# Analysis of PFAS in Drinking Water: Validation Studies of EPA Method 537.1 Using StayClean™ QSight LC-MS/MS

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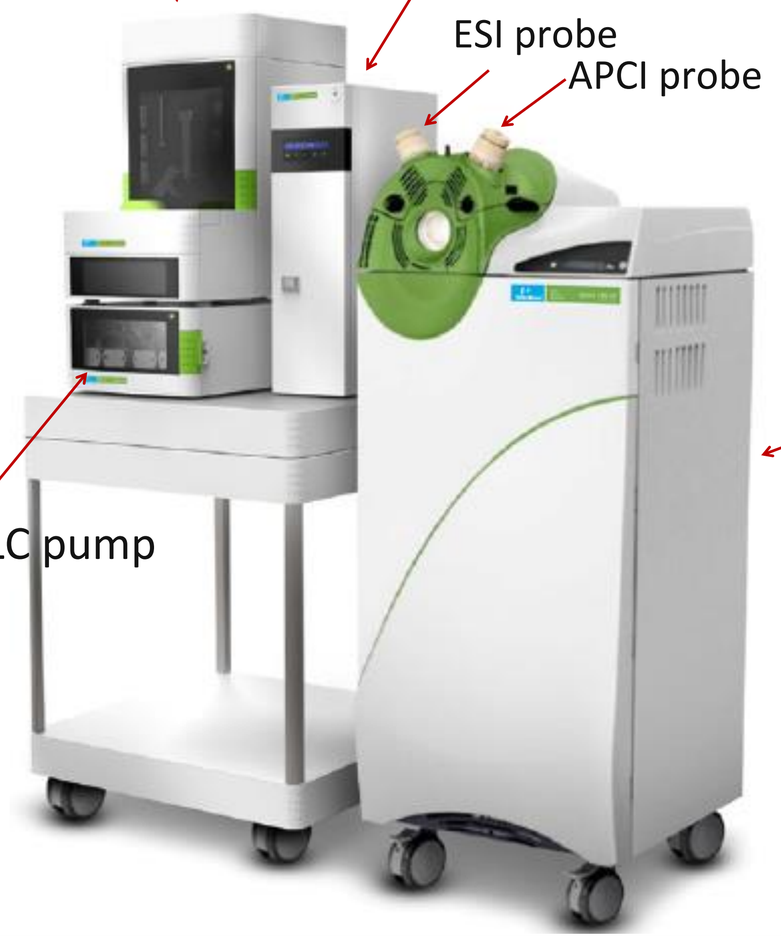
# StayClean™ QSight LC-MS/MS

- Dual Binary LC Pump
  - Two Sets of Mobile Phases
    - A1 and B1 for ESI
    - A2 and B2 for APCI
- Dual ESI/APCI Source
  - ESI for Polars
  - APCI for Non-polars



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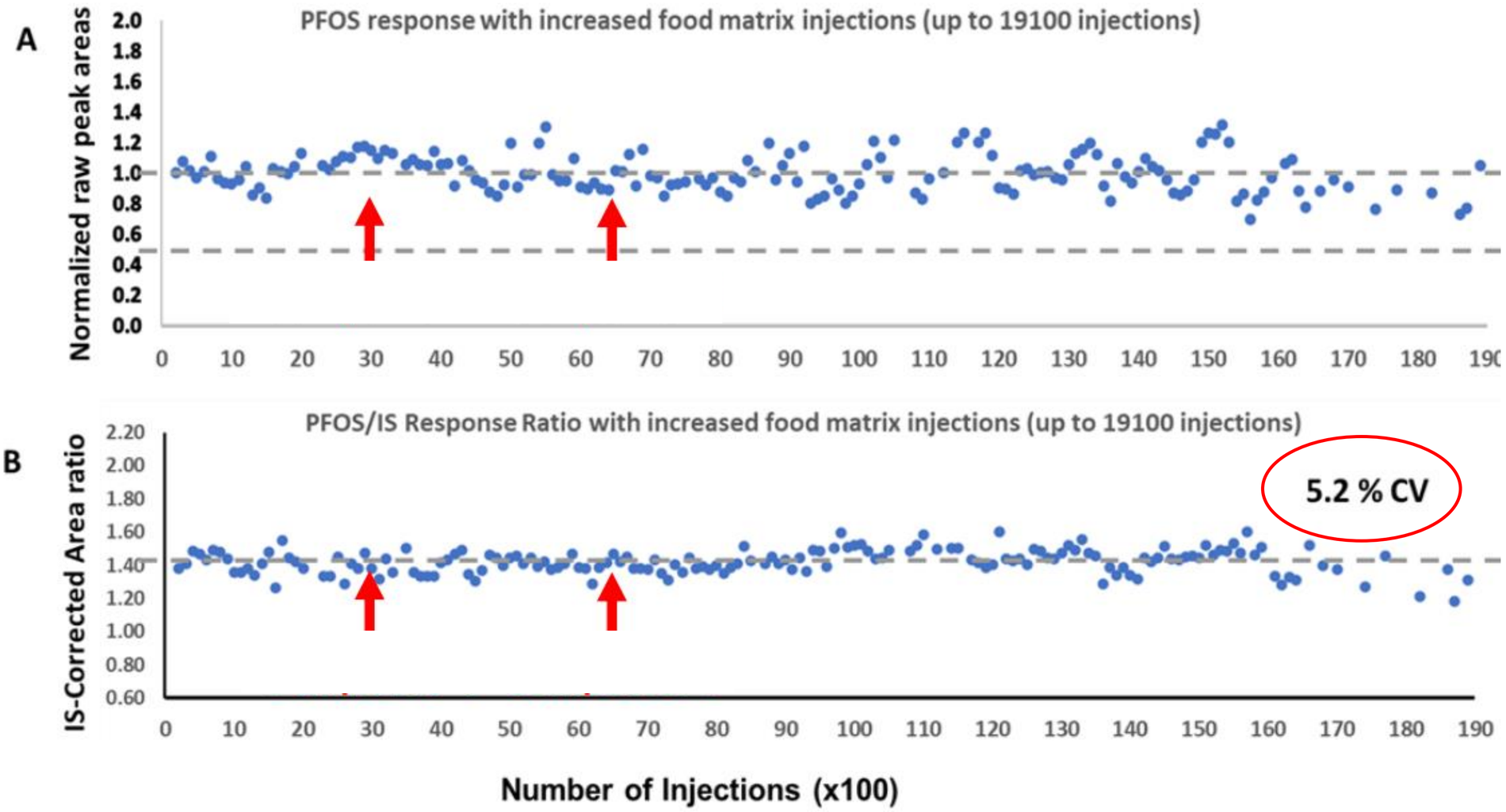
# Robustness: PFAS in Food Matrices (19,100 Continuous Injections)




Salmon, Avocado, Tomato Mix, Spice Powder, Dog/Cat Feed

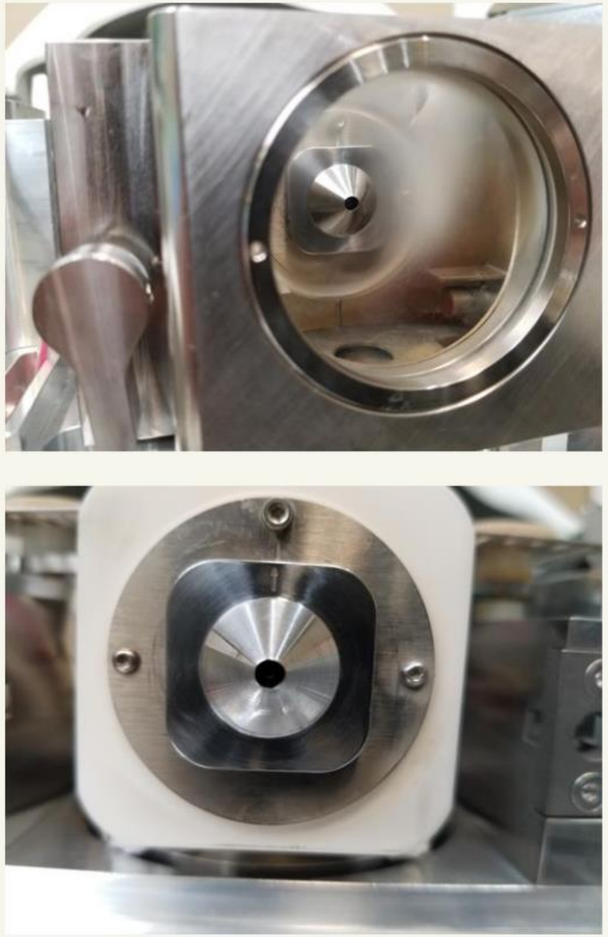
Food Matrices: salmon/avocado/tomato mix, spice powder, dog/cat feed

Preparation using QuEChERS[1] method developed for PFAS analysis in food, but the final SPE step was omitted to maximize sample matrix components in the final matrix extracts

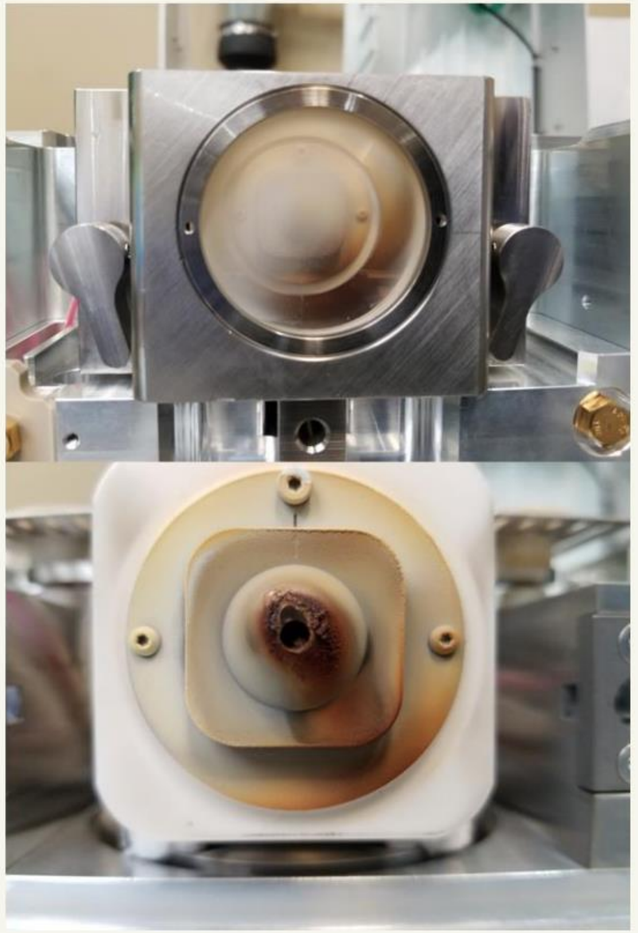
Instrument robustness evaluated by intermittently monitoring solvent QC samples between large blocks of 100 consecutive matrix injections

# Source Images: PFAS in Food Matrices

**Before**

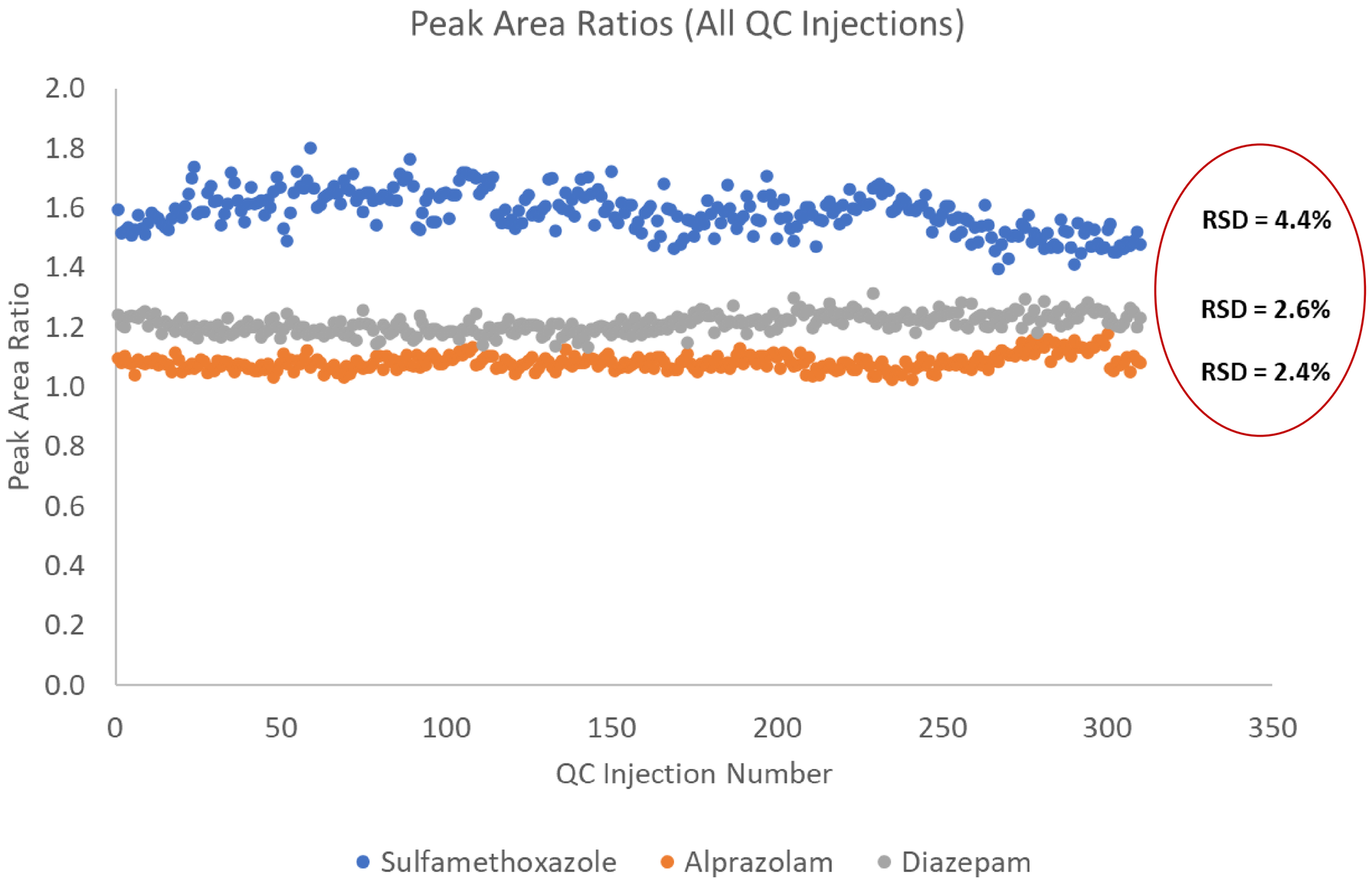


**After**



**After 19,100 Continuous Injections of Salmon, Avocado, Tomato Mix, Spice Powder, Dog/Cat Feed**

# Robustness: 25,500 Continuous Injections of Fetal Bovine Serum




- Protein precipitation of FBS with methanol followed by a 50% dilution with water prior to injecting 5 µL for analysis
- Monitoring 3 analytes and their deuterated standards (1 ng/mL)
- Instrument robustness evaluated by intermittently monitoring SST samples between large blocks of FBS matrix injections

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# Source Images

View from Source Window

Sample Cone

Plenum Chamber

After 25,500 Continuous Injections of Fetal Bovine Serum

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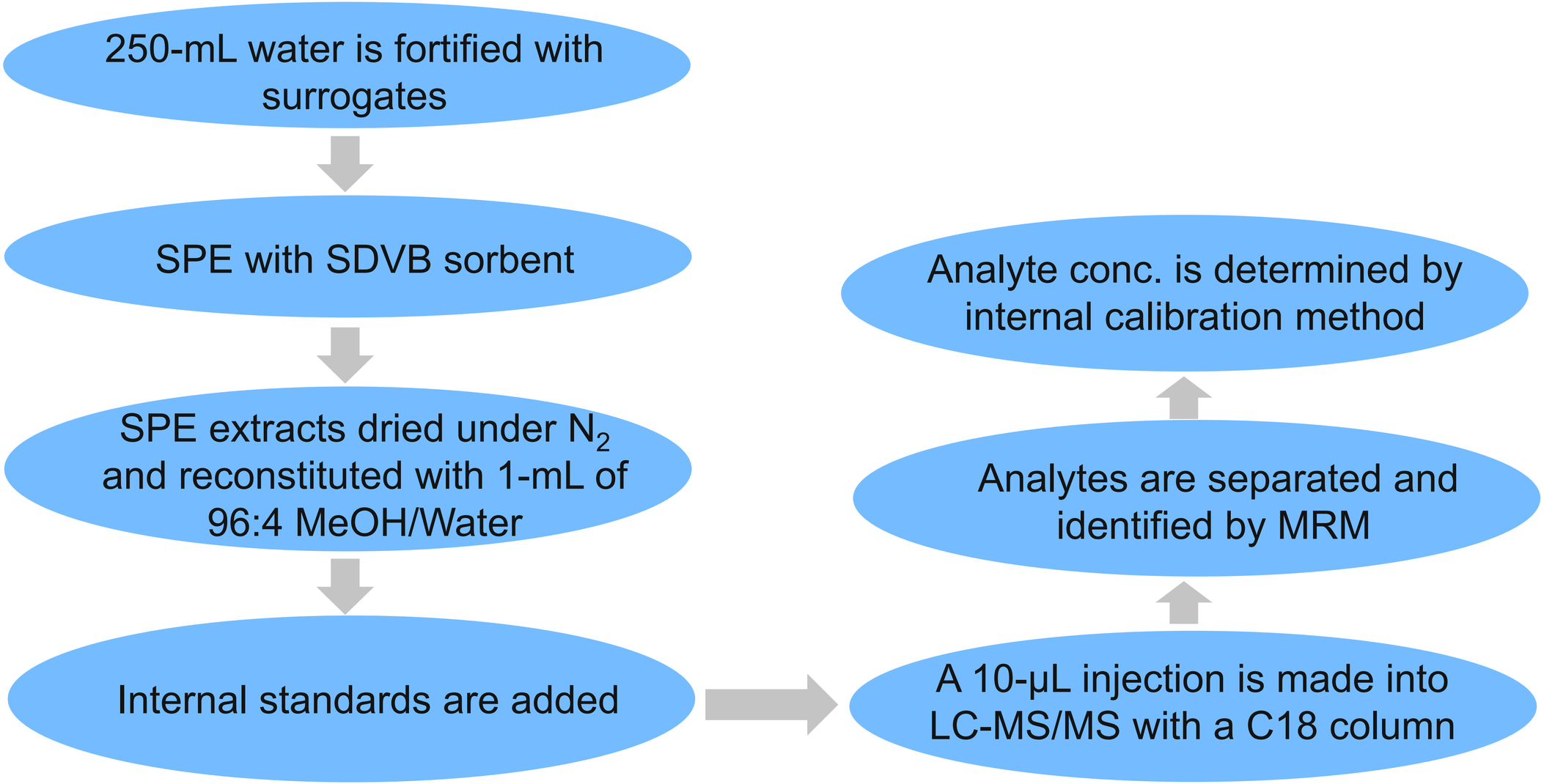
# Summary of PFAS EPA Drinking Water Methods

- EPA Method 537.1
  - Selected linear PFAS
  - 18 PFAS with chain lengths $C_4$-$C_{14}$
  - Isotopic internal standards and reverse phase SPE
- EPA Method 533
  - Short-chain & polar PFAS
  - 25 PFAS with chain length $C_4$-$C_{12}$
  - Addition of more polar fluorotelomers and ether carboxylic acids
  - Isotopic dilution and ion exchange SPE
- EPA Method 1633:
  - Broad range of PFAS in multiple matrices.
  - 40 PFAS in aqueous, solid, biosolids and tissue samples.
  - Isotopic dilution and multiple sample preparation techniques.

# EPA Method 537.1 Summary



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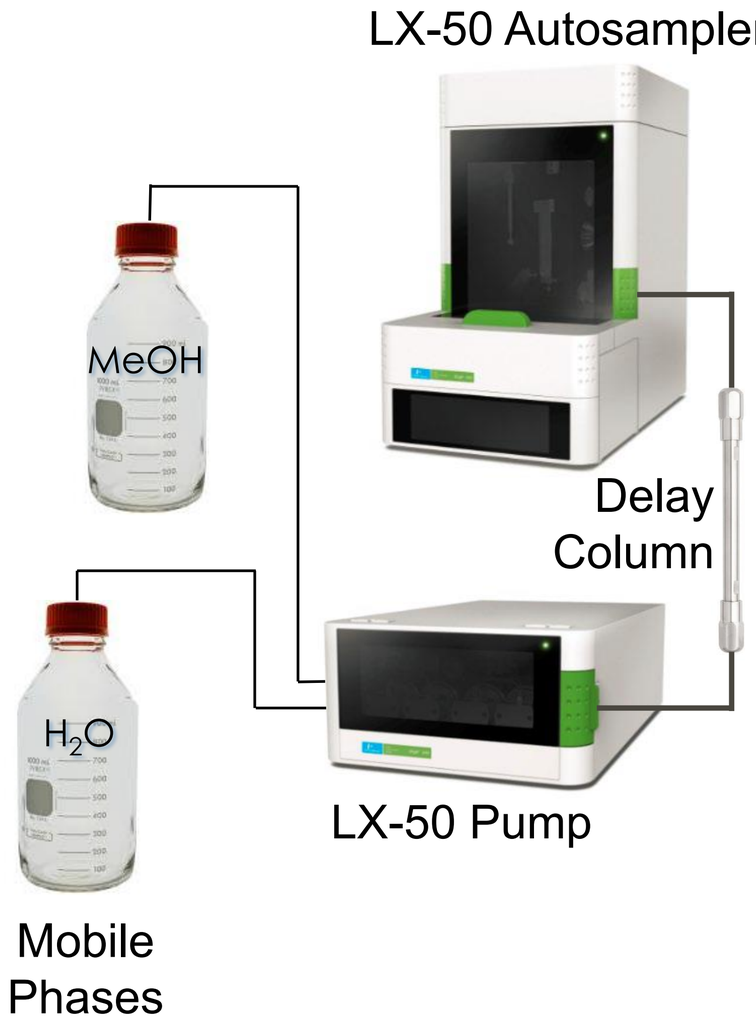
# Major Challenges of EPA Method 537.1

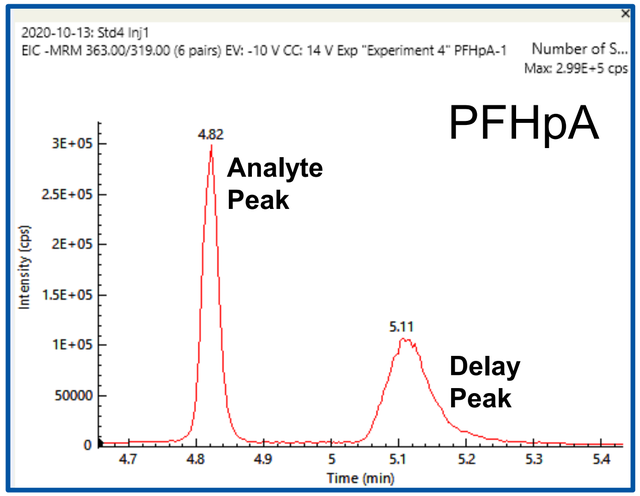
- PFAS ubiquitous, leading to elevated background level
  - Found in clothing, carpet, food packaging, etc.
  - LC-MS and SPE systems constructed from PTFE
  - Glass containers absorb PFAS. Use polyethylene/polypropylene containers
  - Wear nitrile gloves to reduce contamination

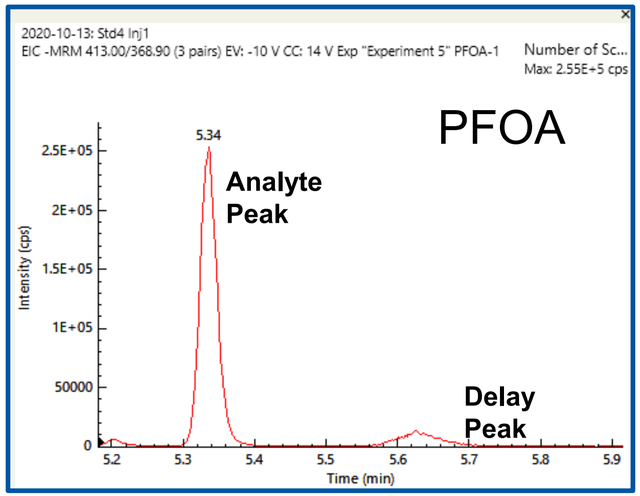
# Remediation Steps to Reduce PFAS Contamination

| Source of Contamination | Remediation |
|---|---|
| Mobile phases | • Purchase LC-MS grade solvents<br>• Use a delay column |
| PTFE parts & tubing in HPLC pump | Use a delay column |
| PTFE Tubing in HPLC autosampler | Replace with PEEK tubing |
| Vials and PTFE lined caps | Use only polyethylene vials and caps |
| PTFE tubing in SPE apparatus | Replace with polyethylene tubing |

# Reducing Background from Pump and Mobile Phases



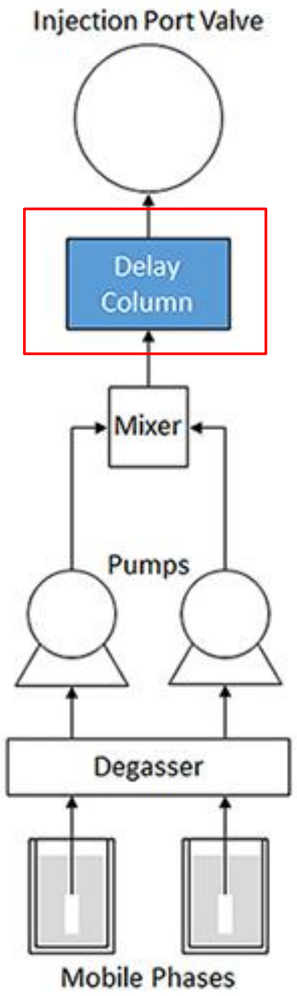



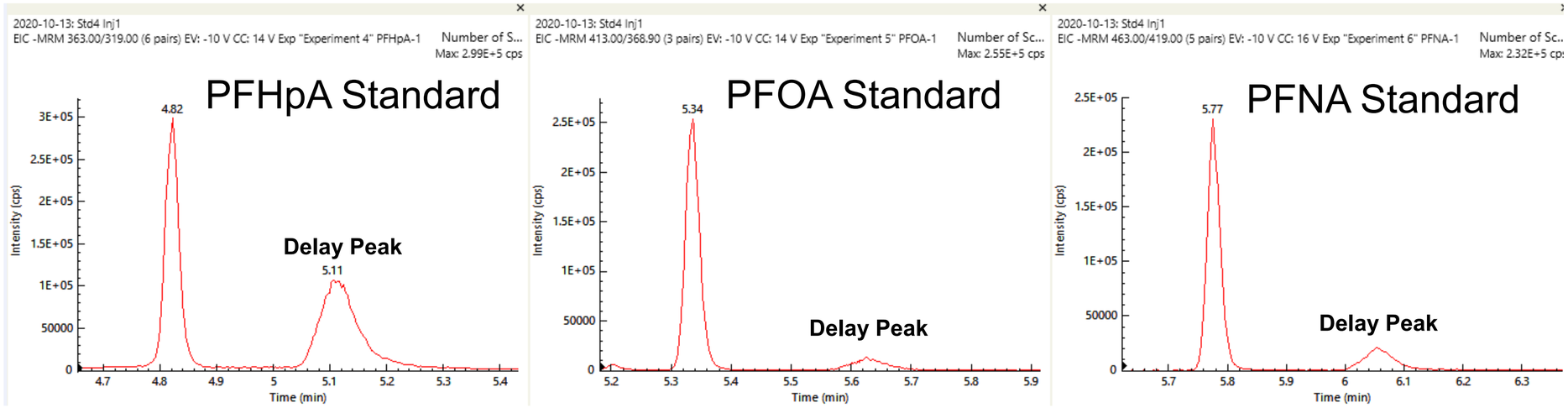






Install a “Delay” column between pump & autosampler

# Reducing Background from Pump and Mobile Phases (Cont'd)

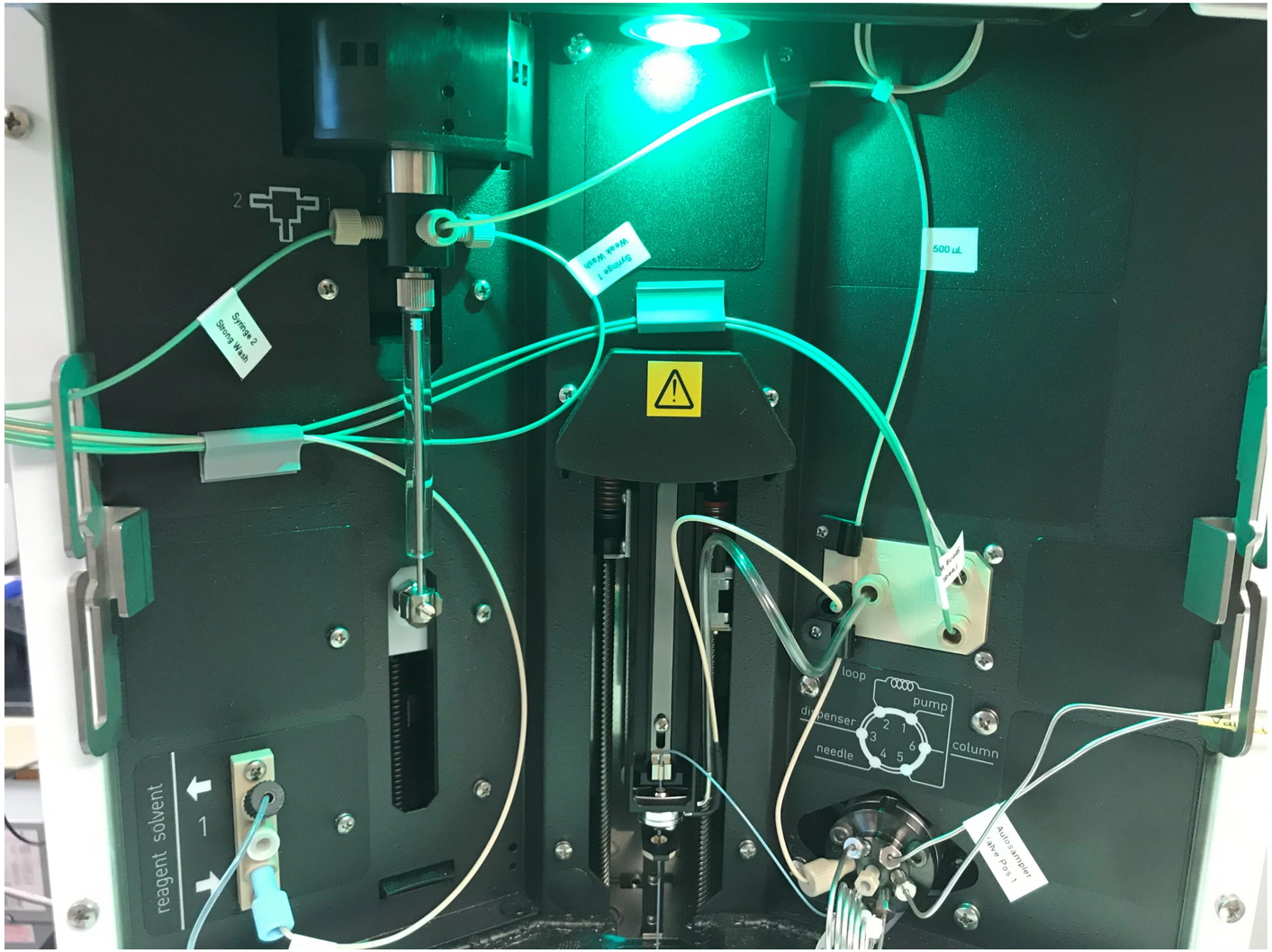



Use a delay column to retain background PFAS interferences from instrument related sources

# Replace PTFE Autosampler Tubing with PEEK

- Tubing kit available
- Can be easily installed by chemist or install engineer



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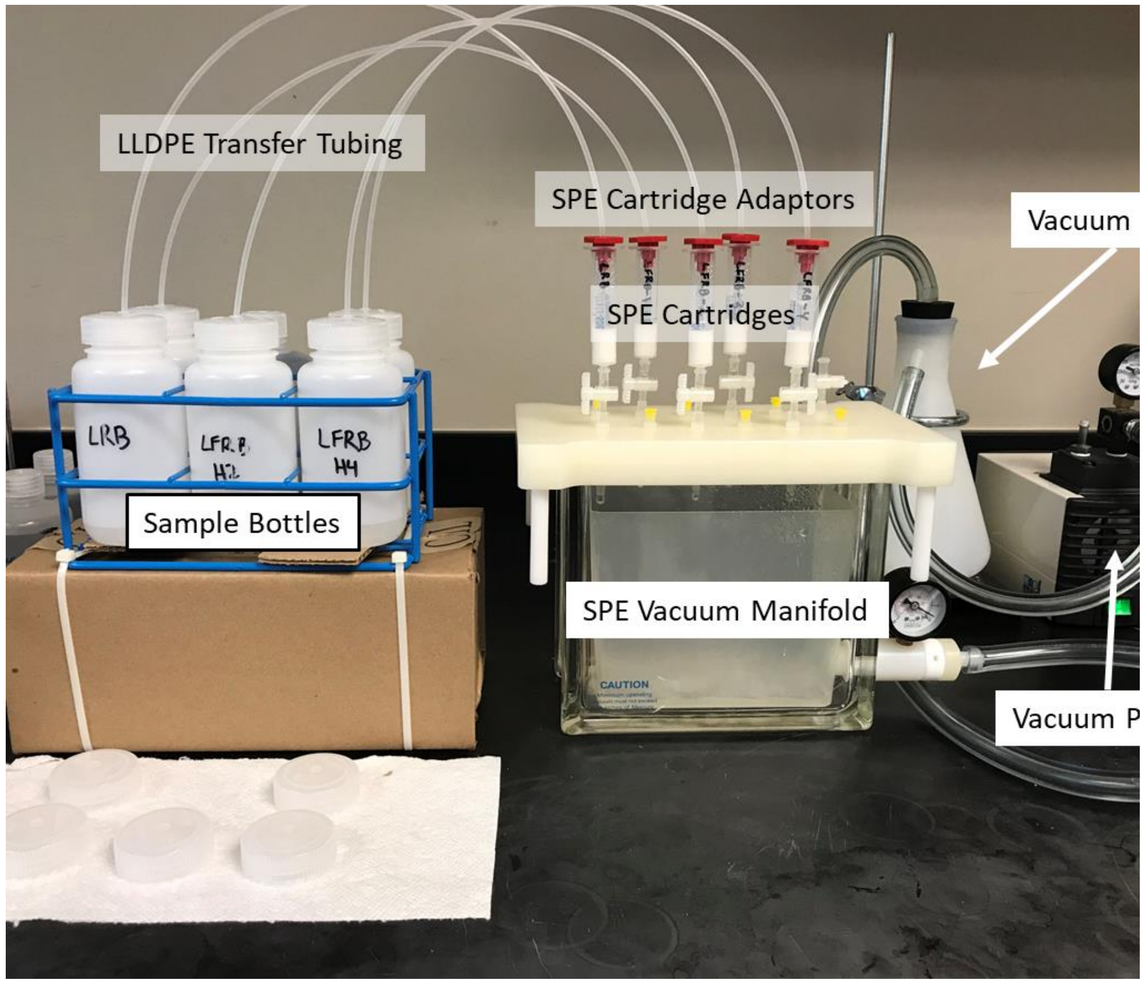
# Manual Large Volume SPE Apparatus

- Eliminate any PTFE or fluoropolymer components that will contribute to PFAS background.
- Replace PTFE transfer tubing with either Linear Low-Density Polyethylene (LLDPE) or PEEK tubing.
- Use stopcocks constructed of polyethylene (PE).
- Collect samples in PE centrifuge tubes.



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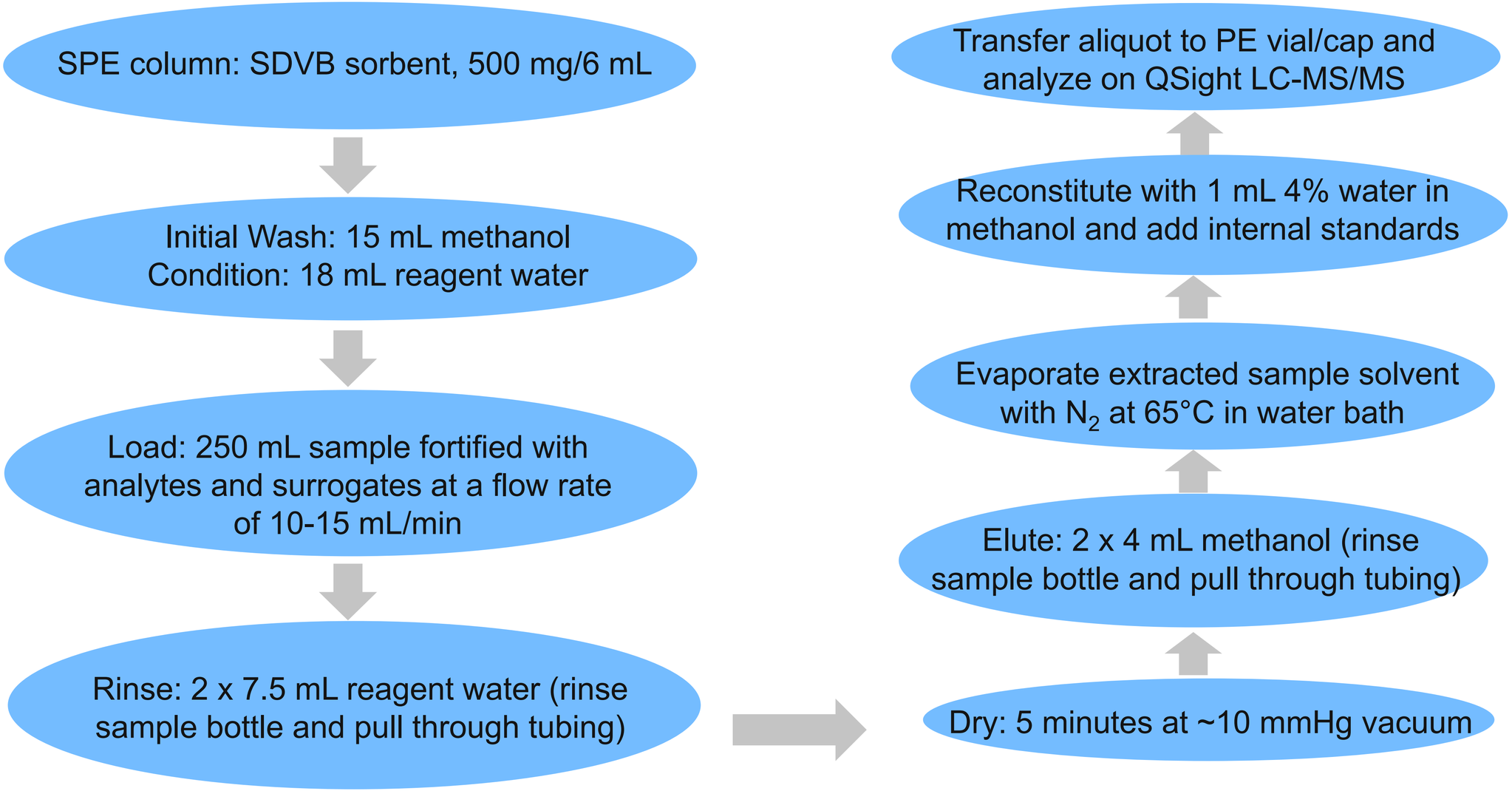
# Sample Preparation Procedure (Manual)



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# Automated SPE Device

- Pre-programmed for EPA methods 537.1, 533 and 1633, etc.
- SPE-03 Automated SPE with MOD-004 for PFAS and applications that require automated rinsing of up to 250mL bottles

# Modified “Fast” HPLC Method

## Original EPA 537.1 LC Method

| Time (min) | % 20 mM ammonium acetate | % Methanol |
|---|---|---|
| Initial | 60.0 | 40.0 |
| 1.0 | 60.0 | 40.0 |
| 25.0 | 10.0 | 90.0 |
| 32.0 | 10.0 | 90.0 |
| 32.1 | 60.0 | 40.0 |
| 37.0 | 60.0 | 40.0 |

**Column**: Waters Atlantis® $C_{18}$, 2.1 x 150 mm, 5.0 μm
**Flow Rate**: 0.3 mL/min
**Injection Volume**: 10 μL
**Runtime**: 37 min

## Modified PerkinElmer EPA 537.1 LC Method

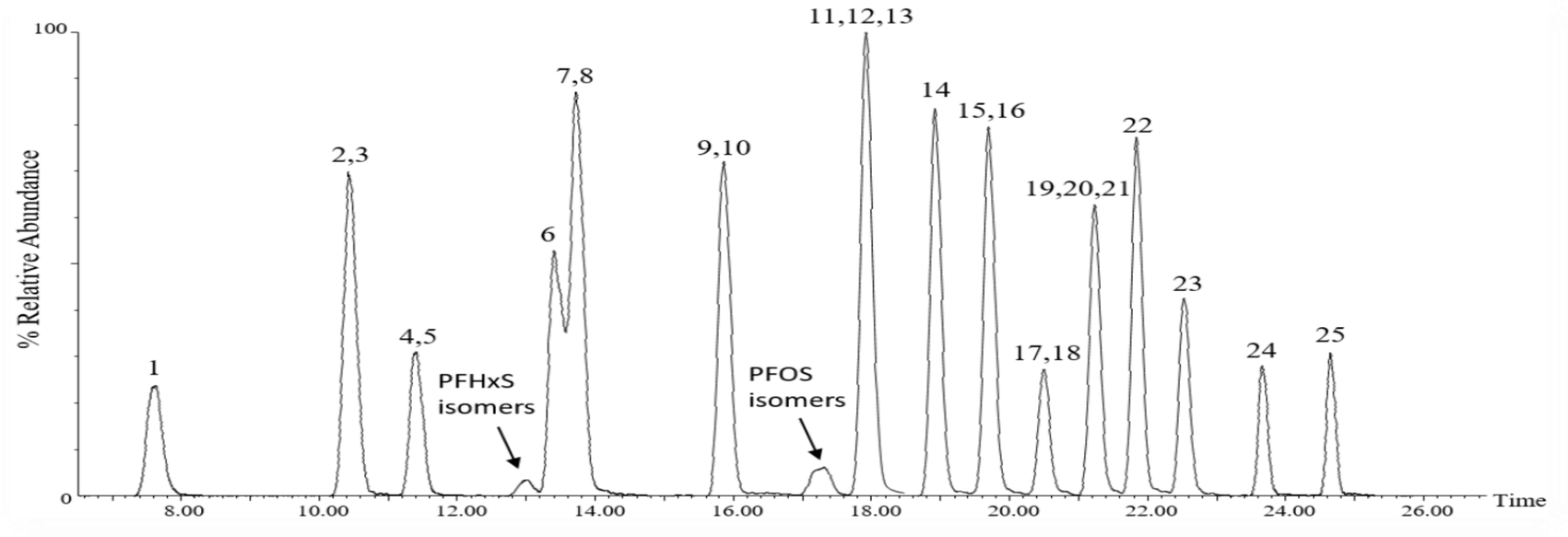
| Time (min) | % 10 mM ammonium acetate | % Methanol |
|---|---|---|
| Initial | 95.0 | 5.0 |
| 0.7 | 95.0 | 5.0 |
| 1.0 | 55.0 | 45.0 |
| 7.0 | 2.0 | 98.0 |
| 8.0 | 2.0 | 98.0 |
| 8.1 | 95.0 | 5.0 |
| 10.0 | 95.0 | 5.0 |

**Column**: Brownlee SPP® $C_{18}$, 4.6 x 75 mm, 2.7 μm
**Flow Rate**: 0.8 mL/min
**Injection Volume**: 10 μL
**Runtime**: 10 min

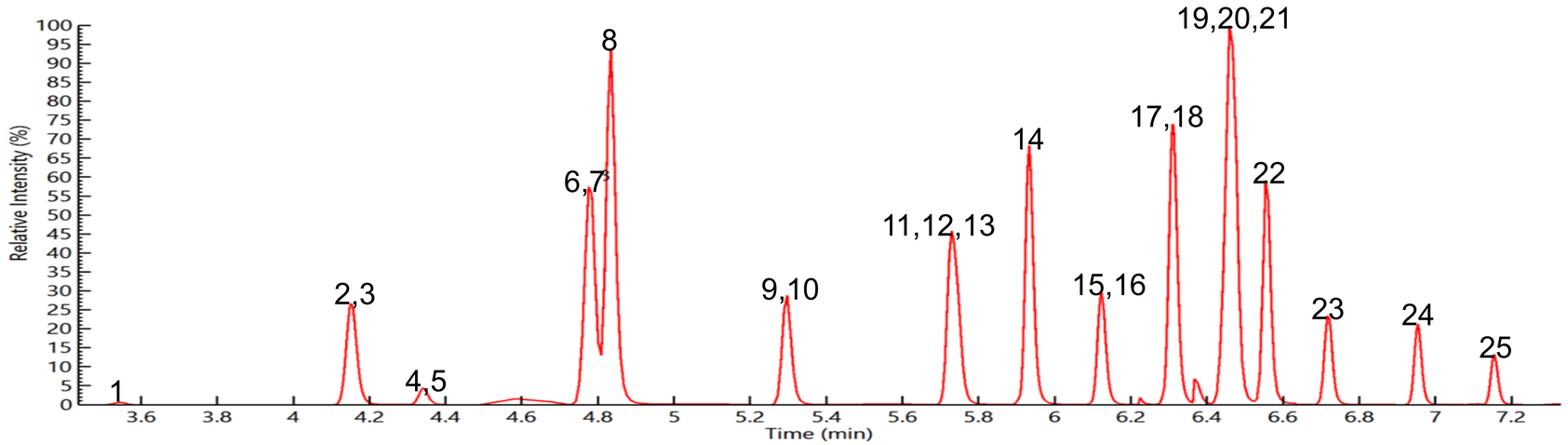
- Runtime reduced from 37 min to 10 min (73% reduction).
- Same retention time order
- Excellent resolution of branched isomers

# Original Method vs. Modified Method

Original EPA method
Total runtime: 37 min.




Mod. PerkinElmer method
Total runtime:10 min.



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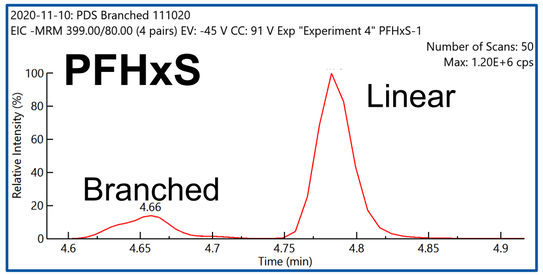
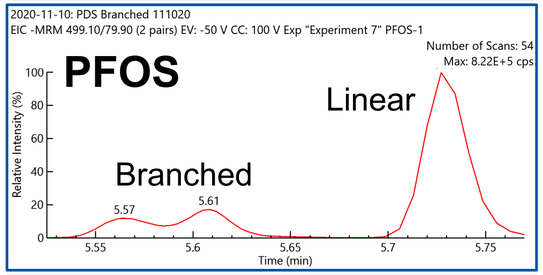
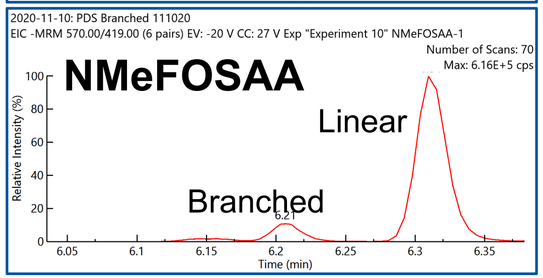
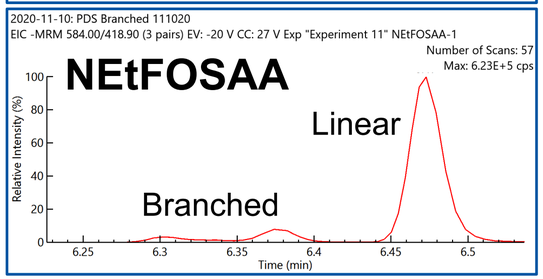
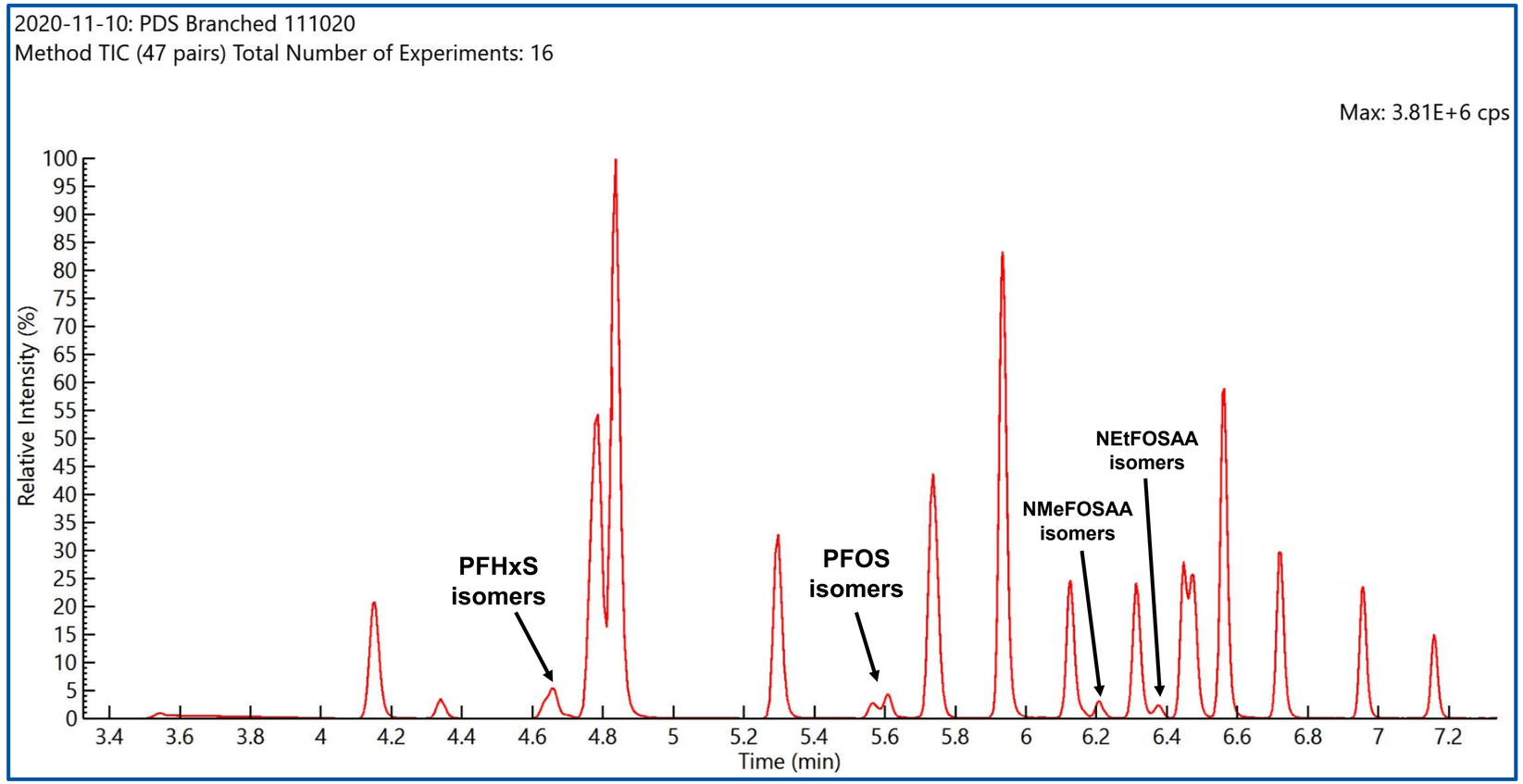
# Baseline Resolution Between Branched & Linear Chain Isomers



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# QSight 220 MS Parameters

- Two MRM experiments per analyte (only quantifier shown here)
- Quantifier/Qualifier ion ratios used to confirm identity
- Dwell times optimized with MRM Time Manager
- Minimum of 10 data points across all peaks

## ESI Source Parameters

| Parameter | Value |
|---|---|
| Polarity | Negative |
| Drying Gas | 110.0 |
| HSID Temperature (°C) | 280.0 |
| Nebulizer Gas 1 | 400.0 |
| Electrospray V1 Negative | -3500.00 |
| Source 1 Temperature (°C) | 350.0 |

## Quantitative MRM Experiments

| Analyte | Q1 Mass | Q2 Mass | Voltages | | |
|---|---|---|---|---|---|
| | | | CE | EV | CCL2 |
| PFBS | 299.5 | 79.8 | 59 | -40 | 250 |
| 13C2-PFHxA (SS) | 315.0 | 270.0 | 13 | -10 | 48 |
| PFHxA | 313.0 | 269.1 | 13 | -10 | 52 |
| 13C3-HFPO-DA (SS) | 286.9 | 168.9 | 12 | -5 | 44 |
| HFPO-DA | 285.0 | 168.9 | 14 | -5 | 40 |
| PFHpA | 363.0 | 319.0 | 14 | -10 | 56 |
| PFHxS | 399.0 | 80.0 | 91 | -45 | 120 |
| ADONA | 377.0 | 251.1 | 17 | -10 | 64 |
| PFOA | 413.0 | 368.9 | 14 | -10 | 68 |
| 13C2-PFOA (IS) | 421.0 | 376.0 | 15 | -5 | 76 |
| PFNA | 463.0 | 419.0 | 16 | -10 | 76 |
| 13C4-PFOS (IS) | 507.0 | 79.9 | 103 | -45 | 124 |
| PFOS | 499.1 | 79.9 | 100 | -50 | 300 |
| 9Cl-PF3ONS | 530.9 | 350.9 | 35 | -30 | 112 |
| 13C2-PFDA (SS) | 515.0 | 469.9 | 16 | -13 | 84 |
| PFDA | 513.0 | 468.9 | 16 | -10 | 84 |
| d3-NMeFOSAA (IS) | 573.0 | 419.0 | 27 | -25 | 104 |
| NMeFOSAA | 570.0 | 419.0 | 27 | -20 | 108 |
| PFUnA | 562.9 | 518.9 | 17 | -10 | 96 |
| d5-NEtFOSAA (SS) | 589.0 | 419.0 | 28 | -20 | 112 |
| NEtFOSAA | 584.0 | 418.9 | 27 | -20 | 96 |
| 11Cl-PF3OUdS | 630.9 | 450.9 | 36 | -40 | 176 |
| PFDoA | 612.9 | 568.9 | 17 | -10 | 104 |
| PFTrDA | 662.9 | 618.9 | 18 | -11 | 104 |
| PFTA | 712.9 | 668.8 | 17 | -10 | 116 |

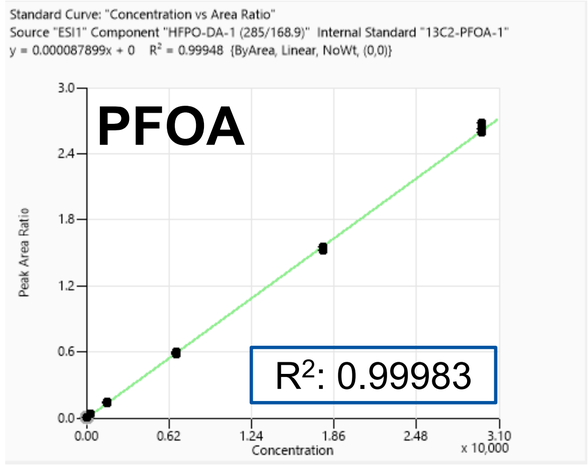
# Calibration Linearity

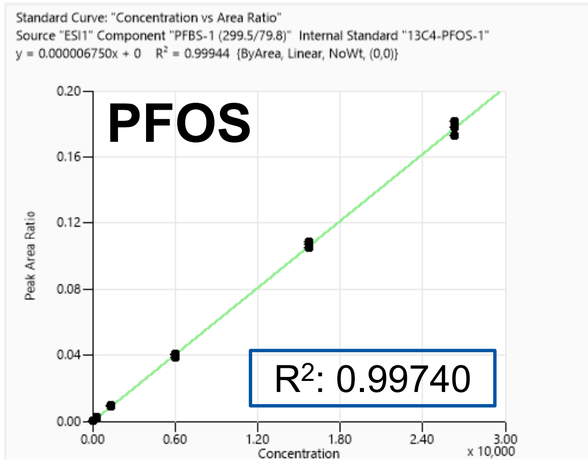
All calibration curves forced through zero as required in method

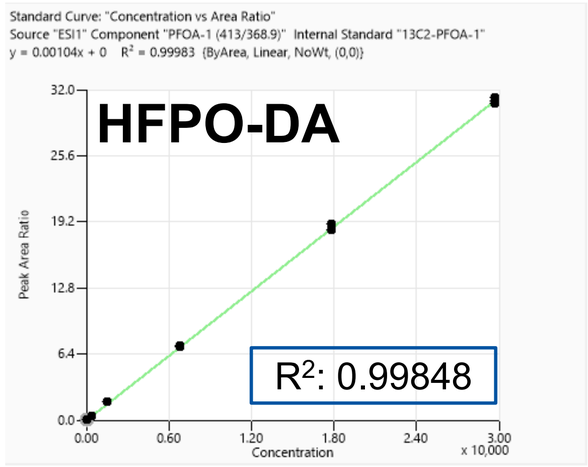
| Compound | Instrument Calibration Range (ng/L)[a] | Method Calibration Range (ng/L)[b] | $R^2$ |
|---|---|---|---|
| PFBS | 16.4 - 26287 | 0.07 - 105.1 | 0.99944 |
| PFHxA | 5.5 - 29703 | 0.02 - 118.8 | 0.99870 |
| $^{13}C_2$-PFHxA | 4.6 - 24752 | 0.02 - 99.0 | 0.99890 |
| $^{13}C_3$-HFPO-DA | 67.5 - 24752 | 0.27 - 99.0 | 0.99923 |
| HFPO-DA | 18.5 - 29703 | 0.07 - 118.8 | 0.99848 |
| PFHpA | 5.5 - 29703 | 0.02 - 118.8 | 0.99840 |
| PFHxS | 5.2 - 28218 | 0.02 - 112.9 | 0.99976 |
| ADONA | 5.2 - 28218 | 0.02 - 112.9 | 0.99904 |
| PFOA | 5.5 - 29703 | 0.02 - 118.8 | 0.99983 |
| PFOS | 5.3 – 28515 | 0.02 - 114.1 | 0.99740 |
| PFNA | 18.5 – 29703 | 0.07 - 118.8 | 0.99926 |
| 9Cl-PF3ONS | 5.1 – 27772 | 0.02 - 111.1 | 0.99979 |
| PFDA | 81.0 – 29703 | 0.32 - 118.8 | 0.99900 |
| $^{13}C_2$-PFDA | 4.6 - 24752 | 0.02 - 99.0 | 0.99880 |
| NMeFOSAA | 5.5 - 29703 | 0.02 - 118.8 | 0.99983 |
| PFUnA | 18.5 - 29703 | 0.07 - 118.8 | 0.99680 |
| NEtFOSAA | 5.5 - 29703 | 0.02 - 118.8 | 0.99680 |
| d5-NEtFOSAA | 18.3 - 99010 | 0.07 - 396.0 | 0.99620 |
| 11Cl-PF3OUdS | 5.2 - 28069 | 0.02 - 112.3 | 0.99972 |
| PFDoA | 18.5 - 29703 | 0.07 - 118.8 | 0.99630 |
| PFTrDA | 5.5 - 29703 | 0.02 - 118.8 | 0.99590 |
| PFTA | 5.5 - 29703 | 0.02 - 118.8 | 0.99670 |

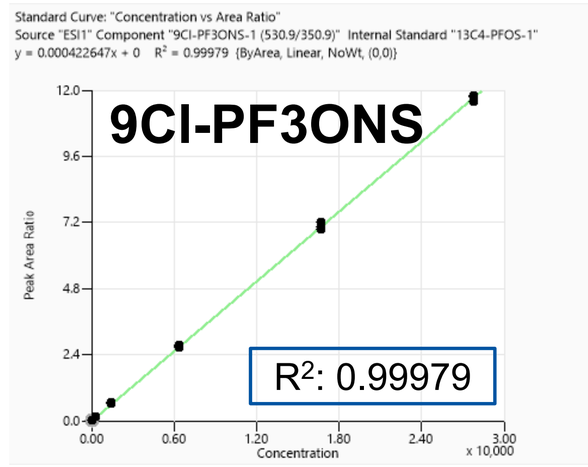
a) Instrument calibration range is the actual concentration range of calibration standards used to determine calibration curves.

b) Method calibration range is determined by multiplying the instrument calibration range by 1/250 to account for the SPE sample preparation/concentration.






Correlation Coefficients ($R^2$) ranges from 0.99670 to 0.99983

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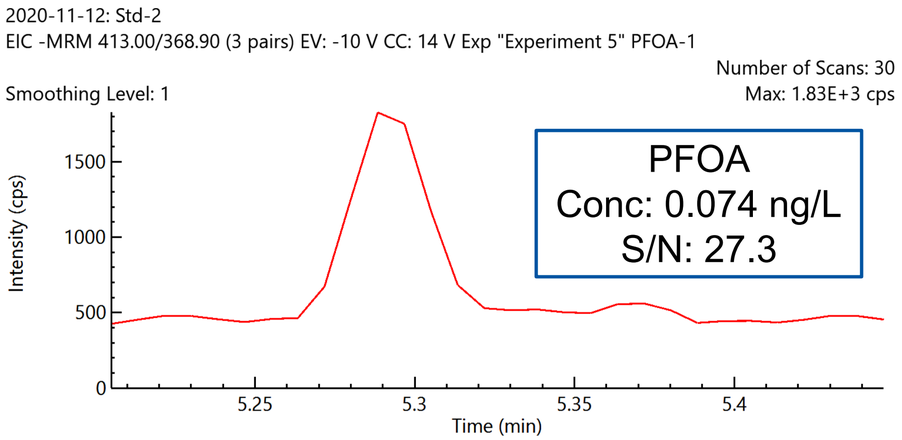
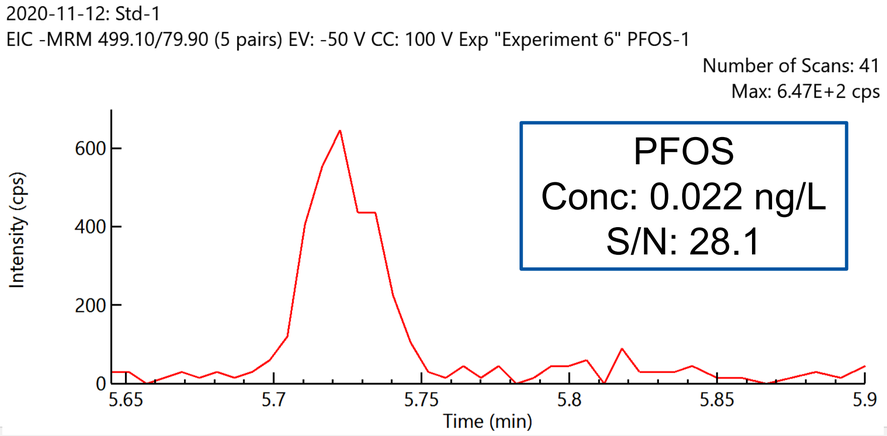
# Instrument Sensitivity (LOQ & LOD)

- LOQ and LOD values estimated from the S/N of calibration standards and adjusted for 250-fold sample concentration
- Most LODs below < 0.08 ng/L demonstrating the MS system exceeds the sensitivity required for this method

| Analyte | LOD (ng/L) | LOQ (ng/L) |
|---|---|---|
| PFBS | 0.012 | 0.040 |
| PFHxA | 0.015 | 0.049 |
| HFPO-DA | 0.029 | 0.098 |
| PFHpA | 0.012 | 0.041 |
| PFHxS | 0.003 | 0.009 |
| ADONA | 0.002 | 0.007 |
| PFOA | 0.016 | 0.053 |
| PFNA | 0.015 | 0.048 |
| PFOS | 0.004 | 0.012 |
| PFNA | 0.014 | 0.004 |
| 9Cl-PF3ONS | 0.004 | 0.013 |
| PFDA | 0.042 | 0.141 |
| NMeFOSAA | 0.002 | 0.007 |
| PFUnA | 0.016 | 0.054 |
| NEtFOSAA | 0.002 | 0.007 |
| 11Cl-PF3OUdS | 0.006 | 0.019 |
| PFDoA | 0.009 | 0.030 |
| PFTrDA | 0.018 | 0.060 |
| PFTA | 0.325 | 1.084 |






Plenty of Sensitivity for EPA Method 537.1

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# Method Detection Limits and LCMRLs

- Detection limits (DL) in this study well below detection limits reported in EPA 537.1
- DL = s x t (n-1, 1-α=0.99)
- LCMRL = Lowest Concentration Minimum Reporting Limit
- LCMRL calculated using EPA calculator

https://www.epa.gov/dwanalyticalmethods/lowest-concentration-minimum-reporting-level-lcmrl-calculator

| Analyte | Experimental DL (ng/L)[a] | EPA 537.1 DL (ng/L)[b] | Experimental LCMRL (ng/L)[c] | EPA 537.1 LCMRL (ng/L)[d] | Experimental MRL (ng/L)[e] |
|---|---|---|---|---|---|
| PFBS | 1.1 | 6.3 | 0.720 | 1.800 | 1.42 |
| PFHxA | 1.6 | 1.7 | 0.930 | 1.000 | 1.00 |
| HFPO-DA | 0.91 | 4.3 | 0.570 | 1.900 | 1.60 |
| PFHpA | 0.41 | 0.63 | 0.100 | 0.710 | 1.60 |
| PFHxS | 0.85 | 2.4 | 0.600 | 1.400 | 0.29 |
| ADONA | 0.10 | 0.55 | 0.10 | 0.880 | 0.28 |
| PFOA | 0.34 | 0.82 | 0.340 | 0.530 | 0.30 |
| PFOS | 1.5 | 2.7 | 1.000 | 1.100 | 1.00 |
| PFNA | 0.98 | 0.83 | 0.500 | 0.700 | 1.60 |
| 9Cl-PF3ONS | 0.95 | 1.8 | 0.680 | 1.400 | 1.50 |
| PFDA | 0.82 | 3.3 | 0.4 | 1.600 | 0.30 |
| NMeFOSAA | 1.9 | 4.3 | 0.220 | 2.400 | 1.00 |
| PFUnA | 0.58 | 5.2 | 0.300 | 1.600 | 1.60 |
| NEtFOSAA | 1 | 4.8 | 0.730 | 2.800 | 1.60 |
| 11Cl-PF3OUdS | 0.45 | 1.5 | 0.390 | 1.500 | 0.28 |
| PFDoA | 0.3 | 1.3 | 0.190 | 1.200 | 0.30 |
| PFTrDA | 1.2 | 0.53 | 0.820 | 0.720 | 4.00 |
| PFTA | 2.1 | 1.2 | 1.500 | 1.100 | 4.00 |

a) Experimental DL was determined from ten LFB replicates fortified at ~1.6 ng/L measured over three days and calculated according to section 9.2.8 in EPA Method 537.1
b) Reference DL values from EPA Method 537.1 rev 2.0 (Table 5) determined from seven LFB replicates fortified at 4.0 ng/L measured over three days and calculated according to section 9.2.8
c) Experimental LCMRLs were determined from ten replicates each at five fortification levels ranging from ~0.2 – 80 ng/L using the EPA LCMRL Calculator.[11]
d) Reference LCMRL values from EPA Method 537.1 rev 2.0 (Table 5).
e) Experimental MRLs were determined from ten LFBs fortified at concentrations ranging from ~0.2 to 4.0 ng/L according to section 9.2.6 of EPA Method 537.1 rev 2.0 using the Half Range prediction interval method with confirmed upper and lower Prediction Interval Results (PIR) ≤150% and ≥50%, respectively.

# % Recovery at Low Concentration

- LFRBs fortified with surrogates and analytes at a conc. of ~1.6 ng/L & ~4.0 ng/L
- Experimental recovery results for ten replicate LFRBs (n=10)
- Experimental recoveries at ~1.6 ng/L range from 86-154%
- Experimental recoveries at ~4.0 ng/L range from 86-108%

| | Experimental Recovery | | | Experimental Recovery | | |
|---|---|---|---|---|---|---|
| Analyte | Fortified Conc. (ng/L) | Mean % Recovery | % RSD | Fortified Conc. (ng/L) | Mean % Recovery | % RSD |
| PFBS | 1.4 | 98 | 1.6 | 3.5 | 106 | 3.6 |
| PFHxA | 1.6 | 115 | 9.6 | 4.0 | 109 | 4.1 |
| HFPO-DA | 1.6 | 86 | 6.7 | 4.0 | 86 | 4.2 |
| PFHpA | 1.6 | 116 | 6.3 | 4.0 | 112 | 1.9 |
| PFHxS | 1.5 | 100 | 4.0 | 3.8 | 105 | 1.3 |
| ADONA | 1.5 | 112 | 4.3 | 3.8 | 110 | 2.4 |
| PFOA | 1.6 | 103 | 2.8 | 4.0 | 107 | 1.4 |
| PFNA | 1.6 | 96 | 10.3 | 4.0 | 114 | 1.9 |
| PFOS | 1.5 | 117 | 6.8 | 3.8 | 109 | 1.7 |
| 9Cl-PF3ONS | 1.5 | 98 | 3.0 | 3.7 | 99 | 3.0 |
| PFDA | 1.6 | 107 | 5.6 | 4.0 | 101 | 5.8 |
| NMeFOSAA | 1.6 | 108 | 5.0 | 4.0 | 103 | 2.4 |
| PFUnA | 1.6 | 117 | 5.9 | 4.0 | 108 | 2.3 |
| NEtFOSAA | 1.6 | 111 | 5.9 | 4.0 | 105 | 3.2 |
| 11Cl-PF3OUdS | 1.5 | 97 | 3.3 | 3.8 | 97 | 4.3 |
| PFDoA | 1.6 | 108 | 5.8 | 4.0 | 104 | 2.7 |
| PFTrDA | 1.6 | 127 | 16.0 | 4.0 | 108 | 3.5 |
| PFTA | 1.6 | 154 | 24.1 | 4.0 | 106 | 2.8 |
| $^{13}C_2$-PFHxA | 40.0 | 93 | 4.6 | 40.0 | 104 | 3.4 |
| $^{13}C_3$-HFPO-DA | 40.0 | 110 | 6.7 | 40.0 | 121 | 3.3 |
| $^{13}C_2$-PFDA | 40.0 | 102 | 5.2 | 40.0 | 105 | 1.9 |
| $d_5$-NEtFOSAA | 160 | 99 | 8.3 | 160 | 106 | 4.2 |

# %Recovery at Medium & High Concentrations

| | Experimental Recovery (n=10) | | | EPA 537.1 Recovery (n=7) | | |
|---|---|---|---|---|---|---|
| Analyte | Fortified Conc. (ng/L) | Mean % Recovery | % RSD | Fortified Conc. (ng/L) | Mean % Recovery | % RSD |
| PFBS | 14.1 | 105 | 4.4 | 16.0 | 90.8 | 6.8 |
| PFHxA | 16.0 | 114 | 2.4 | 16.0 | 101 | 8.0 |
| HFPO-DA | 16.0 | 94 | 1.0 | 16.0 | 97.8 | 1.8 |
| PFHpA | 16.0 | 118 | 1.9 | 16.0 | 105 | 3.3 |
| PFHxS | 15.2 | 107 | 1.4 | 16.0 | 109 | 6.7 |
| ADONA | 15.1 | 116 | 4.0 | 16.0 | 108 | 1.3 |
| PFOA | 16.0 | 109 | 4.4 | 16.0 | 106 | 1.8 |
| PFNA | 16.0 | 108 | 1.7 | 16.0 | 110 | 2.6 |
| PFOS | 15.4 | 116 | 4.6 | 16.0 | 111 | 4.7 |
| 9Cl-PF3ONS | 15.0 | 105 | 3.8 | 16.0 | 108 | 8.8 |
| PFDA | 16.0 | 115 | 4.3 | 16.0 | 111 | 2.4 |
| NMeFOSAA | 16.0 | 111 | 4.9 | 16.0 | 104 | 5.2 |
| PFUnA | 16.0 | 115 | 2.7 | 16.0 | 107 | 2.8 |
| NEtFOSAA | 16.0 | 111 | 3.5 | 16.0 | 97.7 | 6.8 |
| 11Cl-PF3OUdS | 15.1 | 102 | 3.6 | 16.0 | 109 | 3.4 |
| PFDoA | 16.0 | 112 | 3.2 | 16.0 | 101 | 7.2 |
| PFTrDA | 16.0 | 112 | 4.7 | 16.0 | 108 | 2.6 |
| PFTA | 16.0 | 109 | 4.4 | 16.0 | 110 | 0.9 |
| $^{13}C_2$-PFHxA | 40.0 | 100 | 5.9 | 40.0 | 88.5 | 6.4 |
| $^{13}C_3$-HFPO-DA | 40.0 | 95 | 5.6 | 40.0 | 94.5 | 3.2 |
| $^{13}C_2$-PFDA | 40.0 | 104 | 7.2 | 40.0 | 99.1 | 3.4 |
| $d_5$-NEtFOSAA | 160 | 103 | 4.2 | 160 | 90.0 | 2.6 |

Experimental recoveries at 16 ng/L range from 94-116%

| | Experimental Recovery (n=10) | | | EPA 537.1 Recovery (n=7) | | |
|---|---|---|---|---|---|---|
| Analyte | Fortified Conc. (ng/L) | Mean % Recovery | % RSD | Fortified Conc. (ng/L) | Mean % Recovery | % RSD |
| PFBS | 70.8 | 101 | 4.2 | 80.0 | 85.1 | 6.7 |
| PFHxA | 80.0 | 109 | 6.5 | 80.0 | 97 | 4.6 |
| HFPO-DA | 80.0 | 90 | 6.8 | 80.0 | 96.8 | 5.1 |
| PFHpA | 80.0 | 111 | 7.3 | 80.0 | 104 | 2.7 |
| PFHxS | 76.0 | 103 | 3.9 | 80.0 | 107 | 4.4 |
| ADONA | 75.6 | 110 | 6.8 | 80.0 | 106 | 3.6 |
| PFOA | 80.0 | 103 | 4.6 | 80.0 | 104 | 3.1 |
| PFNA | 80.0 | 102 | 4.7 | 80.0 | 104 | 3.6 |
| PFOS | 76.8 | 109 | 7.4 | 80.0 | 107 | 4.8 |
| 9Cl-PF3ONS | 74.8 | 99 | 4.1 | 80.0 | 101 | 3.8 |
| PFDA | 80.0 | 109 | 7.2 | 80.0 | 107 | 3.6 |
| NMeFOSAA | 80.0 | 101 | 3.8 | 80.0 | 102 | 5.4 |
| PFUnA | 80.0 | 108 | 7.0 | 80.0 | 101 | 1.3 |
| NEtFOSAA | 80.0 | 104 | 4.0 | 80.0 | 101 | 2.5 |
| 11Cl-PF3OUdS | 75.6 | 97 | 3.2 | 80.0 | 103 | 6.1 |
| PFDoA | 80.0 | 105 | 7.6 | 80.0 | 107 | 3.7 |
| PFTrDA | 80.0 | 103 | 6.5 | 80.0 | 99.1 | 3.6 |
| PFTA | 80.0 | 101 | 6.6 | 80.0 | 97.2 | 3.6 |
| $^{13}C_2$-PFHxA | 40.0 | 103 | 6.2 | 40.0 | 97.0 | 4.9 |
| $^{13}C_3$-HFPO-DA | 40.0 | 94 | 6.0 | 40.0 | 101 | 9.9 |
| $^{13}C_2$-PFDA | 40.0 | 104 | 6.4 | 40.0 | 106 | 2.7 |
| $d_5$-NEtFOSAA | 160 | 100 | 3.8 | 160 | 99.5 | 4.8 |

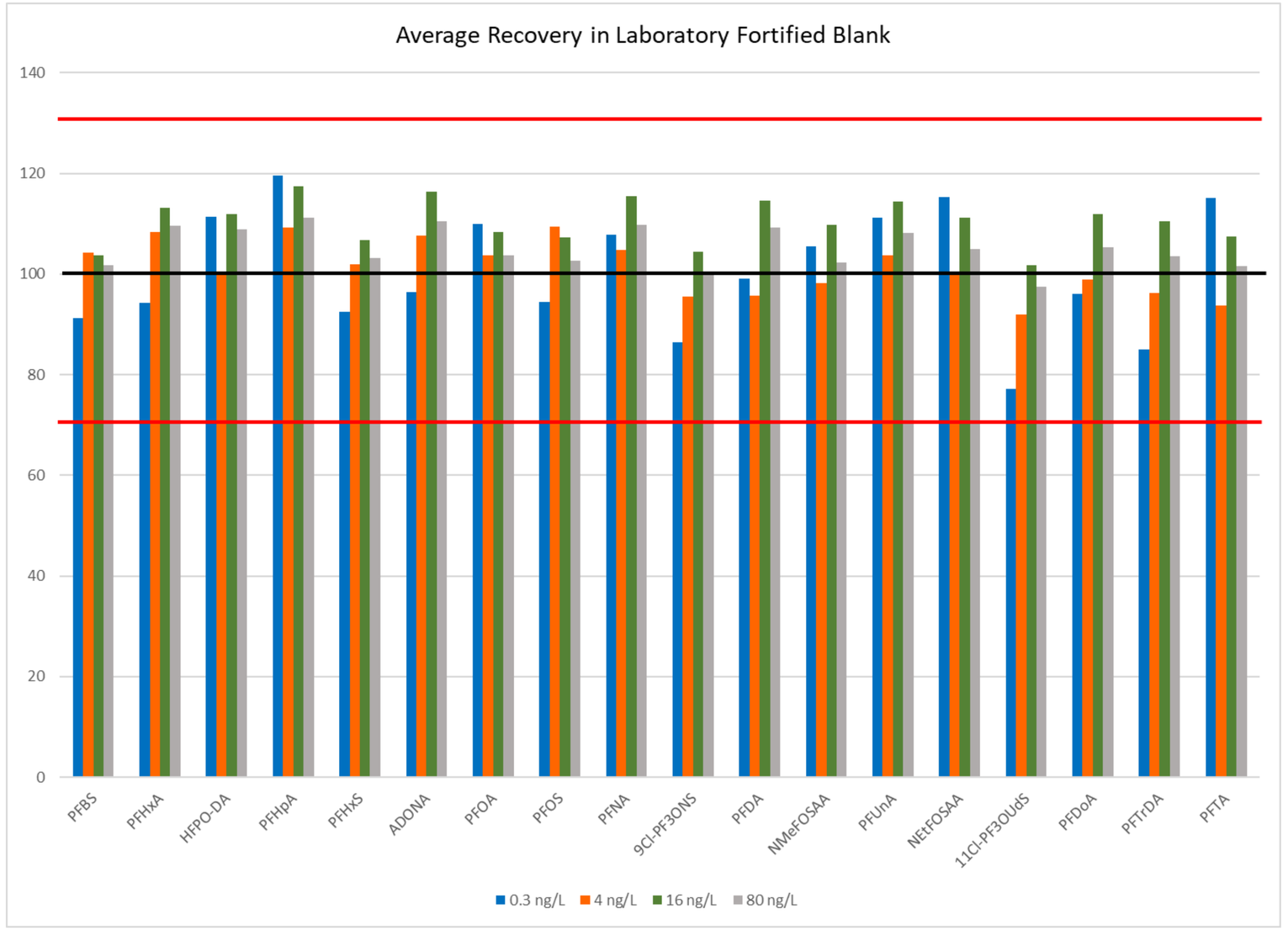
Experimental recoveries at 80 ng/L range from 90-111%



**Recovery results consistent with those reported in Method EPA 537.1**

# PFAS Spiked Recovery Summary

- Spike level at 0.3, 4, 16 and 80 ppt
- Acceptance criteria: 70–130%



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# Field Sample Analysis

- Field samples of tap water were collected from three different municipalities in the Southeast US, and were designated M1, M2 and M3.
- Four field samples and one FRB were collected at each location
- Ongoing QC requirements
  - Laboratory reagent blank (LRB)
  - Continuing calibration check (CCC)
  - Laboratory fortified blank (LFB)
  - Surrogate recovery
  - Laboratory fortified sample matrix (LFSM) and duplicate (LFSMD)
  - Field sample duplicate (FD)

# Field Sample Analyte Test Results

| Analyte | Average FD Conc (ng/L) | | | Average LFSM % Recovery[a] | | | LFSM RPD[b] | | |
|---|---|---|---|---|---|---|---|---|---|
| | M1 | M2 | M3 | M1 | M2 | M3 | M1 | M2 | M3 |
| PFBS | 2.0 | 14.9 | <MRL | 120 | 100 | 119 | 5.6 | 16.0 | 1.4 |
| PFHxA | 1.8 | 2.0 | <MRL | 101 | 95 | 120 | 2.1 | 2.8 | 6.0 |
| HFPO-DA | <MRL | <MRL | <MRL | 116 | 90 | 108 | 4.1 | 18.0 | 1.1 |
| PFHpA | <MRL | <MRL | <MRL | 103 | 88 | 99 | 2.3 | 1.2 | 0.4 |
| PFHxS | 0.32 | 0.56 | <MRL | 89 | 75 | 81 | 5.3 | 0.4 | 0.0 |
| ADONA | <MRL | <MRL | <MRL | 114 | 107 | 111 | 2.5 | 6.8 | 1.3 |
| PFOA | 1.1 | 1.9 | 0.39 | 88 | 78 | 88 | 3.6 | 8.9 | 7.2 |
| PFOS | <MRL | 2.0 | <MRL | 129 | 111 | 126 | 0.1 | 7.0 | 2.9 |
| PFNA | <MRL | <MRL | <MRL | 90 | 82 | 92 | 9.1 | 12.8 | 0.1 |
| 9Cl-PF3ONS | <MRL | <MRL | <MRL | 118 | 97 | 115 | 6.2 | 0.2 | 2.2 |
| PFDA | 0.35 | 0.37 | <MRL | 82 | 128 | 121 | 2.1 | 3.3 | 1.0 |
| NMeFOSAA | <MRL | <MRL | <MRL | 96 | 85 | 94 | 1.7 | 6.5 | 0.7 |
| PFUnA | <MRL | <MRL | <MRL | 75 | 120 | 139 | 0.2 | 1.4 | 5.0 |
| NEtFOSAA | <MRL | <MRL | <MRL | 98 | 84 | 97 | 6.3 | 6.6 | 0.3 |
| 11Cl-PF3OUdS | <MRL | <MRL | <MRL | 57 | 86 | 100 | 9.0 | 2.3 | 4.3 |
| PFDoA | <MRL | <MRL | <MRL | 124 | 118 | 129 | 0.2 | 2.1 | 0.3 |
| PFTrDA | <MRL | <MRL | <MRL | 120 | 106 | 113 | 2.4 | 0.7 | 9.2 |
| PFTA | <MRL | <MRL | <MRL | 94 | 83 | 92 | 6.9 | 1.6 | 19.3 |

% Recovery
acceptance criteria: 70-130%
or 50-150% for low level spike

% RPD
acceptance criteria: ≤30%



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# Field Sample Surrogate %Recovery

| Surrogates | Average FD %Recovery | | | Average LFSM %Recovery | | |
|---|---|---|---|---|---|---|
| | M1 | M2 | M3 | M1 | M2 | M3 |
| $^{13}C_2$-PFHxA | 104 | 112 | 127 | 100 | 106 | 117 |
| $^{13}C_3$-HFPO-DA | 106 | 93 | 103 | 104 | 94 | 97 |
| $^{13}C_2$-PFDA | 76 | 81 | 79 | 81 | 76 | 73 |
| d5-NEtFOSAA | 110 | 106 | 106 | 111 | 106 | 102 |

% Recovery acceptance criteria: 70-130%

# Conclusions

- EPA Method 537.1 requires special equipment and sample handling considerations to minimize the PFAS background to measure analytes at ppt (ng/L) levels.
- Modifications of the QSight LC-MS/MS system and the SPE system are required to perform this method.
- An improved LC method reduces total runtime by 73% (10 min. vs. 37 min.).
- Method detection limits (DL) well below those reported in the EPA method.
- Most Instrument LOQs are <0.060 ppt, confirming that the QSight 220 LC-MS/MS exceeds the sensitivity required to perform Method 537.1.
- Analyte recoveries in LFRBs fortified at 16 and 80 ng/L were all within the range of 94-118% as required in the method with most analyte recoveries between 94-111%.
- Field samples were analyzed with good analyte and surrogate spiked recoveries.
- This method has been implemented and validated at multiple customer sites.
- Instrument robustness with StayClean™ technology would allow injections of thousands of samples with no instrument cleaning and maintenance.

# Thank you very much for attention! Any question?

**Victor Cai**
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Mobile 951-258-2470

# Innovative QSight Design

**Dual Source**
Two independent probes provide true multiplexing flexibility

**StayClean Source**
Self-cleaning design delivers maximum sensitivity and exceptional uptime

**Mass Filters**
High-quality precision rods provide highly stable, precise mass filtering

**UniField Detector**
Patented technology counts positive and negative ions without high-voltage switching

**HSID Interface**
Provides low background and reliable results day after day with equal response at any flow rate

**Laminar Flow Ion Guide**
Highly efficient field-free transmission

**Collision Cell**
Fast, efficient fragmentation (fast MRMs) shortens cycle time with zero crosstalk

**Modular**
Plug-and-play design for ease of service

**Small Footprint, Vertical Design**
Compact 50 cm x 50 cm x 115 cm (no benchtop needed)

**First vertical MS system**
- Dimensions: 50x50x110 cm
- Smallest footprint
- Saves customer lab space

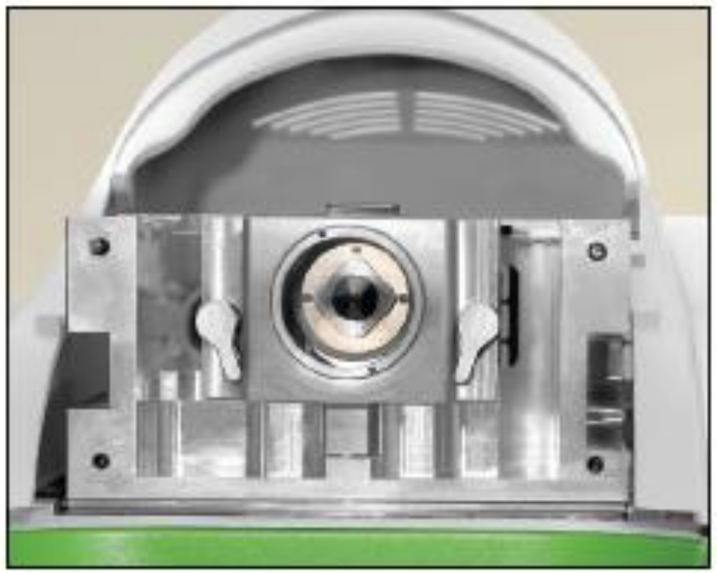
**Modularized design**
- Improved serviceability
- Fast recovery, low down time
- Quick replacement parts

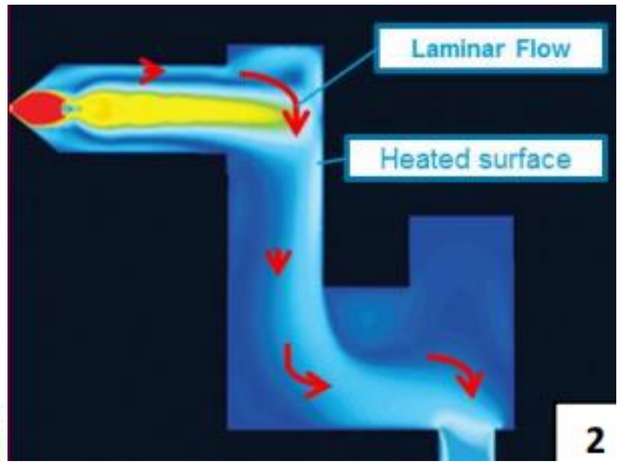
**Smart**
- Full diagnostics
- Remote controlling

**Plug and play design**
- Require minimum tooling
- Reduced cabling by 80%
- Self connecting modules

# How StayClean™ Works?

- Heated Surface Induced Desolvation (HSID)
- Self Clean 24/7
  - Better desolvation
  - Less Maintenance
  - Increased uptime






Self-cleaning Heated Surface Induced Desolvation (HSID)

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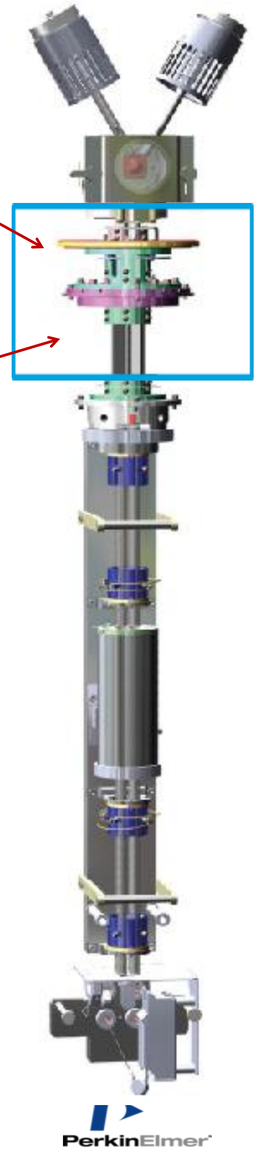
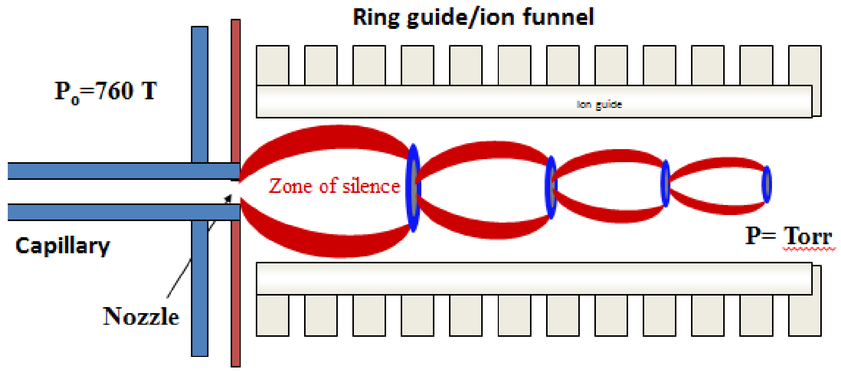
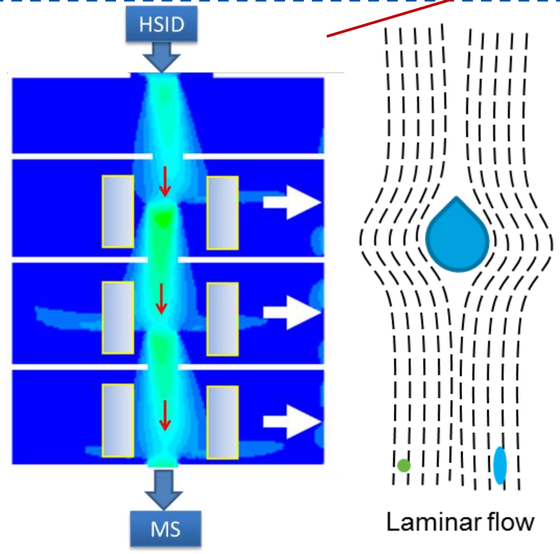
# Laminar Flow Ion Guide (Patent Technology)

- No voltage needed to guild ions
- Ions go with the flow, no mass discrimination
- No voltage re-optimization needed  (Never re-tune ion guide)
- ~98% ion transmission rate






Traditional Ion Guide




Laminar Flow Ion Guide

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# Summary of PFAS EPA Drinking Water Methods

- EPA Method 537.1 (March 2020): Selected Linear PFAS Compounds
  - Targeted analysis of 18 PFAS compounds with chain lengths $C_4$-$C_{14}$ including carboxylic acids, sulfonic acids, sulfonamidoacetic acids and GenX compounds (HFPO-DA)
  - LC/MS/MS method using isotopic internal standards and reverse phase SPE sample preparation

- EPA Method 533 (December 2019): Short-Chain & Polar PFAS Compounds
  - Targeted analysis of 25 PFAS compounds $C_4$-$C_{12}$ expanded with the addition of more polar fluorotelomers and ether carboxylic acids
  - LC/MS/MS method using isotopic dilution and ion exchange SPE sample preparation

- EPA Method 1633 (Draft 2021): Broad range of PFAS in multiple matrices.
  - Targeted analysis of 40 PFAS compounds in aqueous, solid, biosolids and tissue samples.
  - LC/MS/MS using isotopic dilution and multiple sample preparation techniques.

# EPA Method 537.1 Summary

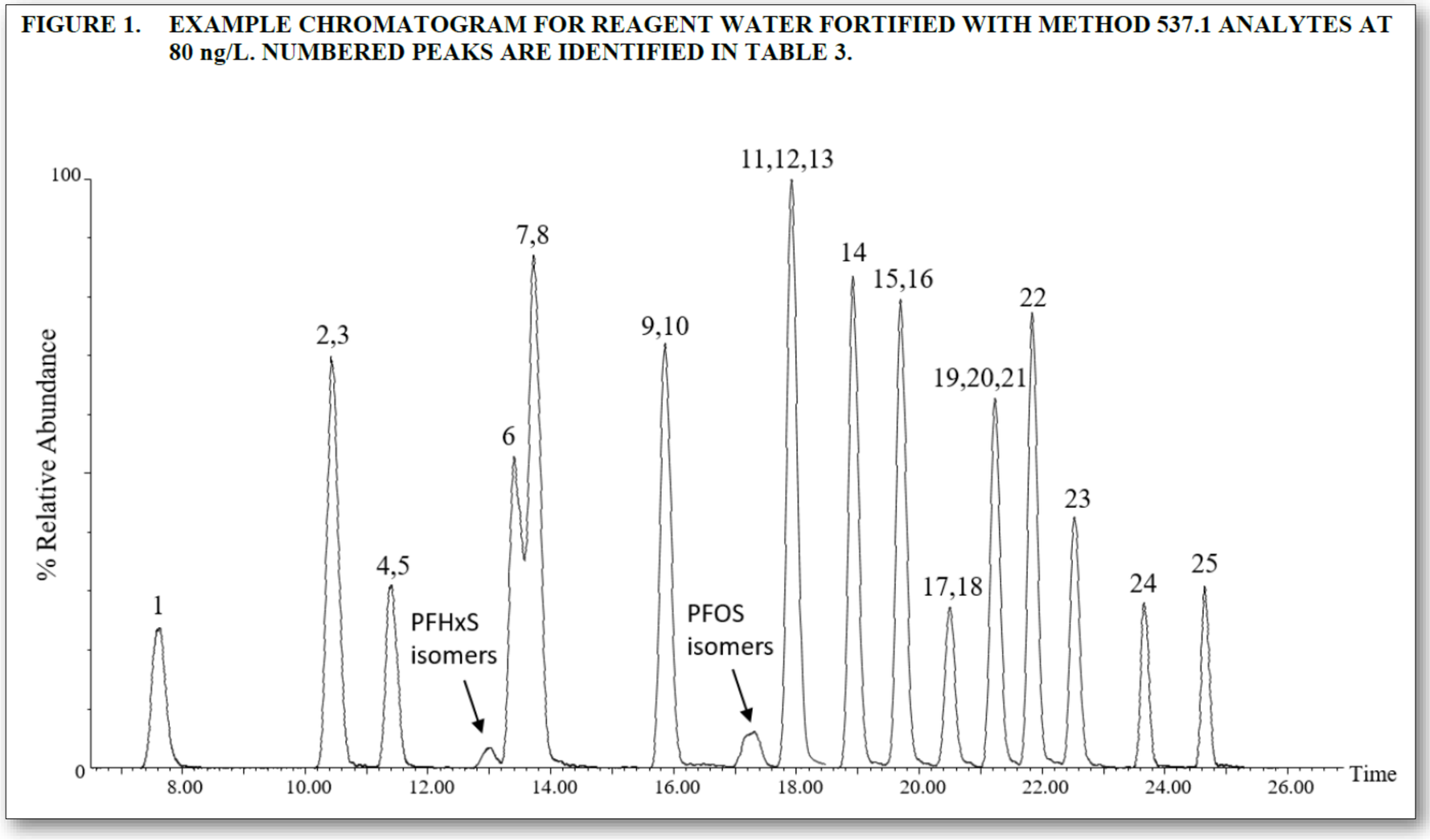
- A 250-mL water sample is fortified with surrogates
- Polystyrenedivinylbenzene (SDVB) phase is required for SPE
- No deviations allowed for SPE extraction
- SPE extracts dried under $N_2$ and reconstituted with 1-mL of 96:4 (vol/vol) MeOH/Water (**250-fold concentration**)
- Internal standards are added
- A 10-µL injection is made into an LC-MS/MS instrument with a C18 column
- Analytes are separated and identified by comparing the acquired mass spectra and retention times to reference spectra and retention times for calibration standards acquired under identical LC-MS/MS conditions
- The concentration of each analyte is determined by using the internal standard technique

# Original EPA 537.1 Chromatogram – 37 min Runtime

Table 3. Method Analytes, Retention Times (RT) and Suggested IS References

| Analyte | Peak # (Fig. 1) | RT (min) | IS# Ref |
|---|---|---|---|
| PFBS | 1 | 7.62 | 2 |
| PFHxA | 2 | 10.42 | 1 |
| HFPO-DA | 4 | 11.38 | 1 |
| PFHpA | 6 | 13.40 | 1 |
| PFHxS | 7 | 13.58 | 2 |
| ADONA | 8 | 13.73 | 1 |
| PFOA | 9 | 15.85 | 1 |
| PFOS | 11 | 17.91 | 2 |
| PFNA | 13 | 17.92 | 1 |
| 9Cl-PF3ONS | 14 | 18.91 | 2 |
| PFDA | 15 | 19.69 | 1 |
| NMeFOSAA | 17 | 20.50 | 3 |
| PFUnA | 19 | 21.21 | 1 |
| NEtFOSAA | 20 | 21.26 | 3 |
| 11Cl-PF3OUdS | 22 | 21.84 | 2 |
| PFDoA | 23 | 22.52 | 1 |
| PFTrDA | 24 | 23.66 | 1 |
| PFTA | 25 | 24.64 | 1 |
| $^{13}C_2$-PFHxA | 3 | 10.42 | 1 |
| $^{13}C_3$-HFPO-DA | 5 | 11.40 | 1 |
| $^{13}C_2$-PFDA | 16 | 19.69 | 1 |
| $d_5$-NEtFOSAA | 21 | 21.24 | 3 |
| $^{13}C_2$-PFOA– IS#1 | 10 | 15.85 | - |
| $^{13}C_4$-PFOS– IS#2 | 12 | 17.91 | - |
| $d_3$-NMeFOSAA–IS#3 | 18 | 20.49 | - |

**FIGURE 1. EXAMPLE CHROMATOGRAM FOR REAGENT WATER FORTIFIED WITH METHOD 537.1 ANALYTES AT 80 ng/L. NUMBERED PEAKS ARE IDENTIFIED IN TABLE 3.**



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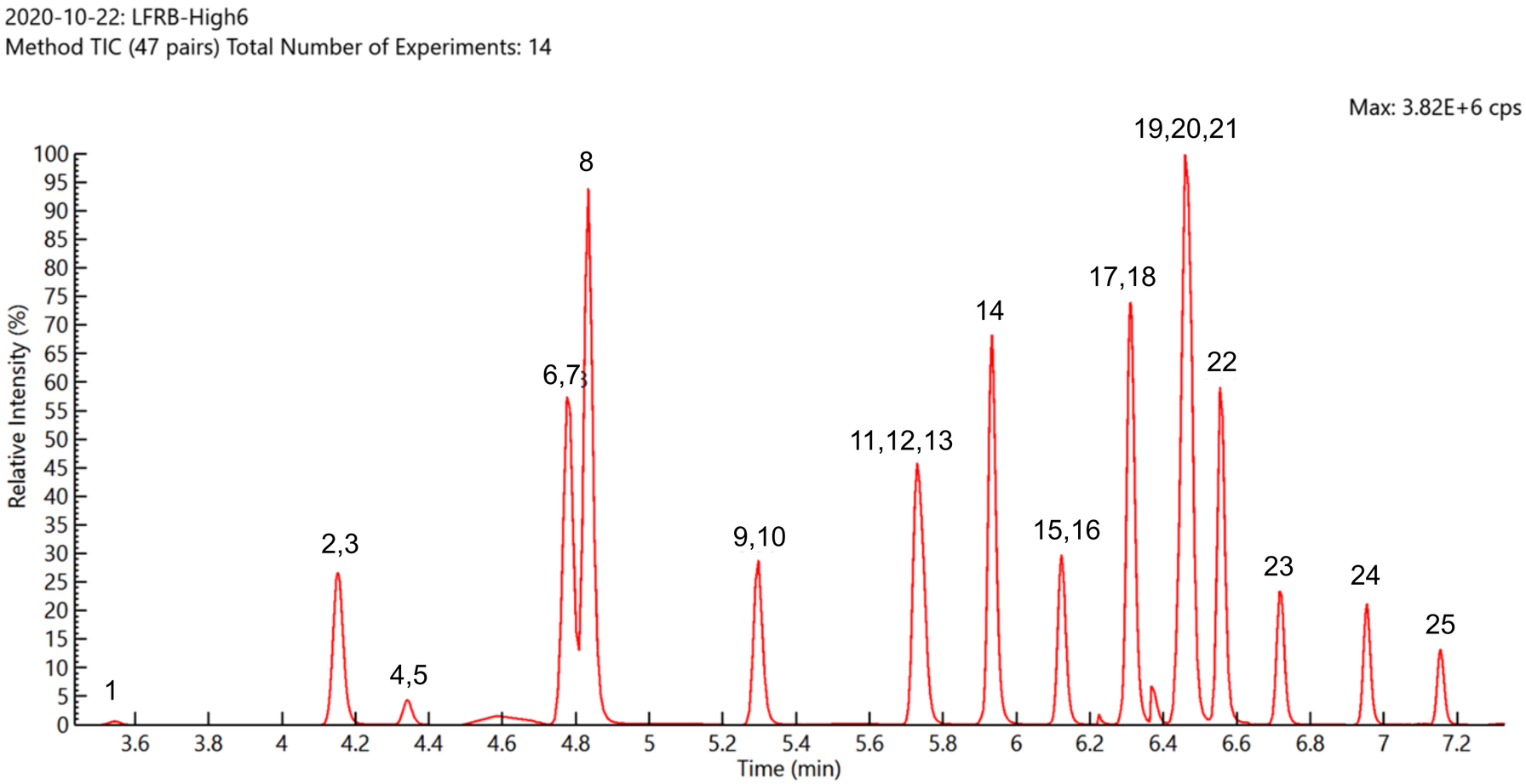
# Modified EPA 537.1 Chromatogram – 10 min Runtime

| Analyte | Peak # | RT (min) | IS# Ref |
|---|---|---|---|
| PFBS | 1 | 3.54 | 2 |
| PFHxA | 2 | 4.15 | 1 |
| HFPO-DA | 4 | 4.34 | 1 |
| PFHpA | 6 | 4.78 | 1 |
| PFHxS | 7 | 4.77 | 2 |
| ADONA | 8 | 4.84 | 1 |
| PFOA | 9 | 5.30 | 1 |
| PFOS | 11 | 5.73 | 2 |
| PFNA | 13 | 5.74 | 1 |
| 9Cl-PF3ONS | 14 | 5.93 | 2 |
| PFDA | 15 | 6.13 | 1 |
| NMeFOSAA | 17 | 6.31 | 3 |
| PFUnA | 19 | 6.45 | 1 |
| NEtFOSAA | 20 | 6.47 | 3 |
| 11Cl-PF3OUdS | 22 | 6.56 | 2 |
| PFDoA | 23 | 6.72 | 1 |
| PFTrDA | 24 | 6.96 | 1 |
| PDTA | 25 | 7.16 | 1 |
| $^{13}C_2$-PFHxA SS#1 | 3 | 4.15 | 1 |
| $^{13}C_3$-HFPO-DA SS#2 | 5 | 4.34 | 1 |
| $^{13}C_2$-PFDA SS#3 | 16 | 6.12 | 1 |
| $d_5$-NEtFOSAA SS#4 | 21 | 6.46 | 3 |
| $^{13}C_2$-PFOA IS#1 | 10 | 5.29 | - |
| $^{13}C_4$-PFOS IS#2 | 12 | 5.74 | - |
| $d_3$-NMeFOSAA IS#3 | 18 | 6.30 | - |



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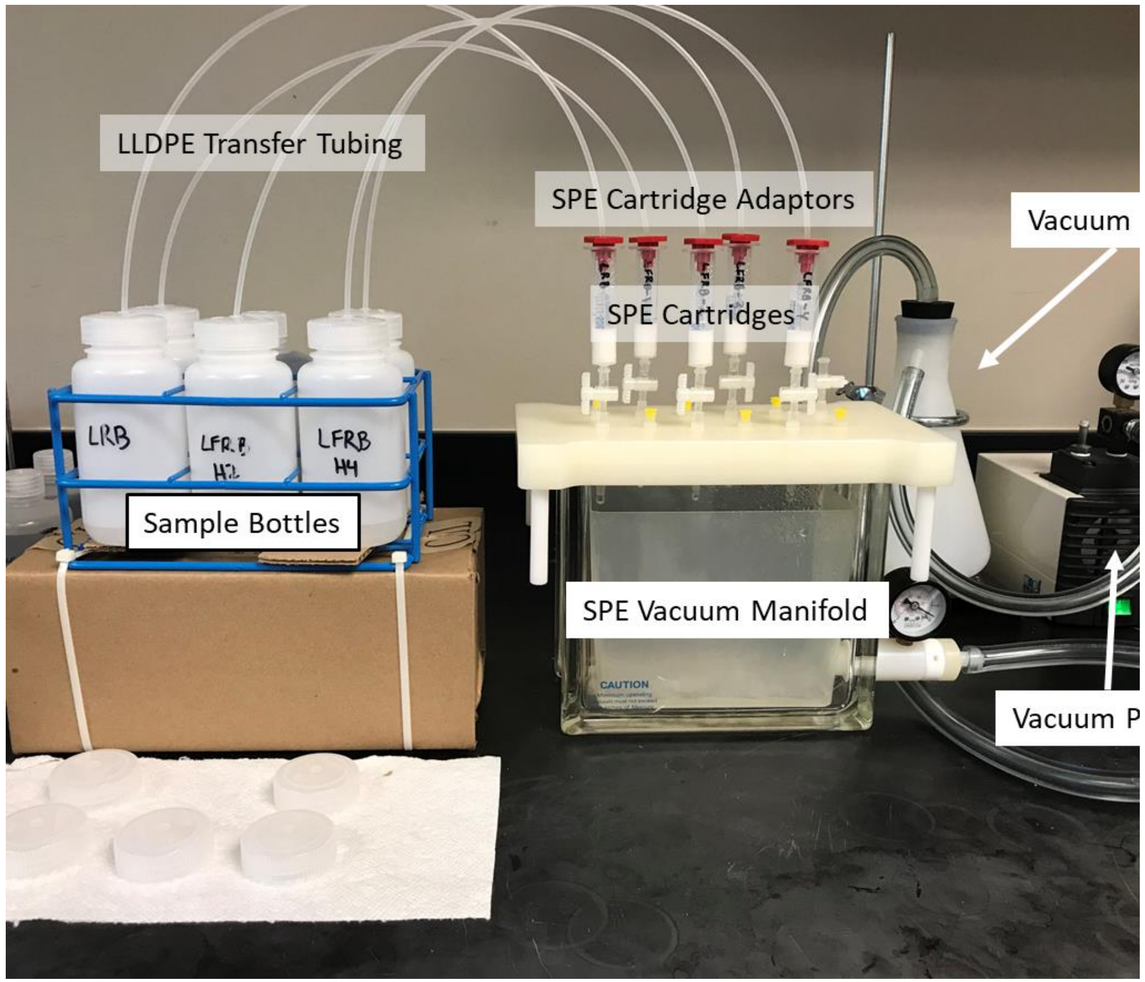
# Manual SPE System Tubing Test

- Do not use PTFE tubing for sample transfer tubing.
- We used 1/8” OD x 1/16” ID linear low density polyethylene tubing (Freelin-Wade).
- Tested 1/8” OD x 1/16” ID PEEK tubing for transfer tubing.
- LLDPE tubing was chosen over PEEK due to flexibility.



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