A Method for the Determination of 30 PFAS in Diverse Human and Animal Foods by LC-MS/MS

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Abstract

Per- and polyfluoroalkyl substances (PFAS) are a class of persistent, bioaccumulative synthetic compounds of growing international concern due to their potential human health and ecological effects [1-5]. This study presents the development and single-laboratory validation of an LC-MS/MS method for the simultaneous determination of 30 PFAS in diverse human and animal food matrices. Sample preparation employs a modified QuEChERS liquid-liquid extraction followed by dispersive solid-phase extraction (dSPE) and solid-phase extraction (SPE) cleanup [6-7]. Three preparation options were developed to accommodate matrices spanning a wide range of moisture content, with historical applications including fruits and vegetables (Option 1), dry pet foods and cooked foods (Option 2), and agricultural products (Option 3).

Validation was conducted across 15 matrices—including clam, lettuce, whole and chocolate milk, eggs, bread, cooked salmon, dry and wet cat and dog foods, chicken feed, alfalfa, corn flour, and corn silage—using duplicate spike recovery experiments at six concentration levels (0.05–5 ng/g). Quantitation employed a partial isotope dilution scheme using 16 isotopically labeled surrogate internal standards, with four additional recovery internal standards added prior to instrumental analysis to monitor extraction efficiency [8]. Initial calibration across eight concentration levels (0.01–25 ng/mL) demonstrated excellent linearity ($r^2 \geq 0.990$) for all analytes. Acceptable spike recoveries (40–120%) were achieved for the majority of analytes across most matrices, with notable exceptions for long-chain sulfonic acids in bread and dry dog food, and persistent contamination issues with 6:2 FTS. Method detection limits (MDLs) were calculated per 40 CFR Appendix B to Part 136 Revision 2 [9] for both method blanks and spiked samples.

Selectivity was demonstrated by chromatographic resolution of three cholic acid interferents (TCDCA, TDCA, TUDCA) from PFOS. Method performance was confirmed through proficiency testing coordinated by the Australian National Measurement Institute (NMI) [10], the U.S. National Institute of Standards and Technology (NIST) [11], and the European Union Reference Laboratory (EURL) [12], yielding consistently acceptable z-scores across multiple years, sample types, and analytes, with an overall average z-score of −0.04 across 208 NMI determinations.

Key Words

PFAS, QuEChERS, SPE, LC-MS/MS

Introduction

Valued for being both hydrophobic and lipophobic, per- and polyfluoroalkyl substances (PFAS) are a class of compounds manufactured for decades and thus useful for a variety of applications. Concern has grown internationally about their persistence, bioaccumulation, and possible human health and ecological effects [1-5].

With expected sample load to include Total Diet Study (TDS) samples [13-14], and a variety of human and animal foods and food ingredients, the method was designed for use in diverse matrices and accordingly validated in a total of 15 matrices. This work is built upon a previous ARHAFL method (LIB4676) validated in a variety of animal foods and forage [15], the then current FDA compendium method (C010.02), which has now been updated to C-010.03 [16], a then unpublished CFSAN method for animal forage (Supplement S1_Silage new protocol 12_10_20), and incorporates an expanded target analyte list. Method performance data is presented herein with conclusions on the validity of the method across the 15 matrices examined.

Also reported are the laboratory's performance on subsequent proficiency test samples (2023, 2024, 2025) [17-19], with lab code numbers of 8, 10 and 18 respectively as well as interlaboratory studies coordinated by the U.S. National Institute of Standards and Technology (NIST), and the European Union Reference Laboratory.

Materials and Methods

Equipment

a. HPLC – Agilent Technologies, 1260 series (Santa Clara, CA)
b. Mass Spectrometer (MS) – Sciex 6500+ triple quadrupole equipped with electrospray ionization (Framingham, MA)
c. HPLC Analytical column – Phenomenex Gemini 3µm, 150mm x 2mm C18 column (Torrance, CA)

d. HPLC Guard column holder and cartridges – Phenomenex SecurityGuard holder and SecurityGuard cartridges, PS C18, 4 mm x 2.0 mm ID
e. HPLC Delay column – Phenomenex Luna 5µm, 50mm x 3mm C18(2) or Gemini 3µm, 50mm x 3mm C18
f. Balance with 0.01 g readability – Sartorius BP 1200 (Bohemia, NY)
g. Sample homogenization – Waring commercial blender pre-rinsed with house reverse osmosis water and methanol (McConnellsburg, PA)
h. Shaker 2010 Geno/Grinder (Spex SamplePrep, Metuchen, NJ)
i. Shaker – Glas-Col digital pulse mixer/vortexer (Terre Haute, IN)
j. Vortexer – Scientific Industries, Inc. Vortex-Genie 2 (Bohemia, NY)
k. Centrifuge – Thermo Fisher Scientific Sorvall legend XFR centrifuge (Waltham, MA)
l. Nitrogen evaporation system – Organomation N-EVAP 24 position nitrogen evaporator (Berlin, MA)
m. Pipettes – Eppendorf Research Plus (0.5 – 10 µL, 10 – 100 µL, 20 – 200 µL, 100 – 1000 µL) (Enfield, CT)
n. Pipette Tips – Eppendorf epT.I.P.S. (0.1 – 10 µL, 2 - 200 µL, 0.05 – 1 mL, and 0.5 – 5 mL)
o. Disposable plastic transfer pipettes (polypropylene; 5.6 and 7.7 mL sizes) – VWR (Radnor, PA)
p. Corning 50 mL polypropylene (PP) conical centrifuge tubes – Thermo Fisher Scientific
q. Corning 15 mL polypropylene (PP) conical centrifuge tubes – Thermo Fisher Scientific
r. Target DP Vial, PP, 300µL – Thermo Fisher Scientific
s. AVCS Clear Membrane Autosampler Caps – Thermo Fisher Scientific
t. Nano filter vials 0.2 µm nylon – Thomson Instrument Company (Oceanside, CA)
u. SPE cartridge – Phenomenex 6 mL Strata-XL-AW 100µm Polymeric Weak Anion SPE Cartridge, 200mg, 50/pk tubes
v. SPE Manifold - Agilent Positive Pressure Manifold 48 Processor (PPM-48)

Test Product

The alfalfa, chicken feed, milk, dry cat food, dry dog food, lettuce, wet cat food, and wet dog food were consumer products purchased from local retailers. The bread, eggs, and chocolate milk were surplus materials prepared by the Kansas City Human and Animal Food Laboratory (KCHAFL) for the Total Dietary Study (TDS) and shipped to ARHAFL. Clam and corn flour were materials originally received by other ARHAFL programs for routine analysis. The corn silage was generously donated by the Arkansas Department of Corrections.

Reagents and Standards

a. Formic acid, reagent grade – Sigma Aldrich (St. Louis, MO)
b. Water, Optima LC/MS grade – Thermo Fisher Scientific

c. Acetonitrile, Optima LC/MS grade - Thermo Fisher Scientific
d. Methanol, HPLC grade - Thermo Fisher Scientific
e. Ammonium acetate, HPLC grade – Thermo Fisher Scientific
f. Ammonium hydroxide certified ACS Plus 14.8N - Thermo Fisher Scientific
g. Native PFAS standard mix (FDA-30MX) – Wellington Laboratories (Guelph, ON, Canada)
h. Isotopically labelled internal standard mix (FDA-12MPFAS) – Wellington Laboratories
i. Sodium 1,1,2,2-D_4-perfluoro-(1,2-$^{13}C_2$)hexanesulfonate (D_4-$^{13}C_2$-4:2 FTS) – Cambridge Isotope Laboratories, Inc. (Tewksbury, MA)
j. Sodium 1,1,2,2-D_4-perfluoro-(1,2-$^{13}C_2$)octanesulfonate (D_4-$^{13}C_2$-6:2 FTS) – Cambridge Isotope Laboratories
k. Sodium 1,1,2,2-D_4-perfluoro-(1,2-$^{13}C_2$)decanesulfonate (D_4-$^{13}C_2$-8:2 FTS) – Cambridge Isotope Laboratories
l. Sodium 1,1,2,2-D_4-perfluoro-(1,2-$^{13}C_2$)dodecanesulfonate (D_4-$^{13}C_2$-10:2 FTS) – Cambridge Isotope Laboratories
m. Perfluoro-n-(1,2,3,4-$^{13}C_4$)octanoic acid (M4PFOA) – Wellington Laboratories
n. Sodium perfluoro-1-(1,2,3,4-$^{13}C_4$)octanesulfonate (M4PFOS) – Wellington Laboratories
o. N-ethyl-D_5-perfluoro-1-octanesulfonamidoacetic acid (D_5-N-EtFOSAA) – Wellington Laboratories
p. Perfluoro-n-(1,2,3,4,5,6,7-$^{13}C_7$)undecanoic acid (M7PFUnA) – Wellington Laboratories
q. Perfluorooctanoic acid, technical mixture containing branched and linear isomers (T-PFOA) – Wellington Laboratories
r. Taurochenodeoxycholic acid (TCDCA) – Ambeed, Inc. (Arlington Heights, IL),
s. Taurodeoxycholic acid (TDCA) – Sigma-Aldrich
t. Tauroursodeoxycholic acid (TUDCA) – EMD Millipore Corp. (Burlington, MA).

Procedures

1. Analytical Standards

   PFAS native and isotopically labelled compounds were purchased from either Wellington Laboratories (Guelph, ON, Canada), or Cambridge Isotope Laboratories, Inc. (Tewksbury, MA). Taurochenodeoxycholic acid (TCDCA) was purchased from Ambeed, Inc. (Arlington Heights, IL), taurodeoxycholic acid (TDCA) from Sigma-Aldrich, Co. (St. Louis, MO), and tauroursodeoxycholic acid (TUDCA) from EMD Millipore Corp. (Burlington, MA).

   Thirty target analytes (Table 1) were evaluated during the study. These targets were received premixed by Wellington (item FDA-30MX - nominal concentration 1000 ng/mL, +/-5% in methanol/isopropanol (2%)/water (<1%)). The product certificate of

analysis (Supplement S2_CoA FDA30) shows actual concentration and form for each component. Working stock solutions were prepared at 100 ng/mL and 10 ng/mL and used to spiking sample matrix as well as calibration standards. Only the linear isomer of each target compound was present in the mix except for PFOS, which included branched and linear isomers. A dilution of a technical PFOA standard (branched and linear isomers) with methanol was prepared to establish the retention times for the branched isomers of this compound.

The determination experiment is a partial isotope dilution scheme using sixteen isotopically labeled surrogate internal standards (Table 2). Twelve of the surrogates were received premixed from Wellington (item FDA-12MPFAS - nominal concentration 2000 ng/mL, +/-5% in methanol/isopropanol (4%)/water (<1%)) while the four labelled FTS compounds (only available from Cambridge) were purchased as individual solutions. A surrogate (SUR) stock solution at 200 ng/mL was prepared by combining 1 mL of the FDA-12MPFAS mix with 0.04 mL of each of the FTS standard solutions (nominal 50,000 ng/mL) and diluting to a final volume of 10mL with methanol.

Four labelled compounds (Table 3) were added as recovery internal standards to the sample just prior to instrumental analysis to evaluate extraction efficiency. A recovery standard (RS) stock solution at 100 ng/mL was prepared by combining 0.02 mL of each of the standard solutions (50,000 ng/mL) and diluting to a final volume of 10 mL with methanol.

Calibration solutions were prepared at eight native concentrations and are shown in Table 4. In addition, solutions of the cholic acids in methanol were prepared at approximately 1 ng/mL for use in establishing their retention times.

2. Mobile Phase and Reagent Preparation

a. 0.6% (v/v) (0.3% (w/v)) Ammonium Hydroxide in Methanol Solution

Add 6 mL of concentrated (14.8 N) ammonium hydroxide to 1000 mL of methanol.

b. 0.05 M Formic Acid in 50:50 Water:Methanol

Spike 1 mL concentrated formic acid into a bottle containing 250 mL LC-MS water and 250 mL LC-MS methanol.

c. Stock 5 M Ammonium Acetate Solution

Weigh 3.85 g of LC-MS-grade ammonium acetate. Dilute to 10 mL with water. Vortex to mix.

d. Mobile Phase A: 5 mM Ammonium Acetate (aq)

Spike 500 µL of the stock 5 M ammonium acetate solution into 500 mL of LC-MS Optima water.

e. Mobile Phase B: 5 mM Ammonium Acetate in 50:50 Methanol:Acetonitrile
Spike 500 µL of the stock 5 M ammonium acetate solution into 500 mL of LC-MS methanol

3. Sample Extraction and Cleanup

QuEChERS Extraction

Note - sample handling*: QuEChERS is a liquid/liquid (water/acetonitrile) extraction technique. Sufficient water is added prior to extraction to wet the sample. After extraction, a salt mixture is added to partition the liquids into separate layers. The water added to wet the sample should be sufficient to produce an excess of water, but not enough so that the salt mixture is completely dissolved.*

The procedure uses three options (shown in Table 5 below) with regards to sample size and amount of added water.

1) If the analyst doesn't have previous experience with a sample, determine the appropriate preparation option using the sample properties and the following tests:

Test 1:

- Is the sample a liquid, colloid, or mechanically homogenizable slurry? [e.g. fruit and vegetable juices, milk etc.] OR
- Does product labelling or literature indicate water content above ~75%? OR
- After homogenization of a solid sample, does it exhibit considerable moisture content? (i.e. does it resemble a liquid or a slurry (e.g. lettuce), or a paste with moisture separating (e.g. wet pet food) after standing for 60s? OR
- After the addition of 5 mL of water and agitation (QuEChERS Extraction, step 6), does the sample dissolve (syrup, honey), the mixture resembles a slurry, or show free-standing water?

If any of the above is true, use Option 1 else continue.

Test 2: Prepare a sample using Option 2 conditions.

- At QuEChERS Extraction, if the matrix swells to the point that mixing in the tube is compromised in step 6, no liquid/liquid bi-layer forms after step 10 etc. (refer to Note - sample handling) OR
- QC checks on surrogate recoveries in duplicate sample preps fail.

If any of the above is true, prepare a sample using Option 3.

Note – workflow recommendation*: If the sample doesn't obviously fall under Option 1, use Case 2 as initial default. If the analyst observes qualitative differences outside their normal experience for Option 2 with an unfamiliar matrix, prepare the sample by Option 3.*

2) Weigh the appropriate amount of homogenized sample from Table 5 into a 50 mL PP centrifuge tube.

a. Prepare one method blank for each prep option represented in the batch with an equivalent amount of water (assume density of 1 g/mL) added in lieu of the sample.

3) Spike with 10 ng of the surrogates (50 µL of 200 $ng \cdot mL^{-1}$ SUR) to make a final concentration of 1 $ng \cdot mL^{-1}$ surrogates in the supernatant.

4) Wait for 30-60 minutes to allow the surrogates to incorporate into the matrix.

5) Add the appropriate amount of water from Table 5 to the tube.

6) Shake vigorously for 1 minute on the Genogrinder, then shake for 30 minutes on the Glas-Col shaker at 900 rpm and 70% pulse to swell the matrix.

7) Add 150 µL of formic acid and 10 mL of acetonitrile.

8) Vigorously shake 1 minute on the Genogrinder.

9) Add QuEChERS salts and vigorously shake for 5 minutes on the Genogrinder

Note - shaking*: Salt pack will clump (vortexing is not violent enough to break up clumps), specifically visually verify that the salts are finely separated after shaking.*

10) Centrifuge for 5 minutes at 10,000 rcf and 15°C.

dSPE cleanup

1) Remove supernatant from QuEChERS extraction and add to a tube containing 150 mg graphitized carbon black (GCB) and 900 mg $MgSO_4$.

2) Agitate the mixture on the vortexer for ~15-30 seconds to suspend the solids and then shake for ~1 minute on the Glas-Col shaker at 900 rpm and 70% pulse.

3) Centrifuge for 5 minutes at 10,000 rcf and 15°C.

4) Transfer supernatant from the dSPE cleanup to a 15 mL PP centrifuge tube.

a) For 5 g sample size preps, transfer 1 mL of supernatant and proceed to step 4.

b) For 1 g sample size preps, transfer 5 mL of supernatant; concentrate the extract to ~1 mL under a gentle stream of nitrogen from a N-Evap (temperature 60 °C) and then proceed to step 4.

5) Dilute the supernatant with 4 mL water.

SPE cleanup

Note – manifold flow: *All flow rates described below are ~ 0.5-1.5 mL per minute or 1-2 drops per second.*

1) Condition SPE cartridge using 6 mL 0.3 % (w/v) NH_4OH in methanol.

2) Condition SPE cartridge using 6 mL HPLC grade H_2O.

3) Load the diluted sample from step 5 of the dSPE cleanup onto the cartridge.

4) Wash with 6 mL HPLC grade H_2O.

5) Wash with 6 mL 0.05 M formic acid in 50:50 water:methanol.

6) Continue to pass nitrogen through the cartridge for ~1 minute to dry it.

7) Place a clean 15 mL PP centrifuge tube under the SPE cartridge.

8) For elution, rinse the tube which previously contained the diluted sample with two 2 mL portions of 0.3% (w/v) NH_4OH in methanol, adding each rinsate to the SPE cartridge.

9) Continue to pass nitrogen through the cartridge until all the eluent has been transferred to the tube.

10) Place under N-Evap (temperature 60 °C) and evaporate to just under 1 mL.

11) Spike with 1 ng recovery standard mixture; bring up to 1 mL with methanol and vortex.

12) Transfer a portion to 0.2 µm filter autosampler vials.

The sample is now ready for instrumental analysis.

4. Instrumental Analysis

A Sciex 6500+ triple quadrupole mass spectrometer (MS/MS) coupled with an Agilent 1260 Infinity II high performance liquid chromatography (HPLC) system was

used for this study. A copy of the instrument acquisition method can be found in Supplement S3_ARL PFAS SLV_Gemini Method_8.17.2022. The LC was modified before use to reduce potential PFAS background. All fluorinated ethylene-propylene (FEP) tubing was replaced with polyetheretherketone (PEEK); stock pump seals were replaced with polyethylene normal phase seals; the stock auto-sampler switching rotor was replaced with a PEEK version; and a delay column (Phenomenex Luna C18(2) 5µm, 50mm x 3mm or Gemini C18 3µm, 50mm x 3mm) was installed between the eluent mixer and the autosampler.

Separation was carried out on a Phenomenex Gemini C18 column (3µm, 150mm x 2mm) with the column compartment at 40°C. Mobile phase A consisted of aqueous 5mM ammonium acetate and mobile phase B was 5mM ammonium acetate in 1:1 methanol/acetonitrile. The elution gradient and flows are shown in Table 6. All injections were 5µL.

Instrument acquisition was controlled with Sciex Analyst 1.7.1 software. Electrospray Ionization (ESI) was utilized. The source was operated in negative mode with a capillary voltage of -3500V, and a temperature of 350°C. Ultra-high purity nitrogen was used as the source (GS1 – 40 psi, GS2 -30 psi), curtain (30 psi), and collision gas (9 psi).

The mass spectrometer was operated in scheduled multiple reaction monitoring (sMRM) mode. Table 7 shows parent and product ions, declustering potential (DP), entrance potential (EP), collision energy (CE), and collision cell exit potential (CXP). The target scan time per MRM was set to 1.4707 seconds with acquisition windows set to 120sec except for analytes with branched isomers which were set to 240sec.

5. Data Processing

All data processing was performed using Sciex OS (versions 1.6.1.29803 and 2.1.6) software. A copy of the data processing method can be found in Supplement S4_2022 SLV Processing Method.

Qualitative confirmation of analyte identity is accomplished by monitoring ion ratios (area of qualitative transition/area of quantitative transition), and retention times. Measured ion ratios are evaluated against the expected ratios (an average calculated from all calibration standards) using a variable tolerance scheme shown in Table 8 [20]. Analyte retention times in validation samples were required to be within 2% of the corresponding retention time in the processing method reference standard. Peaks with signal to noise (S/N) ratios ≥ 10 which also meet ion ratio and retention time tests are considered positive detects.

Eight calibration standard solutions were prepared with native concentrations of 0.01, 0.05, 0.1, 0.5, 1, 5, 10, and 25 ng/mL. For PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFUdS, PFDoS, ADONA, 11-Cl-PF3ONS, 9-Cl-PF3ONS, 4:2 FTS, 6:2 FTS, 8:2 FTS, and 10:2 FTS these concentrations reflect the salt forms used to prepare the standard. Concentrations in the calibration table were corrected to reflect the concentration of the analytes in their acid form by multiplying the nominal concentration times the ratio of molecular weight of acid form divided by the molecular weight of the salt form. Surrogate internal standards and recovery internal standard concentrations were kept constant at 1 ng/mL. Calibration standards were injected in order of least to greatest concentration.

Calibration was accomplished using native peak area data fit to a linear calibration model weighted at 1/x and the fit forced through the origin. Analyte/surrogate internal standard pairings are given in Table 9. Quantitative transitions were previously noted in the MS/MS parameters (Table 7). For analytes with two monitored transitions the qualitative transition also received a calibration fit but determinations are only reported from quantitative transition data.

Surrogate internal standards are entered twice in the calibration table. The first entry is as an internal standard and used to calculate concentrations of associated natives. The second entry is as a surrogate for evaluating extraction efficiency. The mean response ratio of surrogate to recovery standard is used to calculate surrogate recovery with SUR/RS pairings shown in Table 10.

If data for an analyte did not pass qualitative requirements in the low-level standard (calculated concentrations outside ± 50% of the theoretical, missing peak in a quantitative trace, or failed ion ratio), the data point was excluded (‘Used’ box unchecked in the peak table). This evaluation was repeated until the lower limit of quantitation (LLOQ) was established for each analyte.

Both linear and branched alkane isomers of some PFAS can be expected in samples. Most of the target analyte determinations are for only the target’s linear alkane isomer. However, determinations for PFOA, and PFOS represent the sum of branched and linear isomers. For these compounds each quantitative and qualitative transition is entered in the calibration twice. One pair of entries is for the linear isomer only (entries prefixed with “L_”) while the second pair is the sum of branched plus linear isomers (entries prefixed with “Br_”). For the “L_” entries, only the linear isomer peak is integrated and used to generate the ion ratio for qualitative evaluation.

For the “Br_” entries, integration parameters were adjusted to integrate the branched and linear isomers as a single area. To accomplish this, the Peak Noise setting was decreased from the default 40 to 10, and the Peak Splitting factor was increased from the default 2 to 20. An example chromatogram for PFOS with integration shaded in

the mid-level calibration standard is shown in Figure 1. Manual integration was still sometimes required for low level standards or samples. Start and stop integration times from the automatic integration were noted from a mid-level calibration standard and used to guide the manual integration. Tracking of manual integrations was automatic by Sciex OS. Compound determinations are typically only reported from the qualitative transition data of the "Br_" entry and not the "L_".

PFOS was present in the FDA-30MX native solution as a mix of branched and linear isomers while PFOA was present only as the linear isomer. A technical PFOA (T-PFOA) mix of branched and linear isomers was acquired separately and used to establish the retention times of branched isomers for this compound.

Note - PFBA, and PFPeA: *each have only a single MRM transition to monitor, thus ion ratio evaluation was not applicable to these analytes. Because they lack two transitions, these analytes do not meet the minimum FDA requirements for identification in an LC-MS/MS method. Detections for these analytes by this method should be confirmed by a second validated method or appropriately qualified in test reports. In addition, because of the summed integration approach to analytes with branched and linear isomers, ion ratios for these targets are not especially useful in real samples as the ratio of isomers may vary from that in the standard. Consequently, the identification of all components included in the integration for these targets may also not meet normal FDA minimum requirements. However, for purposes of this study determinations for these target analytes in laboratory spiked samples are reported as if they met normal minimum requirements for identification.*

Three cholic acids have been recognized as possible interferents in the determination of PFOS. Taurochenodeoxycholic acid (TCDCA), taurodeoxycholic acid (TDCA), and tauroursodeoxycholic acid (TUDCA) have molecular weights <1 amu from the PFOS [M-H]- (499 m/z) parent ion. Additionally, each contains a sulfonate group and generates the same sulfite radical anion (80 m/z) monitored as the product for PFOS determinations. If not chromatographically resolved from PFOS, they can generate a false positive or bias high determination. Solutions of certified reference materials for the three cholic acids were acquired to demonstrate their separation from PFOS.

Results and Discussion

Validation Criteria:

The validation follows requirements of Guidelines for the Validation of Chemical Methods in Food, Feed, Cosmetics, and Veterinary Products, 3rd Edition, U.S. Food and Drug Administration Foods Program, October 2019 [23] (FVM Guidelines hereafter), Level Two (non-emergency, single laboratory) validation criteria. The FVM Guidelines state, "Validation of new quantitative methods should include at a minimum evaluation of the following performance characteristics: accuracy, precision, selectivity, limit of detection, limit of quantitation, linearity

(or other calibration model), range, measurement uncertainty, ruggedness, confirmation of identity and spike recovery." Spike recovery requirements for a Level Two validation are ≥2 replicates at ≥3 spike levels for ≥3 matrices plus a matrix blank, with acceptable recoveries in the range of 40-120%. Recovery spikes were performed in duplicate at six different spike levels (0.05, 0.15, 0.5, 1.5, 2, and 5ng PFAS/g of sample) in fifteen different matrices: clams (fresh), lettuce, milk (chocolate), milk (whole), wet cat food, wet dog food, chicken feed, corn flour, dry cat food, dry dog food, egg (scrambled), bread, salmon (cooked), alfalfa, silage (corn).

Chromatography:

An example chromatogram from a CS5 calibration standard is shown above in Figure 2. EPA Method 537.1 [21] was previously verified at ARHAFL for PFAS determinations in bottled water samples and has a peak asymmetry requirement for the chromatographic system. As an assessment of the current system, peak asymmetries were calculated according to the equation given in section 9.3.9 of EPA method 537.1 [21] (Figure 3). Calculations for PFOA and PFOS are based on measurements of the respective linear isomer peak only.

Acceptable asymmetry values for the EPA method are 0.8-1.5. All analytes in the present study show good symmetry by this evaluation. Retention times and peak asymmetry values from a CS5 standard in the initial calibration are shown in Table 11.

Initial Calibration:

A copy of the complete calibration results can be found in Supplement S5_20220817_calcurve_sciex template. After applying qualitative requirements to the standard data, PFPeA, PFHxA, PFHpA, PFNA, PFDoA, HFPO-DA, PFHpS, PFDS, PFOSA, 4:2 FTS, and 6:2 FTS had lower limits of quantitation (LLOQ) set to 0.05 ng/mL; all other analytes had LLOQs at the lowest calibration point of 0.01 ng/mL.

All qualitative transition data showed excellent linearity over the calibration range (LLOQ-25ng/mL). Correlation coefficients (r) and coefficient of determination (r^2) values for the calibration fit are shown in Table 12 with all r^2 values exceeding the minimum requirement (≥0.990) for multi analyte/matrix methods.

The calculated analyte concentration divided by the theoretical concentration (expressed as a percentage) was used to assess the accuracy of the calibration. Results are shown in Table 13 below. The accuracy of all the calculated values was within ±30% of the true value for all concentrations above the LLOQ.

Internal standard concentrations in each calibration standard are constant. The relative standard deviation (%RSD) of the areas across all standards was evaluated as an additional precision check on standard preparation, and instrument acquisition and shown below in Table 14.

Identify retention times of PFOA branched vs. linear isomers from a qualitative standard:

Due to the lack of branched PFOA isomers in the calibration standards, identification of the retention times for the branched isomers is necessary to properly integrate PFOA so that determinations represent the sum of branched and linear isomers. The retention times of branched PFOA isomers were identified with each calibration by injecting a technical standard diluted to approximately 1 ng/mL. Figure 4 shows the extracted ion chromatogram for the T-PFOA standard. The linear isomer is the latest to elute (~16.4 minutes) while the earliest branched isomer begins at just after 15 minutes with the major branched components centering around 15.7 minutes.

Selectivity: Resolution between PFOS and cholic acids (TCDCA, TDCA, and TUDCA):

Three cholic acids have been recognized as possible interferents in the determination of PFOS: Taurochenodeoxycholic acid (TCDCA), taurodeoxycholic acid (TDCA), and tauroursodeoxycholic acid (TUDCA). Solutions of the certified reference materials were prepared in methanol and chromatograms of the three compounds were acquired separately. Figure 5 shows an overlay of the three chromatograms.

Accuracy and Precision:

While replicate recovery spikes in matrix provides accuracy and precision data analogous to performance in samples, baseline accuracy and precision for this method was also evaluated sans matrix using spiked method blanks. Three sets of seven native spikes each were fortified at 1 ng PFAS/mL and extracted by each of the three sample preparation options. Accuracy for the three sample preparation options, expressed as average recovery, and precision, expressed as %RSD, is shown in Table 15. For Sample Prep 2 (“5x15”), one of the replicates was identified as an outlier by the Grubb’s test and data is presented both with and without the outlier.

EPA Methods 537.1 [21] and 533 [8] each require an initial demonstration of accuracy and precision using four to seven laboratory fortified blanks to be extracted near the midpoint concentration of the calibration which is similar on procedure to our accuracy and precision baseline. The EPA methods require the average recovery to be ±30% of the true value for accuracy, and the RSD must be less than 20% for precision. Evaluated against those requirements, this extraction and cleanup procedure shows good analyte recovery, excellent repeatability, and little if any bias across analyte chemistries. Box plots of the data with additional detail can be viewed in Supplement S6_Box Plots of Accuracy & Precision Data.

Matrix Blanks:

Reports for all matrix blanks are included in Supplements S7A-Q.

Recovery Spikes:

All fifteen matrices were spiked in duplicate at 0.05, 0.15, 0.5, 1.5, 2, and 5ng PFAS/g of sample, extracted, and evaluated for analyte recovery. A summary of the preparation option(s)

used for each matrix is given in Table 16. Two matrices, bread and salmon, were chosen to receive evaluation by both prep option 2 ("5x15") and option 3 ("1x15").

The FVM Guidelines give 40-120% as an acceptable range of recovery for spikes at method level of 1 part per billion. Results for each spike extraction can be found in Tables 17-33.

MDL/LOQ Evaluation:

Method detection limits (MDL) were calculated per method given in 40 CFR Appendix B to Part 136 Revision 2 [9] where the MDL is defined as "the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results." The procedure requires a minimum of seven method blanks and seven spiked method blanks in at least three batches extracted on at least three separate calendar days and analyzed on at least three separate calendar days. For this study, 10 method blanks were extracted and analyzed by Prep Option 1, 13 by Option 2, and 12 by Option 3. Seven spiked method blanks (0.15 ng PFAS/g of sample) were also extracted by each of the prep options and analyzed. Minimum batch numbers, separate extraction days, and separate analysis days all met or exceeded procedural requirements.

In brief, where the calculated concentration of an analyte in all method blanks is non-zero, a MDL_b value was calculated by multiplying the standard deviation of the concentrations by a coverage factor. Where some but not all concentrations were non-zero, the MDL_b for the analyte is taken to be the max value measured. Where all concentrations were zero, a MDL_b was not applicable. A MDL_s was calculated by multiplying the standard deviation of the analyte's calculated concentration in the spikes by a coverage factor. Finally, the greater of the MDL_s and MDL_b values was taken to be the initial analyte MDL. A summary of this work is shown in Table 34.

In addition, matrix specific MDL values were also determined for all the foods evaluated. Seven or more spikes meeting the procedure's minimum batch numbers, separate extraction days, and separate analysis days were prepared. The results are summarized in Tables 35-37. MDL values were determined for salmon using both Prep Option 2 and 3. Several MDL values denote coming from a spike level of 0.5 ng PFAS/g of sample due to failed qualitative criteria for detection at the 0.15 ng PFAS/g of sample. Several values are also denote coming from as analyte MDL_b values because they were greater than the matrix MDL value from the spikes.

Finally, LOQ values were calculated from the spiked method blank and spiked matrix data as ten times the standard deviation of the calculated concentrations and summarized in Tables 38-40.

Ruggedness:

All extractions were carried out in the same location, lab B118, and were performed by two different analysts both with experience with using QuEChERS, SPE for extraction, and LC-MS/MS analysis. Instrument acquisitions were performed in lab B148 on a single instrument.

Two calibrations were performed during the work and used in data processing. Data analysis was carried out by three different analysts. The analyses were performed across between 08/11/2022 and 09/21/2022 covering multiple days of the week and work hours.

Measurement Uncertainty:

An estimation of the measurement uncertainty was made using the following procedure. The accuracies from the duplicate 0.5, 1.5, 2, and 5 ng/g matrix spikes in clam, lettuce, whole milk, and salmon (5g) were pooled resulting in 40 data points per analyte. The average, standard deviation, and relative standard deviation were calculated for each analyte from the pooled data. The uncertainty was calculated at a 95% confidence level by multiplying the RSD by a coverage factor (k) where k=2.0227 (*t*-value, 95% confidence level, 39 degrees of freedom). Estimated measurement uncertainties are given in Table 41.

Interlaboratory Samples

1. Australian National Measurement Institute (NMI): PT in Food and Biota

   The NMI lab is accredited to ISO 17043 as a proficiency provider. There are few suppliers of PT samples for food matrices. Surplus materials from past NMI PT studies had been utilized in method development and evaluation by ARHAFL in the past so it was natural to utilize them as a provider. Typically, three samples per food PT cycle are offered. Bulk material is spiked by the laboratory with a variety of analytes, homogenized, and tested for stability and homogeneity before being portioned and dispatched to laboratories participating in the study. The ARHAFL three-year NMI Performance History report is available in Supplemental S8 but summarized here.

   AQA 23-15 Lab Code 8 (2023) [17]

   S1: Fish paste – 25 determinations reported ranging in z-score from -0.19 (linear PFHxS) to 1.06 (PFTeDA) with a median value of 0.12.

   S2: Spinach puree – 24 determinations reported ranging in z-score from -1.27 (6:2FTS) to 0.9 (ADONA) with a median value of -0.4.

   S3: Bovine liver paste – 25 determinations reported ranging in z-score from -0.83 (PFOS sum) to 0.08 (analyte) with a median value of -0.26.

   AQA 24-14 Lab Code 10 (2024) [18]

   S1: Prawn paste – 23 determinations reported ranging in z-score from -2.46 (PFUdA) to -0.31 (PFBA) with a median value of -1.7.

   S2: Carrot puree – 19 determinations reported ranging in z-score from -0.71 (PFBS) to 0.67 (PFDA) with a median value of -0.03.

S3: Milk powder – 22 determinations reported ranging in z-score from 0.04 (PFUdA) to 1.95 (PFBA) with a median value of 0.97.

AQA 25-11 Lab Code 18 (2025) [19]

S1: Fish paste – 24 determinations reported ranging in z-score from -0.4 (PFHpA) to 0.89 (PFDS) with a median value of 0.01.

S2: Fruit puree (50% banana, 50% apple) – 23 determinations reported ranging in z-score from -0.95 (PFNA) to 0.97 (PFDS) with a median value of -0.35.

S3: Infant formula – 23 determinations reported ranging in z-score from zero (linear PFHxS) to 2.0 (PFHxA) with a median value of 0.85.

Over the three years of participation, 208 total determinations have been reported with no false positives. Conversely there have been no false negatives. The average z-score for the period is -0.04 indicating that across multiple years and sample types there is little inherent technical bias in the method.

Questionable z-scores for PFUdA, and PFTeDA (-2.21) in prawn paste (24-14, S1) led to an investigation. Due to limited reserve sample and unavailability of surplus sample from NMI, limited conclusions could be drawn. However, it was noted that labs using acetonitrile as an extraction solvent showed bias low results with this sample.

Due to Agency emphasis on these types of products, we draw special attention to the results for the milk powder (24-14, S3) and infant formula (25-11, S3) samples. Here the assigned values were bias low versus spike values by an average of -17.6% in the milk powder, and -17.3% in the infant formula. Individual bias ranges from -5.4% (PFDA) to -29.7% (10:2FTS) in the milk powder, and from +6.6% (PFDA) to -42.6% (PFHxA) in the infant formula. However, our results compared favorably versus the spike values with an average bias of -0.9% (median -3.2%) in milk powder and -3.3% in infant formula (median -3.7%). The final report notes that Laboratory 18 (ARHAFL), “achieved the highest recovery of spiked analytes in the infant formula sample (S3)” and that along with Laboratory 14 (which also pretreated the sample with reagent water) “recovered a higher percentage of the spiked analytes in the infant formula sample S3 than most other laboratories.”

2. NIST: Food Nutrition and Safety Measurements Quality Assurance Program (FNSQAP) Exercise 3 (2023)

   Assessments include Z'_{comm} (Z score with respect to community consensus) and Z_{NIST} (Z score with respect to NIST value) with scores $|Z| \leq 2$ being acceptable.

   RGTM 10225 PFAS in Bovine Milk

Two analytes were reported: PFNA (0.22 ng/g) and PFOS (0.528 ng/g). Both results fell within acceptable performance ranges, with Z'_{comm} scores of 0.7 and 0.8, respectively, and Z_{NIST} scores of -0.7 and 1.4, respectively.

RGTM 10226 PFAS in Chicken Egg

Four analytes were reported: PFHxS (0.259 ng/g), PFNA (15.5 ng/g), PFOA (8.68 ng/g), and PFOS (28.8 ng/g). All Z'_{comm} and Z_{NIST} scores ranged from -0.1 to 1.4.

RM 8695 PFAS in Bovine Tissue

Four analytes were reported: PFHxS (0.070 ng/g), PFNA (1.66 ng/g), PFOA (0.74 ng/g), and PFOS (22.4 ng/g). Scores ranged from -0.1 to 0.8 for Z'_{comm} and -0.5 to 0.8 for Z_{NIST}.

3. EURL: EURL-ILS-BCF_2403-PIM (2024)

Powdered Infant Milk / Formula

ARHAFL reported a total-PFOS result of 0.166 µg/kg against an assigned value of 0.164 µg/kg, yielding a z-score of +0.1. For PFOA, the lab reported 0.284 µg/kg compared to the assigned value of 0.258 µg/kg, resulting in a z-score of +1.0. PFNA was reported at 0.130 µg/kg versus the assigned value of 0.116 µg/kg, also producing a z-score of +1.0. PFHxS came in at 0.047 µg/kg against an assigned value of 0.0422 µg/kg, with a z-score of +0.6. Finally, the upper-bound sum of total-PFOS, PFOA, PFNA, and PFHxS was reported as 0.627 µg/kg compared to the assigned value of 0.593 µg/kg, yielding a z-score of +0.3.

Conclusion

This method is characterized by a calibration that shows excellent linearity, accuracy and precision over a wide working range. The unified sample preparation scheme showed high accuracy and precision across the three options. Cholic acids with known spectral interference with PFOS were shown to be effectively resolved. Tables 42 and 43 summarize analyte validated (V)/ not validated (NV) status in each matrix based on recovery spike data alone.

Recovery spike data supports the core validation conclusion, but additional performance data needs to be considered in the final assessment in several instances:

- PFBA, PFPeA, Br-PFOA, and Br-PFOS all suffer from confirmation of identity problems.
  - For PFBA and PFPeA because of only having a single MRM transition available to monitor. A confirmation method for these analytes will need to be developed and validated. Absent a supplementing confirmation method, analyst practice will be to appropriately qualify these results if reported.

  - For the PFOA and PFOS the process of integrating an extended region of the chromatogram produces an "ion ratio" value that represents a weighted average of multiple ion ratios. However, although attention is brought to the issue here it should also be noted that this practice is entirely consistent with that in the broader PFAS analytical community.
- The requisite number of 6:2 FTS duplicate spikes pass in many of the matrices, but the method blank data and isolated matrix spike examples show an analyte that is out of control because of random contamination. Corroborating data from replicate analysis could generate confidence in reporting detects for this analyte but replicate analysis is not normal laboratory procedure. Analyst practice will be to report this analyte as 'Not Reportable (NR)' absent any corroborating data.
- Several of the long-chain (>C8) sulfonic acids failed recovery spikes in bread and dry dog food. This is presumably due to extraction inefficiency, and not ionization suppression, since the long chain carboxylic acid surrogates also show lower recoveries in this matrix. However, the long-chain carboxylic acids have surrogate internal standards that are better chemical matches; largely result in acceptable native accuracies. In contrast, the long-chain sulfonic acid compounds as yet have no commercially available labelled analogs and are quantified using labelled PFOS as an internal standard.
- Fish tissue has been a commonly available proficiency test or standard reference material matrix but is often restricted in the amount of sample available. Good comparability of results from the 5g and 1g prep options for the fish in this study shows promise for dealing with size limited samples.

Finally, the method has been successfully employed for several thousand TDS samples and a variety of CVM surveillance assignments. Performance across multiple proficiency and inter-laboratory studies have reinforced that the method is accurate and appropriate for deployment across diverse matrices.

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Tables

Table 1. List of method target analytes.

Acronym	Name	CAS	Formula	MW
PFBA	Perfluorobutanoic acid	375-22-4	$C_4F_7O_2$	214
PFPeA	Perfluoropentanoic acid	2706-90-3	$C_5HF_9O_2$	264
PFHxA	Perfluorohexanoic acid	307-24-4	$C_6HF_{11}O_2$	314
PFHpA	Perfluoroheptanoic acid	375-85-9	$C_7HF_{13}O_2$	364
PFOA	Perfluorooctanoic Acid	335-67-1	$C_8HF_{15}O_2$	414
PFNA	Perfluorononanoic acid	375-95-1	$C_9HF_{17}O_2$	464
PFDA	Perfluorodecanoic acid	335-76-2	$C_{10}HF_{19}O_2$	514
PFUnA	Perfluoroundecanoic acid	2058-94-8	$C_{11}HF_{21}O_2$	564
PFDoA	Perfluorododecanoic acid	307-55-1	$C_{12}HF_{23}O_2$	614
PFTrDA	Perfluorotridecanoic acid	72629-94-8	$C_{13}HF_{25}O_2$	664
PFTeDA	Perfluorotetradecanoic acid	376-06-7	$C_{14}HF_{27}O_2$	714
PFBS	Perfluorobutanesulfonic acid	375-73-5	$C_4HF_9O_3S$	300
PFPeS	Perfluoropentanesulfonic acid	2706-91-4	$C_5HF_{11}O_3S$	350
PFHxS	Perfluorohexanesulfonic acid	355-46-4	$C_6HF_{13}O_3S$	400
PFHpS	Perfluoroheptanesulfonic acid	375-92-8	$C_7HF_{15}O_3S$	450
PFOS	Perfluorooctanesulfonic acid	1763-23-1	$C_8HF_{17}O_3S$	500
PFNS	Perfluorononanesulfonic acid	68259-12-1	$C_9HF_{19}O_3S$	550
PFDS	Perfluorodecanesulfonic acid	335-77-3	$C_{10}HF_{21}O_3S$	600
PFUnDS	Perfluoroundecanesulfonic acid	749786-16-1	$C_{11}HF_{23}O_3S$	650

Acronym	Name	CAS	Formula	MW
PFDoS	Perfluorododecanesulfonic acid	79780-39-5	$C_{12}HF_{25}O_3S$	700
PFTrDS	Perfluorotridecanesulfonic acid	791563-89-8	$C_{13}HF_{27}O_3S$	750
FOSA	Perfluorooctanesulfonamide	754-91-6	$C_8H_2F_{17}NO_2S$	499
DONA	4,8-Dioxa-3H-perfluorononanoic acid	919005-14-4	$C_7H_2F_{12}O_4$	378
HFPO-DA	Hexafluoropropylene oxide dimer acid	13252-13-6	$C_6HF_{11}O_3$	330
9Cl-PF3ONS	9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	756426-58-1	$C_8HClF_{16}O_4S$	532
11Cl-PF3OUdS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	763051-92-9	$C_{10}HClF_{20}O_4S$	632
4:2 FTS	1H,1H,2H,2H-Perfluorohexane sulfonic acid	757124-72-4	$C_6H_5F_9O_3S$	328
6:2 FTS	1H,1H,2H,2H-Perfluorooctane sulfonic acid	27619-97-2	$C_8H_5F_{13}O_3S$	428
8:2 FTS	1H,1H,2H,2H-Perfluorodecane sulfonic acid	39108-34-4	$C_{10}H_5F_{17}O_3S$	528
10:2 FTS	1H,1H,2H,2H-Perfluorododecane sulfonic acid	120226-60-0	$C_{12}H_5F_{21}O_3S$	628

Table 2. List of Surrogate Internal Standards.

Name	Acronym
Perfluoro-n-(2,3,4-$^{13}C_3$)butanoic acid	M3PFBA
Perfluoro-n-(3,4,5-$^{13}C_3$)pentanoic acid	M3PFPeA
Perfluoro-n-(1,2,3,4,6-$^{13}C_5$)hexanoic acid	M5PFHxA
Perfluoro-n-($^{13}C_8$)octanoic acid	M8PFOA
Perfluoro-n-(1,2-$^{13}C_2$)undecanoic acid	MPFUdA
Perfluoro-n-(1,2-$^{13}C_2$)dodecanoic acid	MPFDoA
Perfluoro-n-(1,2-$^{13}C_2$)tetradecanoic acid	MPFTeDA
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)($^{13}C_3$)propanoic acid	M3HFPO-DA
Sodium perfluoro-1-(2,3,4-$^{13}C_3$)butanesulfonate	M3PFBS
Sodium perfluoro-1-(1,2,3-$^{13}C_3$)hexanesulfonate	M3PFHxS
Sodium perfluoro-1-($^{13}C_8$) octanesulfonate	M8PFOS
Perfluoro-1-($^{13}C_8$)octanesulfonamide	M8FOSA-I
Sodium $1^2H,1^2H,2^2H,2^2H$-perfluoro-(1,2-$^{13}C_2$)hexanesulfonate*	d4-13C2-4:2 FTS
Sodium $1^2H,1^2H,2^2H,2^2H$-perfluoro-(1,2-$^{13}C_2$)octanesulfonate*	d4-13C2-6:2 FTS
Sodium $1^2H,1^2H,2^2H,2^2H$-perfluoro-(1,2-$^{13}C_2$)decanesulfonate*	d4-13C2-8:2 FTS
Sodium $1^2H,1^2H,2^2H,2^2H$-perfluoro-(1,2-$^{13}C_2$)dodecanesulfonate*	d4-13C2-10:2 FTS

Table 3. List of Recovery Internal Standards.

Name	Acronym
Perfluoro-n-(1,2,3,4-$^{13}C_4$)octanoic acid	M4PFOA
Sodium perfluoro-1-(1,2,3,4-$^{13}C_4$)octanesulfonate	M4PFOS
N-ethyl-d5-perfluoro-1-octanesulfonamidoacetic acid	d5-N-EtFOSAA
Perfluoro-n-[1,2,3,4,5,6,7-$^{13}C_7$]undecanoic acid	M7PFUnA

Table 4. Calibration Standard Composition.

Level	Final [Native] (ng·mL^{-1})	Concentration Native Stock (µg·mL^{-1})	Volume Native Stock (µL)	Volume SUR (µL)	Volume RS (µL)	Volume MeOH (mL)	Final Volume (mL)
CS1	0.01	0.01	10	50	100	9.84	10
CS2	0.05	0.01	50	50	100	9.80	10
CS3	0.1	0.01	100	50	100	9.75	10
CS4	0.5	0.01	500	50	100	9.35	10
CS5	1	0.1	100	50	100	9.75	10
CS6	5	0.1	500	50	100	9.35	10
CS7	10	0.1	1000	50	100	8.85	10
CS8	25	0.1	2500	50	100	7.35	10

Table 5. Sample Preparation Options.

Preparation	**Option 1: "5x5"**	**Option 2: "5x15"**	**Option 3: "1x15"**
Sample size (g)	5	5	1
Water added (mL)	5	15	15
Historical Examples	Fruits, vegetables, juices	Dry pet foods, bread, cooked fish & eggs	Agricultural products, protein powder

Table 6. LC Gradient Method.

Time (min)	**[%B]**	**Flow ($mL \cdot min^{-1}$)**
0	10%	0.300
2	10%	0.300
2.10	40%	0.300
29	99%	0.300
30	99%	0.400
30.10	10%	0.400
33	10%	0.300

Table 7. MS/MS MRM Parameters. Transitions marked with an asterisk are used for quantitation.

Q1 Mass (Da)	Q3 Mass (Da)	Retention Time (min)	ID	DP (volts)	EP (volts)	CE (volts)	CXP (volts)
213	169	6.4	PFBA_1*	-15	-10	-14	-15
263	219	8.38	PFPeA_1*	-14	-10	-13	-5
313	269	10.96	PFHxA_1*	-23	-8	-14	-5
313	119	10.95	PFHxA_2	-23	-10	-30	-13
363	319	13.52	PFHpA_1*	-20	-10	-16	-9
363	169	13.52	PFHpA_2	-20	-10	-25	-10
413	369	15.96	PFOA_1*	-43	-7	-16	-25
413	219	15.96	PFOA_2	-24	-5.5	-23	-25
463	419	18.24	PFNA_1*	-38	-11	-15	-37
463	269	18.23	PFNA_2	-40	-5	-24	-13
513	469	20.28	PFDA_1*	-15	-10	-16	-29
513	269	20.28	PFDA_2	-20	-10	-26	-17
563	519	22.09	PFUdA_1*	-25	-10	-18	-15
563	169	22.08	PFUdA_2	-25	-10	-28	-15
613	569	23.64	PFDoA_1*	-25	-10	-18	-15
613	169	23.64	PFDoA_2	-25	-10	-30	-15
663	619	25.02	PFTrDA_1*	-25	-10	-20	-15
663	169	25.02	PFTrDA_2	-25	-10	-36	-15
713	669	26.31	PFTeDA_1*	-25	-10	-22	-15
713	169	26.31	PFTeDA_2	-25	-10	-38	-15
377	251	14.19	ADONA_1*	-24	-8	-15	-20

Q1 Mass (Da)	Q3 Mass (Da)	Retention Time (min)	ID	DP (volts)	EP (volts)	CE (volts)	CXP (volts)
377	85	14.19	ADONA_2	-20	-7	-39	-10
285	169	11.94	HFPO-DA_1*	-20	-6	-11	-27
285	185	11.94	HFPO-DA_2	-20	-5	-21	-27
299	80	10.12	PFBS_1*	-44	-10	-70	-11
299	99	10.13	PFBS_2	-35	-4	-36	-15
349	99	12.69	PFPeS_1*	-80	-9	-80	-12
349	80	12.69	PFPeS_2	-53	-9	-40	-12
399	80	15.13	PFHxS_1*	-80	-10	-85	-9
399	99	15.13	PFHxS_2	-80	-10	-70	-11
449	99	17.4	PFHpS_1*	-58	-8	-84	-24
449	169	17.39	PFHpS_2	-68	-8	-41	-27
499	80	19.46	PFOS_1*	-150	-4	-120	-10
499	99	19.46	PFOS_2	-150	-4	-100	-10
549	80	21.29	PFNS_1*	-72	-10	-142	-8
549	99	21.29	PFNS_2	-110	-10	-124	-12
599	80	22.87	PFDS_1*	-105	-10	-115	-6
599	99	22.87	PFDS_2	-105	-10	-112	-14
649	80	24.25	PFUdS_1*	-180	-4	-160	-12
649	99	24.25	PFUdS_2	-170	-4	-140	-11
699	80	25.57	PFDoS_1*	-145	-10	-134	-11
699	99	25.57	PFDoS_2	-145	-10	-105	-14
749	80	26.68	PFTrDS_1*	-152	-10	-130	-11

Q1 Mass (Da)	Q3 Mass (Da)	Retention Time (min)	ID	DP (volts)	EP (volts)	CE (volts)	CXP (volts)
749	99	26.68	PFTrDS_2	-152	-10	-118	-9
498	78	22.07	PFOSA_1*	-138	-11	-93	-7
498	169	22.07	PFOSA_2	-148	-13	-43	-15
531	351	20.79	9Cl-PF3ONS_1*	-75	-9	-41	-37
533	353	20.79	9Cl_PF3ONS_2	-75	-9	-41	-37
631	451	23.88	11Cl-PF3OUdS_1*	-20	-10	-42	-6
633	453	23.88	11Cl-PF3OUdS_2	-20	-10	-42	-6
327	307	10.23	4:2 FTS_1*	-50	-6	-28	-24
327	81	10.23	4:2 FTS_2	-40	-11	-62	-10
427	407	15.29	6:2 FTS_1*	-31	-11	-34	-38
427	81	15.29	6:2 FTS_2	-41	-12	-88	-12
527	507	19.76	8:2 FTS_1*	-69	-11	-37	-29
527	81	19.76	8:2 FTS_2	-70	-11	-109	-36
627	607	23.29	10:2 FTS_1*	-54	-6	-46	-48
627	81	23.29	10:2 FTS_2	-68	-6	-129	-15
216	172	6.39	SUR 13C3-PFBA_1*	-17	-8	-12	-14
266	222	8.37	SUR 13C3-PFPeA_1	-17	-6	-11	-28
318	273	10.94	SUR 13C5-PFHxA_1*	-13	-10	-14	-12
318	121	10.94	SUR 13C5-PFHxA_2	-25	-10	-30	-13

Q1 Mass (Da)	Q3 Mass (Da)	Retention Time (min)	ID	DP (volts)	EP (volts)	CE (volts)	CXP (volts)
421	376	15.95	SUR 13C8-PFOA_1*	-36	-8	-13	-20
421	172	15.95	SUR 13C8-PFOA_2	-19	-5	-25	-7
565	520	22.08	SUR M2PFUnA_1*	-75	-10	-18	-11
615	570	23.62	SUR M2PFDoA_1*	-82	-10	-18	-11
715	670	26.3	SUR M2PFTeDA_1*	-90	-10	-22	-11
287	169	11.93	SUR 13C3-HFPO_1*	-31	-5	-10.6	-25
287	185	11.93	SUR 13C3-HFPO_2	-28	-4	-22	-17
302	80	10.11	SUR 13C3-PFBS_1*	-88	-6	-73	-9
302	99	10.12	SUR 13C3-PFBS_2	-85	-6	-36	-8
402	80	15.12	SUR 13C3-PFHxS_1*	-80	-10	-85	-9
402	99	15.12	SUR 13C3-PFHxS_2	-60	-10	-81	-15
507	80	19.45	SUR 13C8-PFOS_1*	-100	-5	-125	-15
507	99	19.45	SUR 13C8-PFOS_2	-100	-5	-100	-15
333	312	10.19	SUR d4-13C2-4:2 FTS_1*	-60	-10	-30	-29
333	82	10.19	SUR d4-13C2-4:2 FTS_2	-60	-10	-63	-12
433	412	15.25	SUR d4-13C2-6:2 FTS_1*	-80	-10	-33	-13

Q1 Mass (Da)	Q3 Mass (Da)	Retention Time (min)	ID	DP (volts)	EP (volts)	CE (volts)	CXP (volts)
433	82	15.25	SUR d4-13C2-6:2 FTS_2	-80	-10	-67	-13
533	512	19.73	SUR d4-13C2-8:2 FTS_1*	-100	-10	-49	-23
533	82	19.73	SUR d4-13C2-8:2 FTS_2	-100	-10	-81	-34
633	612	23.27	SUR d4-13C2-10:2FTS_1*	-100	-10	-45	-19
633	82	23.27	SUR d4-13C2-10:2FTS_2	-100	-10	-85	-10
506	78	22.06	SUR 13-C8-FOSA_1*	-101	-9	-100	-8
589	419	21.84	RS d5-NEtFOSAA_1	-50	-10	-30	-20
589	219	21.84	RS d5-NEtFOSAA_2	-50	-10	-38	-20
499	124	17.5	TDCA_1	-60	-4	-120	-10
499	107	17.5	TDCA_2	-60	-4	-100	-10
570	525	22.06	RS M7PFUnA_1	-75	-10	-18	-11
503	80	19.44	RS 13C4-PFOS_1	-100	-5	-125	-15
503	99	19.44	RS 13C4-PFOS_2	-100	-5	-100	-15
417	372	15.94	RS 13C4-PFOA_1	-36	-8	-13	-20
417	172	15.94	RS 13C4-PFOA_2	-19	-5	-25	-7

Table 8. Ion Ratio (IR) Tolerance.

IR Lower Limit	**IR Upper Limit**	**Acceptable % Difference**
0	0.1	50
0.101	0.2	40
0.201	0.5	35
0.501	1	30

Table 9. Analyte/Internal Standard Pairing.

Analyte	**Internal Standard**
PFBA	13C3-PFBA
PFPeA	13C3-PFPeA
PFHxA	13C5-PFHxA
PFHpA	13C8-PFOA
PFOA	13C8-PFOA
PFNA	13C8-PFOA
PFDA	13C2-PFUdA
PFUdA	13C2-PFUdA
PFDoA	13C2-PFDoA
PFTrDA	13C2-PFTeDA
PFTeDA	13C2-PFTeDA
ADONA	13C3-HFPO-DA
HFPO-DA	13C3-HFPO-DA
PFBS	13C3-PFBS
PFPeS	13C3-PFBS

Analyte	**Internal Standard**
PFHxS	13C3-PFHxS
PFHpS	13C3-PFHxS
PFOS	13C8-PFOS
PFNS	13C8-PFOS
PFDS	13C8-PFOS
PFUdS	13C8-PFOS
PFDoS	13C8-PFOS
PFTrDS	13C8-PFOS
PFOSA	13C8-PFOSA
9Cl-PF3ONS	13C8-PFOS
11Cl-PF3OUdS	13C8-PFOS
4:2 FTS	d4-13C2-4:2FTS
6:2 FTS	d4-13C2-6:2FTS
8:2 FTS	d4-13C2-8:2FTS
10:2 FTS	d4-13C2-10:2FTS

Table 10. Labeled Surrogate/Recovery Standard Pairing.

Labeled Surrogate	Recovery Standard
13C3-PFBA	13C4-PFOA
13C3-PFPeA	13C4-PFOA
13C5-PFHxA	13C4-PFOA
13C8-PFOA	13C4-PFOA
13C2-PFUdA	13C7-PFUdA
13C2-PFDoA	13C7-PFUdA
13C2-PFTeDA	13C7-PFUdA
13C3-HFPO-DA	13C4-PFOA

Labeled Surrogate	Recovery Standard
13C3-PFBS	13C4-PFOS
13C3-PFHxS	13C4-PFOS
13C8-PFOS	13C4-PFOS
13C8-PFOSA	d5-NEtFOSAA
d4-13C2-4:2FTS	d5-NEtFOSAA
d4-13C2-6:2FTS	d5-NEtFOSAA
d4-13C2-8:2FTS	d5-NEtFOSAA
d4-13C2-10:2FTS	d5-NEtFOSAA

Table 11. Retention Times and EPA 537.1 [21] Peak Asymmetry Values from a CS5 Calibration Standard.

Analyte	**Retention Time (minutes)**	**EPA 537.1 Asymmetry Factor**
PFBA	6.11	0.78
PFPeA	8.06	0.86
PFBS	9.69	0.73
4:2 FTS	9.80	0.79
PFHxA	10.51	0.77
HFPO-DA	11.49	0.83
PFPeS	12.22	0.73
PFHpA	13.09	0.98
ADONA	13.79	0.94
PFHxS	14.74	0.99
6:2 FTS	14.93	0.98
PFOA	15.63	1.01
PFHpS	17.07	1.02
PFNA	17.95	1.16
PFOS	19.21	1.03
8:2 FTS	19.54	0.99
PFDA	20.08	1.20
9Cl-PF3ONS	20.57	1.03
PFNS	21.08	1.13
PFOSA	21.77	1.08
PFUdA	21.89	1.17
PFDS	22.68	1.02
10:2 FTS	23.12	1.03
PFDoA	23.46	1.05
11Cl-PF3OUdS	23.71	1.04
PFUdS	24.08	1.19
PFTrDA	24.83	1.08
PFDoS	25.31	1.09
PFTeDA	26.04	1.09
PFTrDS	26.39	1.04

Table 12. Regression Statistics for Initial Calibration.

Analyte	**Slope**	**r**	**r^2**
PFBA	1.50209	0.99975	0.99951
PFPeA	1.46590	0.99999	0.99998
PFHxA	1.31685	0.99995	0.99991
PFHpA	1.66220	0.99995	0.99991
PFOA	1.50162	0.99992	0.99983
PFNA	1.07512	0.99984	0.99968
PFDA	1.72702	0.9984	0.9968
PFUdA	2.20879	0.99967	0.99933
PFDoA	1.76907	0.99962	0.99924
PFTrDA	2.39817	0.99909	0.99818
PFTeDA	2.09342	0.99958	0.99916
ADONA	5.59854	0.99894	0.99788
HFPO-DA	1.38284	0.99952	0.99905
PFBS	1.43838	0.99922	0.99844
PFPeS	0.34741	0.99976	0.99952
PFHxS	1.39436	0.99973	0.99947
PFHpS	0.28371	0.99965	0.9993
L-PFOS	1.18598	0.99997	0.99995
Br-PFOS	1.59360	0.99995	0.99991
PFNS	1.44720	0.9999	0.9998
PFDS	1.21238	0.9998	0.99959
PFUdS	1.16832	0.99993	0.99986
PFDoS	1.16302	0.99993	0.99986
PFTrDS	0.95242	0.99983	0.99967
PFOSA	0.96974	0.99974	0.99947
9Cl-PF3ONS	2.50886	0.99994	0.99987
11Cl-PF3OUdS	2.47939	0.99987	0.99974
4:2 FTS	2.06121	0.99974	0.99947
6:2 FTS	1.27122	0.99955	0.9991
8:2 FTS	2.53927	0.99919	0.99839
10:2 FTS	1.27170	0.9991	0.9982

Table 13. Accuracy of Calibration Concentrations Calculated from the Regression.

Analyte	**0.01 ng·mL^{-1}**	**0.05 ng·mL^{-1}**	**0.1 ng·mL^{-1}**	**0.5 ng·mL^{-1}**	**1 ng·mL^{-1}**	**5 ng·mL^{-1}**	**10 ng·mL^{-1}**	**25 ng·mL^{-1}**
PFBA	LLOQ	88.1	94.2	95.7	99.2	101.0	103.7	98.5
PFPeA	*N/A*	LLOQ	105.3	98.6	100.1	99.3	100.5	100.0
PFHxA	*N/A*	LLOQ	105.2	98.0	101.1	97.8	100.5	100.2
PFHpA	*N/A*	LLOQ	96.8	97.9	97.6	97.7	100.3	100.5
PFOA	LLOQ	89.3	96.5	98.3	100.5	96.6	100.5	100.5
PFNA	*N/A*	LLOQ	107.2	105.9	97.5	96.5	101.9	99.9
PFDA	LLOQ	89.0	99.4	101.3	102.9	106.5	107.7	95.5
PFUdA	LLOQ	97.2	98.8	99.1	100.7	103.6	103.2	98.0
PFDoA	*N/A*	LLOQ	98.5	99.6	102.4	101.9	104.1	97.9
PFTrDA	LLOQ	91.9	104.5	107.2	107.1	107.8	103.1	96.8
PFTeDA	LLOQ	100.7	101.2	101.8	99.9	100.2	104.9	98.0
ADONA	LLOQ	94.4	100.3	103.0	102.5	107.3	105.1	96.4
HFPO-DA	63.9	LLOQ	101.5	103.0	101.5	105.1	103.2	97.6
PFBS	LLOQ	92.9	98.5	102.4	94.3	102.8	106.1	97.2
PFPeS	LLOQ	100.1	101.1	100.5	99.5	100.7	103.6	98.5
PFHxS	LLOQ	93.0	100.8	101.4	104.7	101.6	103.1	98.2
PFHpS	*N/A*	LLOQ	98.0	94.0	103.3	97.9	104.3	98.7
Br-PFOS	LLOQ	93.6	100.5	99.1	102.6	98.5	100.1	100.2
PFNS	LLOQ	87.6	95.6	95.2	100.2	103.3	100.5	99.3
PFDS	*N/A*	LLOQ	90.0	94.9	96.0	96.1	98.6	101.6
PFUdS	LLOQ	93.4	103.4	102.6	103.2	99.4	101.5	99.4
PFDoS	LLOQ	91.4	91.9	92.0	97.5	98.4	101.2	100.2
PFTrDS	LLOQ	88.9	90.5	98.3	99.3	96.4	98.5	101.5
PFOSA	*N/A*	LLOQ	101.4	97.6	100.4	100.2	103.8	98.5
9Cl-PF3ONS	LLOQ	90.5	92.8	96.7	100.2	101.5	101.5	99.2
11Cl-PF3OUdS	LLOQ	92.8	101.0	102.5	102.3	100.1	102.4	98.9
4:2 FTS	*N/A*	LLOQ	109.8	98.9	94.9	95.9	103.0	99.8
6:2 FTS	*N/A*	LLOQ	107.2	88.8	96.3	96.8	104.6	99.1
8:2 FTS	LLOQ	90.8	99.9	95.1	100.0	97.6	107.1	97.8
10:2 FTS	LLOQ	96.0	95.0	96.2	91.3	90.5	98.7	102.9

Table 14. Precision of Internal Standard Areas from the Initial Calibration.

Surrogate	Average Area	σ	%RSD
SUR 13C3-PFBA	4.95E+05	2.27E+04	4.59
SUR 13C3-PFPeA	4.07E+05	1.31E+04	3.22
SUR 13C5-PFHxA	5.42E+05	1.72E+04	3.18
SUR 13C8-PFOA	5.09E+05	1.83E+04	3.60
SUR M2PFUnA	4.22E+05	1.50E+04	3.55
SUR M2PFDoA	4.78E+05	1.15E+04	2.41
SUR M2PFTeDA	3.60E+05	9.08E+03	2.52
SUR 13C3-HFPO	2.80E+05	8.88E+03	3.18
SUR 13C3-PFBS	7.33E+05	3.36E+04	4.58
SUR 13C3-PFHxS	6.55E+05	1.86E+04	2.85
SUR 13C8-PFOS	4.97E+05	2.07E+04	4.17
SUR d4-13C2-4:2 FTS	1.17E+05	4.64E+03	3.97
SUR d4-13C2-6:2 FTS	1.55E+05	6.58E+03	4.23
SUR d4-13C2-8:2 FTS	6.76E+04	2.42E+03	3.58
SUR d4-13C2-10:2FTS	1.01E+05	4.27E+03	4.24
SUR 13-C8-FOSA	8.80E+05	2.57E+04	2.91
RS d5-NEtFOSAA	4.80E+04	1.81E+03	3.76
RS 13C4-PFOS	1.71E+05	4.50E+03	2.64
RS 13C4-PFOA	1.41E+05	3.39E+03	2.41

Table 15. Accuracy and Precision from Native Spike Replicates.

Analyte	Sample Prep 1	Sample Prep 2	Sample Prep 2 (n=6)*	Sample Prep 3
PFBA	95.2 (2.2%)	86.2 (15.3%)	90.9 (4.6%)	96.8 (11.8%)
PFPeA	88.9 (3.0%)	85.7 (14.2%)	90.0 (5.1%)	89.1 (3.6%)
PFHxA	91.0 (2.0%)	85.4 (13.8%)	89.5 (5.0%)	89.5 (3.4%)
PFHpA	90.6 (3.3%)	78.5 (43.7%)	91.3 (6.0%)	88.1 (4.8%)
L_PFOA	87.6 (2.8%)	84.8 (15.7%)	89.7 (4.5%)	86.8 (2.2%)
Br_PFOA	88.9 (2.8%)	85.8 (15.3%)	90.5 (5.0%)	87.8 (2.0%)
PFNA	88.2 (3.0%)	85.8 (15.2%)	90.5 (4.8%)	87.5 (1.6%)
PFDA	93.7 (3.0%)	94.1 (14.8%)	99.3 (2.6%)	100.3 (4.6%)
PFUdA	94.7 (4.2%)	90.9 (14.3%)	95.8 (2.5%)	93.6 (2.4%)
PFDoA	93.6 (3.0%)	88.4 (15.3%)	93.3 (3.8%)	94.2 (3.1%)
PFTrDA	91.3 (4.4%)	86.5 (14.4%)	90.9 (4.7%)	90.2 (3.7%)
PFTeDA	91.4 (3.6%)	87.1 (14.8%)	91.8 (4.1%)	90.4 (2.5%)
ADONA	98.3 (2.8%)	96.3 (13.8%)	101.2 (3.2%)	99.5 (3.0%)
HFPO-DA	93.1 (3.2%)	89.8 (13.7%)	94.3 (3.7%)	92.4 (2.6%)
PFBS	92.1 (4.5%)	87.3 (14.4%)	91.9 (3.8%)	90.7 (5.7%)
PFPeS	89.7 (4.1%)	86.8 (15.2%)	91.5 (4.1%)	91.8 (4.1%)
PFHxS	89.2 (4.1%)	85.6 (14.3%)	90.0 (4.7%)	89.6 (2.8%)
PFHpS	90.3 (2.9%)	86.4 (13.3%)	90.3 (6.3%)	87.6 (4.2%)
L_PFOS	90.2 (3.6%)	87.2 (15.3%)	91.9 (5.2%)	90.1 (2.6%)
Br_PFOS	81.9 (16.4%)	85.6 (17.7%)	89.8 (12.6%)	88.2 (9.5%)
PFNS	87.6 (5.2%)	84.7 (14.5%)	89.1 (4.3%)	87.3 (4.3%)
PFDS	88.7 (4.1%)	84.2 (15.9%)	89.1 (4.5%)	83.2 (4.7%)
PFUdS	84.6 (5.0%)	78.1 (16.3%)	82.5 (6.9%)	78.1 (6.2%)
PFDoS	81.4 (5.5%)	82.6 (17.0%)	87.6 (6.1%)	88.0 (4.0%)
PFTrDS	79.1 (5.4%)	74.8 (16.0%)	79.0 (5.9%)	72.8 (6.0%)
PFOSA	88.6 (3.7%)	86.3 (14.2%)	90.7 (4.4%)	89.2 (3.0%)
9Cl-PF3ONS	89.7 (5.4%)	88.5 (15.6%)	93.4 (5.3%)	90.3 (1.9%)
11Cl-PF3OUdS	90.3 (4.9%)	87.3 (15.3%)	92.0 (6.0%)	86.4 (4.8%)
4:2 FTS	88.7 (5.8%)	85.2 (14.4%)	89.6 (4.5%)	117.0 (29.2%)
6:2 FTS	87.7 (3.4%)	87.5 (15.9%)	92.6 (3.3%)	111.9 (18.9%)
8:2 FTS	94.2 (9.4%)	90.1 (18.3%)	95.5 (9.4%)	89.6 (6.3%)
10:2 FTS	92.4 (3.8%)	84.6 (15.2%)	89.0 (6.8%)	98.5 (13.4%)

Table 16. Prep Option(s) per Matrix Type. Note: Bread and salmon were evaluated by both Prep Options 2 and 3.

Matrix	**Prep Option 1** 5g sample, 5 mL water	**Prep Option 2** 5 g sample, 15 mL water	**Prep Option 3** 1 g sample, 15 mL water
Clam	X		
Lettuce	X		
Milk (chocolate)	X		
Milk (whole)	X		
Wet Cat Food	X		
Wet Dog Food	X		
Chicken Feed		X	
Corn Flour		X	
Dry Cat Food		X	
Dry Dog Food		X	
Egg, hard boiled		X	
Bread		X	X
Salmon, cooked		X	X
Alfalfa			X
Silage			X

Table 17: Native Recoveries (%) from Alfalfa Spiked at 0.05, 0.15, 0.5, 1.5, 2, and 5 ngg^{-1}

Analyte	**0.05**	**0.05**	**0.15**	**0.15**	**0.5**	**0.5**	**1.5**	**1.5**	**2**	**2**	**5**	**5**
PFBA	1680	1852	784	773	263	298	165	165	145	146	100	107
PFPeA	448	420	128	191	131	122	108	105	98	111	90	94
PFHxA	N/A	1040	N/A	N/A	94	98	105	102	100	101	91	90
PFHpA	84	252	73	75	70	77	88	87	80	89	75	75
PFOA	112	148	97	93	88	94	100	99	93	100	85	87
BrPFOA	140	280	128	148	93	112	104	103	95	107	86	88
PFNA	112	144	109	95	101	106	119	122	111	120	106	111
PFDA	164	176	111	104	106	110	114	122	121	123	108	109
PFUdA	88	112	92	87	92	99	107	114	114	117	96	104
PFDoA	116	140	103	105	108	109	127	125	126	126	107	114
PFTrDA	56	64	64	53	70	66	68	76	75	76	67	66
PFTeDA	84	108	85	79	92	96	103	105	111	111	95	101
ADONA	5128	444	110	94	107	113	130	125	127	127	105	116
HFPO-DA	3832	96	83	76	87	92	103	105	100	105	91	96
PFBS	126	208	105	90	90	101	110	106	106	105	91	94
PFPeS	85	106	81	79	93	106	119	121	113	120	110	107
PFHxS	110	127	93	89	89	96	99	102	99	111	87	95
PFHpS	155	147	98	99	91	108	103	111	112	130	92	105
PFOS	99	112	88	82	88	92	101	105	100	107	89	93
Br PFOS	125	491	92	200	120	133	112	117	108	122	90	99
PFNS	79	87	79	76	86	91	104	103	101	109	83	90
PFDS	79	87	80	68	82	82	88	95	93	102	81	89
PFUdS	95	116	83	72	75	79	83	86	85	92	69	80
PFDoS	70	87	63	60	63	70	77	75	74	77	60	77
PFTrDS	58	74	59	63	58	60	70	60	65	70	50	80
PFOSA	84	100	80	77	85	91	102	104	101	107	92	97
9Cl-PF3ONS	73	86	76	73	81	85	94	97	90	101	78	89
11Cl-PF3OUdS	72	93	74	69	78	84	89	96	90	99	75	89
4:2 FTS	145	1225	135	114	90	101	106	114	107	97	101	94
6:2 FTS	1254	93850	2969	947	303	225	146	171	178	157	107	112
8:2 FTS	88	129	82	81	89	92	103	100	106	114	94	99
10:2 FTS	91	108	77	74	82	82	94	94	103	103	77	89

Table 18. Native Recoveries (%) from Clam (fresh) Spiked at 0.05, 0.15, 0.5, 1.5, 2, and 5 ngg^{-1}

Analyte	**0.05**	**0.05**	**0.15**	**0.15**	**0.5**	**0.5**	**1.5**	**1.5**	**2**	**2**	**5**	**5**
PFBA	104	96	172	89	80	104	78	84	75	81	72	74
PFPeA	140	156	125	115	96	95	74	89	79	81	78	76
PFHxA	136	108	104	101	89	87	73	75	79	80	74	75
PFHpA	92	88	81	84	79	79	68	71	74	73	72	70
PFOA	116	120	92	93	82	83	73	75	76	76	73	72
BrPFOA	140	132	95	97	84	84	73	76	76	77	73	72
PFNA	148	136	119	115	102	101	85	92	92	92	90	88
PFDA	104	100	89	87	80	76	69	72	69	77	69	68
PFUdA	100	100	87	91	86	80	75	78	79	77	76	77
PFDoA	92	96	91	87	85	83	71	75	75	77	75	74
PFTrDA	108	112	93	99	82	84	71	74	77	73	76	75
PFTeDA	96	104	85	92	81	82	70	75	76	75	70	72
ADONA	89	89	100	103	93	89	87	87	90	86	85	84
HFPO-DA	76	84	81	81	83	80	73	75	78	76	75	74
PFBS	81	90	87	84	81	81	72	78	75	76	74	72
PFPeS	64	76	88	78	81	80	75	83	78	76	74	72
PFHxS	101	105	96	91	81	81	74	76	77	75	75	72
PFHpS	76	84	88	83	84	83	73	80	78	76	74	77
PFOS	177	168	116	115	89	89	78	78	78	80	73	77
Br PFOS	310	276	152	144	106	103	79	80	78	80	72	75
PFNS	79	79	87	87	83	80	72	74	75	80	71	76
PFDS	79	79	91	83	83	77	74	73	75	77	74	75
PFUdS	74	83	80	79	75	73	70	67	67	70	69	72
PFDoS	74	74	80	81	79	76	69	69	70	71	67	71
PFTrDS	70	66	77	73	74	72	67	65	65	68	66	66
PFOSA	80	84	87	87	83	80	76	78	79	79	75	78
9Cl-PF3ONS	77	77	81	83	79	81	76	75	75	76	74	75
11Cl-PF3OUdS	72	72	83	85	80	79	73	72	77	78	72	72
4:2 FTS	166	158	128	114	113	121	96	103	120	106	104	100
6:2 FTS	88	97	90	91	82	84	81	81	84	86	78	73
8:2 FTS	79	88	92	88	85	85	75	80	81	83	81	80
10:2 FTS	99	95	86	86	89	82	69	73	79	74	76	73

Table 19. Native Recoveries (%) from Chicken Feed Spiked at 0.05, 0.15, 0.5, 1.5, 2, and 5 ngg^{-1}

Analyte	**0.05**	**0.05**	**0.15**	**0.15**	**0.5**	**0.5**	**1.5**	**1.5**	**2**	**2**	**5**	**5**
PFBA	728	704	323	276	146	144	94	95	90	91	80	78
PFPeA	264	268	131	127	94	101	83	83	82	84	78	77
PFHxA	96	856	116	81	110	90	84	85	91	83	81	80
PFHpA	76	212	72	79	88	96	74	81	79	87	73	72
PFOA	104	104	95	92	84	85	77	78	80	78	78	76
BrPFOA	104	100	107	92	82	84	77	79	80	79	78	76
PFNA	104	92	105	111	101	107	94	100	97	103	100	95
PFDA	116	100	97	89	92	89	80	82	85	86	80	81
PFUdA	84	88	95	97	91	95	85	85	87	90	84	85
PFDoA	100	92	95	97	97	94	86	90	88	92	88	81
PFTrDA	88	80	89	88	91	93	89	87	88	90	85	86
PFTeDA	88	84	91	89	89	91	82	80	82	84	81	81
ADONA	93	283	99	99	102	101	93	93	96	98	93	91
HFPO-DA	84	76	84	87	86	89	80	80	83	84	80	80
PFBS	86	90	87	86	81	88	78	79	84	83	79	77
PFPeS	81	76	79	76	80	87	74	75	82	81	75	75
PFHxS	76	84	84	89	85	85	78	82	84	78	79	75
PFHpS	97	88	101	101	107	114	92	92	91	95	98	94
PFOS	82	86	92	89	84	86	79	81	85	84	84	80
Br PFOS	134	112	109	101	85	91	79	81	84	84	83	80
PFNS	79	79	76	86	89	86	75	76	81	82	82	80
PFDS	75	83	83	86	85	84	76	74	74	86	78	78
PFUdS	70	74	76	83	80	78	70	71	74	77	75	75
PFDoS	70	74	76	76	79	79	69	71	72	77	72	69
PFTrDS	66	70	74	77	81	77	68	69	72	77	73	72
PFOSA	76	72	79	83	86	86	78	79	81	82	79	78
9Cl-PF3ONS	81	86	91	94	94	92	78	78	84	86	87	83
11Cl-PF3OUdS	76	85	83	92	95	93	82	84	86	90	88	86
4:2 FTS	2467	2962	882	844	260	256	259	137	194	200	115	108
6:2 FTS	156	79140	421	122	100	115	86	94	76	97	76	84
8:2 FTS	88	171	96	86	92	100	83	87	77	85	80	82
10:2 FTS	87	99	90	79	88	76	84	76	82	83	79	73

Table 20. Native Recoveries (%) from Bread (5g) Spiked at 0.05, 0.15, 0.5, 1.5, 2, and 5 ngg^{-1}

Analyte	**0.05**	**0.05**	**0.15**	**0.15**	**0.5**	**0.5**	**1.5**	**1.5**	**2**	**2**	**5**	**5**
PFBA	296	272	148	149	103	109	87	83	72	81	79	76
PFPeA	396	692	303	232	136	119	99	113	90	93	83	80
PFHxA	96	88	77	93	84	86	80	78	67	78	77	78
PFHpA	88	72	80	77	87	85	80	77	64	76	75	71
PFOA	96	100	84	93	90	85	80	80	66	77	74	74
BrPFOA	172	96	77	93	83	86	79	79	65	78	74	74
PFNA	96	72	81	96	93	83	77	79	65	75	76	71
PFDA	180	160	132	141	113	116	109	101	98	99	109	100
PFUdA	88	68	77	91	86	84	81	79	68	77	78	75
PFDoA	116	104	95	92	94	83	79	75	70	76	78	75
PFTrDA	132	108	120	143	140	124	131	125	95	121	126	128
PFTeDA	192	112	116	113	99	90	84	79	64	78	81	78
ADONA	85	72	85	96	92	89	84	80	73	82	84	78
HFPO-DA	80	68	76	87	88	81	79	79	68	78	79	77
PFBS	86	72	77	84	88	83	77	81	70	79	77	74
PFPeS	72	68	75	86	86	88	79	81	69	77	76	77
PFHxS	80	68	77	87	87	79	81	76	64	77	78	73
PFHpS	88	71	81	87	93	87	83	80	68	82	81	78
PFOS	91	73	80	86	91	78	77	73	65	75	81	79
Br PFOS	108	103	88	92	94	82	79	74	66	75	79	78
PFNS	62	54	55	62	74	65	60	60	52	58	60	60
PFDS	37	37	35	39	44	41	38	37	31	35	34	37
PFUdS	21	25	18	22	24	23	20	21	15	21	19	21
PFDoS	8	8	8	12	12	12	10	11	9	10	10	11
PFTrDS	8	8	7	8	7	7	7	7	6	7	6	7
PFOSA	80	68	75	81	82	81	78	77	69	76	78	75
9Cl-PF3ONS	77	69	76	81	92	79	75	72	64	73	78	75
11Cl-PF3OUdS	38	38	37	41	48	44	39	41	34	40	39	40
4:2 FTS	341	290	162	164	107	106	85	83	72	80	72	70
6:2 FTS	244	215	189	157	112	132	97	102	84	99	99	103
8:2 FTS	117	100	107	119	117	120	106	104	90	99	92	99
10:2 FTS	83	66	81	84	79	76	76	75	61	75	69	77

Table 21. Native Recoveries (%) from Bread (1g) Spiked at 0.05, 0.15, 0.5, 1.5, 2, and 5 ngg^{-1}

Analyte	**0.05**	**0.05**	**0.15**	**0.15**	**0.5**	**0.5**	**1.5**	**1.5**	**2**	**2**	**5**	**5**
PFBA	1020	1080	537	523	208	226	123	119	119	113	95	92
PFPeA	552	552	295	339	137	142	109	109	99	106	88	90
PFHxA	116	120	119	112	92	102	91	90	93	92	84	82
PFHpA	92	84	111	104	84	109	88	83	85	88	84	80
PFOA	112	128	117	103	85	98	91	86	87	88	82	80
BrPFOA	112	116	113	97	85	106	91	88	87	87	83	80
PFNA	84	100	120	109	90	107	94	86	92	91	88	85
PFDA	164	168	153	145	110	132	119	114	124	117	107	107
PFUdA	96	112	119	105	86	102	90	85	87	88	81	81
PFDoA	112	108	112	113	81	105	90	85	83	84	81	82
PFTrDA	176	132	161	133	108	149	115	117	108	103	116	115
PFTeDA	152	144	132	92	79	108	82	84	73	72	80	76
ADONA	93	93	113	100	91	105	93	91	89	91	87	84
HFPO-DA	88	92	109	99	89	100	91	87	91	90	86	82
PFBS	113	113	116	105	88	103	92	87	90	88	86	86
PFPeS	76	89	105	98	88	102	93	88	92	94	86	87
PFHxS	93	89	108	94	86	101	89	90	88	87	89	81
PFHpS	88	88	119	103	91	102	94	89	93	85	90	80
PFOS	99	95	103	101	87	101	95	90	88	88	82	85
Br PFOS	121	147	114	105	91	105	94	90	89	89	82	85
PFNS	75	75	90	76	72	80	77	75	74	70	70	70
PFDS	58	54	66	61	54	55	55	52	53	47	50	50
PFUdS	41	37	47	39	34	38	32	31	30	26	32	32
PFDoS	25	21	27	26	21	22	19	19	18	15	20	20
PFTrDS	12	12	18	16	14	14	12	13	12	10	14	13
PFOSA	84	92	104	89	85	98	90	86	88	87	84	83
9Cl-PF3ONS	90	94	100	97	89	96	93	93	90	88	83	85
11Cl-PF3OUdS	64	64	74	69	58	61	57	54	52	47	56	56
4:2 FTS	346	405	199	198	102	125	103	101	100	100	81	79
6:2 FTS	185	194	189	384	105	158	110	121	123	146	102	104
8:2 FTS	108	125	138	122	118	123	124	112	109	106	113	101
10:2 FTS	95	103	120	98	81	105	87	95	83	81	86	79

Table 22. Native Recoveries (%) from Egg Spiked at 0.05, 0.15, 0.5, 1.5, 2, and 5 ngg^{-1}

Analyte	**0.05**	**0.05**	**0.15**	**0.15**	**0.5**	**0.5**	**1.5**	**1.5**	**2**	**2**	**5**	**5**
PFBA	396	272	203	181	114	110	81	84	84	86	78	78
PFPeA	180	416	103	113	89	86	79	80	79	79	82	81
PFHxA	104	100	85	91	87	84	78	79	79	78	84	82
PFHpA	100	88	87	92	85	84	79	80	79	83	79	82
PFOA	92	100	88	83	79	81	73	74	75	75	76	76
BrPFOA	120	116	93	97	84	83	74	75	75	76	76	76
PFNA	84	88	93	92	87	88	81	85	83	86	83	90
PFDA	96	100	96	96	84	86	80	80	79	83	72	73
PFUdA	88	80	84	84	82	80	77	76	78	79	70	73
PFDoA	84	96	95	87	81	82	76	74	80	80	83	85
PFTrDA	72	76	73	76	77	72	67	67	66	71	79	82
PFTeDA	92	88	87	85	84	82	72	73	74	74	68	74
ADONA	76	76	79	83	82	80	74	76	77	79	78	78
HFPO-DA	84	80	81	85	84	82	75	78	79	82	76	78
PFBS	86	90	83	84	80	81	74	76	79	80	79	79
PFPeS	81	85	82	82	78	83	77	78	82	82	80	80
PFHxS	80	76	86	77	78	76	74	75	80	80	77	77
PFHpS	80	76	90	73	78	74	78	71	83	83	81	79
PFOS	108	99	91	82	81	81	76	77	77	80	79	76
Br PFOS	172	185	111	96	90	91	80	78	77	81	79	77
PFNS	83	87	79	78	78	80	70	71	73	75	74	73
PFDS	83	87	91	84	83	82	75	73	76	77	78	78
PFUdS	79	87	79	86	79	75	73	70	72	73	72	72
PFDoS	78	78	80	80	79	84	71	70	73	75	64	63
PFTrDS	70	78	74	73	70	73	66	66	66	68	62	62
PFOSA	72	84	81	84	86	83	76	77	78	79	72	75
9Cl-PF3ONS	77	86	86	86	82	79	76	72	75	77	76	70
11Cl-PF3OUdS	81	93	88	93	88	90	78	78	82	86	77	75
4:2 FTS	145	149	104	108	102	91	92	86	90	90	82	93
6:2 FTS	97	135	91	83	80	82	77	77	72	72	76	79
8:2 FTS	83	104	92	82	94	82	74	80	75	84	82	82
10:2 FTS	87	87	90	87	74	83	77	80	82	72	78	85

Table 23. Native Recoveries (%) from Dry Cat Food Spiked at 0.05, 0.15, 0.5, 1.5, 2, and 5 ngg^{-1}

Analyte	**0.05**	**0.05**	**0.15**	**0.15**	**0.5**	**0.5**	**1.5**	**1.5**	**2**	**2**	**5**	**5**
PFBA	784	788	327	345	145	151	100	99	90	92	83	84
PFPeA	1080	1144	448	531	188	198	117	113	105	102	90	90
PFHxA	N/A	N/A	112	100	90	84	83	79	76	79	77	83
PFHpA	88	92	76	80	79	74	71	69	67	70	71	72
PFOA	116	124	103	104	91	85	80	78	75	80	80	81
BrPFOA	140	128	121	109	96	92	80	79	76	81	80	81
PFNA	104	92	104	97	102	91	84	87	84	88	87	89
PFDA	120	116	108	108	94	95	87	84	81	79	85	87
PFUdA	96	92	96	93	94	95	86	87	83	84	86	88
PFDoA	96	96	107	105	101	101	91	90	90	90	92	92
PFTrDA	128	120	124	123	115	110	111	111	107	110	108	109
PFTeDA	88	96	95	101	89	90	84	87	82	86	86	86
ADONA	110	102	121	113	110	107	100	108	94	99	101	102
HFPO-DA	88	84	89	92	93	90	82	85	81	81	86	86
PFBS	104	104	90	101	88	92	80	85	77	82	82	85
PFPeS	110	127	95	98	85	88	78	79	76	78	81	80
PFHxS	105	105	96	115	92	91	79	81	78	81	83	83
PFHpS	101	88	98	105	106	103	81	92	85	89	94	104
PFOS	155	129	106	114	95	90	83	81	79	79	85	84
Br PFOS	259	250	177	158	109	96	82	82	77	78	84	81
PFNS	83	83	93	91	89	84	80	77	75	78	83	82
PFDS	87	79	90	90	91	80	78	76	74	76	78	77
PFUdS	70	66	72	74	72	68	66	62	62	62	65	62
PFDoS	54	58	62	66	60	57	56	52	52	53	55	54
PFTrDS	41	45	49	56	52	48	50	45	43	47	49	47
PFOSA	88	84	91	89	91	87	80	82	80	82	83	82
9Cl-PF3ONS	81	73	89	91	90	83	79	76	74	74	78	80
11Cl-PF3OUdS	81	76	91	88	91	85	80	78	73	80	82	78
4:2 FTS	145	149	101	107	89	85	75	67	81	78	76	79
6:2 FTS	219	492	171	125	98	126	87	93	87	88	87	79
8:2 FTS	100	121	110	118	101	103	94	93	96	93	101	96
10:2 FTS	79	91	81	81	89	81	73	77	77	81	77	76

Table 24. Native Recoveries (%) from Dry Dog Food Spiked at 0.05, 0.15, 0.5, 1.5, 2, and 5 ngg^{-1}

Analyte	**0.05**	**0.05**	**0.15**	**0.15**	**0.5**	**0.5**	**1.5**	**1.5**	**2**	**2**	**5**	**5**
PFBA	408	444	204	205	126	119	94	92	87	88	83	83
PFPeA	1176	1276	520	523	221	228	130	124	117	110	97	93
PFHxA	124	116	100	97	87	84	88	83	77	81	78	78
PFHpA	128	120	103	85	91	89	87	85	84	83	83	78
PFOA	128	120	95	103	95	88	87	83	83	84	80	77
BrPFOA	116	148	108	109	94	92	89	81	83	85	82	78
PFNA	96	96	92	91	91	82	84	82	78	80	78	74
PFDA	176	168	115	129	116	110	100	98	98	100	99	101
PFUdA	96	108	93	89	96	94	90	88	89	87	88	89
PFDoA	108	108	95	100	100	97	88	92	83	88	86	88
PFTrDA	160	144	116	108	112	105	103	97	95	96	97	99
PFTeDA	160	148	117	105	99	92	95	89	87	85	90	88
ADONA	97	106	100	104	104	103	105	95	96	101	94	93
HFPO-DA	84	84	88	93	97	91	92	87	85	85	86	82
PFBS	95	104	93	92	90	91	90	84	84	83	85	86
PFPeS	98	85	89	89	87	88	88	80	82	80	83	82
PFHxS	93	93	89	94	91	91	88	84	85	85	88	82
PFHpS	88	88	92	97	103	107	94	87	92	94	97	94
PFOS	168	172	114	118	99	100	91	88	82	85	86	88
Br PFOS	216	190	125	124	100	104	92	90	84	89	88	90
PFNS	71	62	68	71	79	74	69	70	67	70	73	72
PFDS	62	62	61	62	62	65	61	59	58	55	60	59
PFUdS	50	54	51	50	48	52	47	47	45	44	47	47
PFDoS	41	33	37	36	37	38	35	35	35	33	36	35
PFTrDS	29	29	27	30	29	33	29	29	29	27	30	28
PFOSA	88	84	88	84	93	90	87	84	81	82	84	80
9Cl-PF3ONS	86	81	79	83	90	85	80	79	77	78	80	83
11Cl-PF3OUdS	68	64	65	66	65	64	61	64	58	60	62	65
4:2 FTS	166	158	102	108	100	99	85	82	84	79	75	78
6:2 FTS	164	147	109	121	108	100	98	78	88	77	87	87
8:2 FTS	179	167	111	110	100	99	85	87	88	85	83	89
10:2 FTS	120	103	90	87	92	86	87	82	83	83	82	74

Table 25. Native Recoveries (%) from Wet Cat Food Spiked at 0.05, 0.15, 0.5, 1.5, 2, and 5 ngg^{-1}

Analyte	**0.05**	**0.05**	**0.15**	**0.15**	**0.5**	**0.5**	**1.5**	**1.5**	**2**	**2**	**5**	**5**
PFBA	176	192	119	116	98	99	94	92	85	90	93	90
PFPeA	152	184	109	113	99	94	91	90	89	89	95	90
PFHxA	96	96	91	96	92	89	95	92	84	89	89	90
PFHpA	136	124	99	99	101	90	89	90	73	86	90	86
PFOA	100	96	92	95	91	94	87	93	84	87	93	90
BrPFOA	200	192	112	96	99	93	89	96	85	89	92	91
PFNA	96	96	85	85	96	96	98	101	87	94	97	95
PFDA	104	100	99	95	99	98	96	93	88	95	96	95
PFUdA	100	96	91	96	98	96	93	90	87	93	97	96
PFDoA	88	84	95	91	96	94	98	97	93	91	97	92
PFTrDA	92	84	87	84	92	88	90	87	85	84	94	85
PFTeDA	96	88	95	92	100	99	99	99	91	96	100	96
ADONA	80	89	87	87	102	102	100	98	94	96	97	100
HFPO-DA	84	80	87	85	95	98	95	96	91	92	96	91
PFBS	95	81	86	89	88	95	92	95	85	88	100	93
PFPeS	81	72	74	76	84	78	78	81	87	83	88	87
PFHxS	80	80	87	82	94	89	89	90	86	98	98	89
PFHpS	84	88	90	90	93	86	88	90	90	94	101	87
PFOS	121	116	98	99	97	98	96	97	87	90	98	90
Br PFOS	121	125	93	108	98	98	95	96	87	90	97	89
PFNS	83	75	87	84	89	92	93	95	87	92	97	92
PFDS	83	75	80	93	91	93	94	94	89	90	95	89
PFUdS	83	83	83	90	89	94	94	94	86	90	96	90
PFDoS	78	74	80	88	87	90	89	89	79	85	97	85
PFTrDS	74	70	74	81	83	88	87	87	78	82	88	80
PFOSA	84	80	84	81	93	95	94	92	88	89	94	91
9Cl-PF3ONS	81	77	79	80	85	88	89	92	83	85	90	85
11Cl-PF3OUdS	81	85	88	95	96	99	98	99	93	93	104	94
4:2 FTS	137	119	101	94	100	93	88	93	85	91	92	93
6:2 FTS	164	151	114	115	103	113	108	93	87	98	98	99
8:2 FTS	121	113	113	117	113	115	122	113	109	114	122	116
10:2 FTS	83	83	87	86	95	85	95	90	79	87	94	92

Table 26. Native Recoveries (%) from Wet Dog Food Spiked at 0.05, 0.15, 0.5, 1.5, 2, and 5 ngg^{-1}

Analyte	**0.05**	**0.05**	**0.15**	**0.15**	**0.5**	**0.5**	**1.5**	**1.5**	**2**	**2**	**5**	**5**
PFBA	312	124	95	93	90	88	89	85	86	83	89	90
PFPeA	252	340	147	140	108	111	94	94	93	94	93	93
PFHxA	108	100	91	84	89	88	95	87	85	85	85	79
PFHpA	88	72	81	75	84	77	80	79	76	74	79	82
PFOA	112	104	89	89	92	85	88	86	85	86	88	86
BrPFOA	128	128	99	108	97	93	90	87	86	86	88	86
PFNA	96	96	89	91	98	92	94	90	89	91	91	89
PFDA	108	116	96	100	99	94	97	92	98	91	100	97
PFUdA	84	76	89	91	98	90	95	93	89	86	94	91
PFDoA	100	88	91	89	90	92	99	94	89	88	92	92
PFTrDA	84	84	87	89	95	96	93	90	86	87	91	90
PFTeDA	96	108	92	93	97	99	101	95	92	95	96	97
ADONA	93	89	99	94	99	101	104	98	99	96	99	94
HFPO-DA	88	88	88	88	94	92	94	91	89	91	92	91
PFBS	86	90	90	86	92	95	90	86	87	89	87	93
PFPeS	85	81	89	84	91	91	92	89	87	89	90	89
PFHxS	80	84	89	86	89	93	92	85	90	84	88	88
PFHpS	67	88	90	94	91	89	87	85	90	84	84	92
PFOS	91	99	92	85	88	90	89	90	82	87	93	93
Br PFOS	108	121	95	92	88	92	89	90	83	87	92	92
PFNS	79	83	86	80	89	89	90	89	90	87	91	96
PFDS	79	87	80	81	88	92	90	90	83	85	91	95
PFUdS	83	87	86	86	85	88	84	88	85	83	89	89
PFDoS	62	74	70	73	73	80	78	80	75	76	79	80
PFTrDS	66	70	69	70	76	76	77	75	74	73	80	78
PFOSA	76	76	88	83	89	85	89	86	85	88	86	89
9Cl-PF3ONS	73	77	83	76	86	85	81	88	79	84	87	83
11Cl-PF3OUdS	81	85	89	88	91	93	93	91	90	90	94	91
4:2 FTS	124	124	97	95	94	93	92	85	91	85	90	84
6:2 FTS	173	181	125	128	108	101	93	95	89	96	91	90
8:2 FTS	92	117	96	108	110	127	104	123	112	107	110	111
10:2 FTS	83	95	86	83	89	94	90	87	85	86	86	91

Table 27. Native Recoveries (%) from Chocolate Milk Spiked at 0.05, 0.15, 0.5, 1.5, 2, and 5 ngg^{-1}

Analyte	**0.05**	**0.05**	**0.15**	**0.15**	**0.5**	**0.5**	**1.5**	**1.5**	**2**	**2**	**5**	**5**
PFBA	316	384	141	164	109	110	87	84	83	83	78	80
PFPeA	80	132	88	97	87	86	77	76	78	76	79	78
PFHxA	100	128	85	96	90	90	83	79	80	77	79	79
PFHpA	76	96	87	89	90	90	80	77	75	77	76	78
PFOA	92	104	85	91	89	87	78	77	74	75	74	78
BrPFOA	112	136	103	95	99	94	81	79	76	78	76	78
PFNA	84	80	88	88	93	92	83	82	78	79	80	81
PFDA	100	108	87	88	98	92	80	80	81	83	82	84
PFUdA	76	84	77	76	88	87	77	77	78	77	79	78
PFDoA	76	84	83	81	91	85	79	75	77	77	78	77
PFTrDA	84	88	76	80	78	82	75	71	74	74	72	76
PFTeDA	80	84	77	80	84	82	75	75	73	75	76	76
ADONA	85	85	87	92	94	93	88	83	87	83	83	84
HFPO-DA	76	76	84	81	91	90	80	77	79	80	78	80
PFBS	77	86	78	84	88	88	82	81	80	80	77	84
PFPeS	81	85	74	82	82	86	81	77	78	79	78	82
PFHxS	76	80	82	79	90	87	76	77	72	77	81	76
PFHpS	92	80	77	83	91	83	81	76	76	80	83	83
PFOS	86	82	88	89	88	88	83	79	75	78	84	81
Br PFOS	121	95	98	99	90	91	84	78	76	78	83	80
PFNS	75	66	80	79	90	83	80	76	74	73	81	78
PFDS	75	75	84	90	92	89	86	71	70	70	82	74
PFUdS	70	79	83	86	88	83	83	72	73	73	78	78
PFDoS	70	66	73	77	80	82	76	68	68	71	73	75
PFTrDS	70	70	77	75	83	83	78	70	69	70	75	74
PFOSA	68	80	80	80	87	89	79	78	76	77	78	83
9Cl-PF3ONS	73	73	81	81	87	87	83	73	69	74	81	77
11Cl-PF3OUdS	76	76	85	88	90	90	91	78	79	77	87	82
4:2 FTS	137	145	100	101	96	85	78	80	77	74	80	77
6:2 FTS	5785	7468	1937	2694	672	750	285	284	226	229	140	155
8:2 FTS	88	104	78	86	94	93	81	84	82	77	82	77
10:2 FTS	83	99	81	88	83	87	82	70	77	73	77	75

Table 28. Native Recoveries (%) from Whole Milk Spiked at 0.05, 0.15, 0.5, 1.5, 2, and 5 ngg^{-1}

Analyte	**0.05**	**0.05**	**0.15**	**0.15**	**0.5**	**0.5**	**1.5**	**1.5**	**2**	**2**	**5**	**5**
PFBA	124	132	103	96	92	88	77	81	80	81	85	82
PFPeA	156	176	108	103	89	93	83	79	81	78	83	83
PFHxA	108	104	93	88	91	91	83	83	84	82	86	83
PFHpA	88	76	100	81	88	84	78	82	82	76	82	81
PFOA	112	100	89	87	88	88	77	79	79	77	82	77
BrPFOA	120	176	95	96	93	95	79	81	81	78	82	78
PFNA	96	104	88	89	91	88	82	92	86	81	84	86
PFDA	112	104	92	89	86	86	77	77	78	81	84	78
PFUdA	92	92	81	83	92	84	83	77	81	81	84	82
PFDoA	96	96	92	81	92	88	83	83	80	81	87	83
PFTrDA	80	76	83	79	88	83	78	81	82	78	80	80
PFTeDA	88	88	88	83	88	84	80	78	81	78	80	78
ADONA	89	89	94	86	99	92	89	84	88	90	89	85
HFPO-DA	88	84	87	85	92	88	82	81	81	82	86	84
PFBS	90	81	92	86	91	83	78	80	79	80	85	82
PFPeS	81	89	91	89	91	85	81	79	81	82	85	83
PFHxS	80	76	89	80	94	84	83	84	81	80	83	81
PFHpS	84	80	90	78	91	86	80	85	82	80	81	80
PFOS	91	82	85	85	88	89	82	81	81	83	87	84
Br PFOS	121	103	92	98	91	90	82	81	81	83	84	84
PFNS	87	71	83	82	88	86	80	82	79	82	87	80
PFDS	83	75	81	84	87	85	80	82	81	77	86	81
PFUdS	87	70	80	81	81	78	75	76	74	78	80	76
PFDoS	87	78	85	81	85	84	79	80	77	79	82	79
PFTrDS	78	70	80	78	84	81	77	79	79	77	82	77
PFOSA	80	72	87	81	90	86	80	81	79	80	84	82
9Cl-PF3ONS	90	81	91	89	89	91	79	88	86	89	89	87
11Cl-PF3OUdS	93	76	95	83	93	90	82	86	87	89	90	86
4:2 FTS	132	132	102	98	89	94	80	85	83	74	78	84
6:2 FTS	126	2100	121	109	134	97	86	83	79	95	91	98
8:2 FTS	92	88	90	82	95	83	83	84	76	82	93	84
10:2 FTS	108	87	90	80	78	86	83	79	72	76	82	84

Table 29. Native Recoveries (%) from Lettuce Spiked at 0.05, 0.15, 0.5, 1.5, 2, and 5 ngg^{-1}

Analyte	**0.05**	**0.05**	**0.15**	**0.15**	**0.5**	**0.5**	**1.5**	**1.5**	**2**	**2**	**5**	**5**
PFBA	156	148	107	105	79	86	74	74	77	75	79	79
PFPeA	344	436	216	175	114	121	85	97	82	82	80	83
PFHxA	108	112	93	87	77	83	75	75	75	78	78	80
PFHpA	120	148	100	107	80	88	82	79	79	78	85	79
PFOA	100	100	84	84	73	77	75	74	73	76	78	75
BrPFOA	96	96	92	93	73	76	76	74	76	77	78	74
PFNA	92	108	93	103	84	95	89	82	82	84	93	86
PFDA	104	88	92	83	74	88	73	69	71	73	75	72
PFUdA	76	72	84	83	75	85	78	76	74	78	78	76
PFDoA	84	76	79	84	76	84	76	77	76	76	77	76
PFTrDA	72	76	76	73	70	77	69	72	65	71	69	72
PFTeDA	80	80	87	83	72	81	73	73	72	73	75	75
ADONA	76	80	83	85	78	88	75	79	80	80	78	77
HFPO-DA	80	80	84	81	76	86	77	76	76	79	80	77
PFBS	86	86	86	84	75	83	75	77	76	78	81	76
PFPeS	76	72	85	79	76	82	77	77	77	80	80	79
PFHxS	76	72	80	82	72	86	78	78	73	76	76	78
PFHpS	80	84	85	88	75	93	85	79	79	84	87	86
PFOS	82	82	85	78	78	82	77	74	74	75	75	74
Br PFOS	95	99	98	79	79	86	78	75	74	74	75	74
PFNS	75	71	79	78	71	76	77	73	73	73	74	71
PFDS	75	79	80	80	69	80	75	73	77	75	81	73
PFUdS	70	70	79	79	70	77	72	72	72	71	74	69
PFDoS	74	70	73	74	67	74	67	66	69	68	71	64
PFTrDS	70	70	77	73	63	77	68	68	69	70	72	66
PFOSA	72	76	80	80	74	79	77	77	73	76	75	76
9Cl-PF3ONS	73	77	74	74	75	79	74	74	70	72	75	70
11Cl-PF3OUdS	89	81	81	82	76	83	74	77	75	76	80	75
4:2 FTS	141	154	114	102	83	91	79	77	81	85	82	82
6:2 FTS	4258	7157	1512	1589	511	494	207	206	171	177	125	123
8:2 FTS	113	113	93	106	82	102	83	71	82	82	86	90
10:2 FTS	87	83	80	84	70	79	70	68	77	70	78	78

Table 30. Native Recoveries (%) from Salmon (5 g) Spiked at 0.05, 0.15, 0.5, 1.5, 2, and 5 ngg^{-1}

Analyte	**0.05**	**0.05**	**0.15**	**0.15**	**0.5**	**0.5**	**1.5**	**1.5**	**2**	**2**	**5**	**5**
PFBA	216	280	163	173	105	101	87	81	82	79	80	79
PFPeA	104	92	137	121	93	90	87	76	78	77	79	79
PFHxA	92	116	96	112	96	98	91	80	87	80	82	80
PFHpA	84	120	93	93	92	88	84	76	75	75	74	78
PFOA	96	104	92	101	90	88	83	73	75	73	76	76
BrPFOA	128	188	100	99	94	86	85	73	77	74	77	77
PFNA	112	128	115	123	108	105	106	90	93	91	91	96
PFDA	88	96	91	103	86	89	82	77	78	80	80	77
PFUdA	104	128	96	109	88	91	81	81	76	82	78	83
PFDoA	92	108	97	99	89	92	88	77	76	81	80	81
PFTrDA	104	108	105	108	96	106	83	81	89	82	89	87
PFTeDA	72	92	83	93	84	84	76	78	74	79	72	81
ADONA	76	85	92	100	88	91	88	75	83	73	82	77
HFPO-DA	72	88	88	95	86	88	83	77	76	77	79	80
PFBS	77	86	92	96	89	91	87	77	82	75	79	79
PFPeS	81	89	92	92	88	90	87	80	78	78	82	77
PFHxS	76	84	91	96	85	84	78	75	77	77	75	78
PFHpS	76	97	90	91	86	86	80	76	79	81	76	85
PFOS	99	108	93	111	88	85	83	75	76	75	79	80
Br PFOS	108	121	106	119	90	88	83	89	76	84	78	81
PFNS	75	87	89	100	86	86	84	78	77	78	85	81
PFDS	79	83	88	97	85	82	83	85	75	83	80	80
PFUdS	66	74	74	81	72	72	72	74	62	70	66	67
PFDoS	41	49	47	45	42	44	56	61	39	54	42	43
PFTrDS	49	62	53	59	53	49	69	63	44	62	49	44
PFOSA	92	108	91	97	87	88	81	79	75	76	78	80
9Cl-PF3ONS	77	94	86	100	85	84	84	77	74	78	76	78
11Cl-PF3OUdS	72	76	85	88	76	79	79	80	70	80	73	76
4:2 FTS	141	158	131	110	91	101	105	83	85	89	84	88
6:2 FTS	97	109	102	97	90	85	81	82	79	76	77	83
8:2 FTS	75	88	93	107	94	100	92	87	79	94	82	97
10:2 FTS	95	91	97	109	89	88	85	77	75	78	82	88

Table 31. Native Recoveries (%) from Salmon (1 g) Spiked at 0.05, 0.15, 0.5, 1.5, 2, and 5 ngg^{-1}

Analyte	**0.05**	**0.05**	**0.15**	**0.15**	**0.5**	**0.5**	**1.5**	**1.5**	**2**	**2**	**5**	**5**
PFBA	1056	1020	481	459	234	227	131	141	126	118	111	100
PFPeA	112	96	93	96	113	89	97	94	95	92	99	91
PFHxA	156	164	119	107	110	92	98	96	96	95	94	90
PFHpA	108	112	95	89	106	90	96	95	94	94	96	91
PFOA	124	124	99	92	103	88	92	92	91	91	92	86
BrPFOA	156	168	100	95	104	89	94	92	91	92	92	86
PFNA	152	144	113	108	121	110	113	109	107	112	111	109
PFDA	128	112	89	89	94	78	86	87	86	86	83	80
PFUdA	160	156	112	107	117	100	103	101	102	102	99	94
PFDoA	124	116	108	95	114	96	102	99	101	98	101	96
PFTrDA	148	160	109	123	136	117	100	93	112	122	139	94
PFTeDA	120	112	101	91	110	93	99	96	98	95	97	95
ADONA	97	93	92	89	106	89	97	94	97	90	95	88
HFPO-DA	104	100	93	89	107	91	98	96	98	94	99	93
PFBS	135	126	107	95	110	97	96	96	96	90	97	93
PFPeS	110	110	95	91	108	93	96	97	96	93	96	93
PFHxS	101	118	93	91	98	89	95	94	94	96	97	89
PFHpS	113	88	97	90	105	93	101	95	95	96	97	94
PFOS	207	194	105	116	110	96	94	97	102	94	96	89
Br PFOS	668	703	273	283	155	145	106	110	112	104	100	92
PFNS	100	96	87	93	98	92	94	96	99	94	95	89
PFDS	116	116	102	102	114	97	104	102	104	102	100	98
PFUdS	157	124	90	98	99	82	92	91	86	83	76	86
PFDoS	70	54	70	48	59	42	67	65	50	50	45	71
PFTrDS	62	49	63	47	49	45	70	85	56	49	37	83
PFOSA	132	128	101	99	105	95	97	99	93	94	97	92
9Cl-PF3ONS	103	107	96	93	104	97	91	97	101	92	95	90
11Cl-PF3OUdS	106	106	95	96	106	93	95	100	97	97	90	97
4:2 FTS	166	171	114	114	125	99	108	105	100	108	106	101
6:2 FTS	295	396	617	348	204	98	102	116	121	94	105	102
8:2 FTS	138	121	107	110	115	101	117	118	115	110	116	113
10:2 FTS	116	91	105	97	105	82	94	99	101	95	92	97

Table 32. Native Recoveries (%) from Corn Flour Spiked at 0.05, 0.15, 0.5, 1.5, 2, and 5 ngg^{-1}

Analyte	**0.05**	**0.05**	**0.15**	**0.15**	**0.5**	**0.5**	**1.5**	**1.5**	**2**	**2**	**5**	**5**
PFBA	92	100	77	76	73	77	74	69	72	72	72	72
PFPeA	104	68	136	100	93	83	75	74	76	76	74	74
PFHxA	96	92	77	83	78	75	82	73	76	77	74	75
PFHpA	60	60	63	61	64	64	60	59	61	61	60	63
PFOA	84	88	75	75	71	74	72	64	71	66	66	70
BrPFOA	92	100	77	81	74	76	73	65	72	67	67	70
PFNA	108	108	92	91	91	96	94	85	90	88	88	91
PFDA	128	124	99	95	100	91	81	75	77	80	79	80
PFUdA	100	76	79	81	80	85	82	74	74	77	77	78
PFDoA	92	92	79	83	88	82	79	76	83	77	78	77
PFTrDA	92	92	88	83	84	88	84	78	78	85	81	84
PFTeDA	76	88	79	76	78	80	75	72	75	80	74	76
ADONA	80	89	89	86	94	94	93	85	89	89	86	86
HFPO-DA	72	72	76	79	79	81	77	73	76	77	75	75
PFBS	77	81	74	75	78	77	78	67	74	76	72	71
PFPeS	81	85	82	79	82	85	85	78	77	81	79	79
PFHxS	68	72	75	70	76	78	74	73	75	74	75	71
PFHpS	63	67	73	69	72	75	71	67	74	71	69	72
PFOS	78	78	72	80	78	76	76	77	75	73	76	77
Br PFOS	116	95	80	88	81	78	77	77	75	73	75	76
PFNS	79	71	71	76	73	76	74	72	71	70	74	73
PFDS	70	66	70	70	73	70	68	72	70	68	71	72
PFUdS	70	62	63	65	68	68	70	67	65	63	66	65
PFDoS	54	58	58	60	59	57	59	57	58	55	57	57
PFTrDS	53	58	56	62	59	58	56	56	56	54	56	56
PFOSA	68	72	75	72	75	77	74	69	73	73	73	72
9Cl-PF3ONS	73	81	77	84	79	81	79	80	80	77	80	78
11Cl-PF3OUdS	68	72	72	79	76	76	76	77	74	73	76	74
4:2 FTS	175	179	118	110	87	110	82	82	77	75	75	83
6:2 FTS	126	97	81	86	79	80	71	73	71	71	69	73
8:2 FTS	92	96	89	79	84	85	81	81	84	82	86	79
10:2 FTS	91	91	73	91	82	73	83	83	81	75	79	88

Table 33. Native Recoveries (%) from Corn Silage Spiked at 0.05, 0.15, 0.5, 1.5, 2, and 5 ngg^{-1}

Analyte	**0.05**	**0.05**	**0.15**	**0.15**	**0.5**	**0.5**	**1.5**	**1.5**	**2**	**2**	**5**	**5**
PFBA	180	180	101	107	86	94	67	72	64	70	71	72
PFPeA	1012	984	309	384	146	164	135	101	80	88	78	75
PFHxA	132	140	92	96	90	97	72	76	69	74	74	75
PFHpA	116	100	79	89	83	90	64	71	67	71	73	75
PFOA	132	116	95	88	84	91	63	71	66	70	73	70
BrPFOA	124	116	89	88	89	96	63	72	67	71	73	71
PFNA	104	100	88	85	92	99	70	78	74	78	83	81
PFDA	112	100	87	87	84	85	63	71	66	73	73	73
PFUdA	92	92	77	81	82	88	68	70	68	71	71	73
PFDoA	104	100	84	88	94	96	67	76	72	77	78	78
PFTrDA	96	88	71	75	76	77	63	68	62	69	67	61
PFTeDA	92	92	79	79	83	87	67	73	67	72	73	70
ADONA	106	93	87	89	95	97	77	84	78	79	82	81
HFPO-DA	88	84	77	80	82	85	67	72	67	71	73	73
PFBS	108	95	77	78	85	88	68	68	63	69	71	69
PFPeS	89	89	78	78	85	88	69	73	67	72	74	74
PFHxS	97	84	75	77	81	83	64	73	68	71	74	73
PFHpS	84	76	70	77	81	79	65	64	68	68	73	72
PFOS	86	86	78	78	84	85	69	71	64	70	73	73
Br PFOS	181	198	119	108	89	102	70	73	67	73	72	73
PFNS	91	79	71	72	80	83	65	67	62	66	66	67
PFDS	83	75	73	75	82	87	66	64	61	67	67	71
PFUdS	83	79	70	73	76	79	62	61	61	63	66	66
PFDoS	74	66	59	62	68	72	55	56	52	57	56	59
PFTrDS	78	66	66	64	75	74	55	61	59	60	61	62
PFOSA	80	80	75	76	79	86	66	68	65	69	73	70
9Cl-PF3ONS	86	73	73	73	79	86	65	64	62	68	66	69
11Cl-PF3OUdS	93	85	74	81	84	88	70	71	67	71	72	73
4:2 FTS	333	316	162	174	109	134	84	82	72	96	82	88
6:2 FTS	299	366	130	227	109	145	63	89	76	82	82	111
8:2 FTS	150	129	97	97	99	96	81	79	72	79	72	73
10:2 FTS	141	128	98	105	90	105	75	79	68	69	74	77

Table 34. Initial MDL Determination.

Analyte	**Prep Option 1**	**Prep Option 2**	**Prep Option 3**
PFBA	230[b]	140[s]	650[b]
PFPeA	150 [s]	83 [s]	110 [s]
PFHxA	82 [s]	42 [s]	68[b]
PFHpA	67 [s]	30 [s]	30 [s]
PFOA	78 [s]	30 [s]	23[b]
BrPFOA	82 [s]	55[b]	49[b]
PFNA	72 [s]	26 [s]	21 [s]
PFDA	110 [s]	26[b]	32[b]
PFUdA	91 [s]	27 [s]	19 [s]
PFDoA	78 [s]	24 [s]	23 [s]
PFTrDA	90 [s]	30 [s]	57 [s]
PFTeDA	94 [s]	23 [s]	31 [s]
ADONA	78 [s]	19 [s]	27 [s]
HFPO-DA	74 [s]	26 [s]	29 [s]
PFBS	59 [s]	25 [s]	37 [s]
PFPeS	53 [s]	16 [s]	26 [s]
PFHxS	64 [s]	26 [s]	28 [s]
PFHpS	77 [s]	33 [s]	23 [s]
PFOS	69 [s]	30 [s]	30 [s]
Br PFOS	75 [s]	120 [s]	86[b]
PFNS	75 [s]	31 [s]	35 [s]
PFDS	67 [s]	51 [s]	48 [s]
PFUdS	73 [s]	50 [s]	66 [s]
PFDoS	70 [s]	30 [s]	58 [s]
PFTrDS	110 [s]	46 [s]	43 [s]
PFOSA	160[*s]	130[*s]	81[*s]
9Cl-PF3ONS	68 [s]	26 [s]	31 [s]
11Cl-PF3OUdS	81 [s]	40 [s]	67 [s]
4:2 FTS	50 [s]	32 [s]	43[b]
6:2 FTS	3800[b]	110[b]	3300[b]
8:2 FTS	64 [s]	16 [s]	34 [s]
10:2 FTS	1800 [s]	310[b]	51 [s]

[b]Initial value = MDL_b

[s]Initial value = MDL_s

[*]Determined from 0.5ng/g spike.

Table 35. Matrix MDL Values: Sample Prep 1.

Analyte	Clam	Lettuce	Milk, Whole	Milk, Chocolate	Wet Cat Food	Wet Dog Food
PFBA	230[1]	230[1]	230[1]	230[1]	230[1]	230[1]
PFPeA	100	190	29	34	66	100
PFHxA	61	28	22[1]	22[1]	41	28
PFHpA	44	27	33	21[1]	56	37
PFOA	39	30	22[1]	22[1]	54	37
BrPFOA	47[1]	47[1]	47[1]	47[1]	57	50
PFNA	60	32	10	16	38	38
PFDA	29	36	30	23[1]	46	61
PFUdA	25	14	11	20	28	46
PFDoA	18	22	21	13[1]	27	38
PFTrDA	52	35	18	17	38	59
PFTeDA	27	20	21	12	35	48
ADONA	36	16	18	14	26	52
HFPO-DA	27	18	12	11	23	45
PFBS	21	21	18	11	31	39
PFPeS	22	15	14	21	18	37
PFHxS	29	21	23	5	30	38
PFHpS	110[2]	27	18	17	39	45
PFOS	22[1]	32	22[1]	22[1]	29	37
Br PFOS	77	120	73	82	82[2]	37
PFNS	31	12	12	14	37	40
PFDS	33	15	17	27	30	37
PFUdS	35	26	17	15	30	44
PFDoS	26	11	24	14	35	33
PFTrDS	24	19	7	14	24	28
PFOSA*	170[2]	210[2]	120[2]	110[2]	24	120[2]
9Cl-PF3ONS	28	18	21	12	24	35
11Cl-PF3OUdS	25	15	22	20	32	39
4:2 FTS	36[1]	36[1]	36[1]	36[1]	36[1]	69[2]
6:2 FTS	3800[1]	3800[1]	3800[1]	4900	3800[1]	3800[1]
8:2 FTS	19	46	26	69[2]	70	180[2]
10:2 FTS	24	27	150[2]	24	32	31

[1]MDL Value is the MDL_B Value

[2]MDL Value Calculated From the 0.5ppb Spike Level

Table 36. Matrix MDL Values: Sample Prep 2.

Analyte	Bread, Wheat	Chicken Feed	Corn Flour	Dry Cat Food	Dry Dog Food	Egg	Salmon, 5g
PFBA	84[1]	84[1]	84[1]	210	84[1]	84[1]	94
PFPeA	240	55	120	940	1000	34	62
PFHxA	25	39	30	41	33	17	34
PFHpA	24	300[2]	270[2]	28	31	15[1]	22
PFOA	28	23	29	29	29	21[1]	34
BrPFOA	55[1]	55[1]	55[1]	55[1]	55[1]	55[1]	56
PFNA	40	23	8[1]	23	27	10	20
PFDA	91	43	26[1]	28	38	34	40
PFUdA	23	25	18	35	33	10	28
PFDoA	140[2]	12	40	37	26	14	25
PFTrDA	63	28	41	64	44	24	53
PFTeDA	41	14	29	36	52	18	21
ADONA	17	26	60	53	31	10	25
HFPO-DA	18	210[2]	21	45[2]	27	10	19
PFBS	13	10	120[2]	24	17	6	20
PFPeS	17	15	13	31	20	10	15
PFHxS	16	14	22	44	20	15	30
PFHpS	23	660[2]	90[2]	81[2]	170[2]	26	15
PFOS	21	16[1]	19	80	20	16[1]	36
Br PFOS	120[1]	54	120[1]	120[1]	120[1]	120[1]	120[1]
PFNS	17	15	17	32	14	16	28
PFDS	10	17	21	33	17	15	24
PFUdS	12	21	19	33	19	30	16
PFDoS	63[2]	20	12	24	24	22	33
PFTrDS	3	14	15	20	18	13	44
PFOSA*	160[2]	170[2]	120[2]	58[2]	19	92[2]	18
9Cl-PF3ONS	18	29	12	25	11	9	25
11Cl-PF3OUdS	17	18	18	33	17	22	15
4:2 FTS	130[2]	N/A	140[2]	23	20[1]	20[1]	38
6:2 FTS	280	450	110[1]	220[2]	140	520	110[1]
8:2 FTS	66	28	26	61	130[2]	33	29
10:2 FTS	310[1]	310[1]	310[1]	310[1]	310[1]	310[1]	310[1]

[1]MDL Value is the MDL_B Value

[2]MDL Value Calculated From the 0.5ppb Spike Level

Table 37. Matrix MDL Values: Sample Prep 3.

Analyte	Alfalfa	Salmon, 1g	Silage, Corn
PFBA	650[1]	650[1]	650[1]
PFPeA	190	72	910
PFHxA	N/A	68[1]	120
PFHpA	28	41	90
PFOA	45	29	90
BrPFOA	120	49[1]	90
PFNA	36	29	100
PFDA	72	32[1]	97
PFUdA	210[2]	47	81
PFDoA	32	49	86
PFTrDA	110	84	82
PFTeDA	31	39	89
ADONA	43	24	100
HFPO-DA	29	35	230[2]
PFBS	250[2]	35	74
PFPeS	29	29	80
PFHxS	250[2]	30	77
PFHpS	440[2]	30	68
PFOS	32	46	69
Br PFOS	86[1]	310	91
PFNS	33	30	78
PFDS	26	48	77
PFUdS	44	44	79
PFDoS	240[2]	37	73
PFTrDS	78	33	72
PFOSA*	240[2]	130[2]	240[2]
9Cl-PF3ONS	34	33	84
11Cl-PF3OUdS	26	43	90
4:2 FTS	53	43[1]	N/A
6:2 FTS	3300[1]	3300[1]	3300[1]
8:2 FTS	27	84[2]	130
10:2 FTS	280[2]	44	120

[1]MDL Value is the MDL_B Value

[2]MDL Value Calculated From the 0.5ppb Spike Level

Table 38. Limit of Quantification by Matrix – Sample Prep 1.

Analyte	Clam	Lettuce	Milk, Whole	Milk, Chocolate	Wet Cat Food	Wet Dog Food
PFBA	730	730	730	730	730	730
PFPeA	470	610	470	470	470	470
PFHxA	260	260	260	260	260	260
PFHpA	210	210	210	210	210	210
PFOA	250	250	250	250	250	250
BrPFOA	260	260	260	260	260	260
PFNA	230	230	230	230	230	230
PFDA	350	350	350	350	350	350
PFUdA	290	290	290	290	290	290
PFDoA	250	250	250	250	250	250
PFTrDA	290	290	290	290	290	290
PFTeDA	300	300	300	300	300	300
ADONA	250	250	250	250	250	250
HFPO-DA	240	240	240	240	240	240
PFBS	190	190	190	190	190	190
PFPeS	170	170	170	170	170	170
PFHxS	210	210	210	210	210	210
PFHpS	360	250	250	250	250	250
PFOS	220	220	220	220	220	220
Br PFOS	240	370	240	260	370	240
PFNS	240	240	240	240	240	240
PFDS	210	210	210	210	210	210
PFUdS	230	230	230	230	230	230
PFDoS	220	220	220	220	220	220
PFTrDS	350	350	350	350	350	350
PFOSA*	550	680	520	520	520	520
9Cl-PF3ONS	220	220	220	220	220	220
11Cl-PF3OUdS	260	260	260	260	260	260
4:2 FTS	160	160	160	160	250	220
6:2 FTS	12000	12000	12000	16000	12000	12000
8:2 FTS	200	200	200	220	220	560
10:2 FTS	5800	5800	5800	5800	5800	5800

Table 39. Limit of Quantification by Matrix – Sample Prep 2.

Analyte	Bread, Wheat	Chicken Feed	Corn Flour	Dry Cat Food	Dry Dog Food	Egg	Salmon, 5g
PFBA	440	440	440	680	440	440	440
PFPeA	770	260	370	3000	3300	260	260
PFHxA	130	130	130	130	130	130	130
PFHpA	97	960	880	97	98	97	97
PFOA	96	96	96	96	96	96	110
BrPFOA	180	180	180	180	180	180	180
PFNA	130	82	82	82	86	82	82
PFDA	290	140	210	110	120	110	130
PFUdA	85	85	85	110	100	85	89
PFDoA	440	77	130	120	82	77	79
PFTrDA	200	95	130	200	140	95	170
PFTeDA	130	75	92	110	160	75	75
ADONA	62	84	190	170	99	62	78
HFPO-DA	83	660	83	140	85	83	83
PFBS	79	79	370	79	79	79	79
PFPeS	53	49	49	100	63	49	49
PFHxS	81	81	81	140	81	81	95
PFHpS	110	2100	290	260	530	110	110
PFOS	94	94	94	250	94	94	120
Br PFOS	370	370	370	370	370	370	370
PFNS	100	100	100	100	100	100	100
PFDS	160	160	160	160	160	160	160
PFUdS	160	160	160	160	160	160	160
PFDoS	200	96	96	96	96	96	100
PFTrDS	150	150	150	150	150	150	150
PFOSA*	500	540	410	410	410	410	410
9Cl-PF3ONS	82	94	82	82	82	82	82
11Cl-PF3OUdS	130	130	130	130	130	130	130
4:2 FTS	400	N/A	440	100	100	100	120
6:2 FTS	900	1400	330	690	430	1700	320
8:2 FTS	210	89	81	200	400	110	92
10:2 FTS	990	990	990	990	990	990	1600

Table 40. Limit of Quantification by Matrix – Sample Prep 3.

Analyte	**Alfalfa**	**Salmon, 1g**	**Silage, Corn**
PFBA	2100	2100	2100
PFPeA	620	350	2900
PFHxA	N/A	220	370
PFHpA	97	130	290
PFOA	140	92	290
BrPFOA	380	160	290
PFNA	110	92	320
PFDA	230	100	310
PFUdA	680	150	260
PFDoA	100	160	270
PFTrDA	340	270	260
PFTeDA	100	130	280
ADONA	140	86	320
HFPO-DA	94	110	720
PFBS	790	120	230
PFPeS	92	91	260
PFHxS	800	97	250
PFHpS	1400	95	220
PFOS	100	150	220
Br PFOS	270	980	290
PFNS	110	110	250
PFDS	150	150	250
PFUdS	210	210	250
PFDoS	750	180	230
PFTrDS	250	140	230
PFOSA*	780	410	770
9Cl-PF3ONS	110	100	270
11Cl-PF3OUdS	210	210	290
4:2 FTS	170	140	N/A
6:2 FTS	11000	11000	11000
8:2 FTS	110	270	430
10:2 FTS	890	160	380

Table 41. Measurement Uncertainty

Analyte	**U**
PFBA	0.24
PFPeA	0.23
PFHxA	0.15
PFHpA	0.13
PFOA	0.12
BrPFOA	0.15
PFNA	0.16
PFDA	0.15
PFUdA	0.12
PFDoA	0.13
PFTrDA	0.22
PFTeDA	0.13
ADONA	0.15
HFPO-DA	0.11
PFBS	0.11
PFPeS	0.10
PFHxS	0.11
PFHpS	0.12
PFOS	0.12
Br PFOS	0.18
PFNS	0.13
PFDS	0.11
PFUdS	0.11
PFDoS	0.36
PFTrDS	0.29
PFOSA	0.11
9Cl-PF3ONS	0.15
11Cl-PF3OUdS	0.15
4:2 FTS	0.25
6:2 FTS	1.65
8:2 FTS	0.17
10:2 FTS	0.15

Table 42. Analyte Validation Summary by Matrix (Part 1). V = validated, NV = not validated.

Analyte	Alfalfa	Clam	Chicken Feed	Bread (5 g)	Bread (1 g)	Egg	Dry Cat Food	Dry Dog Food
PFBA	V	V	V	V	V	V	V	V
PFPeA	V	V	V	V	V	V	V	NV
PFHxA	V	V	V	V	V	V	V	V
PFHpA	V	V	V	V	V	V	V	V
PFOA	V	V	V	V	V	V	V	V
BrPFOA	V	V	V	V	V	V	V	V
PFNA	V	V	V	V	V	V	V	V
PFDA	V	V	V	V	V	V	V	V
PFUdA	V	V	V	V	V	V	V	V
PFDoA	V	V	V	V	V	V	V	V
PFTrDA	V	V	V	NV	V	V	V	V
PFTeDA	V	V	V	V	V	V	V	V
ADONA	NV	V	V	V	V	V	V	V
HFPO-DA	V	V	V	V	V	V	V	V
PFBS	V	V	V	V	V	V	V	V
PFPeS	V	V	V	V	V	V	V	V
PFHxS	V	V	V	V	V	V	V	V
PFHpS	V	V	V	V	V	V	V	V
PFOS	V	V	V	V	V	V	V	V
Br PFOS	NV	V	V	V	V	V	V	V
PFNS	V	V	V	V	V	V	V	V
PFDS	V	V	V	NV	V	V	V	V
PFUdS	V	V	V	NV	NV	V	V	V
PFDoS	V	V	V	NV	NV	V	V	NV
PFTrDS	V	V	V	NV	NV	V	V	NV
PFOSA	V	V	V	V	V	V	V	V
9Cl-PF3ONS	V	V	V	V	V	V	V	V
11Cl-PF3OUdS	V	V	V	NV	V	V	V	V
4:2 FTS	V	V	NV	V	V	V	V	V

Analyte	Alfalfa	Clam	Chicken Feed	Bread (5 g)	Bread (1 g)	Egg	Dry Cat Food	Dry Dog Food
6:2 FTS	NV	V	V	V	NV	V	V	V
8:2 FTS	V	V	V	V	NV	V	V	V
10:2 FTS	V	V	V	V	V	V	V	V

Table 43. Analyte Validation Summary by Matrix (Part 2). V = validated, NV = not validated.

Analyte	Wet Cat Food	Wet Dog Food	Chocolate Milk	Whole Milk	Lettuce	Salmon (5 g)	Salmon (1 g)	Corn Flour	Corn Silage
PFBA	V	V	V	V	V	V	NV	V	V
PFPeA	V	V	V	V	V	V	V	V	NV
PFHxA	V	V	V	V	V	V	V	V	V
PFHpA	V	V	V	V	V	V	V	V	V
PFOA	V	V	V	V	V	V	V	V	V
BrPFOA	V	V	V	V	V	V	V	V	V
PFNA	V	V	V	V	V	V	V	V	V
PFDA	V	V	V	V	V	V	V	V	V
PFUdA	V	V	V	V	V	V	V	V	V
PFDoA	V	V	V	V	V	V	V	V	V
PFTrDA	V	V	V	V	V	V	NV	V	V
PFTeDA	V	V	V	V	V	V	V	V	V
ADONA	V	V	V	V	V	V	V	V	V
HFPO-DA	V	V	V	V	V	V	V	V	V
PFBS	V	V	V	V	V	V	V	V	V
PFPeS	V	V	V	V	V	V	V	V	V
PFHxS	V	V	V	V	V	V	V	V	V
PFHpS	V	V	V	V	V	V	V	V	V
PFOS	V	V	V	V	V	V	V	V	V
Br PFOS	V	V	V	V	V	V	V	V	V
PFNS	V	V	V	V	V	V	V	V	V
PFDS	V	V	V	V	V	V	V	V	V
PFUdS	V	V	V	V	V	V	V	V	V
PFDoS	V	V	V	V	V	V	V	V	V
PFTrDS	V	V	V	V	V	V	V	V	V
PFOSA	V	V	V	V	V	V	V	V	V
9Cl-PF3ONS	V	V	V	V	V	V	V	V	V
11Cl-PF3OUdS	V	V	V	V	V	V	V	V	V
4:2 FTS	V	V	V	V	V	V	V	V	V

Analyte	Wet Cat Food	Wet Dog Food	Chocolate Milk	Whole Milk	Lettuce	Salmon (5 g)	Salmon (1 g)	Corn Flour	Corn Silage
6:2 FTS	V	V	NV	V	NV	V	NV	V	V
8:2 FTS	V	V	V	V	V	V	V	V	V
10:2 FTS	V	V	V	V	V	V	V	V	V

Figures

Figure 1. Integration example for the quantitative transition of target analyte PFOS encompassing branched and linear isomers.

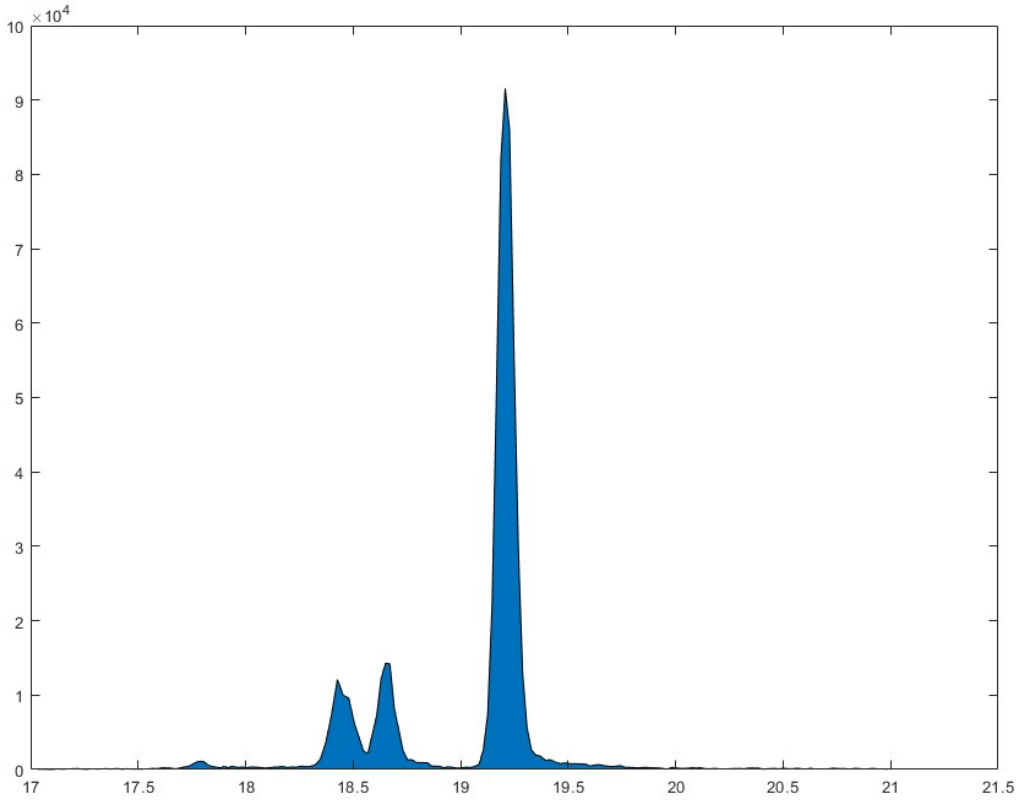


Figure 2. Reference chromatogram of a CS5 (1 ng/mL) calibration standard. Expected analyte retention times are listed in Table 11.

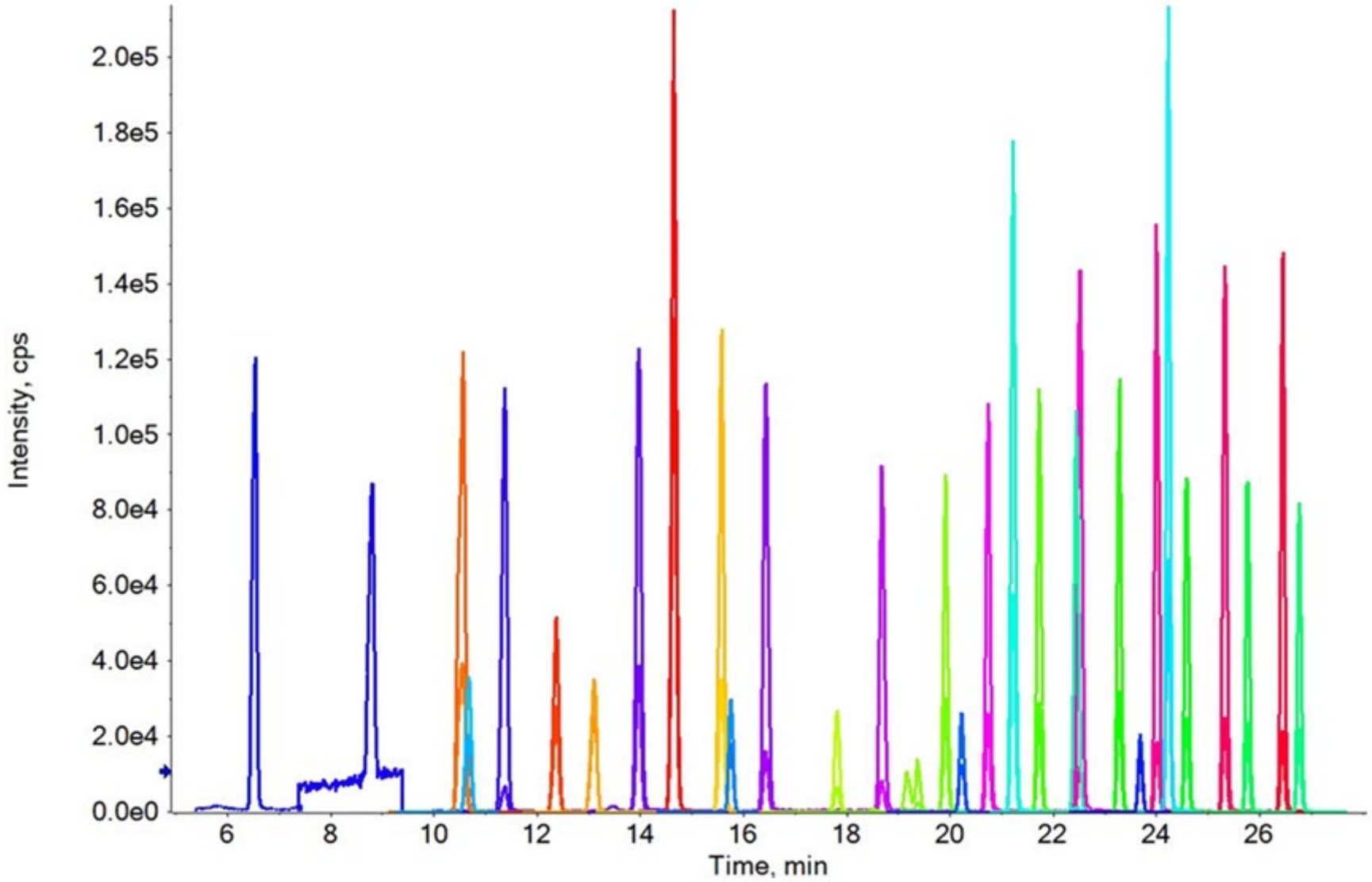
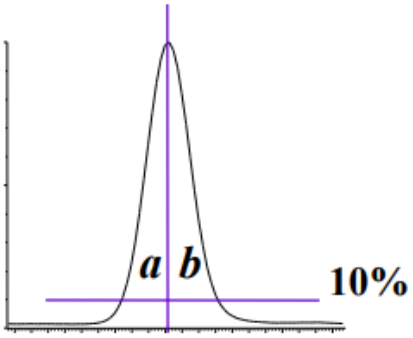


Figure 3. EPA Method 537.1 [21] Peak Asymmetry Calculation

$$A_s = \frac{b}{a}$$



where:

A_s = peak asymmetry factor

B = width of the back half of the peak measured (at 10% peak height) from the trailing edge of the peak to a line dropped perpendicularly from the peak apex

a = the width of the front half of the peak measured (at 10% peak height) from the leading edge of the peak to a line dropped perpendicularly from the apex.

Figure 4. Branched and Linear PFOA Isomer Retention Times.

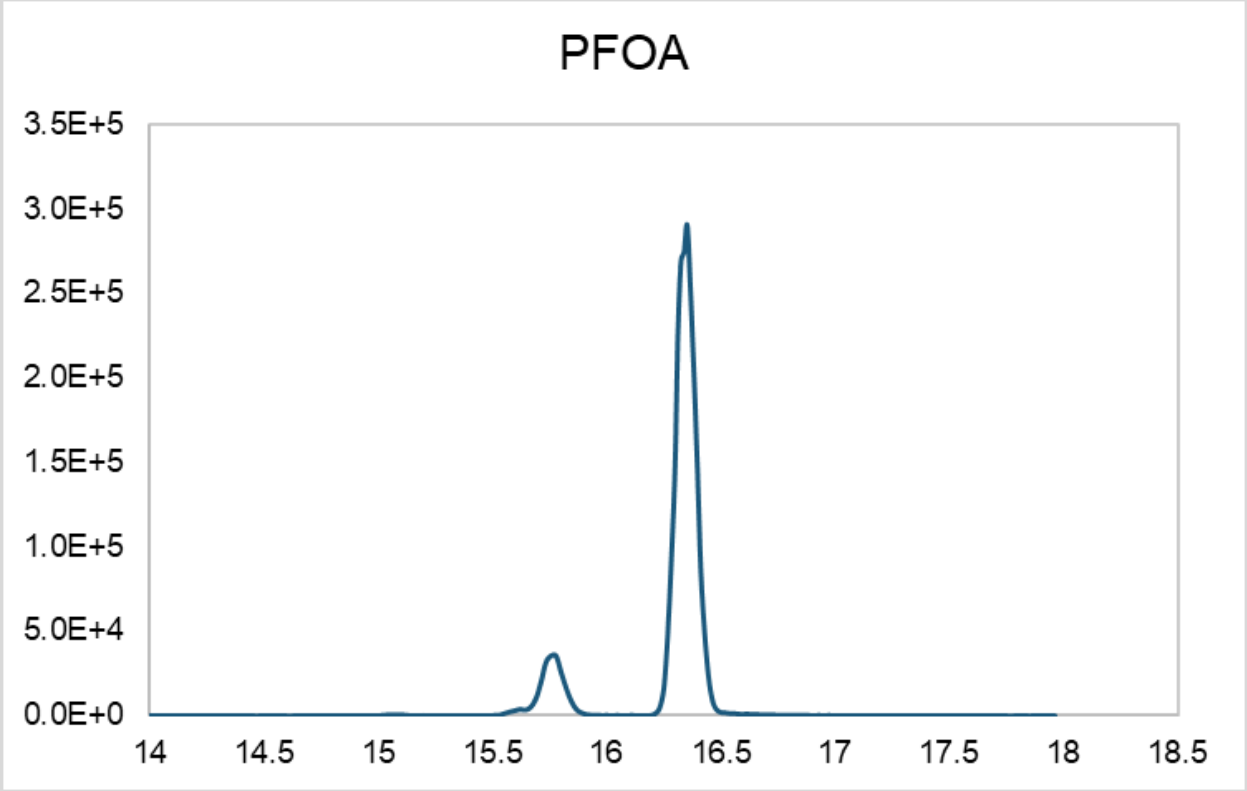
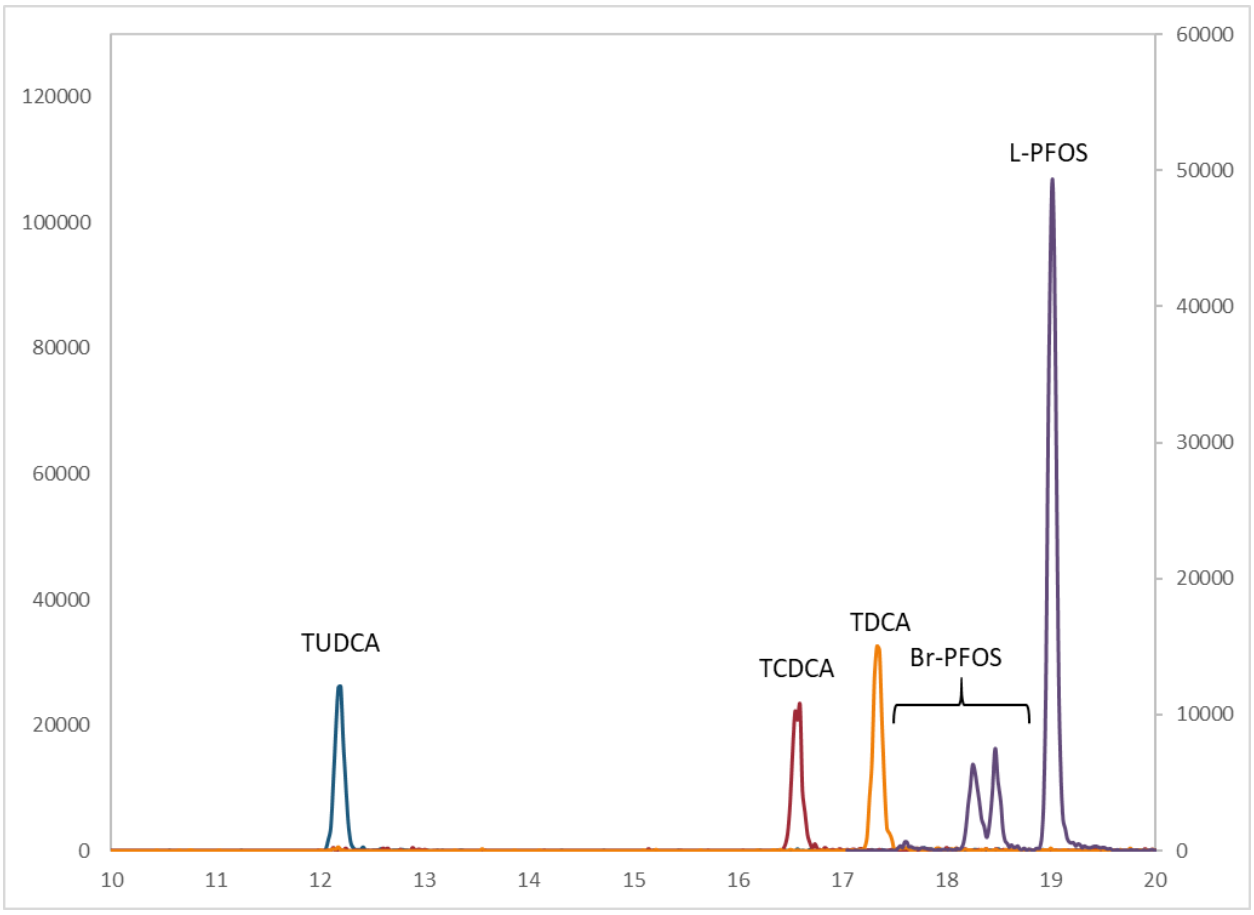


Figure 5. Resolution between potential cholic acid interferents of PFOS (chromatogram overlays).



Supplemental material

Separate PDF.