Sample Preparation Solutions for PFAS Analysis in Environmental Samples

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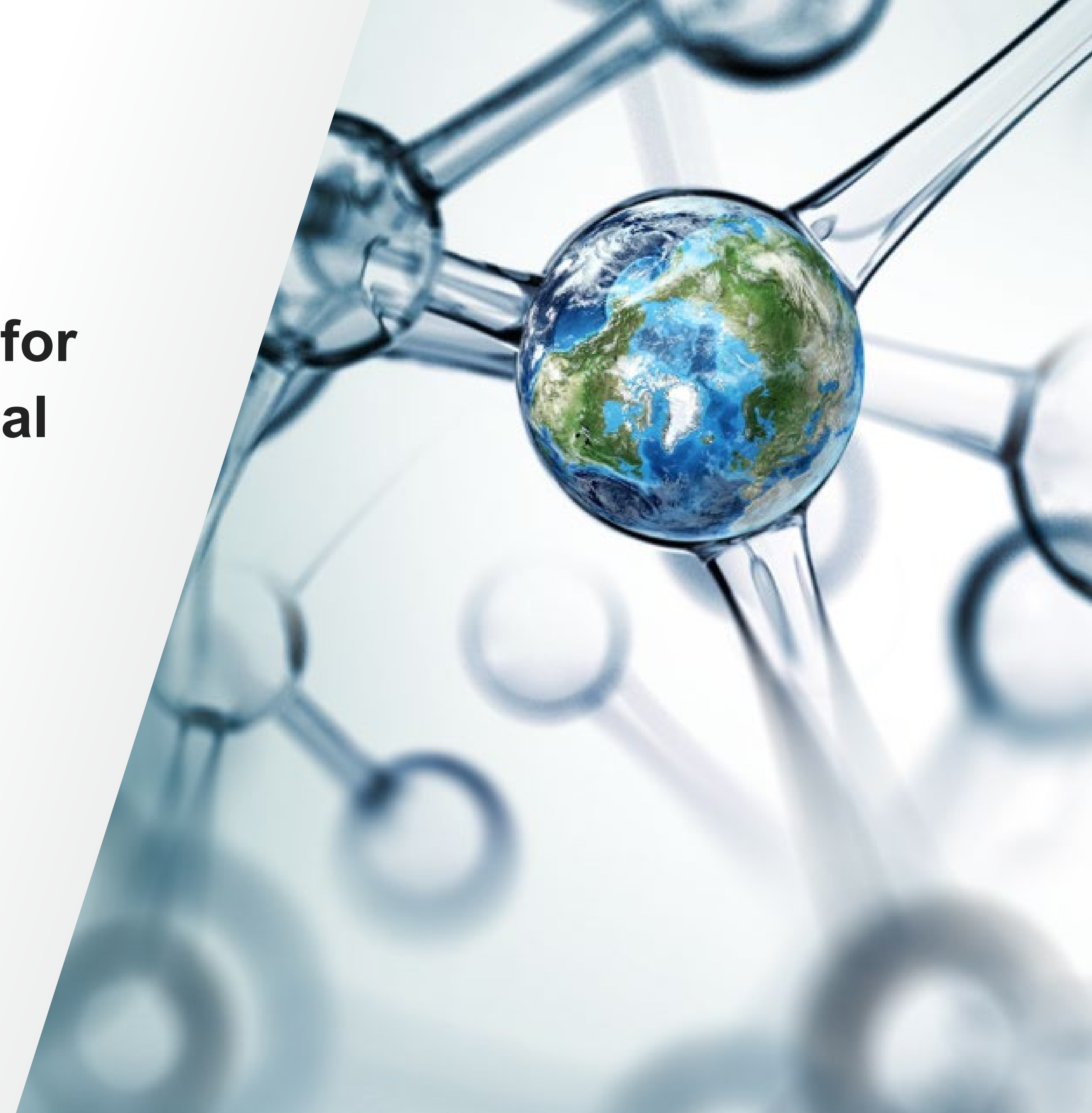


The world leader in serving science

Automated PFAS Workflows

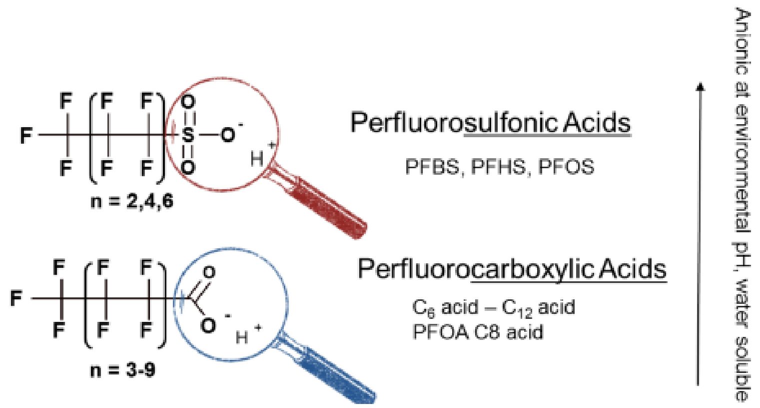
Outline

- 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 by direct aqueous injection
  - 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**lkyl **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

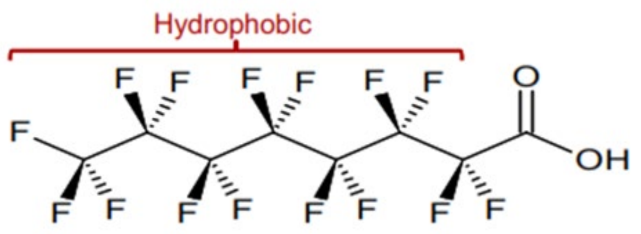


Perfluorosulfonic Acids

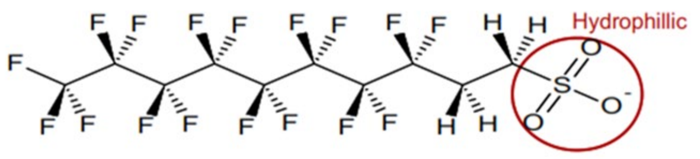
PFBS, PFHS, PFOS

Perfluorocarboxylic Acids

C_6 acid – C_{12} acid
PFOA C8 acid



Perfluorooctanoic acid
- PFOA
- Teflon®



8:2 Fluorotelomer sulfonate
- 8:2 FTS

Individual PFAS molecule is determined by chain length and functional group

Overview of Thermo Fisher Scientific PFAS Workflows

ThermoFisher
SCIENTIFIC

Soil

Water

Unknown profiling

Targeted

Unknown profiling

Screening

Extraction and analysis of poly- and perfluoroalkyl substances (PFAS) from soil

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

EPA Method 537.1 using automated SPE followed by LC-Q Exactive Orbitrap MS

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

ASE 350

ASE 350

SolEx WAX

AutoTrace 280 PFAS

AutoTrace 280 PFAS playbook

Accucore RP-MS

Acclaim 120 C18

Vanquish Duo

Altis

Fortis

SolEx WAX SPE Cartridges

AutoTrace 280, DIA, and Equan 850

Accucore RP-MS or Acclaim 120 C18 Column

Vanquish Flex/Core HPLC + PFAS-free kit

TSQ Fortis, TSQ Altis

Chromeleon, Trace Finder, Compound Discoverer

Orbitrap Exploris 120, 240

Orbitrap Exploris 120, 240

Triplus equan 850 autosampler Brochure

+

Combustion IC

PFAS by CIC Workflow

Orbitrap

Chromeleon

TraceFinder

Compound Discoverer

PFAS Solutions

Setting a new horizon for PFAS workflow applications brochure

www.thermofisher.com/pfas-testing

Legend

Webpage

Brochure

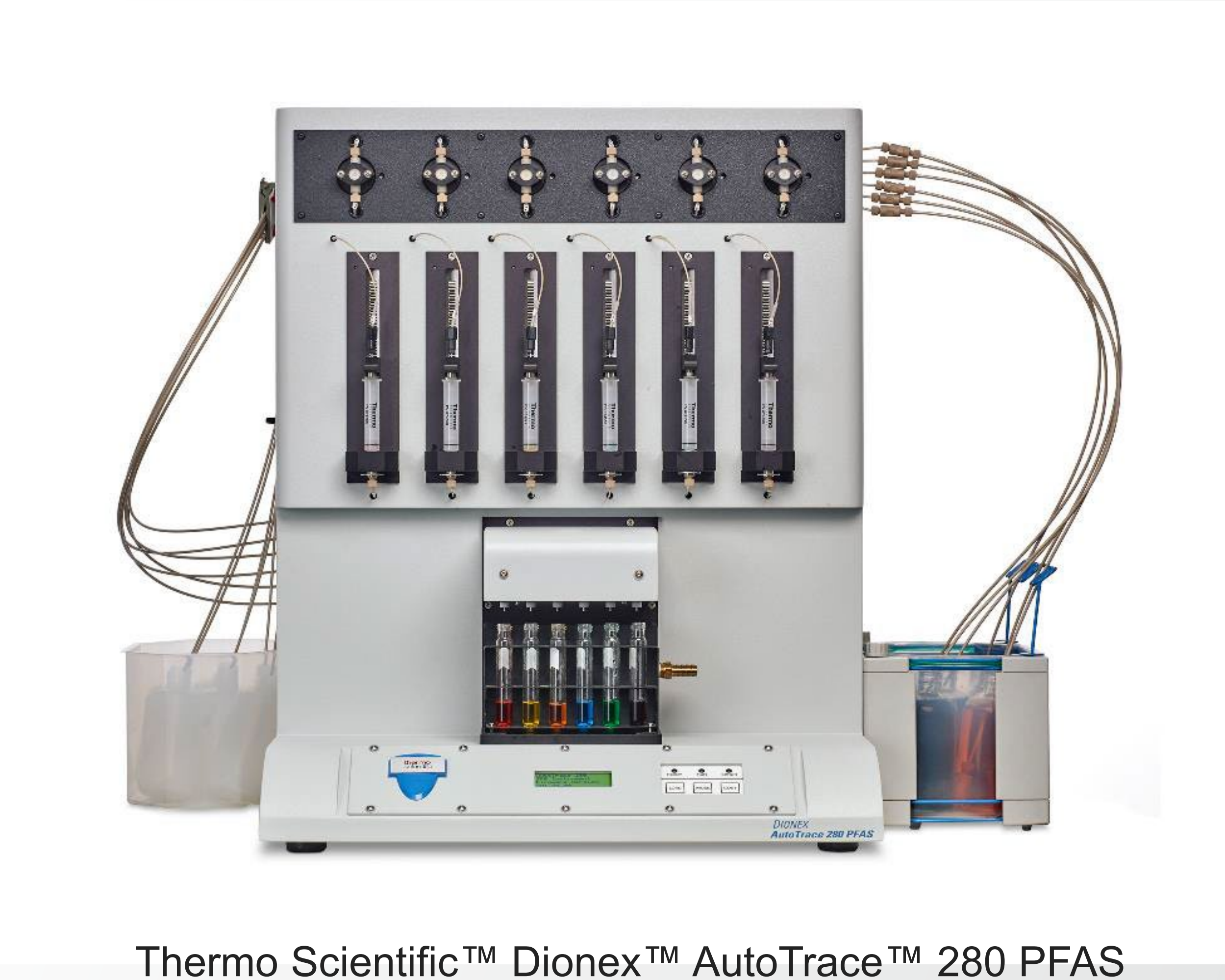
App Note

Playbook

Sample Prep Devices for Large Sample Volumes

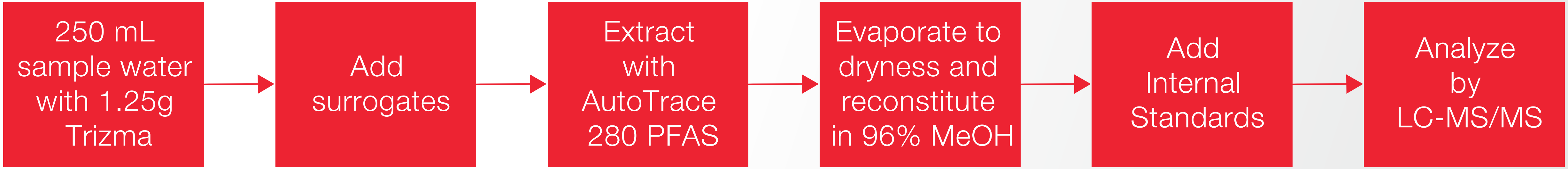
Sample Extraction and Clean up

Vacuum Manifold



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

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



250 mL sample water with 1.25g Trizma

Add surrogates

Extract with AutoTrace 280 PFAS

Evaporate to dryness and reconstitute in 96% MeOH

Add Internal Standards

Analyze by LC-MS/MS

ThermoFisher
SCIENTIFIC

Solid Phase Extraction Method

Keeping cartridge sorbent wet is very important

Conditioning

15 mL Methanol then 18 mL H_2O.
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_2O
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

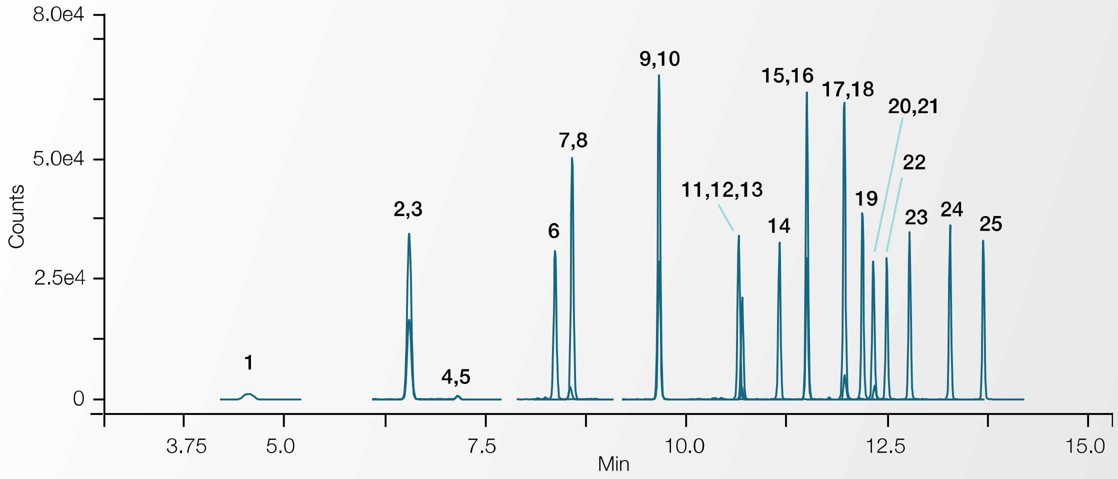
- AutoTrace 280 PFAS
  - Pumps are set at a constant flow
  - Ensures cartridges do not dry on critical steps
  - Precise consistency run to run
  - Push “start” and have a cup of coffee

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



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

All recoveries and precision are well with in the method requirements

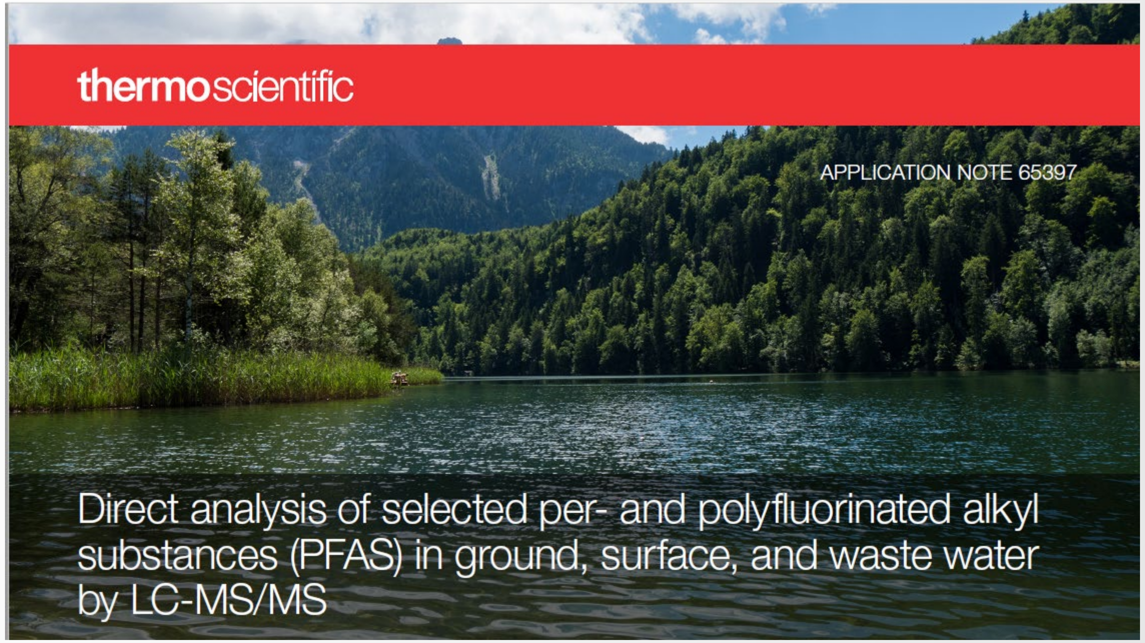
- Recovery must be 70 – 130%
- RSD < 20%

Direct injection sample analysis for PFAS

Non-potable groundwater, surface water, and wastewater testing protocols SW-846 Method 8327

- Direct injection of samples is easy and requires only minimal sample handling
- Reduces manual labor and increases efficiency
- Minimizes risk of sample contamination during a pre-concentration step
- *Is a requirement in several published methods*

- Note: This method requires greater LC-MS/MS sensitivity due to no sample preconcentration



thermo scientific

APPLICATION NOTE 65397

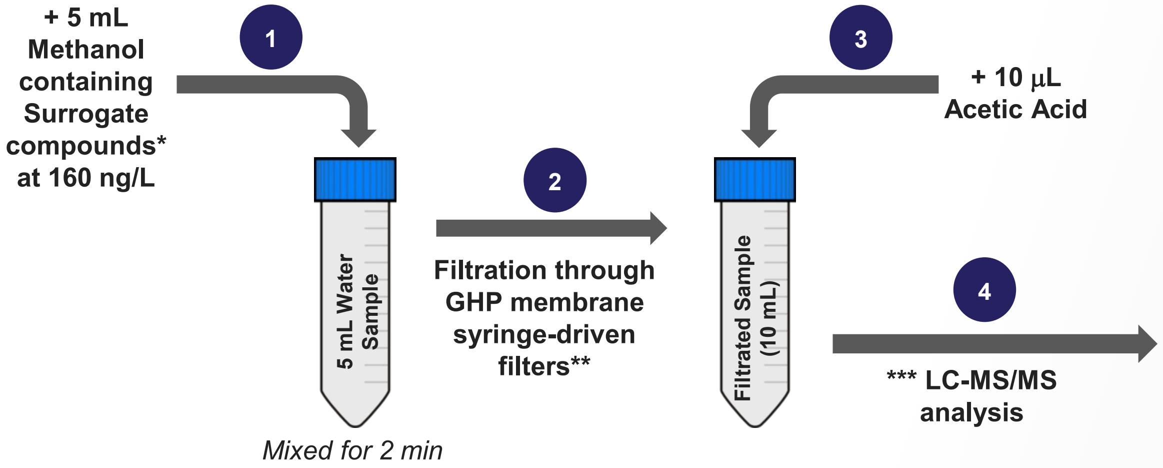
Direct analysis of selected per- and polyfluorinated alkyl substances (PFAS) in ground, surface, and waste water by LC-MS/MS

Application Note 65397

Direct Analysis of Selected Per- and Polyfluorinated Alkyl Substances (PFAS) in Ground, Surface, and Waste Water by LC-MS/MS (thermofisher.com)

Sample processing workflow – US EPA Method 8327

Preparation for direct injection analysis



* All standards were obtained form Wellington Laboratories

**Acrodisc GxF/0.2 µm GHP membrane syringe-driven filters were washed twice with LC-MS grade methanol (2x 10 mL) and acetonitrile (2x 10 mL)

*** Silanized-amber glass autosampler vials sealed with polypropylene caps were free of contaminants and interferences

Thermo Scientific Vanquish Flex Binary UHPLC system fitted with PFC-free kit and interfaced with Thermo Scientific **TSQ Altis Plus** mass spectrometer

An Alternate Liquid Chromatography Set-Up for Large Volume Injections

Vanquish Core HPLC system setup

Custom Injection Program

- Sample loop: 1000 µL
- Sandwich injection
- In needle mixing

Strong Solvent Loop

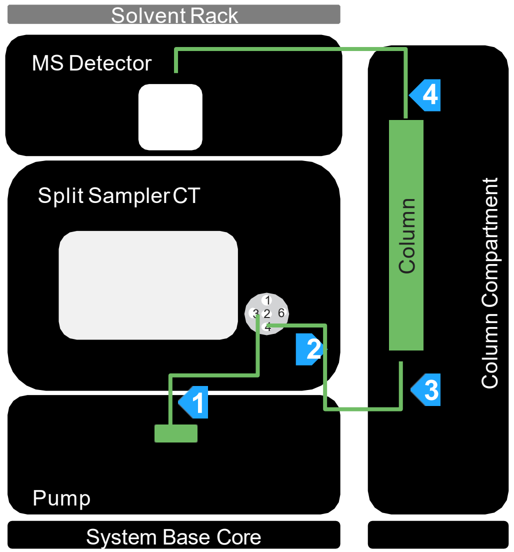
- Volume: 46.2 µL

Capillary

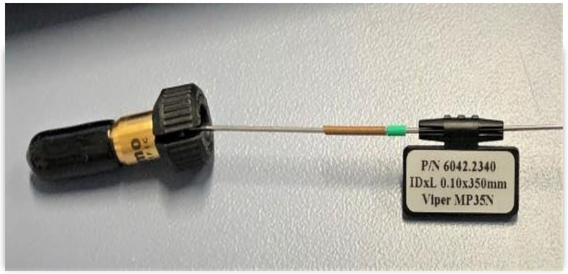
- Sampler-column
- Viper MP35N

Delay Column

- Accucore™ aQ, 3.0 x 50 mm, 2.6 µm)

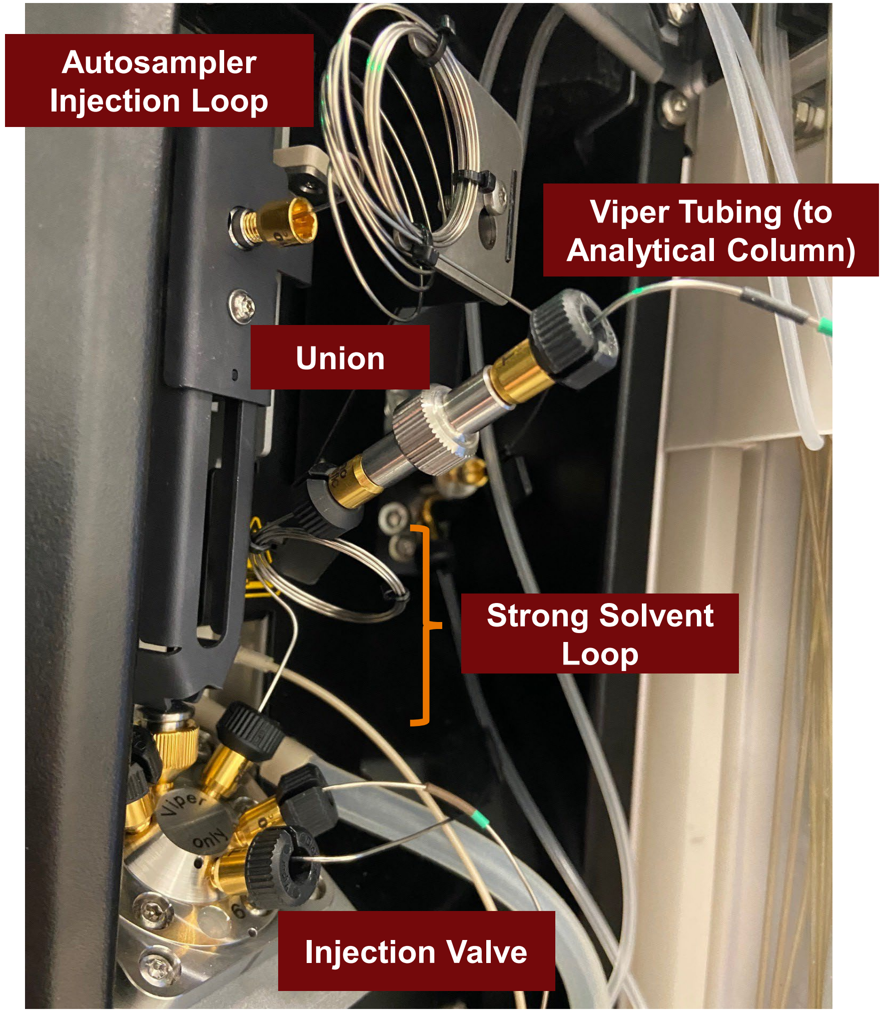


#	Connection between	Description
1	Pump Out – Port 1	0.18 x 350mm, SST, P/N 6040.2375
2	Port 2 – Viper Union	Strong Solvent Loop, SST, P/N 6036.2200
3	Viper Union – Column Inlet	0.10 x 350 mm, MP35N, P/N 6042.2340
4	Column Outlet - Detector	0.10 x 450 mm, MP35N, P/N 6042.2340

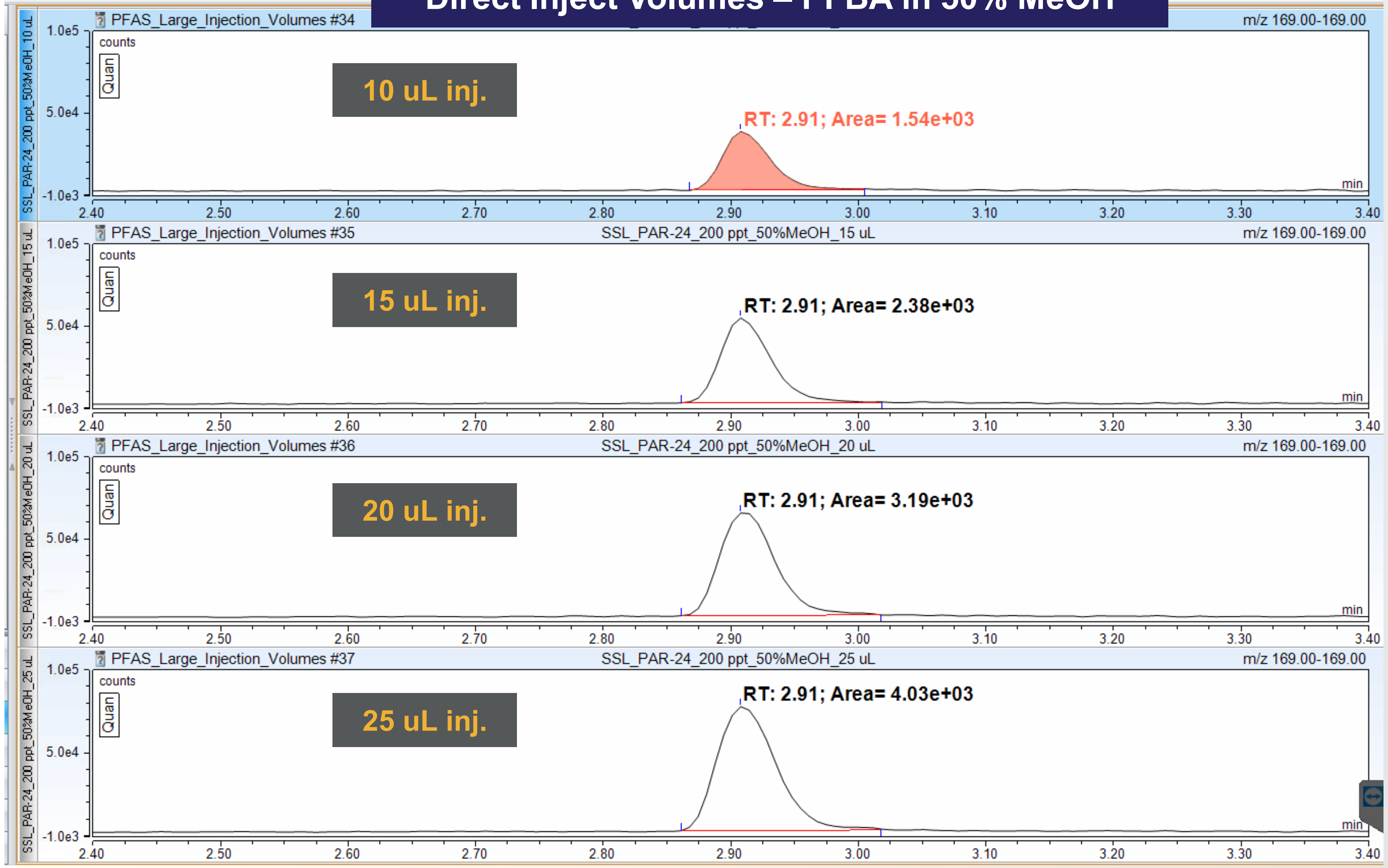


Experimental – Liquid Chromatography

Strong Solvent Loop added in autosampler: Large volume direct injections



Direct Inject Volumes – PFBA in 50% MeOH

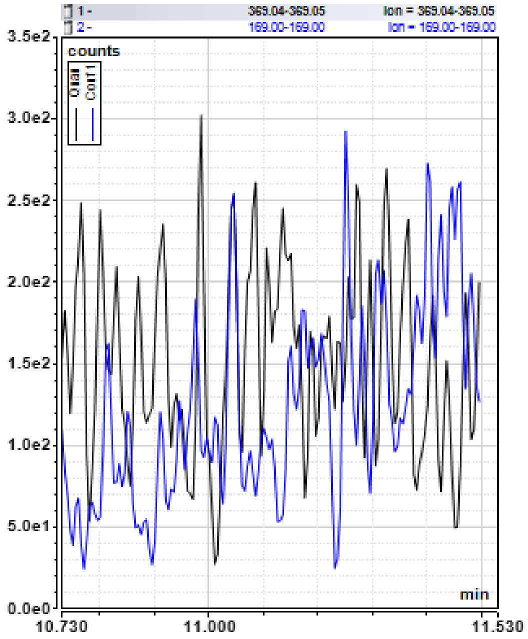


Peak shape for PFBA is maintained up to 25 uL inj. of 50% MeOH solution

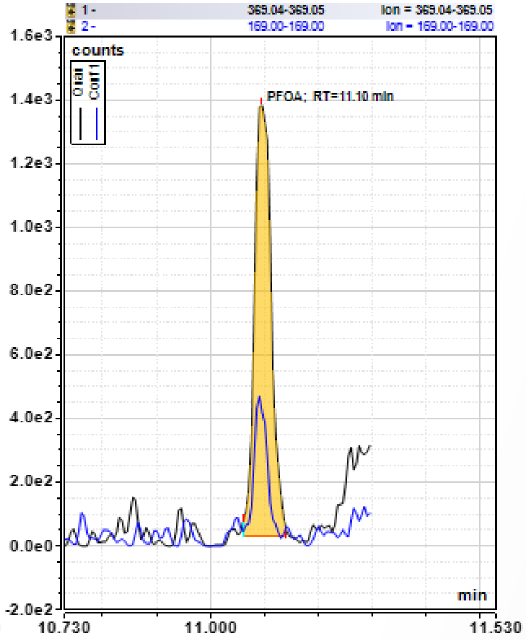
Low-level quantitation using the direct inject method

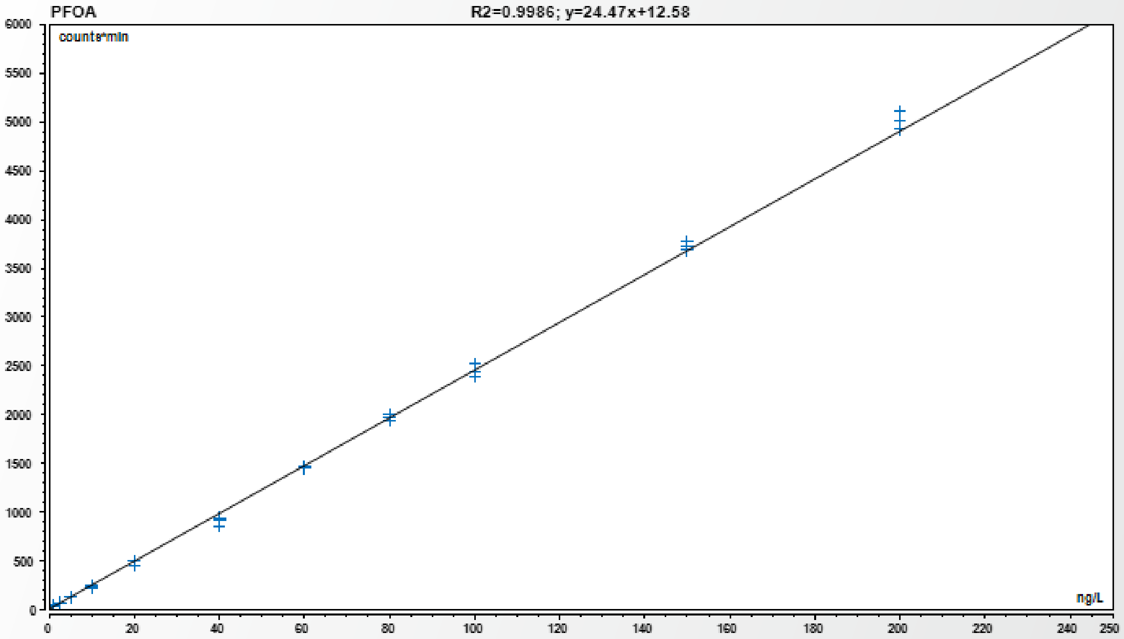
TSQ Altis MS results for PFOA analysis in reagent water following EPA Method 8327

Reagent blank



1 ppt*
25 fg on column





*2-fold dilution was not taken into consideration

LLOQ = 1 ppt on TSQ Altis Plus MS, 5-times lower than the EPA 8327 reporting limit

TriPlus RSH EQuan 850 Autosampler- Online Solution

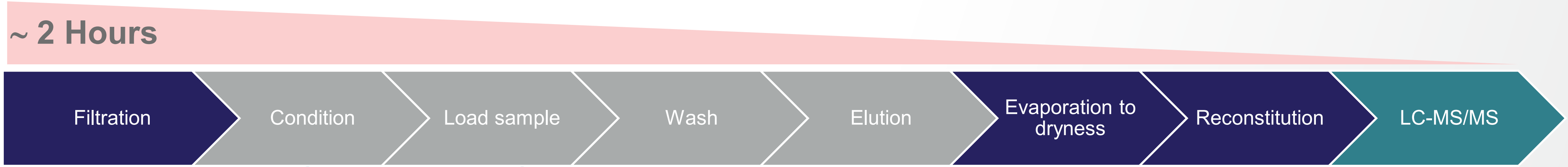
Automated high-throughput LC-MS solution for the analysis of contaminants in environmental water, drinking water and beverages at low ng/L levels

- **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 µL

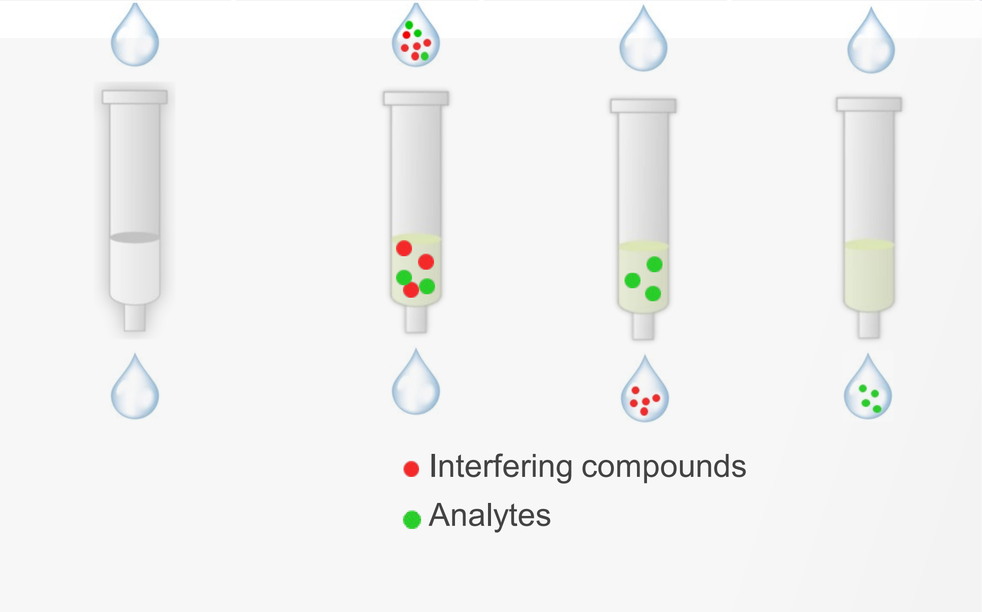
Find out more at **thermofisher.com/EQuan850**

Offline *vs.* Online Sample preparation

Conventional Method: Offline Sample Preparation

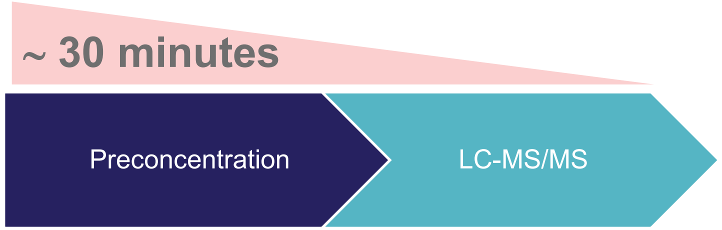

~ 2 Hours

Filtration → Condition → Load sample → Wash → Elution → Evaporation to dryness → Reconstitution → LC-MS/MS


🔴 Interfering compounds

🟢 Analytes

TriPlus RSH EQuan 850: Online Sample Preparation

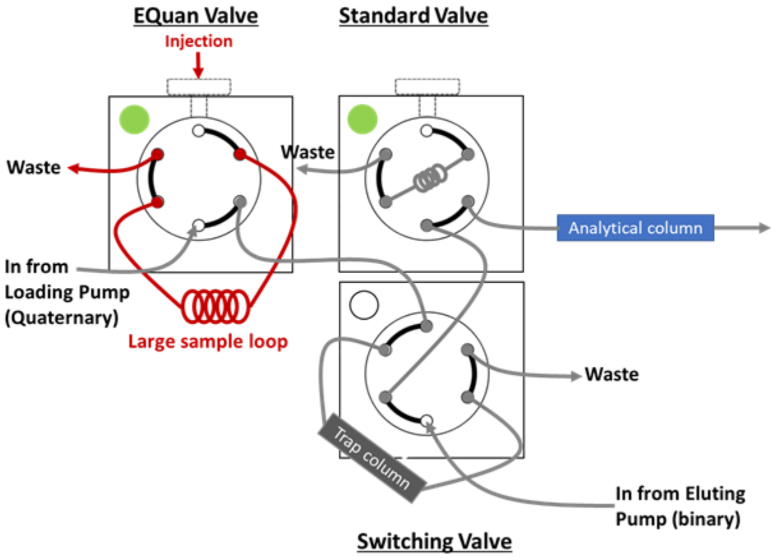

~ 30 minutes

Preconcentration → LC-MS/MS

◀ Analysis time is reduced from hours to minutes

Online Sample Pre-Concentration: How it Works

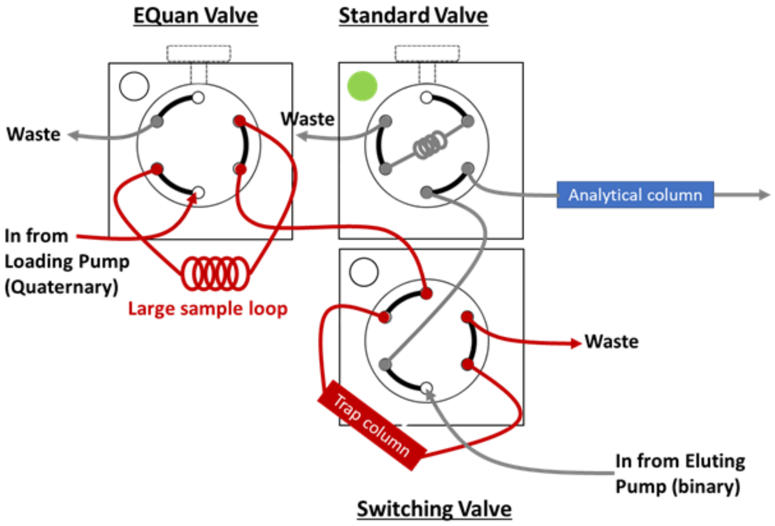
EQuan Injection Mode: Red Flow Path



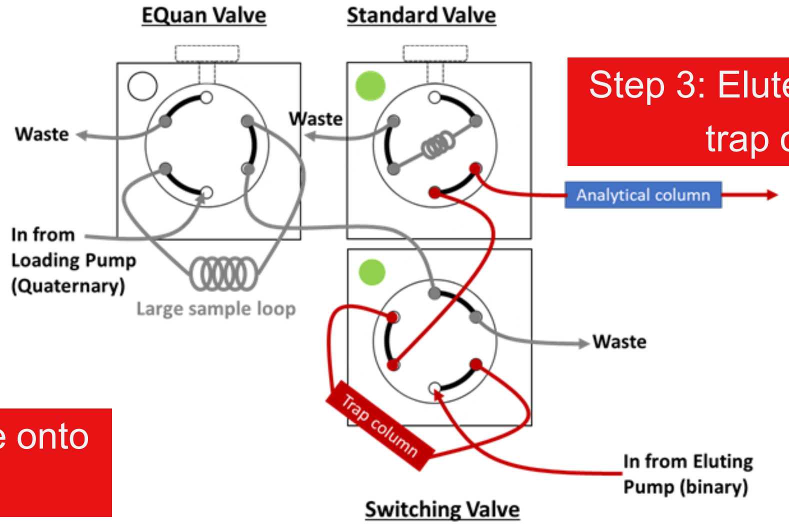
Step 1: Inject and load the sample into large sample loop

up to 20 mL

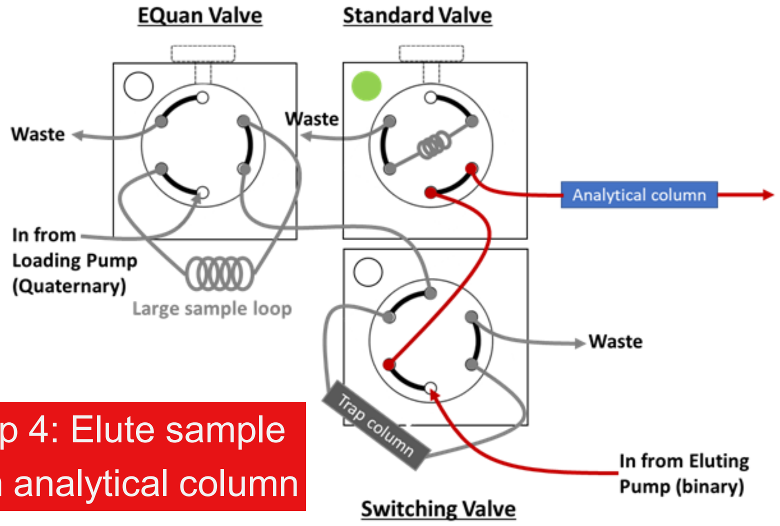
Step 2: Load sample onto trap column



Step 3: Elute sample from trap column



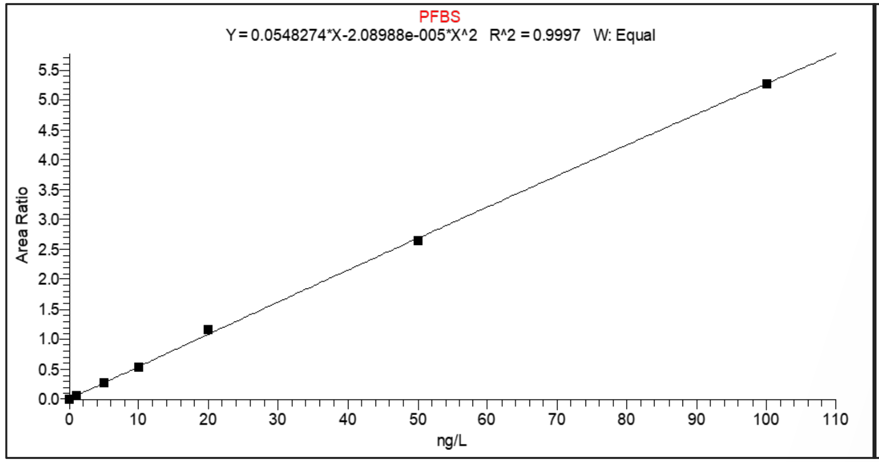
Step 4: Elute sample from analytical column

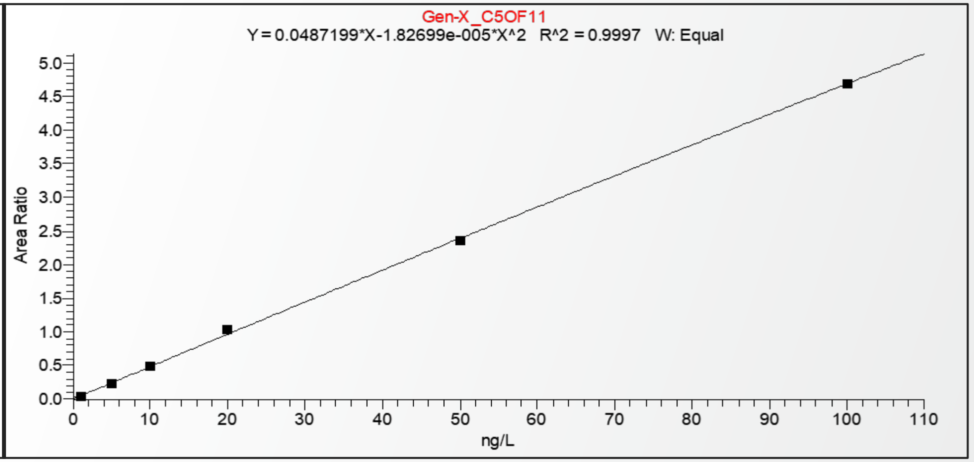


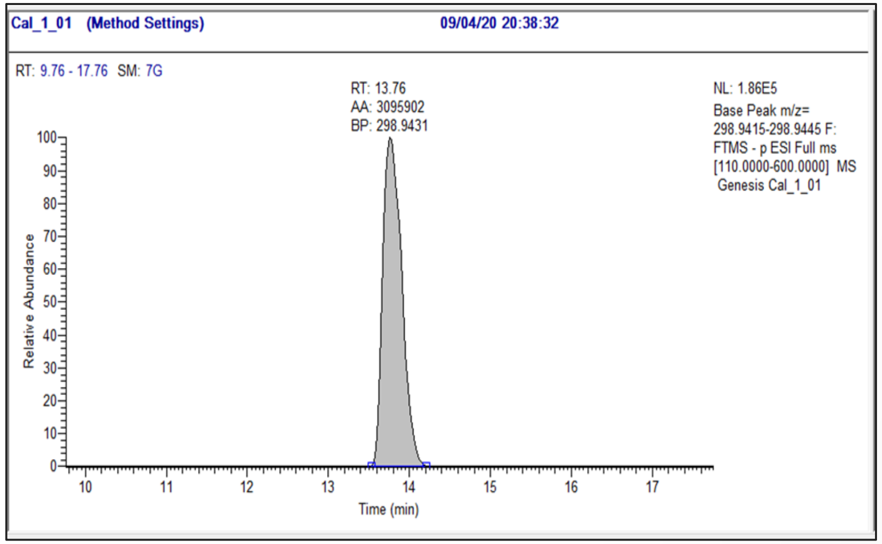
Sensitivity and Linearity- EQuan 5ml Injection- QE Focus

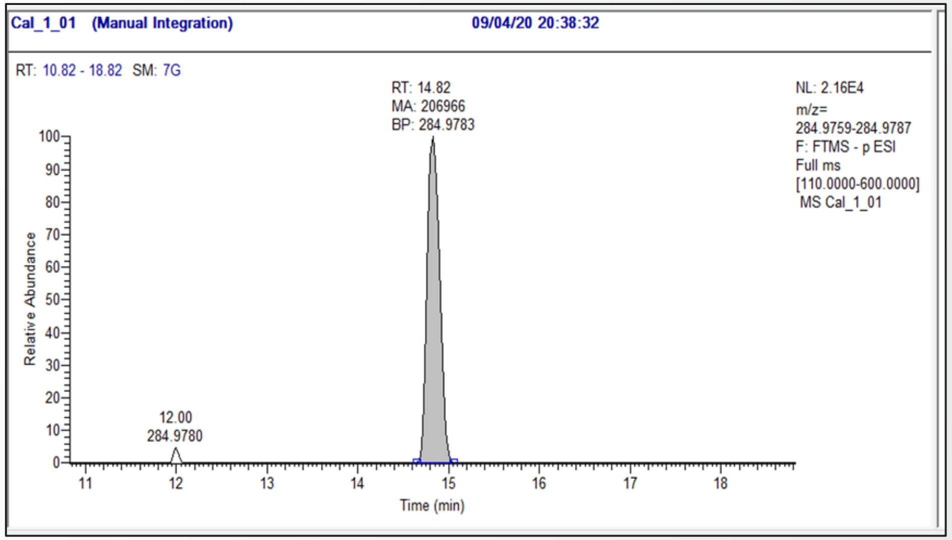
Pentafluorobutane Sulfonate 1 - 100ng/L

GenX 1 - 100ng/L





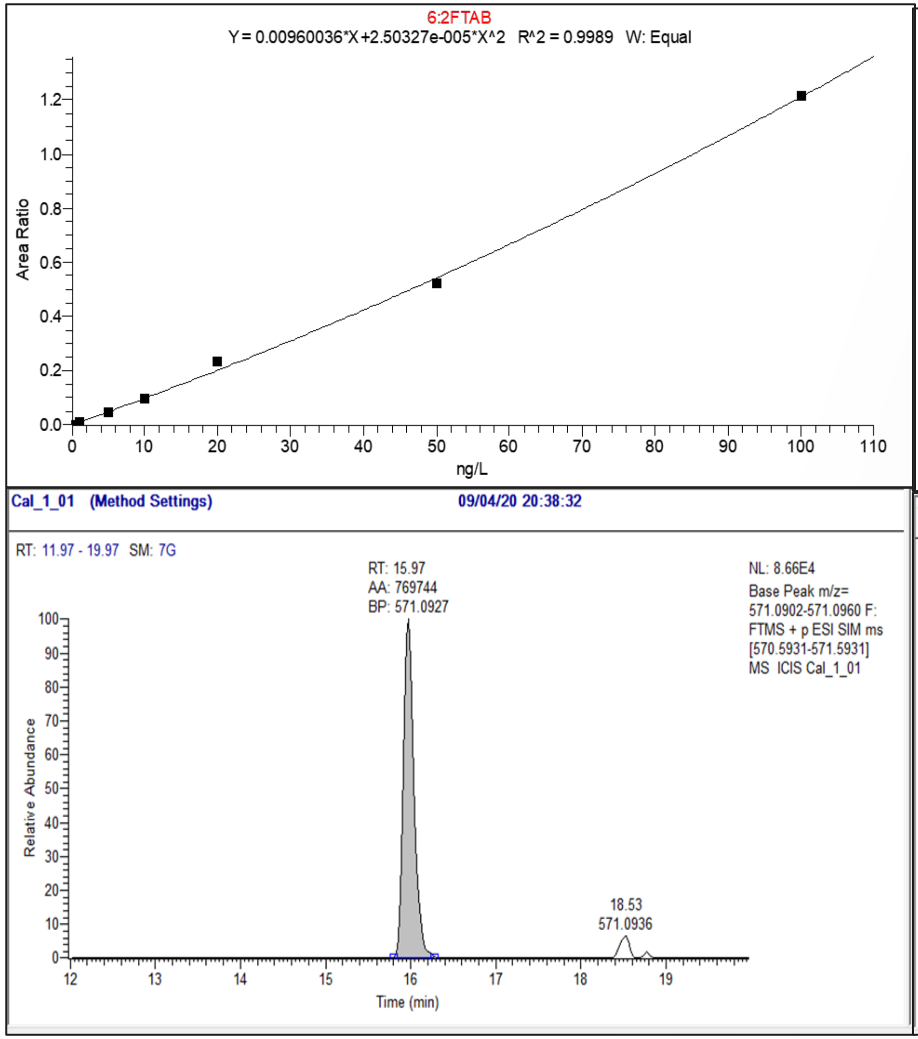




Data Courtesy of John Quick ALS Environmental - Coventry

Sensitivity and Linearity- EQuan 5ml Injection- QE Focus

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



6:2FTAB

Y = 0.00960036*X+2.50327e-005*X^2 R^2 = 0.9989 W: Equal

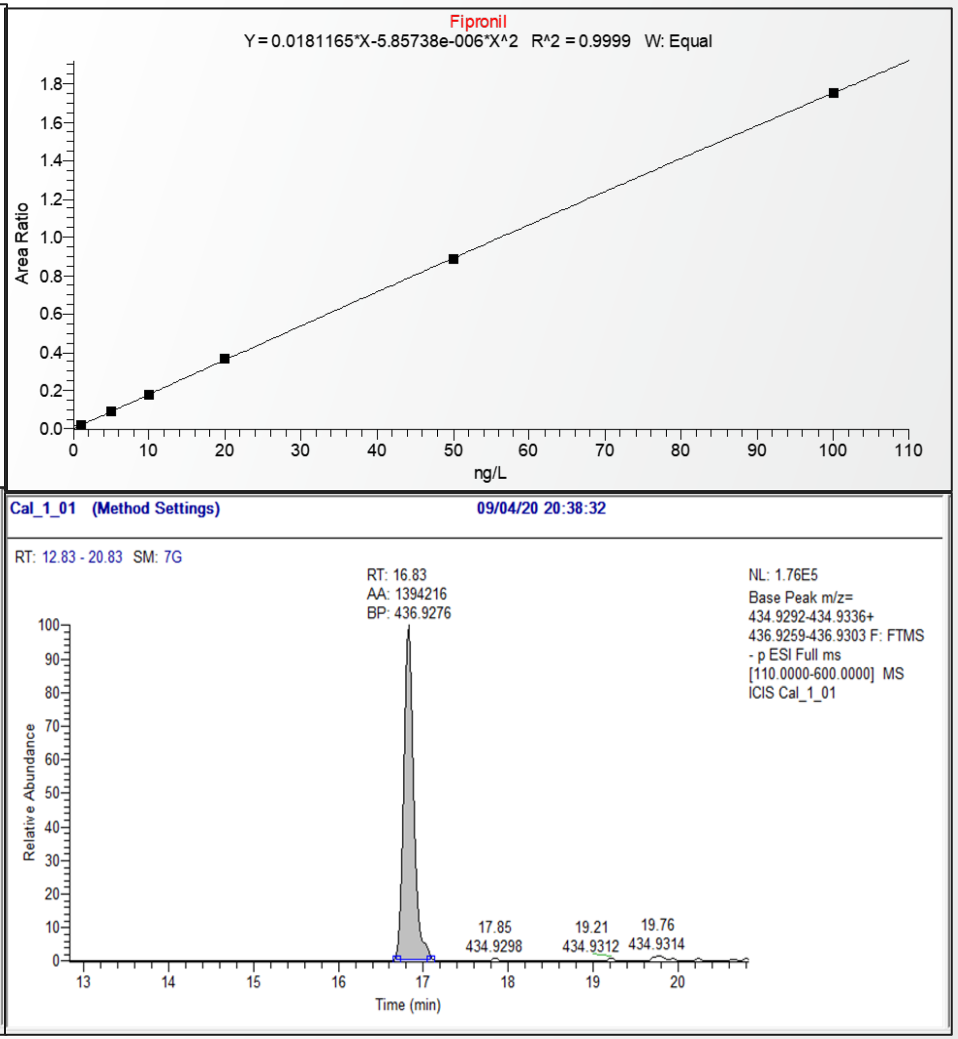
Cal_1_01 (Method Settings) 09/04/20 20:38:32

RT: 11.97 - 19.97 SM: 7G

RT: 15.97
AA: 769744
BP: 571.0927

NL: 8.66E4
Base Peak m/z= 571.0902-571.0960 F: FTMS + p ESI SIM ms [570.5931-571.5931] MS ICIS Cal_1_01

Fipronil 1 - 100ng/L



Fipronil

Y = 0.0181165*X-5.85738e-006*X^2 R^2 = 0.9999 W: Equal

Cal_1_01 (Method Settings) 09/04/20 20:38:32

RT: 12.83 - 20.83 SM: 7G

RT: 16.83
AA: 1394216
BP: 436.9276

NL: 1.76E5
Base Peak m/z= 434.9292-434.9336+ 436.9259-436.9303 F: FTMS - p ESI Full ms [110.0000-600.0000] MS ICIS Cal_1_01

Data Courtesy of John Quick ALS Environmental - Coventry

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

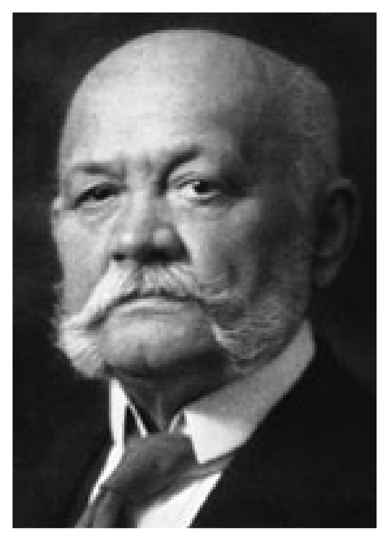
Method Validation Results – EQuan Continued

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	%Bias
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

Data Courtesy of John Quick ALS Environmental - Coventry

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

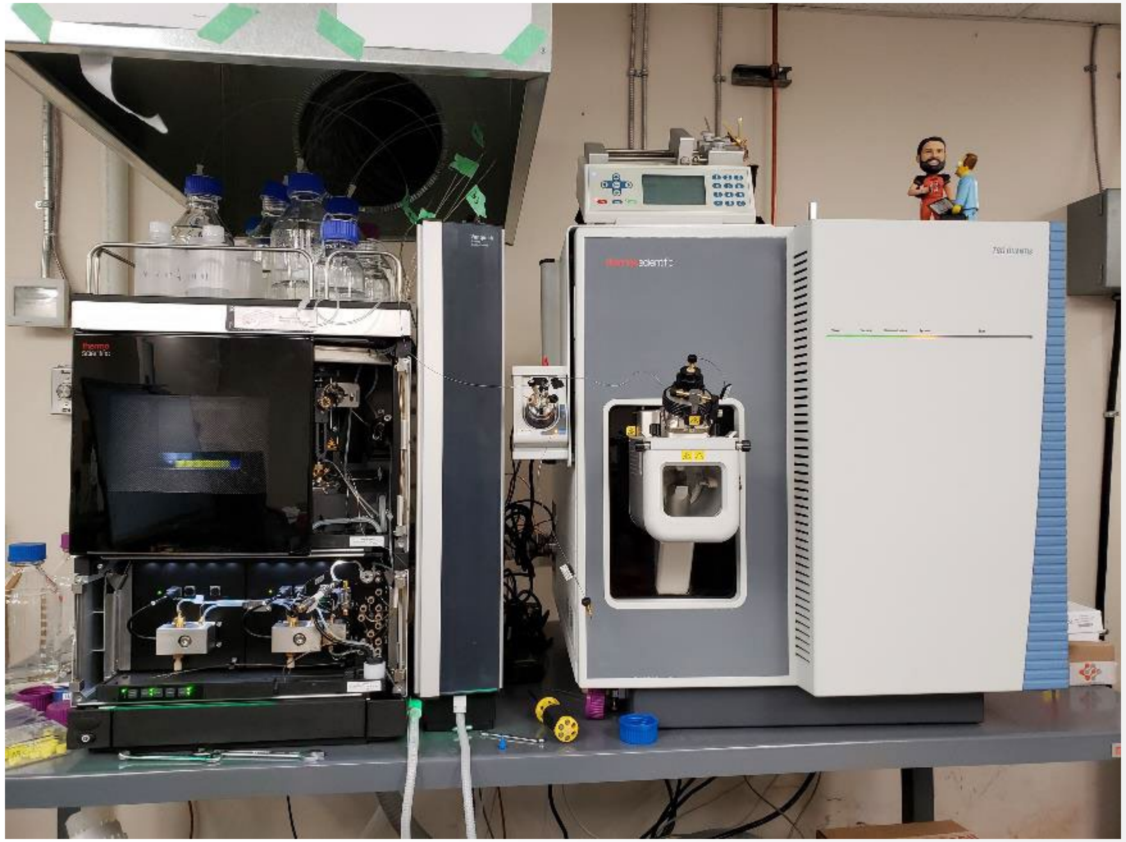
Accelerated Solvent Extraction (ASE) for PFAS

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

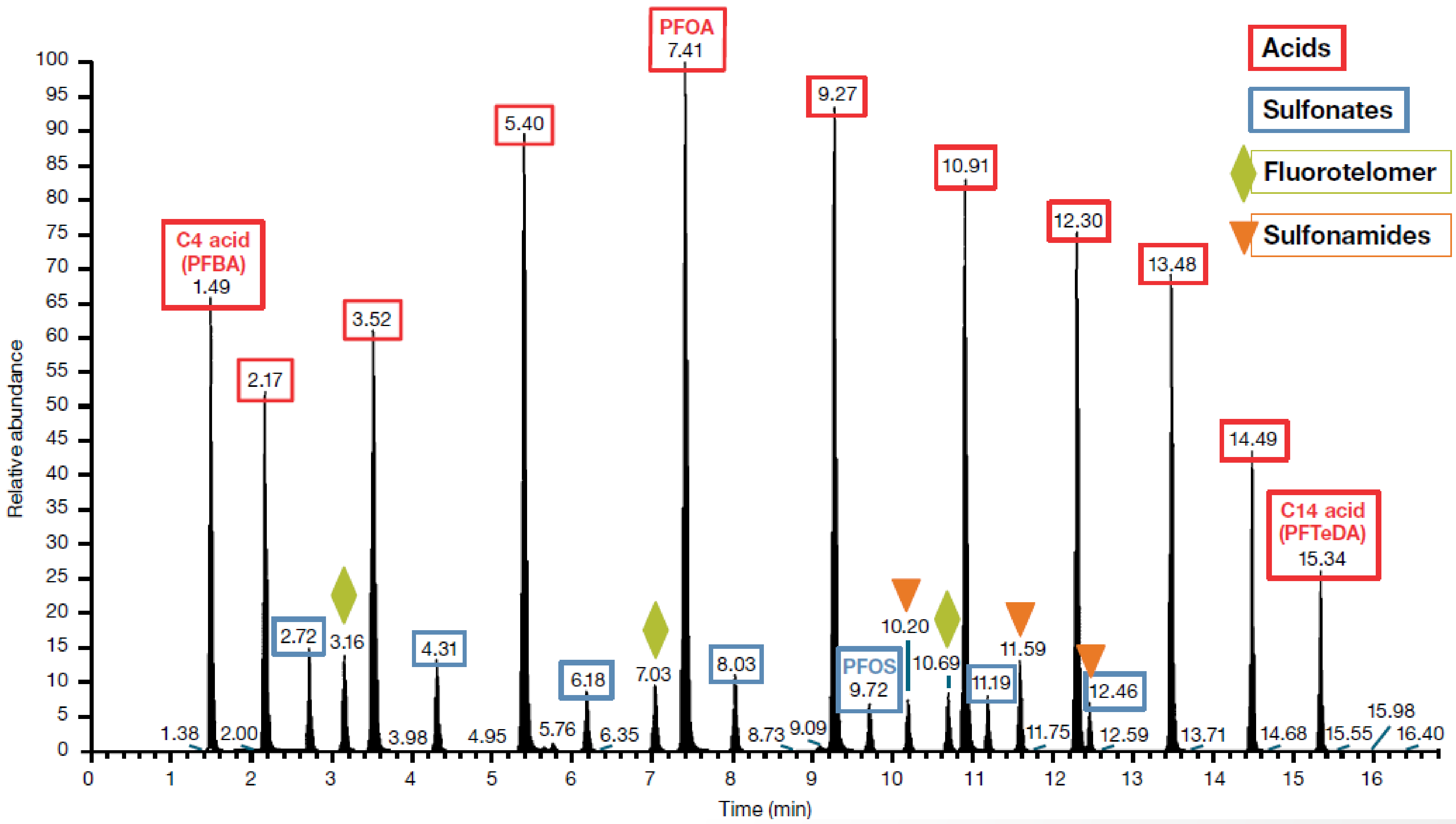
Analytical Instrumentation

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

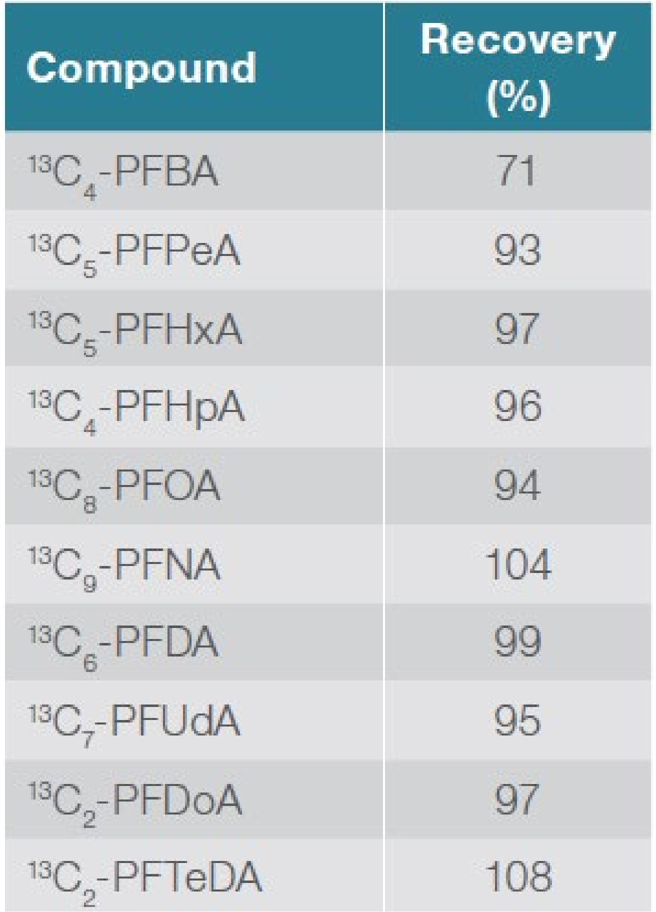


Thermo Fisher Scientific™ TSQ Quantis™ Mass Spectrometer

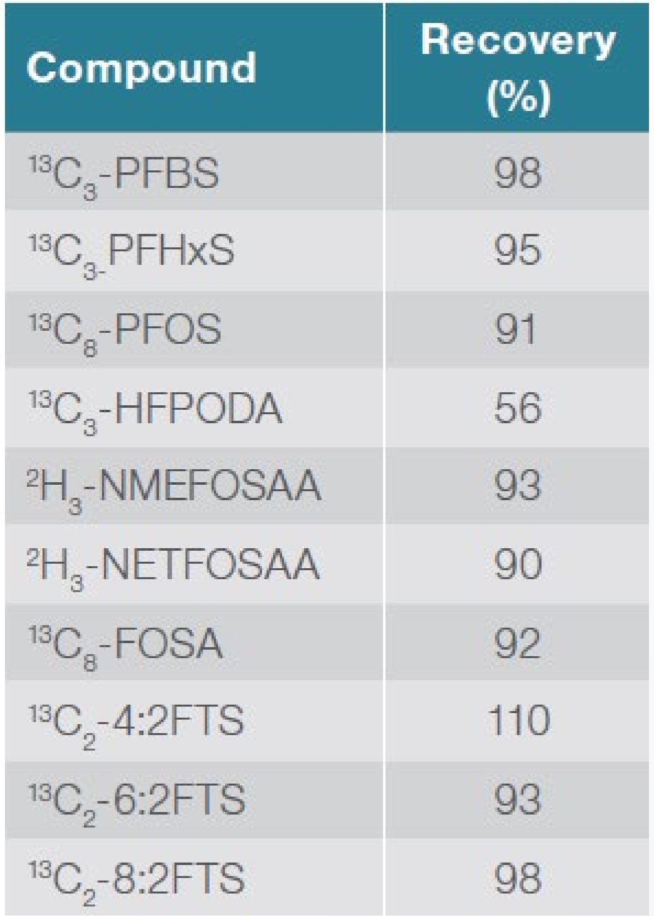
PFAS results using ASE 350



PFAS Recovery



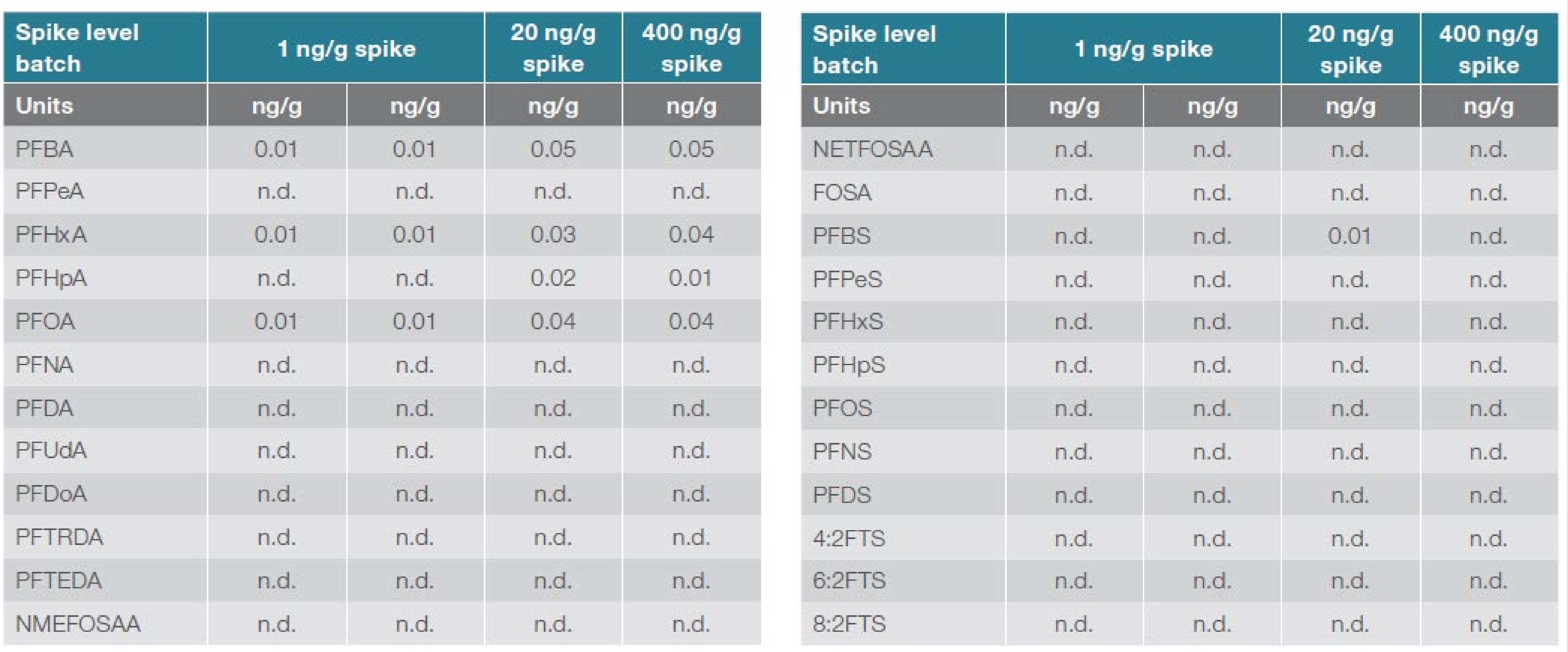
Compound	Recovery (%)
$^{13}C_{4}$-PFBA	71
$^{13}C_{5}$-PFPeA	93
$^{13}C_{5}$-PFHxA	97
$^{13}C_{4}$-PFHpA	96
$^{13}C_{8}$-PFOA	94
$^{13}C_{9}$-PFNA	104
$^{13}C_{6}$-PFDA	99
$^{13}C_{7}$-PFUdA	95
$^{13}C_{2}$-PFDoA	97
$^{13}C_{2}$-PFTeDA	108



Compound	Recovery (%)
$^{13}C_{3}$-PFBS	98
$^{13}C_{3\text{-}}$PFHxS	95
$^{13}C_{8}$-PFOS	91
$^{13}C_{3}$-HFPODA	56
$^{2}H_{3}$-NMEFOSAA	93
$^{2}H_{3}$-NETFOSAA	90
$^{13}C_{8}$-FOSA	92
$^{13}C_{2}$-4:2FTS	110
$^{13}C_{2}$-6:2FTS	93
$^{13}C_{2}$-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
Units	**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.
PFDoA	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
Units	**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

EXTREVA ASE Key Benefits

Streamlined Sample Extraction

(Combines sample extraction, clean-up and concentration)

Combined Footprint

(Extraction and Evaporation System in one platform)

Increased Laboratory Productivity

(Parallel Extraction of up to 4 samples at one, reduces cost per sample)

Complete Workflow from Sample to Vial

(True walk-away technology)

Increased productivity, better consistancy & reduces costs

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.

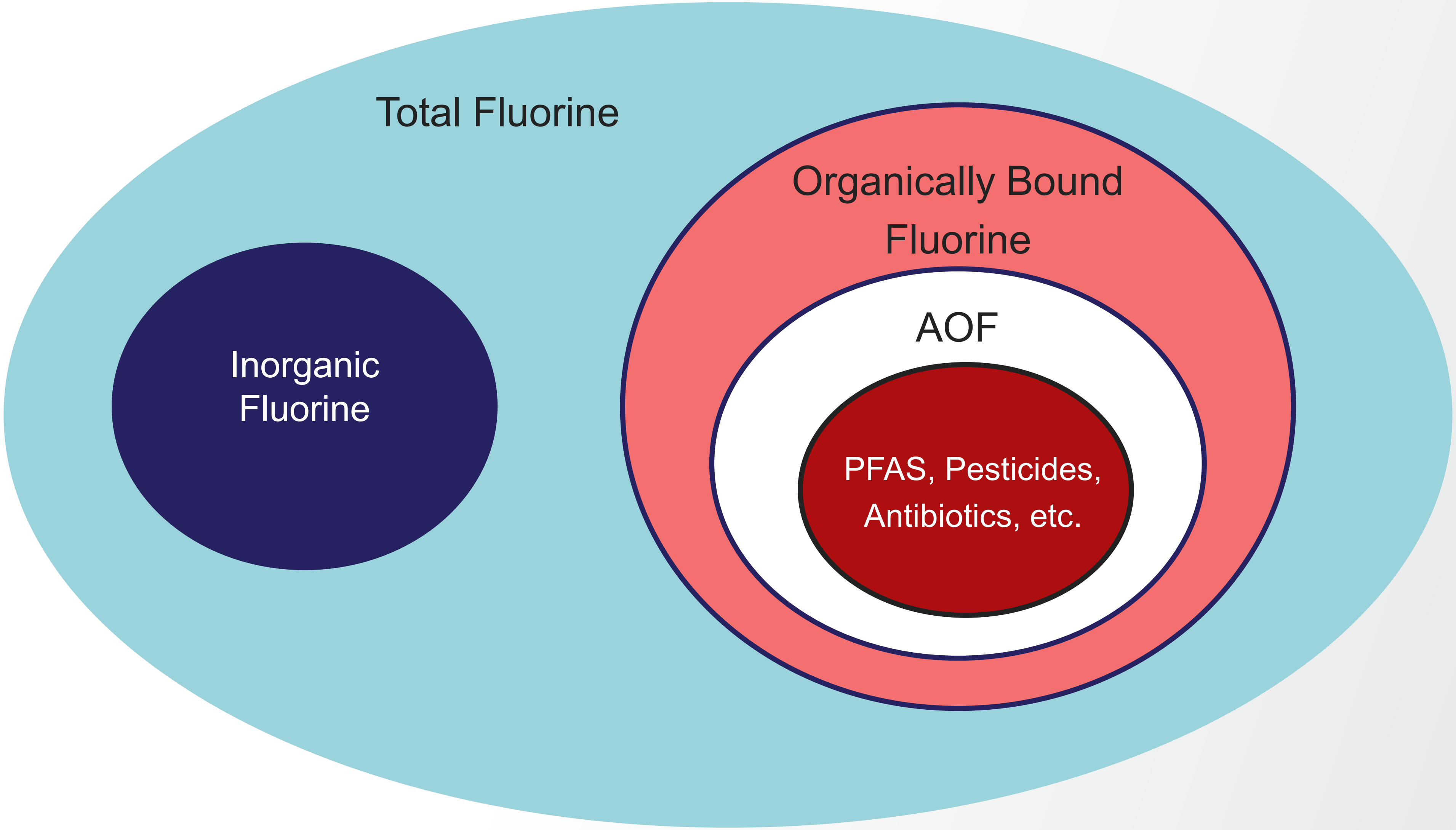
Ion Chromatograph

Gas Absorption Unit

Furnace

Solid/Liquid Autosampler

Distribution of Fluorine in the Environment


Total Fluorine

Inorganic Fluorine

Organically Bound Fluorine

AOF

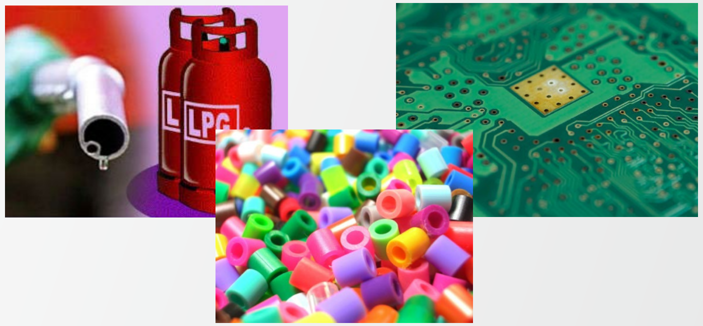
PFAS, Pesticides, Antibiotics, etc.

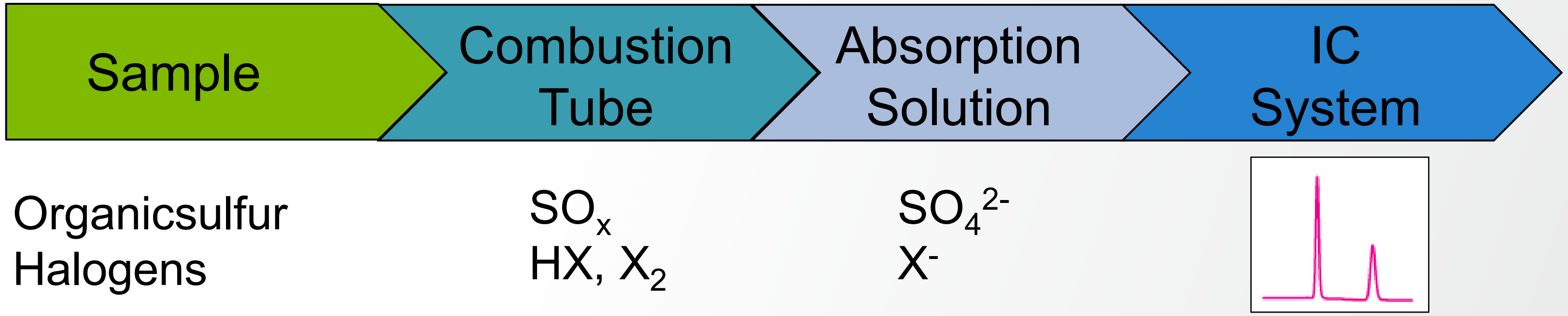
Analytical method for the determination of AOF

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





Sample → Combustion Tube → Absorption Solution → IC System

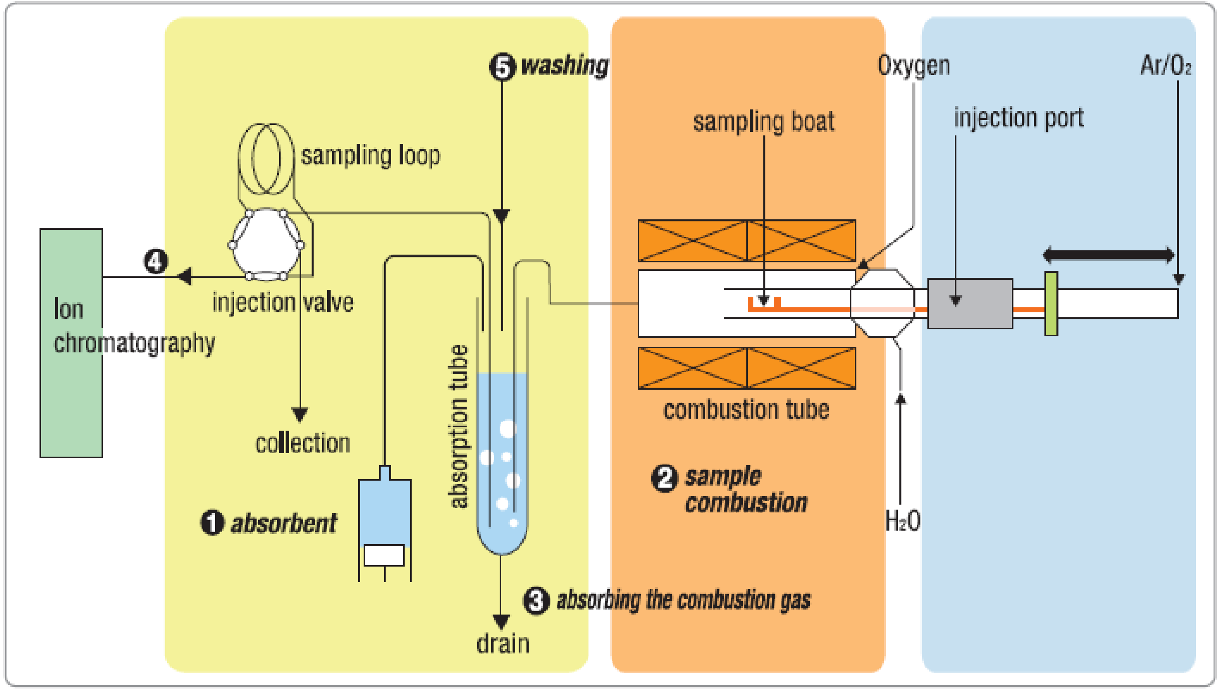
Organicsulfur
Halogens

SO_x
HX, X_2

SO_4^{2-}
X^-

CIC theory

Sample | Sulfur → **In the combustion tube** | SOx → **In the absorbent** | SO_4^{2-} → Ion Chromatograph
Sample | Halogen → **In the combustion tube** | HX, X_2 → **In the absorbent** | X^- → Ion Chromatograph

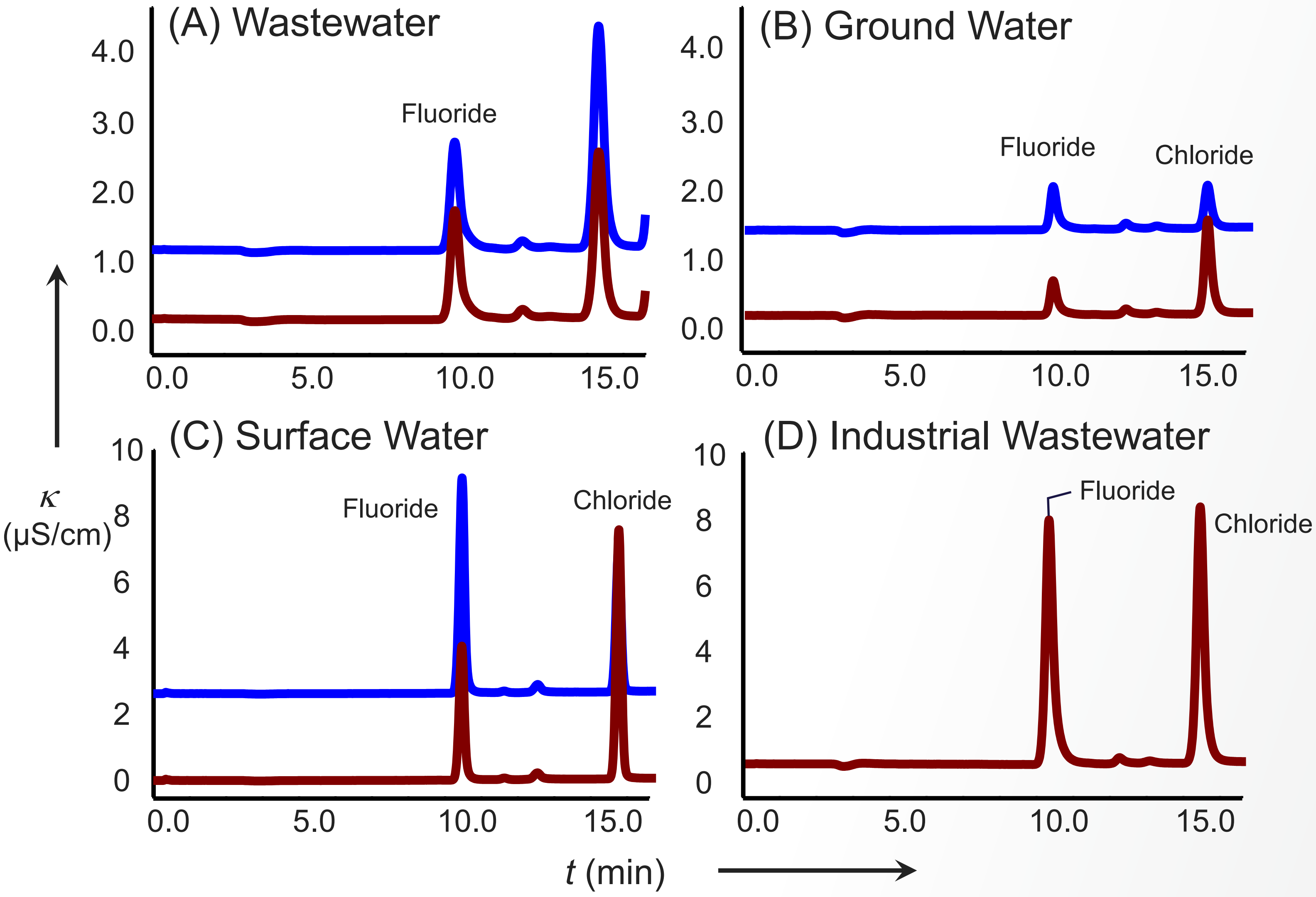


Process Flowchart

1. set absorbent
2. pyrohydrolytic combustion of sample
3. combusted gas is absorbed by absorbent
4. absorbent is injected into the Ion chromatograph
5. clean absorption tube

Schematic of a CIC system

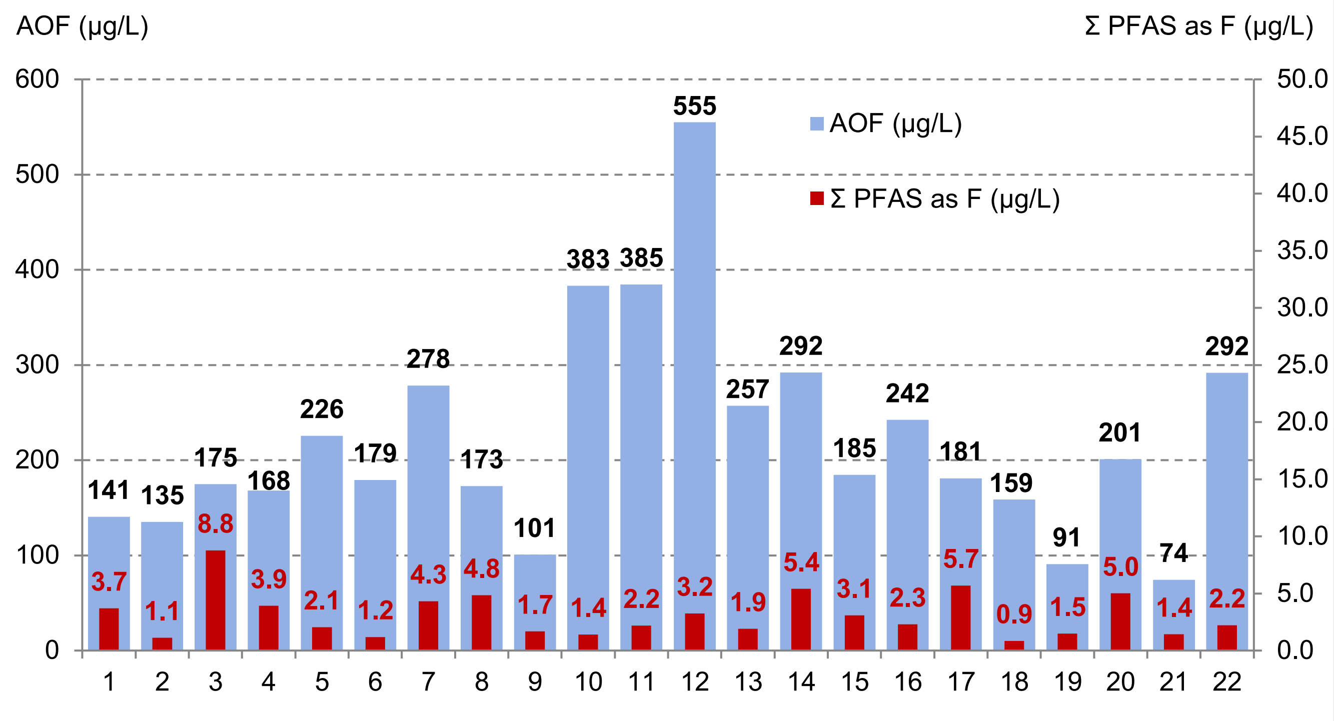
Non-Targeted Complemental Determination of PFAS in Aqueous Samples



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 (Σ of PFAS as F) are shown.

AOF in Aqueous Environmental Samples

Thermo Fisher
SCIENTIFIC

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

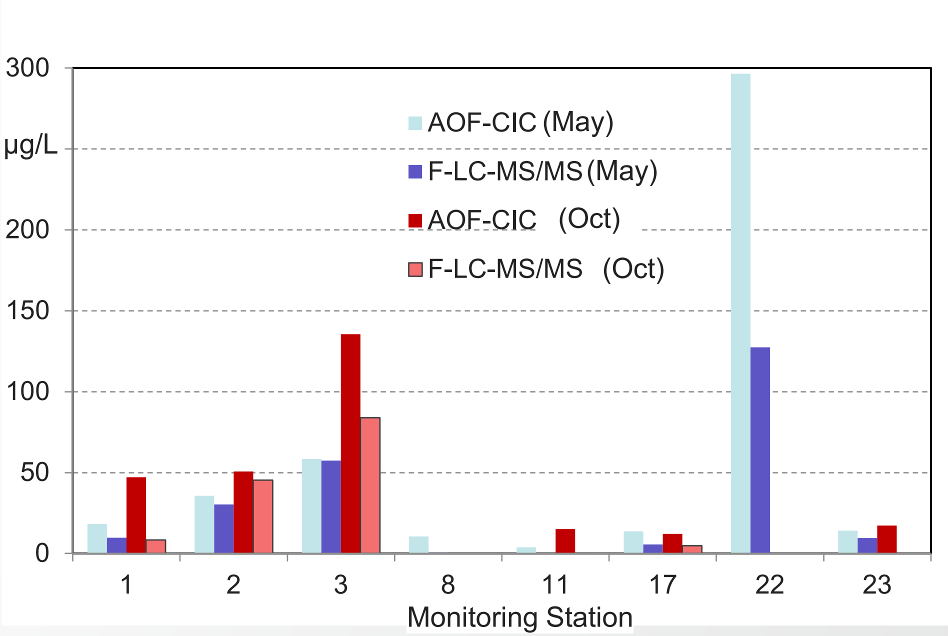
- Matrix: PFAS contaminated surfacewater
- 23 monitoring stations (May and October 2015)
- 14 individual PFAS targeted *(DIN 38407-42, 2011)*

AOF (µg/L): < 2-300 µg/L

F-PFAS: 0.01-130 µg/L

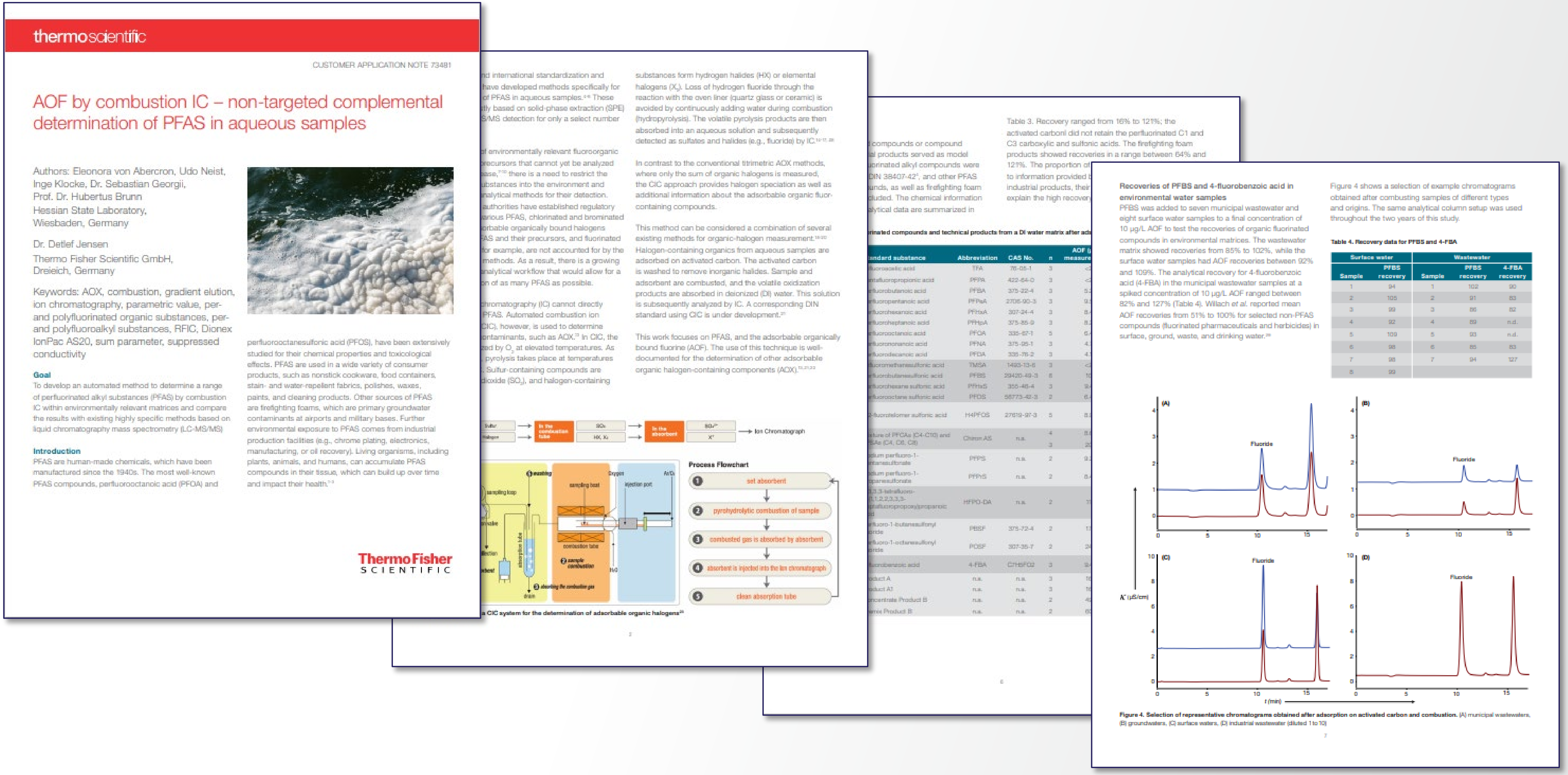
Samples with AOF Results above 10 µg/L

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 µg/L

Customer Application Note: AOF by combustion IC



CUSTOMER APPLICATION NOTE 73481

AOF by combustion IC – non-targeted complemental 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, RFIC, 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.[1-3]

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substances form hydrogen halides (HX) or elemental halogens (X_2). Loss of hydrogen fluoride through the reaction with the oven liner (quartz glass or ceramic) is avoided by continuously adding water during combustion (hydropyrolysis). The volatile pyrolysis products are then absorbed into an aqueous solution and subsequently detected as sulfates and halides (e.g., fluoride) by IC.[10-17, 28]

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 fluor-containing compounds.

This method can be considered a combination of several existing methods for organic-halogen measurement.[18-20] 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 oxidization products are absorbed in deionized (DI) water. This solution is subsequently analyzed by IC. A corresponding DIN standard using CIC is under development.[21]

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).[13,21,22]

Process Flowchart

1. set absorbent
2. pyrohydrolytic combustion of sample
3. combusted gas is absorbed by absorbent
4. absorbent is injected into the Ion Chromatograph
5. clean absorption tube

a CIC system for the determination of adsorbable organic halogens[20]

Table 3. Recovery ranged from 16% to 121%; the activated carbonl 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

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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% (Table 4). Willach *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.[28]

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

Surface water		Wastewater		
Sample	PFBS recovery	Sample	PFBS recovery	4-FBA recovery
1	94	1	102	90
2	105	2	91	83
3	99	3	86	82
4	92	4	89	n.d.
5	109	5	93	n.d.
6	98	6	85	83
7	98	7	94	127
8	99			

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

Thank you