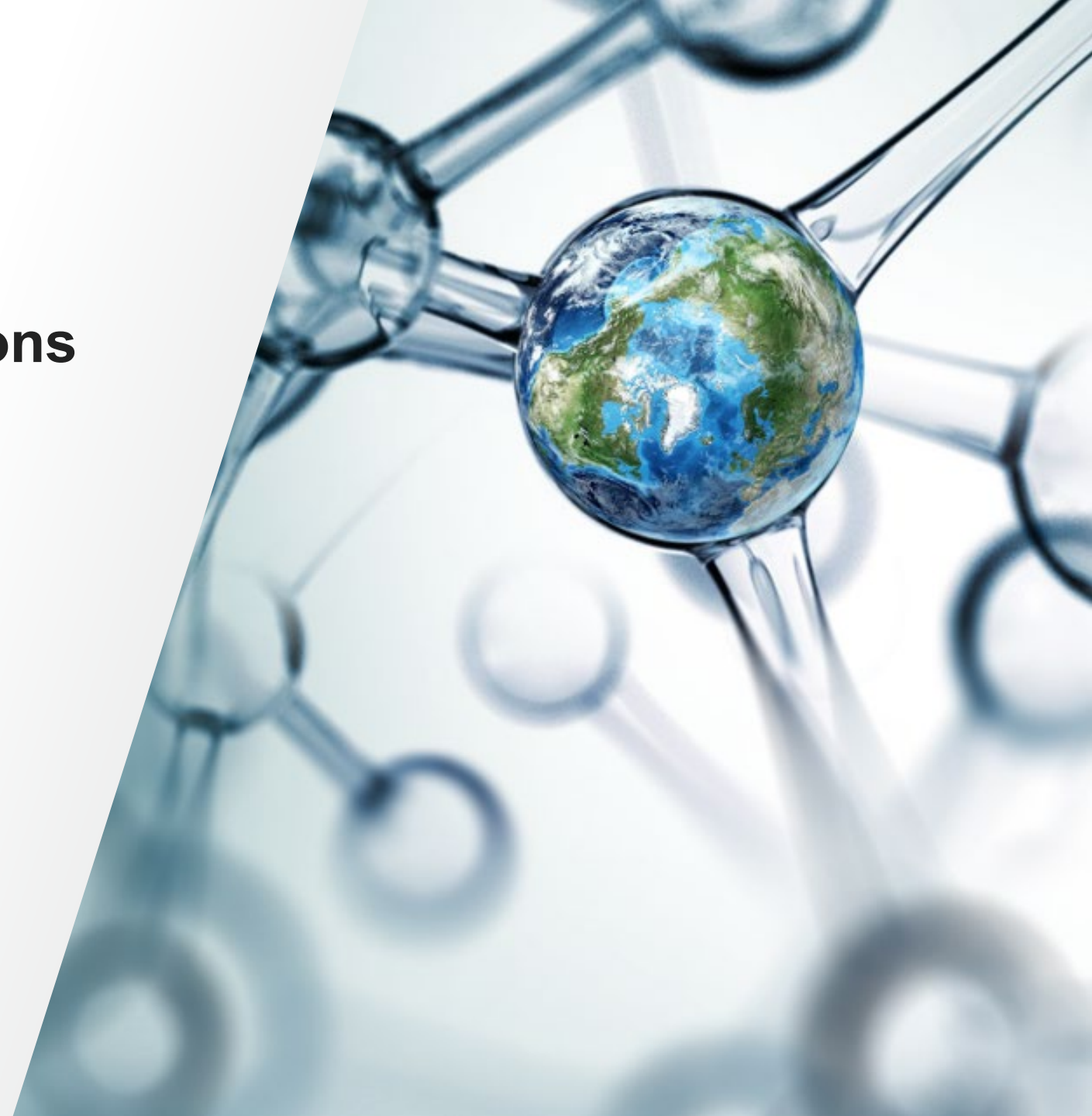


# Automated Preparation Solutions for PFAS Analysis in Environmental Samples

Ed George– Thermo Fisher Scientific  
Environmental, Food and Beverage Market Manager  
NEMC 2022- Lunch Seminar  
Crystal City, VA

 The world leader in serving science



# Automated PFAS Workflows

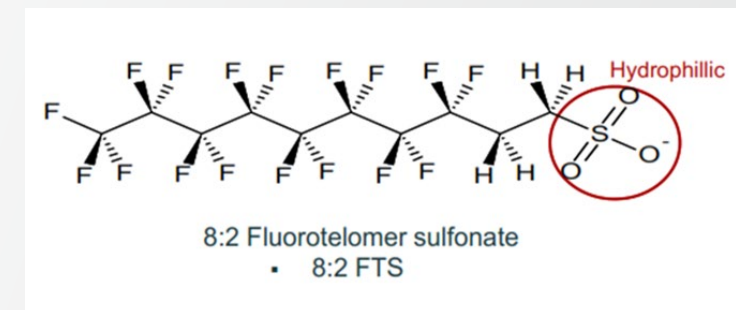
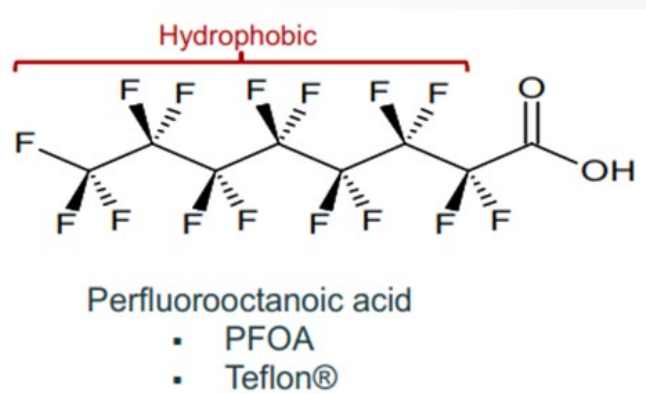
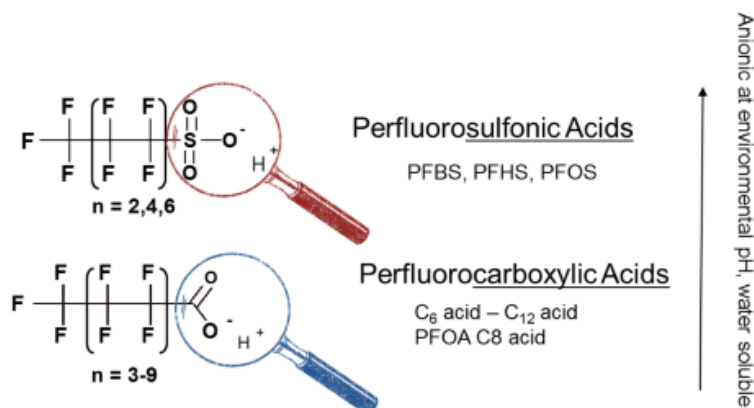
## Outline

- Background
- Overall Solutions for PFAS offered by Thermo Fisher Scientific
- Automated Sample Preparation Solutions for Environmental Samples
  - Water sample analysis with the Autotrace 280 (off-line solid phase extraction)
  - Water sample analysis with the Equan 850 Autosampler (on-line solid phase extraction)
  - Soil analysis with the ASE 350
  - Screening samples with Combustion Ion Chromatography (CIC)

# Background

- PFAS = **P**er- and **P**oly- **F**luorinated **A**lky **S**ubstances
  - Class of structurally similar compounds
  - Hydrophobic C-F chain of various lengths with hydrophilic functional group on the end
  - Shorter carbon chains → More water soluble
  - Longer carbon chain → Less water soluble

>9000 varieties more are being discovered



Individual PFAS molecule is determined by chain length and functional group

# Overview of Thermo Fisher Scientific PFAS Workflows

Soil

Unknown profiling

[Extraction and analysis of poly- and perfluoroalkyl substances \(PFAS\) from soil](#)

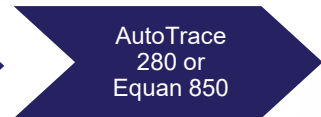
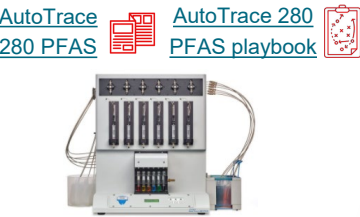


Targeted

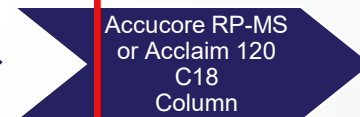
[Determination of per- and polyfluorinated alkyl substances \(PFAS\) in drinking water EPA 533](#)



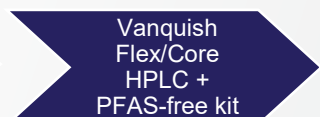
[Determination of per- and polyfluorinated alkyl substances \(PFAS\) in drinking water EPA 537.1](#)



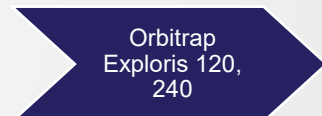
[Accucore RP-MS](#)  
[Acclaim 120 C18](#)



[Vanquish Duo](#)



[Altis](#)  
[Fortis](#)

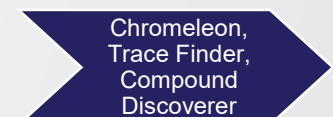
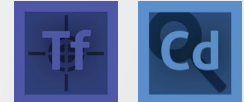
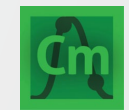


Orbitrap

## PFAS Solutions

[Setting a new horizon for PFAS workflow applications brochure](#)

[www.thermofisher.com/pfas-testing](http://www.thermofisher.com/pfas-testing)



[Chromleon](#)

[TraceFinder](#)

[Compound Discoverer](#)

Water

Unknown profiling

[EPA Method 537.1 using automated SPE followed by LC-Q Exactive Orbitrap MS](#)

Screening

[AOF by combustion IC – non-targeted complementary determination of PFAS in aqueous samples](#)



[PFAS by CIC Workflow](#)

## Legend

Webpage

Brochure

App Note

Playbook

# Sample Prep Devices for Large Sample Volumes

Sample  
Extraction  
and Clean up



Vacuum Manifold



Thermo Scientific™ Dionex™ AutoTrace™ 280 PFAS  
Solid-Phase Extraction Instrument

# Solid Phase Extraction (SPE) for EPA methods 537/537.1





# Solid Phase Extraction Method

Keeping cartridge sorbent wet is very important

## Conditioning

15 mL Methanol then 18 mL H<sub>2</sub>O.  
Cartridges can not go dry. 1-minute soak time might be required for each to aid recovery.

⌚ Time ~ 10 to 15 min

Flow rate is critical, too quickly will cause loss of analytes

## Sample loading

Load 250 mL of sample through at 10 to 15 mL/min.  
Do not let cartridge go dry during loading.

⌚ Time ~ 17 to 25 min

Elution speed must be controlled otherwise analytes will stay on the sorbent

## Cartridge elution

Rinse bottles and elute SPE cartridges with two 4 mL aliquots of MeOH. Elution speed is to be done in dropwise fashion (20 drops/mL).

⌚ Time ~ 10 min

## Concentration

Dry sample and reconstitute with 1 mL 96/4% MeOH:H<sub>2</sub>O and Internal Standard



# Vacuum SPE vs. AutoTrace 280 PFAS SPE Instrument

It's automated!

- Vacuum SPE
  - Problems maintaining consistent flow
  - Cannot let it run dry – affects the flow rate and performance
  - Inconsistent volumes run to run
  - Requires constant attendance
- AutoTrace 280 PFAS
  - Pumps are set at a constant flow
  - Ensures cartridges do not dry on critical steps
  - Precise consistency run to run
  - Push “start” and have a cup of coffee





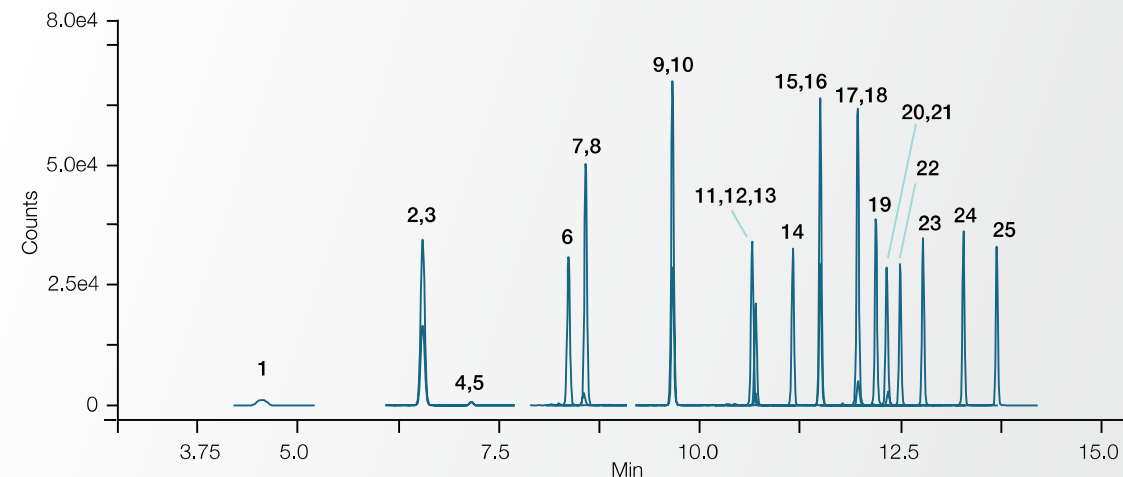
# AutoTrace 280 PFAS SPE Instrument for Liquid Samples

- Sample and reagent tubing is PEEK
- Positive pressure instead of vacuum
- Method stored on the AutoTrace 280 PFAS SPE Instrument
  - No PC required
- Walk-up operation- Parallel sample processing steps
- Significant labor savings
  - Minimal user interaction required
  - Analysts can accomplish other lab tasks
  - Lower costs due to increased efficiency
- Better data quality
- Lower risk of rerunning samples



# EPA 537.1 Performance Data using AutoTrace 280 PFAS SPE Instrument

Peak number	Analyte	Fortified Conc. (ng/L)	Mean Recovery (%)	RSD	Fortified Conc. (ng/L)	Mean Recovery (%)	RSD
1	PFBS	16.0	107	3.3	80.0	<b>98.3</b>	<b>3.6</b>
2,3*	PFHxA	16.0	108	2.3	80.0	<b>106</b>	<b>2.6</b>
4,5*	HFPO-DA	16.0	84.1	7.5	80.0	<b>88.6</b>	<b>6.3</b>
6	PFHpA	16.0	113	2.7	80.0	<b>117</b>	<b>1.3</b>
7	PFHxS	16.0	120	3.4	80.0	<b>123</b>	<b>2.1</b>
8	ADONA	16.0	117	2.5	80.0	<b>121</b>	<b>1.1</b>
9,10*	PFOA	16.0	113	2.5	80.0	<b>119</b>	<b>1.6</b>
11	PFNA	16.0	114	2.9	80.0	<b>118</b>	<b>2.1</b>
12,13*	PFOS	16.0	113	4.5	80.0	<b>117</b>	<b>2.9</b>
14	9Cl-PF3ONS	16.0	96.1	4.1	80.0	<b>103</b>	<b>2.6</b>
15*,16	PFDA	16.0	105	3.2	80.0	<b>111</b>	<b>2.1</b>
17*,18	NMeFOSAA	16.0	103	5.2	80.0	<b>110</b>	<b>5.2</b>
19	PFUnA	16.0	96.8	5.0	80.0	<b>103</b>	<b>3.1</b>
20*21	NEtFOSAA	16.0	100	9.9	80.0	<b>104</b>	<b>2.3</b>
22	11Cl-PF3OUdS	16.0	88.5	5.5	80.0	<b>97.1</b>	<b>4.8</b>
23	PFDoA	16.0	89.8	4.4	80.0	<b>97.3</b>	<b>3.4</b>
24	PFTTrA	16.0	89.6	3.8	80.0	<b>95.8</b>	<b>3.7</b>
25	PFTA	16.0	89.0	4.8	80.0	<b>98.1</b>	<b>3.3</b>



Precision and accuracy (n=6) of PFAS in fortified drinking water

All recoveries and precision are well with in the method requirements

- Recovery must be 70 – 130%
- RSD < 20%

# TriPlus RSH EQuan 850 Autosampler- Online Solution

**Automated high-throughput LC-MS solution** for the analysis of contaminants in environmental water, drinking water and beverages at low ng/L levels

- **Online sample pre-concentration**
  - 2 LC pumps: Loading and Eluting
  - 2 injection valves and 1 switching valve
  - 2 LC columns
- **High injection volumes**
  - 1 – 20 mL
- **Standard injection volumes**
  - 1-100  $\mu$ L

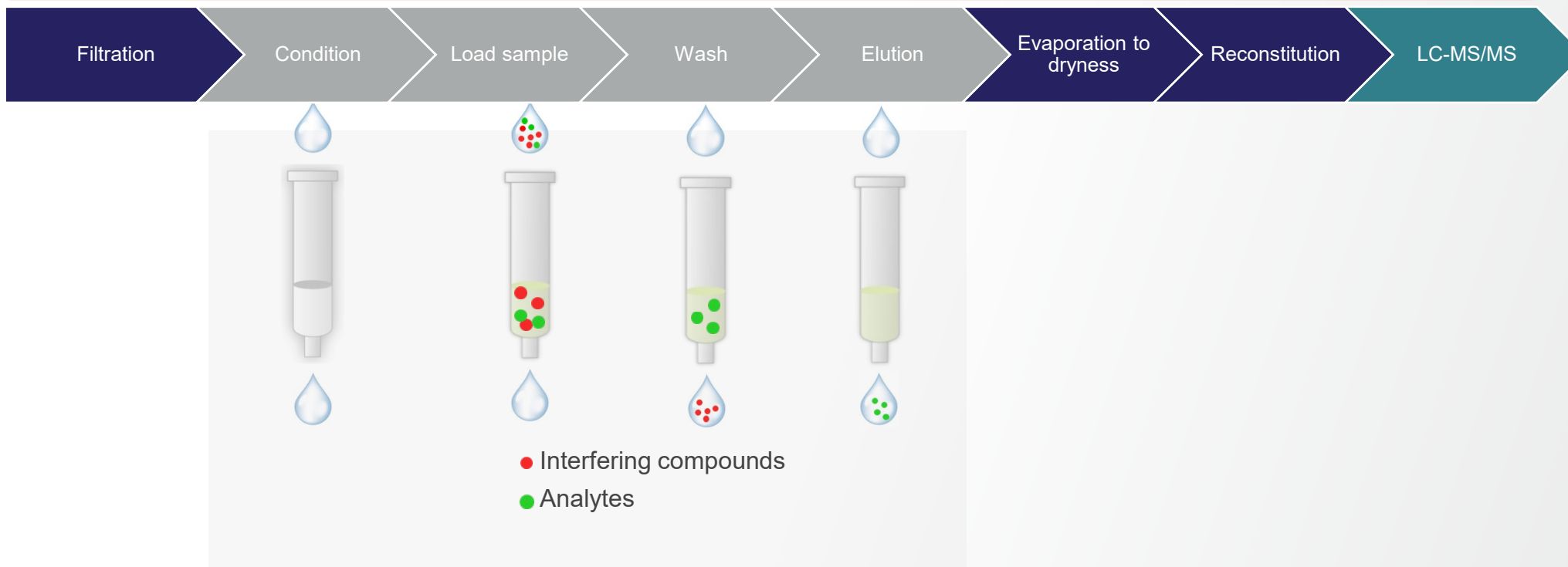
Find out more at [thermofisher.com/EQuan850](https://www.thermofisher.com/EQuan850)



# Offline vs. Online Sample preparation

## Conventional Method: Offline Sample Preparation

~ 2 Hours



## TriPlus RSH EQuan 850: Online Sample Preparation

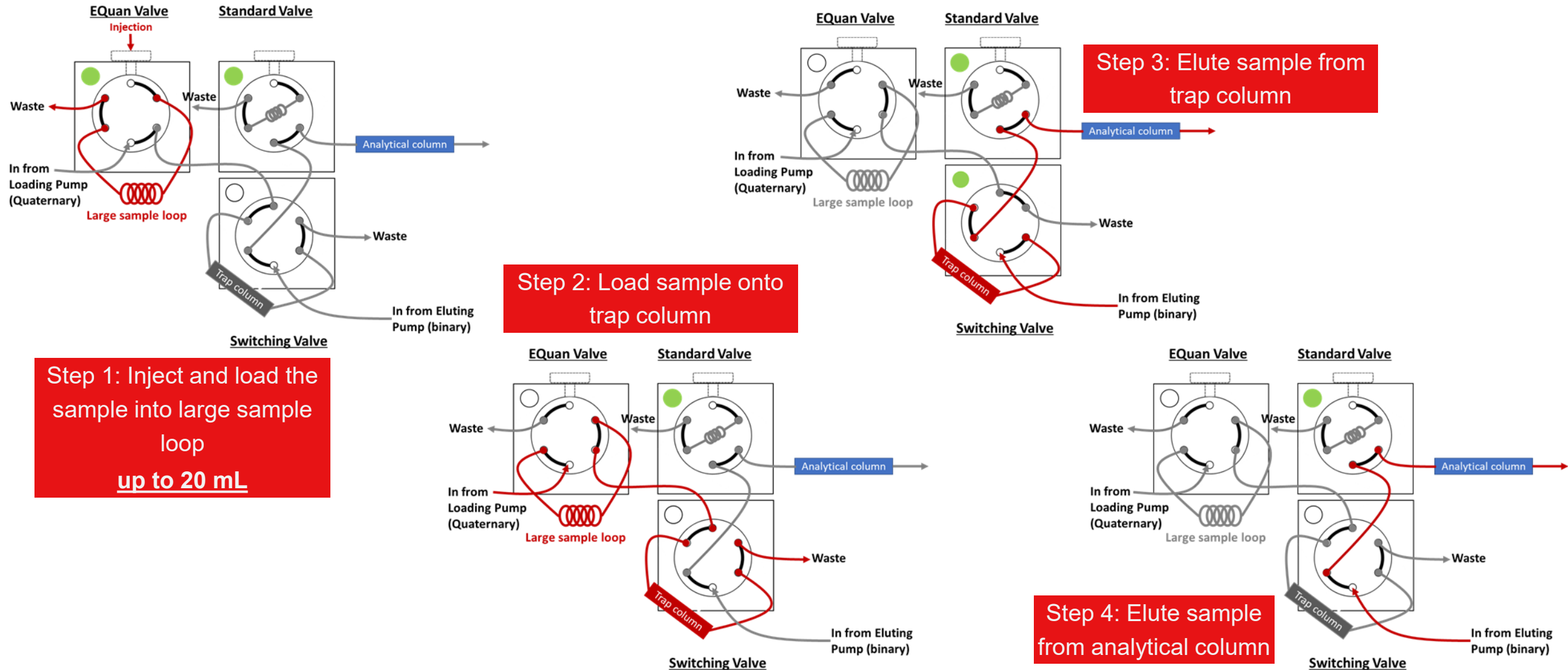
~ 30 minutes



Analysis time is reduced from hours to minutes

# Online Sample Pre-Concentration: How it Works

## EQuan Injection Mode: Red Flow Path

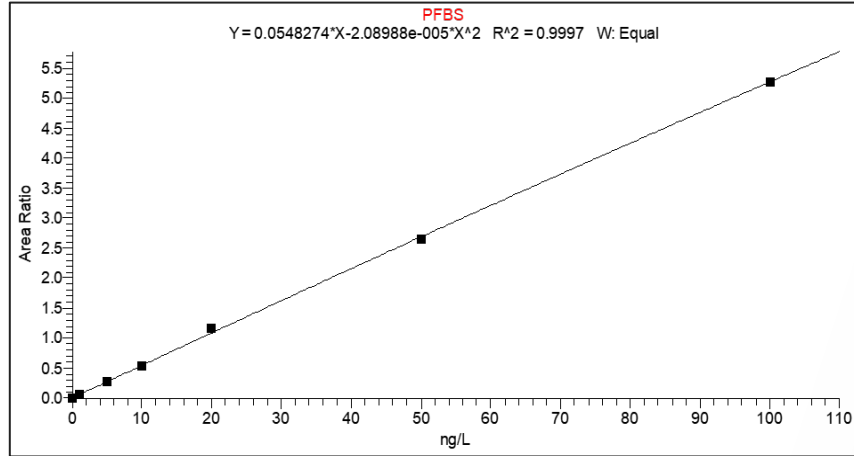




# Sensitivity and Linearity- EQuan 5ml Injection- QE Focus

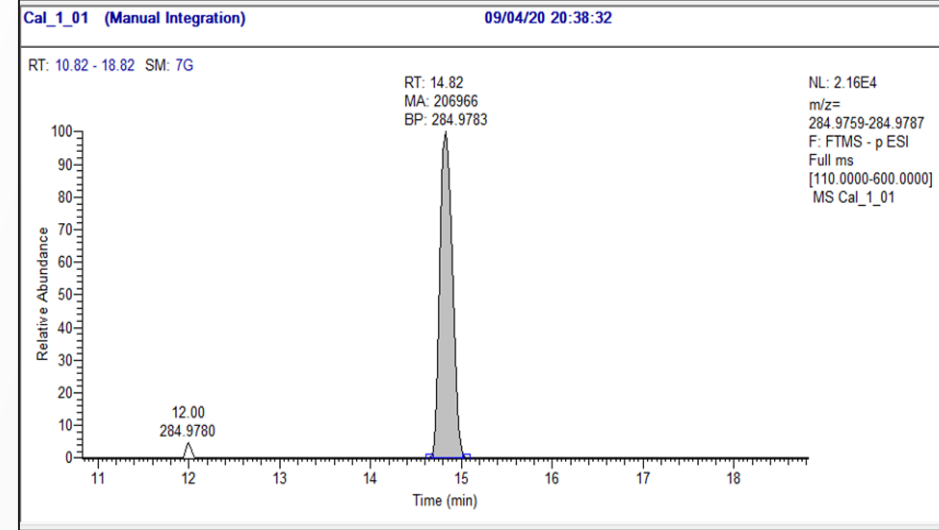
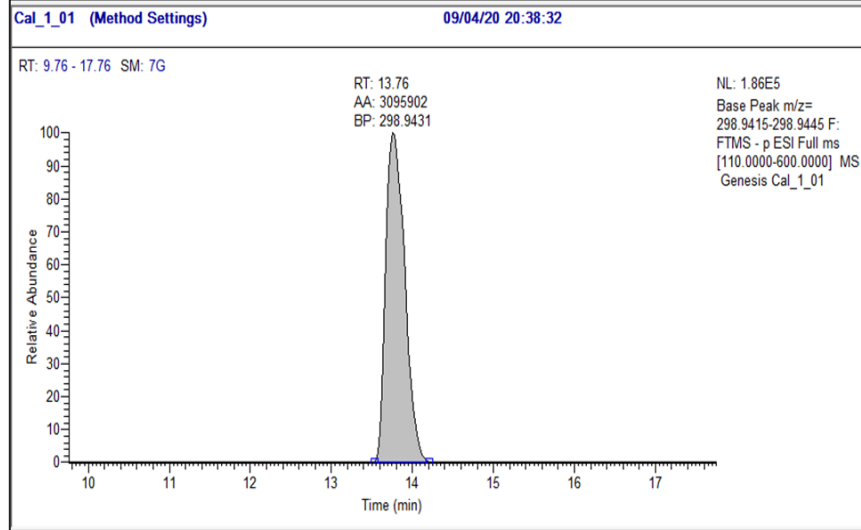
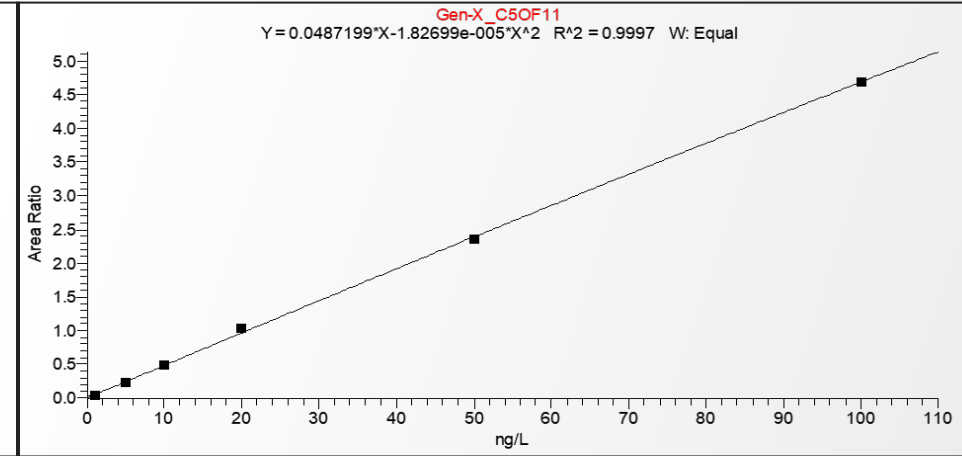
Pentafluorobutane Sulfonate

1 - 100ng/L



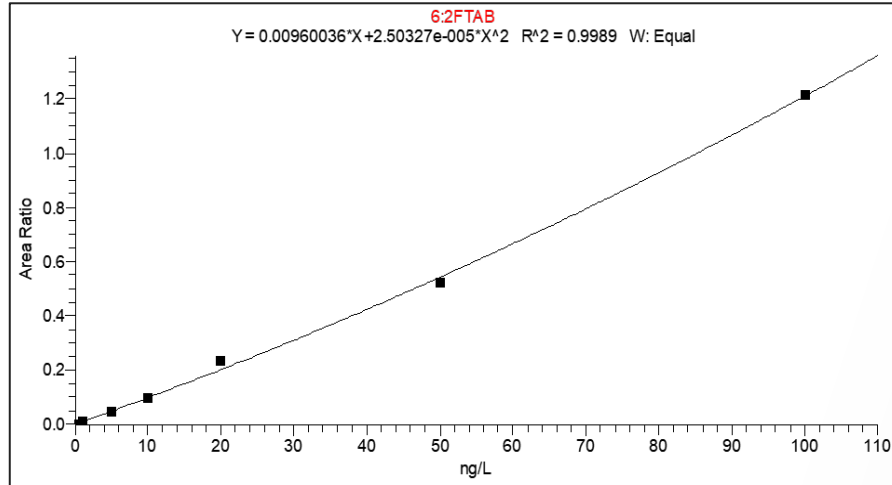
GenX

1 - 100ng/L

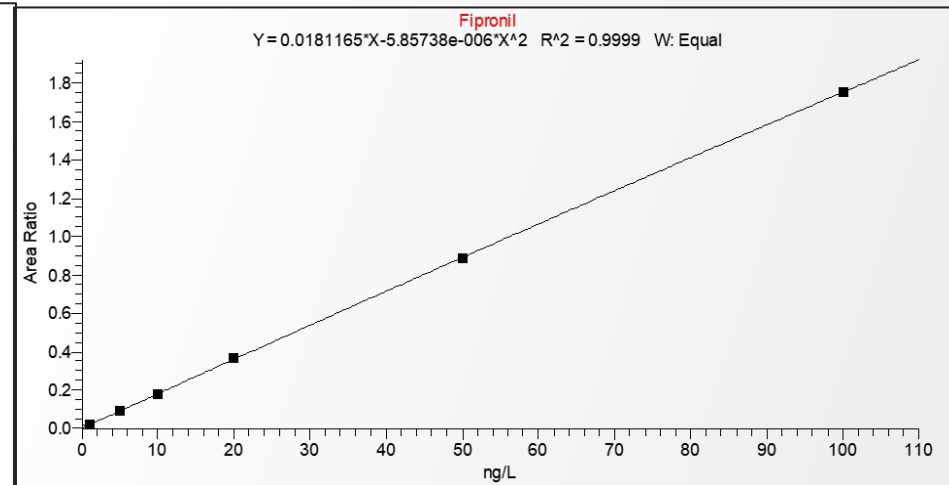


# Sensitivity and Linearity- EQuan 5ml Injection- QE Focus

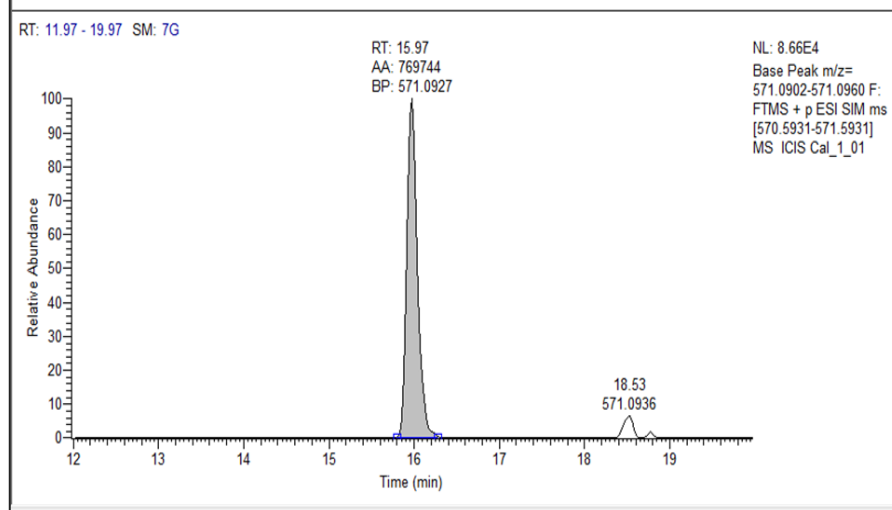
6:2 FTAB (SIM) 1 - 100ng/L



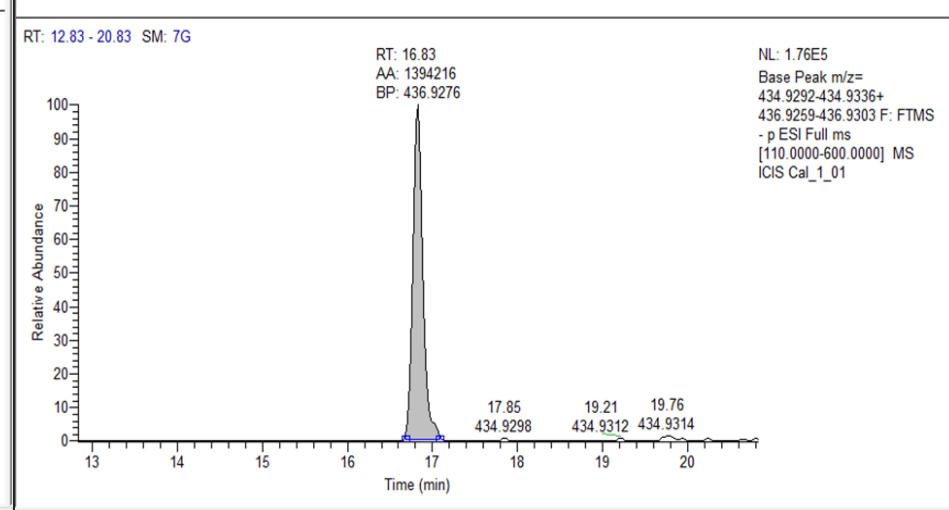
Fipronil 1 - 100ng/L



Cal\_1\_01 (Method Settings) 09/04/20 20:38:32



Cal\_1\_01 (Method Settings) 09/04/20 20:38:32



# Method Validation Results- EQuan

Compound	Cal Range (ng/L)	Treated Sewage 10% Cal range		Treated Sewage 60% Cal Range		Surface Water 60% Cal range		Crude Sewage 60% Cal Range	
		%RSD	%Rec	%RSD	%Rec	%RSD	%Rec	%RSD	%Rec
Ranitidine	10-1000	3.99	94.7	4.91	101	3.98	98.5	6.93	99.3
Benzotriazole	10-1000	10.61*	106.0*	9.61*	95.7*	4.26	103.1	5.49	104.4
Imidacloprid	1-100	3.14	96.9	1.61	101	1.64	99.6	6.95	98.8
Bisphenol S	10-1000	3.09	97.1	3.03	99.8	2.61	99.3	6.18	97.7
PFPeA	1-100	6.46	100	3.43	102	2.18	102	6.62	99.7
Climbazole	10-1000	2.84	96.5	3.73	101	2.35	101	7.37	98.7
PFBS	1-100	2.93	96.8	2.24	99.2	1.34	99.1	6.60	98.4
PFHxA	1-100	2.33	97.1	3.33	101	2.28	100	6.38	97.7
GenX	1-100	4.78	95.9	3.04	99.9	1.58	101	6.92	98.5
PFHpA	1-100	2.29	95.7	2.42	99.2	1.49	99.1	7.52	97.8
PFHxS	1-100	3.46	94.8	2.68	96.8	1.08	97.3	6.73	96.1
6:2FTAB	1-100	18.19	93.9	9.73	98.2	9.70	128	12.50	109
6:2FTS	1-100	2.60	95.3	2.32	99.1	1.69	101	6.95	94.9
PFOA	0.1-10	4.54	84.0	5.70	105	2.53	102	2.48	102
PFOS	0.1-10	*	*	5.38	118	2.92	101	11.27	118
Fipronil	1-100	2.55	95.5	2.79	100	1.77	101	5.83	99.2
Triclocarban	10-1000	5.28	96.2	3.93	98.5	2.49	98.9	7.25	98.2

Samples centrifuged at 4000 rpm if suspended sediment visible; [\*] PFOS present in matrix

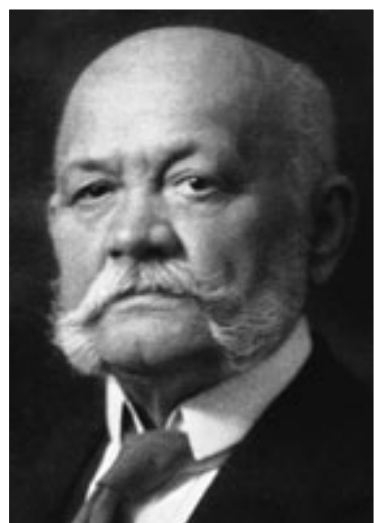
Data Courtesy of John Quick ALS Environmental - Coventry

# Method Validation Results – EQuan Continued

Compound	LOD, ug/L				MRL	Low Std (20% Cal range)		High Std (80% cal range)	
	Treated Sewage	Surface Water	Ground Water	Crude Sewage		ug/L	%RSD	%Bias	%RSD
Ranitidine	0.00890	0.00230	0.000804	0.0225	0.1	3.10	-2.89	2.87	-0.63
Benzotriazole	0.944	0.0140	0.00399	0.361	0.1	5.43	-1.24	2.26	-0.59
Imidacloprid	0.00205	0.000462	0.000293	0.00644	0.001	4.57	-2.81	1.53	-0.43
Bisphenol S	0.00426	0.00243	0.00284	0.0233	0.01	4.52	-3.87	2.30	-0.57
PFPeA	0.00191	0.000623	0.000332	0.00467	0.001	4.11	-2.35	2.13	-0.22
Climbazole	0.00297	0.00170	0.00149	0.0110	0.1	3.91	-1.39	1.98	-0.29
PFBS	0.000426	0.0000973	0.000179	0.00176	0.001	2.37	-2.52	2.21	-0.48
PFHxA	0.00126	0.000292	0.000192	0.00159	0.001	4.24	-2.99	1.32	-0.70
GenX	0.00129	0.000334	0.000147	0.00816	0.001	4.07	-2.81	1.13	-1.87
PFHpA	0.000591	0.000230	0.000158	0.00137	0.001	2.37	-2.81	2.21	-0.35
PFHxS	0.000424	0.0000788	0.000107	0.00112	0.001	2.37	-3.63	1.94	-0.94
6:2FTAB	0.00535	0.000507	0.000995	0.0221	0.001	8.26	0.76	8.76	-4.30
6:2FTS	0.00249	0.000326	0.000176	0.00176	0.001	2.21	-1.73	2.21	1.39
PFOA	0.00108	0.000232	0.0000668	0.000594	0.00009	2.37	-4.04	2.01	-0.38
PFOS	0.00830	0.000151	0.0000233	0.0200	0.00009	10.01	-3.95	4.45	-0.77
Fipronil	0.000939	0.000216	0.000234	0.00227	0.01	6.47	-3.14	2.03	0.28
Triclocarban	0.00132	0.00110	0.00115	0.00736	0.1	4.83	-1.99	1.63	0.30

Samples centrifuged at 4000 rpm if suspended sediment visible

# Soil Analysis- In the Beginning There Was Soxhlet...



Franz von Soxhlet  
(1848 – 1926)



*de facto* standard for solvent extraction

Slow, high solvent usage



# Now . . . Accelerated Solvent Extraction

- Automates sample preparation for solid and semisolid samples using solvents at elevated temperatures and pressure.
- Operates above the boiling point of extraction solvents by using sealed extraction cells.
- pH Hardened pathways allows use of strong acids and bases for sample pretreatment
- Well established and proven technique that is superior to Soxhlet and approved for U.S. EPA Method 3545A.



**Thermo Scientific™ Dionex™ ASE™ 350  
Accelerated Solvent Extractor system**

# Accelerated Solvent Extraction (ASE) for PFAS

Thermo Fisher Scientific™ Dionex™ ASE 350™ Accelerated Solvent Extractor



- **Extraction Conditions**
- 2g Soil + 10g Diatomaceous Earth
- Extraction Solvent: Methanol
- Temperature: 100 °C
- Pressure: 1600 psi
- Heat Time: 5 min
- Static Time: 5 min
- Flush Volume: 70%
- Purge Time: 120 s
- Static Cycles: 3
- Total Extraction Time: 25 min per sample

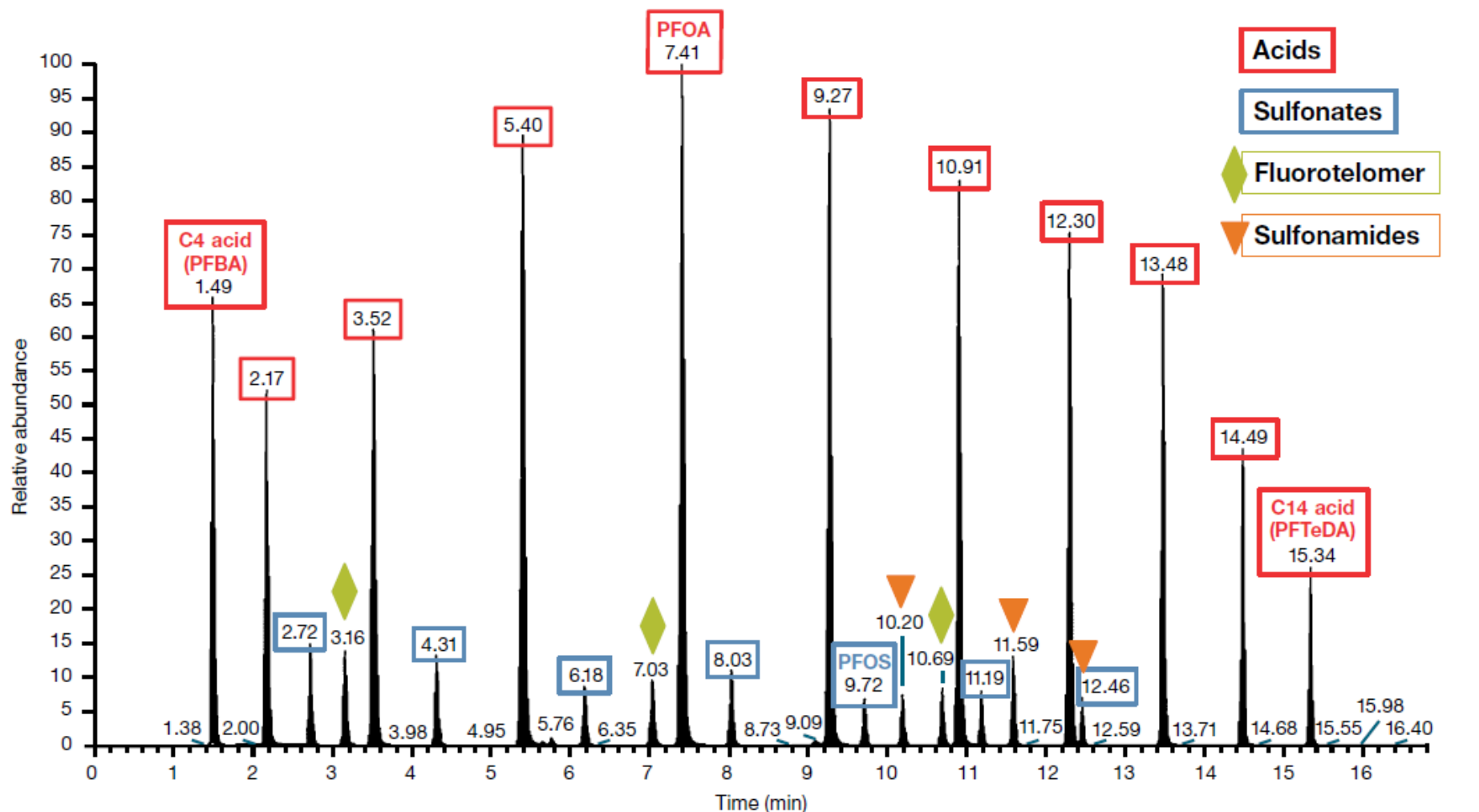
# Analytical Instrumentation

## Thermo Fisher Scientific™ Vanquish™ HPLC System with PFC Free Kit



## Thermo Fisher Scientific™ TSQ Quantis™ Mass Spectrometer

# PFAS results using ASE 350



# PFAS Recovery

Compound	Recovery (%)
<sup>13</sup> C <sub>4</sub> -PFBA	71
<sup>13</sup> C <sub>5</sub> -PFPeA	93
<sup>13</sup> C <sub>5</sub> -PFHxA	97
<sup>13</sup> C <sub>4</sub> -PFHpA	96
<sup>13</sup> C <sub>8</sub> -PFOA	94
<sup>13</sup> C <sub>9</sub> -PFNA	104
<sup>13</sup> C <sub>6</sub> -PFDA	99
<sup>13</sup> C <sub>7</sub> -PFUdA	95
<sup>13</sup> C <sub>2</sub> -PFDoA	97
<sup>13</sup> C <sub>2</sub> -PFTeDA	108

Compound	Recovery (%)
<sup>13</sup> C <sub>3</sub> -PFBS	98
<sup>13</sup> C <sub>3</sub> -PFHxS	95
<sup>13</sup> C <sub>8</sub> -PFOS	91
<sup>13</sup> C <sub>3</sub> -HFPODA	56
<sup>2</sup> H <sub>3</sub> -NMEFOSAA	93
<sup>2</sup> H <sub>3</sub> -NETFOSAA	90
<sup>13</sup> C <sub>8</sub> -FOSA	92
<sup>13</sup> C <sub>2</sub> -4:2FTS	110
<sup>13</sup> C <sub>2</sub> -6:2FTS	93
<sup>13</sup> C <sub>2</sub> -8:2FTS	98

- Excellent Recoveries between 71% and 110%
- Only exception is HFPO-DA;



# Analysis of Blanks

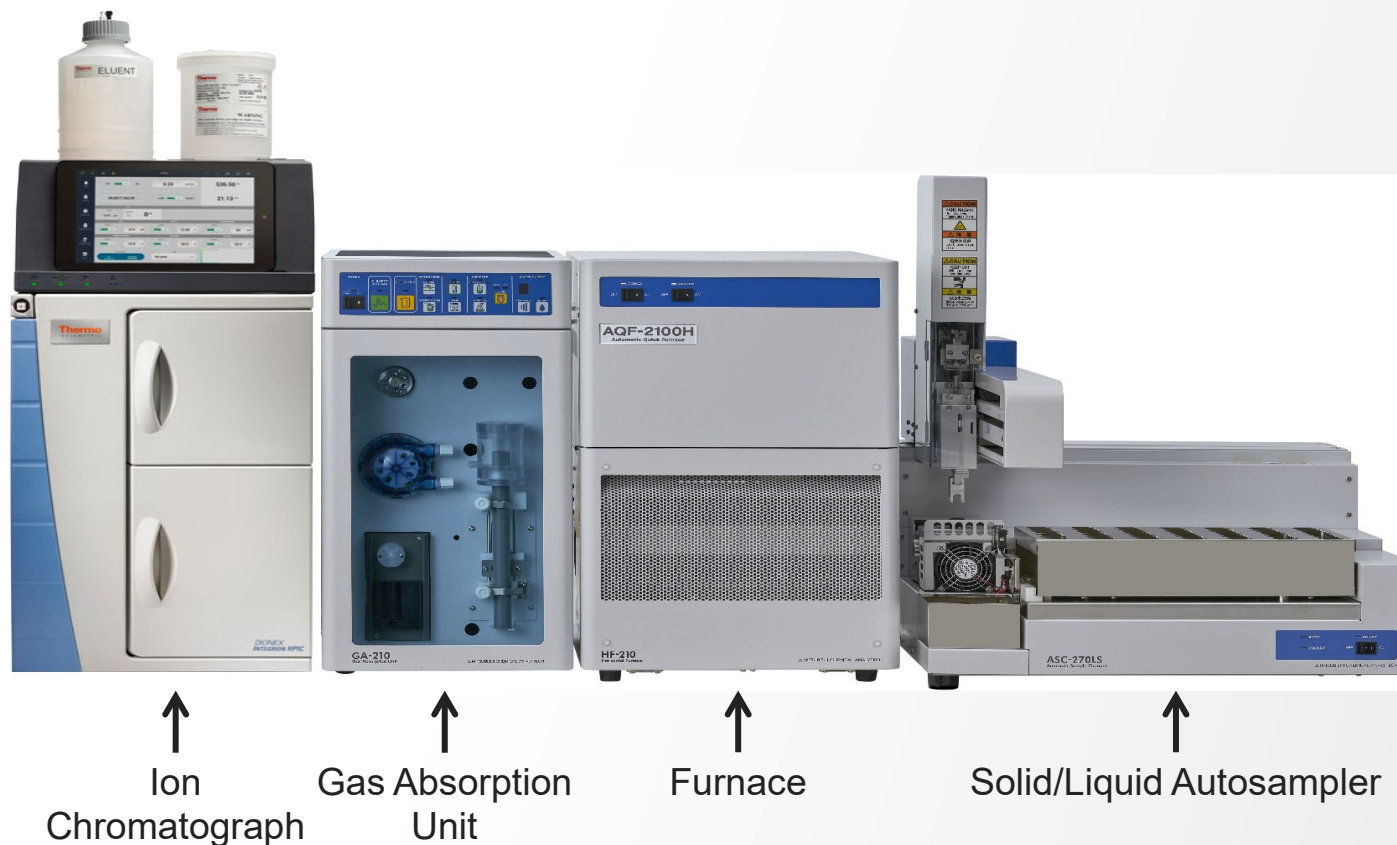
Spike level batch	1 ng/g spike		20 ng/g spike	400 ng/g spike
	ng/g	ng/g	ng/g	ng/g
PFBA	0.01	0.01	0.05	0.05
PFPeA	n.d.	n.d.	n.d.	n.d.
PFHxA	0.01	0.01	0.03	0.04
PFHpA	n.d.	n.d.	0.02	0.01
PFOA	0.01	0.01	0.04	0.04
PFNA	n.d.	n.d.	n.d.	n.d.
PFDA	n.d.	n.d.	n.d.	n.d.
PFUdA	n.d.	n.d.	n.d.	n.d.
PFDaA	n.d.	n.d.	n.d.	n.d.
PFTRDA	n.d.	n.d.	n.d.	n.d.
PFTEDA	n.d.	n.d.	n.d.	n.d.
NMEFOSAA	n.d.	n.d.	n.d.	n.d.

Spike level batch	1 ng/g spike		20 ng/g spike	400 ng/g spike
	ng/g	ng/g	ng/g	ng/g
NETFOSAA	n.d.	n.d.	n.d.	n.d.
FOSA	n.d.	n.d.	n.d.	n.d.
PFBS	n.d.	n.d.	0.01	n.d.
PFPeS	n.d.	n.d.	n.d.	n.d.
PFHxS	n.d.	n.d.	n.d.	n.d.
PFHpS	n.d.	n.d.	n.d.	n.d.
PFOS	n.d.	n.d.	n.d.	n.d.
PFNS	n.d.	n.d.	n.d.	n.d.
PFDS	n.d.	n.d.	n.d.	n.d.
4:2FTS	n.d.	n.d.	n.d.	n.d.
6:2FTS	n.d.	n.d.	n.d.	n.d.
8:2FTS	n.d.	n.d.	n.d.	n.d.

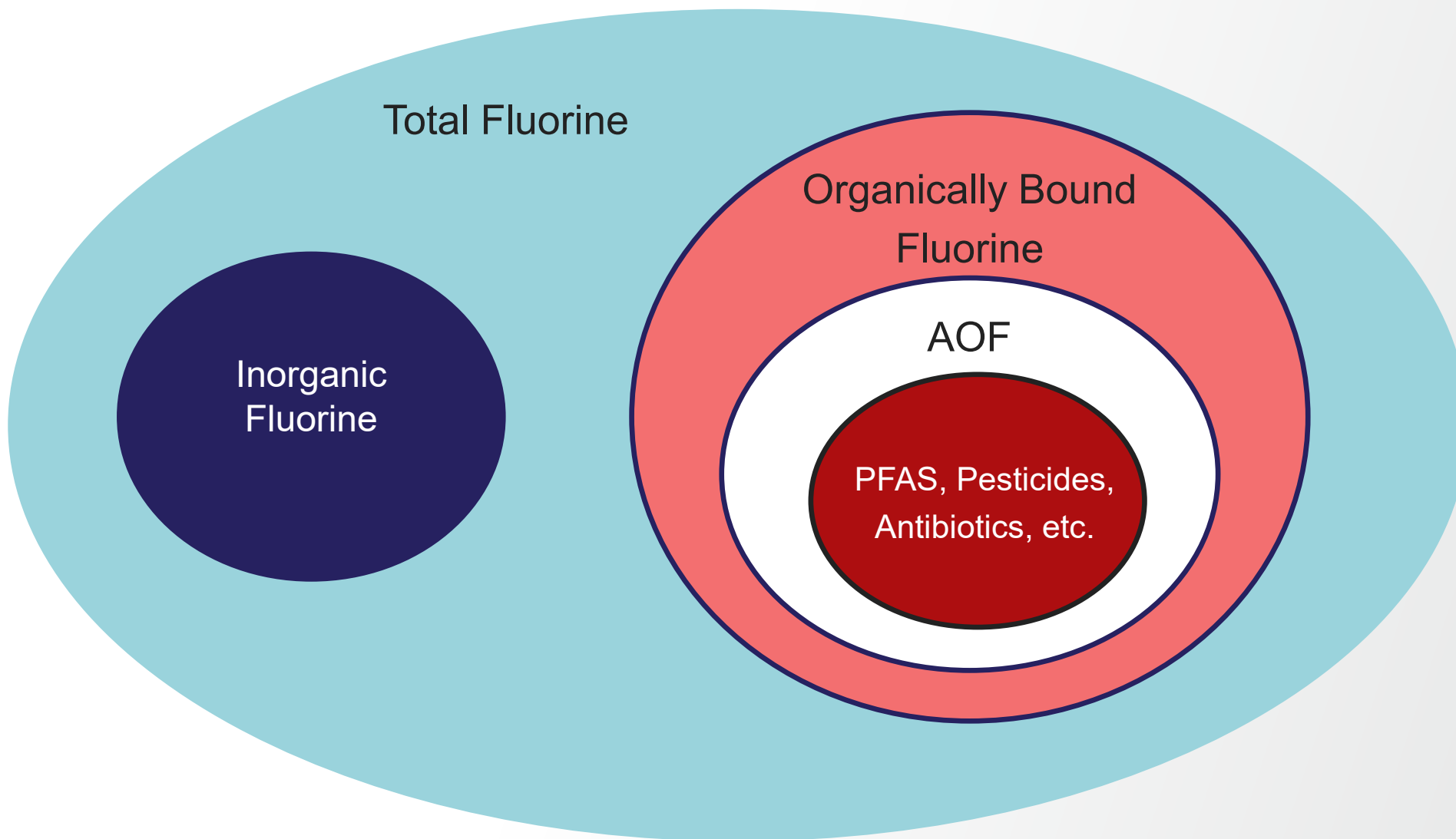
Blanks are very clean  
Very little background PFAS

# Combustion IC- Complement to Other PFAS Methods

- The AOF-CIC-method, as a complement to existing approaches, provides an easy-to-use and economically attractive way to generate a cumulative parameter, and can help to optimize the utilization of the more expensive LC-MS/MS and GC-MS/MS instrumentation by selecting and only analyzing “suspicious” samples.



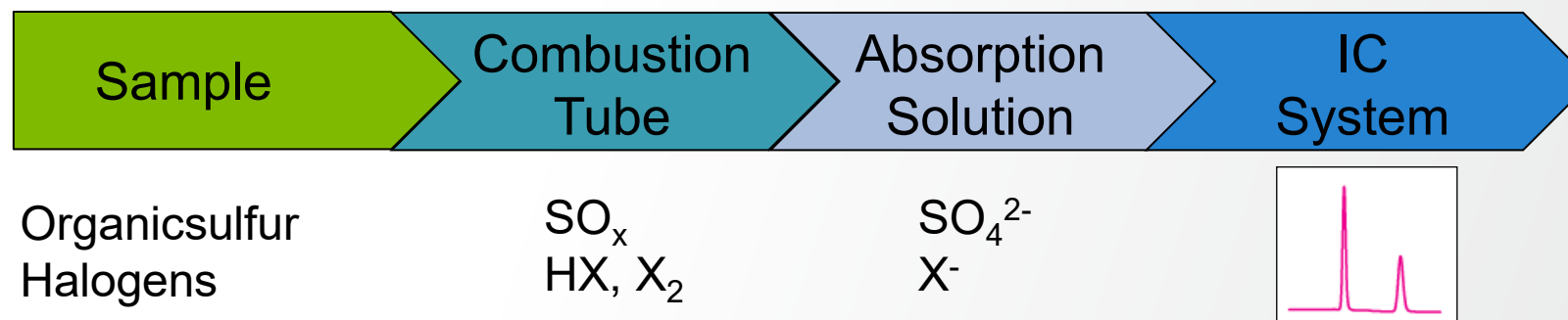
# Distribution of Fluorine in the Environment



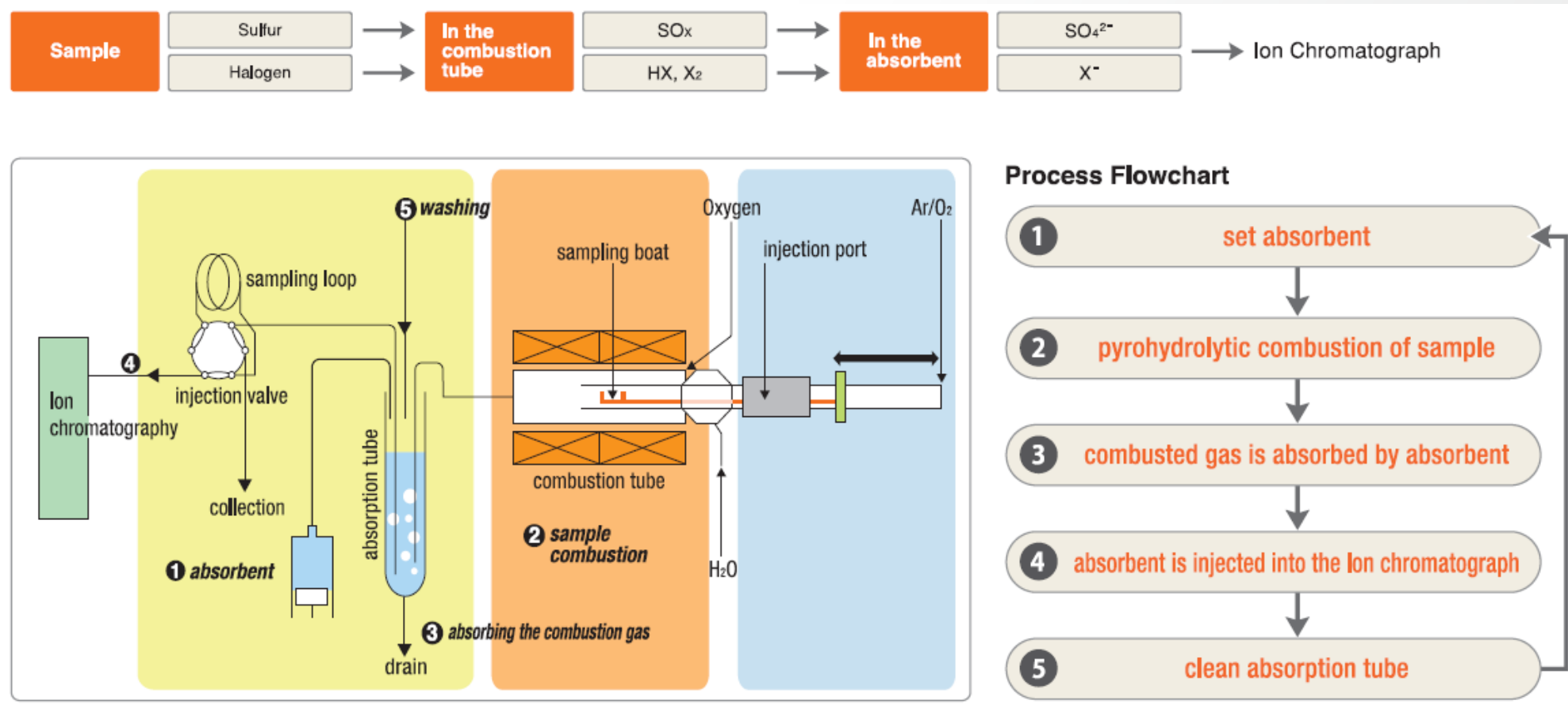
# Analytical method for the determination of AOF

## What is CIC?

- Combination of Ion Chromatography (IC) with an automated sample preparation step (Combustion)
  - Combustion Ion Chromatography (CIC)
- Total S, F, Cl, Br in Liquid, Solid and Gas Samples
- Environmental, Polymers, Raw Materials, Oil, Fuel, Coal
- Standard Methods: ASTM, DIN, ISO, Others



# CIC theory

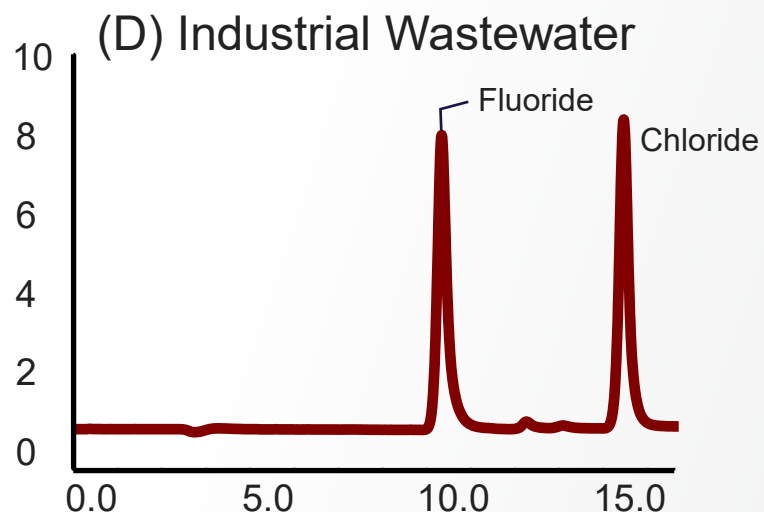
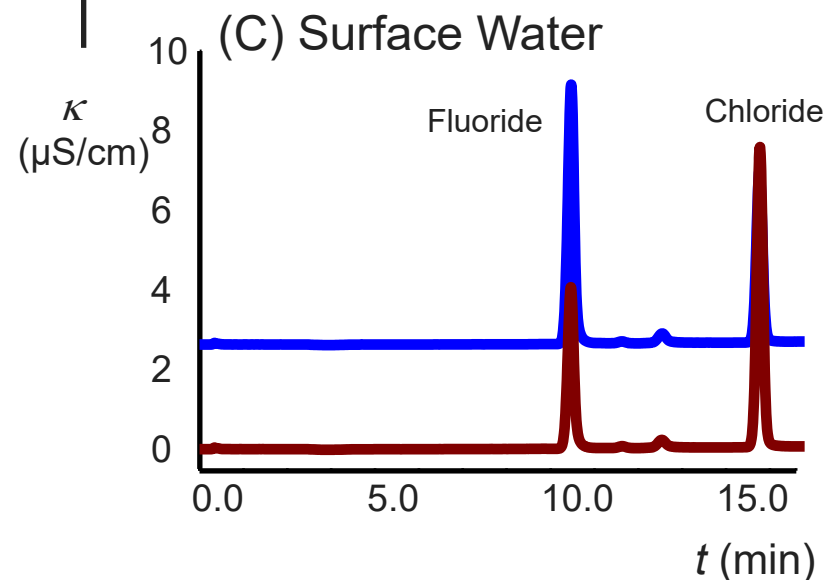
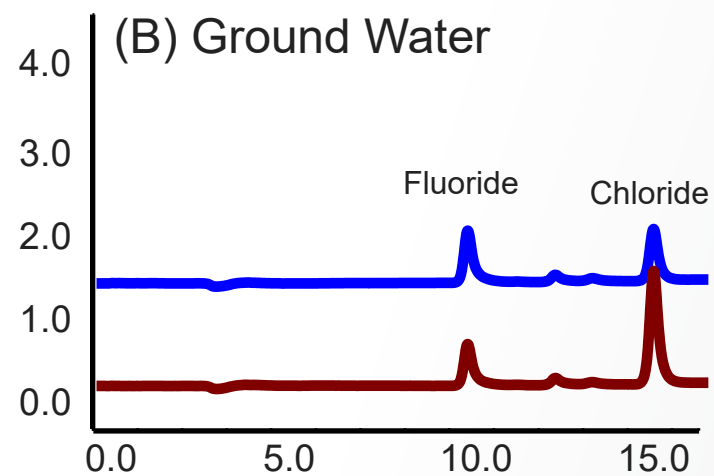
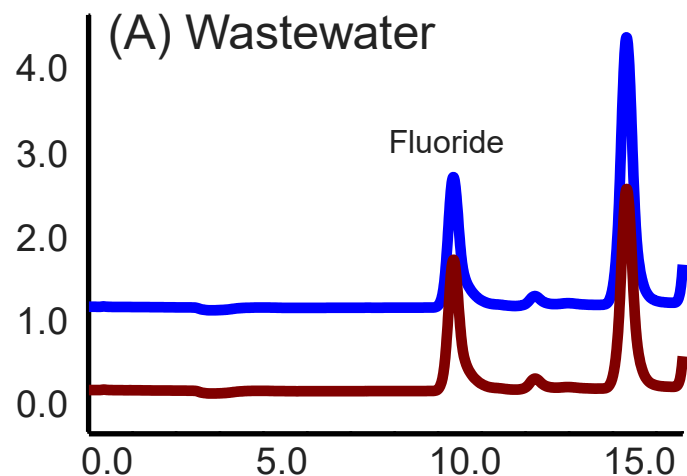


Schematic of a CIC system





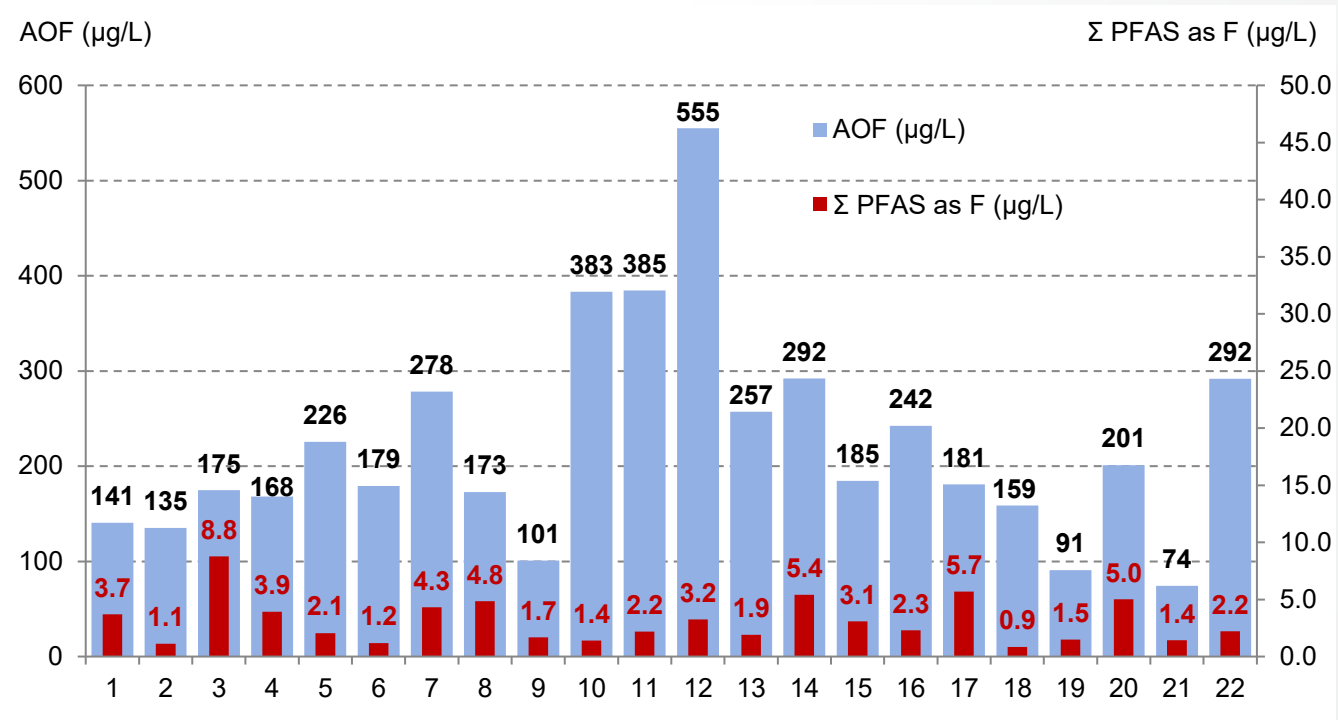
# Non-Targeted Complementary Determination of PFAS in Aqueous Samples



Columns	Dionex IonPac AG20 (2 × 50 mm) and Dionex IonPac AS20 (2 × 250 mm)
Eluent source	KOH Eluent Generator
KOH-Gradient	KOH-Gradient
Run time	44 min
Flow rate	0.25 mL/min
Injection volume	250 μL
Temperature	30 °C (column temperature) 35 °C (detector cell temperature)
Backpressure	~ 2200 psi (100 psi = 0.6894 MPa)
Suppressed conductivity detection	Dionex AERS (2 mm), timed constant current mode
Background conductance	< 0.5 μS/cm

# AOF in Aqueous Environmental Samples

## AOF in Industrial wastewater samples



### AOF and total F-PFAS in Industrial Wastewater over one year (n=22, 2016-2017)

The individual AOF values and the sum of the PFAS of each sample, calculated as fluorine ( $\Sigma$  of PFAS as F) are shown.

# AOF in Aqueous Environmental Samples

## AOF in and targeted Analysis (LC-MS/MS)

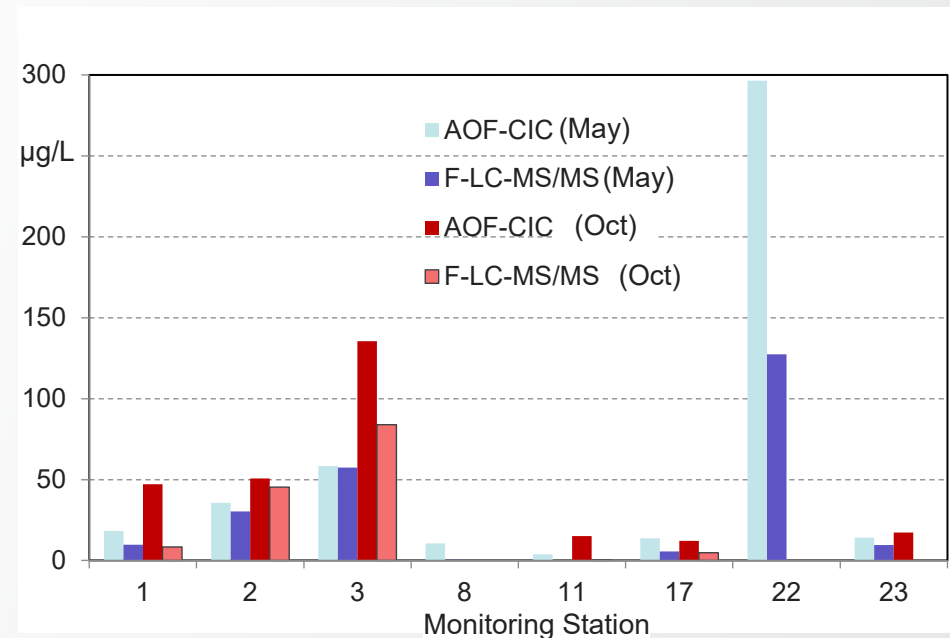
- Matrix: PFAS contaminated surfacewater
- 23 monitoring stations (May and October 2015)
- 14 individual PFAS targeted (*DIN 38407-42, 2011*)

AOF ( $\mu\text{g/L}$ ): < 2-300  $\mu\text{g/L}$

F-PFAS: 0.01-130  $\mu\text{g/L}$

Samples with AOF Results above 10  $\mu\text{g/L}$

In general, 50% of the AOF values were reflected by the targeted F-PFAS results.



Comparison AOF and F-PFAS. Measuring Stations with AOF > 10  $\mu\text{g/L}$

# Customer Application Note: AOF by combustion IC

thermoscientific

CUSTOMER APPLICATION NOTE 73481

## AOF by combustion IC – non-targeted complementary determination of PFAS in aqueous samples

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Keywords: AOX, combustion, gradient elution, ion chromatography, parametric value, per- and polyfluorinated organic substances, per- and polyfluoroalkyl substances, PFIC, Dionex IonPac AS20, sum parameter, suppressed conductivity

### Goal

To develop an automated method to determine a range of perfluorinated alkyl substances (PFAS) by combustion IC within environmentally relevant matrices and compare the results with existing highly specific methods based on liquid chromatography mass spectrometry (LC-MS/MS)

### Introduction

PFAS are human-made chemicals, which have been manufactured since the 1940s. The most well-known PFAS compounds, perfluorooctanoic acid (PFOA) and



perfluorooctanesulfonic acid (PFOS), have been extensively studied for their chemical properties and toxicological effects. PFAS are used in a wide variety of consumer products, such as nonstick cookware, food containers, stain- and water-repellent fabrics, polishes, waxes, paints, and cleaning products. Other sources of PFAS are firefighting foams, which are primary groundwater contaminants at airports and military bases. Further environmental exposure to PFAS comes from industrial production facilities (e.g., chrome plating, electronics, manufacturing, or oil recovery). Living organisms, including plants, animals, and humans, can accumulate PFAS compounds in their tissue, which can build up over time and impact their health.<sup>1,2</sup>

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and international standardization and have developed methods specifically for the determination of PFAS in aqueous samples.<sup>3-5</sup> These are mostly based on solid-phase extraction (SPE) followed by GC-MS detection for only a select number

of environmentally relevant fluoroorganic precursors that cannot yet be analyzed easily.<sup>6,7</sup> There is a need to restrict the substances into the environment and analytical methods for their detection. Authorities have established regulatory limits for various PFAS, chlorinated and brominated organically bound halogens (AOB) and their precursors, and fluorinated organics, for example, are not accounted for by the methods. As a result, there is a growing analytical workflow that would allow for the determination of as many PFAS as possible.

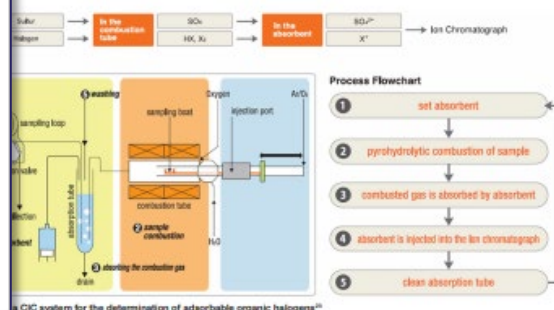
Ion chromatography (IC) cannot directly determine PFAS. Automated combustion ion chromatography (CIC), however, is used to determine PFAS. In CIC, the sample is oxidized by O<sub>2</sub> at elevated temperatures. As a result, pyrolysis takes place at temperatures up to 1000 °C. Sulfur-containing compounds are oxidized to sulfur dioxide (SO<sub>2</sub>), and halogen-containing

substances form hydrogen halides (HX) or elemental halogens (X<sub>2</sub>). Loss of hydrogen fluoride through the reaction with the oven liner (quartz glass or ceramic) is avoided by continuously adding water during combustion (hydrolysis). The volatile pyrolysis products are then absorbed into an aqueous solution and subsequently detected as sulfates and halides (e.g., fluoride) by IC.<sup>10-12</sup>

In contrast to the conventional titrimetric AOX methods, where only the sum of organic halogens is measured, the CIC approach provides halogen speciation as well as additional information about the adsorbable organic fluorine-containing compounds.

This method can be considered a combination of several existing methods for organic-halogen measurement.<sup>10-12</sup> Halogen-containing organics from aqueous samples are adsorbed on activated carbon. The activated carbon is washed to remove inorganic halides. Sample and adsorbent are combusted, and the volatile oxidation products are absorbed in deionized (DI) water. This solution is subsequently analyzed by IC. A corresponding DIN standard using CIC is under development.<sup>13</sup>

This work focuses on PFAS, and the adsorbable organically bound fluorine (AOF). The use of this technique is well-documented for the determination of other adsorbable organic halogen-containing components (AOX).<sup>12,13,14</sup>



compounds or compound classes. The model compounds served as model compounds were DIN 38407-42<sup>2</sup>, and other PFAS compounds, as well as firefighting foam products. The chemical information and analytical data are summarized in

Table 3. Recovery ranged from 16% to 121%; the activated carbon did not retain the perfluorinated C1 and C3 carboxylic and sulfonic acids. The firefighting foam products showed recoveries in a range between 64% and 121%. The proportion of information provided to industrial products, their explain the high recovery

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Standard substance	Abbreviation	CAS No.	n	AOF (%)
perfluoroacetic acid	PFA	76-05-1	3	<2
perfluoropropionic acid	PFPA	422-54-0	3	<2
perfluorobutanoic acid	PFBA	375-22-4	3	91
perfluoropentanoic acid	PFPA	2705-90-3	3	51
perfluorohexanoic acid	PFHxA	307-34-4	3	81
perfluoroheptanoic acid	PFHpA	375-85-9	3	81
perfluorooctanoic acid	PFOPA	335-87-1	5	61
perfluorononanoic acid	PFNA	375-95-1	3	41
perfluorodecanoic acid	PFDA	335-79-2	3	41
perfluorododecanoic acid	PFDDA	1460-13-6	3	<2
perfluorotetradecanoic acid	PFTDA	29420-49-3	6	11
perfluorohexanesulfonic acid	PFHxS	350-48-4	3	31
perfluorooctanesulfonic acid	PFOS	95773-42-3	2	61
perfluorodecane sulfonic acid	PFDS	27619-97-3	5	81
Mixture of PFOA (C4-C10) and PFAS (C4, C8, C16)	Chrom AS	n.a.	4	21
perfluorooctylmethanesulfonate	PFOMeS	n.a.	2	91
perfluorooctylsulfonate	PFOS	n.a.	2	81
2,3,3,3-tetrafluoro-1,1,2,2,3,3,3-heptafluoropropanoic acid	PFPO-DA	n.a.	2	11
perfluoro-1-butanesulfonyl fluoride	PFBSF	375-72-4	2	11
perfluoro-1-octanesulfonyl fluoride	POSF	307-35-7	2	21
perfluorobenzoic acid	4-FBA	CH <sub>2</sub> PF <sub>2</sub> O <sub>2</sub>	3	31
Product A	n.a.	n.a.	3	11
Product A1	n.a.	n.a.	3	71
Product A2	n.a.	n.a.	2	41
Product B	n.a.	n.a.	2	81
Product B1	n.a.	n.a.	2	81

### Recoveries of PFBS and 4-fluorobenzoic acid in environmental water samples

PFBS was added to seven municipal wastewater and eight surface water samples to a final concentration of 10 µg/L AOF to test the recoveries of organic fluorinated compounds in environmental matrices. The wastewater matrix showed recoveries from 85% to 102%, while the surface water samples had AOF recoveries between 92% and 109%. The analytical recovery for 4-fluorobenzoic acid (4-FBA) in the municipal wastewater samples at a spiked concentration of 10 µg/L AOF ranged between 82% and 127%. Wilach et al. reported mean AOF recoveries from 51% to 100% for selected non-PFAS compounds (fluorinated pharmaceuticals and herbicides) in surface, ground, waste, and drinking water.<sup>20</sup>

Figure 4 shows a selection of example chromatograms obtained after combusting samples of different types and origins. The same analytical column setup was used throughout the two years of this study.

Table 4. Recovery data for PFBS and 4-FBA

Sample	Surface water		Wastewater	
	PFBS recovery	4-FBA recovery	PFBS recovery	4-FBA recovery
1	94	92	102	92
2	105	91	91	83
3	99	86	86	82
4	92	89	n.d.	n.d.
5	109	93	n.d.	n.d.
6	98	85	83	83
7	98	94	127	127
8	99	94	102	102

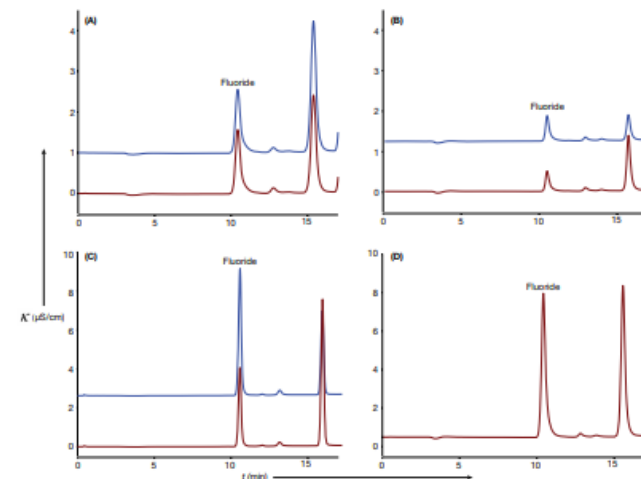


Figure 4. Selection of representative chromatograms obtained after adsorption on activated carbon and combustion. (A) municipal wastewater, (B) groundwater, (C) surface water, (D) industrial wastewater (diluted 1 to 10)

# Thank you

