutanoic acid	375-22-4
PFPeA (C5 Acid)	Perfluoropentanoic acid	2706-90-3
PFHxA (C6 Acid)	Perfluorohexanoic acid	307-24-4
PFHpA (C7 Acid)	Perfluoroheptanoic acid	375-85-9
PFOA (C8 Acid)	Perfluorooctanoic acid	335-67-1
PFNA (C9 Acid)	Perfluorononanoic acid	375-95-1
PFDA (C10 Acid)	Perfluorodecanoic acid	335-76-2
PFUnA (C11 Acid)	Perfluoroundecanoic acid	2058-94-8
PFDoA (C12 Acid)	Perfluorododecanoic acid	307-55-1
PFTrDA (C13 Acid)	Perfluorotridecanoic acid	72629-94-8
PFBS (C4 Sulfonate)	Perfluorobutanesulfonic acid	375-73-5
PFHS (C6 Sulfonate)	Perfluorohexanesulfonic acid	355-46-4
PFOS (C8 Sulfonate)	Perfluorooctanesulfonic acid	1763-23-1
FBSA (C4 Sulfonamide	Perfluorobutanesulfonamide	30334-69-1
FOSA (C8 Sulfonamide)	Pefluorooctanesulfonamide	754-91-6

The Minimum Reporting Level (MRL) is the Limit of Quantitation (LOQ) that meets Data Quality Objectives (DQOs) that are developed based on the intended use of this method.

Method Flexibility – This is a performance-based method and may be generally applied to the determination of perfluorinated compounds in water matrices when analysis batch quality control (QC) criteria are met[2]. Each set of samples are prepared in an analysis batch with calibration standards, LCSs, blanks, and continuing calibration check standards analyzed on the same instrument during a time period that begins and ends with the analysis of the appropriate continuing calibration check standards. The laboratory is permitted to modify the LC column, mobile phase composition, LC conditions, and MS/MS conditions. Method modifications should be considered to improve method performance or to meet data quality objectives for the study. In all cases where method modifications are implemented, the batch

[1] The method is supported by validation with internal standard calibration for C4-C13 PFCAs, C4, C6, and C8 PFSAs, and C8 perfluoroalkane sulfonamide in laboratory control samples under 3M method validation E11-0667.

[2] Guidance for establishing method QC Criteria based on a.) FDA May 2001, "Guidance for Industry, Bioanalytical Method Validation", b.) EPA Method 537, and c.) European Commission: Guidance for Generating and Reporting Methods of Analysis in Support of Pre-registration Data Requirements for Annex II (Part A, section 4) and Annex III (Part A,section 5) of Directive 91/414, SANCO/3029/99 rev. 4 (11/07/00).

analytical QCs (section 9) must be completed and pass QC acceptance criteria (section 13) if the data from the analytical batch are to be reported.

2 Method Summary

Water samples are analyzed as neat aqueous sample or as solvent diluted aqueous samples by direct injection using LC/MS/MS. Samples containing heavy particulate may not be suitable for analysis by this method. Samples containing suspended particulate should be centrifuged or filtered prior to removing a sample aliquot or diluting with solvent. The water sample is mixed well prior to removing an aliquot or diluting, if necessary, with ASTM Type I water, HPLC water, other suitable water, or solvent (methanol).

Quantitation is by stable isotope internal standard calibration in laboratory reagent water. All perfluorinated compounds (PFCs) target analyte concentrations of perfluorosulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs) are reported as anions and corrected for their salt or free acid forms. Alternatively, quantitation may be performed by external standard calibration.

This is a performance-based method. Method uncertainty for each target analyte is determined for each analytical batch using multiple laboratory control spikes at multiple concentrations. This method also requires that the precision and accuracy for each sample be determined using field matrix spikes to verify that the method is applicable to each sample matrix.

Calibration standards for PFUnA, PFDoA, PFTrDA, and FOSA have been found to be unstable for more than 2 days in 100% water. Samples requiring analysis for these compounds by this method should be diluted 1:1 with methanol and analyzed against a calibration curve prepared in 1:1 synthetic groundwater:MeOH.

3 Definitions

3.1 Analysis Batch

A set of study samples that are prepared with calibration standards, laboratory control samples, and procedural blanks, and analyzed on the same instrument during a time period that begins and ends with the analysis of the appropriate continuing calibration check standards.

3.2 Analytical Sample

A portion of a laboratory sample prepared for analysis.

3.3 Calibration Standard

A solution prepared by spiking a known volume of the Working Standard (WS) into a predetermined amount of ASTM Type I, HPLC grade water, or other suitable water (i.e. matrix water), and analyzed according to this method. Calibration standards are used to calibrate the instrument response with respect to analyte concentration.

3.4 Laboratory Duplicate Sample (LDS, or Lab Dup)

A laboratory duplicate sample is a separate aliquot of a sample taken in the analytical laboratory that is analyzed separately with identical procedures. Analysis of LDSs 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.

3.5 Field Blank (FB)/Trip Blank (TB)

ASTM Type I, HPLC grade water, or other suitable 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 TB is to determine if test substances or other interferences are present in the field environment. This sample is also referred to as a Trip Blank.

3.6 Field Duplicate Sample (FDS, Field Dup)

A sample collected in duplicate at the same time from the same location as the sample. The FDS is handled under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analysis of the FDS 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.

3.7 Field Matrix Spike (FMS)

A sample to which known quantities of the target analytes, ISs and SRSs are added to the sample bottle in the laboratory before the bottles are sent to the field for collection of aqueous samples. A known, specific volume of sample must be added to the 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 is analyzed to ascertain if any matrix effects, interferences, or stability issues may complicate the interpretation of the sample analysis.

3.8 Trip Blank Matrix Spike (TBMS)

An aliquot of ASTM Type I, HPLC grade water, or other suitable water, to which known quantities of the target analytes, ISs and SRSs are added in the laboratory prior to the shipment of the collection bottles. The TBMS is analyzed exactly like a study sample to help determine if the method is in control and whether a loss of analyte or analytical bias could be attributed to sample holding time, sample storage and/or shipment issues. A low and high TBMS are appropriate when expected sample concentrations are not known or may vary.

3.9 Internal Standard (IS)

A compound added to each study sample, calibration standard, laboratory control samples, and procedural blanks at a consistent level (typically around 1 ng/mL). The internal standard(s) are stable isotope labeled versions of the target analytes. The area count ratio of the target analyte to the internal standard is used for calibration. Surrogate ISs are applied when stable isotope ISs of target analytes are unavailable. A surrogate IS is not necessarily a stable isotope labeled version of the target analyte, but is treated as an internal standard for quantitation.

3.10 Laboratory Control Sample (LCS)

An aliquot of control matrix to which known quantities of the target analytes, ISs and SRSs (when applicable) are added in the laboratory at the time when samples are aliquotted. At least three levels (two levels for SRSs) in triplicate are included, one generally at the low end of the calibration curve and one near the mid range and the upper end of the curve. The LCSs are analyzed exactly like a laboratory sample to determine whether the stability of the standards. LCSs should be prepared each day samples are aliquoted.

3.11 Laboratory Matrix Spike (LMS)

A laboratory matrix spike is an aliquot of a sample to which known quantities of target analytes, ISs and SRSs (when applicable) are added in the laboratory. The LMS is analyzed exactly like a laboratory sample to determine whether the sample matrix contributes bias to the analytical results. The endogenous concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LMS corrected for these concentrations. LMSs are optional for analysis of aqueous samples.

3.12 Laboratory Sample

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

3.13 Limit of Quantitation (LOQ)

The lower limit of quantitation (LLOQ) for an analytical batch is the lowest concentration that can be reliably quantitated within the specified limits of precision and accuracy. The LLOQ is generally selected as the lowest non-zero standard in the calibration curve that meets method acceptance criteria. The LLOQ for each target analyte is established for each analysis batch as the lowest calibration standard with area counts at least twice that of the average area counts of the procedural blanks.

The upper limit of quantitation (ULOQ) for an analytical batch is the highest concentration that can be reliably quantitated within the specified limits of precision and accuracy. The highest standard in the calibration curve that meets method acceptance criteria is defined as the ULOQ.

3.14 Method/Procedural Blank

An aliquot of control matrix 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.

3.15 Sample

A sample is an aliquot removed from a larger quantity of material intended to represent the original source material.

3.16 Stock Standard Solution (SSS)

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

3.17 Surrogate Internal Standard

An IS that is not necessarily a stable isotopically labeled target analyte, but is treated as an internal standard for quantitation. Surrogate ISs are used when isotopically labeled counterparts of the target analyte are not commercially or readily available.

3.18 Surrogate Recovery Standard (SRS)

An isotopically labeled standard, not used as an internal standard, that is added to each sample and appropriate QC sample as a means to evaluate the method performance for a chemical class of compounds (e.g., PFSAs, PFCAs).

3.19 Working Standard (WS)

A solution of several analytes prepared in the laboratory from SSSs 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. The analyst should wear gloves, a lab coat, and safety glasses to prevent exposure to chemicals that might be present.

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

The analyst must be familiar with the laboratory equipment and potential hazards including, but not limited to, the use of solvents, pressurized gas and solvent lines, high voltage, and vacuum systems. Refer to the appropriate equipment procedure or operator manual for additional information and cautions.

5 Interferences

During sample preparation and analysis, major potential contaminant sources are reagents and glassware. 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 or minimized 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

6.1 Instrumentation

Analytical balance capable of reading to 0.0001g

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

6.2 Supplies and Materials

Sample collection bottles—HDPE (e.g., Nalgene™) wide-mouth bottles with screw cap.
Note: Do not use fluorinated or Teflon® bottles or lined caps.

Coolers or boxes for sample shipment.

15-mL and 50-mL disposable polypropylene centrifuge tubes.

Class A pipettes and volumetric flasks, various.

2 mL HPLC autovials

Disposable pipettes, polypropylene or glass as appropriate

Centrifuge capable of spinning 15-mL and 50-mL polypropylene tubes at 3000 rpm.

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

Water – Milli-Q, HPLC grade, or other suitably appropriate sources

Calcium Acetate - A.C.S. Reagent Grade

Magnesium Acetate - A.C.S. Reagent Grade

Methanol – HPLC grade

Ammonium Acetate – A.C.S. Reagent Grade

7.2 Representative Target Analytes, ISs, and SRSs

PFBA, Heptafluorobutyric Acid, (C_4 Perfluorinated Acid)

PFPeA, Nonafluoropentanoic Acid (C_5 Perfluorinated Acid)

PFHxA, Perfluorohexanoic Acid (C_6 Perfluorinated Acid)

PFHpA, Tridecafluoroheptanoic Acid, (C_7 Perfluorinated Acid)

PFOA, Ammonium perfluorooctanoate, (C_8 Perfluorinated Acid)

PFNA, Heptadecafluorononanoic Acid, (C_9 Perfluorinated Acid)

PFDA, Nonadecafluorodecanoic Acid (C_{10} Perfluorinated Acid)

PFUnA, Perfluoroundecanoic Acid, (C_{11} Perfluorinated Acid)

PFDoA, Perfluorododecanoic Acid, (C_{12} Perfluorinated Acid)

PFTrDA, Perfluorotridecanoic Acid, (C_{13} Perfluorinated Acid)

FBSA, Perfluorobutanesulfonamide

FOSA, Perfluorooctanesulfonylamide

PFBS, Potassium Perfluorobutanesulfonate

PFHS, Perfluorohexanesulfonate

PFOS, Potassium perfluorooctanesulfonate

PFOA [1,2, 3, 4-^{13}C], $^{13}C_4$-isotopically labeled perfluorooctanoic acid (SRS)

PFOS [1,2, 3, 4-^{13}C], $^{13}C_4$-isotopically labeled Perfluorooctanesulfonate (SRS)

PFUnA [1,2-^{13}C], $^{13}C_2$-isotopically labeled Perfluoroundecanoic acid (SRS)

A custom mix of ISs in a methanolic solution containing ([1,2,3,4-$^{13}C_4$]PFBA, [1,2-$^{13}C_2$]PFHxA, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA, [1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA, [1,2-$^{13}C_2$]PFDA, [1,2,3,4,5,6,7-$^{13}C_7$]PFUnA, [1,2-$^{13}C_2$]PFDoA, [1,2,3-$^{13}C_3$]PFHS, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOS, and [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOSA (Wellington Laboratories, Guelph, ON) in combination with added ([1,2,3,4,5-$^{13}C_5$]PFPeA, ([1,2,3,4-$^{13}C_4$]PFHpA, and [$^{18}O_2$]PFBS can be used to prepare a stock IS solution. Alternatively, individual stable isotope ISs can be used to prepare a stock IS mixture.

Other ISs can be applied.

7.3 Reagent Preparation

2 mM Ammonium acetate solution (Analysis)—Weigh 0.3 g of Ammonium acetate and dissolve in 2.0 L of reagent water.

Synthetic Groundwater (containing 25 ppm Ca and Mg) – Weigh 0.61 g of Calcium Acetate and 0.92 g of Magnesium Acetate and dissolve in 6.0 L of reagent water.

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

7.4 Stock Standard Solution (SSS) and Working Standard Solution Preparation

The following standard preparation procedure serves as an example. Weighed amounts and final volumes 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.

100 µg/mL target analyte SSSs—Weigh out 10 mg of analytical standard ***(corrected for percent salt, acid [ETS-4-031] and purity)*** and dilute to 100 mL with methanol or other suitable solvent, in a 100 mL volumetric flask. Transfer to a 125 mL LDPE bottle or other suitable container. Prepare a separate solution for each analyte. Expiration dates and storage conditions of stock solutions should be assigned in accordance with laboratory standard operating procedure. An example of purity and salt correction is given below for PFOS.

$$\text{salt correction factor} = \frac{\text{molecular weight of anion}}{\text{moclecular weight of salt}}$$

$$\text{PFOS } (K^+)\text{salt correction factor} = \frac{499}{538} = 0.9275$$

10 mg $C_8F_{17}SO_3K^+$ with purity 90% = 8.35 mg $C_8F_{17}SO_3^-$ (10 mg*0.90*0.9275=8.35 mg)

10 µg/mL (10,000 ng/mL) mixed working standard—Add 5.0 mL each of the 100 µg/mL SSSs to a 50 mL volumetric flask and bring up to volume with solvent.

1 µg/mL (1,000 ng/mL) mixed working standard—Add 0.5 mL of the 100 µg/mL SSSs to a 50 mL volumetric flask and bring up to volume with solvent.

0.1 µg/mL (100 ng/mL) mixed standard—Add 0.05 mL of the 100 µg/mL SSSs to a 50 mL volumetric flask and bring up to volume with solvent.

Storage Conditions—Store all SSSs and working standards in accordance with laboratory standard operating procedure or in a refrigerator at 4°±2°C for a maximum period of 6 months from the date of preparation.

7.5 Calibration Standards

Calibration can be performed by IS or external calibration. Using the working standards described above, prepare calibration solutions in ASTM Type I water, HPLC water, other suitable water, or a mixture of solvent and water using the information in Table 2 as a guideline. Note: Volumes of water or water/solvent mixtures and working standards may be adjusted to meet the data quality objectives addressed in the general project outline. Calibration levels other than those listed below can be prepared as needed.

For the quantitation of PFOA and PFOS, reference materials of certified mixed linear and branched isomer are preferred. Alternately, reference materials of primarily linear isomers of PFOA and/or PFOS may be used, however, when quantitating with predominantly linear reference standards, additional LCS samples containing both linear and branched isomers of PFOA and PFOS are required[3].

7.5.1 Internal Standard (IS) and Surrogate Recovery Standard (SRS)

For IS calibration, stable isotope internal standards of each target analyte or appropriate surrogate ISs should be spiked at the same level in all calibration standards. Once the calibration standards have been prepared as stated above in Section 7.5, all calibration standards are spiked with a separate internal standard spiking solution. Typically the

[3] A report summarizing an assessment of the use of reference standards containing certified linear and branched isomers of PFOA/PFOS can be found in 3M report E11-0560.

concentration of the internal standard is consistent with the internal standard concentration expected in the samples being prepared, usually 1 ng/mL. The concentration of the internal standard spiking solution is typically 2 µg/mL. A separate zero point or method blank is typically prepared at the same time as the calibration standards, using the same solution used to prepare the standards (ASTM Type I water, HPLC water, other suitable water, or a solvent/water mixture), and is spiked with the internal standard at the same concentration as the calibration curve, typically at 1 ng/mL.

If the samples being analzyed were pre-spiked with SRSs, the calibration curve prepared in Section 7.5 is spiked with a separate SRS spiking solution. Typically, the sample bottles are spiked with a SRS at 0.1 ng/mL. The final calibration curve must consist of at least six calibration points after analysis. The following table provides an example of spike concentrations and volumes used to achieve a multi-point extracted calibration curve with internal standard and surrogate standard.

Table 1 lists recommended stable isotope internal standards for several PFSA and PFCA target compounds. A custom mix of isotopically labeled target analytes in a methanolic solution containing ([1,2,3,4-$^{13}C_4$]PFBA, [1,2-$^{13}C_2$]PFHxA, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA, [1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA, [1,2,3,4,5,6-$^{13}C_6$]PFDA, [1,2,3,4,5,6,7-$^{13}C_7$]PFUnA, [1,2-$^{13}C_2$]PFDoA, [1,2,3-$^{13}C_3$]PFHS, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOS, and [1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA (Wellington Laboratories, Guelph, ON) in combination with added ([1,2,3,4,5-$^{13}C_5$]PFPeA, ([1,2,3,4-$^{13}C_4$]PFHpA, and [$^{18}O_2$]PFBS can be used to prepare a stock IS solution. Alternative sources of certified stable isotope labeled target analytes are applicable. Alternatively, individual stable isotope ISs can be used to prepare a stock IS mixture. The table below lists the recommended stable isotope ISs and SRSs applied in the method. Other stable isotope ISs and SRSs of target analytes not listed in the table may be used if supported by validation and/or analysis batch QCs meeting method acceptance criteria (e.g., [$^{13}C_2$]-PFOA). The same internal standard should be used for a given analyte throughout the entire project/study. Note: some of the compounds listed below are appropriate to use as surrogate ISs when a stable isotope IS of a target analyte is not available. Generally, surrogate isotopically labeled PFCAs are used for PFCAs, and surrogate isotopically labeled PFSAs are used for PFSAs.

Table 2 provides examples of spike concentrations and volumes used to achieve a multi-point calibration curve with ISs and SRSs.

Table 1. Stable Isotope PFCAs and PFSAs used for ISs and SRSs

Compound Name	*Synonym or Acronym*	*Analytical Purpose*	*Reference Standard Source*
$^{13}C_4$-Perfluorobutanoic acid	[1,2,3,4-$^{13}C_4$]PFBA	IS for PFBA	Wellington Labs (Mix or Individual)
$^{13}C_4$-Perfluoropentanoic acid	[1,2,3,4,5-$^{13}C_5$]PFPeA	IS for PFPeA	Wellington Labs (Mix or Individual)
$^{13}C_2$-Perfluorohexanoic acid	[1,2 -$^{13}C_2$]PFHxA	IS for PFHxA	Wellington Labs (Mix or Individual)
$^{13}C_4$-Perfluoroheptanoic acid	[1,2,3,4-$^{13}C_4$]PFHpA	IS for PFHpA	Wellington Labs (Mix or Individual)
$^{13}C_8$-Perfluorooctanoic acid	[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA	IS for PFOA and [1,2,3,4 $^{13}C_4$]PFOA	Wellington Labs (Mix or Individual)
$^{13}C_9$-Perfluorononanoic acid	[1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA	IS for PFNA	Wellington Labs (Mix or Individual)
$^{13}C_6$-Perfluorodecanoic acid	[1,2,3,4,5,6 -$^{13}C_6$]PFDA	IS for PFDA	Wellington Labs (Mix or Individual)
$^{13}C_7$-Perfluoroundecanoic acid	[1,2,3,4,5,6,7 -$^{13}C_7$]PFUnA	IS for PFUnA	Wellington Labs (Mix or Individual)
$^{13}C_2$-Perfluorododecanoic acid	[1,2 -$^{13}C_2$]PFDoA	IS for PFDoA, *PFTA	Wellington Labs (Mix or Individual)
$^{18}O_2$-Ammonium Perfluorobutane sulfonate	[$^{18}O_2$]PFBS	IS for PFBS	RTI International (Individual)
$^{13}C_3$-Ammonium Perfluorohexane sulfonate	[1,2,3-$^{13}C_3$]PFHS	IS for PFHS	Wellington Labs (Mix or Individual)
$^{13}C_8$-Sodium Perfluorooctane sulfonate	[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOS	IS for PFOS and PFOS[1,2,3,4 $^{13}C_4$].	Wellington Labs (Mix or Individual)
$^{13}C_8$-Perfluorooctanesulfonamide	[1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA	IS for FOSA	Wellington Labs (mix) RTI International (Individual)
$^{13}C_4$-Perfluorooctanoic acid	[1,2,3,4-$^{13}C_4$]PFOA	SRS for all PFCAs: C4-C8	Wellington
$^{13}C_2$-Perfluoroundecanoic acid	[1,2 -$^{13}C_2$]PFUnA	SRS for all PFCAs C9-C13	Wellington
$^{13}C_8$-Perfluorooctane sulfonate	[1,2,3,4-$^{13}C_4$]PFOS	SRS for all PFSAs: C4, C6, and C8	Wellington

Table 2. Example Preparation of Calibration Curve with ISs and SRSs

Sample Description	*Concentration of WS, µg/mL*	*Volume of WS, µL*	*Volume of IS (2 µg/mL), µL*	*Concentration of Surrogate, µg/mL*	*Volume of Surrogate, µL*	*Volume of ASTM Type I Water, or other suitable solvent (1), mL*
0.025 ng/mL curve point	0.10	25	50	0.20	12.5	100
0.030 ng/mL curve point	0.10	30	50	0.20	15	100
0.04 ng/mL curve point	0.10	40	50	0.20	20	100
0.05 ng/mL curve point	0.10	50	50	0.20	25	100
0.1 ng/mL curve point	0.10	100	50	0.20	50	100
0.25 ng/mL curve point	0.10	250	50	0.20	125	100
0.5 ng/mL curve point	1.0	50	50	0.20	250	100
1 ng/mL curve point	1.0	100	50	0.20	500	100
2.5 ng/mL curve point	10.0	25	50	10.0	25	100
5.0 ng/mL curve point	10.0	50	50	10.0	50	100
10.0 ng/mL curve point	10.0	100	50	10.0	100	100
25.0 ng/mL curve point	10.0	250	50	10.0	NA	100
50.0 ng/mL curve point	10.0	500	50	10.0	NA	100
75.0 ng/mL curve point	10.0	750	50	10.0	NA	100
100 ng/mL curve point	10.0	1000	50	10.0	NA	100

N/A - Not Applicable
(1) Samples requiring analysis for PFUnA, PFDoA, PFTrDA, and FOSA should be analyzed against a calibration curve prepared in 1:1 synthetic groundwater:MeOH.

8 Sample Collection and Bottle Preparation

Sample collection bottles are prepared by 3M Environmental Laboratory (or subcontract supplier) personnel for shipment at ambient temperature to the collection site. Typically, four separate collection bottles are associated with a single collection site: sample, field duplicate sample, low field matrix spike, and high field matrix spike. Alternatively, the sample and field duplicate sample may contain SRSs in lieu of additional target analyte low field matrix spike and target analyte high field matrix spike samples. Depending on the scope of the project, additional replicates of the field sample and field matrix spikes may be added. Also, it is not uncommon for additional mid-level field matrix spikes to be collected if the expected sample concentrations are truly unknown or could span a large concentration range.

High-density polyethylene (HDPE) wide-mouth Nalgene bottles are used for the sample collection containers. (Volumes of the bottles may vary depending on how much sample is required to meet data quality objectives.) Sample collection volumes are project specific and based on data quality objectives. The Nalgene bottles do not require any pretreatment prior to use. Typically, placement of a sample bottle volumetric "fill to here" line is done by using a sample bottle marker template. Alternatively, bottles may be weighed prior to bottle preparation and weighed again after samples have been collected.

All bottles should be clearly labeled to indicate its intended use as a sample, field sample duplicate, low field matrix spike, high field matrix spike, sample/SRS field matrix spike, field duplicate sample/SRS field matrix spike, trip blank, or trip blank matrix spike. If each location has different designated spike levels, the label should also clearly indicate the sample location designation. Generally, a set of bottles for a given collection site are prepared then grouped together in plastic bags for organizational purposes. For each sample collection event, at least one set of trip blank and trip blank matrix spikes are prepared.

Bottle preparation should be documented in a Note to File or on a sample preparation worksheet and should include the following information: date prepared, total number of bottles prepared, number of sample sites, the standard identification numbers and spike volumes used to prepare spiked bottles, the "fill to here" volume, and any other pertinent information needed for reconstructibility of the data. The Note to File will be included in the final data package for the project.

Samples are collected in the field and shipped to the laboratory at ambient temperature.

8.1 Field Matrix Spike Sample (FMS)

Field matrix spike samples are a requirement of the method. A FMS sample is defined as a QC sample to which known quantities of appropriate target analytes are added to the sample bottle in the field or in the laboratory before the bottles are sent to the field. The sample and field duplicate sample may contain appropriate SRSs in lieu of target analyte FMS samples. Sample quantities are determined volumetrically or gravimetrically. A known, specific volume or weight of sample is added to the sample container without rinsing. Volumetric sample measurements may be acquired by a laboratory applied "fill to this level" line on the outside of the sample container. Target analyte FMS samples should be spiked at approximately 0.5-10 times the expected analyte concentration in the sample. If the expected range of analyte concentrations is unknown, multiple spikes at varying levels may be prepared to increase the likelihood that a spike at an appropriate level is made. Typically a low and a high target analyte spike are prepared for each sampling location. In those instances where SRSs are to be used in lieu of target analyte FMS samples, the sample and field duplicate sample are spiked at approximately 2-5 times the target LOQ. The FMS is analyzed to ascertain if matrix effects or sample holding time contributes bias to the analytical results. For the sample bottles designated for matrix spikes, an appropriate volume of matrix spiking solution is added to the empty bottle prior to sampling. The volume of spike solution added should produce the desired final concentration of target analytes once the bottle is filled with sample to the "fill to here line". The matrix spiking solution(s) should be prepared in a suitable solvent and contain all of the appropriate target analytes, ISs, and SRSs. The target analyte matrix spiking solution is often the same as the working standards used to create the calibration standards. An example of a bottle spike is given below.

"Fill to here" volume = 200 mL (A 250 mL Nalgene bottle is used)

Desired Field Spike Concentration = 0.25 ng/mL

500 µL of a 0.1 µg/mL spiking solution (containing the target analytes) is added to the bottle and the bottle cap promptly sealed.

8.2 Internal Standard and Surrogate Recovery Standard

If analysis of a surrogate recovery standard (SRS) is included in the project objectives, an appropriate volume of a surrogate standard solution is added to all the bottles prior to sampling and SPE. Typically sample bottles are spiked with surrogate recovery standards at a final desired spike concentration of 0.1 ng/mL.

If quantitation by internal standard (IS) is included in the project objective, an appropriate volume of internal standard solution is added to all the bottles prior to sampling and SPE. Typically sample bottles are spiked with internal standard at a final desired spike concentration of 1 ng/mL.

For the trip blank, the SRS spike and IS spike is added to the bottle and then ASTM Type I water (HPLC grade reagent water or other suitable water may used) is added to the "fill to here" line. The bottle is capped and sealing tape may be placed around the outer edge of the cap. Trip blank matrix spikes are prepared by adding the appropriate volume of target analyte spiking solution, IS, and SRS spiking solutions and filling the bottle to the desired volume with the appropriate water and capping and sealing the cap.

9 Quality Control and Data Quality Objectives

9.1 Data Quality Objectives

This method and required quality control samples is designed to generate data accurate to ±30% with a targeted LOQ of 0.025 ng/mL. Any deviations from the quality control measures spelled out below will be documented in the raw data and footnoted in the final report.

9.2 Method/Procedural Blanks

The method/procedural blank is zero point calibration standard (which includes ISs) analyzed in a regular basis with each analysis batch. At a minimum, method blanks are analyzed prior to instrument calibration, prior to the analysis of CCV samples, after every 10 sample injections, and at the end of the analytical run.

The mean area count or area ratios when using internal standard calibration, for each analyte in the method blanks must be less than 50% of the area count counts or area ratios when using internal standard calibration, of the LOQ standard. The standard deviation of the area counts, or area ratios when using internal standard calibration, of these method blanks should be calculated. A specific %RSD acceptance criteria is not specified but is assessed on an analytical batch basis. If the mean area counts or area ratios when using internal standard calibration, of the method blanks exceed 50% of the LOQ standard, then the LOQ must be raised to the first standard level in the curve that meets criteria. Method blanks may be eliminated if technical justification can be provided (e.g. the procedural blank was analyzed after an unexpectedly high level sample). If any procedural blanks are removed from the LOQ determination, document in the raw data and report as appropriate. Laboratory Sample Replicates / Field Duplicate Sample

Typically, samples are collected in duplicates in the field. The relative percent difference (RPD) of duplicate samples should be ≤20% for the precision of sample preparation and analysis to be considered in control. Replicate samples not meeting the ≤20% RPD criteria are flagged and reported as outside of QC acceptance criteria.

9.3 Laboratory Matrix Spikes (LMSs)

LMSs may be performed in lieu of FMSs if FMSs have previously been performed for the sample matrix. Additionally, LMSs may be performed in lieu of FMSs for a sample matrix if the FMS levels were not appropriate for determining spike recoveries relative to endogenous levels of target analytes and appropriate SRSs. Generally, each sample location represents a different sample and sample matrix. LMSs are prepared for each sample and analyzed to determine the matrix effect on spike recovery efficiency of each target analyte and appropriate SRSs. LMSs should be prepared at a minimum of one level and in duplicate. LMS concentrations should be prepared at approximately 0.5-10 times the endogenous concentration or approximately 4-10 times the LOQ concentration of each target analyte.

Lab matrix spike recoveries should fall within ± 30% of expected values. Sample data with LMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria. Data with LMS recovery outside of ±50% of the expected value are reported as NR, where NR is defined as "Not Reportable" data outside of QC acceptance criteria.

9.4 Lab Control Sample

Lab control spikes are prepared for each analysis batch to determine method accuracy and precision. LCSs should be prepared at three levels in triplicate for each target analyte and at a minimum of two levels in triplicate for appropriate SRSs. Low lab control spikes should be prepared at a concentration in the range of approximately four to ten times higher than the targeted lower LOQ, the mid lab control spikes should be prepared at a concentration near the mid-point of the calibration curve and the high lab control spikes at approximately 80% of the upper LOQ. For each target analyte and SRSs, the percent relative standard deviation (method precision) for each control spike level must be less than or equal to 20% and the average recovery (method accuracy) for each control spike level must be 80-120%. Sample data for target analytes outside of the laboratory control spike acceptance criteria will be handled as follows:

If the average recovery of a spiking level falls outside method acceptance, but at least 67% (6 out of 9) of LCS samples are within 20% of their respective nominal value (33% of the QC samples, not all replicates at the same concentration, may be outside 20% of nominal value), the average recovery will be flagged as outside method acceptance criteria. All LCS samples will be control charted as per ETS-4-026. If the average recovery of one of the spiking levels exceeded the analytical method uncertainty as determined by ETS-12-012, that analytical batch uncertainty will be expanded for that particular study.

If more than 67% of the LCS samples fail to meet method acceptance criteria, the data will not be reported.

Calibration standards consisting of mixed branched and linear isomer PFOS/PFOA are preferred. However, for PFOS/PFOA target analytes, if the calibration standards are comprised of predominantly linear isomers only, at least one level of triplicate LCSs should be prepared using PFOS/PFOA which contains a mix of linear and branched isomers. These LCSs will be used to demonstrate quantitative equivalency (or quantitative bias) of the isomeric mix when using a predominantly linear standard for calibration. The mixed linear and branched isomer PFOS/PFOA LCSs recoveries should fall within ± 30% of expected values. Alternatively, in lieu of mixed branched and linear isomer PFOS/PFOA LCSs, mixed branched and linear isomer PFOS/PFOA TBMSs may be applied to demonstrate method accuracy and precision.

9.5 Field Matrix Spikes (FMSs) / Surrogate Recovery Standards (SRSs)

FMSs are prepared for each sampling location and analyzed to determine the matrix effect and sample holding time on the spike recovery of each target analyte and/or appropriate SRS. Generally, each sample location represents a different sample and sample matrix.

FMSs are QC samples to which known quantities of appropriate target analytes are added to the sample bottle in the laboratory before the bottles are sent to the field. Typically a low and a high target analyte FMS are prepared for each sampling location. The sample and field duplicate sample may contain appropriate SRSs in lieu of target analyte low field matrix spike and target analyte high field matrix spike samples.

Field matrix spike method acceptance criteria are recoveries within ±30% of the expected value. If FMS recovery (target analyte or SRS spike) is outside of ±30% of the expected value or could not be assessed because the FMS (target analyte) was spiked at an inappropriate level, the sample result is reported as follows:

1.) If target analyte FMS recovery could not be assessed because the FMS's were at an inappropriate level, then Laboratory Matrix Spikes (LMS) may be substituted. If LMS recoveries are within ±30% the data are reportable and flagged to indicate that the FMS spikes levels were inappropriate.

2.) If multiple target analyte FMS's were prepared on a sample and the closest FMS level to the reported sample meets the ±30% acceptance criteria but additional FMS's are outside the ±30% acceptance range, the data are reportable and flagged to indicate that while there were failing FMS's, the uncertainty will not be expanded since the most appropriate spike level passed.

3.) If the target analyte FMS recoveries are outside of the ±30% acceptance range but at least 30 acceptable historical reportable FMS sample results are available, the data may be reported but flagged with an expanded uncertainty and as not meeting FMS criteria.

4.) Sample data with FMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria with an expanded uncertainty.

5.) If FMS recovery is outside of ±50%, the sample result is reported as NR, where NR is defined as "Not Reportable" due to noncompliant QC results.

The targeted fortification levels should be at least 50% of the endogenous level and less than 10 times the endogenous level to be used without justification to determine the statement of accuracy for analytical results.

Note: It is possible for bottles utilized for Field Matrix Spike samples to be under-filled or over-filled during sample collection. Since this scenario will effect the actual concentration of the FMS sample (surrogate and internal standard concentrations will also be effected, if used), it is important that any obvious under-filling or over-filling of sample bottles be documented in the data package and taken into account in the FMS, ISs, or SRSs recovery calculations. Samples over-filled or under-filled by more than 10% will be require recalculation of the FMS, ISs, and SRS true values.

The average of the sample and the field duplicate should be used to calculate the recovery.

10 Procedures

10.1 Water Sample Preparation

This method is applicable to water samples. Samples containing heavy particulate may not be suitable for analysis by this method. Samples containing suspended particulate should be centrifuge prior to removing a sample aliquot, or filtered.

- Thoroughly mix sample before removing an aliquot and placing in a labeled autovial.
- Dilute sample, if necessary, with ASTM Type I water, HPLC water, other suitable water, or solvent (methanol).
- Lab control spikes are prepared for each analysis batch to determine method accuracy and precision. LCSs should be prepared at three levels in triplicate for each target analyte and at a minimum of two levels in triplicate for appropriate SRSs. Low lab control spikes should be prepared at a concentration in the range of approximately four to ten times higher than the targeted lower LOQ, the mid lab control spikes should be prepared at a concentration near the mid-point of the calibration curve and the high lab control spikes at approximately 80% of the upper LOQ. For IS quantitation, stable isotope internal standards of each target analyte or appropriate surrogate ISs should be spiked at the same level as the samples being analyzed, in all LCSs.
- If LCSs are being prepared using synthetic groundwater, allow the LCSs samples to equilibrate for a minimum of 4 hours before aliquoting for analysis or diluting with solvent (methanol).

11 Sample Analysis - LC/MS/MS

11.1 Instrument Setup

Note: In this example, an Applied Biosystems Sciex API 4000 (API 5000 or API 5500) Tandem Mass Spectrometer (LC/MS/MS) is used. Other brands/models of LC/MS/MS instruments as well as single quadrupole mass spectrometers (LC/MS) may be used as long as the method acceptance 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: Applied Biosystems API 4000, API 5000, or API 5500

Ion Source: Turbo Ion Spray (ABS)

Mode: Electrospray Negative

Scan Type: MRM (Multiple Reaction Monitoring)

Computer: Dell DHM

Software: Windows 2000 or Windows XP, Analyst 1.4.2 or higher versions

HPLC: Agilent Series 1100,1200, or 1290

Agilent Quaternary Pump

Agilent Vacuum Degasser

Agilent Autosampler

Agilent Column Oven

Note: One or more C18 HPLC analytical columns (2.1 mm x 100 mm, 5µm or 2.1 mm x 50 mm, 5µm) may be attached on-line after the purge valve and before the sample injection port to retard and separate any residue contaminants that may be in the mobile phase and/or HPLC system.

HPLC Column: Betasil C18, 4.6mm x 100mm, 5µm (ThermoElectron Corporation)

Column Temperature: 35°C

Injection Volume: 5µL

Mobile Phase (A): 2mM Ammonium Acetate in ASTM Type I water (See 7.3)

Mobile Phase (B): Methanol

Table 3. Liquid Chromatography Gradient Program.

Step Number	*Total Time (min)*	*Flow Rate (µL/min)*	*Percent A (2 mM ammonium acetate)*	*Percent B (Methanol)*
0	0	750	97.0	3.0
1	2.0	750	97.0	3.0
2	14.5	750	5.0	95.0
3	15.5	750	5.0	95.0
4	16.5	750	97.0	3.0
5	20.0	750	97.0	3.0

Note: Other HPLC gradients may be used as long as the method criteria and project data quality objectives 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.

Table 4 Suggested MRM Transitions for Target Analytes, Surrogates, and Internal Standards

Analyte	*Analyte Description*	*Mass Transition Q1 (amu)*	*Mass Transition Q3 (amu)*
PFBA (C4 Acid)	Target	213	169
PFPeA (C5 Acid)	Target	263	219
PFHxA (C6 Acid)	Target	313	269, 119
PFHpA (C7 Acid)	Target	363	319, 169
PFOA (C8 Acid)	Target	413	369, 219, 169
PFNA (C9 Acid)	Target	463	419, 169, 219
PFDA (C10 Acid)	Target	513	469, 269, 219
PFUnA (C11 Acid)	Target	563	519, 269, 219
PFDoA (C12 Acid)	Target	613	569, 169, 319
PFTA (C13 Acid)	Target	663	619, 369, 319
FBSA (C4 Sulfonamide)	Target	298	78
FOSA (C8 Sulfonamide)	Target	498	78
PFBS (C4 Sulfonate)	Target	299	99, 80
PFHS (C6 Sulfonate)	Target	399	99, 80
PFOS (C8 Sulfonate)	Target	499	80, 99, 130
[1,2,3,4 -$^{13}C_4$]PFBA	IS for PFBA	217	172
[1,2,3,4,5 -$^{13}C_5$]PFPeA	IS for PFPeA	268	223
[1,2 -$^{13}C_2$]PFHxA	IS for PFHxA	315	270
[1,2,3,4- $^{13}C_4$]PFHpA	IS for PFHpA	367	322
[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA	IS for PFOA	421	376
[1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA	IS for PFNA	472	427
[1,2,3,4,5,6 -$^{13}C_6$]PFDA	IS for PFDA	519	474
[1,2,3,4,5,6,7 -$^{13}C_7$]PFUnA	IS for PFUnA	570	525
[1,2 -$^{13}C_2$]PFDoA	IS for PFDoA and PFTA	615	570
[$^{18}O_2$]PFBS	IS for PFBS	303	84
[1,2,3-$^{13}C_3$]PFHS	IS for PFHS	402	80
[1,2,3,4- $^{13}C_4$]PFOS	IS for PFOS	503	80
[1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA	IS for FOSA	507	80
[1,2,3,4-$^{13}C_4$]PFOA	Surrogate (C4-C8 Acids)	417	372
[1,2,3,4- $^{13}C_4$]PFOS	Surrogate(Sulfonates, FOSA)	503	80
[1,2 -$^{13}C_2$]PFUnA	Surrogate (C9-C13 Acids)	565	520

Multiple transitions for monitoring the analytes is an option. The use of one daughter ion is acceptable if data sensitivity and selectivity is achieved and provided that retention time criteria are met to assure adequate specificity. While the daughter ions may be chosen at the discretion of the analyst, mass transition 99 is suggested for PFOS. Quantitation may be performed using the total ion chromatogram (TIC, or summed MRMs) for a given analyte. For example, the PFOA TIC would sum all three of the monitored transitions. 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 and the gradient, column, guard column(s) used 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.

11.2 Calibration Curve

Quantitation is by internal standard or external standard calibration. Calibration standards may be prepared in ASTM Type I, HPLC water, other suitable water, or a solvent/water mixture. If internal standard calibration does not meet calibration acceptance criteria, external calibration can be applied. See Table 1 for

recommended application of available internal standards. Quantitation of PFOA and PFOS is by summed analyte-specific mass transitions.

Analyze the standard curve prior to each set of samples. If internal standards were added to the calibration standards area ratios are used to generate the calibration curve. The standard curve may be plotted using a linear regression ($y = mx + b$), weighted 1/x or unweighted, or by quadratic fit ($y = ax^2 + bx + c$), weighted 1/x or unweighted, using suitable software. 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.

High and/or low points may be excluded from the calibration curves to provide a better fit over the 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 (or area ratio if quantitating by IS) are not at least twice that of the average area counts (or area ratio if quantitating by IS) of method and/or solvent blanks. The coefficient of determination (r^2) value for the calibration curve must be greater than or equal to 0.990 (or a correlation coefficient (r) of 0.995). Each point in the curve must be within ±25% of the theoretical concentration with the exception of the LLOQ, which may be within ±30%. 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.

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

11.3 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. Samples must be bracketed by passing CCVs or the calibration curve and a passing CCV to be reportable.

11.4 System Suitability

A minimum of three system suitability samples should be injected at the beginning of each analytical run, prior to the analysis of the calibration curve. Typically these samples are at a concentration near the mid-level of the calibration curve and are repeated injections from one autosampler vial. It is suggested that the system suitability injections have area counts or area ratios when using internal standard calibration, with a target RSD of ≤5% and a target retention time RSD of ≤2%. There is no defined acceptability limit on these results as the %RSD value is dependent on the number of MRM transitions being monitored in the LC/MS/MS run or time period. Ultimately, any effects on these parameters for the System Suitability samples will also be evident on all standards and QC samples analyzed as part of the analysis batch. Any effect of system suitability is incorporated within QC acceptance criteria.[4]

11.5 Sample Analysis and QCs

For each analysis batch, the instrument analysis run sequence should include an initial calibration curve, samples, FDSs, interspersed blanks, interspersed CCVs, appropriate QCs (i.e., LCSs, LMSs, FMSs, TBMSs, and TBs), and a final CCV or calibration curve bracketing samples and appropriate QCs

Inject the same volume (between 5 - 100µL) of each standard, analytical sample and blank into the instrument (unless an on-instrument sample dilution is desired).

Samples containing analytes that are quantitated above the concentration of the highest standard in the curve should be further diluted and reanalyzed.

[4] 3M Environmental Laboratory study E08-0096 evaluated the effect on these results as a function of the number of MRMs being monitored.

12 Data Analysis and Calculations

The chromatography analysis software will typically calculate the amount of target analyte in the sample extracts using the established calibration curve.

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

$$\text{LCS\% recovery} = \frac{\text{LCS Concentration } (\frac{ng}{mL})}{\text{Spike Concentration } (\frac{ng}{mL})} * 100\%$$

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

$$\text{LMS \% recovery} = \frac{\text{LMS Concentration } (\frac{ng}{mL}) - \text{Concentration of Sample } (\frac{ng}{mL})}{\text{Spike Concentration } (\frac{ng}{mL})} * 100\%$$

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

$$\text{Recovery} = \frac{\text{Total analyte found (ng/mL)} - \text{Average analyte found in sample (ng/mL)}}{\text{Analyte added (ng/mL)}} \times 100$$

13 Analysis Batch Method Performance Criteria

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 the final report if the Technical Manager (non-GLP study) or Study Director (GLP study) chooses to report 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 appropriate. 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 – Analysis Batch

A minimum of three system suitability samples should be injected at the beginning of each analytical run. These samples are run prior to the calibration curve. It is suggested that the system suitability injections have area counts with a target RSD of ≤5% and a target retention time RSD of ≤2%. There is no defined acceptability limit on these results as the %RSDs are dependent on the number of MRM transitions being monitored in the LC/MS/MS run or time period. Any effect of system suitability is incorporated in the QC acceptance criteria.

13.2 Calibration and Limit of Quantitation (LOQ) – Analysis Batch

Calibration Curve: The coefficient of determination (r^2) value for the calibration curve must be greater than or equal to 0.990 corresponding to a correlation coefficient (r) = 0.995. Each point in the curve must be within ±25% of the theoretical concentration with the exception of the LLOQ, which may be within ±30%.

CCV Performance: The calibration standards that are interspersed throughout the analytical sequence are evaluated as continuing calibration verifications in addition to being part of the calibration curve. The accuracy

of each curve point must be within 25% of the theoretical value (within 30% for lowest curve point). Samples that are bracketed by CCVs not meeting these criteria must be reanalyzed.

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 average area counts for all prepared procedural blank(s). By definition, the measured value of the LLOQ must be within 30% of the theoretical value.

Demonstration of Specificity: Specificity is demonstrated by chromatographic retention time (within 4% of standard) and the mass spectral response of unique ions.

13.3 Blanks – Method/Procedural Blanks and Trip

Method/Procedural Blanks: Multiple procedural blanks should be interspersed throughout the analysis batch and the analytical sequence. At a minimum, method blanks are analyzed prior to instrument calibration, prior to the analysis of CCV samples, after every 10 sample injections, and at the end of the analytical run.

The mean area counts (or area ratios when using IS calibration) for each analyte must be less than 50% of the area count of the LOQ standard. If the area counts of the procedural blanks exceed 50% of the LOQ standard, then the LOQ must be raised to the first standard level that meets criteria.

Trip Blank: A trip blank of ASTM Type I water (or lab equivalent) is prepared in a sample container in the laboratory and treated as a sample, including exposure to shipping, sampling site conditions, storage, preservation and all analytical procedures. The trip blanks results for each analyte are included with the reported sample results.

13.4 Data Accuracy and Precision – Analysis Batch

Lab Control Spikes: The average recovery at each LCS level for each target analyte and appropriate SRS should be within 80-120% and the percent relative standard deviation of the recoveries must be less than or equal to 20%. If the average recovery of a spiking level falls outside method acceptance, but at least 67% (6 out of 9) of LCS samples are within 20% of their respective nominal value (33% of the QC samples, not all replicates at the same concentration, may be outside 20% of nominal value), the average recovery will be flagged as outside method acceptance criteria. All LCS samples will be control charted as per ETS-12-012. If the average recovery of one of the spiking levels exceeded the analytical method uncertainty as determined by ETS-12-012, that analytical batch uncertainty will be expanded for that particular study. The average recovery at each LCS level for mixed branched/linear isomer PFOA and PFOS should be within 70-130% and the percent relative standard deviation of the recoveries must be less than or equal to 20%.

Field Duplicates: The relative percent difference (RPD) of duplicate samples should be less than 20% for the precision of sample preparation and analysis to be considered in control. Replicate samples not meeting the 20% RPD criteria are flagged and reported as outside of QC acceptance criteria.

Field Matrix Spikes: FMS acceptance criteria are recoveries within ±30% of the expected value for each target analyte and appropriate SRS. Sample data with FMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria. Data with FMS recovery outside of ±50% of the expected value are reported as NR, where NR is defined as "Not Reportable" data outside of QC acceptance criteria. If FMS recovery could not be assessed because FMSs were at an inappropriate level, then Laboratory Matrix Spikes (LMSs) may be substituted. If LMS recoveries are within ±30% for each target analyte and SRSs the data are reportable but flagged as not meeting the FMS method acceptance criteria.

13.5 Analytical Method Uncertainty

Analytical method uncertainty for each target analyte and SRS is determined with control charted historical analysis batch LCS data for the method and reported with each analysis batch.[5] Uncertainty determinations

[5] Method uncertainty based on INTERNATIONAL ANS/ISO/IED STANDARD 17025 reference (GUM, Guide to the Expression of Uncertainty in Measurement). Method application demonstrated in ETS-12-012, citing references: a.) EURACHEM/CITAC Guide, "Quantifying Uncertainty in Analytical Measurement," Second Edition; Editors: S.L.R. Ellison, M. Rosslein, and A. Williams. b.)Georgian, Thomas, "Estimation of Laboratory Analytical Uncertainty Using Laboratory Control Samples," Environmental Testing &

are based on INTERNATIONAL ANS/ISO/IED STANDARD 17025 reference (GUM, Guide to the Expression of Uncertainty in Measurement) and described in ETS-12-012. At least thirty data points are required for determining analytical method uncertainty. The method uncertainty is defined as 2x the standard deviation of the percent recoveries of the pooled lab control spikes. While all LCS data points are control charted, only the most recent fifty data points are used for determining the method uncertainty.

When less than thirty LCS data points have been generated for a given analyte, the analysis batch LCSs are used to determine the data uncertainty. If FMSs meet the ±30% recovery criteria at a level appropriate to the endogenous level, and the LCS meet the ±20% recovery criteria, then the uncertainty of the data is determined as within 100±20%.

Analysis batch sample data with FMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria with expanded uncertainties. Data with FMS recovery outside of ±50% of the expected value are reported as NR, where NR is defined as "Not Reportable" data outside of QC acceptance criteria. If FMS recovery could not be assessed because FMSs were at an inappropriate level, then Laboratory Matrix Spikes (LMSs) may be substituted. If LMS recoveries are within ±30% for each target analyte and appropriate SRSs the data are reportable but flagged as not meeting the FMS method acceptance criteria with uncertainties of ±30%. If FMS do not meet the ±30% recovery criteria, and historical FMS data does not exist, the analytical uncertainty is evaluated on a sample-by-sample basis, the data may be reported with expanded uncertainty and are flagged.

13.6 Quantitation of PFOA/PFOS – Analysis Batch

Calibration standards consisting of mixed branched and linear isomer PFOS/PFOA are preferred. Quantitation is performed by integrating the linear and branched isomers together. Alternately, the linear and branched isomers can be integrated separately, applying the appropriate true value to each calibration curve point for each isomer. The LCS and samples are then quantitated by integrating the linear and branched isomers separately (requires separate analytical results files) and quantitating the resulting peak against the linear or branched calibration curve. The results from both integrations are then summed to produce the final result. Integrating the linear and branched isomers separately may be helpful for those samples where the linear/branched ratios do not closely match those of the reference standards.

However, for PFOS/PFOA target analytes, if the calibration standards are comprised of predominantly linear isomers only the method requires the addition of LCSs of mixed branched/linear isomer PFOS/PFOA. The purpose of including these LCSs is to demonstrate quantitative equivalency (or quantitative bias) of the isomeric mix when using a predominantly linear PFOS or PFOA standard for calibration. Alternatively, in lieu of mixed branched and linear isomer PFOS/PFOA LCSs, mixed branched and linear isomer PFOS/PFOA TBMSs may be applied to demonstrate method accuracy and precision.

An alternate method of quantitation can be performed whereby only the linear isomer of PFOS/PFOA is integrated and used for generating the calibration curve. The LCS and samples are then quantitated by integrating the linear and branched isomers separately (requires separate analytical results files) and quantitating the resulting peak against the linear calibration curve. The results from both integrations are then summed to produce the final result. Integrating the linear and branched isomers separately reduces the on-column concentration for those samples that contain both linear and branched isomers of PFOA/PFOS. This ensures that the concentration detected is within the a range of the calibration curve that is comparable regardless of whether the calibration curve was generated using predominantly linear isomers of PFOS/PFOA or linear plus branched isomers of PFOS/PFOA.

14 Pollution Prevention and Waste Management

Waste generated when performing this method will be disposed of appropriately. The original samples will be archived at the 3M Environmental Laboratory in accordance with internal procedures.

Analysis, November/December 2000. c.)Taylor, B.N. and CE. Kuyatt, NIST Technical Note 1297, 1994 Edition: "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results."d.)Adams, T.M., "A2LA Guide for the Estimation of Measurement Uncertainty in Testing", July 2002.

15 Records

Each data package generated for a study must include all supporting information for reconstruction of the data. Information for the data package must include, but is not limited to the following items: study or project number, sample and standard prep sheets/records, instrument run log (instrument batch records, instrument acquisition method, summary pages), instrument results files, chromatograms, calibration curves, and data calculations.

16 Affected Documents

None.

17 Revisions

Revision Number	Summary of Changes
1	*Section 1. Included the use of internal standard calibration by this method.* *Section 2. Included the use of internal standard calibration by this method. Included the use of a solvent/water mixture when analyzing for PFUnA, PFDoA, PFTrDA, and FOSA.* *Section 3. Added definitions for internal standard, surrogate internal standard, and surrogate recovery standard.* *Section 6.Removed the details regarding the instrument parameters to section 10 of the method.* *Section 7. Updated reference standards to include internal standards and surrogates. Changed concentration levels for working standards and included the use of internal standards and surrogates.* *Section 8. Inserted a new section on sample bottle preparation.* *Section 9 Quality Control. This section was previously section 10 in ETS-8-044.0. Updated QC criteria to be consistent with method ETS-8-154.4.* *Section 10 Procedures. This section was previously section 8 (Sample Handling) in ETS-8-044.0. Added detail regarding the preparation of LCSs. Included the use of methanol as a dilution solvent.* *Section 11 Sample Analysis. This section was previously section 10 in ETS-8-044.0. Included the details regarding the instrument parameters.* *Section 12 Data Analysis and Calculations. This section was previously section 11 in ETS-8-044.0. Removed the equation for calculating the analytes concentration, indicating that this is done by the instrument software.* *Section 13 Method Performance. This section was previously section 12 in ETS-8-044.0. Updated QC criteria to be consistent with ETS-8-154.4. Added information on the determination of analytical method uncertainty and quantitation of PFOA/PFOS.* *Section 14 Pollution Prevention. This section was previously section 13 in ETS-8-044.0.* *Section 15 Records. This section was previously section 14 in ETS-8-044.0.* *Section 16 Affected Documents. This section was previously section 15 in ETS-8-044.0.* *Section 17 Revisions. This section was previously section 16 in ETS-8-044.0.*

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GLP10-01-01, Interim Report 32: Analysis of PFOA in Groundwater Samples from New On-Site Wells - Adjacent to the 3M Decatur Wastewater Treatment Plant (WWTP) April 2012

Study Title

Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program

Data Requirement

EPA TSCA Good Laboratory Practice Standards 40 CFR Part 792

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Interim Report Completion Date

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Project Identification

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A2LA ACCREDITED

The testing reported herein meet the requirements of ANSI/ISO/IEC 17025:2005 "General Requirements for the Competence of Testing and Calibration Laboratories", in accordance with the A2LA Testing Certificate # 2052.01. Testing that complies with this International Standard also meets principles of ISO 9001:2000.

Testing Cert #2052.01

This page has been reserved for specific country requirements.

GLP COMPLIANCE STATEMENT

Report Title: GLP10-01-01, Interim Report 32; Analysis of PFOA in Groundwater Samples from New On-Site Wells – Adjacent to the 3M Decatur Wastewater Treatment Plant (WWTP) April 2012.

Study: Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program.

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

- These are environmental samples where there is no specific test substance, no specific test system and no dosing of a test system.
- The reference substances have not been characterized under the GLPs and the stability under storage conditions at the test site have not been determined under GLPs.

Gary Hohenstein — 5/7/12

Gary Hohenstein, Sponsor Representative — Date

Jaisimha Kesari — 5/18/12

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

QUALITY ASSURANCE STATEMENT

Report Title: GLP10-01-01, Interim Report 32; Analysis of PFOA in Groundwater Samples from New On-Site Wells – Adjacent to the 3M Decatur Wastewater Treatment Plant (WWTP) April 2012.

Study: Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program.

This report and the accompanying data were audited by the 3M Environmental Laboratory Quality Assurance Unit (QAU), as indicated below. The findings were reported to the principal analytical investigator (P.A.I.), laboratory management and study director.

Inspection Dates	Phase	Date Reported to	
		Testing Facility Management	Study Director
4/20/12	Data and Report	4/26/12	4/26/12

Casey Norwell 5-1-12

QAU Representative Date

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1 Study Information

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3M Company

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Study Location

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Study Dates

Study Initiation: March 8, 2010
Interim Report 32 Experimental Termination: April 14, 2012
Interim Report Completion: Date of Interim Report Signing

Location of Archives

All original raw data and the analytical report have been archived at the 3M Environmental Laboratory according to 40 CFR Part 792. The test substance and analytical reference standard reserve samples are archived at the 3M Environmental Laboratory according to 40 CFR Part 792

2 Summary

The 3M Environmental Laboratory received groundwater samples from six new on-site temporary residuum monitoring wells in the vicinity of the 3M Decatur facility Wastewater Treatment Plant (WWTP) in Decatur, AL. A total of twenty-eight sample bottles were received at the 3M Environmental Laboratory for perfluorooctanoate (PFOA) analysis and included duplicate groundwater samples and two field matrix spike (FMS) samples from each sampling location. Samples also included one trip blank containing Milli-Q™ water and appropriate trip blank spikes and one equipment rinseate blank. The equipment rinseate blank did not have FMS samples prepared for determination of PFOA recovery. All samples were logged into the laboratory information management system (LIMS) under project GLP10-01-01-32. The groundwater samples and trip blanks were received from Weston personnel on April 9, 2012. All of the samples were prepared and analyzed for PFOA following 3M Environmental Laboratory Method ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds in Water by LC/MS/MS; Direct Injection Analysis".

The average measured PFOA concentrations are summarized in Table 1. The trip blank was below the lower limit of quantitation (LLOQ) of 0.0240 ng/mL, indicating adequate control of sample contamination during shipping and sample collection. The analytical uncertainty was estimated at ± 23%.

Table 1. Summarized PFOA Results (Residuum Monitoring Wells, April 2012)

Sample ID	Avg. PFOA Concentration (ng/mL)	Relative Percent Difference
DAL GW TW1R 120405	103	1.9
DAL GW TW2R 120405	1070	6.6
DAL GW TW3R 120405	2260	13
DAL GW TW4R 120405	107	2.8
DAL GW TW5R 120405	369	6.8
DAL GW TW6R 120405	238	0.42
DAL GW TW3R Rinseate Blank	<0.240	N/A
DAL-GW-TRIP01 Blank	<0.240	N/A

NA; not applicable
The analytical uncertainty for PFOA was estimated at ± 23%.

3 Introduction

This analytical study was conducted as part of the Phase 3 Environmental Monitoring and Assessment Program for the 3M facility located in Decatur, Alabama. The objective of the overall program is to gain information regarding concentrations of perfluorooctanoate (PFOA) in various environmental media such as groundwater, soils and sediments that are associated with and near the Decatur facility. This analytical study was conducted to analyze groundwater samples collected from six new temporary on-site residuum monitoring wells located adjacent to the 3M Decatur WWTP for PFOA in an effort to characterize regional groundwater conditions.

The 3M Environmental Laboratory prepared sample bottles (250 mL high-density polyethylene) which were shipped to Decatur, AL Weston personnel prior to field sampling. Sample bottle sets for each groundwater sampling location included a field sample, field sample duplicate, and two field spike samples. Each empty container for groundwater samplings was marked with a "fill to here" line to

produce a final sample volume of 200 mL. Containers designated for field matrix samples were fortified with an appropriate matrix spike solution containing PFOA prior to being sent to the field for sample collection. All sample bottles included the addition of $^{13}C_8$-PFOA (internal standard) at a nominal concentration of 1 ng/mL and $^{13}C_4$-PFOA (surrogate recovery standard) at a nominal concentration of 0.1 ng/mL. Due to the level of PFOA detected in the samples, neither the internal standard nor the surrogate recovery standard was utilized during sample analysis. Laboratory matrix spikes were prepared for sampling locations TW2, TW3, TW5, and TW6 since the field matrix spike levels were not appropriate for these four sampling locations. See section 8.8 of the report for field matrix spike levels. See section 8.9 of the report for laboratory matrix spike levels.

Samples were prepared and analyzed according to the procedure defined in 3M Environmental Laboratory method ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds in Water by LC/MS/MS; Direct Injection Analysis".

Table 1 summarizes the average PFOA concentration for the duplicate ground water samples collected, and for the trip blank and aqueous rinseate blank sample. Tables 10-17 summarize the individual sample results and the associated FMS or LMS recoveries. All results for the quality control samples prepared and analyzed with the samples are reported and discussed elsewhere in this report.

4 Test & Control Substances

There was not a test substance or control substances in the classic sense of a GLP study. This study was purely analytical in nature.

5 Reference Substances

The analytical reference substances used for this study are listed below.

Reference Substance	PFOA (Linear+Branched)	PFOA (Linear+Branched)	$^{13}C_8$-PFOA	$^{13}C_8$-PFOA
Chemical Name	Perfluorooctanoate	Perfluorooctanoate	Perfluorooctanoate	Perfluorooctanoate
Chemical Formula	$C_7F_{15}COOH$	$C_8HF_{15}O_2$	$^{13}C_8HF_{15}O_2$	$^{13}C_8HF_{15}O_2$
Identifier	CAS # 95328-99-7	CAS #335-67-1	MPFC-C-0511	MPFC-C-0112
Use	Target Analyte Reference Standard	FMS Reference Standard	Internal Standard	Internal Standard
Source	Wellington	Sigma-Aldrich	Wellington	Wellington
Expiration Date	03/17/2014	7/27/2016	05/25/2014	01/24/2015
Storage Conditions	Frozen	Frozen	Frozen	Frozen
Chemical Lot Number	TPFOA0311	MKBD4574V	052411	012312
TCR Number	TCR11-0042	TCR11-0029	TCR11-0016	TCR12-0004
Physical Description	Liquid	Powder	Liquid	Liquid
Purity	98.3%	96.8%	NA (1)	NA (1)

(1) Compound is part of a custom mixture of mass-labeled perfluorinated compounds at a concentration of 5.0 µg/mL.

6 Test System

There was not a test system for this study in the classic sense of a GLP study. This study was conducted for analysis of ground water samples collected from wells located in Decatur, AL by Weston Solutions, Inc. personnel. Samples for this study are "real world" environmental samples.

Table 2. Sample Description Key Code.

String Number	String Descriptor	Example
Example	*DAL-GW-TW1R-0-120405*	
1	*Sample Location*	*DAL= Decatur, Alabama*
2	*Sample Type*	*GW = Ground Water*
3	*Well ID*	*Example: TW1R*
4	*Sampling Date*	*120405– April 5, 2012*
5	*Sample Type*	*0=primary sample* *DB=duplicate sample* *LS = low spike* *HS = high spike*

7 Method Summary

7.1 Method

Analysis for all analytes was completed following 3M Environmental Laboratory method ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds In Water by High Performance Liquid Chromatography/Mass Spectrometry Direct Injection Analysis".

7.2 Sample Collection

Samples were collected in 250 mL Nalgene™ (high-density polyethylene) bottles prepared at the 3M Environmental Laboratory. Sample bottles associated with GLP10-01-01-32 were returned to the laboratory at ambient conditions on April 9, 2012. Samples were stored refrigerated at the laboratory after receipt. A set of laboratory prepared Trip Blank and Trip Blank field matrix spikes were sent with the set of sample collection bottles.

7.3 Sample Preparation

All samples were initially diluted 1:10 by diluting 1 mL of a well mixed sample with 9 mL of Milli Q water and analyzed on 4/12/12.

Sampling locations TW2, TW3, TW5, and TW6 were re-analyzed on 4/26/12, and included the preparation of a laboratory matrix spike with each sample set. Location TW2R was diluted 1:50 by diluting 0.2 mL of the well mixed sample with 9.8 mL of Milli Q water, and included a 1000 ppb LMS. Location TW3R was diluted 1:100 by diluting 0.1 mL of the well mixed sample with 9.9 mL of Milli Q water, and included a 2000 ppb LMS. Locations TW5R and TW6R were diluted 1:10 by diluting 1.0 mL of the well mixed sample with 9.0 mL of Milli Q water, and included a 200 ppb LMS.

7.4 Analysis

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

raw data hard copies placed in the final data packet, and are briefly described below in **Table 3, Table 4** and **Table 5.**

Table 3. Instrument Parameters.

Instrument Name	ETS Ginger	ETS Buster
Analytical Method Followed	ETS-8-044.1	ETS-8-044.1
Analysis Date	4/12/12	4/26/12
Liquid Chromatograph	Agilent 1100	Agilent 1100
Guard column	Betasil C18 (4.6 mm X 100 mm), 5µ	Betasil C18 (4.6 mm X 100 mm), 5µ
Analytical column	Betasil C18 (4.6 mm X 100 mm), 5µ	Betasil C18 (4.6 mm X 100 mm), 5µ
Injection Volume	10 µL	5 µL
Mass Spectrometer	Applied Biosystems API 5000	Applied Biosystems API 4000
Ion Source	Turbo Spray	Turbo Spray
Electrode	Turbo ion electrode	Turbo ion electrode
Polarity	Negative	Negative
Software	Analyst 1.4.2	Analyst 1.4.2

Table 4. Liquid Chromatography Conditions.

Step Number	*Total Time (min)*	*Flow Rate (µL/min)*	*Percent A (2 mM ammonium acetate)*	*Percent B (Methanol)*
ETS-8-044.1 Analysis				
0	0.0	750	97.0	3.0
1	2.0	750	97.0	3.0
2	14.5	750	5.0	95.0
3	15.5	750	5.0	95.0
4	16.5	750	97.0	3.0
5	20.0	750	97.0	3.0

Table 5. Mass Transitions.

Analyte	*Mass Transition Q1/Q3*	*Reference Material Structure*
PFOA	*413/369*	*Linear + Branched*
	413/219	
	413/169	
Dwell time was 50 (4/12/12) or 100 (4/26/12) msec for each transition. The individual transitions were summed to produce a "total ion chromatogram" (TIC), which was used for quantitation.		

8 Analytical Results

8.1 Calibration

Samples were analyzed against an external standard calibration curve. Calibration standards were prepared by spiking known amounts of the stock solution containing PFOA (reference standard containing both linear and branched isomers) into Milli Q water. Standards ranging from 0.0250 ng/mL to 100 ng/mL (nominal) were analyzed on 4/12/12 while only standards ranging from 1.0 ng/mL to 100

ng/mL (nominal) were analyzed on 4/26/12. A quadratic, 1/x weighted, calibration curve of the peak area counts was used to fit the data for each analyte. The data were not forced through zero during the fitting process. Calculating the standard concentrations using the peak area confirmed accuracy of each curve point. Each curve point was quantitated using the overall calibration curve and reviewed for accuracy. Method calibration accuracy requirements of 100±25% (100±30% for the lowest curve point) were met for all analytes. The correlation coefficient (r) was greater than 0.995 for PFOA for both the 4/12/12 and 4/26/12 analysis.

8.2 System Suitability

A calibration standard was analyzed four times at the beginning of the analytical sequence to demonstrate overall system suitability. The acceptance criteria of less than or equal to 5% relative standard deviation (RSD) for peak area and retention time criteria of less than or equal to 2% RSD was met for PFOA for both the 4/12/12 and 4/26/12 analysis.

8.3 Limit of Quantitation (LOQ)

The LOQ for this analysis is the lowest non-zero calibration standard in the curve that meets linearity and accuracy requirements and for which the area counts are at least twice those of the appropriate blanks. The nominal LOQ for PFOA can be found in Table 6.

Table 6. Limit of Quantitation (LOQ).

Analysis Date	*PFOA ng/mL*
4/12/12	0.240 [1]
	1.20 [2]
4/26/12	9.58 [3]
	47.9 [4]
	95.8 [5]

(1) A 1:10 dilution factor was applied to LOQ.
(2) A 1:50 dilution factor was applied to LOQ.
(3) A 1:10 dilution factor was applied to LOQ.
(4) A 1:50 dilution factor was applied to LOQ
(5) A 1:100 dilution factor was applied to LOQ.

8.4 Continuing Calibration

During the course of each analytical sequence, continuing calibration verification samples (CCVs) were analyzed to confirm that the instrument response and the initial calibration curve were still in control. All CCVs met method criteria of 100% ± 25% for PFOA for both the 4/12/12 and 4/26/12 analysis.

8.5 Blanks

Three types of blanks were prepared and analyzed with the samples: method procedural blanks, a trip blank, and an equipment rinseate blank. Method procedural blank results were reviewed and used to evaluate method performance and to determine the LOQ for PFOA. The trip blank reflects the shipping and sample collection conditions the sample bottles and samples experience. The equipment rinseate blank is an aqueous sample that reflect the efficiency of equipment cleaning in the field between different sample collections and are proof of no cross contamination of samples from the equipment.

8.6 Lab Control Spikes (LCSs)

Low, mid, and high lab control spikes were prepared for the PFOA and analyzed in triplicate. LCSs were prepared by spiking known amounts of PFOA into 10 mL of Milli-Q water to produce the desired concentration. The spiked water samples were then analyzed in the same manner as the samples. The method acceptance criteria, average of LCS at each level should be within 100% ± 20% with an RSD ≤20%, were met for PFOA.

The following calculations were used to generate data in Table 7 for laboratory control spikes:

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

$$\text{LCS\% RSD} = \frac{\text{standard deviation LCS replicates}}{\text{average LCS recovery}} * 100\%$$

Table 7. Laboratory Control Spike Recovery.

ETS-8-044.1 Analyzed 4/12/12	*PFOA (Linear + Branched)*		
Lab ID	***Spiked Concentration (ng/mL)***	***Calculated Concentration (ng/mL)***	***%Recovery***
LCS-120411-1	0.477	0.435	91.2
LCS-120411-2	0.477	0.444	93.2
LCS-120411-3	0.477	0.452	94.7
Average ± %RSD	**93.0% ± 1.9%**		
LCS-120411-4	4.77	4.56	95.5
LCS-120411-5	4.77	4.70	98.4
LCS-120411-6	4.77	4.61	96.7
Average ± %RSD	**96.9% ± 1.5%**		
LCS-120411-7	28.7	25.3	88.1
LCS-120411-8	28.7	24.9	86.9
LCS-120411-9	28.7	25.7	89.5
Average ± %RSD	**88.2% ± 1.5%**		

Table 7 continued. Laboratory Control Spike Recovery.

ETS-8-044.1 Analyzed 4/26/12	*PFOA (Linear + Branched)*		
Lab ID	*Spiked Concentration (ng/mL)*	*Calculated Concentration (ng/mL)*	*%Recovery*
LCS-120426-1	4.77	4.36	91.4
LCS-120426-2	4.77	4.35	91.2
LCS-120426-3	4.77	4.33	90.7
Average ± %RSD	**91.1% ± 0.40%**		
LCS-120426-4	19.1	15.5	81.4
LCS-120426-5	19.1	15.6	81.8
LCS-120426-6	19.1	15.8	82.6
Average ± %RSD	**81.9% ± 0.75%**		
LCS-120426-7	47.7	42.4	88.9
LCS-120426-8	47.7	39.9	83.6
LCS-120426-9	47.7	39.7	83.3
Average ± %RSD	**85.3% ± 3.7%**		

8.7 Analytical Method Uncertainty

Analytical uncertainty is based on historical QC data that is control charted and used to evaluate method accuracy and precision. The method uncertainty is calculated following ETS-12-012.2. The standard deviation is calculated for the set of accuracy results (in %) obtained for the QC samples. The expanded uncertainty is calculated by multiplying the standard deviation by a factor of 2, which corresponds to a confidence level of 95%.

Table 8. Analytical Method Uncertainty.

Analyte	Method	Standard Deviation	Method Uncertainty
PFOA	ETS-8-044.1	11.3	±23%

8.8 Field Matrix Spikes (FMS)

Low and high field matrix spikes were collected at each sampling point to verify that the analytical method is applicable to the collected matrix. Field matrix spikes were generated by adding a measured volume of field sample to a container spiked by the laboratory with PFOA (reference standard containing both linear and branched isomers) prior to shipping sample containers for sample collection. Field matrix spike recoveries within method acceptance criteria of 100±30% confirm that "unknown" components in the sample matrix do not significantly interfere with the extraction and analysis of the analytes of interest. Field matrix spike concentrations must be 50% of the sample concentration to be considered an appropriate field spike. Field matrix spikes are presented in section 9 of this report.

Table 9. Field Matrix Spike Levels.

Sampling Location	Spike Level	PFOA, ng/mL
All Locations and Trip Blank	Low	10
	High	100

The following calculation was used to calculate the field matrix spike recovery in Section 9 of the report:

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

8.9 Laboratory Matrix Spike (LMS)

Due to the high level of PFOA detected in sampling locations TW2, TW3, TW5, and TW6, the FMS spike levels were not appropriate and laboratory matrix spikes (LMS) samples were prepared to verify that the analytical method is applicable to the collected matrix. Laboratory matrix spikes were generated by adding a measured volume of PFOA (reference standard containing both linear and branched isomers) to an aliquot of the primary sample. Since all samples required dilution prior to sample analysis, the laboratory matrix spike added was based on the on-column instrument concentration.

Sampling location TW2; the primary sample (GLP10-01-01-32-005) was diluted 1:50, to which 19.1 ng/mL of PFOA was added for a LMS concentration of 956 ng/mL.

Sampling location TW3; the primary sample (GLP10-01-01-32-009) was diluted 1:100, to which 19.1 ng/mL of PFOA was added for a LMS concentration of 1912 ng/mL.

Sampling location TW5; the primary sample (GLP10-01-01-32-017) was diluted 1:10, to which 19.1 ng/mL of PFOA was added for a LMS concentration of 191 ng/mL.

Sampling location TW6; the primary sample (GLP10-01-01-32-017) was diluted 1:10, to which 19.2 ng/mL of PFOA was added for a LMS concentration of 191 ng/mL.

Lab matrix spike recoveries within method acceptance criteria of 100±30% confirm that "unknown" components in the sample matrix do not significantly interfere with the extraction and analysis of the analytes of interest. Lab matrix spike concentrations must be 50% of the sample concentration to be considered an appropriate field spike. Lab matrix spikes are presented in section 9 of this report.

The following calculation was used to calculate the lab matrix spike recovery in Section 9 of the report:

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

9 Data Summary and Discussion

The tables below summarize the sample results and field or lab matrix spike recoveries for the sampling locations as well as the Trip Blanks. Results and average values are rounded to three significant figures according to EPA rounding rules. Because of rounding, values may vary slightly from those listed in the raw data. Field matrix spike recoveries meeting the method acceptance criteria of ± 30%, demonstrate that the method was appropriate for the given matrix and their respective quantitative ranges.

Table 10. DAL GW TW1R 120405

		PFOA	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery
GLP10-01-01-32-001	DAL-GW-TW1R-0-120405	102	NA
GLP10-01-01-32-002	DAL-GW-TW1R-DB-120405	104	NA
GLP10-01-01-32-003	DAL-GW-TW1R-LS-120405	108	NC
GLP10-01-01-32-004	DAL-GW-TW1R-HS-120405	182	79.0
Average Concentration (ng/mL) ± %RPD		103 ng/mL ± 1.9%	

NA = Not Applicable
NC = Not Calculated; the sample concentration is greater than 2x the spike level.
Samples analyzed on 4/12/12 using a 1:10 dilution factor.

Table 11. DAL GW TW2R 120405

		PFOA	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery
GLP10-01-01-32-005	DAL-GW-TW2R-0-120405	1030	NA
GLP10-01-01-32-006	DAL-GW-TW2R-DB-120405	1100	NA
GLP10-01-01-32-005 LMS; 956 ppb	DAL-GW-TW2R-0-LMS	1820	79.0
Average Concentration (ng/mL) ± %RPD		1070 ng/mL ± 6.6%	

NA = Not Applicable
Samples analyzed on 4/26/12 using a 1:50 dilution factor.

Table 12. DAL GW TW3R 120405

		PFOA	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery
GLP10-01-01-32-009	DAL-GW-TW3R-0-120405	2110	NA
GLP10-01-01-32-010	DAL-GW-TW3R-DB-120405	2400	NA
GLP10-01-01-32-009 LMS; 1912 ppb	DAL-GW-TW3R-0-LMS	3680	74.5
Average Concentration (ng/mL) ± %RPD		2260 ng/mL ± 13%	

NA = Not Applicable
Samples analyzed on 4/26/12 using a 1:100 dilution factor.

Table 13. DAL GW TW4R 120405

		PFOA	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery
GLP10-01-01-32-013	DAL-GW-TW4R-0-120405	105	NA
GLP10-01-01-32-014	DAL-GW-TW4R-DB-120405	108	NA
GLP10-01-01-32-015	DAL-GW-TW4R-LS-120405	114	NC
GLP10-01-01-32-016	DAL-GW-TW4R-HS-120405	184	77.5
Average Concentration (ng/mL) ± %RPD		107 ng/mL ± 2.8%	

NA = Not Applicable
NC = Not Calculated; the sample concentration is greater than 2x the spike level.
Samples analyzed on 4/12/12 using a 1:10 dilution factor.

Table 14. DAL GW TW5R 120405

		PFOA	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery
GLP10-01-01-32-017	DAL-GW-TW5R-0-120405	381	NA
GLP10-01-01-32-018	DAL-GW-TW5R-DB-120405	356	NA
GLP10-01-01-32-017 LMS; 191 ppb	DAL-GW-TW5R-0-LMS	515	76.7
Average Concentration (ng/mL) ± %RPD		369 ng/mL ± 6.8%	

NA = Not Applicable
Samples analyzed on 4/26/12 using a 1:10 dilution factor.

Table 15. DAL GW TW6R 120405

		PFOA	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery
GLP10-01-01-32-021	DAL-GW-TW6R-0-120405	238	NA
GLP10-01-01-32-022	DAL-GW-TW6R-DB-120405	237	NA
GLP10-01-01-32-021 LMS; 191 ppb	DAL-GW-TW6R-0-LMS	387	78.3
Average Concentration (ng/mL) ± %RPD/RSD		238 ng/mL ± 0.42%	

NA = Not Applicable
Samples analyzed on 4/12/12 using a 1:10 dilution factor.

Table 16. DAL GW TRIP01 120405

		PFOA	
3M LIMS ID	*Description*	*Concentration (ng/mL)*	*%Recovery*
GLP10-01-01-32-026	DAL-GW-TRIP01-0-120405	<0.240	NA
GLP10-01-01-32-027	DAL-GW-TRIP01-LS-120405	8.80	88.0
GLP10-01-01-32-028	DAL-GW-TRIP01-HS-120405	90.5	90.5

NA = Not Applicable
NC = Not Calculated; the sample concentration is greater than 2x the spike level.
Samples analyzed on 4/12/12 using a 1:10 dilution factor.

Table 17. Rinseate Blank

		PFOA	
3M LIMS ID	*Description*	*Concentration (ng/mL)*	*%Recovery*
GLP10-01-01-32-025	DAL-GW-TW3R-RB-120405	<0.240	NA

NA = Not Applicable
Samples analyzed on 4/12/12 using a 1:10 dilution factor.

9 Conclusion

Laboratory control spikes and field matrix spikes were used to determine the analytical method accuracy and precision for PFOA. Analysis was successfully completed following 3M Environmental Laboratory method ETS-8-044.1 described herein.

10 Data/Sample Retention

All remaining samples and associated project data (hardcopy and electronic) will be archived according to 3M Environmental Laboratory standard operating procedures.

11 Attachments

Attachment A: Protocol Amendment 32 (General Project Outline)

Attachment B: Representative Chromatograms and Calibration Curves

Attachment C: Analytical Method – ETS-8-044.1

12 Signatures

5/2/2012
Cleston Lange, Ph.D., 3M Principal Analytical Investigator — Date

4 MAY 2012
William K. Reagen, Ph.D., 3M Environmental Laboratory Manager — Date

Gary Hohenstein
5/7/12
Gary Hohenstein, 3M Sponsor Representative — Date

5/18/12
Jaisimha Kesari, Study Director — Date

ATTACHMENT A: PROTOCOL AMENDMENT

Study Title

Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program

PROTOCOL AMENDMENT NO. 32

Amendment Date:
March 28, 2012

Performing Laboratory
3M Environmental, Health, and Safety Operations
3M Environmental Laboratory
Building 260-5N-17
Maplewood, MN 55144-1000

Laboratory Project Identification
GLP10-01-01

Sampling Event

New On-Site Wells - Adjacent to 3M Decatur WWTP

This amendment modifies the following portion of protocol:

"Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program"

PROTOCOL READS:

No changes to the wording of the protocol are required.

AMEND TO READ:

No changes to the wording of the protocol are required. This amendment only addresses and documents the addition of the General Project Outline (GPO) for the collection and analysis of groundwater samples as part of the 3M Decatur Phase 3 Program for PFOA (GLP10-01-01). The anticipated sample collection will occur around the timeframe of the week of April 2, 2012. The groundwater samples for this sampling event will be entered into the 3M Environmental Laboratory LIMS as project GLP10-01-01-32 and reported as interim report GLP10-01-01-32, (reflecting study GLP10-01-01 and amendment -32).

Reason:

The reason for this amendment is to document the General Project Outline (GPO) which describes the anticipate groundwater sample collection event for six new on-site temporary residuum monitoring wells in the vicinity of the Wastewater Treatment Plant (WWTP) at the 3M Decatur facility.

The GPO is three pages in length and included as attached to this amendment form.

Amendment Approval

Gary Hohenstein, Sponsor Representative — Date 4/5/12

Cleston C. Lange, Principal Analytical Investigator — Date 3/29/2012

William Reagen, EHS Opns Environmental Lab Management — Date 2 April 2012

Jaisimha Kesari P.E., DEE, Study Director — Date 4/12/12

3M Environmental Health & Safety Operations, Environmental Laboratory

General Project Outline

To:	Gary Hohenstein, 3M EHS&Opns
From:	Susan Wolf, 3M EHS&Opns; Environmental Lab
cc:	William Reagen, 3M EHS&Opns; Environmental Lab
	Cleston Lange, 3M EHS&Opns; Environmental Lab
	Jai Kesari, Weston Solutions
Date:	March 28, 2012
Subject:	Analysis of Perfluorooctanoic Acid (PFOA) in Groundwater, Soil and Sediment for the 3M Decatur Phase 3 Site-Related Monitoring Program; GLP Interim Report 32; New On-Site Wells – Adjacent to the 3M Decatur Wastewater Treatment Plant (WWTP)

1 General Project Information

Contacts	**3M Sponsor Representative** Gary Hohenstein 3M EHS Operations 3M Building 224-5W-03 Saint Paul, MN 55144-1000 Phone: (651) 737-3570 gahohenstein@mmm.com **3M Environmental Laboratory Management** William K. Reagen 3M EHS Opns, Environmental Laboratory 260-5N-17 651 733-9739 wkreagen@mmm.com **Principal Analytical Investigator** Cleston Lange 3M EHS Opns, Environmental Laboratory 260-5N-17 651 733-9860 cclange@mmm.com **Sampling Coordinator** Timothy Frinak Weston Solutions Timothy.frinak@westonsolutions.com Phone: (334)-332-9123
Lab Request Number	**GLP10-01-01-32**
Six Digit Department Number	Dept #530711, Project #0022674449
Project Schedule/Test Dates	Sampling scheduled for the week of April 2, 2012

All verbal and written correspondence will be directed to Gary Hohenstein and Jai Kesari.

2 Background Information and Project Objective(s)

The 3M EHS Operations Laboratory (3M Environmental Lab) will receive and analyze groundwater samples collected from six new temporary on-site residuum monitoring wells located adjacent to the 3M Decatur WWTP for Perfluorooctanoic Acid (PFOA). Analyses will be conducted under the GLP requirements of EPA TSCA Good Laboratory Practice Standards 40 CFR 792.

Groundwater samples will be collected by Weston Solutions personnel the week of April 2, 2012. The 3M Environmental Laboratory will prepare the sample bottles with all required spikes to ensure that results for PFOA are of a known precision and accuracy. The final report will be submitted to Gary Hohenstein and Jai Kesari upon completion under interim report GLP10-01-01-32.

3 Project Schedule

Sample collection bottles will be prepared by 3M Environmental Laboratory for sampling the week of April 2, 2012. Sample bottles will be shipped in coolers overnight to 3M Decatur for arrival on Friday, March 30, 2012. Sample bottles should be stored refrigerated on-site until sample collection.

Martin Smith \ Weston Trailer
3M Decatur Plant
1400 State Docks Road
Decatur, Alabama 35601

4 Test Parameters

The targeted limit of quantitation will be **0.025 ng/mL** (ppb) for PFOA.

Six sampling locations have been specified; TW1R, TW2R, TW3R, TW4R, TW5R, and TW6R. These are new wells with no historical sampling values for estimating field matrix spike levels, however, information received from Weston indicates that locations TW3R, TW4R and potentially TW5R, are expected to have higher concentrations based on the expected groundwater gradients in the area of these wells and field observations. Given the limited information on expected levels, at each sampling location, a total of four sample bottles will be collected (sample, sample duplicate low field matrix spike and high field matrix spike). The low field matrix spike will be prepared at 10 ng/mL and the high field matrix spike will be prepared at 100 ng/mL. The "fill to here" line on each 250 mL Nalgene bottle will be 200 mL. One set of trip blanks consisting of reagent-grade water as well as a low and high trip blank spike will be prepared at the 3M Environmental Laboratory and sent to the sampling location with the other bottles. All sample bottles will include the addition of $^{13}C_8$-PFOA (internal standard) at a nominal concentration of 1 ng/mL. All sample bottles will also include the addition of $^{13}C_4$-PFOA (surrogate spike) at a nominal concentration of 0.1 ng/mL. One additional bottle will be prepared to be used for the preparation of the equipment rinseate blank. A 500-mL bottle of laboratory reagent water will be sent with the sample bottles to be used to generate the rinseate blank sample.

5 Test Methods

Samples will be prepared and analyzed by LC/MS/MS following ETS-8-044.1 "Method of Analysis for the Determination of Perfluorinated Compounds In Water by LC/MS/MS; Direct Injection Analysis".

The data quality objectives for these studies are quantitative results for the target analytes with an analytical accuracy of 100±30%. Field matrix spikes not yielding recoveries within 100±30% will be addressed in the report and the final accuracy statement may be adjusted accordingly.

Where applicable, samples will be analyzed against an internal standard calibration curve. Each curve point will contain isotopically-labeled perfluorocarboxylic acids and perfluorosulfonic acids at a nominal concentration of 1 ng/mL. The calibration curve will be generated by taking the ratio of the standard peak area counts over the internal standard peak area counts to fit the data for each analyte.

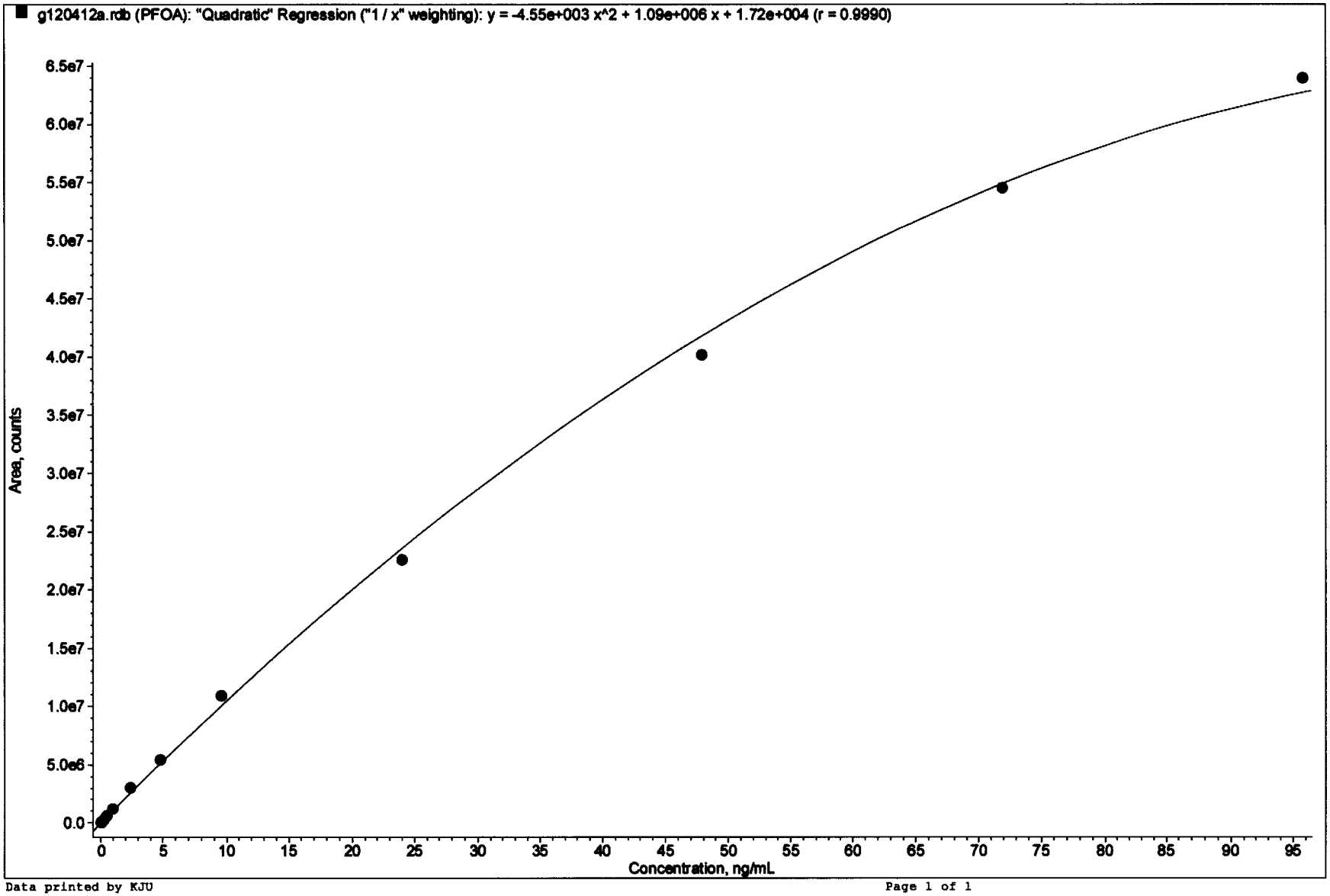
6 Reporting Requirements

For each sampling location, the report will contain the results for the sample, sample duplicate, and field matrix spike. Trip blank and trip blank spike will be reported for the sampling event as will any equipment/rinseate blanks prepared in the field. Laboratory control spikes of reagent water prepared at the time of sample extraction will also be reported and used to evaluate the overall method accuracy and precision. Method blanks of reagent water prepared at the time of sample extraction will be used to determine the method detection limit.

ATTACHMENT B: REPRESENTATIVE SAMPLE CHROMATOGRAMS AND CALIBRATION CURVE(S)

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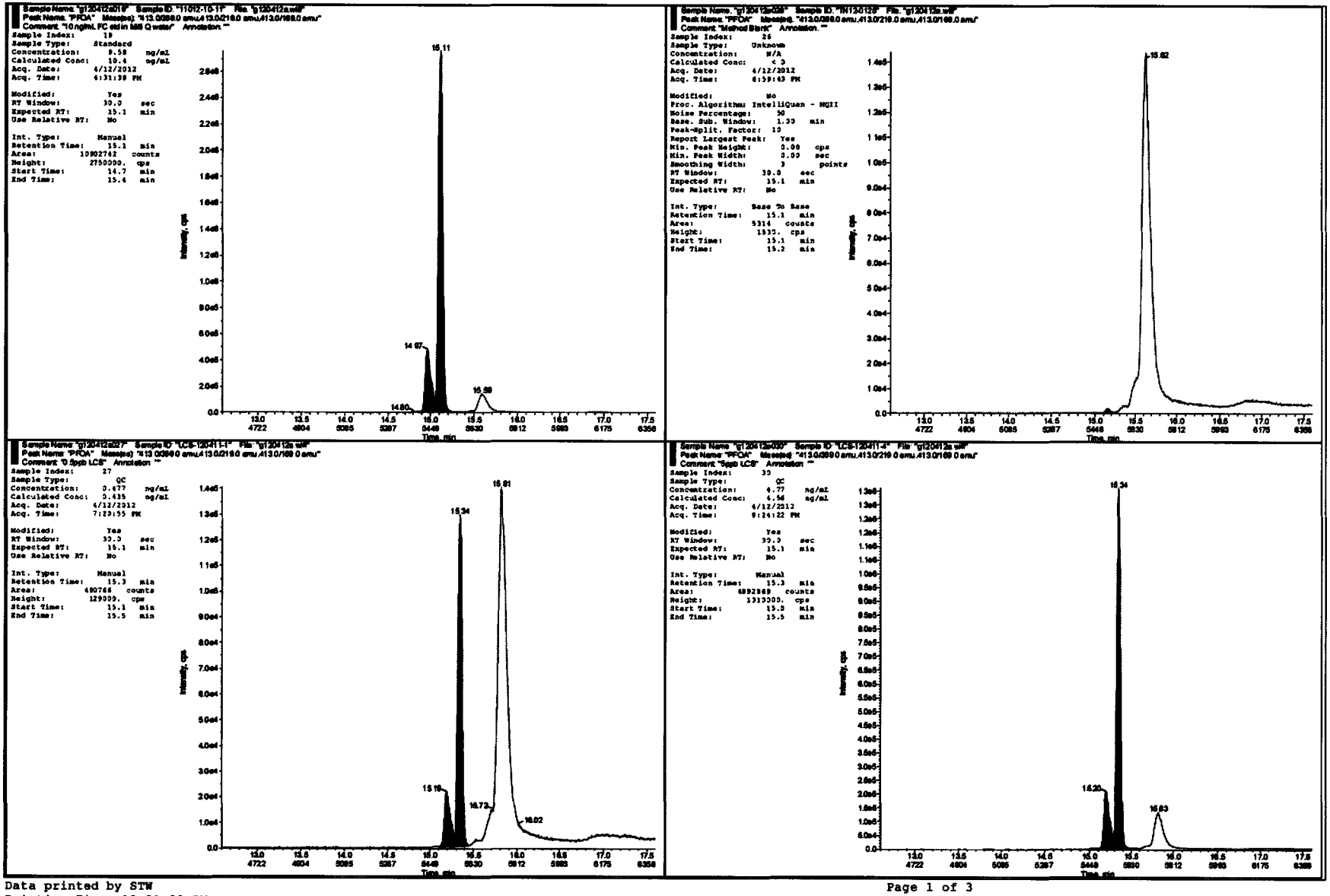


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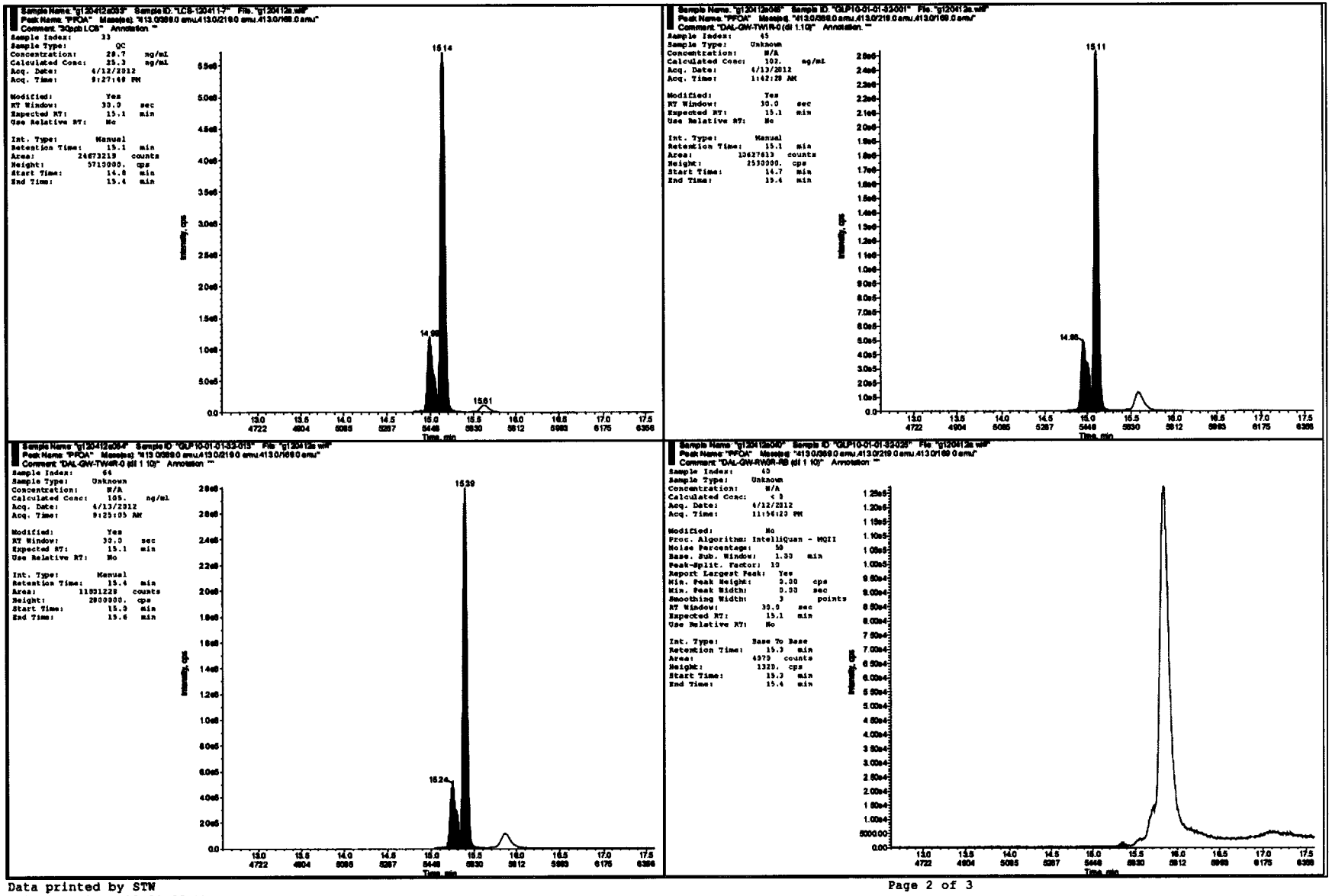
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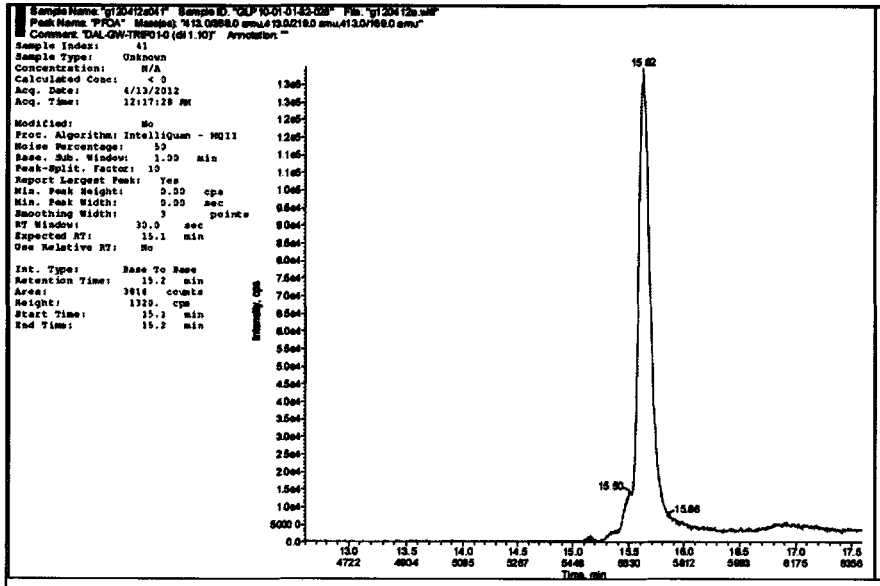
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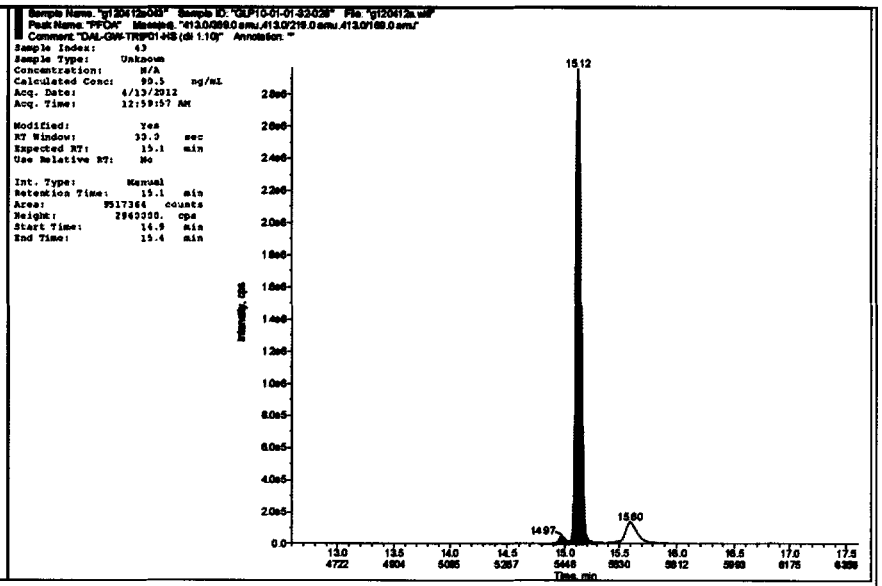


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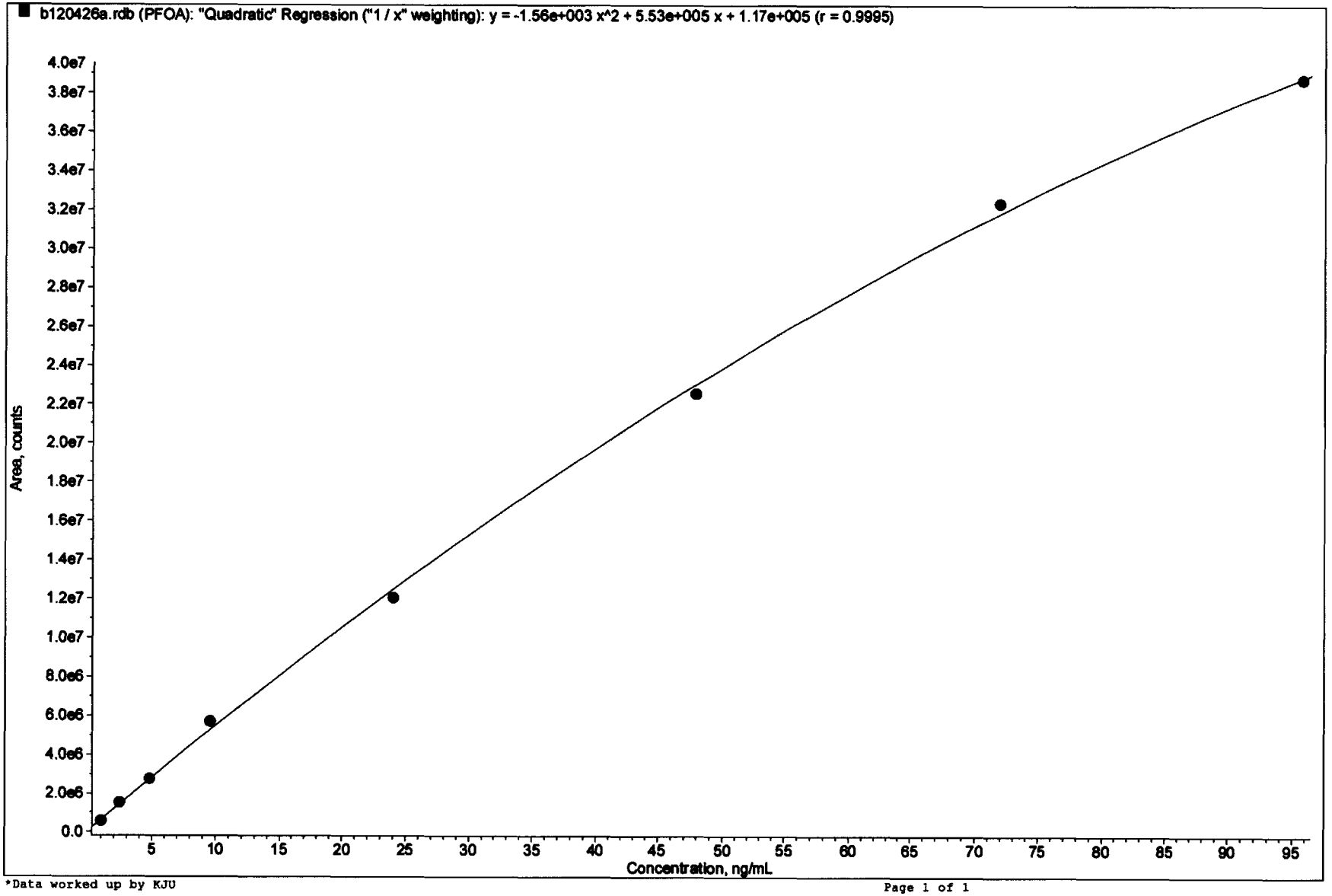


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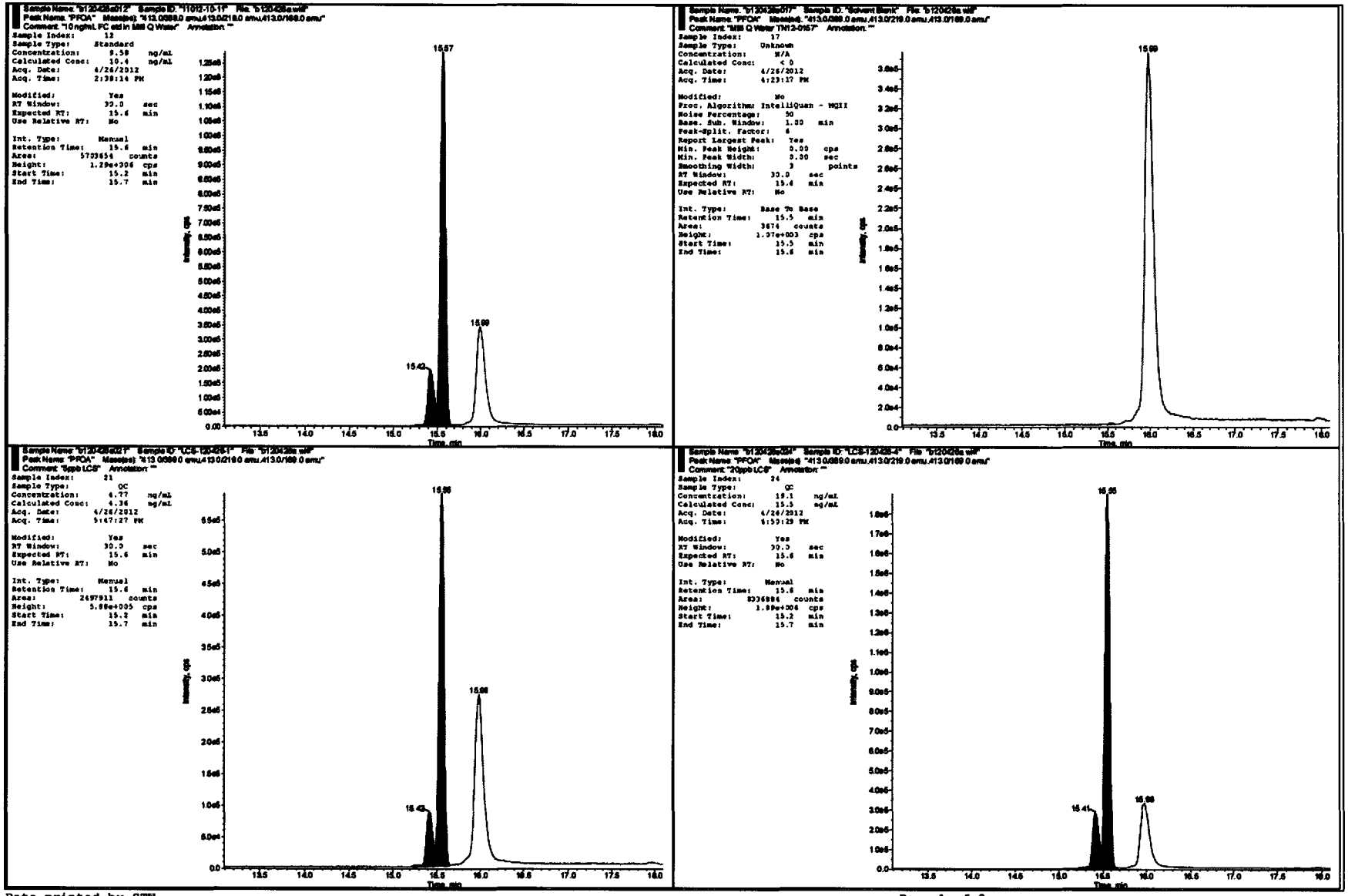
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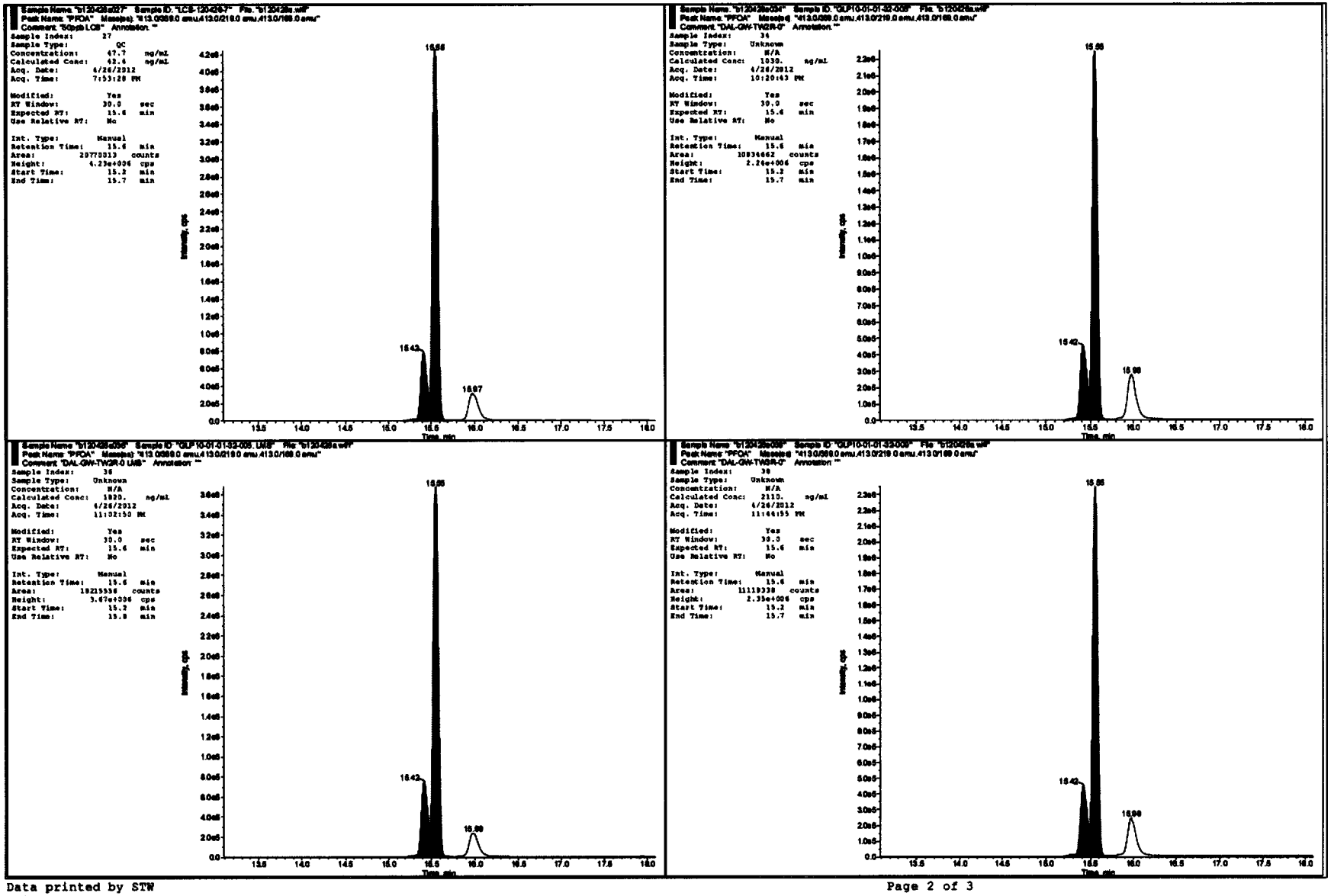
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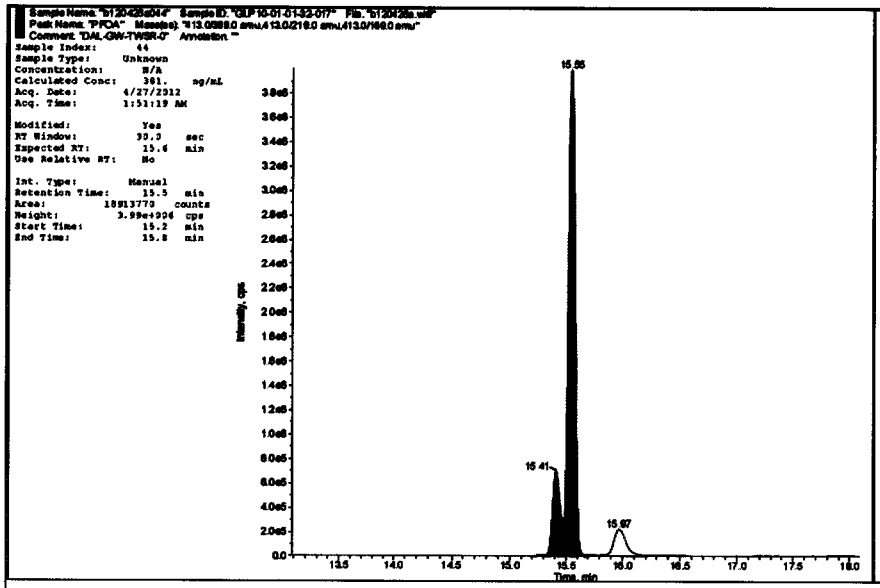
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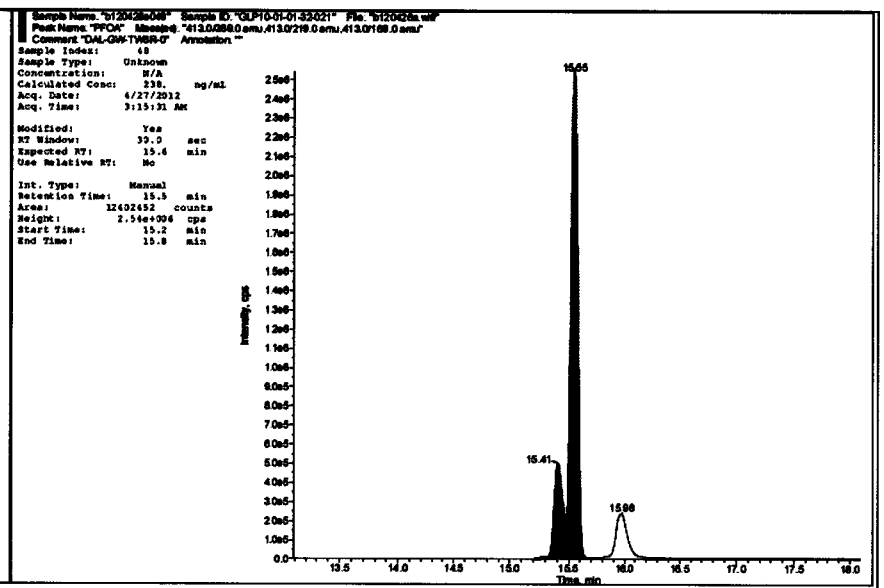


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ATTACHMENT C: ANALYTICAL METHOD(S)

3M Environmental Laboratory

Method

Method of Analysis for the Determination of Perfluorinated Compounds in Water by LC/MS/MS; Direct Injection Analysis

Method Number: ETS-8-044.1

Adoption Date: 4/12/07

Effective Date: 11/9/11

Approved By:

9 NOV 2011

William K. Reagen, Technical Director, Environmental Laboratory — Date

1 Scope and Application

This method describes the direct injection analysis of perfluorinated compounds (PFCs) from water matrices using high-performance liquid chromatography tandem mass spectrometry (HPLC/MS/MS). The method is generally applicable but not limited to the measurement of perfluoroalkyl sulfonamides and perfluorinated alkyl acids (PFAAs) such as perfluorosulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs) (Table 1). Water samples containing heavy particulate may require preparation by an alternate method such as ETS-8-154 "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates In Water By Solid Phase Extraction and High Performance Liquid Chromatography/Mass Spectrometry". The method is applicable to both external standard and internal standard calibration[1].

Table 1. Representative Target Analytes

Acronym	*Analyte*	*Chemical Abstract Services Registry Number (CASRN)*
PFBA (C4 Acid)	Perfluorobutanoic acid	375-22-4
PFPeA (C5 Acid)	Perfluoropentanoic acid	2706-90-3
PFHxA (C6 Acid)	Perfluorohexanoic acid	307-24-4
PFHpA (C7 Acid)	Perfluoroheptanoic acid	375-85-9
PFOA (C8 Acid)	Perfluorooctanoic acid	335-67-1
PFNA (C9 Acid)	Perfluorononanoic acid	375-95-1
PFDA (C10 Acid)	Perfluorodecanoic acid	335-76-2
PFUnA (C11 Acid)	Perfluoroundecanoic acid	2058-94-8
PFDoA (C12 Acid)	Perfluorododecanoic acid	307-55-1
PFTrDA (C13 Acid)	Perfluorotridecanoic acid	72629-94-8
PFBS (C4 Sulfonate)	Perfluorobutanesulfonic acid	375-73-5
PFHS (C6 Sulfonate)	Perfluorohexanesulfonic acid	355-46-4
PFOS (C8 Sulfonate)	Perfluorooctanesulfonic acid	1763-23-1
FBSA (C4 Sulfonamide	Perfluorobutanesulfonamide	30334-69-1
FOSA (C8 Sulfonamide)	Pefluorooctanesulfonamide	754-91-6

The Minimum Reporting Level (MRL) is the Limit of Quantitation (LOQ) that meets Data Quality Objectives (DQOs) that are developed based on the intended use of this method.

Method Flexibility – This is a performance-based method and may be generally applied to the determination of perfluorinated compounds in water matrices when analysis batch quality control (QC) criteria are met[2]. Each set of samples are prepared in an analysis batch with calibration standards, LCSs, blanks, and continuing calibration check standards analyzed on the same instrument during a time period that begins and ends with the analysis of the appropriate continuing calibration check standards. The laboratory is permitted to modify the LC column, mobile phase composition, LC conditions, and MS/MS conditions. Method modifications should be considered to improve method performance or to meet data quality objectives for the study. In all cases where method modifications are implemented, the batch

[1] The method is supported by validation with internal standard calibration for C4-C13 PFCAs, C4, C6, and C8 PFSAs, and C8 perfluoroalkane sulfonamide in laboratory control samples under 3M method validation E11-0667.

[2] Guidance for establishing method QC Criteria based on a.) FDA May 2001, "Guidance for Industry, Bioanalytical Method Validation", b.) EPA Method 537, and c.) European Commission: Guidance for Generating and Reporting Methods of Analysis in Support of Pre-registration Data Requirements for Annex II (Part A, section 4) and Annex III (Part A,section 5) of Directive 91/414, SANCO/3029/99 rev. 4 (11/07/00).

analytical QCs (section 9) must be completed and pass QC acceptance criteria (section 13) if the data from the analytical batch are to be reported.

2 Method Summary

Water samples are analyzed as neat aqueous sample or as solvent diluted aqueous samples by direct injection using LC/MS/MS. Samples containing heavy particulate may not be suitable for analysis by this method. Samples containing suspended particulate should be centrifuged or filtered prior to removing a sample aliquot or diluting with solvent. The water sample is mixed well prior to removing an aliquot or diluting, if necessary, with ASTM Type I water, HPLC water, other suitable water, or solvent (methanol).

Quantitation is by stable isotope internal standard calibration in laboratory reagent water. All perfluorinated compounds (PFCs) target analyte concentrations of perfluorosulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs) are reported as anions and corrected for their salt or free acid forms. Alternatively, quantitation may be performed by external standard calibration.

This is a performance-based method. Method uncertainty for each target analyte is determined for each analytical batch using multiple laboratory control spikes at multiple concentrations. This method also requires that the precision and accuracy for each sample be determined using field matrix spikes to verify that the method is applicable to each sample matrix.

Calibration standards for PFUnA, PFDoA, PFTrDA, and FOSA have been found to be unstable for more than 2 days in 100% water. Samples requiring analysis for these compounds by this method should be diluted 1:1 with methanol and analyzed against a calibration curve prepared in 1:1 synthetic groundwater:MeOH.

3 Definitions

3.1 Analysis Batch

A set of study samples that are prepared with calibration standards, laboratory control samples, and procedural blanks, and analyzed on the same instrument during a time period that begins and ends with the analysis of the appropriate continuing calibration check standards.

3.2 Analytical Sample

A portion of a laboratory sample prepared for analysis.

3.3 Calibration Standard

A solution prepared by spiking a known volume of the Working Standard (WS) into a predetermined amount of ASTM Type I, HPLC grade water, or other suitable water (i.e. matrix water), and analyzed according to this method. Calibration standards are used to calibrate the instrument response with respect to analyte concentration.

3.4 Laboratory Duplicate Sample (LDS, or Lab Dup)

A laboratory duplicate sample is a separate aliquot of a sample taken in the analytical laboratory that is analyzed separately with identical procedures. Analysis of LDSs 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.

3.5 Field Blank (FB)/Trip Blank (TB)

ASTM Type I, HPLC grade water, or other suitable 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 TB is to determine if test substances or other interferences are present in the field environment. This sample is also referred to as a Trip Blank.

3.6 Field Duplicate Sample (FDS, Field Dup)

A sample collected in duplicate at the same time from the same location as the sample. The FDS is handled under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analysis of the FDS 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.

3.7 Field Matrix Spike (FMS)

A sample to which known quantities of the target analytes, ISs and SRSs are added to the sample bottle in the laboratory before the bottles are sent to the field for collection of aqueous samples. A known, specific volume of sample must be added to the 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 is analyzed to ascertain if any matrix effects, interferences, or stability issues may complicate the interpretation of the sample analysis.

3.8 Trip Blank Matrix Spike (TBMS)

An aliquot of ASTM Type I, HPLC grade water, or other suitable water, to which known quantities of the target analytes, ISs and SRSs are added in the laboratory prior to the shipment of the collection bottles. The TBMS is analyzed exactly like a study sample to help determine if the method is in control and whether a loss of analyte or analytical bias could be attributed to sample holding time, sample storage and/or shipment issues. A low and high TBMS are appropriate when expected sample concentrations are not known or may vary.

3.9 Internal Standard (IS)

A compound added to each study sample, calibration standard, laboratory control samples, and procedural blanks at a consistent level (typically around 1 ng/mL). The internal standard(s) are stable isotope labeled versions of the target analytes. The area count ratio of the target analyte to the internal standard is used for calibration. Surrogate ISs are applied when stable isotope ISs of target analytes are unavailable. A surrogate IS is not necessarily a stable isotope labeled version of the target analyte, but is treated as an internal standard for quantitation.

3.10 Laboratory Control Sample (LCS)

An aliquot of control matrix to which known quantities of the target analytes, ISs and SRSs (when applicable) are added in the laboratory at the time when samples are aliquotted. At least three levels (two levels for SRSs) in triplicate are included, one generally at the low end of the calibration curve and one near the mid range and the upper end of the curve. The LCSs are analyzed exactly like a laboratory sample to determine whether the stability of the standards. LCSs should be prepared each day samples are aliquoted.

3.11 Laboratory Matrix Spike (LMS)

A laboratory matrix spike is an aliquot of a sample to which known quantities of target analytes, ISs and SRSs (when applicable) are added in the laboratory. The LMS is analyzed exactly like a laboratory sample to determine whether the sample matrix contributes bias to the analytical results. The endogenous concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LMS corrected for these concentrations. LMSs are optional for analysis of aqueous samples.

3.12 Laboratory Sample

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

3.13 Limit of Quantitation (LOQ)

The lower limit of quantitation (LLOQ) for an analytical batch is the lowest concentration that can be reliably quantitated within the specified limits of precision and accuracy. The LLOQ is generally selected as the lowest non-zero standard in the calibration curve that meets method acceptance criteria. The LLOQ for each target analyte is established for each analysis batch as the lowest calibration standard with area counts at least twice that of the average area counts of the procedural blanks.

The upper limit of quantitation (ULOQ) for an analytical batch is the highest concentration that can be reliably quantitated within the specified limits of precision and accuracy. The highest standard in the calibration curve that meets method acceptance criteria is defined as the ULOQ.

3.14 Method/Procedural Blank

An aliquot of control matrix 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.

3.15 Sample

A sample is an aliquot removed from a larger quantity of material intended to represent the original source material.

3.16 Stock Standard Solution (SSS)

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

3.17 Surrogate Internal Standard

An IS that is not necessarily a stable isotopically labeled target analyte, but is treated as an internal standard for quantitation. Surrogate ISs are used when isotopically labeled counterparts of the target analyte are not commercially or readily available.

3.18 Surrogate Recovery Standard (SRS)

An isotopically labeled standard, not used as an internal standard, that is added to each sample and appropriate QC sample as a means to evaluate the method performance for a chemical class of compounds (e.g., PFSAs, PFCAs).

3.19 Working Standard (WS)

A solution of several analytes prepared in the laboratory from SSSs 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. The analyst should wear gloves, a lab coat, and safety glasses to prevent exposure to chemicals that might be present.

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

The analyst must be familiar with the laboratory equipment and potential hazards including, but not limited to, the use of solvents, pressurized gas and solvent lines, high voltage, and vacuum systems. Refer to the appropriate equipment procedure or operator manual for additional information and cautions.

5 Interferences

During sample preparation and analysis, major potential contaminant sources are reagents and glassware. 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 or minimized 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

6.1 Instrumentation

Analytical balance capable of reading to 0.0001g

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

6.2 Supplies and Materials

Sample collection bottles—HDPE (e.g., Nalgene™) wide-mouth bottles with screw cap.
Note: Do not use fluorinated or Teflon® bottles or lined caps.

Coolers or boxes for sample shipment.

15-mL and 50-mL disposable polypropylene centrifuge tubes.

Class A pipettes and volumetric flasks, various.

2 mL HPLC autovials

Disposable pipettes, polypropylene or glass as appropriate

Centrifuge capable of spinning 15-mL and 50-mL polypropylene tubes at 3000 rpm.

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

Water – Milli-Q, HPLC grade, or other suitably appropriate sources

Calcium Acetate - A.C.S. Reagent Grade

Magnesium Acetate - A.C.S. Reagent Grade

Methanol – HPLC grade

Ammonium Acetate – A.C.S. Reagent Grade

7.2 Representative Target Analytes, ISs, and SRSs

PFBA, Heptafluorobutyric Acid, (C_4 Perfluorinated Acid)

PFPeA, Nonafluoropentanoic Acid (C_5 Perfluorinated Acid)

PFHxA, Perfluorohexanoic Acid (C_6 Perfluorinated Acid)

PFHpA, Tridecafluoroheptanoic Acid, (C_7 Perfluorinated Acid)

PFOA, Ammonium perfluorooctanoate, (C_8 Perfluorinated Acid)

PFNA, Heptadecafluorononanoic Acid, (C_9 Perfluorinated Acid)

PFDA, Nonadecafluorodecanoic Acid (C_{10} Perfluorinated Acid)

PFUnA, Perfluoroundecanoic Acid, (C_{11} Perfluorinated Acid)

PFDoA, Perfluorododecanoic Acid, (C_{12} Perfluorinated Acid)

PFTrDA, Perfluorotridecanoic Acid, (C_{13} Perfluorinated Acid)

FBSA, Perfluorobutanesulfonamide

FOSA, Perfluorooctanesulfonylamide

PFBS, Potassium Perfluorobutanesulfonate

PFHS, Perfluorohexanesulfonate

PFOS, Potassium perfluorooctanesulfonate

PFOA [1,2, 3, 4-^{13}C], $^{13}C_4$-isotopically labeled perfluorooctanoic acid (SRS)

PFOS [1,2, 3, 4-^{13}C], $^{13}C_4$-isotopically labeled Perfluorooctanesulfonate (SRS)

PFUnA [1,2-^{13}C], $^{13}C_2$-isotopically labeled Perfluoroundecanoic acid (SRS)

A custom mix of ISs in a methanolic solution containing ([1,2,3,4-$^{13}C_4$]PFBA, [1,2-$^{13}C_2$]PFHxA, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA, [1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA, [1,2-$^{13}C_2$]PFDA, [1,2,3,4,5,6,7-$^{13}C_7$]PFUnA, [1,2-$^{13}C_2$]PFDoA, [1,2,3-$^{13}C_3$]PFHS, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOS, and [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOSA (Wellington Laboratories, Guelph, ON) in combination with added ([1,2,3,4,5-$^{13}C_5$]PFPeA, ([1,2,3,4-$^{13}C_4$]PFHpA, and [$^{18}O_2$]PFBS can be used to prepare a stock IS solution. Alternatively, individual stable isotope ISs can be used to prepare a stock IS mixture.

Other ISs can be applied.

7.3 Reagent Preparation

2 mM Ammonium acetate solution (Analysis)—Weigh 0.3 g of Ammonium acetate and dissolve in 2.0 L of reagent water.

Synthetic Groundwater (containing 25 ppm Ca and Mg) – Weigh 0.61 g of Calcium Acetate and 0.92 g of Magnesium Acetate and dissolve in 6.0 L of reagent water.

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

7.4 Stock Standard Solution (SSS) and Working Standard Solution Preparation

The following standard preparation procedure serves as an example. Weighed amounts and final volumes 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.

100 µg/mL target analyte SSSs—Weigh out 10 mg of analytical standard ***(corrected for percent salt, acid [ETS-4-031] and purity)*** and dilute to 100 mL with methanol or other suitable solvent, in a 100 mL volumetric flask. Transfer to a 125 mL LDPE bottle or other suitable container. Prepare a separate solution for each analyte. Expiration dates and storage conditions of stock solutions should be assigned in accordance with laboratory standard operating procedure. An example of purity and salt correction is given below for PFOS.

$$\text{salt correction factor} = \frac{\text{molecular weight of anion}}{\text{moclecular weight of salt}}$$

$$\text{PFOS } (K^+) \text{salt correction factor} = \frac{499}{538} = 0.9275$$

10 mg $C_8F_{17}SO_3K^+$ with purity 90% = 8.35 mg $C_8F_{17}SO_3^-$ (10 mg*0.90*0.9275=8.35 mg)

10 µg/mL (10,000 ng/mL) mixed working standard—Add 5.0 mL each of the 100 µg/mL SSSs to a 50 mL volumetric flask and bring up to volume with solvent.

1 µg/mL (1,000 ng/mL) mixed working standard—Add 0.5 mL of the 100 µg/mL SSSs to a 50 mL volumetric flask and bring up to volume with solvent.

0.1 µg/mL (100 ng/mL) mixed standard—Add 0.05 mL of the 100 µg/mL SSSs to a 50 mL volumetric flask and bring up to volume with solvent.

Storage Conditions—Store all SSSs and working standards in accordance with laboratory standard operating procedure or in a refrigerator at 4°±2°C for a maximum period of 6 months from the date of preparation.

7.5 Calibration Standards

Calibration can be performed by IS or external calibration. Using the working standards described above, prepare calibration solutions in ASTM Type I water, HPLC water, other suitable water, or a mixture of solvent and water using the information in Table 2 as a guideline. Note: Volumes of water or water/solvent mixtures and working standards may be adjusted to meet the data quality objectives addressed in the general project outline. Calibration levels other than those listed below can be prepared as needed.

For the quantitation of PFOA and PFOS, reference materials of certified mixed linear and branched isomer are preferred. Alternately, reference materials of primarily linear isomers of PFOA and/or PFOS may be used, however, when quantitating with predominantly linear reference standards, additional LCS samples containing both linear and branched isomers of PFOA and PFOS are required[3].

7.5.1 Internal Standard (IS) and Surrogate Recovery Standard (SRS)

For IS calibration, stable isotope internal standards of each target analyte or appropriate surrogate ISs should be spiked at the same level in all calibration standards. Once the calibration standards have been prepared as stated above in Section 7.5, all calibration standards are spiked with a separate internal standard spiking solution. Typically the

[3] A report summarizing an assessment of the use of reference standards containing certified linear and branched isomers of PFOA/PFOS can be found in 3M report E11-0560.

concentration of the internal standard is consistent with the internal standard concentration expected in the samples being prepared, usually 1 ng/mL. The concentration of the internal standard spiking solution is typically 2 µg/mL. A separate zero point or method blank is typically prepared at the same time as the calibration standards, using the same solution used to prepare the standards (ASTM Type I water, HPLC water, other suitable water, or a solvent/water mixture), and is spiked with the internal standard at the same concentration as the calibration curve, typically at 1 ng/mL.

If the samples being analzyed were pre-spiked with SRSs, the calibration curve prepared in Section 7.5 is spiked with a separate SRS spiking solution. Typically, the sample bottles are spiked with a SRS at 0.1 ng/mL. The final calibration curve must consist of at least six calibration points after analysis. The following table provides an example of spike concentrations and volumes used to achieve a multi-point extracted calibration curve with internal standard and surrogate standard.

Table 1 lists recommended stable isotope internal standards for several PFSA and PFCA target compounds. A custom mix of isotopically labeled target analytes in a methanolic solution containing ([1,2,3,4-$^{13}C_4$]PFBA, [1,2-$^{13}C_2$]PFHxA, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA, [1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA, [1,2,3,4,5,6-$^{13}C_6$]PFDA, [1,2,3,4,5,6,7-$^{13}C_7$]PFUnA, [1,2-$^{13}C_2$]PFDoA, [1,2,3-$^{13}C_3$]PFHS, [1,2,3,4,5,6,7,8-$^{13}C_8$]PFOS, and [1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA (Wellington Laboratories, Guelph, ON) in combination with added ([1,2,3,4,5-$^{13}C_5$]PFPeA, ([1,2,3,4-$^{13}C_4$]PFHpA, and [$^{18}O_2$]PFBS can be used to prepare a stock IS solution. Alternative sources of certified stable isotope labeled target analytes are applicable. Alternatively, individual stable isotope ISs can be used to prepare a stock IS mixture. The table below lists the recommended stable isotope ISs and SRSs applied in the method. Other stable isotope ISs and SRSs of target analytes not listed in the table may be used if supported by validation and/or analysis batch QCs meeting method acceptance criteria (e.g., [$^{13}C_2$]-PFOA). The same internal standard should be used for a given analyte throughout the entire project/study. Note: some of the compounds listed below are appropriate to use as surrogate ISs when a stable isotope IS of a target analyte is not available. Generally, surrogate isotopically labeled PFCAs are used for PFCAs, and surrogate isotopically labeled PFSAs are used for PFSAs.

Table 2 provides examples of spike concentrations and volumes used to achieve a multi-point calibration curve with ISs and SRSs.

Table 1. Stable Isotope PFCAs and PFSAs used for ISs and SRSs

Compound Name	*Synonym or Acronym*	*Analytical Purpose*	*Reference Standard Source*
$^{13}C_4$-Perfluorobutanoic acid	[1,2,3,4-$^{13}C_4$]PFBA	IS for PFBA	Wellington Labs (Mix or Individual)
$^{13}C_4$-Perfluoropentanoic acid	[1,2,3,4,5-$^{13}C_5$]PFPeA	IS for PFPeA	Wellington Labs (Mix or Individual)
$^{13}C_2$-Perfluorohexanoic acid	[1,2 -$^{13}C_2$]PFHxA	IS for PFHxA	Wellington Labs (Mix or Individual)
$^{13}C_4$-Perfluoroheptanoic acid	[1,2,3,4-$^{13}C_4$]PFHpA	IS for PFHpA	Wellington Labs (Mix or Individual)
$^{13}C_8$-Perfluorooctanoic acid	[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA	IS for PFOA and [1,2,3,4 $^{13}C_4$]PFOA	Wellington Labs (Mix or Individual)
$^{13}C_9$-Perfluorononanoic acid	[1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA	IS for PFNA	Wellington Labs (Mix or Individual)
$^{13}C_6$-Perfluorodecanoic acid	[1,2,3,4,5,6 -$^{13}C_6$]PFDA	IS for PFDA	Wellington Labs (Mix or Individual)
$^{13}C_7$-Perfluoroundecanoic acid	[1,2,3,4,5,6,7 -$^{13}C_7$]PFUnA	IS for PFUnA	Wellington Labs (Mix or Individual)
$^{13}C_2$-Perfluorododecanoic acid	[1,2 -$^{13}C_2$]PFDoA	IS for PFDoA, *PFTA	Wellington Labs (Mix or Individual)
$^{18}O_2$-Ammonium Perfluorobutane sulfonate	[$^{18}O_2$]PFBS	IS for PFBS	RTI International (Individual)
$^{13}C_3$-Ammonium Perfluorohexane sulfonate	[1,2,3-$^{13}C_3$]PFHS	IS for PFHS	Wellington Labs (Mix or Individual)
$^{13}C_8$-Sodium Perfluorooctane sulfonate	[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOS	IS for PFOS and PFOS[1,2,3,4 $^{13}C_4$].	Wellington Labs (Mix or Individual)
$^{13}C_8$-Perfluorooctanesulfonamide	[1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA	IS for FOSA	Wellington Labs (mix) RTI International (Individual)
$^{13}C_4$-Perfluorooctanoic acid	[1,2,3,4-$^{13}C_4$]PFOA	SRS for all PFCAs: C4-C8	Wellington
$^{13}C_2$-Perfluoroundecanoic acid	[1,2 -$^{13}C_2$]PFUnA	SRS for all PFCAs C9-C13	Wellington
$^{13}C_8$-Perfluorooctane sulfonate	[1,2,3,4-$^{13}C_4$]PFOS	SRS for all PFSAs: C4, C6, and C8	Wellington

Table 2. Example Preparation of Calibration Curve with ISs and SRSs

Sample Description	*Concentration of WS, µg/mL*	*Volume of WS, µL*	*Volume of IS (2 µg/mL), µL*	*Concentration of Surrogate, µg/mL*	*Volume of Surrogate, µL*	*Volume of ASTM Type I Water, or other suitable solvent (1), mL*
0.025 ng/mL curve point	0.10	25	50	0.20	12.5	100
0.030 ng/mL curve point	0.10	30	50	0.20	15	100
0.04 ng/mL curve point	0.10	40	50	0.20	20	100
0.05 ng/mL curve point	0.10	50	50	0.20	25	100
0.1 ng/mL curve point	0.10	100	50	0.20	50	100
0.25 ng/mL curve point	0.10	250	50	0.20	125	100
0.5 ng/mL curve point	1.0	50	50	0.20	250	100
1 ng/mL curve point	1.0	100	50	0.20	500	100
2.5 ng/mL curve point	10.0	25	50	10.0	25	100
5.0 ng/mL curve point	10.0	50	50	10.0	50	100
10.0 ng/mL curve point	10.0	100	50	10.0	100	100
25.0 ng/mL curve point	10.0	250	50	10.0	NA	100
50.0 ng/mL curve point	10.0	500	50	10.0	NA	100
75.0 ng/mL curve point	10.0	750	50	10.0	NA	100
100 ng/mL curve point	10.0	1000	50	10.0	NA	100

N/A - Not Applicable
(1) Samples requiring analysis for PFUnA, PFDoA, PFTrDA, and FOSA should be analyzed against a calibration curve prepared in 1:1 synthetic groundwater:MeOH.

8 Sample Collection and Bottle Preparation

Sample collection bottles are prepared by 3M Environmental Laboratory (or subcontract supplier) personnel for shipment at ambient temperature to the collection site. Typically, four separate collection bottles are associated with a single collection site: sample, field duplicate sample, low field matrix spike, and high field matrix spike. Alternatively, the sample and field duplicate sample may contain SRSs in lieu of additional target analyte low field matrix spike and target analyte high field matrix spike samples. Depending on the scope of the project, additional replicates of the field sample and field matrix spikes may be added. Also, it is not uncommon for additional mid-level field matrix spikes to be collected if the expected sample concentrations are truly unknown or could span a large concentration range.

High-density polyethylene (HDPE) wide-mouth Nalgene bottles are used for the sample collection containers. (Volumes of the bottles may vary depending on how much sample is required to meet data quality objectives.) Sample collection volumes are project specific and based on data quality objectives. The Nalgene bottles do not require any pretreatment prior to use. Typically, placement of a sample bottle volumetric "fill to here" line is done by using a sample bottle marker template. Alternatively, bottles may be weighed prior to bottle preparation and weighed again after samples have been collected.

All bottles should be clearly labeled to indicate its intended use as a sample, field sample duplicate, low field matrix spike, high field matrix spike, sample/SRS field matrix spike, field duplicate sample/SRS field matrix spike, trip blank, or trip blank matrix spike. If each location has different designated spike levels, the label should also clearly indicate the sample location designation. Generally, a set of bottles for a given collection site are prepared then grouped together in plastic bags for organizational purposes. For each sample collection event, at least one set of trip blank and trip blank matrix spikes are prepared.

Bottle preparation should be documented in a Note to File or on a sample preparation worksheet and should include the following information: date prepared, total number of bottles prepared, number of sample sites, the standard identification numbers and spike volumes used to prepare spiked bottles, the "fill to here" volume, and any other pertinent information needed for reconstructibility of the data. The Note to File will be included in the final data package for the project.

Samples are collected in the field and shipped to the laboratory at ambient temperature.

8.1 Field Matrix Spike Sample (FMS)

Field matrix spike samples are a requirement of the method. A FMS sample is defined as a QC sample to which known quantities of appropriate target analytes are added to the sample bottle in the field or in the laboratory before the bottles are sent to the field. The sample and field duplicate sample may contain appropriate SRSs in lieu of target analyte FMS samples. Sample quantities are determined volumetrically or gravimetrically. A known, specific volume or weight of sample is added to the sample container without rinsing. Volumetric sample measurements may be acquired by a laboratory applied "fill to this level" line on the outside of the sample container. Target analyte FMS samples should be spiked at approximately 0.5-10 times the expected analyte concentration in the sample. If the expected range of analyte concentrations is unknown, multiple spikes at varying levels may be prepared to increase the likelihood that a spike at an appropriate level is made. Typically a low and a high target analyte spike are prepared for each sampling location. In those instances where SRSs are to be used in lieu of target analyte FMS samples, the sample and field duplicate sample are spiked at approximately 2-5 times the target LOQ. The FMS is analyzed to ascertain if matrix effects or sample holding time contributes bias to the analytical results. For the sample bottles designated for matrix spikes, an appropriate volume of matrix spiking solution is added to the empty bottle prior to sampling. The volume of spike solution added should produce the desired final concentration of target analytes once the bottle is filled with sample to the "fill to here line". The matrix spiking solution(s) should be prepared in a suitable solvent and contain all of the appropriate target analytes, ISs, and SRSs. The target analyte matrix spiking solution is often the same as the working standards used to create the calibration standards. An example of a bottle spike is given below.

"Fill to here" volume = 200 mL (A 250 mL Nalgene bottle is used)

Desired Field Spike Concentration = 0.25 ng/mL

500 µL of a 0.1 µg/mL spiking solution (containing the target analytes) is added to the bottle and the bottle cap promptly sealed.

8.2 Internal Standard and Surrogate Recovery Standard

If analysis of a surrogate recovery standard (SRS) is included in the project objectives, an appropriate volume of a surrogate standard solution is added to all the bottles prior to sampling and SPE. Typically sample bottles are spiked with surrogate recovery standards at a final desired spike concentration of 0.1 ng/mL.

If quantitation by internal standard (IS) is included in the project objective, an appropriate volume of internal standard solution is added to all the bottles prior to sampling and SPE. Typically sample bottles are spiked with internal standard at a final desired spike concentration of 1 ng/mL.

For the trip blank, the SRS spike and IS spike is added to the bottle and then ASTM Type I water (HPLC grade reagent water or other suitable water may used) is added to the "fill to here" line. The bottle is capped and sealing tape may be placed around the outer edge of the cap. Trip blank matrix spikes are prepared by adding the appropriate volume of target analyte spiking solution, IS, and SRS spiking solutions and filling the bottle to the desired volume with the appropriate water and capping and sealing the cap.

9 Quality Control and Data Quality Objectives

9.1 Data Quality Objectives

This method and required quality control samples is designed to generate data accurate to ±30% with a targeted LOQ of 0.025 ng/mL. Any deviations from the quality control measures spelled out below will be documented in the raw data and footnoted in the final report.

9.2 Method/Procedural Blanks

The method/procedural blank is zero point calibration standard (which includes ISs) analyzed in a regular basis with each analysis batch. At a minimum, method blanks are analyzed prior to instrument calibration, prior to the analysis of CCV samples, after every 10 sample injections, and at the end of the analytical run.

The mean area count or area ratios when using internal standard calibration, for each analyte in the method blanks must be less than 50% of the area count counts or area ratios when using internal standard calibration, of the LOQ standard. The standard deviation of the area counts, or area ratios when using internal standard calibration, of these method blanks should be calculated. A specific %RSD acceptance criteria is not specified but is assessed on an analytical batch basis. If the mean area counts or area ratios when using internal standard calibration, of the method blanks exceed 50% of the LOQ standard, then the LOQ must be raised to the first standard level in the curve that meets criteria. Method blanks may be eliminated if technical justification can be provided (e.g. the procedural blank was analyzed after an unexpectedly high level sample). If any procedural blanks are removed from the LOQ determination, document in the raw data and report as appropriate. Laboratory Sample Replicates / Field Duplicate Sample

Typically, samples are collected in duplicates in the field. The relative percent difference (RPD) of duplicate samples should be ≤20% for the precision of sample preparation and analysis to be considered in control. Replicate samples not meeting the ≤20% RPD criteria are flagged and reported as outside of QC acceptance criteria.

9.3 Laboratory Matrix Spikes (LMSs)

LMSs may be performed in lieu of FMSs if FMSs have previously been performed for the sample matrix. Additionally, LMSs may be performed in lieu of FMSs for a sample matrix if the FMS levels were not appropriate for determining spike recoveries relative to endogenous levels of target analytes and appropriate SRSs. Generally, each sample location represents a different sample and sample matrix. LMSs are prepared for each sample and analyzed to determine the matrix effect on spike recovery efficiency of each target analyte and appropriate SRSs. LMSs should be prepared at a minimum of one level and in duplicate. LMS concentrations should be prepared at approximately 0.5-10 times the endogenous concentration or approximately 4-10 times the LOQ concentration of each target analyte.

Lab matrix spike recoveries should fall within ± 30% of expected values. Sample data with LMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria. Data with LMS recovery outside of ±50% of the expected value are reported as NR, where NR is defined as "Not Reportable" data outside of QC acceptance criteria.

9.4 Lab Control Sample

Lab control spikes are prepared for each analysis batch to determine method accuracy and precision. LCSs should be prepared at three levels in triplicate for each target analyte and at a minimum of two levels in triplicate for appropriate SRSs. Low lab control spikes should be prepared at a concentration in the range of approximately four to ten times higher than the targeted lower LOQ, the mid lab control spikes should be prepared at a concentration near the mid-point of the calibration curve and the high lab control spikes at approximately 80% of the upper LOQ. For each target analyte and SRSs, the percent relative standard deviation (method precision) for each control spike level must be less than or equal to 20% and the average recovery (method accuracy) for each control spike level must be 80-120%. Sample data for target analytes outside of the laboratory control spike acceptance criteria will be handled as follows:

If the average recovery of a spiking level falls outside method acceptance, but at least 67% (6 out of 9) of LCS samples are within 20% of their respective nominal value (33% of the QC samples, not all replicates at the same concentration, may be outside 20% of nominal value), the average recovery will be flagged as outside method acceptance criteria. All LCS samples will be control charted as per ETS-4-026. If the average recovery of one of the spiking levels exceeded the analytical method uncertainty as determined by ETS-12-012, that analytical batch uncertainty will be expanded for that particular study.

If more than 67% of the LCS samples fail to meet method acceptance criteria, the data will not be reported.

Calibration standards consisting of mixed branched and linear isomer PFOS/PFOA are preferred. However, for PFOS/PFOA target analytes, if the calibration standards are comprised of predominantly linear isomers only, at least one level of triplicate LCSs should be prepared using PFOS/PFOA which contains a mix of linear and branched isomers. These LCSs will be used to demonstrate quantitative equivalency (or quantitative bias) of the isomeric mix when using a predominantly linear standard for calibration. The mixed linear and branched isomer PFOS/PFOA LCSs recoveries should fall within ± 30% of expected values. Alternatively, in lieu of mixed branched and linear isomer PFOS/PFOA LCSs, mixed branched and linear isomer PFOS/PFOA TBMSs may be applied to demonstrate method accuracy and precision.

9.5 Field Matrix Spikes (FMSs) / Surrogate Recovery Standards (SRSs)

FMSs are prepared for each sampling location and analyzed to determine the matrix effect and sample holding time on the spike recovery of each target analyte and/or appropriate SRS. Generally, each sample location represents a different sample and sample matrix.

FMSs are QC samples to which known quantities of appropriate target analytes are added to the sample bottle in the laboratory before the bottles are sent to the field. Typically a low and a high target analyte FMS are prepared for each sampling location. The sample and field duplicate sample may contain appropriate SRSs in lieu of target analyte low field matrix spike and target analyte high field matrix spike samples.

Field matrix spike method acceptance criteria are recoveries within ±30% of the expected value. If FMS recovery (target analyte or SRS spike) is outside of ±30% of the expected value or could not be assessed because the FMS (target analyte) was spiked at an inappropriate level, the sample result is reported as follows:

1.) If target analyte FMS recovery could not be assessed because the FMS's were at an inappropriate level, then Laboratory Matrix Spikes (LMS) may be substituted. If LMS recoveries are within ±30% the data are reportable and flagged to indicate that the FMS spikes levels were inappropriate.

2.) If multiple target analyte FMS's were prepared on a sample and the closest FMS level to the reported sample meets the ±30% acceptance criteria but additional FMS's are outside the ±30% acceptance range, the data are reportable and flagged to indicate that while there were failing FMS's, the uncertainty will not be expanded since the most appropriate spike level passed.

3.) If the target analyte FMS recoveries are outside of the ±30% acceptance range but at least 30 acceptable historical reportable FMS sample results are available, the data may be reported but flagged with an expanded uncertainty and as not meeting FMS criteria.

4.) Sample data with FMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria with an expanded uncertainty.

5.) If FMS recovery is outside of ±50%, the sample result is reported as NR, where NR is defined as "Not Reportable" due to noncompliant QC results.

The targeted fortification levels should be at least 50% of the endogenous level and less than 10 times the endogenous level to be used without justification to determine the statement of accuracy for analytical results.

Note: It is possible for bottles utilized for Field Matrix Spike samples to be under-filled or over-filled during sample collection. Since this scenario will effect the actual concentration of the FMS sample (surrogate and internal standard concentrations will also be effected, if used), it is important that any obvious under-filling or over-filling of sample bottles be documented in the data package and taken into account in the FMS, ISs, or SRSs recovery calculations. Samples over-filled or under-filled by more than 10% will be require recalculation of the FMS, ISs, and SRS true values.

The average of the sample and the field duplicate should be used to calculate the recovery.

10 Procedures

10.1 Water Sample Preparation

This method is applicable to water samples. Samples containing heavy particulate may not be suitable for analysis by this method. Samples containing suspended particulate should be centrifuge prior to removing a sample aliquot, or filtered.

- Thoroughly mix sample before removing an aliquot and placing in a labeled autovial.
- Dilute sample, if necessary, with ASTM Type I water, HPLC water, other suitable water, or solvent (methanol).
- Lab control spikes are prepared for each analysis batch to determine method accuracy and precision. LCSs should be prepared at three levels in triplicate for each target analyte and at a minimum of two levels in triplicate for appropriate SRSs. Low lab control spikes should be prepared at a concentration in the range of approximately four to ten times higher than the targeted lower LOQ, the mid lab control spikes should be prepared at a concentration near the mid-point of the calibration curve and the high lab control spikes at approximately 80% of the upper LOQ. For IS quantitation, stable isotope internal standards of each target analyte or appropriate surrogate ISs should be spiked at the same level as the samples being analyzed, in all LCSs.
- If LCSs are being prepared using synthetic groundwater, allow the LCSs samples to equilibrate for a minimum of 4 hours before aliquoting for analysis or diluting with solvent (methanol).

11 Sample Analysis - LC/MS/MS

11.1 Instrument Setup

Note: In this example, an Applied Biosystems Sciex API 4000 (API 5000 or API 5500) Tandem Mass Spectrometer (LC/MS/MS) is used. Other brands/models of LC/MS/MS instruments as well as single quadrupole mass spectrometers (LC/MS) may be used as long as the method acceptance 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: Applied Biosystems API 4000, API 5000, or API 5500

Ion Source: Turbo Ion Spray (ABS)

Mode: Electrospray Negative

Scan Type: MRM (Multiple Reaction Monitoring)

Computer: Dell DHM

Software: Windows 2000 or Windows XP, Analyst 1.4.2 or higher versions

HPLC: Agilent Series 1100,1200, or 1290

Agilent Quaternary Pump

Agilent Vacuum Degasser

Agilent Autosampler

Agilent Column Oven

Note: One or more C18 HPLC analytical columns (2.1 mm x 100 mm, 5µm or 2.1 mm x 50 mm, 5µm) may be attached on-line after the purge valve and before the sample injection port to retard and separate any residue contaminants that may be in the mobile phase and/or HPLC system.

HPLC Column: Betasil C18, 4.6mm x 100mm, 5µm (ThermoElectron Corporation)

Column Temperature: 35°C

Injection Volume: 5µL

Mobile Phase (A): 2mM Ammonium Acetate in ASTM Type I water (See 7.3)

Mobile Phase (B): Methanol

Table 3. Liquid Chromatography Gradient Program.

Step Number	*Total Time (min)*	*Flow Rate (µL/min)*	*Percent A (2 mM ammonium acetate)*	*Percent B (Methanol)*
0	0	750	97.0	3.0
1	2.0	750	97.0	3.0
2	14.5	750	5.0	95.0
3	15.5	750	5.0	95.0
4	16.5	750	97.0	3.0
5	20.0	750	97.0	3.0

Note: Other HPLC gradients may be used as long as the method criteria and project data quality objectives 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.

Table 4 Suggested MRM Transitions for Target Analytes, Surrogates, and Internal Standards

Analyte	*Analyte Description*	*Mass Transition Q1 (amu)*	*Mass Transition Q3 (amu)*
PFBA (C4 Acid)	Target	213	169
PFPeA (C5 Acid)	Target	263	219
PFHxA (C6 Acid)	Target	313	269, 119
PFHpA (C7 Acid)	Target	363	319, 169
PFOA (C8 Acid)	Target	413	369, 219, 169
PFNA (C9 Acid)	Target	463	419, 169, 219
PFDA (C10 Acid)	Target	513	469, 269, 219
PFUnA (C11 Acid)	Target	563	519, 269, 219
PFDoA (C12 Acid)	Target	613	569, 169, 319
PFTA (C13 Acid)	Target	663	619, 369, 319
FBSA (C4 Sulfonamide)	Target	298	78
FOSA (C8 Sulfonamide)	Target	498	78
PFBS (C4 Sulfonate)	Target	299	99, 80
PFHS (C6 Sulfonate)	Target	399	99, 80
PFOS (C8 Sulfonate)	Target	499	80, 99, 130
[1,2,3,4 -$^{13}C_4$]PFBA	IS for PFBA	217	172
[1,2,3,4,5 -$^{13}C_5$]PFPeA	IS for PFPeA	268	223
[1,2 -$^{13}C_2$]PFHxA	IS for PFHxA	315	270
[1,2,3,4- $^{13}C_4$]PFHpA	IS for PFHpA	367	322
[1,2,3,4,5,6,7,8-$^{13}C_8$]PFOA	IS for PFOA	421	376
[1,2,3,4,5,6,7,8,9-$^{13}C_9$]PFNA	IS for PFNA	472	427
[1,2,3,4,5,6 -$^{13}C_6$]PFDA	IS for PFDA	519	474
[1,2,3,4,5,6,7 -$^{13}C_7$]PFUnA	IS for PFUnA	570	525
[1,2 -$^{13}C_2$]PFDoA	IS for PFDoA and PFTA	615	570
[$^{18}O_2$]PFBS	IS for PFBS	303	84
[1,2,3-$^{13}C_3$]PFHS	IS for PFHS	402	80
[1,2,3,4- $^{13}C_4$]PFOS	IS for PFOS	503	80
[1,2,3,4,5,6,7,8-$^{13}C_8$]FOSA	IS for FOSA	507	80
[1,2,3,4-$^{13}C_4$]PFOA	Surrogate (C4-C8 Acids)	417	372
[1,2,3,4- $^{13}C_4$]PFOS	Surrogate(Sulfonates, FOSA)	503	80
[1,2 -$^{13}C_2$]PFUnA	Surrogate (C9-C13 Acids)	565	520

Multiple transitions for monitoring the analytes is an option. The use of one daughter ion is acceptable if data sensitivity and selectivity is achieved and provided that retention time criteria are met to assure adequate specificity. While the daughter ions may be chosen at the discretion of the analyst, mass transition 99 is suggested for PFOS. Quantitation may be performed using the total ion chromatogram (TIC, or summed MRMs) for a given analyte. For example, the PFOA TIC would sum all three of the monitored transitions. 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 and the gradient, column, guard column(s) used 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.

11.2 Calibration Curve

Quantitation is by internal standard or external standard calibration. Calibration standards may be prepared in ASTM Type I, HPLC water, other suitable water, or a solvent/water mixture. If internal standard calibration does not meet calibration acceptance criteria, external calibration can be applied. See Table 1 for

recommended application of available internal standards. Quantitation of PFOA and PFOS is by summed analyte-specific mass transitions.

Analyze the standard curve prior to each set of samples. If internal standards were added to the calibration standards area ratios are used to generate the calibration curve. The standard curve may be plotted using a linear regression ($y = mx + b$), weighted 1/x or unweighted, or by quadratic fit ($y = ax^2 + bx + c$), weighted 1/x or unweighted, using suitable software. 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.

High and/or low points may be excluded from the calibration curves to provide a better fit over the 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 (or area ratio if quantitating by IS) are not at least twice that of the average area counts (or area ratio if quantitating by IS) of method and/or solvent blanks. The coefficient of determination (r^2) value for the calibration curve must be greater than or equal to 0.990 (or a correlation coefficient (r) of 0.995). Each point in the curve must be within ±25% of the theoretical concentration with the exception of the LLOQ, which may be within ±30%. 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.

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

11.3 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. Samples must be bracketed by passing CCVs or the calibration curve and a passing CCV to be reportable.

11.4 System Suitability

A minimum of three system suitability samples should be injected at the beginning of each analytical run, prior to the analysis of the calibration curve. Typically these samples are at a concentration near the mid-level of the calibration curve and are repeated injections from one autosampler vial. It is suggested that the system suitability injections have area counts or area ratios when using internal standard calibration, with a target RSD of ≤5% and a target retention time RSD of ≤2%. There is no defined acceptability limit on these results as the %RSD value is dependent on the number of MRM transitions being monitored in the LC/MS/MS run or time period. Ultimately, any effects on these parameters for the System Suitability samples will also be evident on all standards and QC samples analyzed as part of the analysis batch. Any effect of system suitability is incorporated within QC acceptance criteria.[4]

11.5 Sample Analysis and QCs

For each analysis batch, the instrument analysis run sequence should include an initial calibration curve, samples, FDSs, interspersed blanks, interspersed CCVs, appropriate QCs (i.e., LCSs, LMSs, FMSs, TBMSs, and TBs), and a final CCV or calibration curve bracketing samples and appropriate QCs

Inject the same volume (between 5 - 100µL) of each standard, analytical sample and blank into the instrument (unless an on-instrument sample dilution is desired).

Samples containing analytes that are quantitated above the concentration of the highest standard in the curve should be further diluted and reanalyzed.

[4] 3M Environmental Laboratory study E08-0096 evaluated the effect on these results as a function of the number of MRMs being monitored.

12 Data Analysis and Calculations

The chromatography analysis software will typically calculate the amount of target analyte in the sample extracts using the established calibration curve.

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

$$\text{LCS\% recovery} = \frac{\text{LCS Concentration } (\frac{ng}{mL})}{\text{Spike Concentration } (\frac{ng}{mL})} * 100\%$$

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

$$\text{LMS \% recovery} = \frac{\text{LMS Concentration } (\frac{ng}{mL}) - \text{Concentration of Sample } (\frac{ng}{mL})}{\text{Spike Concentration } (\frac{ng}{mL})} * 100\%$$

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

$$\text{Recovery} = \frac{\text{Total analyte found (ng/mL) - Average analyte found in sample (ng/mL)}}{\text{Analyte added (ng/mL)}} \times 100$$

13 Analysis Batch Method Performance Criteria

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 the final report if the Technical Manager (non-GLP study) or Study Director (GLP study) chooses to report 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 appropriate. 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 – Analysis Batch

A minimum of three system suitability samples should be injected at the beginning of each analytical run. These samples are run prior to the calibration curve. It is suggested that the system suitability injections have area counts with a target RSD of ≤5% and a target retention time RSD of ≤2%. There is no defined acceptability limit on these results as the %RSDs are dependent on the number of MRM transitions being monitored in the LC/MS/MS run or time period. Any effect of system suitability is incorporated in the QC acceptance criteria.

13.2 Calibration and Limit of Quantitation (LOQ) – Analysis Batch

Calibration Curve: The coefficient of determination (r^2) value for the calibration curve must be greater than or equal to 0.990 corresponding to a correlation coefficient (r) = 0.995. Each point in the curve must be within ±25% of the theoretical concentration with the exception of the LLOQ, which may be within ±30%.

CCV Performance: The calibration standards that are interspersed throughout the analytical sequence are evaluated as continuing calibration verifications in addition to being part of the calibration curve. The accuracy

of each curve point must be within 25% of the theoretical value (within 30% for lowest curve point). Samples that are bracketed by CCVs not meeting these criteria must be reanalyzed.

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 average area counts for all prepared procedural blank(s). By definition, the measured value of the LLOQ must be within 30% of the theoretical value.

Demonstration of Specificity: Specificity is demonstrated by chromatographic retention time (within 4% of standard) and the mass spectral response of unique ions.

13.3 Blanks – Method/Procedural Blanks and Trip

Method/Procedural Blanks: Multiple procedural blanks should be interspersed throughout the analysis batch and the analytical sequence. At a minimum, method blanks are analyzed prior to instrument calibration, prior to the analysis of CCV samples, after every 10 sample injections, and at the end of the analytical run.

The mean area counts (or area ratios when using IS calibration) for each analyte must be less than 50% of the area count of the LOQ standard. If the area counts of the procedural blanks exceed 50% of the LOQ standard, then the LOQ must be raised to the first standard level that meets criteria.

Trip Blank: A trip blank of ASTM Type I water (or lab equivalent) is prepared in a sample container in the laboratory and treated as a sample, including exposure to shipping, sampling site conditions, storage, preservation and all analytical procedures. The trip blanks results for each analyte are included with the reported sample results.

13.4 Data Accuracy and Precision – Analysis Batch

Lab Control Spikes: The average recovery at each LCS level for each target analyte and appropriate SRS should be within 80-120% and the percent relative standard deviation of the recoveries must be less than or equal to 20%. If the average recovery of a spiking level falls outside method acceptance, but at least 67% (6 out of 9) of LCS samples are within 20% of their respective nominal value (33% of the QC samples, not all replicates at the same concentration, may be outside 20% of nominal value), the average recovery will be flagged as outside method acceptance criteria. All LCS samples will be control charted as per ETS-12-012. If the average recovery of one of the spiking levels exceeded the analytical method uncertainty as determined by ETS-12-012, that analytical batch uncertainty will be expanded for that particular study. The average recovery at each LCS level for mixed branched/linear isomer PFOA and PFOS should be within 70-130% and the percent relative standard deviation of the recoveries must be less than or equal to 20%.

Field Duplicates: The relative percent difference (RPD) of duplicate samples should be less than 20% for the precision of sample preparation and analysis to be considered in control. Replicate samples not meeting the 20% RPD criteria are flagged and reported as outside of QC acceptance criteria.

Field Matrix Spikes: FMS acceptance criteria are recoveries within ±30% of the expected value for each target analyte and appropriate SRS. Sample data with FMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria. Data with FMS recovery outside of ±50% of the expected value are reported as NR, where NR is defined as "Not Reportable" data outside of QC acceptance criteria. If FMS recovery could not be assessed because FMSs were at an inappropriate level, then Laboratory Matrix Spikes (LMSs) may be substituted. If LMS recoveries are within ±30% for each target analyte and SRSs the data are reportable but flagged as not meeting the FMS method acceptance criteria.

13.5 Analytical Method Uncertainty

Analytical method uncertainty for each target analyte and SRS is determined with control charted historical analysis batch LCS data for the method and reported with each analysis batch.[5] Uncertainty determinations

[5] Method uncertainty based on INTERNATIONAL ANS/ISO/IED STANDARD 17025 reference (GUM, Guide to the Expression of Uncertainty in Measurement). Method application demonstrated in ETS-12-012, citing references: a.) EURACHEM/CITAC Guide, "Quantifying Uncertainty in Analytical Measurement," Second Edition; Editors: S.L.R. Ellison, M. Rosslein, and A. Williams. b.)Georgian, Thomas, "Estimation of Laboratory Analytical Uncertainty Using Laboratory Control Samples," Environmental Testing &

are based on INTERNATIONAL ANS/ISO/IED STANDARD 17025 reference (GUM, Guide to the Expression of Uncertainty in Measurement) and described in ETS-12-012. At least thirty data points are required for determining analytical method uncertainty. The method uncertainty is defined as 2x the standard deviation of the percent recoveries of the pooled lab control spikes. While all LCS data points are control charted, only the most recent fifty data points are used for determining the method uncertainty.

When less than thirty LCS data points have been generated for a given analyte, the analysis batch LCSs are used to determine the data uncertainty. If FMSs meet the ±30% recovery criteria at a level appropriate to the endogenous level, and the LCS meet the ±20% recovery criteria, then the uncertainty of the data is determined as within 100±20%.

Analysis batch sample data with FMS recovery outside of ±30% but within ±50% of the expected value are flagged and reported as outside of QC acceptance criteria with expanded uncertainties. Data with FMS recovery outside of ±50% of the expected value are reported as NR, where NR is defined as "Not Reportable" data outside of QC acceptance criteria. If FMS recovery could not be assessed because FMSs were at an inappropriate level, then Laboratory Matrix Spikes (LMSs) may be substituted. If LMS recoveries are within ±30% for each target analyte and appropriate SRSs the data are reportable but flagged as not meeting the FMS method acceptance criteria with uncertainties of ±30%. If FMS do not meet the ±30% recovery criteria, and historical FMS data does not exist, the analytical uncertainty is evaluated on a sample-by-sample basis, the data may be reported with expanded uncertainty and are flagged.

13.6 Quantitation of PFOA/PFOS – Analysis Batch

Calibration standards consisting of mixed branched and linear isomer PFOS/PFOA are preferred. Quantitation is performed by integrating the linear and branched isomers together. Alternately, the linear and branched isomers can be integrated separately, applying the appropriate true value to each calibration curve point for each isomer. The LCS and samples are then quantitated by integrating the linear and branched isomers separately (requires separate analytical results files) and quantitating the resulting peak against the linear or branched calibration curve. The results from both integrations are then summed to produce the final result. Integrating the linear and branched isomers separately may be helpful for those samples where the linear/branched ratios do not closely match those of the reference standards.

However, for PFOS/PFOA target analytes, if the calibration standards are comprised of predominantly linear isomers only the method requires the addition of LCSs of mixed branched/linear isomer PFOS/PFOA. The purpose of including these LCSs is to demonstrate quantitative equivalency (or quantitative bias) of the isomeric mix when using a predominantly linear PFOS or PFOA standard for calibration. Alternatively, in lieu of mixed branched and linear isomer PFOS/PFOA LCSs, mixed branched and linear isomer PFOS/PFOA TBMSs may be applied to demonstrate method accuracy and precision.

An alternate method of quantitation can be performed whereby only the linear isomer of PFOS/PFOA is integrated and used for generating the calibration curve. The LCS and samples are then quantitated by integrating the linear and branched isomers separately (requires separate analytical results files) and quantitating the resulting peak against the linear calibration curve. The results from both integrations are then summed to produce the final result. Integrating the linear and branched isomers separately reduces the on-column concentration for those samples that contain both linear and branched isomers of PFOA/PFOS. This ensures that the concentration detected is within the a range of the calibration curve that is comparable regardless of whether the calibration curve was generated using predominantly linear isomers of PFOS/PFOA or linear plus branched isomers of PFOS/PFOA.

14 Pollution Prevention and Waste Management

Waste generated when performing this method will be disposed of appropriately. The original samples will be archived at the 3M Environmental Laboratory in accordance with internal procedures.

Analysis, November/December 2000. c.)Taylor, B.N. and CE. Kuyatt, NIST Technical Note 1297, 1994 Edition: "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results."d.)Adams, T.M., "A2LA Guide for the Estimation of Measurement Uncertainty in Testing", July 2002.

15 Records

Each data package generated for a study must include all supporting information for reconstruction of the data. Information for the data package must include, but is not limited to the following items: study or project number, sample and standard prep sheets/records, instrument run log (instrument batch records, instrument acquisition method, summary pages), instrument results files, chromatograms, calibration curves, and data calculations.

16 Affected Documents

None.

17 Revisions

Revision Number	Summary of Changes
1	*Section 1. Included the use of internal standard calibration by this method.* *Section 2. Included the use of internal standard calibration by this method. Included the use of a solvent/water mixture when analyzing for PFUnA, PFDoA, PFTrDA, and FOSA.* *Section 3. Added definitions for internal standard, surrogate internal standard, and surrogate recovery standard.* *Section 6.Removed the details regarding the instrument parameters to section 10 of the method.* *Section 7. Updated reference standards to include internal standards and surrogates. Changed concentration levels for working standards and included the use of internal standards and surrogates.* *Section 8. Inserted a new section on sample bottle preparation.* *Section 9 Quality Control. This section was previously section 10 in ETS-8-044.0. Updated QC criteria to be consistent with method ETS-8-154.4.* *Section 10 Procedures. This section was previously section 8 (Sample Handling) in ETS-8-044.0. Added detail regarding the preparation of LCSs. Included the use of methanol as a dilution solvent.* *Section 11 Sample Analysis. This section was previously section 10 in ETS-8-044.0. Included the details regarding the instrument parameters.* *Section 12 Data Analysis and Calculations. This section was previously section 11 in ETS-8-044.0. Removed the equation for calculating the analytes concentration, indicating that this is done by the instrument software.* *Section 13 Method Performance. This section was previously section 12 in ETS-8-044.0. Updated QC criteria to be consistent with ETS-8-154.4. Added information on the determination of analytical method uncertainty and quantitation of PFOA/PFOS.* *Section 14 Pollution Prevention. This section was previously section 13 in ETS-8-044.0.* *Section 15 Records. This section was previously section 14 in ETS-8-044.0.* *Section 16 Affected Documents. This section was previously section 15 in ETS-8-044.0.* *Section 17 Revisions. This section was previously section 16 in ETS-8-044.0.*

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