SITE CHACTERIZATION SAMPLING
FOR CONTAMINATED MATERIAL MANAGEMENT PURPOSES
PR0P0SED MEDICAL READINESS FACILITY
TRUAX FIELD
APRIL 10, 2020

For project XGFG 139001 soil and groundwater samples will be collected at the locations shown on the attached map. All samples will be tested for the full range of volatile organic chemicals and the included list of PFAS compounds. This field information will be used to develop a contaminated materials management plan. The management plan will describe the reuse or disposal of contaminated soil and/or groundwater generated during site preparation and building construction.

SAMPLING:
Two discrete soil samples will be collected from each boring at depths of: 1-2 feet below ground surface and 1 foot above the water table; Four sample locations are shown on attached map for total of eight soil samples

Groundwater samples will be collected from each boring: samples can be grab samples using a direct push method, permanent wells are not required; four sample locations for a total of four water samples.

ANALYSIS
All soil and groundwater samples will be analyzed at a lab, approved by the Department, to conduct volatile organic chemical and PFAS analysis. QA/QC requirements will be laboratory specific.

WISCONSIN DEPARTMENT OF NATURAL RESOURCES
NOTICE OF FINAL GUIDANCE & CERTIFICATION

Pursuant to ch. 227, Wis. Stats., the Wisconsin Department of Natural Resources has finalized and hereby certifies the following guidance document.

DOCUMENT ID

EA-19-0001

DOCUMENT TITLE

Wisconsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Expectations

PROGRAM/BUREAU

Certification Services / Environmental Analysis & Sustainability

STATUTORY AUTHORITY OR LEGAL CITATION

Wis. Stats. s. 299.11 and Wis. Admin. Code s. NR 149.41 (2)

DATE SENT TO LEGISLATIVE REFERENCE BUREAU (FOR PUBLIC COMMENTS)

9.16.19

DATE FINALIZED

12.16.19

DNR CERTIFICATION

I have reviewed this guidance document or proposed guidance document and I certify that it complies with sections 227.10 and 227.11 of the Wisconsin Statutes. I further certify that the guidance document or proposed guidance document contains no standard, requirement, or threshold that is not explicitly required or explicitly permitted by a statute or a rule that has been lawfully promulgated. I further certify that the guidance document or proposed guidance document contains no standard, requirement, or threshold that is more restrictive than a standard, requirement, or threshold contained in the Wisconsin Statutes.

Signature

Date 12/10/2019

Wisconsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Expectations

- Version 12.16.2019 -

Per- and Polyfluorinated Alkyl Substances (PFAS) Analysis Using Isotope Dilution by LC/MS/MS

The purpose of this document is to provide the expectations that will help the Program determine if a laboratory's method is considered suitable for analysis of PFAS in aqueous (non-potable water) and non-aqueous matrices for Wisconsin.

The Program has the legal authority under NR 149.41 (2) to determine whether the method selected by a laboratory is suitable for the matrix, type of analyte, expected level of analyte, regulatory limit, and anticipated interferences in the sample, when methods are not prescribed by covered programs under NR 149 or permits issued by the department.

Once the EPA publishes their 1600 series isotope dilution method, the Program will defer to that method for certification.

Potable water samples are analyzed utilizing EPA 537.1.

{F} = when "{F}" is listed after an expectation and the expectation is not met, then qualify the associated results on the test report. The qualifier can refer the data user to the narrative where detail is provided that indicates what the non-conformance was, and if known, the possible effects on the sample results.

Definitions are provided in Section **X, "Definitions,"** of this document.

I. Sample Handling

1. Instruct sample collectors to collect grab samples in high density polyethylene or polypropylene containers. {F} Avoid polytetrafluoroethylene (PTFE) containers and contact with PTFE surfaces.

2. Instruct sample collectors to collect an equipment blank when using equipment in the field to collect samples. {F}

3. Instruct sample collectors not to fill aqueous sample containers completely.

4. There is no chemical preservation necessary, just temperature preservation. Instruct sample collectors to ship aqueous and solid samples at above their freezing point to 6 °C. {F} Instruct sample collectors to ship tissue samples frozen. {F} Measure and document the temperature of aqueous and solid samples at sample receipt. Tissue samples received frozen can be documented as "frozen" at sample receipt.

5. Store aqueous and solid samples at above their freezing point to 6 °C at the laboratory. {F} Store tissue samples at less than or equal to -10 °C at the laboratory. {F} Store all extracts at 0 – 6 °C at the laboratory. {F}

6. Aqueous and solid sample holding times are within 28 days from collection to extraction and within 30 days from extraction to analysis. {F} Tissue sample holding times are within 1 year from collection to extraction and within 30 days from extraction to analysis. {F}

7. Rinse aqueous sample containers and all extract containers after transfers with one or more rinses of polar solvent to remove any PFAS that may have been adsorbed to container walls.

8. Thoroughly vortex or mix extracts and standards before transfer or aliquoting to remove any PFAS that may have been adsorbed to container walls.

9. Thoroughly vortex autosampler vials before loading the autosampler to remove any PFAS that may have adsorbed to container walls.

II. Initial Demonstration of Capability (IDC)

1. All analysts performing testing are expected to pass an IDC. If analysts perform only the extraction steps, then they are expected to pass the extraction portion of an IDC. If analysts perform only the analysis steps, then they are expected to pass the analysis portion of an IDC.

2. Analyze standards of all target (native) analytes and extracted internal standards (EIS) to determine retention times of the linear and branched isomers.

3. Analyze a method blank. The results are expected to be less than one-half the method reporting limit (MRL).

4. Assess precision and recovery by performing the entire procedure on four laboratory control samples (LCS) spiked at a midrange concentration of the initial calibration for each target (native) analyte. The average recovery is expected to be within 65-135%, and the RSD is expected to be less than or equal to 30%.

5. Assess recovery of the extracted internal standards (EIS) in each LCS. Except for FOSA, NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE, EIS recoveries are expected to be within 50–150%. For FOSA, NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE, EIS recoveries are expected to be within 20 – 150%.

III. Field Quality Control Samples

1. **Equipment blanks** (one per sampling event when equipment is used in the field to collect samples) – The results are expected to be less than the highest of the following {F}:

    a. 1/2 the MRL
    b. 1/10 the sample concentration

    It is not necessary to qualify equipment blank detections between the MDL and one-half the MRL.

2. **Field blanks** (one per sampling event for each sampling site) – The results are expected to be less than the highest of the following {F}:

    a. 1/2 the MRL
    b. 1/10 the sample concentration

    It is not necessary to qualify field blank detections between the MDL and one-half the MRL.

3. **Field duplicates** (one per sampling event for each sampling site) – The RPDs are expected to be less than or equal to 30% when analyte concentrations are greater than twice the MRL. {F} The RPDs are expected to be less than or equal to 50% when analyte concentrations are the MRL and twice the MRL. {F}

IV. Batch Quality Control Samples

1. **Method blank** (one per batch) – The results are expected to be less than the highest of the following {F}:

    a. 1/2 the MRL
    b. 1/10 the sample concentration

    It is not necessary to qualify method blank detections between the MDL and one-half the MRL.

    Method blanks are processed along with and under the same conditions, including all sample preparation steps (i.e. filtering, centrifuging), as the associated samples in the preparation batch.

2. **Laboratory control sample** (one per batch) – Spike with all target (native) analytes.

    Laboratory control samples are processed along with and under the same conditions, including all sample preparation steps (i.e. filtering, centrifuging), as the associated samples in the preparation batch.

    For aqueous and solids batches, spike the LCS at a low range (1 – 2x MRL) in each batch, or the laboratory may rotate spike concentrations between three consecutive batches alternating low range, midrange, and high range. Midrange and high range are relative to the initial calibration range. For aqueous and solid batches, the recoveries are expected to be within 60-135%, except for the low range (1 – 2x MRL) where the recoveries are expected to be within 50-150%. {F}

    For tissue batches, spike the LCS at midrange. For tissue batches the recoveries are expected to be within 60-135% with the following exceptions: for PFHxDA, PFODA, and NMeFOSA, the recoveries are expected to be within 50-135%; for PFDS, PFDoS, and 4:2 FTS, the recoveries are expected to be within 40-135%. {F}

3. **Extracted internal standards (EIS)** – Spike field samples and all quality control samples (preparation and instrument) with internal standards. The recoveries of these internal standards are used to adjust target (native) analyte concentrations. These isotopically labeled internal standards are added to the sample at the very beginning of the procedure, before extraction, centrifuging, filtering or phase separation takes place.

    In order to report quantitative results for the target (native) analytes using the EIS, a minimum signal to noise ratio of 10:1 is expected for each EIS. Do not report results with a qualifier if this minimum is not achieved.

    Except for FOSA, NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE, the EIS recoveries are expected to be within 25-150% in samples. For FOSA, NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE, these EIS recoveries are expected to be within 10-150% in samples. Once enough data points have been collected, the laboratory may develop their own statistical limits for these five EIS in samples. The statistical limits can be different than 10–150% as long as the expected minimum 10:1 signal to noise ratio is maintained for each EIS.

    If any EIS recoveries are outside of limits in a sample, reinject the sample. If the EIS recovery fails again, the data may be reported with a qualifier. {F}

    Use exact isotopically labeled analogs for the EIS where commercially available. As of December 2019, at least 25 of the 36 PFAS for which Wisconsin is offering certification are available as exact isotopically labeled analogs of the target (native) analytes. As of December 2019, the following 11 PFAS do not have exact isotopically labeled analogs commercially available and are therefore not currently necessary: PFTriA, PFODA, PFPeS, PFHpS, PFNS, PFDS, PFDoS, 10:2 FTSA, DONA, 9Cl-PF3ONS, and 11Cl-PF3OUdS.

For these 11 PFAS without an exact isotopically labeled analog commercially available, use an alternate EIS. The alternate EIS is expected to be isotopically labeled and is expected to be a chemically similar analyte that is close in retention time to the target (native) analyte. The alternate EIS may be from the same functional group as the target (native) analyte or have the same chain length as the target (native) analyte (whichever gives better performance). Typically, the alternate EIS comes from those EIS that are already in use. The same EIS can be used for more than one target (native) analyte.

V. Calibration (Initial and Continuing)

1. Perform initial calibration at setup and after an ICV or CCV standard failure. If an ICV or CCV standard fails, the laboratory may immediately analyze two additional consecutive ICV or CCV standards. If either of the two fails, or if immediate analysis is not possible, it is expected that a new initial calibration is performed. If both pass, then sample analysis can continue without a new initial calibration. If a CCV fails high and there are no detections in the associated samples, then analysis can proceed.

2. Initial calibration functions are expected to be as follows:

    a. Calibration factors have an RSD that is less than or equal to 20%.
    b. Linear regressions have a coefficient of determination that is greater than or equal to 0.99 and use a minimum of five non-zero concentration standards.
    c. Quadratic regressions have a coefficient of determination that is greater than or equal to 0.99 and use a minimum of six non-zero concentration standards.
    d. Do not force linear and quadratic regressions through zero.
    e. For each calibration standard, reprocess the target (native) analyte against the chosen calibration function. The reprocessed recoveries are expected to be within 70–130% of their actual concentrations, except for the lowest concentration standard, whose reprocessed recoveries are expected to be within 50–150% of their actual concentrations.

3. It is expected that sample analysis is not performed if the initial calibration fails.

4. Analyze standards of all target (native) analytes and EIS to determine retention times of the linear and branched isomers. Analyze branched isomers that have commercially available standards. As of December 2019, the following PFAS are commercially available as branched isomer analytical (quantitative) standards: PFHxS, PFOS, NMeFOSAA, and NEtFOSAA. As of December 2019, PFOA is commercially available as a branched isomer technical grade (qualitative) standard.

5. When an initial calibration is performed, it is expected that the midrange standard is used to establish absolute retention times. When an initial calibration is not performed, it is expected that the first CCV is used to establish absolute retention times.

6. Retention times of the target (native) analytes and the EIS are expected to fall within 0.4 minutes of the established absolute retention times. Comparison of the target (native) analyte and EIS retention times can help determine if analyte shifts occurred due to matrix effects.

7. **ICV (2nd source)** – It is expected that the ICV is performed with each new initial calibration before sample analysis. The ICV is analyzed after the ICB. As of December 2019, the following PFAS may be difficult to find as second sources and are therefore not currently necessary: PFHxDA, PFODA, PFDoS, NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE. Recoveries in the ICV are expected to be within 70-130%. It is expected that sample analysis is not performed if the ICV fails.

8. **ICB** – It is expected that the ICB is analyzed immediately after the highest standard in the initial calibration and before the ICV to demonstrate the instrument is free from levels of contaminants that would bias results. The results of the ICB are expected to be less than one-half the MRL.

9. **CCV** – It is expected that CCVs are performed at the beginning and end of each analysis batch and after every 10 field samples.

    a. It is expected that the concentrations in the first CCV on non-initial calibration days are at the MRL.
    b. Target (native) analyte recoveries are expected to be within 50-150% for the CCV analyzed at the MRL.
    c. Target (native) analyte recoveries for all other CCVs are expected to be within 70-130%.
    d. It is expected that samples results are only reported when bracketed by passing CCVs unless the recovery failure is high and there are no detections of that analyte in the associated samples.

10. **CCB** – It is expected that the CCB is analyzed immediately after each CCV to demonstrate the instrument is free from levels of contaminants that would bias results. If method blanks or reagent blanks are analyzed after a CCV instead of a CCB, then it is expected that the CCB limits are used for assessment. The results of the CCBs are expected to be less than one-half the MRL.

11. It is expected that the same EIS as those used in samples are added to the initial calibration standards, ICV, CCVs, ICBs, and CCBs at the same concentration used in samples. The calibration standards (initial and continuing) are not extracted like samples. Since there is no matrix effect or extraction performed on these instrument quality control samples, the recoveries of the EIS are expected to be within 50 – 150%.

VI. Aqueous Sample Extraction

1. Extract the entire sample received in the sample container in which it was collected unless the exceptions listed below apply.

    a. Samples received at extremely high PFAS concentrations may be subsampled. {F}
    b. If more sample volume is received than what can be extracted through the solid phase extraction (SPE) cartridge, then subsampling is allowed. {F}

    Adsorption of target (native) analytes to sample collection container walls is known to occur in aqueous samples. Extract the entire aqueous sample volume. Subsampling of aqueous samples from the sample collection container is discouraged and can result in significant loss of longer-chain PFAS (e.g. carboxylic acids ≥ C9, sulfonic acids ≥ C7).

2. Spike the sample in the sample bottle it was received in by adding the EIS. Cap, invert and mix. It is expected that the EIS that are spiked into the sample are provided sufficient time to equilibrate in the sample before further processing. This allows the EIS time to disperse proportionally into the liquid phase and solid phase – same as the target (native) analytes and thereby providing a more accurate result. Add the EIS before any extraction, centrifuging, filtering or phase separation takes place.

    Biphasic and problematic sample matrices may have to use a different spiking procedure. It is best for the laboratory to contact the client prior to spiking and extraction to determine the best course of action to meet their data quality objectives. In these events, include detail in the narrative as to why spiking into the sample bottle was not possible, what was done instead, and if known, the possible effects on the sample results. {F}

3. If particulates in the sample have to be removed before using SPE, centrifuge the sample and take the liquid phase through the SPE. Samples should only be centrifuged when the suspended solids content visually appears to be high enough, by chemist inspection, that it would cause the SPE cartridge to clog.

   The laboratory could consider creating a "percent solids reference sample" that would include the minimum solids the laboratory has tested that would clog the SPE cartridge and use it to compare it to field samples. For reference, the Department of Defense has indicated that samples with percent solids greater than one percent may require centrifuging before performing the SPE procedure. Ideally, the entire sample is extracted, including the suspended solids.

4. If aqueous samples with a solid phase are centrifuged, the solid phase of the sample is expected to be a plug at the bottom of the container. It is expected that the solid phase remains in the container when rinsing the container walls with the polar elution solvent. Rinsing the container walls would therefore also include rinsing of the solids. If the polar elution solvent disrupts the solid phase significantly, the container can be centrifuged again before removing the solvent for use during the elution step of the SPE procedure.

5. If a total sample concentration is needed and there are significant solids in the sample, the initial spike of EIS into the sample container is sufficient for both phases. There is no need to re-spike the solid phase with EIS if it is being extracted separately.

6. Using filters to separate the solid phase from the liquid phase is discouraged unless there is data to demonstrate that the filters used do not result in contamination greater than one-half the MRL.

7. In the cases where a filter is used to separate the solid phase from the liquid phase, it is expected that the filter would also be rinsed to remove any potentially adsorbed PFAS. The filtrate is then added to the SPE cartridge during the elution step.

8. The data quality objectives from the data user should determine whether the solid phase of the sample has to be extracted or not. Not analyzing the solid phase may lead to a low bias in total sample concentration. Analyzing the liquid phase only would provide a liquid sample concentration result. It is expected that the laboratory would make it clear to the data user whether the reported concentrations are a total or liquid concentration sample result.

9. Determine sample volume by marking the sample level on the bottle or by weighing. It is expected that sample volumes would not be measured with a graduated cylinder. Sample volumes are expected to be measured and not assumed by container size.

   When the sample has significant solids, the laboratory should account for the weight or volume displaced by the solids in the initial sample volume determination and include this information in the test report.

10. Use an appropriate SPE cartridge for the target (native) analytes reported. A weak anion exchange cartridge has been shown to work with the PFAS for which Wisconsin is offering certification.

11. One or more rinses of polar solvent can be used for quantitative transfers. Rinse the sample bottle and cap with elution solvent, pour the solvent from each rinse through the SPE cartridge during the elution step, and collect the filtrate for analysis.

12. Bring to a quantitative final volume with the final injection solvent and vortex well.

VII. Non-Aqueous Sample Extraction

1. Homogenize the entire solid sample received in the sample container in which it was collected in by stirring the solids with a clean spatula or other suitable implement. This would help ensure that a representative subsample is taken.

2. For tissues (e.g. fish, wildlife), the target tissue (liver, fillet, whole fish) is isolated from the rest of the tissue sample. The target (isolated) tissue is ground and is typically provided to the analyst as a subsample. At the time of sample preparation, the analyst is to further homogenize the subsample by stirring with a clean spatula or other suitable implement. This would help ensure that a representative subsample is taken.

3. Spike a portion of the homogenized subsample by adding the EIS directly onto the sample. It is expected that the solvent used to carry the EIS spike onto the sample be allowed to evaporate prior to addition of the extraction solution.

4. Extract the PFAS from the non-aqueous samples with an appropriate solution prior to clean-up.

5. Use an appropriate clean-up cartridge (i.e. ENVI-Carb, W-AX, …) to remove the organic analytes extracted from the soil matrix. More than one type of clean-up cartridge can be used.

6. Use a clean-up cartridge on the fish tissue extract to eliminate known interferences with PFOS (e.g. bile acids such as taurodeoxycholic acid (TDCA)).

7. Ensure that all transfers are quantitative by solvent-rinsing with the elution solvent.

8. Bring to a quantitative final volume with the final injection solvent and vortex thoroughly.

VIII. Sample Analysis

1. Use an LC/MS/MS that is capable of negative ion ESI, produces unique product ions within retention time windows, and is able to provide a minimum of 10 scans across each peak.

2. Perform mass calibration such that the range of masses associated with all precursor and product ions are bracketed for both the primary and confirmation transitions. Documentation is expected to be available to demonstrate that the mass calibration covers this range. Calibrate the mass scale using the calibration analytes and procedure from the instrument manufacturer.

3. Analyte identification is performed using retention times, Signal/Noise ratio, Quantitation Parent Ion to Quantitation Daughter Ion (Quantitation Ion Transition), Confirmation Parent Ion to Confirmation Daughter Ion (Confirmation Ion Transition) and the Ion Transition Ratio.

4. Calculate sample results for the target (native) analytes that have exact isotopically labeled standards using isotope dilution (recovery correction using the EIS).

5. Calculate sample results for the target (native) analytes that do not have exact isotopically labeled standards using an alternate extracted isotopically labeled standard and internal standard quantitation recovery correction (recovery correction using the alternate EIS).

6. Use analytical (quantitative) standards containing both branched and linear isomers where commercially available. The analytical branched isomer standards are included in the initial calibration the same as the linear isomer

standards. Branched isomers in samples are quantitated against these analytical branched isomer standards. To calculate the target (native) analyte result, sum the resulting concentrations of all branched and linear isomers that have corresponding analytical standards.

7. Where analytical standards are not available for the branched isomers, use qualitative (technical grade) standards to identify the branched isomer using retention times, transitions, and ion transition ratios. Quantitate target (native) analytes that use qualitative branched isomer standards by integrating the branched and linear isomer peaks and sum the peak areas to get a total area. Calculate the target (native) analyte concentration using the linear isomer.

   Do not include branched isomer peaks in the initial calibration when qualitative standards are used, and do not use calibration functions from the qualitative branched isomer standards to quantitate branch isomer concentrations.

8. It is expected that the target (native) analytes that have exact labeled analogs would elute within 0.1 min of their analogs. {F}

9. Have a written policy on how retention time windows are established.

10. It is expected that the method reporting limit (MRL) concentration would not be below the lowest standard concentration in the initial calibration.

11. The MDL is expected to be less than the MRL.

12. Report sample results and all quality control blank results to the MDL and include the MRL with each result. Qualify results reported between the MDL and MRL as estimated concentrations.

    Example 1: MDL = 0.6, MRL = 2, sample result = 0.4. Report as:

Result	MDL	MRL
<0.6	0.6	2.0

    Example 2: MDL = 0.6, MRL = 2, sample result = 0.8. Report as:

Result	MDL	MRL
0.8 J	0.6	2.0

13. The MDL for PFOS and PFOA in non-potable waters are each expected to be no higher than 2 ng/L.

14. It is expected that high density polyethylene or polypropylene autosampler vials are single injection use only unless they are immediately recapped.

15. It is expected that all sample results are reported from a response that is no higher than the highest response in the initial calibration, except for samples that saturate the instrument. If supplemental EIS is needed to quantitate dilutions, qualify the results that used the supplemental EIS (in this case, true isotope dilution was not achieved).

16. It is expected that sample results that saturate the instrument are reported with “E” flags. {F}

17. For target (native) analytes, the Signal to Noise (S/N) ratio is expected to be greater than or equal to 3:1 for quantitation ions and confirmation ions. If the S/N is not achieved, it is expected that the peak would not be used in any way and the analyte would be reported as “not detected.”

18. All analytes that have two transitions are expected to include two transitions ions in the analysis (precursor ion to quantitation ion and precursor ion to confirmation ion). Use the confirmation ion for positive analyte identification. The department has provided a list of target (native) analytes and confirmation ions in section **XII**, "**Wisconsin Laboratory Accreditation Program PFAS Certification Offerings with Ions,"** of this document.

19. Assess primary and secondary ion transition ratios. It is expected that recoveries be within 50–150% of the value calculated from the midrange standard in the ICAL on ICAL days or from the beginning CCV on non-ICAL days. {F}

    The transition ratio = $\frac{\text{quantitation ion abundance}}{\text{confirmation ion abundance}}$ or $\frac{\text{confirmation ion abundance}}{\text{quantitation ion abundance}}$

    Either ratio protocol presented above can be used, but it is expected that the protocol is consistently used for all analytes.

    When the ion ratio fails, it is expected that the target (native) analytes would still be reported but qualify them as failing the ion ratio. {F} The ion transition ratio can help identify if bias is present. Ratios can be outside of limits due to interferences or the presence of branched isomers that are in the sample but not in the quantitation standards.

20. Document the primary and confirmation transitions and the ion transition ratio.

21. It is expected that the following transitions are used for quantitation of the following analytes [precursor – product] unless a technically justified reason is used and documented:

    a. PFOA 413-369
    b. PFOS 499-80
    c. PFHxS 399-80
    d. PFBS 299-80
    e. 4:2 FTS 327-307
    f. 6:2 FTS 427-407
    g. 8:2 FTS 527-507
    h. NEtFOSAA 584-419
    i. NMeFOSAA 570-419

22. The laboratory is expected to determine at what concentration the instrument has carryover at concentrations greater than one-half the MRL. The laboratory is expected to have a documented procedure to bring the instrument back in control after encountering a sample with carryover. PFAS have demonstrated a delayed release in the system.

23. Report results in acid form.

24. Verify standard purity and ensure that any standards with less than 98% purity are corrected for in the calculations.

25. Mass correct salt content in all calibration standards purchased as salts.

26. Perform a moisture analysis on solid samples (on a subsample different than that used for extraction) and adjust the final concentration of solid samples for the percent moisture.

27. If only the liquid phase of a biphasic sample was extracted, report the results as liquid concentration results instead of total sample concentration results. The lab should report the weight of the solid phase not prepared in this case. This can be detailed in the narrative.

28. If the data quality objective is to obtain a total sample concentration and the sample is biphasic, then extract and analyze both phases.

29. Do not subtract quality control blank values from sample result values.

30. Integrate linear and branched isomers in the samples in the same manner as the standards.

31. Include the following elements in the laboratory SOP:

    a. The extracted internal standards used to calculate the result of each target (native) analyte reported.
    b. The mass used for the precursor ion for each analyte.
    c. The mass used for the product quantitation ion for each analyte.
    d. The mass used for the product confirmation ion for each analyte.
    e. Instructions for conditioning and elution of the SPE cartridge.
    f. Indicate which branched isomers are calculated using the linear isomer standard.

32. PFOA and PFOS WP PT samples are necessary for aqueous (non-potable water) certification of PFOA and PFOS. To obtain the 36-analyte group for aqueous (non-potable water) or non-aqueous from Wisconsin, analyze a PT with a minimum of 6 PFAS that include PFOA and PFOS. It is expected that 80% of the spiked analytes pass.

33. Requirements in NR 149 still apply to this analysis unless otherwise specified in this document.

AS NEW INFORMATION IS PROVIDED BY THE EPA, THIS DOCUMENT WILL BE UPDATED.

IX. Other Considerations

1. Screen a separate aliquot of sample received prior to preparation of a quantitative analysis.
2. Prior to any quantitative analysis, at least one, if not multiple instrument blanks should be analyzed to assess the system for potential contamination. These instrument blanks should include EIS to enable quantitation of the contamination.
3. Evaluate all containers, water, reagents, solvents, materials, SPE cartridges, and equipment as sources of contamination. The lab should be able to demonstrate that these items are not introducing unacceptable positive or negative bias.
4. Supplies should be tested on a lot-by-lot basis.
5. Avoid contact with glassware.
6. Avoid any Teflon including Teflon lined caps.
7. Flush water purification system with 3 liters of reagent water before using.
8. Use LC PEEK tubing and stainless-steel frits.
9. Use polypropylene transfer lines.
10. Replace mobile phase after 48 hours of preparation.
11. Store standards in the containers they were received in and at the storage conditions recommended by the manufacturer.
12. Store solid PFSA standards in a desiccator as they can hydrate over time.
13. PFCA standards in methanol solution may undergo esterification to methyl esters. Ideally, purchase PFCA standard solutions in methanol that contain four mole equivalents of NaOH. Use basic methanol (0.3% NH_4OH v/v in methanol) rather than straight methanol for all standard dilutions to avoid this potential problem.
14. PFSA standards that are ^{18}O-labelled may exchange with water and therefore reducing purity.
15. To establish retention times, analyze individual standards of each analyte. Analyze a mixed standard of all analytes to confirm their separation and identification.
16. Validate each individual standard and labeled standard by analysis to confirm its identity and the absence of significant impurities.
17. Certified standards have been known to vary by as much as 20% between vendors. The laboratory should be able to demonstrate that the standards being used are of known and defensible quality.
18. Some certified standards are less than 90% pure and often contain impurities that are other PFAS being analyzed.
19. EIS should be 96% or greater purity. When the impurity consists of an unlabeled analyte, the EIS can result in a background artifact that is present in every sample, standard, and blank if the EIS is spiked at excessive concentrations.
20. Different certified standards can have different isomer content.
21. Calibration standards are solvent based only. Matrix matched calibration standards (such as those that include sand or fish tissue) should not be used for isotope dilution methods.
22. If the site where samples are being collected is considered a “newer” spill and source apportionment is one of the data quality objectives, ship the samples with dry ice. PFAS transformation can occur if the samples are not frozen.
23. Although matrix spikes and matrix spike duplicates (MS/MSDs) are not necessary, analyzing them would help with assessing measurement bias for those target (native) analytes that do not have exact labeled isotope analogs.
24. Solid samples should not be air dried unless required by a QAPP.
25. Perform solid and fish tissue PT samples.

X. Definitions

Confirmation Ion - one of the fragment ions (product ions) used to help qualitatively confirm presence of the analyte. The product ion chosen is typically one of the remaining ions with high sensitivity and minimum interferences, after the quantitation ion has been chosen. Not all precursor ions provide confirmation ions.

Extraction batch – a set of one to 20 environmental samples of the same certification matrix with a maximum time of 24 hours between the start of processing of the first and last samples in the batch.

Extracted Internal Standards (EIS) - isotopically labeled internal standards that undergo the same extraction and analysis as the other analytes in the sample. The EIS are added to the sample at the very beginning of the procedure before extraction, centrifugation, filtering, or phase separation. Ideally, these are exact isotopically labeled analogs of the target (native) analyte so that identical behavior can be assumed. The recoveries of these standards are used to adjust the target (native) analyte results.

Internal Standard Dilution Quantitation - measurement of native analytes using an alternate analog (surrogate) isotope (one that has the same chemical behavior and is close in retention time to the native analyte) thus providing a close approximation of matrix effects and losses that can occur during the preparatory and analytical procedures. The native analyte concentration is adjusted for the recovery of the alternate analog isotope. An alternate analog isotope is typically used when an exact analog isotope is not available.

Method Detection Limit (MDL) – the minimum measured concentration of a substance that is reported with 99% confidence that the measured concentration is distinguishable from method blank results. The MDL is generated according to the procedure specified in the latest revision of 40 CFR Part 136, Appendix B. The MDL is expected to meet S/N ratio, ion transition ratio, and both quantitation and confirmation ions.

Method Reporting Limit (MRL) – the minimum concentration reported as a quantitative value for a method analyte in a sample following analysis. This defined concentration is expected to be no lower than the concentration of the lowest calibration standard for that analyte and is only used if the recovery in the lowest standard is within 50 – 150%.

Native Analyte - the analyte being tested in the matrix of interest. It is also the analyte for which a result would be reported. It is defined as native to distinguish it from analyte standards added during the test procedure. Native analyte is also referred to as “target analyte” or “reported analyte.”

Precursor Ion – the deprotonated molecule of the analyte. The precursor ion is mass selected and fragmented to produce distinctive product ions of smaller m/z.

Product Ion – one of the fragment ions produced from the precursor ion.

Quantitation Ion – one of the fragment ions (product ions) used to quantitate analyte concentrations. The product ion chosen is typically one of high sensitivity and minimum interferences.

True Isotope Dilution Quantitation – measurement of native analytes using an exact analog (surrogate) isotope of the native analyte thus eliminating differences in chemical behavior. The native analyte concentration is adjusted for the recovery of the exact analog isotope that has been included in the preparatory and analytical procedures.

XI. Wisconsin Laboratory Accreditation Program PFAS Certification Offerings – 5.1.19

#	Acronym	Name	CAS #	# carbons	Acronyms (other)
Carboxylic Acids					
1	PFBA	Perfluorobutanoic acid	375-22-4	4	
2	PFPeA	Perfluoropentanoic acid	2706-90-3	5	
3	PFHxA	Perfluorohexanoic acid	307-24-4	6	
4	PFHpA	Perfluoroheptanoic acid	375-85-9	7	
5	PFOA	Perfluorooctanoic acid	335-67-1	8	
6	PFNA	Perfluorononanoic acid	375-95-1	9	
7	PFDA	Perfluorodecanoic acid	335-76-2	10	
8	PFUnA	Perfluoroundecanoic acid	2058-94-8	11	PFUdA, PFUnDA
9	PFDoA	Perfluorododecanoic acid	307-55-1	12	PFDoDA
10	PFTriA	Perfluorotridecanoic acid	72629-94-8	13	PFTrA, PFTrDA
11	PFTeA	Perfluorotetradecanoic acid	376-06-7	14	PFTeDA
12	PFHxDA	Perfluorohexadecanoic acid	67905-19-5	16	
13	PFODA	Perfluorooctadecanoic acid	16517-11-6	18	
Sulfonic Acids					
14	PFBS	Perfluorobutanesulfonic acid	375-73-5	4	
15	PFPeS	Perfluoropentanesulfonic acid	2706-91-4	5	
16	PFHxS	Perfluorohexanesulfonic acid	355-46-4	6	
17	PFHpS	Perfluoroheptanesulfonic acid	375-92-8	7	
18	PFOS	Perfluorooctanesulfonic acid	1763-23-1	8	
19	PFNS	Perfluorononanesulfonic acid	68259-12-1	9	
20	PFDS	Perfluorodecanesulfonic acid	335-77-3	10	
21	PFDoS	Perfluorododecanesulfonic acid	79780-39-5	12	PFDoDS
22	4:2 FTSA	4:2 Fluorotelomer sulfonic acid	757124-72-4	6	
23	6:2 FTSA	6:2 Fluorotelomer sulfonic acid	27619-97-2	8	
24	8:2 FTSA	8:2 Fluorotelomer sulfonic acid	39108-34-4	10	
25	10:2 FTSA	10:2 Fluorotelomer sulfonic acid	120226-60-0	12	
Sulfonamides, Sulfomidoacetic acids, Sulfonamidoethanols					
26	FOSA	Perfluorooctane sulfonamide	754-91-6	8	PFOSA
27	NMeFOSA	N-Methyl perfluorooctane sulfonamide	31506-32-8	9	MeFOSA
28	NEtFOSA	N-Ethyl perfluorooctane sulfonamide	4151-50-2	10	EtFOSA
29	NMeFOSAA	N-Methyl perfluorooctane sulfonamidoacetic acid	2355-31-9	11	MeFOSAA
30	NEtFOSAA	N-Ethyl perfluorooctane sulfonamidoacetic acid	2991-50-6	12	EtFOSAA

31	NMeFOSE	N-Methyl perfluorooctane sulfonamidoethanol	24448-09-7	11	MeFOSE
32	NEtFOSE	N-Ethyl perfluorooctane sulfonamidoethanol	1691-99-2	12	EtFOSE
Replacement Chemicals					
33	HFPO-DA	Hexafluoropropylene oxide dimer acid [1]	13252-13-6	6	PFPrOPrA
34	DONA	4,8-Dioxa-3H-perfluorononanoic acid [2]	919005-14-4	7	
35	9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid [3]	756426-58-1	8	F-53B Major
36	11Cl-PF3OUdS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid [4]	763051-92-9	10	F-53B Minor

	1 - Also referred to as "GenX"
	2 - Also available as the ammonium salt = ADONA (Ammonium 4,8-dioxa-3H-perfluorononanoate) # 958445-44-8
	3 - Also available as the potassium salt = Potassium, 9-chlorohexadecafluoro-3-oxanone-1-sulfonate # 73606-19-6
	4 - Also available as the potassium salt = Potassium, 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate # 83329-89-9

XII. Wisconsin Laboratory Accreditation Program PFAS Certification Offerings with Ions – 10.27.19

The masses presented are expected to be used, although if other masses are used for the precursor or product ions, the reason is expected to be documented (such as interferences). If the confirmation ion is weak (S/N < 3), it does not have to be used but instrument optimization can increase the S/N.

#	Acronym	Name	CAS #	Precursor Ion Mass	Primary Product Ion Mass	Suggested Confirmation Product Ion Mass
Carboxylic Acids						
1	PFBA	Perfluorobutanoic acid	375-22-4	**213**	**169**	**None**
2	PFPeA	Perfluoropentanoic acid	2706-90-3	**263**	**219**	**69, None**
3	PFHxA	Perfluorohexanoic acid	307-24-4	**313**	**269**	**119**
4	PFHpA	Perfluoroheptanoic acid	375-85-9	**363**	**319**	**169**
5	PFOA	Perfluorooctanoic acid	335-67-1	**413**	**369**	**169**
6	PFNA	Perfluorononanoic acid	375-95-1	**463**	**419**	**219**
7	PFDA	Perfluorodecanoic acid	335-76-2	**513**	**469**	**219**
8	PFUnA	Perfluoroundecanoic acid	2058-94-8	**563**	**519**	**269**
9	PFDoA	Perfluorododecanoic acid	307-55-1	**613**	**569, 319**	**569, 369, 319, 269, 169**
10	PFTriA	Perfluorotridecanoic acid	72629-94-8	**663**	**619**	**369, 319, 269, 169**
11	PFTeA	Perfluorotetradecanoic acid	376-06-7	**713**	**669**	**369, 319, 269, 169**
12	PFHxDA	Perfluorohexadecanoic acid	67905-19-5	**813**	**769**	**369, 319, 269, 219, 169**
13	PFODA	Perfluorooctadecanoic acid	16517-11-6	**913**	**869**	**369, 319, 269, 219, 169**
Sulfonic Acids						
14	PFBS	Perfluorobutanesulfonic acid	375-73-5	**299**	**80**	**99**
15	PFPeS	Perfluoropentanesulfonic acid	2706-91-4	**349**	**80**	**99**
16	PFHxS	Perfluorohexanesulfonic acid	355-46-4	**399**	**80**	**99**
17	PFHpS	Perfluoroheptanesulfonic acid	375-92-8	**449**	**99, 80**	**99, 80**
18	PFOS	Perfluorooctanesulfonic acid	1763-23-1	**499**	**80**	**99**
19	PFNS	Perfluorononanesulfonic acid	68259-12-1	**549**	**80**	**99**
20	PFDS	Perfluorodecanesulfonic acid	335-77-3	**599**	**99, 80**	**99, 80**
21	PFDoS	Perfluorododecanesulfonic acid	79780-39-5	**699**	**80**	**99, 62**
22	4:2 FTSA	4:2 Fluorotelomer sulfonic acid	757124-72-4	**327**	**307**	**81, 80**
23	6:2 FTSA	6:2 Fluorotelomer sulfonic acid	27619-97-2	**427**	**407**	**81, 80**
24	8:2 FTSA	8:2 Fluorotelomer sulfonic acid	39108-34-4	**527**	**507**	**81, 80**
25	10:2 FTSA	10:2 Fluorotelomer sulfonic acid	120226-60-0	**627**	**607**	**587, 81, 80**

Sulfonamides, Sulfomidoacetic acids, Sulfonamidoethanols						
26	FOSA	Perfluorooctane sulfonamide	754-91-6	**498**	**78**	**478, 169, None**
27	NMeFOSA	N-Methyl perfluorooctane sulfonamide	31506-32-8	**512**	**169**	**219**
28	NEtFOSA	N-Ethyl perfluorooctane sulfonamide	4151-50-2	**526**	**169**	**219**
29	NMeFOSAA	N-Methyl perfluorooctane sulfonamidoacetic acid	2355-31-9	**570**	**419**	**512, 483**
30	NEtFOSAA	N-Ethyl perfluorooctane sulfonamidoacetic acid	2991-50-6	**584**	**419**	**526, 483**
31	NMeFOSE	N-Methyl perfluorooctane sulfonamidoethanol	24448-09-7	**616**	**59**	**122, None**
32	NEtFOSE	N-Ethyl perfluorooctane sulfonamidoethanol	1691-99-2	**630**	**59**	**136, None**
Replacement Chemicals						
33	HFPO-DA	Hexafluoropropylene oxide dimer acid	13252-13-6	**329**	**285, 169**	**285, 169, None**
34	DONA	4,8-Dioxa-3H-perfluorononanoic acid	919005-14-4	**377**	**251**	**85, None**
35	9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	756426-58-1	**531**	**351**	**83, None**
36	11Cl-PF3OUdS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	763051-92-9	**631**	**451**	**99, None**

NOTE: ISO 21675, SW 8327, and Wellington Laboratories provide precursor, product and confirmation ions for many of the extracted internal standards

Mass Source
EPA 537.1
DoD QSM 5.3
Janice Willey
EPA-821-R-11-007, PFAS in Sludge/Biosolids
ISO 21675
SW 8327
Wellington Laboratories
Confirmation mass have multiple sources