7.2.6 Non-regenerating PFOA / PFOS reduction testing

This protocol is designed for non-regenerable POU and POE devices using anion exchange media.

7.2.6.1 PFOA / PFOS reduction claim

Claims for PFOA / PFOS reduction may be made when tested in accordance with Section 7.2.6 as long as maximum effluent concentrations in Table 7.A are not exceeded.

Table 7.A – PFOA / PFOS reduction requirements

<table>
<thead>
<tr>
<th>Substance</th>
<th>Influent challenge (mg/L)</th>
<th>Maximum effluent concentration (mg/L)</th>
<th>USEPA method(s)</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA (perfluorooctanoic acid) and PFOS (perfluorooctane sulfonate)(^1)</td>
<td>0.0015 ± 30%</td>
<td>0.00007(^2)</td>
<td></td>
<td>PFOA and PFOS</td>
</tr>
<tr>
<td>PIPAA (as N)</td>
<td>10 ± 10%</td>
<td>Influent &lt;20%</td>
<td>300</td>
<td>N/A</td>
</tr>
</tbody>
</table>

\(^1\) Influent challenge levels for PFOS were based on the upper percentile concentration per EPA's UCMR3 occurrence data (2013-2015) (the concentration for which there is high probability [P <0.01] that 99 percent of the population will be exposed to waters of lower concentration). Influent challenge levels for PFOA were based on the upper percentile concentration of private well and public water supply sampling in Hoosick Falls New York (the concentration for which there is high probability [P <0.10] that 90 percent of the population will be exposed to waters of lower concentration). This influent concentration is higher than the maximum concentration per EPA's UCMR3 occurrence data (2013-2015). PFOS and PFOA will be added gravimetrically in a ratio of 5 parts PFOA to 10 parts PFOS by weight to achieve the total influent concentration.

\(^2\) Total of both PFOS and PFOA. Based on USEPA Health Advisory level which includes a margin of protection for the most sensitive populations.

7.2.6.2 Apparatus

Refer to 7.1.2 Figure 2 for an example of the test apparatus.

7.2.6.3 Analytical methods

All analyses shall be conducted in accordance with the applicable methods referenced in Section 2.

7.2.6.4 Premature filter plugging

If a product prematurely plugs prior to the completion of the required test volume, the volume of the final sample point collected prior to plugging becomes the final test volume to determine capacity.

Applicable actions to remediate premature filter plugging for this tests method are contained in Annex H, Sections H.1, H.2, H.3, and H.6.

7.2.6.5 PFOA / PFOS reduction test water

a) A water supply shall be treated by reverse osmosis, then shall be treated by deionization (RO/DI) water and shall have a conductivity of less than 2 µS / cm.
b) All chemical additions shall take place either after the test tank is filled with the RO/DI water, or while the test tank is being filled. Reagent grade chemicals shall be used for all additions to adjust the RO/DI water to meet the following specific characteristics:

| Parameter           | Target value | Overall average tolerance | Single point tolerance
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_4^{2-}$</td>
<td>200 mg/L</td>
<td>± 20%</td>
<td>± 30%</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>10 mg/L</td>
<td>± 10%</td>
<td>± 20%</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>100 mg/L</td>
<td>± 20%</td>
<td>± 30%</td>
</tr>
<tr>
<td>alkalinity as CaCO$_3$</td>
<td>200 mg/L</td>
<td>± 20%</td>
<td>± 30%</td>
</tr>
<tr>
<td>PFOA</td>
<td>0.0005 mg/L</td>
<td>± 10%</td>
<td>± 20%</td>
</tr>
<tr>
<td>PFOS</td>
<td>0.0010 mg/L</td>
<td>± 10%</td>
<td>± 20%</td>
</tr>
<tr>
<td>temperature</td>
<td>20 °C (68 °F)</td>
<td>± 2.5 °C (± 5 °F)</td>
<td>—</td>
</tr>
<tr>
<td>turbidity</td>
<td>&lt; 1 NTU</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>pH</td>
<td>7.5</td>
<td>± 0.5</td>
<td>—</td>
</tr>
</tbody>
</table>

1 Equals average influent challenge concentration variability plus one of the following, in order of availability:
1. Acceptable continuing calibration verification (CCV) limits stated in the appropriate USEPA method.
2. Acceptable spike recoveries as stated in the appropriate USEPA method.
3. Opinion of laboratory professionals - no guidance available in USEPA method.

\[ PFOA = \text{Perfluorooctanoic acid} \]
\[ PFOS = \text{Perfluorooctanesulfonic acid} \]

\[ \text{NaHCO}_3 \]
\[ \text{NaCl} \]

Table 7.B – PFOA / PFOS influent water characteristics

\[ \text{NaOH} \]

\[ \text{MgSO}_4 \]

\[ \text{HCl} \]

\[ \text{NaNO}_3 \]

\[ \text{CaCO}_3 \]

\[ \text{H}_2 \text{O} \]

c) Dissolve enough sodium bicarbonate (NaHCO$_3$) in RO/DI water to achieve a test tank concentration of 336 mg/L NaHCO$_3$. This should be equivalent to 200 mg/L of alkalinity expressed as CaCO$_3$. Stir and transfer the solution to the test tank.

d) Adjust the pH of the test tank solution using hydrochloric acid (HCl) or sodium hydroxide (NaOH) to 7.5 ± 0.5. Record the amount HCl used.

e) Dissolve enough magnesium sulfate (MgSO$_4$·7H$_2$O) in RO/DI water to achieve test tank concentrations of 200 mg/L. Sodium Sulfate (NaSO$_4$·7H$_2$O) may be substituted for 75% of the magnesium sulfate if the presence of hardness interferes with the proper operation of the device under test.

f) Dissolve enough NaNO$_3$ in the RO/DI water to achieve 69 mg/L of sodium nitrate. This shall produce 10 mg/L nitrate nitrogen.

g) Dissolve enough perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid PFOS in RO/DI water to achieve test tank concentration of 0.0005 mg/L of PFOA and 0.0010 mg/L of PFOS

h) Mix and measure the final pH, and adjust as needed. Mixing shall be minimized thereafter throughout the duration of the test.

i) Dissolve enough sodium chloride (NaCl) in RO/DI water to achieve a test tank concentration of 100 mg/L of chloride. Balance this number with the amount of chlorides added from the HCl for pH control to maintain a target of 100 mg/L. Stir and transfer to the test tank.

j) Each tank of water prepared shall have all of the parameters specified in Table 7.B verified by analytical methods.
7.2.6.6 Cycle time

The systems shall be operated on a 50%-on / 50%-off cycle basis with a 15 to 40 min cycle, up to 16 h per 24 h period, followed by an 8 h rest under pressure (a 10%-on / 90%-off cycle may be used if requested by the manufacturer for POU systems but for POE systems only 50%-on / 50%-off cycle shall be used).

7.2.6.7 Method – POU

Two systems shall be conditioned using the PFOA / PFOS reduction water specified in Section 7.2.6.5 with the test contaminant present. The conditioning volume shall be excluded from the volume measured as the influent challenge volume for capacity and sample point determination.

7.2.6.7.1 Plumbed-in systems without reservoirs and all faucet-mounted systems

Two systems shall be conditioned in accordance with the manufacturer’s instructions and Section 7.2.6.7.

The systems shall be tested using the influent challenge water at the maximum flow rate attainable by setting an initial dynamic pressure of 410 ± 20 kPa (60 ± 3 psi). The pressure shall not be readjusted although the system may experience some change in dynamic pressure. The operating cycle specified in Section 7.2.6.6 shall be used.

7.2.6.7.1.1 Refrigerator filters without integral flow control

Chemical reduction testing for refrigerator filters without an integral automatic fixed flow-rate control shall be performed at a controlled flow rate that is equal to or greater than the rated service flow of the refrigerator filter system and refrigerator plumbing.

7.2.6.7.1.2 Refrigerator filters without integral flow control, with water dispenser and ice maker

If the refrigerator filter does not include an integral automatic fixed flow-rate control, and supplies water to both a water dispenser and an ice maker, then any chemical reduction testing shall be performed at a controlled flow rate equal to or greater than the tested flow rate of the icemaker or the tested flow rate of the water dispenser, whichever is greater.

7.2.6.7.2 Plumbed-in systems with reservoirs

Two systems shall be conditioned in accordance with the manufacturer’s instructions and Section 7.2.6.7.

The system shall be tested using the influent challenge water at the maximum flow rate attainable by setting an initial dynamic pressure of 410 ± 20 kPa (60 ± 3 psi). The pressure shall be readjusted although the system may experience some change in dynamic pressure. Where the design of the system does not lend itself to the operating cycle specified in Section 7.2.6.6, the operating cycle shall be a repetitive complete filling and emptying of the reservoir. It is acceptable to run this cycle continuously for 24 h per day.
7.2.6.7.3 Nonplumbed pour-through-type batch treatment systems

Two systems shall be conditioned in accordance with the manufacturer’s instructions and Section 7.2.6.7.

If the effluent reservoir capacity is equal or greater than two times the volume of the influent reservoir, multiple successive influent reservoir fills shall be performed until the remaining volume in the effluent reservoir is less than the influent reservoir volume. The resulting volume for each filling of the effluent reservoir shall be the batch volume. If the volume of the effluent reservoir is less than two times the volume of the influent reservoir, the batch volume shall be the influent reservoir volume.

Example:

<table>
<thead>
<tr>
<th>Influent volume (L)</th>
<th>Effluent volume (L)</th>
<th>Batch (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.8</td>
<td>1.0</td>
</tr>
<tr>
<td>1.2</td>
<td>2.5</td>
<td>2.4</td>
</tr>
<tr>
<td>1.4</td>
<td>4.0</td>
<td>2.8</td>
</tr>
</tbody>
</table>

7.2.6.7.3.1 Systems with a manufacturer’s recommended use pattern

Two systems shall be tested using the appropriate influent challenge water using the manufacturer’s use pattern. The use pattern shall include information about the rest period between the fillings. The rest period after the influent reservoir has drained given by the manufacturer shall not exceed 75 min and include a tolerance of at least ± 15 min. The systems shall be operated up to 16 h per 24 h period, followed by an 8 h rest period. Exceptions to the rest period are permissible for laboratory operational needs (e.g., water preparation, equipment malfunctions).

7.2.6.7.3.2 Systems without a manufacturer’s recommended use pattern

Two systems shall be tested using the appropriate influent challenge water. The systems shall be operated up to 16 h per 24 h period, followed by an 8 h rest period. The test cycle shall include a rest period of 30 to 90 min after the influent reservoir has drained. The total volume per day shall be limited to 10 batches. Exceptions to the rest period are permissible for laboratory operational needs (e.g., water preparation, equipment malfunctions).

7.2.6.7.3.3 Mouth drawn drinking water treatment units

Products meeting the definition for mouth drawn drinking water treatment unit shall be evaluated using the method specified in Annex F.

Two systems shall be conditioned in accordance with the manufacturer’s instructions and Section 7.2.6.7

7.2.6.7.3.4 Squeeze bottle drinking water treatment units

Products meeting the definition for squeeze drawn drinking water treatment unit shall be evaluated using the method specified in Annex G.

Two systems shall be conditioned in accordance with the manufacturer’s instructions and Section 7.2.6.7

7.2.6.8 Method – POE – Full scale units
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Two systems shall be conditioned in accordance with the manufacturer's instructions using the PFOA / PFOS reduction water specified in Section 7.2.6.5. The systems shall be tested using the influent challenge water (Section 7.2.6.5) at the rated service flow at an initial dynamic pressure of 410 ± 20 kPa (60 ± 3 psi). The pressure shall not be readjusted although the system may experience some change in dynamic pressure. The flow rate shall be controlled to the rated service flow or the maximum flow rate achievable through the entire test, but if the flow rate cannot be maintained at greater than 25% of the rated service flow, the test shall be terminated. The operating cycle specified in Section 7.2.6.6 shall be used.

7.2.6.9 Sampling

The effluent of the test system shall be sampled after a minimum of one bed volume has passed through the column or ½ of the cycle ON time has passed, whichever is greater.

7.2.6.9.1 Inorganic sampling – Nitrate nitrogen

For systems with performance-indication devices, influent and effluent samples shall be collected for nitrate nitrogen analysis at 5%, 10%, 15%, 20%, 25%, 50%, 75%, 100%, and 120% of the estimated capacity. For systems without performance indication device, influent and effluent samples shall be collected for nitrate analysis at 5%, 10%, 15%, 20%, 25%, 50%, 75%, 100%, 180% and 200% of the estimated capacity.

7.2.6.9.2 PFOA and PFOS

For systems with performance-indication devices, during the "on" portion of the cycle, influent and effluent samples shall be collected for PFOA and PFOS analysis at the start of the test (after the passage of 10 unit volumes) and at 25%, 50%, 75%, 100%, and 120% of the estimated capacity. For systems without performance indication device, during the "on" portion of the cycle, influent and effluent samples shall be collected for PFOA and PFOS analysis at the start of the test (after the passage of 10 unit volumes) and at 50%, 100%, 150%, 180% and 200% of the estimated capacity.
Annex F
(normative)

Test method for PFOA and PFOS
by LC/MS in Electrospray Negative Ionization Mode

F.1 Summary of method

PFOA and PFOS are direct injected on to the analytical column. The analytes are then analyzed by LC/MS/MS in electrospray negative mode.

F.2 Definitions

F.2.1 internal stock standard solution (ISS): A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source that is added to all of the samples at a constant concentration.

F.2.2 stock standard solution (SS): A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

F.2.3 working calibration standard (WCS): A solution prepared from the stock standard solution. The calibration solutions are used to calibrate the instrument response with respect to analyte concentration.

F.2.4 matrix spike (MS): A quality control sample composed of a known amount of standard is added to a sample before the analysis to access the effect the matrix has on the performance of measurement process.

F.2.5 matrix spike duplicate (MSD): A quality control sample composed of a known amount of standard is added to a sample, analyzed with a matrix spike to access the effect the matrix has on the precision of the measurement process.

F.2.6 continuing calibration verification (CCV): An analytical standard prepared from the same source as the calibration curve that is analyzed periodically after the sample to verify the accuracy of the existing calibration of the analytes.

F.2.7 limit of detection (LOD): The lowest detection of a substance that can be distinguished from the absence of that substance within a stated confidence limit.

F.3 Interferences

Interferences can occur depending on the composition of the sample water.
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F.4 Safety

Before attempting this procedure, the analyst should be familiar with the proper operation of the LCMS system and the data acquisition systems or should be closely supervised by an experienced analyst.

The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard. Exposure to these chemicals should be minimized.

F.5 Reagents

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Description</th>
<th>Catalog No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Analytical balance</td>
<td>Mettler Toledo XS105 or equivalent</td>
</tr>
<tr>
<td>1</td>
<td>Vortex genie</td>
<td>Fisher #12-812 or equivalent</td>
</tr>
<tr>
<td>1</td>
<td>Sonicator</td>
<td>WWR #75T or equivalent</td>
</tr>
<tr>
<td>1</td>
<td>Pipette 2-20 ul</td>
<td>Biohit Serial #8508399 or equivalent</td>
</tr>
<tr>
<td>1</td>
<td>Pipette 20-200 ul</td>
<td>Biohit Serial #8520007 or equivalent</td>
</tr>
<tr>
<td>1</td>
<td>Pipette 100-1000 ul</td>
<td>Biohit Serial #8514462 or equivalent</td>
</tr>
<tr>
<td>1</td>
<td>Pipette 10 mL</td>
<td>Eppendorf Serial #4360944 or equivalent</td>
</tr>
<tr>
<td>As needed</td>
<td>40 mL VOC vial and caps</td>
<td>VWR or equivalent</td>
</tr>
<tr>
<td>As needed</td>
<td>8 mL amber vial and caps</td>
<td>VWR #66010-482 or equivalent</td>
</tr>
<tr>
<td>As needed</td>
<td>Graduated cylinders</td>
<td>VWR or equivalent</td>
</tr>
<tr>
<td>As needed</td>
<td>Erlenmeyer flasks</td>
<td>VWR #89001-952 or equivalent</td>
</tr>
<tr>
<td>As needed</td>
<td>100 mL volumetric flasks with PTFE stoppers</td>
<td>VWR #89001-956 or equivalent</td>
</tr>
<tr>
<td>As needed</td>
<td>10 mL volumetric flasks with PTFE stoppers</td>
<td>VWR #89001-956 or equivalent</td>
</tr>
<tr>
<td>As needed</td>
<td>5/4&quot; Disposable Transfer pipettes</td>
<td>VWR #14672-200 or equivalent</td>
</tr>
<tr>
<td>As needed</td>
<td>Optima LCMS Methanol</td>
<td>Fisher Scientific A456-4 or equivalent</td>
</tr>
<tr>
<td>1</td>
<td>Stir Plate</td>
<td>Corning Serial #440933 or equivalent</td>
</tr>
<tr>
<td>As needed</td>
<td>Autosampler vials with pre-slit caps</td>
<td>Phenomenex #AHO-7507 or equivalent</td>
</tr>
<tr>
<td>1</td>
<td>triple quadrupole mass spectrometer</td>
<td>Thermo TSQ Vantage or equivalent</td>
</tr>
<tr>
<td>1</td>
<td>UPLC and autosampler</td>
<td>Thermo Transced TLX2 or equivalent</td>
</tr>
<tr>
<td>As needed</td>
<td>XBridge C18 5 (\mu)m (3.0 x 50 mm) analytical column</td>
<td>Waters #186003112 or equivalent</td>
</tr>
<tr>
<td>As needed</td>
<td>Optima LCMS Water</td>
<td>Optima LCMS Water Fisher Scientific W6-4 or equivalent</td>
</tr>
<tr>
<td>As needed</td>
<td>Ammonium Acetate &gt;=99%</td>
<td>Sigma Aldrich 17836 or equivalent</td>
</tr>
<tr>
<td>As needed</td>
<td>Mobile Phase Bottle</td>
<td>Fisherbrand FB-800-100 or equivalent</td>
</tr>
</tbody>
</table>

NOTE — See Table 8 for list of chemical standards

F.5.1 Eluting pump mobile phase B (methanol)
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- Add 1000 mL of Optima LCMS methanol or equivalent to a mobile phase bottle.
- Label with contents and preparation date. Solution is viable for up to one month at room temperature.

F.5.2 Eluting Pump mobile phase A (10mm ammonium acetate in optima LCMS water)
- Add 1000 mL of Optima LCMS water or equivalent to a mobile phase bottle.
- Add 0.7708g of Ammonium Acetate to Optima LCMS water in mobile phase bottle and shake.
- Label with contents and preparation date. Solution is viable for up to one week at room temperature.

F.5.3 Preparation of Standards

F.5.3.1 Preparation of 2000 μg/mL stock standard(s)
- Stock standards from pure reference standards
- Add about 20 mg of the reference standard to a 40 mL VOC vial, recording actual mass.
- Adjust mass based upon purity and salt content.
- Add 10.0 mL of Optima methanol and vortex, or sonicate as necessary to dissolve.
- Calculate the concentration by the following equation:

\[
\text{concentration}[\mu g/mL] = \left( \frac{\text{mass}[mg]}{10mL} \right) \times \left( \frac{1000\mu g}{1mg} \right) \times \left( \frac{\text{Purity}[:]}{100} \right) \times \left( \frac{\text{FW of free base or acid}}{\text{FW of salt}} \right)
\]

F.5.3.2 Stock standards from solution
- Many stock standards are available as a 1.0 mg/mL solution from commercial vendors. The analyst has the option of using them if they choose.
- Prepare secondary stock standard in methanol as needed using the following equation:

\[ (C_1)(V_1) = (C_2)(V_2) \]

Where:
- \( C_1 \) = concentration of stock standard (ng/mL)
- \( V_1 \) = volume of stock standard (mL)
- \( C_2 \) = concentration of working standard (ng/mL)
- \( V_2 \) = volume of working standard (mL)

F.5.3.3 Preparation of 20 μg/L PFOA and PFOS stock standard (SS) compounds in Optima water
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--- Prepare a stock standard (SS) as specified in Table L.1. The analyst shall make dilutions of the 2000 µg/mL individual primary stock solutions to the 20 µg/mL solutions used in Table 1. The analyst has the option of preparing the 20 µg/ml Stock Standard Solution Mixture using other analytical dilution protocols.

--- Add 40 ml of Optima Water to a vial.

--- Using the table below, prepare each calibration standard by adding appropriate aliquot volume for each standard to the 40 mL VOC vial.

--- Label with contents and preparation date. Solution is viable for 6 months.

--- Store Solution in 40 mL VOC vial at -20°C.

Table F.1 - Negative pharma compounds stock standard preparation (SS) – Optima water

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (µg/mL)</th>
<th>Alquot (µL)</th>
<th>Final volume (mL)</th>
<th>Final Concentration (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA</td>
<td>20</td>
<td>40</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>PFOS</td>
<td>20</td>
<td>40</td>
<td>40</td>
<td>20</td>
</tr>
</tbody>
</table>

F.5.3.4 Preparation of 1000 µg/mL Individual Internal standard stock solutions.

--- Stock Internal Standards from pure reference standards

--- Add about 10 mg of the Internal Standard to a 40 mL VOC vial, recording actual mass.

--- Adjust mass based upon purity and salt content.

--- Add 10.0 ml of Optima methanol and vortex or sonicate as necessary to dissolve.

--- Calculate the concentration by the following the equation in F.5.3.1. The analyst will need to dilute the 1000 µg/mL individual Internal Standard stock solutions to a concentration of 1000 ng/mL to be used in Table 2. The analyst has the option of preparing the 1000 ng/L Stock Standard Solution Mixture using other analytical dilution protocols.

F.5.3.5 Preparation of 2000 ng/L Internal Standard Mixture in 95/5 (v/v) Optima water/methanol

--- Using Table F.2 below. Prepare the internal standard mixture by adding appropriate aliquot volume for each individual internal standard to a 40ml VOC vial.

--- Add 38.64 ml of diluent 95/5 (v/v) Optima water/methanol. Stir to mix.

--- Label with contents and preparation date. The Internal Standard solution is viable until a noticeable decrease in response is observed.

--- Store Solution at 4°C.
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Table F.2 - Internal standard solution preparation - Optima water

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (ng/mL)</th>
<th>Aliquot (µL)</th>
<th>Final volume (mL)</th>
<th>Final Concentration (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA-13C8</td>
<td>1000</td>
<td>80</td>
<td>40</td>
<td>2000</td>
</tr>
<tr>
<td>PFOS-13C8</td>
<td>1000</td>
<td>80</td>
<td>40</td>
<td>2000</td>
</tr>
</tbody>
</table>

F.5.3.6 Preparation of PFOA and PFOS working standard (WCS).

— Use the PFOA and PFOS stock standard (SS) prepared in F.5.3.4 to prepare working standards in Table F.3.

— Prepare each working standard by adding appropriate aliquot volume and diluent for each standard to a 40 mL VOA.

— Label with contents and preparation date. Solution is viable for 1 month or when a noticeable decrease in response is observed.

— Store Solution in 40 mL VOA vial at 4°C.

Table F.3: PFOA and PFOS working calibration standard solutions (WCS) – optima water

<table>
<thead>
<tr>
<th>Standard ID</th>
<th>Spike conc. (µg/L)</th>
<th>Aliquot volume (µL)</th>
<th>Final volume (mL)</th>
<th>Final concentration (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>20 µg/L</td>
<td>2000</td>
<td>40</td>
<td>1000</td>
</tr>
<tr>
<td>500</td>
<td>20 µg/L</td>
<td>1000</td>
<td>40</td>
<td>500</td>
</tr>
<tr>
<td>250</td>
<td>20 µg/L</td>
<td>500</td>
<td>40</td>
<td>250</td>
</tr>
<tr>
<td>100</td>
<td>20 µg/L</td>
<td>200</td>
<td>40</td>
<td>100</td>
</tr>
<tr>
<td>50</td>
<td>20 µg/L</td>
<td>100</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>20</td>
<td>20 µg/L</td>
<td>40</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>10</td>
<td>20 µg/L</td>
<td>20</td>
<td>40</td>
<td>10</td>
</tr>
</tbody>
</table>

F.5.3.7 Preparation of Matrix Spike Samples

— Preparation of matrix spike samples in effluent sample water.

— Prepare a matrix spike (MS) and matrix spike duplicate (MSD) from one of the effluent samples.

— Prepare the matrix spike (MS) and matrix spike duplicate (MSD) to a concentration of 350 ng/L using the 20 ng/mL Pharma compound stock standard (SS).
F.5.4 Sample collection, preservation, and storage

Samples shall be preserved with 8 to 10 mg of sodium thiosulfate per 125 mL of sample at time of sampling. Samples are stored at 4°C.

F.5.4.1 Standard, sample, and blank preparation

F.5.4.2 Standard Preparation

— Pipette 1800 μL of standards into a 2-mL autosampler vial for each standard.
— Pipette 100 μL of the 2000 ng/L internal standard solution to each of the standards.
— Pipette 9 μL of concentrated formic acid into each vial.
— Vortex all standards for 15 seconds.
— Inject sample into LC/MS/MS.

F.5.4.3 Sample and blank preparation

— Pipette 1800 μL of blank Optima water and samples into a 2-mL autosampler vial.
— Pipette 100 μL of the 2000 ng/L internal standard solution to each of blanks and samples in the 2-mL autosampler vial.
— Pipette 9 μL of concentrated formic acid into each vial.
— Vortex all standards, blanks, and samples for 15 seconds.
— Inject samples into LC/MS/MS.

F.5.4.4 LC/MS/MS instrument conditions

Example run conditions are listed below for LC-MS-MS analysis performed with a Thermo Scientific Transcend TLX-2 Turbulent Flow system interfaced with Thermo Scientific TSQ Quantiva triple quadrupole mass spectrometer using SRM in negative mode. Analysts are encouraged to optimize specific conditions for their instrument configuration.

— Negative pharma compounds chromatographic conditions:
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- Analytical column: Waters Xbridge C18.5μm (3.0 x 50 mm)
- Injection volume: 2000 μL
- Mobile phase eluting pump:
  - 10 mM Ammonium Acetate in Optima water
  - Optima methanol
- TSQ Vantage Ion Source Setting:

**Table F.4 – Turbulent flow and UPLC conditions for negative PFOA and PFOS analysis**

<table>
<thead>
<tr>
<th>Load pump (Pharma)</th>
<th>Eluting pump (pharma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start</td>
<td>Seconds</td>
</tr>
<tr>
<td>0.00</td>
<td>25</td>
</tr>
<tr>
<td>0.42</td>
<td>400</td>
</tr>
<tr>
<td>7.08</td>
<td>60</td>
</tr>
<tr>
<td>8.08</td>
<td>60</td>
</tr>
<tr>
<td>9.08</td>
<td>260</td>
</tr>
<tr>
<td>13.42</td>
<td>240</td>
</tr>
</tbody>
</table>

Total method duration – 17.42 minutes

- Spray Voltage: 2500 volts
- Vaporizer Temperature: 400 degrees C
- Sheath Gas Pressure: 50
- Aux Gas Pressure: 11
- Ion Transfer Tube: 350 degrees C
- Declustering Voltage: 0
- Polarity: ES

**Table F.5 - MS Compound dependent parameters**

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS #</th>
<th>Supplier</th>
<th>MRM transition</th>
<th>Dwell (sec)</th>
<th>Collision energy</th>
<th>S-Lens</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA</td>
<td>335-67-1</td>
<td>Sigma Aldrich</td>
<td>413.02 &gt; 369.11</td>
<td>0.05</td>
<td>10</td>
<td>52</td>
</tr>
<tr>
<td>PFOA - 13C8</td>
<td>NA</td>
<td>Cambridge Isotopes</td>
<td>421.05 &gt; 376.11</td>
<td>0.05</td>
<td>10</td>
<td>55</td>
</tr>
<tr>
<td>PFOS</td>
<td>1763-23-1</td>
<td>Sigma Aldrich</td>
<td>498.99 &gt; 80.22</td>
<td>0.05</td>
<td>46</td>
<td>160</td>
</tr>
<tr>
<td>PFOS - 13C8</td>
<td>NA</td>
<td>Cambridge Isotopes</td>
<td>507.03 &gt; 80.22</td>
<td>0.05</td>
<td>46</td>
<td>160</td>
</tr>
</tbody>
</table>

**F.5.5 Sample analysis**
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--- Analyze four control blanks to condition the system, then the calibration standards, reagent blank, LFB, Second source, a blank, the samples, a matrix spike (MS) and matrix spike duplicated (MSD), and continuing calibration verification (CCV) at a minimum for every 10 samples being analyzed.

--- The sample concentrations are estimated using internal standard (least squares linear regression) with a $1/X^2$ weighting.

F.5.6. Report limit determination

--- The report limit is determined by the following equation:

\[
\text{Report Limit} = \frac{\text{ng}}{\text{L}} = \text{Low standard concentration} \times \text{Dilution}
\]

F.5.7 Quality control

--- Calibration criteria for quantitative analysis

--- Each sample batch run will contain a minimum of 3 calibration standards. If the lowest standard is excluded, the reporting limits will be adjusted accordingly.

--- The calibration curve correlation coefficient 0.995 or better. Or $R^2 \geq 0.99$.

--- A method blank will be run after calibration standards. The area ratio for any peak present in the retention window of a target analyte should be less than 80% of the area ratio of the lowest standard. We have found background levels of compounds of interest in the method reagents that may sometimes affect our ability to meet this requirement.

--- If the method blank area ratio is greater than 80% of the area ratio of the lowest standard, and no samples are greater than the lowest standard, then note and report.

--- If the method blank area ratio is greater than 80% of the area ratio of the lowest standard, and the samples concentration is greater than the method blank, then reanalyze the method blank. If it is again greater than 80% of the lowest standard, investigate the cause of the failure and re-analyze the samples.

--- Acceptance criteria for quality control samples.

--- Percent recoveries for MS and MSD are calculated. Average percent recoveries should fall within established control limits or $\pm 30\%$ if control limits have not been established.

\[
\% \text{ recovery} = \frac{\text{observed value} - \text{nominal value}}{\text{nominal value}} \times 100\%
\]
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— The relative percent difference (RPD) for MS and MSD are calculated:
RPDs should fall within established control limits or ± 30% if control limits have not been established:

\[ RPD = \frac{(MS - MSD)}{(MS + MSD)} \times 20 \]

— A Bracket standard (CCV) prepared at a midrange concentration will be run after every ten samples. The percent recovery for the bracket standard should be within ±20%.

**F.5.8 Peer review**

All data shall be subject to appropriate peer review to ensure data integrity and compliance with QC criteria outlined in F.5.7.

Any deviations from the above procedure shall be documented.