Learn How to Analyze Extended List of PFAS Including Ultrashort-Chain (C2-C3) PFAS

Shun-Hsin Liang – Senior Scientist, LC Applications
Mike Chang – Business Development Manager, Environmental Market
Outline

• PFAS Panel

• Restek’s Analytical Solutions
  • Raptor C18 and PFAS Delay Column

• Method Development for Ultrashort-Chain and Alternative PFAS
  • Reversed-Phase & HILIC Methodology

• Conclusions
PFAS (Per- and Polyfluoroalkyl Substances)

Perfluoroalkylcarboxylic Acid (PFCA)
Perfluoroalkylsulfonic Acid (PFSA)
X:2 Telomer Sulfonic Acid (X:2 FTS)

Surfactant
- Processing aid
- Mist suppressant
- Fire fighting foam
- Cleaning Products

Raw Material
- Perfluoroctanesulfonamide (FOSA)
- Perfluoroctanesulfonamido-ethanol (FOSE)

Environmental Transformation
- Perfluoroctanesulfonamido-acetic acid (FOSAA)
- Telomer Carboxylic Acid (X:2 FTA)
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Restek’s PFAS Analytical Solution

Raptor C18
1.8µm, 50x2.1mm

Mobile Phase A:
5mM ammonium acetate in water

Mobile Phase B:
Methanol

Gradient:
<table>
<thead>
<tr>
<th>Time (min)</th>
<th>%B</th>
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<tr>
<td>0.00</td>
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<td>6.00</td>
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<td>6.50</td>
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<td>6.51</td>
<td>20</td>
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<td>8.00</td>
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Flow Rate: 0.4 mL/min

Column Temp.: 40 °C

Ion Mode: ESI-

Diluent: 80:20 Methanol:Water

Concentration: 5-50 ng/mL

Injection Volume: 2 µL

8 min
Perfluoroalkylcarboxylic Acid

Perfluoroalkylsulfonic Acid

PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrDA, PFTeDA, PFHxDA, PFODA, PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS

(C4), (C10), (C18)
Fluorotelomer Sulfonate

Perfluoroalkylsulfonamidoethanol

Perfluoroalkylsulfonamidoacetic acid

Perfluoroalkylsulfonamide

Fluorotelomer Carboxylic Acid
Restek’s PFAS Analytical Solution

**Raptor C18**
1.8µm, 50x2.1mm

**Mobile Phase A:**
- 5mM ammonium acetate in water

**Mobile Phase B:**
- Methanol

**Gradient:**

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- 40 °C

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- 80:20 Methanol:Water

**Concentration:**
- 5-50 ng/mL

**Injection Volume:**
- 2 µL

8 min
EPA 537 and Updated 537.1 Method (Drinking Water)

EPA 537 Method (2009)

EPA 537.1 Method (2018)

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Peak # (Fig. 1)</th>
<th>RT (min)</th>
<th>IS# Ref</th>
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<td>PFBS</td>
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<td>PFHxA</td>
<td>2</td>
<td>10.42</td>
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<td>HFPO-DA</td>
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<td>PFHpA</td>
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<td>PFHxS</td>
<td>7</td>
<td>13.58</td>
<td>2</td>
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<td>ADONA</td>
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<td>PFOA</td>
<td>9</td>
<td>15.85</td>
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<td>PFOS</td>
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<td>d5-NMeFOSAA-IS#3</td>
<td>18</td>
<td>20.49</td>
<td>-</td>
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</tbody>
</table>
Restek's PFAS Analytical Solution

PFOA and PFOS Alternatives

Perfluoroalkyl ether carboxylic acids (PFECAs)

Hexafluoropropylene oxide dimer acid (HFPO-DA) GenX

ammonium 4,8-dioxa-3H-perfluorononanoate (ADONA)

Polyfluoroalkyl ether Sulfonates (PFESAs)

F-53B (9-chlorohexadecafluoro-3-oxanonane-1-sulfonate) (9Cl-PF3ONS)

(11-chloroeicosafluoro-3-oxanonane-1-sulfonate) (11Cl-PF3OUdS)
EPA 537.1 Method (Drinking Water) on Raptor C18

Raptor C18
2.7µm, 50x2.1mm

10 min

37 min

EPA 537.1 Method (2018)

Raptor C18
2.7µm, 50x2.1mm

10 min

37 min
Outline

• PFAS Panel

• **Restek’s Analytical Solutions**
  - Raptor C18 and **PFAS Delay Column**

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  - Reversed-Phase & HILIC Methodology

• Conclusions
Restek’s PFAS Analytical Solution

Interference Removal (Delay Column)

Note: This diagram represents a generic LC-MS/MS workflow. The exact location of the PFAS Delay Column installation may vary, however, it must be installed between the mobile phase mixer and the autosampler injector as shown in the diagram.
Blank Injections and Interferences

40 min equilibration

10 min equilibration

50 ppt standard

PFDa

PFUnA

PFDA

PFNA

PFOA

PFDa

PFUnA

PFDA

PFNA

PFOA
Blank Injections and Interferences

40 min equilibration

- PFDa
- PFUnA
- PFDA
- PFNA
- PFOA

10 min equilibration

- PFDa
- PFUnA
- PFDA
- PFNA
- PFOA

With the PFAS Delay Column
Blank Injections and Interferences

15 min equilibration

1 min equilibration

10 ppt standard

PFOA

PFOA

PFOA
Blank Injections and Interferences

15 min equilibration

1 min equilibration

With the PFAS Delay Column

PFOA

With the PFAS Delay Column

PFOA

Gone!
Restek’s PFAS Analytical Solution

Interference Removal (PFAS Delay Column)

System independent solution – compatible w/ both HPLC, UHPLC systems with max pressure of 1,034 bar/15,000 psi

50 ppt standard injection

Blank (30 min equilibration)
Outline

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Ultrashort-Chain, Alternative, and Legacy PFAS Analysis

UltraShort–Chain PFAS

- Trifluoroacetic acid (TFA)
- Perfluoropropionic acid (PFPrA)
- Perfluoroethane sulfonate (PFEtS)
- Perfluoropropane sulfonate (PFPrS)

Detected in different water matrices (snow, rain, river, and tap water)

1. PFPrA is up to 45% of the total PFAS in rain and snow samples (USA, France, Japan)
2. C2-C3 accounted for >40% of the total PFAS in rain samples (Canada)
3. TFA is the most abundant PFAS in rainwater (Japan)
4. PFEtS and PFPrS are detected in aqueous film-forming foam (AFFF)

Analytical methods for investigation on the sources and environmental levels
Direct Injection Method Evaluation

Raptor C18
2.7µm, 100x3.0mm

UltraShort & Short Chain PFAS

- Perfluoropropionic acid (PFPrA)
- Perfluorobutanoic acid (PFBA)
- Perfluoropropane sulfonate (PFPrS)
- Perfluorobutane sulfonate (PFBS)

Legacy PFAS

- Perfluorooctanoic acid (PFOA)
- Perfluorooctanesulfonic acid (PFOS)

PFOA and PFOS Alternatives

- Perfluoroalkyl ether carboxylic acids (PFECAs)
  - Hexafluoropropylene oxide dimer acid (HFPO-DA)
  - ammonium 4,8-dioxa-3H-perfluorononanoate (ADONA)

- Polyfluoroalkyl ether Sulfonates (PFESAs)
  - (9-chlorohexadecafluoro-3-oxanonane-1-sulfonate) (9Cl-PF3ONS)
  - (11-chloroeicosafluoro-3-oxanonane-1-sulfonate) (11Cl-PF3OuD S)
Direct Injection Method Evaluation

**Calibration Range:**

- 5 – 400 ng/L (LLOQ: 5 ng/L)
- 10 – 400 ng/L (for PFPrA; LLOQ: 10 ng/L)

**Precision & Accuracy of Spiked Water Samples:**

1. Tap water
2. River water (Chicago)
3. Groundwater
4. POTW water (Effluent)
Direct Injection Method Evaluation

Sample Preparation:

- 250 µL water sample or standard
- 250 µL 40/60 LC-MS water / methanol
- 5 µL internal standard

(polypropylene vial)

(5 ng/mL $^{13}$C$_2$-PFHxA, $^{13}$C$_2$-PFOA, $^{13}$C$_4$-PFOS in methanol)
### LC Conditions: (Shimadzu Nexera X2)

<table>
<thead>
<tr>
<th>Mobile Phase A</th>
<th>Mobile Phase B</th>
</tr>
</thead>
<tbody>
<tr>
<td>5mM ammonium acetate in water</td>
<td>methanol</td>
</tr>
</tbody>
</table>

#### Gradient

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>%B</th>
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<tbody>
<tr>
<td>0.00</td>
<td>20</td>
</tr>
<tr>
<td>7.00</td>
<td>95</td>
</tr>
<tr>
<td>9.00</td>
<td>95</td>
</tr>
<tr>
<td>9.01</td>
<td>20</td>
</tr>
<tr>
<td>11.00</td>
<td>20</td>
</tr>
</tbody>
</table>

- **Injection:** 10 µL
- **Flow Rate:** 0.25 mL/min
- **Run Time:** 11 min
- **Column Temp.:** 40°C

### MS Conditions: (AB Sciex 4500)

- **Ion Mode:** Negative ESI
- **Curtain Gas:** 20
- **Collision Gas:** 10
- **IonSpray Voltage:** -2000
- **Temperature:** 450°C
- **Ion Source Gas1:** 30
- **Ion Source Gas1:** 30

<table>
<thead>
<tr>
<th>Peak</th>
<th>MRM</th>
<th>RT</th>
<th>IS</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFPrA</td>
<td>162.9/119.0</td>
<td>2.75</td>
<td>$^{13}$C$_2$-PFHxA</td>
</tr>
<tr>
<td>PFBA</td>
<td>212.8/169.0</td>
<td>4.70</td>
<td>$^{13}$C$_2$-PFOA</td>
</tr>
<tr>
<td>PFPrS</td>
<td>248.8/79.6</td>
<td>5.13</td>
<td>$^{13}$C$_2$-PFHxA</td>
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<td>PFBS</td>
<td>298.8/79.9</td>
<td>6.13</td>
<td>$^{13}$C$_2$-PFHxA</td>
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<td>HFPO-DA</td>
<td>285.0/168.9</td>
<td>6.92</td>
<td>$^{13}$C$_2$-PFOA</td>
</tr>
<tr>
<td>DONA</td>
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<td>$^{13}$C$_2$-PFOA</td>
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<tr>
<td>PFOA</td>
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<td>$^{13}$C$_2$-PFOA</td>
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<td>PFOS</td>
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<td>$^{13}$C$_4$-PFOS</td>
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<td>9Cl-PF3ONS</td>
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<td>13C$_2$-PFOA</td>
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<td>-</td>
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<tr>
<td>13C$_4$-PFOS</td>
<td>503.0/80.0</td>
<td>8.01</td>
<td>-</td>
</tr>
</tbody>
</table>

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**80 ppt standard**

![Graph of chromatogram showing peaks for various PFAS compounds](chart.png)

- **PFPrA**
- **PFBA**
- **PFPrS**
- **PFBS**
- **HFPO-DA**
- **DONA**
- **PFOA**
- **PFOS**

---

**Website:** [www.restek.com](http://www.restek.com)

**Product:** Pure Chromatography
# Direct Injection Method Evaluation

## Analytes in Unspiked Water Samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>PFPrA</th>
<th>PFBA</th>
<th>PFPrS</th>
<th>PFBS</th>
<th>HFPO-DA</th>
<th>DONA</th>
<th>PFOA</th>
<th>PFOS</th>
<th>9Cl-PF3ONS</th>
<th>11Cl-PF3OUDS</th>
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</thead>
<tbody>
<tr>
<td>Tap Water</td>
<td>ND</td>
<td>1.1</td>
<td>ND</td>
<td>ND</td>
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<td>ND</td>
<td>ND</td>
<td>ND</td>
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<tr>
<td>River Water</td>
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<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Groundwater</td>
<td>9.0</td>
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<td>ND</td>
<td>2.6</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
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<td>POTW</td>
<td>11.7</td>
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<td>3.1</td>
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<td>ND</td>
<td>15.0</td>
<td>6.0</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

**PFPrA in Unspiked Waters**

![Reagent Water](image1.png)

![Ground Water](image2.png)

![River Water](image3.png)

![POTW Water](image4.png)
# Direct Injection Method Evaluation

## Analytes in Unspiked Water Samples

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<th>PFBA</th>
<th>PFPrS</th>
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<th>DONA</th>
<th>PFOA</th>
<th>PFOS</th>
<th>9Cl-PF3ONS</th>
<th>11Cl-PF3OUdS</th>
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<tr>
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<td>ND</td>
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<tr>
<td>River Water</td>
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<td>ND</td>
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<td>ND</td>
<td>ND</td>
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<td>Groundwater</td>
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<td>ND</td>
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<tr>
<td>POTW</td>
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<td>6.0</td>
<td>ND</td>
<td>ND</td>
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</tbody>
</table>

### PFBA in Unspiked Waters

- **Tap Water**
- **River Water**
- **Ground Water**
- **POTW Water**
- **Reagent Water**
Direct Injection Method Evaluation

PFAS Delay Column + Raptor C18 2.7µm, 100x3.0mm

PFOA contamination in the LC System

Reagent Water Injection with Delay Column

Reagent Water Injection With No Delay Column (2-minute equilibration)

PFOA in Unspiked Waters

POTW Water (With Delay Column)
Analyte Peak Intensity at LLOQ

- PFBA: 10 ppt
- PFPrS: 5 ppt
- C2-PFHxS: 5 ppt
- DONA: 5 ppt
- HFPO-DA: 5 ppt
- PFOA: 5 ppt
- PFOS: 5 ppt
- 9Cl-PF3ONS: 5 ppt
- 11Cl-PF3OUdS: 5 ppt

*Note: LLOQ stands for Lower Limit of Quantitation.*

**Analyte:**
- PFBA
- PFPrS
- C2-PFHxS
- DONA
- HFPO-DA
- PFOA
- PFOS
- 9Cl-PF3ONS
- 11Cl-PF3OUdS

**Peak Intensity at LLOQ:**
- PFBA: 10 ppt
- PFPrS: 5 ppt
- C2-PFHxS: 5 ppt
- DONA: 5 ppt
- HFPO-DA: 5 ppt
- PFOA: 5 ppt
- PFOS: 5 ppt
- 9Cl-PF3ONS: 5 ppt
- 11Cl-PF3OUdS: 5 ppt

**Software:**
- RESTEK Pure Chromatography
- Website: www.restek.com
Direct Injection Method Evaluation

**Linearity**

For PFPrS:

\[ y = 0.00527x + 0.00108 \quad (r = 0.99959) \quad \text{(weighting: } 1/x) \]

For 11Cl-PF3OUdS:

\[ y = -7.64307 \times 10^{-6}x^2 + 0.01194x + 0.00361 \quad (r = 0.99850) \quad \text{(weighting: } 1/x) \]
# Direct Injection Method Evaluation

## Accuracy & Precision

<table>
<thead>
<tr>
<th>Matrices</th>
<th>Tap Water</th>
<th>River Water</th>
<th>Ground Water</th>
<th>POTW Water</th>
<th>Reagent Water</th>
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</thead>
<tbody>
<tr>
<td>Conc. (ng/L)</td>
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<td>80</td>
<td>10*</td>
<td>80</td>
<td>10*</td>
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<tr>
<td>PFPrA</td>
<td>96.9 (11.0)</td>
<td>105 (3.91)</td>
<td>105 (6.57)</td>
<td>95.4 (6.84)</td>
<td>92.0 (9.54)</td>
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<tr>
<td>PFBA</td>
<td>99.3 (9.19)</td>
<td>108 (1.81)</td>
<td>108 (5.20)</td>
<td>110 (1.70)</td>
<td>104 (8.21)</td>
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<tr>
<td>PFPrS</td>
<td>100 (4.24)</td>
<td>107 (3.14)</td>
<td>103 (6.71)</td>
<td>105 (2.64)</td>
<td>105 (8.48)</td>
</tr>
<tr>
<td>PFBS</td>
<td>101 (5.20)</td>
<td>106 (1.84)</td>
<td>99.7 (7.54)</td>
<td>105 (2.10)</td>
<td>100 (6.57)</td>
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<tr>
<td>HFPO-DA</td>
<td>96.2 (7.86)</td>
<td>102 (4.64)</td>
<td>96.2 (4.99)</td>
<td>105 (3.94)</td>
<td>95.0 (3.59)</td>
</tr>
<tr>
<td>ADONA</td>
<td>101 (6.23)</td>
<td>106 (3.82)</td>
<td>97.6 (6.36)</td>
<td>106 (2.32)</td>
<td>98.4 (2.68)</td>
</tr>
<tr>
<td>PFOA</td>
<td>105 (8.65)</td>
<td>105 (3.70)</td>
<td>108 (12.1)</td>
<td>107 (3.63)</td>
<td>108 (9.66)</td>
</tr>
<tr>
<td>PFOS</td>
<td>99.3 (2.10)</td>
<td>108 (4.24)</td>
<td>112 (1.87)</td>
<td>107 (4.93)</td>
<td>101 (2.96)</td>
</tr>
<tr>
<td>9Cl-PF3ONS</td>
<td>95.6 (4.60)</td>
<td>106 (5.93)</td>
<td>105 (5.37)</td>
<td>110 (8.20)</td>
<td>97.2 (4.52)</td>
</tr>
<tr>
<td>11Cl-PF3OuDS</td>
<td>114 (8.78)</td>
<td>112 (8.91)</td>
<td>102 (15.0)</td>
<td>91.5 (2.34)</td>
<td>96.7 (5.99)</td>
</tr>
</tbody>
</table>

* 20 ng/L for PFPrA;  # 10 ng/L for PFPrA

% Recovery 80 – 120 %

% RSD < 15 %

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[RESTEK](https://www.restek.com) Pure Chromatography
Outline

• PFAS Panel
• Restek’s Analytical Solutions
  • Raptor C18 and PFAS Delay Column
• Method Development for Ultrashort-Chain and Alternative PFAS
  • Reversed-Phase & HILIC Methodology
• Conclusions
Method Development with A Hybrid Ion-Exchange/HILIC Column

*Single Ligand, Multi-functionalities*
Ultrashort-Chain, Short-Chain, and Legacy PFAS Analysis

Hybrid Ion-Exchange/HILIC Column

400 ppt in 50:50 water:methanol

**LC Conditions : (Shimadzu Nexera X2)**

| Mobile Phase A | 10mM ammonium acetate in water |
| Mobile Phase B | 50:50 acetonitrile:methanol     |

<table>
<thead>
<tr>
<th>Gradient</th>
<th>Time (min)</th>
<th>%B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>6.00</td>
<td>95</td>
<td></td>
</tr>
</tbody>
</table>

**Injection** 10 µL

**Flow Rate** 0.4 mL/min

**Run Time** 6 min

**Column Temp.** 40°C

[Graph showing PFAS analysis]
Comprehensive PFAS Analysis
Hybrid Ion-Exchange/HILIC Column

Perfluorooalkylsulfonic Acid
- PFOS
- PFBA
- PFPrS
- PFBS

Perfluorooalkylcarboxylic Acid
- PFOA
- PFPrA
- TFA

Perfluorooalkyl Ether Carboxylic Acid
- 9Cl-PF3ONS
- 11Cl-PF3Ouds
- ADONA
- HFPO-DA

Perfluorooalkyl Ether Sulfonic Acid
- FOSA

Perfluorooalkylsulfonamide
- N-MeFOSAA
- N-EtFOSAA

Fluorotelomer Sulfonate
- 4:2 FTS
- 10:2 FTS
- 8:2 FTS
- 6:2 FTS

Fluorotelomer Sulfonamide
- N-MeFOSAA

Di-substituted Polyfluorooalkyl Phosphate Ester
- 6:2 diPAP
- 8:2 diPAP
- 6:2/8:2 diPAP

6:2 diPAP
Ultrashort-Chain, Short-Chain, and Legacy PFAS Analysis

Hybrid Ion-Exchange/HILIC Column

TFA is everywhere

10ppt standard  RO H₂O  DI H₂O  LC/MS Grade H₂O

EMSURE® MeOH  JT Baker MeOH  Brand A MeOH  Brand B MeOH  Brand C MeOH  Brand D MeOH

RESTEK

Pure Chromatography
Conclusions

• Use **Raptor C18 column** for PFAS monitoring including C3 ultrashort-chain compounds

• Use **PFAS delay column** to block PFAS contamination

• Use **HILIC/Ion-Exchange column** for PFAS monitoring including C2 ultrashort-chain compounds
Acknowledgement

**LC R&D:**
- Xiaoning Lu
- Vernon C. Bartlett
- Connor Flannery
- Ahren Green
- Terry S. Reid

**EPA (Region 5):**
- Larry Zintek
Thanks for Your Attention

Visit us at Booth # 31