# Sampling Plan

*February 2016*

## Perfluorinated Compound Sampling Plan

***Former ChemFab***
**North Bennington, VT**
(SMS Site # 2016-4630)

*Prepared For:*

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# 1.0 INTRODUCTION

Weston & Sampson Engineers, Inc., (Weston & Sampson) was retained by the Vermont Department of Environmental Conservation (VTDEC) to prepare this work plan for sampling of existing water supply wells in the vicinity of the Former ChemFab facility (Site) at 1030 Water Street, North Bennington, Vermont (SMS #2016-4630). The Site is generally located on **Figure 1**. **Figure 2** shows the area of interest for this sampling effort.

The Site operated as a manufacturing facility which utilized perfluorinated compounds (PFCs) for a number of years into the early 2000's. PFCs include 2 major subcategories of compounds, perfluorooctane sulfonates (PFOS) and perfluorooctanoic acids (PFOA). PFCs are used as "surface active agents" in high temperature applications. Products which utilized PFCs include waterproofing on garments, non-stick cooking surfaces, wiring, cleaning products and fire fighting foams. PFOS has not been manufactured in the United States since 2002. However, PFOS is still present in imported good and PFOAs remain in use.

Potential releases of PFCs through atmospheric deposition and poor handling at the ChemFab facility may have resulted in environmental impacts surrounding the facility. The immediate concern is the potential for bedrock aquifer contamination which could result in exposure of nearby residents via their drilled water supply wells. It is not currently known if releases occurred at the facility. However, recently collected data from a similar former ChemFab facility in nearby Hoosick Falls, New York indicates that the potential for adverse environmental impact exists.

To assess the potential for PFC presence in the bedrock aquifer the VTDEC proposes collecting water quality samples from 4 nearby residential water supply wells. The 2 closest public water supply wells will also be sampled. The water samples will be submitted to an EPA approved laboratory for analysis of 19 PFCs. The locations of the nearby residential water supply wells proposed for sampling are shown on **Figure 3**. The proposed public water supply wells to be sampled are shown of **Figure 4**.

This sampling plan has been designed to collect representative data necessary to determine if the Site has caused PFC concentrations in drinking water above applicable standards. The work plan has been developed in a manner to allow its execution by any properly trained personnel. The work required will be performed by Weston & Sampson with particular attention paid to minimizing the potential for "false positive" results. Due to PFCs extreme persistence in the environment, they are nearly ubiquitous and specific sampling and analytical protocols must be followed to assure accurate results.

# 2.0 DATA QUALITY OBJECTIVES

## 2.1 PFC Data Quality Objectives

Currently neither the EPA or Vermont Department of Health have regulatory drinking water quality standards for PFCs. The VTDOH was consulted by the VTDEC Project Manager, Richard Spiese to determine a guidance value for drinking water. Lori Cragin, MS, PhD of VTDOH responded via e-mail on February 9, 2016 as shown below:

> "*…The Health Department's proposed drinking water guidance value for PFOA is 20 ppt (ng/L). This value is consistent with Health's Drinking Water Guidance (Guidance), and is based on the most sensitive receptor, a child 0-1 year old. The proposed guidance value is based on the non-cancer endpoint. We looked at the cancer endpoint and determined that derivation of the proposed value based on the noncancer endpoint is most protective. Consistent with the Guidance, the proposed value is based on ingestion only, with a Relative Source Contribution of 20% incorporated to account for potential exposure to PFOA from other sources. EPA's provisional health advisory for PFOA of 100 ppt (ng/L) is based on adult assumptions instead of the child. All other inputs (RfD, RSC) are the same as what Health is proposing…*"

PFC water quality guidance concentrations for the EPA are presented in their Third Unregulated Contaminant Monitoring Rule (UMCR-3). Guidance concentrations for the PFCs listed range from 10 to 40 ng/l.

Laboratory analytical methods must meet the VTDOH and EPA guidance levels referenced above. We proposed to utilize Northern Lake Service, Inc. (NLS) for sample analyses via EPA Method 537. NLS is approved by EPA to meet the Third Unregulated Contaminant Monitoring Rule (UMCR-3).

The summary table below presents the VTDOH and EPA guideline concentrations and NLS EPA 537 detection and reporting limits. The proposed analysis method will meet the guideline concentrations for VTDOH and EPA.

**PFC QUANTIFICATION LIMITS AND DRINKING WATER GUIDELINE CONCENTRATIONS**

| Analyte Description | CAS # | Units | RL | MDL | VTDOH | EPA- UMCR3 |
|---|---|---|---|---|---|---|
| Perfluoroheptanoic acid (PFHpA) | 375-85-9 | ng/L | 10 | 3.3 | NG | 10 |
| Perfluorooctanoic acid (PFOA) | 335-67-1 | ng/L | 20 | 6.7 | 20 | 20 |
| Perfluorononanoic acid (PFNA) | 375-95-1 | ng/L | 20 | 6.7 | NG | 20 |
| Perfluorobutanesulfonic acid (PFBS) | 375-73-5 | ng/L | 90 | 30.0 | NG | 90 |
| Perfluorohexanesulfonic acid (PFHxS) | 355-46-4 | ng/L | 30 | 10.0 | NG | 30 |
| Perfluorooctanesulfonic acid (PFOS) | 1763-23-1 | ng/L | 40 | 13.3 | NG | 40 |

NG - No guidline concentration available

## 2.2 VOC Data Quality Objectives

VOC samples will be analyzed by NLS via EPA Method 524.2. The quantification limits will meet the latest Vermont Groundwater Enforcement Standards, Vermont Health Advisories and EPA Maximum Contaminant Levels (MCLs) as defined in the Groundwater Protection Rule and Strategy, 2/25/05.

## 2.3 Quality Assurance and Quality Control

Quality Assurance/Quality Control (QA/QC) for the field sampling will be provided through several methods:

1) PFC blanks will be collected at each sampling point. A sample location blank will be analyzed if PFCs are detected at concentrations greater than 1/3 of the reporting limit. (Concentrations of PFCs between 1/3 of the reporting limit and the reporting limit will be reported as estimated)
2) A single duplicate sample from a randomly selected sample location will be analyzed by Methods 537 and 524.2.
3) A trip blank will be collected for 524.2 analysis.

Laboratory QA/QC will be provided as indicated in their SOP included in **Appendix** B. We will evaluate the data with respect to project decisions; uncertainty within the decisions; and, quality criteria required for the data, specifically precision, accuracy, representativeness, completeness, comparability and sensitivity (PARCCS).

## 3.0 SAMPLE METHODOLOGY

All sampling will be performed in accordance with the Standard Operating Procedure (SOP) included in **Appendix A**. Access to the sampling will be arranged by the VTDEC. The SOP addresses methods for direct sampling of a water supply via either a spigot or tap. Where possible, the samples will be obtained from before the pressure tank/first storage vessel. Otherwise the sample will be obtained from the tap nearest the pressure tank. Screens/aerators will be removed from the tap prior to initiating purging. The water supply will be run for at least 15 minutes prior to sampling to assure any stagnant water in the distribution lines is purged. The samples will be collected in the laboratory provided containers, labeled, placed on ice and a chain of custody completed. The secured samples will be shipped to Northern Lake Service, Inc. for analyses within 24 hours of collection.

An inventory of building materials and items used/stored in the immediate area of the sampling location will be made. The property owner will also be interviewed to determine if potential PFC containing materials are typically used/stored in the general area.

## 4.0 SAMPLE LOCATION SELECTION

The VTDEC has identified 4 preferred residential drinking water supply wells and 2 public water supply wells for collection of water samples. The locations of the preferred sample locations are shown on **Figures 3** and **4**. The general locations for the samples have been selected to achieve 2 objectives:

- Evaluate bedrock water quality from wells closest to the potential PFC source (ChemFab).
- Determine if PFC impacts are observed in representative public water supply wells serving the Bennington and North Bennington area.

If access is not obtained for the preferred residential well locations, access to other nearby residential water supply wells will be attempted. Several alternative residential well locations are shown on **Figure 3**.

Access to the public water supply locations has been obtained by the VTDEC.

## 5.0 REPORTING

A report presenting all data collected, mapping of the locations of each sample, building inventory and water quality compared to the VTDOH and EPA guideline concentrations for PFCs and the VTGWES for VOCs. Conclusions and recommendations regarding the impact of PFCs on the water supplies sampled will be presented, along with recommendations regarding the need for additional assessment of PFC and VOC impacts if deemed necessary.

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# FIGURES

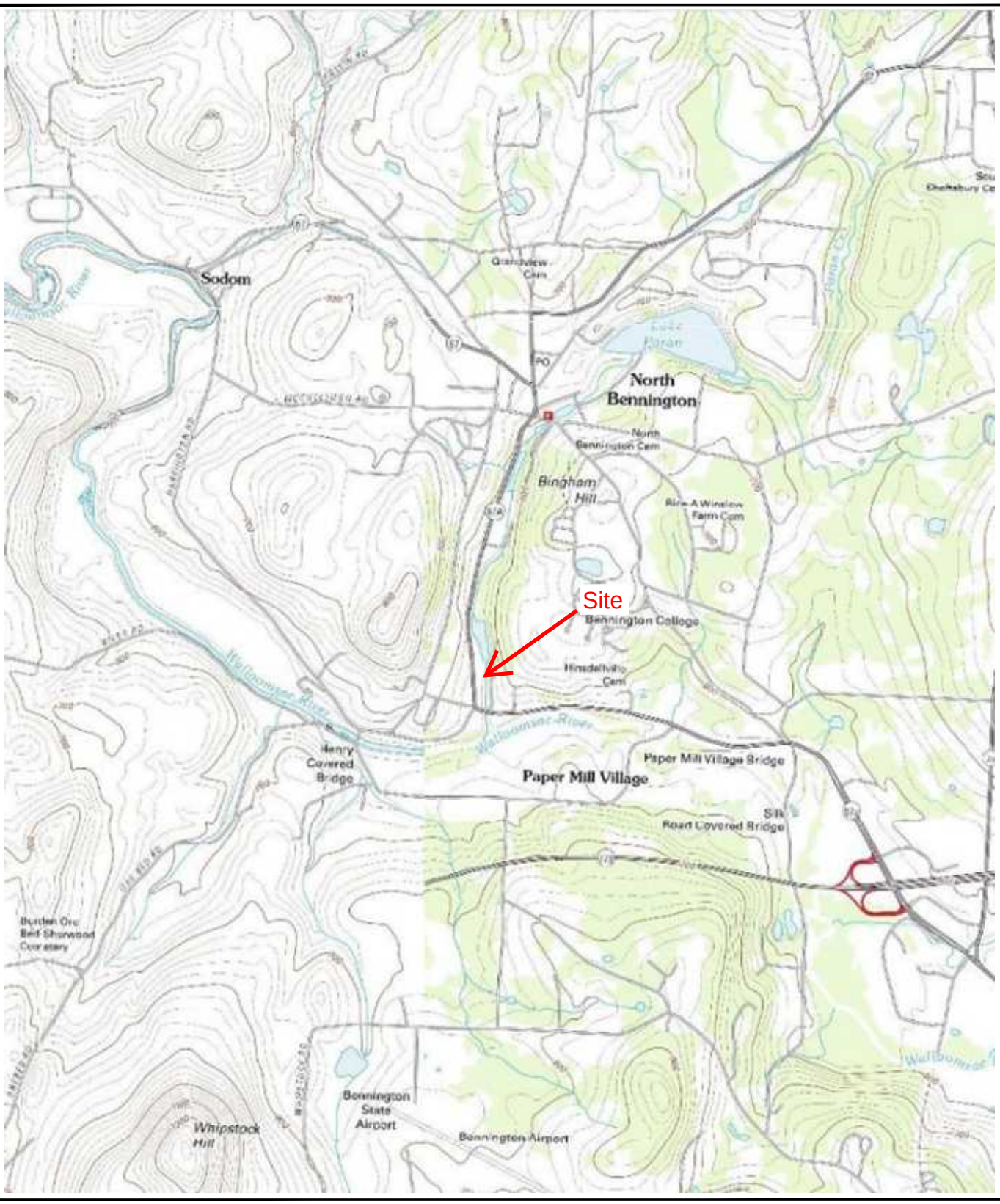


Figure 1
Locus Map

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Figure 2
Aerial Photo

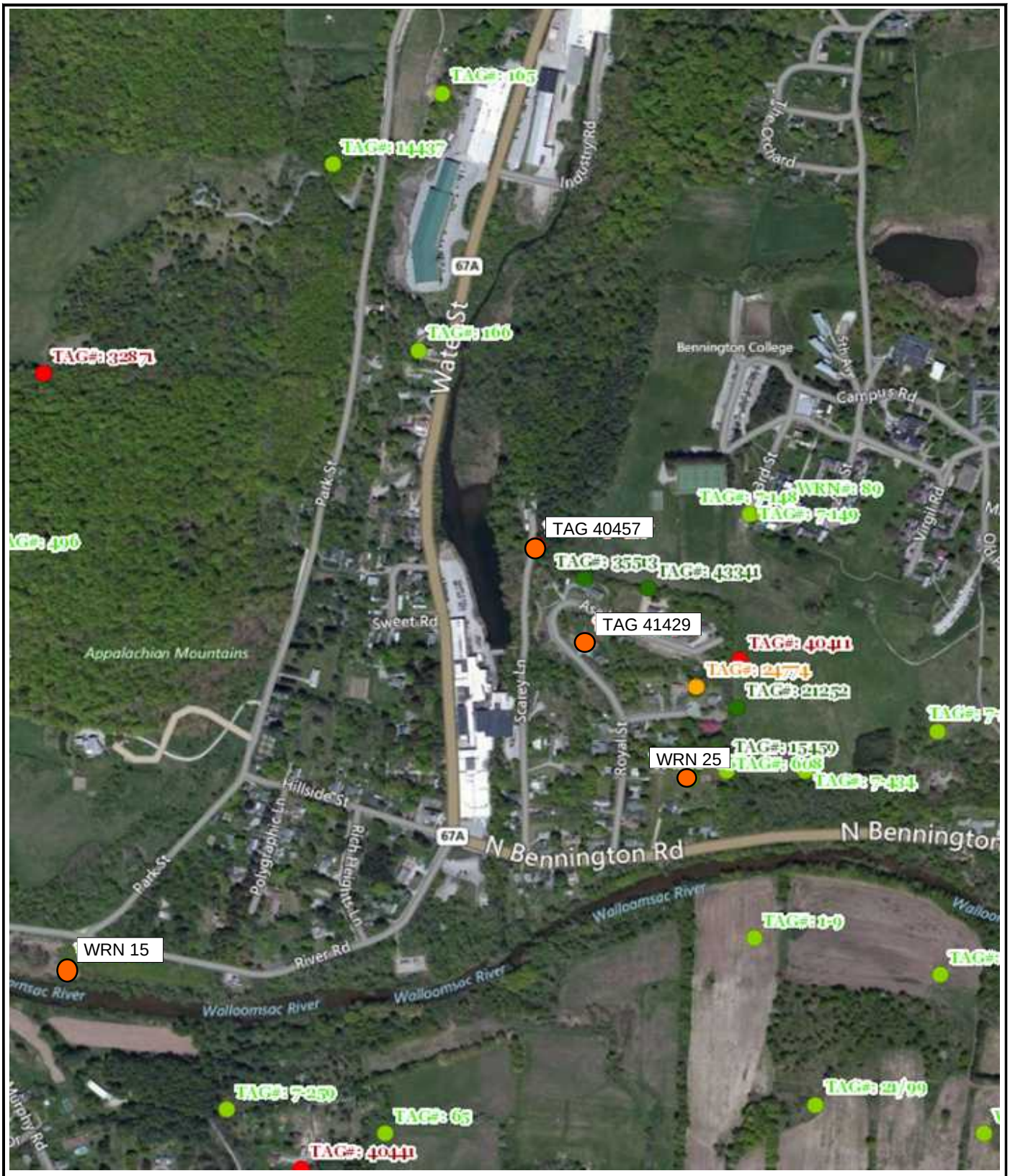


Figure 3

# Private Wells

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Wells To Be Sampled

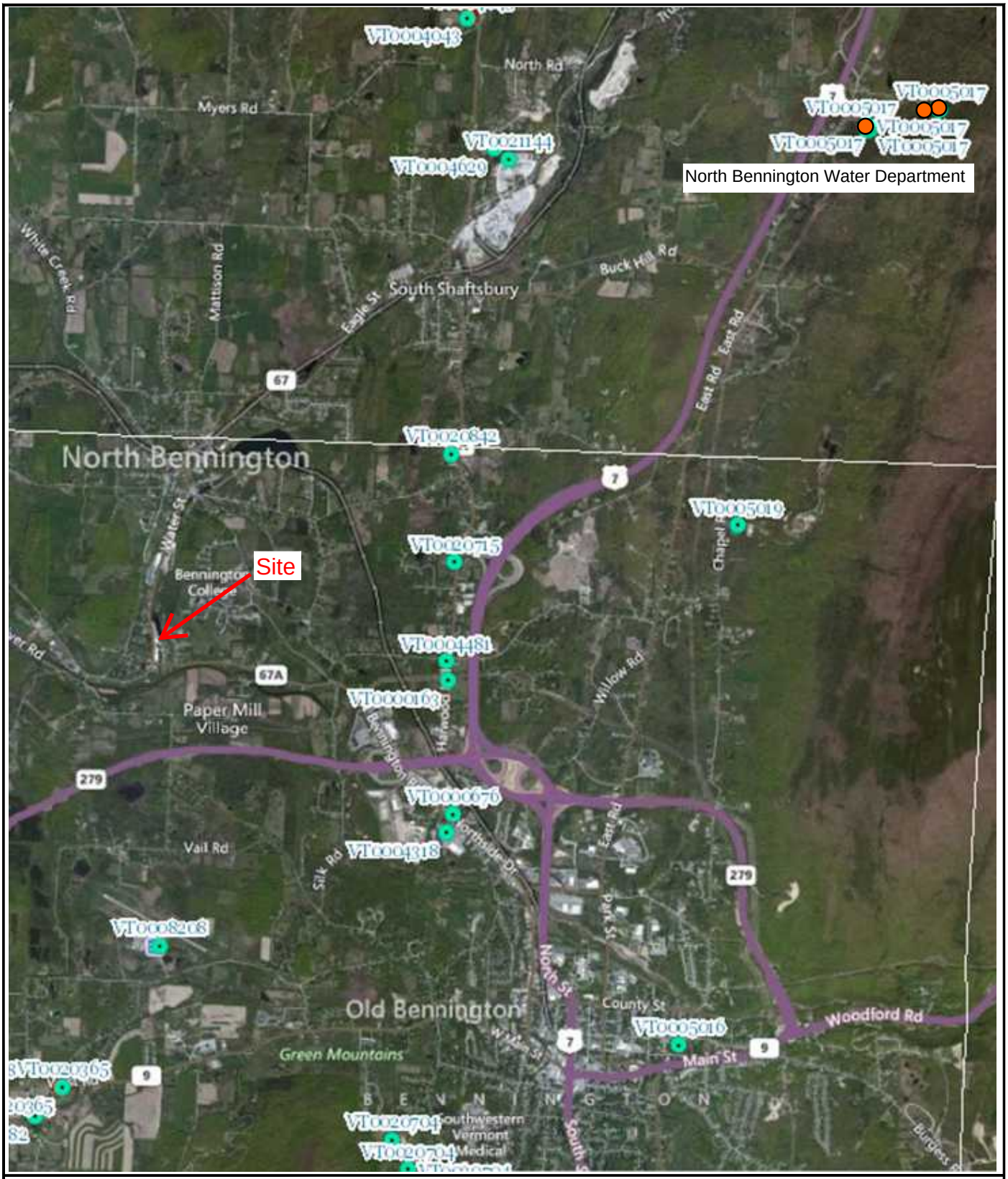


Figure 4
# Public Wells

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Wells To Be Sampled

# APPENDIX A

# SOP 16: Standard Operating Procedure for Water Supply Sampling for Perfluorinated Compounds

| | |
|---|---|
| Purpose: | Water supply water sampling from a pre-existing sample port/tap for laboratory analysis for the presence of perfluorinated compounds (PFCs). |
| Applicable for: | Water supply sampling while in the field for laboratory analysis at Northern Lake Service, Inc ONLY. |
| Not applicable for: | Soil, surface water, and groundwater samples. |

| PREREQUISITES | MATERIALS NEEDED |
|---|---|
| None, unless otherwise noted by Project Engineer. | ✓ Sampling Plan<br>✓ Slotted Pliers andPadding<br>✓ Laboratory provided bottles and blanks<br>✓ Field notebook (NOT WRITE IN THE RAIN)<br>✓ Latex gloves<br>✓ Cooler and ice |

## PROCEDURE

1) Sampler must assure that no potential PFC containing materials are utilized during sampling. No materials containing Teflon, Goretex, or other waterproofing can be utilized while sampling. Extra care to assure clothing, storage containers, and sampling equipment does not contain potential PFC sources must be taken.

2) Remove any screens, aerators or diverters from the selected sampling tap and initiate cold water flow at approximately 2 to 3 gallons per minute for at least 10 minutes.

3) Don latex gloves.

4) Open Method 537 Sample Kit Ziploc bag. Locate the full bottle, marked “blank water” and the empty bottle clearly marked “field blank.” Carefully uncap each bottle. This is best done with one person holding the bottles firmly and the other uncapping both bottles and maintaining the caps upright while the next step is performed. Dispense the content of the full “blank water” bottle into the empty “field blank” bottle. Recap both bottles. Return the blank bottles to the bag before proceeding.

5) Adjust sample tap flow to ensure slow, constant flow of less than ½ gallon per minute. Write the sample point descriptor (i.e. EP 1) on each of the remaining empty bottles with indelible ink (Sharpie). Carefully fill one of the bottles to near the top. Do not overflow the bottles during sample collection. Securely recap the bottle. Fill recap and return the first bottle to the bag before repeating this process with the

other empty bottle. Return all bottles to the Ziploc bag before proceeding to the next bag.

6) Record all relevant information and observations about the sample location including an inventory of potential PFC containing items in the area nearby the sampling point, if any exist.

7) Complete the chain-of-custody form.

8) Place bottles in the shipping container, add cooler blocks and packing materials sufficient to keep samples cool and protected from damage during shipping.

9) Place COC in a Ziplok bag and place atop the samples prior to sealing shipping container.

# APPENDIX B

## I. METHOD TITLE: EPA Method 537 – Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)

## II. METHOD SCOPE AND APPLICATION

A. Parameters: Method 537 is used to determine concentrations of selected perfluorinated alkyl acids (PFAAs) that are extracted from an aqueous sample matrix using a solid phase extraction cartridge. See attachment IV for compound list.

B. Matrix: Method 537 is used to determine concentrations of PFAAs in drinking water matrices.

C. NLS Test Codes: Descriptions

1. 15620 – UCMR3 by EPA Method 537
2. 15625 **–** UCMR3 by EPA Method 537 Solid Phase Extraction

D. Method Detection Limit (MDL) Study Procedure: The MDLs for EPA Method 537 will be statistically determined according to 40 CFR, Part 136, Appendix B, Rev 1.1, if required. The MDLs and the Limit of Quantitation (LOQs), if performed, are listed in the attached table (attachment IV). The Minimum Reporting Levels (MRL) are also listed for the six UCMR3 compounds: PFBS, PFHpA, PFHxS, PFNA, PFOS, and PFOA. The MDL determination is not required for the UCMR3 monitoring program. No results below the MRL will be reported to the EPA during the analysis of UCMR3 samples. For monitoring programs outside the scope of UCMR3, an MDL study will be performed if required.

## III. REFERENCES

A. Method 537 - Version 1.1, September 2009. Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)

## IV. METHOD SUMMARY

A. PFAAs are extracted from drinking water matrices using solid phase extraction. Final volume is always 1 mL of 96/4% (vol/vol) methanol/water. The extracts are injected via autosampler into the HPLC system pathway, utilizing a C18 column. The column is held at 30$^{o}$C to optimize compound separation. As the compounds elute from the column, they are analyzed using tandem mass spectrometry (MS/MS). Data is reprocessed, entered into a LIMS sample template, and reviewed by a co-worker prior to being archived.

## V. DEFINITIONS

A. AB Sciex Model API4000 or Varian Model 1200L Quadrupole Mass Spectrometer (MS/MS): Instrument capable of negative ion electrospray ionization (ESI) at an LC flow rate of 0.3 mL/min. Nitrogen or Argon is introduced as the collisionally activated dissociation (CAD) gas. Must be capable of producing a minimum of 10 scans across the chromatographic peak when operated in MS/MS mode.

B. Shimadzu or Varian Liquid Chromatograph (LC): The instrument that is capable of injecting 4-5 uL aliquots and performing binary linear gradients at a constant flow rate of 0.3 mL/min.

C. Laboratory Reagent Blank (WBLK): Clean sample matrix that is extracted and analyzed exactly like a sample. Method blanks are used to demonstrate that the extraction and analysis are free of contamination.

D. Initial Calibration (ICAL): Known standards that are prepared at different concentrations to determine a linear range of the LC/MS/MS. Sample amounts are calculated using a linear regression or quadratic calibration curve forced through zero. The curve may be weighted.

E. Initial Calibration Verification (ICV): The Quality Control Sample is a second source standard that is injected immediately after the ICAL and the Low-Level CCV. The ICV verifies the ICAL.

F. Continuing Calibration Verification (CCV): The Continuing Calibration Check is a known standard that is analyzed prior to sample analysis. The concentration of the initial low-level CCV will be at or below the MRL. A final CCV will bracket every ten samples rotating between a mid and high concentration calibration standard.

G. Laboratory Control Spike (LCS): The Laboratory Fortified Blank is a clean sample matrix to which MRL level concentrations of the target compound is added prior to extraction and analyzed exactly like a sample. Spike recoveries are calculated and are used to verify the laboratory's ability to perform an analysis on a clean matrix.

H. Matrix Spike and Matrix Spike Duplicate (MS/MSD): The Laboratory Fortified Sample Matrix and Laboratory Fortified Sample Matrix Duplicate is an environmental sample matrix to which a known MRL level and a mid level concentration of the target compounds are added on a rotational basis prior to extraction and analyzed exactly like a sample. Spike and relative percent difference recoveries (RPD) are calculated and are used to indicate potential recovery problems due to sample matrix.

I. Internal Standard (ISTD): The appropriate non-target compound that is added at a known concentration to each ICAL, ICV, CCV, WBLK, client sample, LCS, and MS/MSD prior to analysis. Comparing target ion areas against ISTD ion areas are used to quantify the concentrations of compounds.

J. Surrogate (SURR): The appropriate non-target compound that is added to all ICAL, ICV, and CCV prior to analysis. Also added to each WBLK, client sample, LCS, and MS/MSD prior to extraction. Surrogate recoveries are calculated and determine the efficiency of the entire process.

## VI. INTERFERENCES

A. Matrix/Chemical Interferences: Interference may come from solvents, reagents, glassware, sample bottles or caps, MS hardware, LC hardware, PTFE products, preservatives, or solid phase extraction cartridges. PFAAs may build up in the LC solvent lines while idle. 100% MeOH should be flushed through the system daily before initiating a sequence. The extracts and instrumentation must be free from contamination. If contamination is present the source must be identified and corrected. Extraction materials are washed in hot, soapy water, tap water rinsed, methanol rinsed, and solvent rinsed before use. Please refer to Extraction Quicknotes (attachment V) for further details. PFAA standards, extracts and samples will be prepared and stored in polypropylene containers.

B. Compound carryover may occur when a clean sample is analyzed after a sample containing a high concentration. Reanalysis of this sample should be performed for confirmation.

## VII. SAMPLE COLLECTION/PRESERVATION/SHIPMENT/STORAGE

A. Bottle Preparation and Sampling: Sample bottles are purchased "pre-cleaned" and are quality tested in-house to verify the bottles are free of contamination. Samples are collected in duplicate 250 mL polypropylene bottles with polypropylene screw caps containing 1.175g Trizma Hydrochloride and 0.075g Tris (Hydroxymethyl) Aminomethane for dechlorination and preservation. For specific information regarding sample receipt requirements, refer to the NLS UCMR3 sample receipt SOP. If any of the samples do not meet the stated criteria at login, the sample will be discarded. If no additional samples are available, the client is contacted and must resample. The pH is verified at receiving to confirm a pH of approximately 7.0. Any sample that does not have a pH of approximately 7 will be rejected. If no duplicate bottles are available or all bottles fail the pH criteria, the client is contacted and must resample. Residual chlorine testing is performed at receiving. Any sample that has residual chlorine present will be rejected. If no duplicate bottles are available, the client is contacted and must resample. After use, polypropylene bottles are recycled or discarded.

B. Storage

1. Sample Refrigeration – Aqueous samples are stored at 0-6°C in the walk-in cooler until time of extraction. No organic standards are stored in the walk-in cooler.

2. Extracts are stored on the shelving unit, at room temperature, in the instrument room until instrument analysis.

3. After analysis, extracts are stored on the shelving unit in the instrument room until discarded.

C. Holding Times

1. Extraction: Samples must be extracted within 14 days of sample collection. Any samples that are not extracted within 14 days must be recollected.

2. Analysis: Extracts must be analyzed within 28 days after extraction. Any extracts that are not analyzed within 28 days must be recollected.

## VIII. SAFETY

A. Special Precautions - Many of the PFAA analytes are either suspected or known carcinogens and must be treated with great care. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The material safety data sheet (MSDS) for chemical handling is available to all analysts and should be read. A ventilation hood with adjustable sash must be used to contain solvent fumes. Use nitrile gloves to avoid contact with standards, samples, and solvents. Always wear safety glasses.

## IX. EQUIPMENT AND MATERIALS

A. Extraction Room Equipment: Please see detailed Extraction Quicknotes (attachment V) for procedure, equipment, materials, and solvents.

B. Instrumentation: The LC/MS/MS analytical system consists of a AB Sciex API4000 quadropole mass spectrometer (SCILCMSMS) connected to a Shimadu Prominance LC Pump (2) Model LC-20ADXR (Shipump.1 & Shipump.2) with Prominance autosampler Model SIL-20ACXR (ShiAS.1) with chiller. System includes AB Sciex Analyst 1.5.2 software with Hotfixes to February 2011for instrument control, data acquisition, and reduction. An alternate LC/MS/MS analytical system consists of a Varian 1200L quadropole mass spectrometer (VARLCMSMS) connected to a Varian Prostar LC Pump (2) Model 210 (Varpump.1 & Varpump.2) with Varian Prostar autosampler Model 420 (VarAS.5). System includes Varian MS Workstation version 6.9 for instrument control, data acquisition, and reduction.

C. Column: Waters Atlantis dC18 5um 2.1x150mm or equivalent.

## X. REAGENTS AND STANDARDS

A. Reagent Purity Specifications: Analytical standards should be purchased from a reputable supplier. Solvents used during extraction should be of sufficient high purity to permit use without affecting accuracy. Only LC/MS grade methanol is used during the extraction and in the preparation of standards. Only LC/MS grade methanol is used to prepare 96/4% (vol/vol) methanol/reagent water. Deionized water is used for laboratory reagent blanks and laboratory control spikes. Only LCMS grade ammonium acetate is used to prepare 20mM ammonium acetate/reagent water.

B. Standards Preparation Specifications: Stock standards are purchased from a reliable supplier and accompanied with a certificate of analysis that verifies the sample concentration and preparation date for a specific lot number. The certificate of analysis must be kept in a file for a complete record of the standard preparation. Lot numbers and labels (if available) are recorded and attached in the Semi-Volatiles Standards Preparation Logbook (attachment I).

C. Standards Preparation Directions

1. Working Solution Preparation: A 10-90 mg/L stock standard is used to make a 500-4500 ug/L working solution by adding 250 uL of stock solution to 4.75 mL 96/4% (vol/vol) methanol/DI water into a 10 mL polypropylene container. The working solution is used to prepare serial dilutions for the ICAL and CCVs. It is also used as the spiking solution for LCS, MS,and MSD. All stock standards and working solutions are recorded in the Semi-Volatiles Standards Preparation Logbook (attachment I). All stock standards and working solutions are labeled with the expiration date, standard concentration, and reference logbook number and page.

2. Initial Calibration Curve (ICAL) Setup: From the 500-4500 ug/L working solution, perform a serial dilution into 6 calibration levels using polypropylene autosampler vials.

| Calibration Level | Amount of 500-4500 ug/L working std (uL) | Amount of 96/4% MeOH/DI water (uL) |
|---|---|---|
| 1 | 2.5 | 487.5 |
| 2 | 5 | 485 |
| 3 | 10 | 480 |
| 4 | 20 | 470 |
| 5 | 40 | 450 |
| 6 | 50 | 440 |

Add 5 uL of 1000 ug/L internal standard ($^{13}$C-PFOA and $^{13}$C-PFOS) mix and 5 uL of surrogate ($^{13}$C-PFHxA and $^{13}$C-PFDA) mix to each calibration level. The ISTD and SURR primary dilution standard mixes are added to each ICAL, CCV, and ICV.

3. Internal standard (ISTD) mix and surrogate (SURR) primary dilution mix preparation: The 1000 ug/L ISTD and SURR mixes are prepared individually in 4 mL polypropylene containers by adding 40 uL of each stock 50 ug/mL to 2 mL 96/4% MeOH/ DI water. The Final ISTD and SURR mix concentration is 10 ug/L.

4. Continuing Calibration Verification Standard (CCV) Setup: From the working standard prepare a low-level CCV concentration equivalent to the initial calibration level 1. This will yield a final concentration equal to or less than the MRL for each compound. The low-level CCV is analyzed prior to any samples in the sequence. A bracketing CCV is prepared and rotated between the mid and high-level concentration calibration standard. The mid-level CCV concentration is equivalent to initial calibration level 4. The high-level CCV concentration is equivalent to initial calibration level 5. CCV must be analyzed after every 10 samples and/or at the end of the sample sequence.

5. Initial Calibration Verification Standard (ICV) Setup: From a second source standard, prepare a mid-level concentration equivalent to initial calibration level 4 to verify the ICAL. NLS uses a secondary supplier to prepare the ICV. Detailed ICV preparation can be found in the Semi-Volatiles Standards Preparation Logbook (attachment I).

D. Storage Conditions: All stock standards are stored in the extraction room freezer (C) at -15°C to -20°C. All primary dilution standards consisting of the internal, surrogate, working, and ICV standard mixes are held at room temperature to prevent adsorption of analytes onto polypropylene container surfaces.

E. Second Source Standards: To assure quality results, the ICAL standard is made from a different supplier source stock standard than the ICV stock standard.

F. Shelf life: Stock standards from neat material should be replaced within 6 months. Working standards should be replaced within 6 months. Internal standard and surrogate standard stock solutions should be replaced within 6 months. Internal standard primary dilution mix should be replaced within 2 months. Surrogate standard primary dilution mix must be replaced within 1 year.

## XI. SAMPLE PREPARATION PROCEDURE

A. Extraction Preparation

1. Approximately 250 mL of liquid is passed through a Phenomenex Strata SDB-L (part# 8B-S014-HCH) cartridge. The compounds are eluted from the cartridge with methanol. The extract is concentrated to dryness under a gentle stream of nitrogen in a heated water bath (60- 65$^{o}$C) then brought up to a final volume of 1 mL with 96:4% (vol:vol) methanol/DI water. Please refer to Extraction Quicknotes (attachment V) for further details.

2. A laboratory reagent blank (WBLK) is included with every extraction batch up to 20 samples.

3. A laboratory control spike (LCS) is included with every extraction batch up to 20 samples. The LCS is spiked at or below the MRL. A 5 uL aliquot of the 500 ug/L *537 CAL* standard is added to the sample resulting in a true concentration of 0.01 ug/L.

4. A matrix spike and matrix spike duplicate (MS/MSD) are included with every extraction batch up to 20 samples. Analyte concentrations in the MS/MSD are rotated between MRL and mid calibration levels. For MRL level concentrations, 5 uL of the 500 ug/L *537 CAL* standard is added to the sample resulting in a true concentration of 0.01 ug/L. For mid-level concentrations, 40 uL of the 500 ug/L *537 CAL* standard is added to the sample resulting in a true concentration of 0.08 ug/L.

5. The appropriate surrogate (SURR) amount is added to each laboratory reagent blank, client sample, laboratory control spike, matrix spike, and matrix spike duplicate prior to extraction. A 10 uL aliquot of the 1000 ug/L *537 SURR* standard yields a true concentration of 10 ug/L.

6. The appropriate internal standard (ISTD) amount is added to the final extract of each laboratory reagent blank, client sample, laboratory control spike, matrix spike, and matrix spike duplicate. A 10 uL aliquot of the 1000 ug/L *537 ISTD* standard yields a true concentration of 10 ug/L.

7. Upon receipt of a new lot of extraction cartridges and prior to extraction of client samples, the new lot is tested. A WBLK and LCS are extracted. The WBLK must be less than 1/3 the MRL and the LCS must be within QC limits.

B. Final Sample Preparation: All samples are brought up to a final volume of 1 mL with 96:4% (vol:vol) methanol/DI water. Instrument dilutions are made if target compound concentrations are above the highest calibration standard.

C. See Extraction Quicknotes (attachment V) for detailed extraction procedure.

## XII. INSTRUMENT ANALYSIS

A. All LC/MS/MS operating conditions can be found in the beginning pages of the Instrument Run Logbook. See actual acquisition method for all HPLC parameters and MS segment descriptions. All acquisition methods are saved and archived in the group network folder named “Lx10 / u / archive / SciLCMSMS-537” or “Lx10 / u / archive / VarLCMSMS-537”.

B. Integration Events: Integration events are set before the calibration curve is calculated. Integration events remain constant for the initial calibration, quality control sample, blank, samples, laboratory control spike, matrix spike, and matrix spike duplicate. The analyst determines if manual integrations are needed for proper peak integration. For the manual integration policy, please refer to the NLS Manual Chromatographic Peak Integration Procedure.

C. Sample/Standard Presentation to Instrument: All sample extracts are stored in 4 mL polypropylene containers and labeled with sample number, extraction date, and method number. All standards and sample extracts must be delivered to the 0.5 mL polypropylene autosampler vials. All calibration levels must be injected with 5 uL of the 1000 ug/L *537 ISTD* and *537 SURR* mixes for every 500 uLs of solution for a final concentration of 10 ug/L each. The vials are placed into a 70-position autosampler tray. A 4 uL aliquot of sample is injected into the HPLC sample pathway by the Shimadzu Prominance autosampler Model SIL-20ACXR or equivalent. The autosampler chiller keeps all of the standards and sample extracts at a constant temperature of 15$^{o}$C. The analytical loading sequence is shown in attachment VII on page 19.

## XIII. CALCULATIONS

A. General Calculations

1. The concentration of each analyte is calculated using the internal standard technique (peak areas vs. concentration). Calibration points are fitted using either linear or quadratic regression forced through zero. The curve may be weighted. PFHxS and PFOS have multiple chromatographic peaks containing both linear and branched isomers. All peaks observed must be integrated and summed.

2. Final Liquid Concentration:

$$\text{Concentration}\ (\mu\text{g/L}) = \frac{(C)(FV)(D)}{(VE)}$$

Where: C = Concentration from Calibration Curve (ug/L).
FV = Final Extract Volume (mL).
D = Dilution factor.
VE = Volume Extracted (mL)

3. Analyte standard solutions are purchased in solution or as neat material. PFHxS and PFOS must contain both linear and branched isomers. PFHxS and PFOS are available as corresponding salts. These salts are acceptable materials as along as the measured mass is corrected for the salt content per the equation below:

$$\text{Mass}_{\text{acid}} = \text{Measured Mass}_{\text{salt}} \times \text{MW}_{\text{acid}} / \text{MW}_{\text{salt}}$$

Where: $\text{MW}_{\text{acid}}$ = the molecular weight of PFAA
$\text{MW}_{\text{salt}}$ = the molecular weight of salt

B. Significant figures: Sample results are reported to two significant figures. Performance Evaluations are reported to three significant figures. The results entered into the template are automatically rounded to the specified number in the reporting template.

C. Dilutions: Dilutions will be performed on final volumes of .2 mL or .5 mL of 96/4% (vol/vol) methanol/DI water. For example: A 2x dilution will be 100-uL of sample to 100-uL of 96/4% (vol/vol) methanol/DI water. A 5x dilution will be 100-uL of sample to 400-uL of 96/4% (vol/vol) methanol/DI water. Additional internal standard must be added to both to match the original concentration. A 2x dilution requires an additional 1 uL of ISTD. A 5x dilution requires an additional 1 uL of ISTD.

## XIV. METHOD PERFORMANCE

A. There are several requirements that must be met to insure that this procedure generates accurate and reliable data. Further specifications may be found in the Laboratory Quality Control Manual and specific Standard Operating Procedures.

1. The analyst must read and understand this procedure with written documentation maintained in his/her training file.

2. An initial demonstration of capability (IDC) must be performed. An additional IDC will be performed if any personnel or instrument changes occur. A record of the IDC will be maintained in his/her file with written documentation from the Laboratory Manager and Quality Assurance Officer.

3. An initial minimum reporting level (MRL) study will be completed. An additional MRL study will be performed if any personnel or instrument changes occur. Refer to method templates for current MRL limits.

4. The qualitative identification of a compound is based on retention time and mass spectrum comparison to a user defined spectra library.

5. Periodic performance evaluation (PE) samples are analyzed to demonstrate continuing competence.

6. Update the LC/MS/MS user defined spectra library periodically and following significant instrument maintenance.

## XV. QUALITY CONTROL

A. Laboratory Reagent Blank: A laboratory reagent blank (WBLK) is analyzed with every extraction batch up to 20 samples. If the method blank has a target concentration greater than 1/3 the MRL, the contamination source must be found and the samples must be re-extracted. If no duplicate samples are available for re-extraction, or are past holding time, the EPA will be contacted for acceptance guidance.

B. Initial Calibration: A 6-point initial calibration (ICAL) is performed when it has been demonstrated that continuing calibration verification standards, laboratory control spikes, matrix spikes, and matrix spike duplicates fail to meet QC requirements. A new ICAL may also be necessary when new standards are used or major instrument maintenance has been performed. The % recovery for each calibration point must be 70-130% of the compounds true value except for ICAL#1, this lowest point must be 50-150%. When these criteria are met the initial calibration is considered valid.

1. If one point fails, the analyst must determine if a single calibration point is an outlier. To do this the analyst must display the curve to screen and visually inspect all calibration points. This inspection may show that a single calibration point is an outlier and removal of that point would yield an acceptable calibration. Analysts must keep in mind that low-point concentration removal is prohibited as this may lead to significant low concentration quantitative errors. NLS currently performs a 6-point calibration. By removing a mid-point or high level, a 5-point calibration is considered valid. Removal of this outlier requires the analyst to document the potential cause. A brief description of the cause must be included on the Initial Calibration report.

C. Initial Calibration Verification: Following the instrument initial calibration and a low-level CCV, an Initial Calibration Verification (ICV) or Quality Control Sample is injected. This is a second source standard used to verify the initial calibration. The second source ICV compounds must recover within 70-130% the expected value. In the event of a failing ICV, a new ICAL must be analyzed and a new ICV injected.

D. Continuing Calibration Verification: A Continuing Calibration Verification (CCV) or Continuing Calibration Check standard is analyzed prior to sample analysis. This initial low-level CCV will be at or below the MRL. The low-level CCV must be within 50-150% of the true value. A bracketing CCV is analyzed after every 10 samples and/or at the end of the sequence. The bracketing CCV will rotate between the medium and high concentration calibration standard. The mid-level and high-level CCV must be within 70-130% of the true value. All surrogate recoveries must be 70-130% of the true value. Data is not valid if the low-level CCV is <50% of the true value or the medium and high level concentration CCVs are <70% of the true value. If the CCV fails because the concentration is greater than 130% (150% for the low-level CCV) for a particular analyte, and the samples show a no detect for that analyte, no detects may be reported. In any other case data is not valid and the laboratory must re-analyze, re-extract, or request a resample.

E. Laboratory Control Spike: A laboratory control spike (LCS) or Laboratory Fortified Blank is included with every extraction batch up to 20 samples. The appropriate spike amount is added to the LCS prior to extraction. The concentration of the LCS will be at or below the MRL. Laboratory control spike recoveries must be 50-150%. Data is not valid if the LCS does not meet acceptance criteria. The laboratory must re-analyze, re-extract, or request a resample.

F. Matrix Spike/Duplicate: A matrix spike and matrix spike duplicate (MS/MSD) or Laboratory Fortified Sample Matrix / Laboratory Fortified Sample Matrix Duplicate is included with every extraction batch up to 20 samples. The appropriate spike amount is added to the MS/MSD prior to the extraction. The concentration of the MS/MSD will rotate between low and mid levels. The low-level MS/MSD will be at a concentration at or near the MRL, but no greater than 2x the MRL. The low-level MS/MSD must recover within 50-150% of the true value and have a RPD < 50. The mid-level MS/MSD will be at a concentration near the mid point of the ICAL. The mid-level MS/MSD must recover within 70-130% of the true value and have a RPD <30. If the accuracy or precision of the MS/MSD falls outside the designated ranges and the CCV and LCS are shown to be in control, the sample result is labeled as “suspect/matrix” and the client results are flagged.

G. Internal Standards: The appropriate internal standard (ISTD) amount is added to each ICAL, CCV, ICV, WBLK, client sample, LCS, MS, and MSD prior to analysis. Internal standard area counts for all CCV, ICV, WBLK, client sample, LCS, MS, and MSD must be 70-140% of the peak area in the most recent CCV, **and** 50-150% of the average area in the ICAL. In the event there is no previous CCV present, for instance the initial low-level CCV after an ICAL, the low-level CCV must recover within 70-130% of the last ICAL standard analyzed. If the instrument is suspected of causing ISTD failures, the samples must be repeated after problem sources are found and corrected. Data is not valid if the ISTD in any sample does not meet acceptance criteria. The laboratory must re-analyze, re-extract, or request a resample.

H. Surrogates: The appropriate surrogate (SURR) amount is added to each ICAL, ICV, and CCV prior to analysis. The surrogate is also added to each WBLK, client sample, LCS, MS, and MSD prior to extraction. Surrogate recoveries for all ICAL, ICV, CCV, WBLK, client sample, LCS,

MS, and MSD must be 70%-130%. Recoveries are tracked and recorded through the Laboratory Information Management System (LIMS). If the instrument is suspected of causing SURR failures, the samples must be repeated after problem sources are found and corrected. If sample matrix is suspect and the SURR recovers above or below acceptable limits, the sample will be re-extracted if holding time permits. If the re-extracted surrogate results are similar to the initial results, the sample result is labeled as "suspect/matrix" and the client results are flagged. If the sample is past the 14-day holding time, the EPA will be contacted for acceptance guidance.

I. Peak Asymmetry Factor: A peak asymmetry factor must be calculated for the first two eluting peaks every time an initial calibration curve is generated. The peak asymmetry factor for the first two eluting peaks must be 0.8 to 1.5.

## XVI. RECORDS AND REPORTING DATA

A. Logbook entry

1. Semi-Volatiles Standards Preparation Logbook (attachment I) is filled out every time a new stock standard solution is opened or prepared. If an adhesive label is available with the stock standard solution it should be attached to the page containing the information about the standard prepared. This label is then traceable to the certificate of analysis for a complete record.

2. Instrument Run Logbook (attachment II) Documents the analytical run list including ICAL, ICV, CCV, WBLK, client sample, LCS, MS, and MSD.

3. Instrument Maintenance Logbook (attachment III) documents all maintenance done to the instrument.

4. Extraction Logbook (attachment VI) documents all extraction including initial sample volumes, final extract volumes, spiking solutions, solvents lot numbers, cartridge lot numbers, sample numbers, and quality control.

B. Sample Calculation: Text files generated by the instrument software are extracted into an in-house calculation program known as Quantit. The Quantit program calculates final reporting concentrations for all samples and QC data points. QC data points are automatically transferred to the LIMS system.

C. Method Detection limits and Reporting limits: The MDLs for EPA Method 537 will be statistically determined according to 40 CFR, Part 136, Appendix B, Rev 1.1, if required. For additional references on MDL determination see Analytical Detection Limit Guidance, WDNR OTS, April 1996 draft.

D. Qualifiers or comments used if data is to be flagged:

1. The matrix spike recovered above/below QC limits due to suspect/matrix

2. The matrix spike duplicate RPD recovered above QC limits due to suspect/matrix.

3. The surrogate recovered above/below QC limits due to suspect/matrix.

E. LIMS Entry: The laboratory information system contains all of the data that appears on the final analytical reports. Results are entered into the LIMS system under template entry. Enter the

appropriate template name, sample number, date, time, dilution factor (MRL will not be adjusted), analyst initials, and testcode. By entering a testcode, the sample will be removed from the benchsheet. Enter all final results including surrogate recoveries and commit data. If there are any additional footnotes, comments or qualifiers enter this information under the notes category. A copy of the template is included with the raw data for peer review.

F. Client Reports: Final client templates automatically print with the final client report.

G. Data Peer Review: An individual, different from the person organizing the data, reviews the data folder. This person reviews sample template entry and the contents of the folder. The reviewer also files the folders in the appropriate file cabinet.

H Data archiving or filing: Archiving of data should be performed on a regular basis. Data files are transferred to LX10\u\archive\ SciLCMSMS-537 on the network. When the network archive is full the LIMS department stores the data on tape. These files are stored at the bank.

I. Hard Copy Archiving: Processed data reports are printed for each sample analyzed. All data compiled from an instrument run should be kept in a separate file folder. Information kept in the file folder includes calibration summary, reagent blanks, quality control, sample data, extraction log, instrument log, and sample template. Folder is labeled with the date of the analytical run, method number, and instrument. Folders are stored in the file cabinets. When file cabinets are full the folders are transferred to a labeled bankers box and stored in the basement archives.

## XVII. CLEAN UP/POLLUTION PREVENTION/WASTE MANAGEMENT

A. Lab Work Area: Samples should always be returned to the refrigerator after use. Also, any materials, reagents, supplies or standards should be returned to their proper location. The lab area in general should always be kept clean and free from clutter.

B. Sample and Standard Disposal: Samples are disposed of in accordance with procedures determined in the Quality Management Plan. Aqueous samples, after extraction, are emptied down the drain and the sample bottles recycled. Duplicate samples are not discarded for four weeks after the client report has been sent. Standards and extracts are emptied into a solvent waste jug. The auto-sampler vials are discarded into a glass jug that is later disposed. The solvent contents are removed from the premises by a licensed waste hauler.

C. Equipment and Glassware: Equipment is kept clean and dust free. Occasional cleaning may be needed to ensure equipment is free from dust and other debris. Glassware should be washed and rinsed immediately after use.

D. Pollution prevention: Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

E. Chemicals: The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

F. Waste Management Practice: The Environmental Protection Agency (USEPA) requires that laboratory waste management practice be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. The agency urges laboratories to protect the air, water and land by minimizing and controlling all releases from hoods, and bench operations, complying with the letter and spirit of any waste discharge permit and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions.

## XVIII. MAINTENANCE/TROUBLESHOOTING

A. Maintenance procedures and frequency: All maintenance is recorded in the Instrument Maintenance Logbook (attachment III)

1. As needed wipe inside of spray chamber and electrospray needle tip with MeOH.
2. As needed clean the spray shield with stainless steel cleaner and wipe with MeOH.
3. As needed replace the LC column.
4. Replace every six months the Rough Pump Oil.
5. As needed check the Air and Nitrogen generator filters and replace.

B. **Note**: Daily maintenance items that are not recorded in the maintenance log.

1. Check for air bubbles in sample delivery tubing.
2. Replace mobile phase
3. Refill pump rinse vials

## XIX. ATTACHMENTS

A. Attachment I – page 13: Semi-Volatiles Standards Preparation Logbook

B. Attachment II – page 14: Instrument Run Logbook

C. Attachment III – page 15: Instrument Maintenance Logbook

D. Attachment IV- page 16: Table with LOD, LOQ, and MRL for water

E. Attachment V- page 17: Extraction Quicknotes

F. Attachment VI- page 18: Extraction Logbook

G. Attachment VII- page 19: Analytical Sequence

NORTHERN LAKE SERVICE, INC.
ORGANIC ANALYSIS
STANDARDS PREPARATION LOGBOOK

BOOK: 960004
PAGE:

| Line No. | Date | Vendor/Lot No. | Compound / Mixture | Exp. Date | Stock Conc. | Dilution/Prep | * Solvent/Lot No. | Final Conc. | Analyst | Discard Date | Discarded By |
|---|---|---|---|---|---|---|---|---|---|---|---|
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* Solvent Key: A = Acetonitrile H = Hexane M = Methanol

Comments:

Org-30 (2/96)

Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography /Tandem Mass Spectrometry (LC/MS/MS)

**NORTHERN LAKE SERVICE, INC.**
***SciLCMSMS INSTRUMENT RUN LOG***
***EPA METHOD 537 DRINKING WATER ANALYSIS LOGBOOK***

BOOK: 120009
PAGE: _____

| Date: | Method / Quantitation Method | Analyst: | Calibration Date: |
|---|---|---|---|
| / / | EPA 537 / | | / / |

| File No. | Sample Number | Dilution Factor | Comments / Repeats |
|---|---|---|---|
| 1 | | | |
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| 4 | | | |
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| All Area Counts Must Be Within: | Internal Standard Area Counts | C13-PFOS | C13-PFOA | Standards Reference | Book # | Page # | Line # |
|---|---|---|---|---|---|---|---|
| 70 – 140% of Most Recent CCV and 50 – 150% of Average ICAL | Ave. ICAL | | | ISTD Mix: | | | |
| | Previous Day CCV | | | SURR Mix: | | | |
| | This Analysis CCV 1 | | | 537 Calibration Mix: | | | |
| | This Analysis CCV 2 | | | 537 ICV Mix: | | | |
| | This Analysis CCV 3 | | | Peak Asymmetry Factor for the first two eluting peaks must be 0.8 to 1.5 midpoint ICAL only | | | |
| | Samples analyzed within 28 days after extraction? Yes No | | | Peak #1 calculated peak Asymmetry Factor | | | |
| | Notes: See Quantit area sheets for outliers | | | Peak #2 calculated peak Asymmetry Factor | | | |

Org (03/2012)

**NORTHERN LAKE SERVICE**

***AB Sciex LC/MS/MS ANALYTICAL SYSTEM MAINTENANCE LOG***
***GENERAL MAINTENANCE & REPAIR LOGBOOK***

BOOK: 110023
PAGE: _____

| Maintenance Performed | Date | Initials |
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Org-75 (5/2007)

TEMPLATE REPORT: 537UCMR3 **Perfluorinated Chemicals by EPA 537 UCMR3 Safe Drinking Water** 05/23/12 Page 1 of

**Analysis**

| PEAK | LOD | LOQ | MRL | UNITS | PCODE | ESORT | RSORT | MCL | NR | TYPE |
|---|---|---|---|---|---|---|---|---|---|---|
| C13-PFHxA | | | | | q | .1 | 7 | | | SURR |
| C13-PFDA | | | | | q | .3 | 8 | | | SURR |
| perfluorobutanesulfonic acid (PFBS) | .09 | .09 | .09 | ug/L | | 1 | 1 | | | PEAK |
| perfluoroheptanoic acid (PFHpA) | .01 | .01 | .01 | ug/L | | 2 | 2 | | | PEAK |
| perfluorohexanesulfonic acid (PFHxS) | .03 | .03 | .03 | ug/L | | 3 | 3 | | | PEAK |
| perfluorooctanoic acid (PFOA) | .02 | .02 | .02 | ug/L | | 4 | 4 | | | PEAK |
| perfluorononanoic acid (PFNA) | .02 | .02 | .02 | ug/L | | 5 | 5 | | | PEAK |
| perfluorooctanesulfonic acid (PFOS) | .04 | .04 | .04 | ug/L | | 6 | 6 | | | PEAK |

# 537 Solid Phase Extraction Quick Notes

**A. Clean-Up**

1. All polypropylene beakers, 250mL polypropylene graduated cylinder, collection vials, and caps must be:
   a. Detergent washed and tap water rinsed.
   b. Rinsed with HPLC grade MeOH twice.
   c. Final rinse with LCMS grade MeOH.
2. The transfer tubes should be pre-cleaned before each extraction round by pulling15 mL of LCMS grade MeOH through each followed by 20 mL of DI water (see Sample Prep 1 for DI water). Do this by using the SPE cartridges from the previous extraction round. Remove and discard the cartridge and wipe both outside ends of the tubes with LCMS grade MeOH.
3. Clean each stainless steel nitrogen tube on the NEVAP with LCMS grade MeOH.
4. Triple rinse the 10 mL extraction syringe with LCMS grade MeOH.

**B. Sample Prep**

1. Fill pre-cleaned polypropylene beakers for the LCS and blank with 250 mL of DI water from the Pure Lab Ultra system located in the SemiVol instrument room. Allow 3 L to run before collecting. (Also collect one beaker full to be used in the extraction process.)

a. Add 1.175 g of Trizma HCL and .075 g of Tris(Hdroxymethyl) Aminomethane to the blank and LCS.

2. Mark the sample level on the bottles for later volume determination.
3. To the LCS add 5uL of the 537 CAL standard.*
4. The MS/MSD spike volume must rotate between 5uL and 40uL of the 537 CAL standard.*
5. To each sample and QC add 10uL of Surrogate.*

**C. Extraction**

1. Set up the 12 position SPE system with new Phenomenex Strata SDB-L (part# 8B-S014-HCH) cartridges in place.
2. Rinse each cartridge with 15 mL of LCMS grade MeOH. **DO NOT ALLOW TO GO DRY.**
3. Rinse with 18 mL of DI water collected from step 1 of Sample Prep. **DO NOT ALLOW TO GO DRY.**
4. Add 4-5 mL of DI water and leave in cartridge.
5. Attach pre-cleaned sample transfer tubes.
6. Pull sample through cartridge at a rate of 10-15 mL/min. 250 mL should take 17-25 min. **DO NOT ALLOW TO GO DRY.**
7. After sample has been pulled through, rinse everything with **two** 7.5 mL aliquots of DI water and pull through cartridge.
8. Dry each cartridge for 5 min at high vacuum.
9. Place rack with 10 mL pre-cleaned polypropylene collection vials into the manifold.
10. Add 4 mL of LCMS grade MeOH to each sample bottle/ QC beaker being sure to rinse the sides of each, as well as the outside of the transfer tubes.
11. Pull through at a drop wise rate.
12. Repeat steps 10 and 11.
13. Leave the cartridges on the transfer tubes to use in the transfer tube Clean Up step 2.
14. Place 10 mL collection vials on the NEVAP set at 60-65°C and concentrate to dryness with nitrogen.
15. Remove and add 990 uL of 96:4% MeOH:DI water solution.*
16. Add 10 uL of ISTD, cap, and vortex for about 10seconds.
17. Store the final extracts in the instrument room at room temperature.
18. Use a graduated cylinder to determine sample volume marked on sample containers.

*NOTE: A Microman pipette with designated polypropylene tips must be used when spiking the SURR, ISTD, CAL spike, and 96:4% solution.

*NORTHERN LAKE SERVICE, INC.*
***EPA METHOD 537 LC/MS/MS SOLID PHASE EXTRACTION LOGBOOK***

BOOK: 120011
PAGE: _____

Date: _____ Analyst: _____

| Line No. | NLS Sample Identification | INITIAL Volume | FINAL Volume | ISTD Volume | SURR Volume | 537 - Spike Volume | Comments |
|---|---|---|---|---|---|---|---|
| 1 | BLK_ | 250 mL | 1 mL | | | | Extraction Blank |
| 2 | LCS_ | 250 mL | 1 mL | | | | Lab Control Spike |
| 3 | MS_ | | | | | | Matrix Spike (LFSM) |
| 4 | MSD_ | | | | | | Matrix Spike Duplicate (LFSMD) |
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| Extraction Items | Supplier | Lot # |
|---|---|---|
| Trizma Hydrochloride (1.175g) | | |
| Tris (Hydroxymethyl) Aminomethane (.075g) | | |
| Extraction Cartridges | | |
| MeOH | | |

| Additional Extraction Items | Book # | Page # | Line # |
|---|---|---|---|
| 96:4% (vol/vol) MeOH in DI | | | |
| | | | |
| | | | |

| Standards Reference | Book # | Page # | Line # |
|---|---|---|---|
| Internal Standard Mix | | | |
| Surrogate Standard Mix | | | |
| 537 Spike Mix (537 CAL) | | | |
| | | | |

Org (3/2012)

Laboratory Name: Northern Lake Service EPA Lab ID Code: WI00034

# Method 537 Analytical Sequence

## Internal Standard

Internal standards area counts are monitored during each analysis day. The Internal Standards of any chromatographic run must not deviate from the most recent CCC by +40% or - 30% and must not deviate by more than +/- 50% of the average measured area during the initial calibration.

## Surrogate

All surrogates in the CCC, QCS, LRB, Field Samples, LFB, LFSM, and LFSMD all must recover between 70-130%.

## Daily Instrument Performance Checks

| Injection # | Sample description |
|---|---|
| 1 | Instrument Blank |
| 2 | Low-Level CCC (MRL Level) |
| 3 | Laboratory Reagent Blank (LRB) |
| 4 | Laboratory Fortified Blank (LFB) |
| 5 | LFSM of Field Sample |
| 6 | LFSMD of Field Sample |
| 7-16 | Field Samples 1-10 |
| 17 | Mid-Level CCC |
| 18-27 | Field Samples 11-20 |
| 28 | High-Level CCC |

ICAL note: If a 6-point ICAL is analyzed. Injection #1 is an Instrument Blank. Injection #2-#7 is the ICAL. Injection #8 is a Cleanup Blank (CBLK) to verify there is no carryover is present. Injection #9 is a Low-Level CCC. Injection #10 is a second source Quality Control Standard (QCS). Injection #11 is a Laboratory Reagent Blank (LRB).

Please note: The LFB will be spiked at the low calibration concentration. The LFSM and LFSMD will rotate between low and a mid-level calibration concentration.