

Analysis of Per/Polyfluoroalkyl Substances (PFAS) in Drinking Water Using the Agilent Ultivo Triple Quadrupole LC/MS

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Per/Poly Fluoroalkyl Substances (PFAS) in Water



- PFASs widely used and can be sourced from:
 - Fire-fighting foams
 - Non-stick cookware
 - Food packaging
 - Manufacturing
- USEPA drinking water health advisories for PFOA and PFOS 70 ng/L in drinking water
- Individual US State guidelines 13 – 32 ng/L PFOS and PFOA in water.
- US EPA Method 537 → 14 PFAS compounds

Overview



Two methods for detecting PFAS compounds in drinking water using the Ultivo LC/TQ

Method 1

- 17 PFAS Compounds
- EPA 537 sample preparation

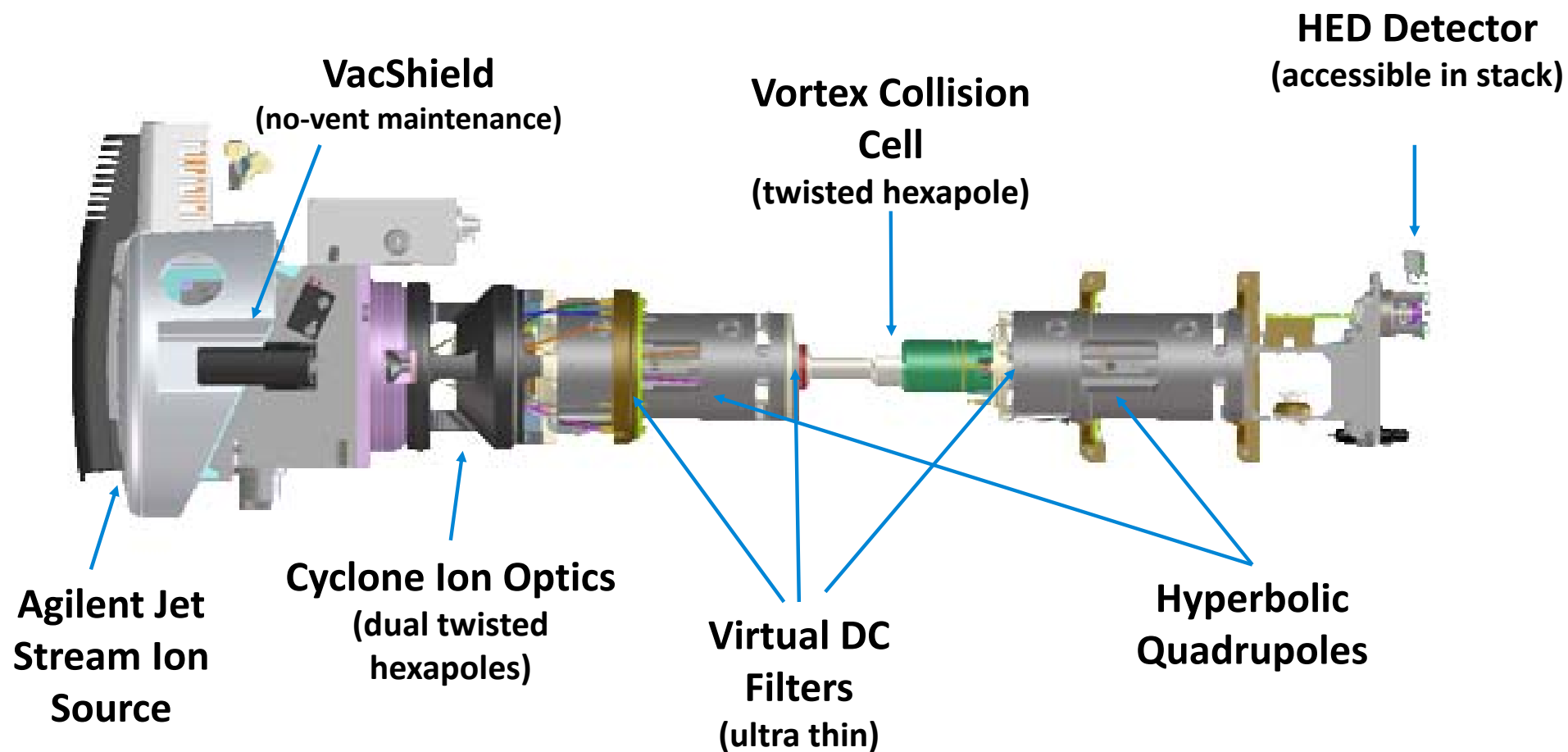
Method 2

- 51 Trace Organic Contaminants Including 10 PFAS compounds
- Online SPE

The New Ultivo Triple Quad LC/MS

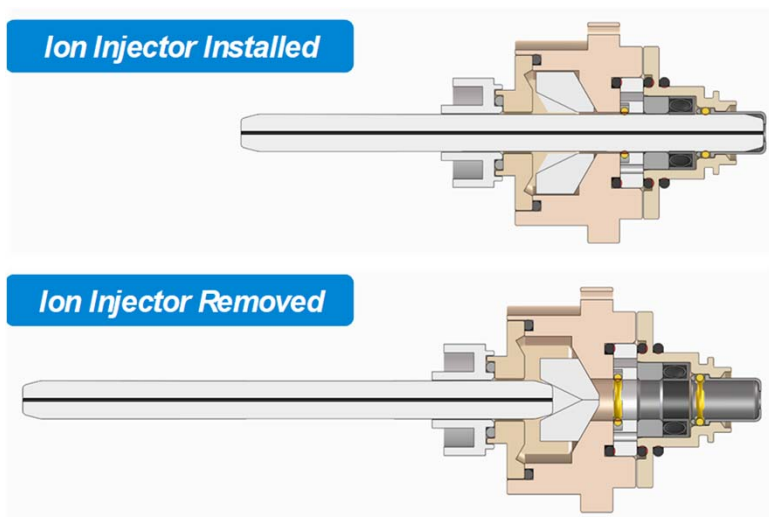


Ultivo: Space-saving, Sensitive, Robust & Powerful

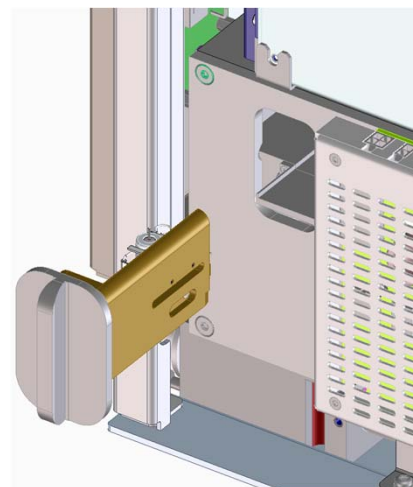


Ultivo – Reduced Downtime

- ✓ Fast Autotune <10 minutes!
- ✓ Vac Shield: Change capillary without venting
- ✓ Accessible maintenance features



New Vac Shield Technology



Easy Change Detector Assembly

Software Features for High Throughput

- ✓ Real time diagnostics
 - ✓ Capillary health
 - ✓ Spray stability
 - ✓ Source Cleanliness
- ✓ Clearer callouts for entry errors

CAV (V)	CE (V)	Average Dwell (ms)	Polarity	
3	0	1002	Positive	
3	10	325.26	Positive	
3	10	325.26	Positive	
3	0	138.9	Positive	
3	15	138.9	Positive	
3	24	82.98	Positive	
3	12	82.98	Positive	

Total MRMs	504
Minimum Concurrent MRMs	1
Maximum Concurrent MRMs	104
Minimum Dwell Time (ms)	5.62
	1002
Minimum Cycle Time (ms)	521.52
Cycle time (ms):	1002
☐ Override RT window (min)	1

Agilent MassHunter Workstation Data Acquisition

File View Sample Worklist Method Tools Help

Layout: Default(sys).lyt Method: 062017_Robustnes Worklist: dy_robustness test

Instrument Status

Multisampler Run EMF ✓

2.00 µL P1-E-1

8 °C [8 °C]

Binary Pump Run EMF ✓

66.71 33.29 0.400 mL/min

209.06 bar

Column Comp. ? Run EMF ✓

On Off

45.10°C [45.0°C] 45.11°C [45.0°C]

QQQ Run EMF ✓

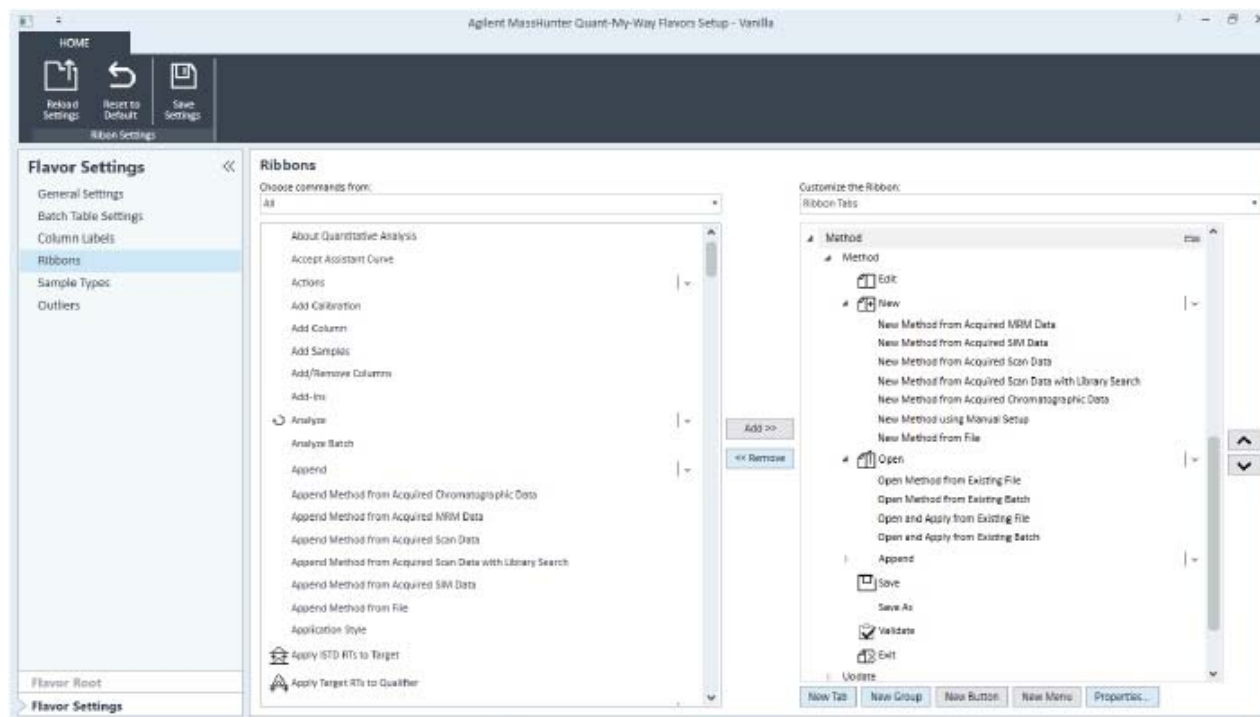
AJS ESI

Run 0.61 / 4.00 min

Instrument Run On Off

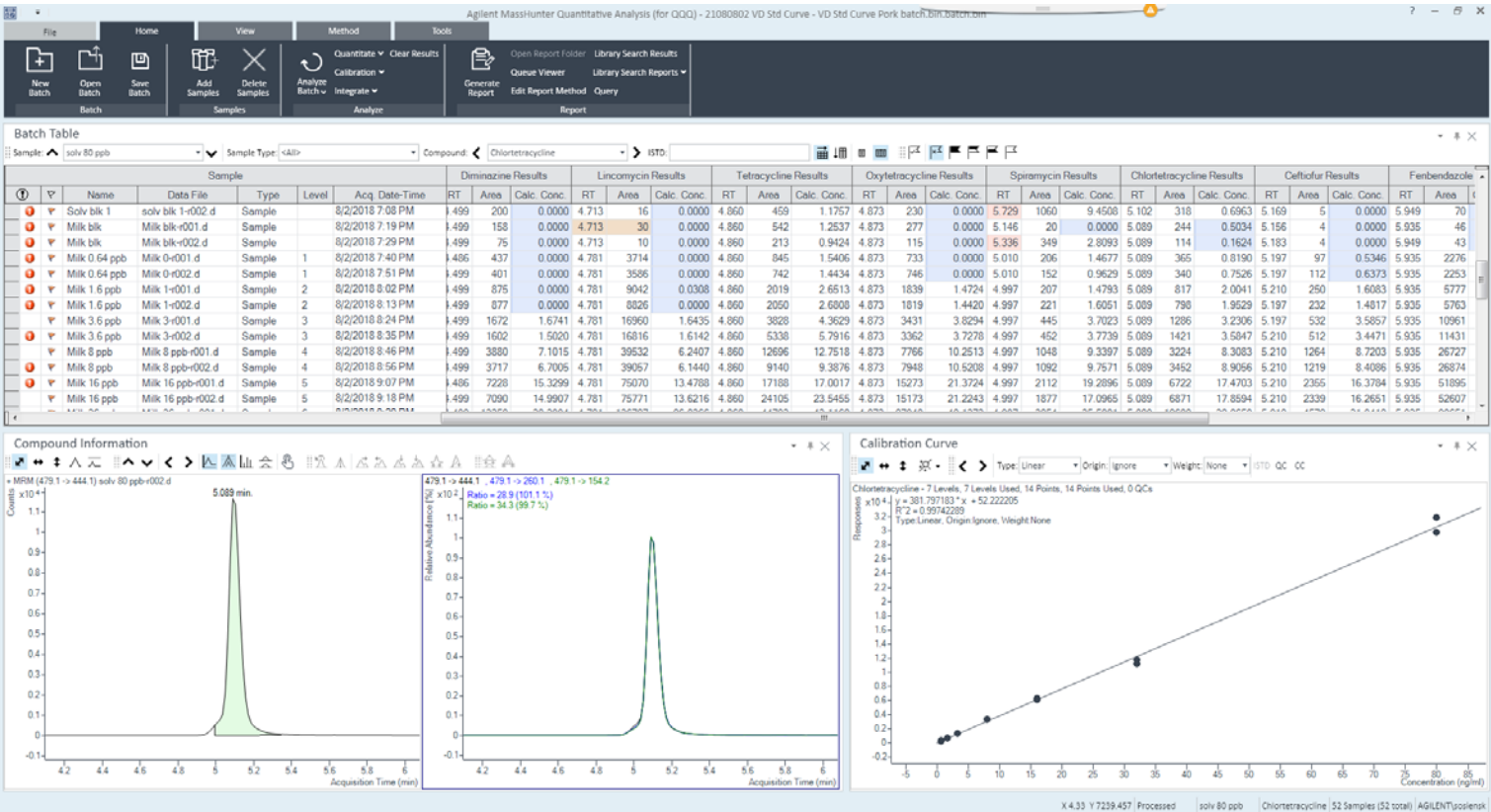
Software Features for High Throughput

- Quant-My-Way: customize the user interface for data analysis.



Faster, easier, error-free data analysis, review and reporting by novice operators.

Quant-My-Way



Analysis of Per/Polyfluoroalkyl Substances (PFAS) in Drinking Water Using the Agilent Ultivo Triple Quadrupole LC/MS

Application Note: 5991-8969EN



Analysis Method

- 17 PFAS compounds in drinking water.
 - All 14 from USEPA 537 method.
 - Additional compounds PFDoA, PFPeA, and PFBA
 - Full list included in Application note 5991-8969EN
- 250mL water samples
 - Extracted with Agilent Weak Anion Exchange (WAX) cartridges.
 - Similar to US EPA 537 Method Conditions
 - Extracts concentrated to dryness with nitrogen
 - Reconstituted w/ 96:4 (v/v) Methanol/Water
 - IS added



Instrumentation

- 1290 Infinity II LC
 - Analytical Column: Zorbax Eclipse plus C18 3.0x50mm, 1.8 μ m
 - Mobile Phase A: H₂O and
 - Mobile Phase B: 95:5 MeOH/H₂O, 5mM Ammonium Acetate
 - Flow Rate: 0.4 ml/min
 - Injection Volume: 5 μ L
- Ultivo Triple Quadrupole MS in negative ionization mode.
 - Dynamic MRM



Overcoming Potential Contamination

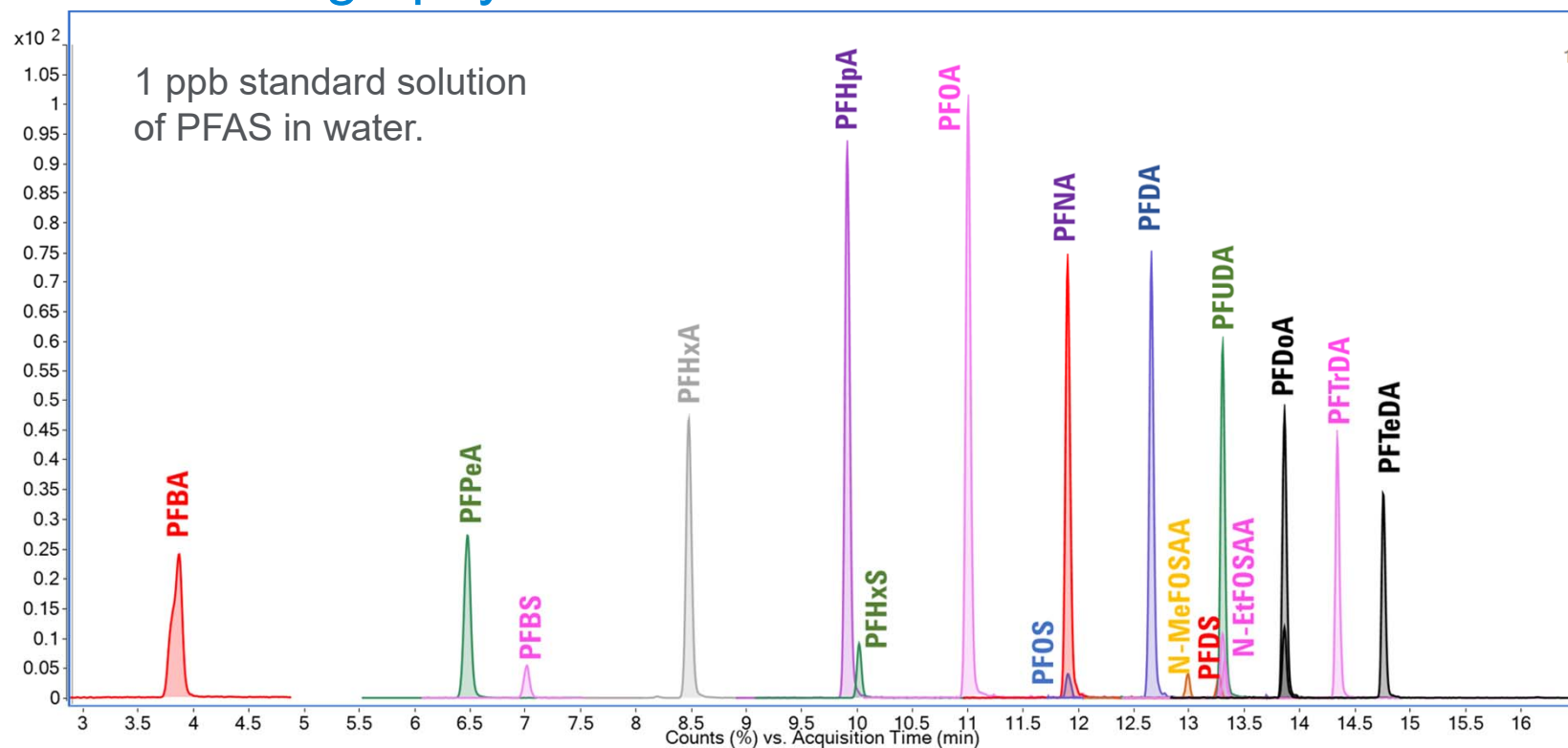
PFASs could potentially be used in LC and component manufacturing processes

Changes to the system:

- Delay Column: Zorbax Eclipse plus C18 4.6x50mm, 3.5 μ m
- Vials: 1 mL polypropylene vials
- Caps: Snap top polypropylene caps

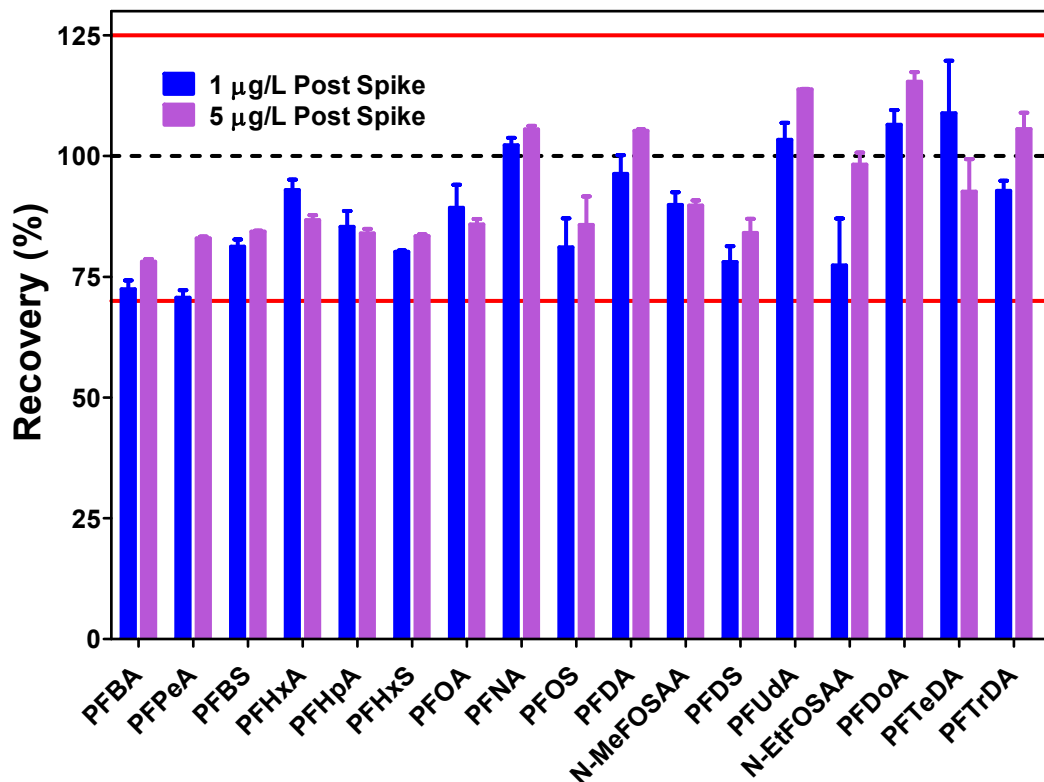


PFAS Chromatography



- Good chromatographic separation and S/N with 1 ppb standard solution.
- EPA Method 537 → 35 to 37 min analytical run time
- This method is less than 22 minutes.

Recovery of PFAS Compounds in Water

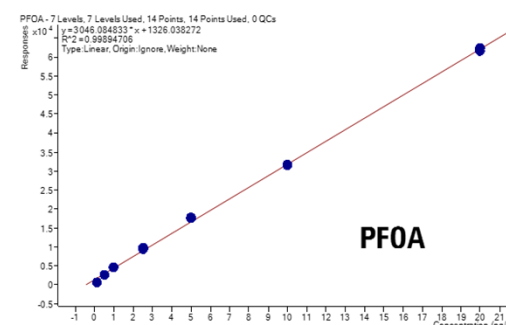
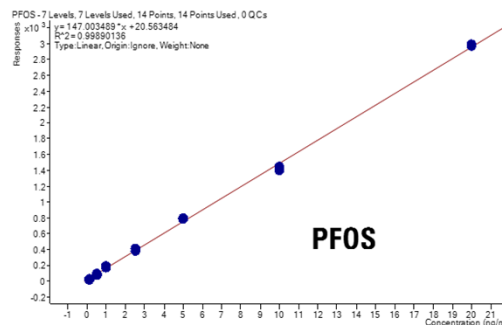


- Recovery 70-120% for all compounds at 1 µg/L and 5 µg/L spiking levels
- RSD%: 0.3-10.8% for all compounds at both spiking levels (5 replicates).

Linearity of PFAS Compounds

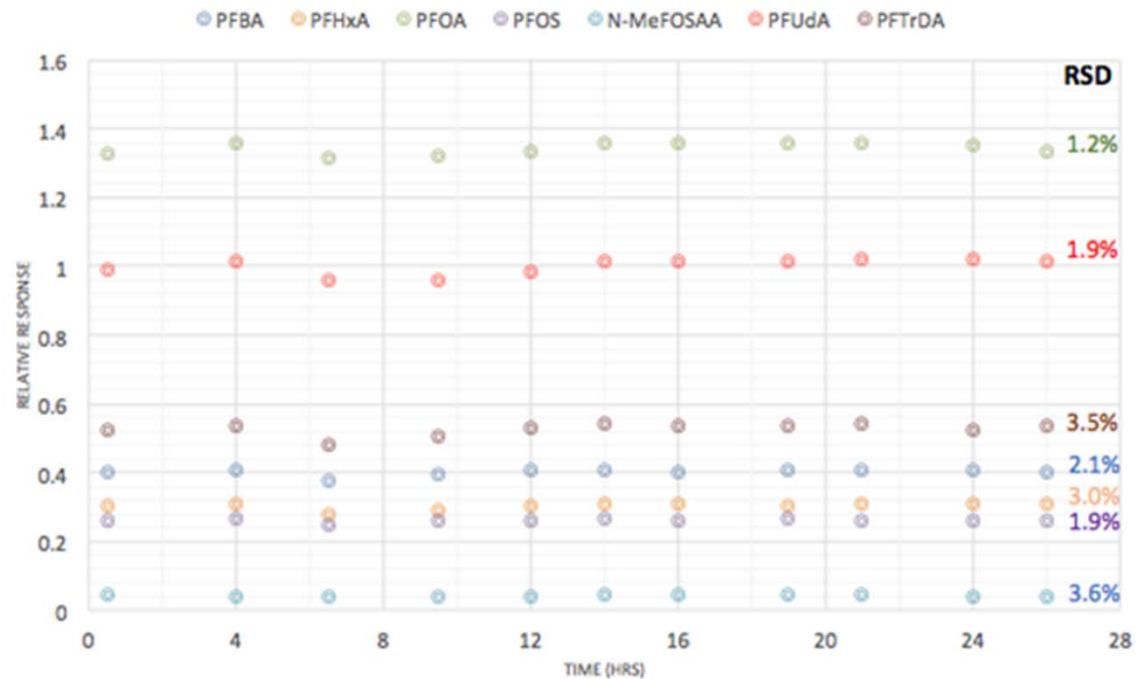
Compound	R ²	CCV RSD (%)
PFBA	0.9965	2.1
PFPeA	0.9996	2.7
PFBS	0.9964	3.1
PFHxA	0.9988	3.0
PFHpA	0.9985	3.4
PFHxS	0.9995	1.7
PFOA	0.9971	1.2
PFOS	0.9991	1.9
PFNA	0.9811	3.7
PFDA	0.9941	3.6
N-MeFOSAA	0.9999	3.6
PFDS	0.9999	2.3
PFUdA	0.9940	2.3
N-EtFOSAA	0.9996	5.2
PFDoA	0.9974	3.6
PFTTrDA	0.9984	3.5
PFTeDA	0.9986	3.2

- Excellent Linearity for 0.2 – 100 µg/L calibration curves.
- R² > 0.99 for all compounds, based on average of 3 calibration curves run over 1 month period.
- Linearity over 1 month highly stable.

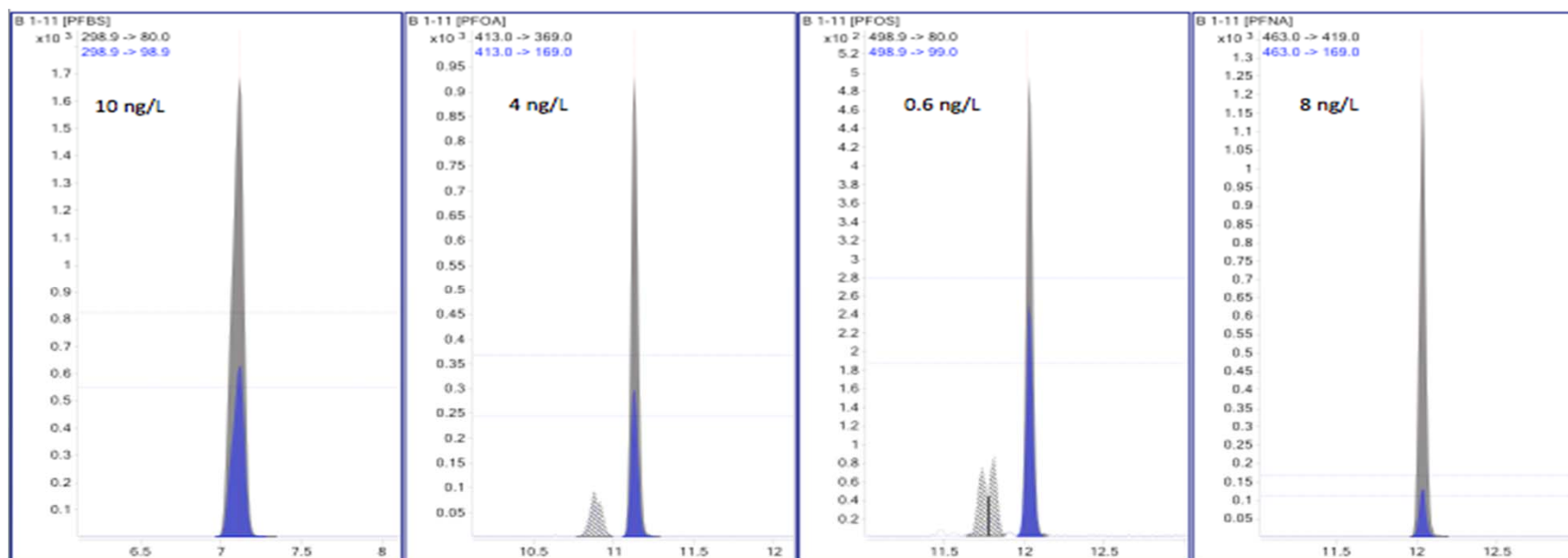


Continuous Calibration Verification

- Calibration sample run after every ten samples - required by US EPA 537.
- CCV samples at 1 ppb level were calculated for a 26 hour batch.
- 94% of Analytes have less than 5% RSD at 1ppb.
- Very stable over 26 hour experiment.



Analysis of Real Water Samples



- Drinking water sample sourced from California
- 4 PFAS compounds detected

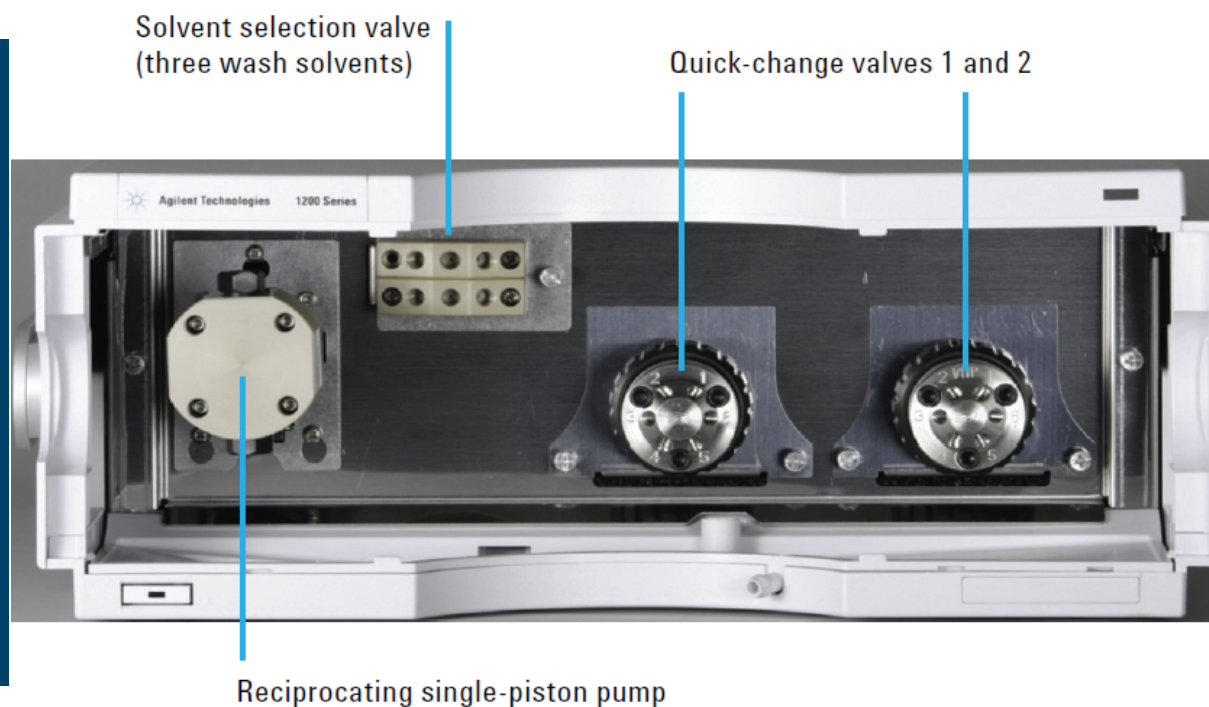
Conclusions

- Ultivo can exceed the sensitivity requirements for PFAS detection in drinking water.
- This method is robust both in standard curve and check sample evaluations.
- Shorter runtime and less sample volume than traditional methods.



Sensitive Detection of Trace Organic Contaminants in Water Using Agilent 1290 Infinity FlexCube Online SPE and Agilent Ultivo Triple Quadrupole LC/MS

Application Note: 5991-8767EN



Ultivo: Even more powerful with Flex Cube Online SPE

- Automated sample pre-concentration
- Fits neatly into LC Stack
- Operated using Agilent MassHunter Software
- Many phases compatible with Online SPE format

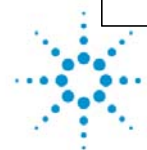


Detection of Trace Level Pharmaceuticals in Drinking Water by Online SPE Enrichment with the Agilent 1200 Infinity Series Online-SPE Solution



Comparison of Online SPE Analysis and Direct Injection of Trace Level Estrogens in Drinking Water with the Agilent 6460 and Agilent 6490 Triple Quadrupole LC/MS Systems

The Agilent 1200 Infinity Series Online SPE Solution for the Highest Sensitivity



Quantitation of Trace Level Emerging Contaminants in Water Using Online SPE with LC/MS/MS



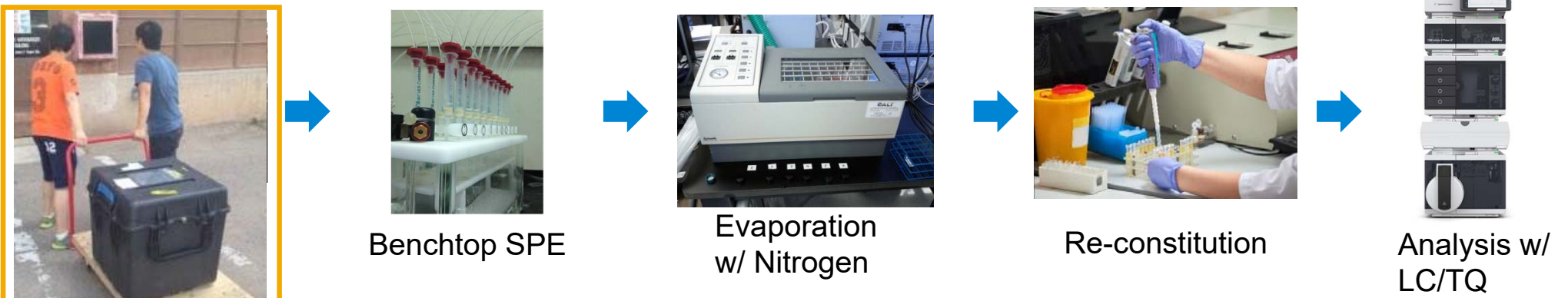
On-line SPE Enrichment of Trace Organic Contaminants in Water and Juices



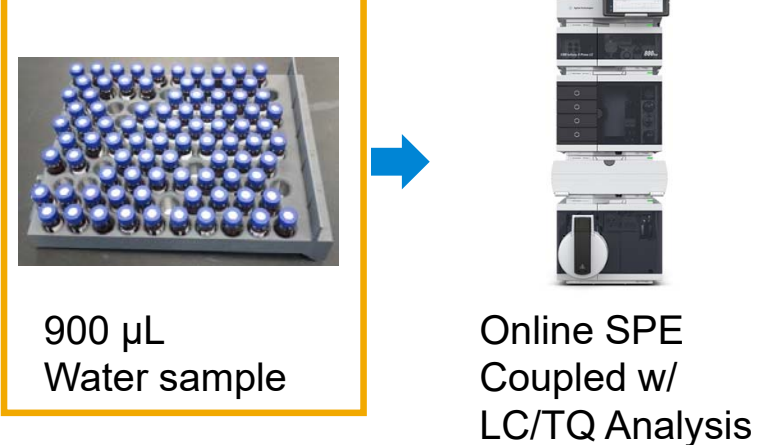
High Sensitivity Detection of Pesticides in Water Using Online SPE Enrichment

Comparing Methods:

Conventional SPE:



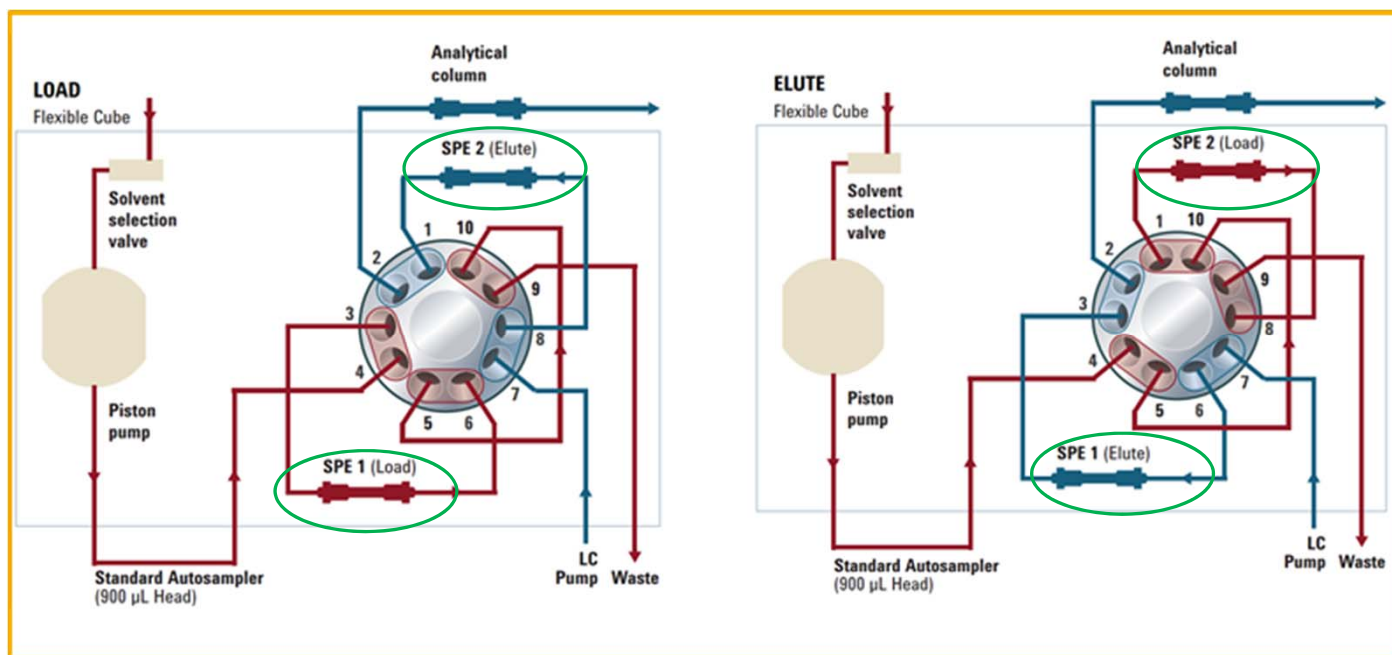
Online SPE:



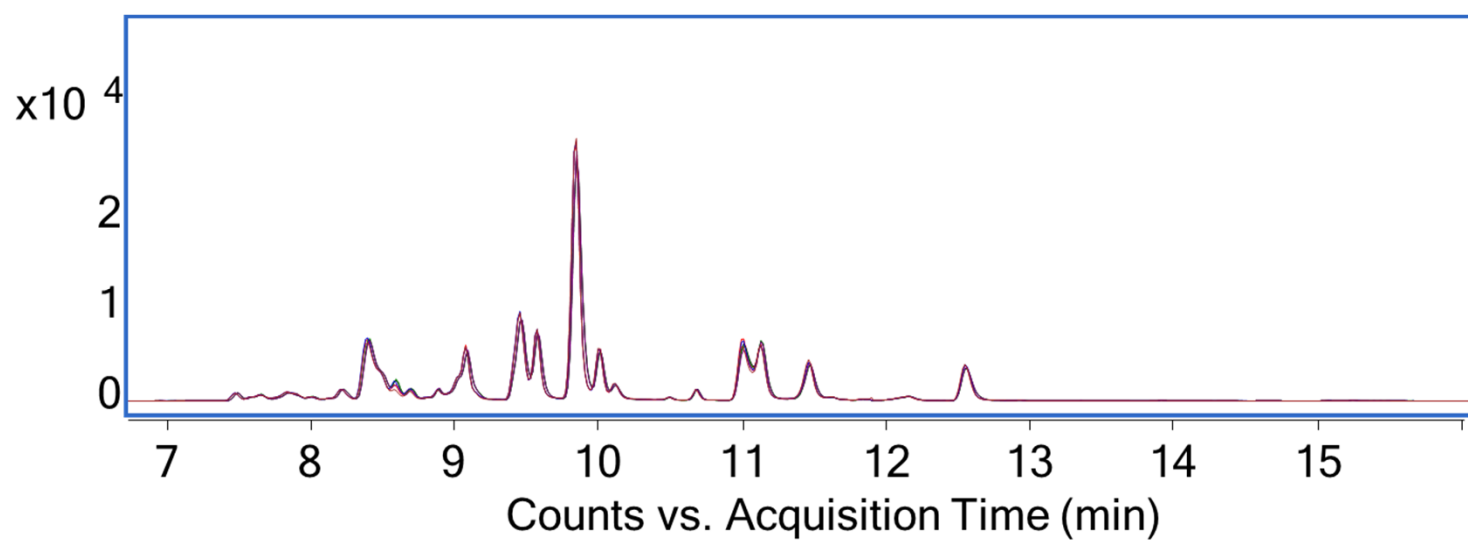
Online SPE Wins:

- ✓ Sample volume
- ✓ Number of steps
- ✓ Potential error
- ✓ Cost
- ✓ Your time

Valve System



Excellent Reproducibility of Dual Cartridge System



Chromatographic overlay of 6 injections at 20 ng/L with alternating enrichment cartridges

Trace Organic Compounds in Drinking Water (51 Analytes)



Pesticides/Metabolites

3-Hydroxy Carbofuran

Alachlor

DEET

Disulfoton-Sulfoxide

Ethion

Fenamiphos

Indoxacarb

Metalaxyl

Mevinphos (Cis)

Methomyl

Oxadixyl

Propoxur

Vamidothion sulfoxide

Blue=EPA 540

PFASs (Neg ESI)

PFBS

PFDA

PFDxA

PFHpA

PFHxA

PFHxS

PFNA

PFOA

PFPeA

PFUdA

Pharmaceuticals

Carbamazepine

Diclofenac

Diltiazem

Gemfibrozil

Hydrocortisone

Ibuprofen

Norgestrel

Primidone

Propanolol

Simazine

Sulfamethoxazole

Testosterone

Triclocarban

Trimethoprim

Other Chemicals

Caffeine

Benzotriazole

Diphenylhydramine

Propylparaben

TCEP

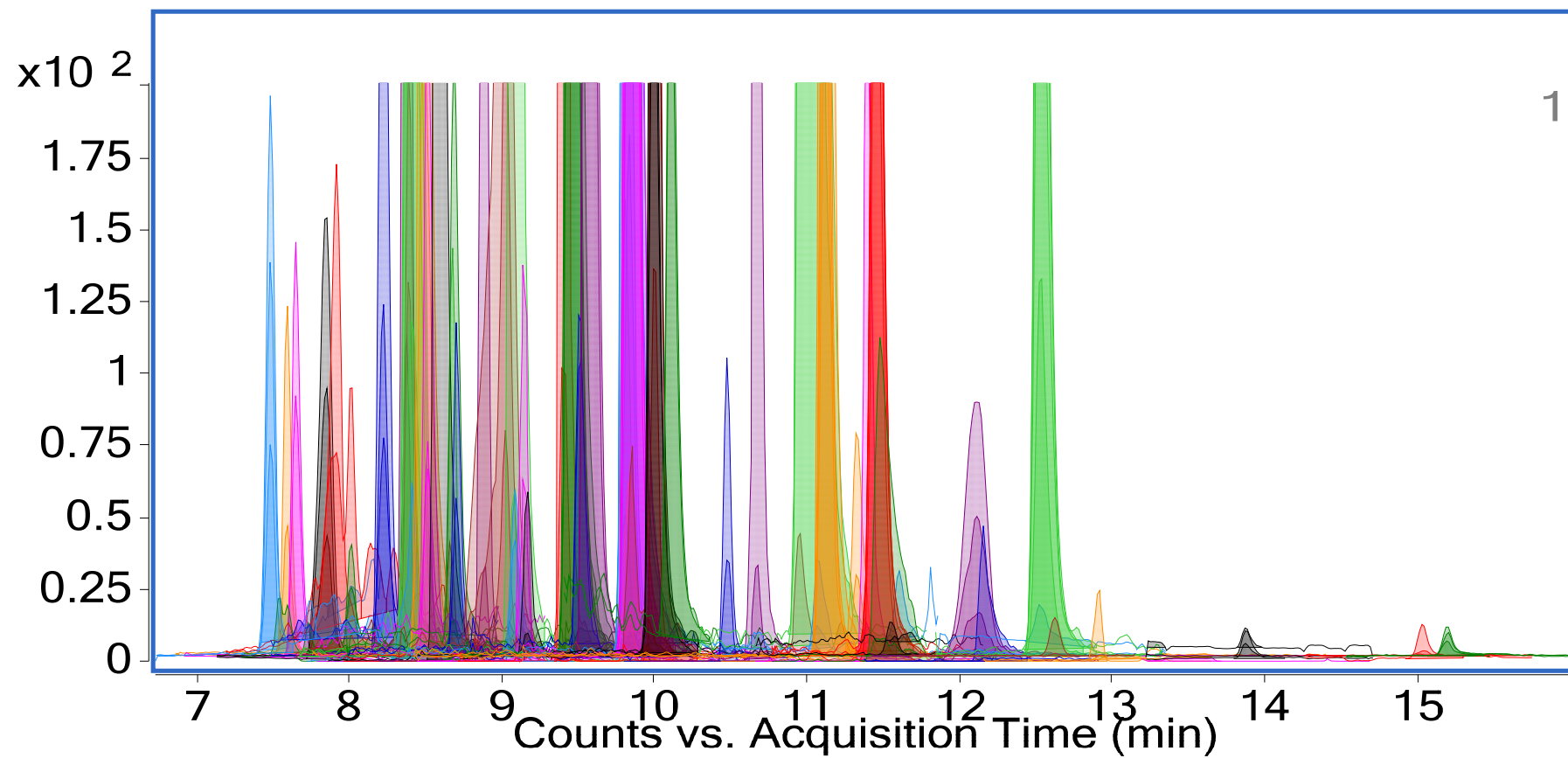
Trace Organic Compounds in Drinking Water

- 51 representative compounds
- 1260 Infinity II HPLC
 - Column: Poroshell 120 EC C18, 3.0 x 50 mm, 2.7 μ m (p/n 699975-302)
 - Mobile Phases: H₂O (1mM NH₄OAc + 0.1mM NH₄F + 0.01% HOAc) and ACN (0.01% HOAc)
 - Flow Rate: 0.4 ml/min
- Flex Cube Online SPE
 - **900uL** injection volume.
 - No bench-top sample pretreatment.
 - SPE Cartridge: PLRP, 2.1x12.5mm
 - Load: H₂O, 0.1% Formic Acid
 - Clean: 1:1 ACN/IPA
- Fast → 21 min total (including post time)!

AJS Source and MS Parameters

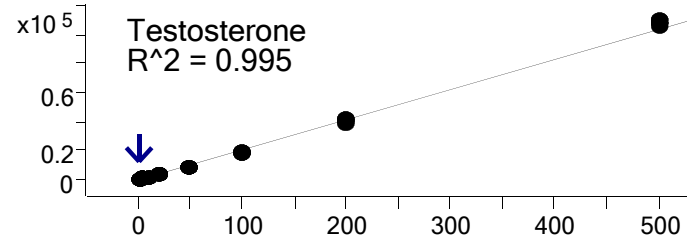
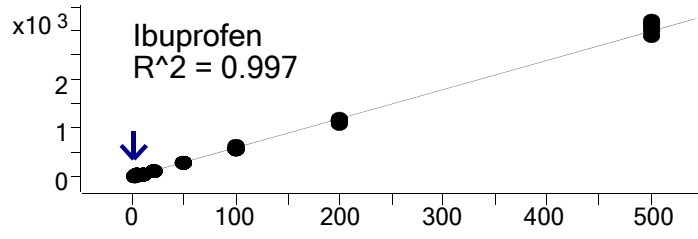
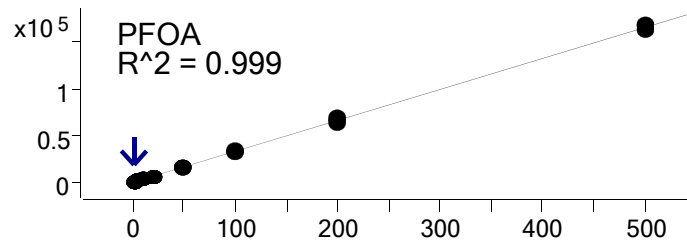
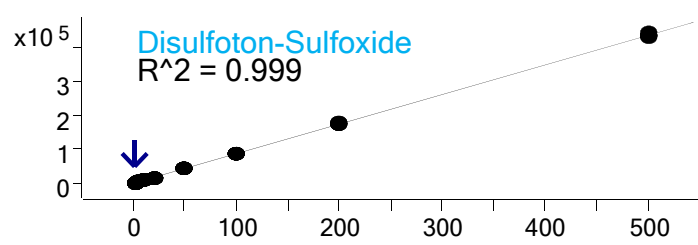
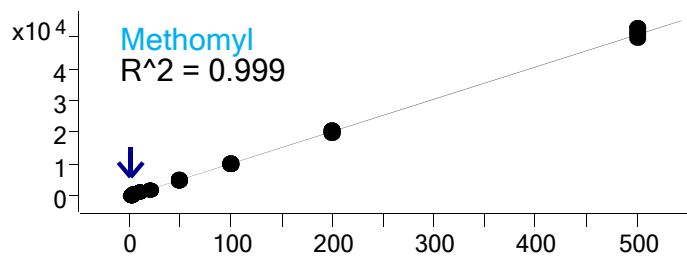
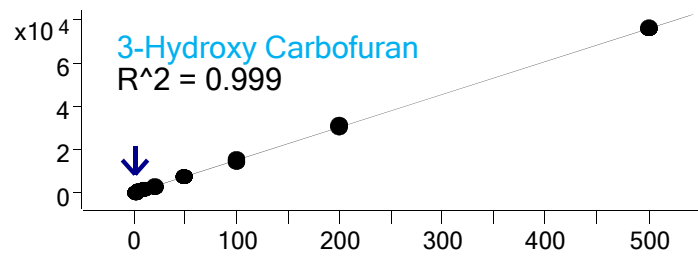
Drying Gas Temp	250°C
Drying gas Flow	11L/min
Sheath Gas Temp	375°C
Sheath Gas Flow	12L/min
Nebulizer Pressure	45 psi
Nozzle Voltage (V)	500 (+); 500 (-)
Capillary Voltage (V)	4000 (+); 3500 (-)

Excellent Signal Response



Signal response at 10 ppt with 900 uL injection

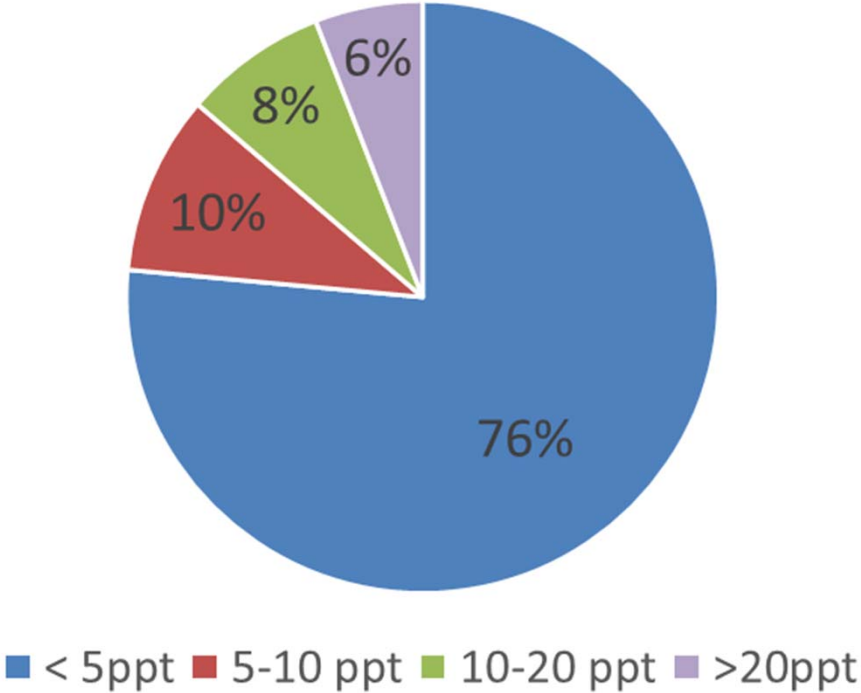
Excellent Dynamic Range (1.25 ng/L to 500 ng/L)



Concentration (pg/ml)

Concentration (pg/ml)

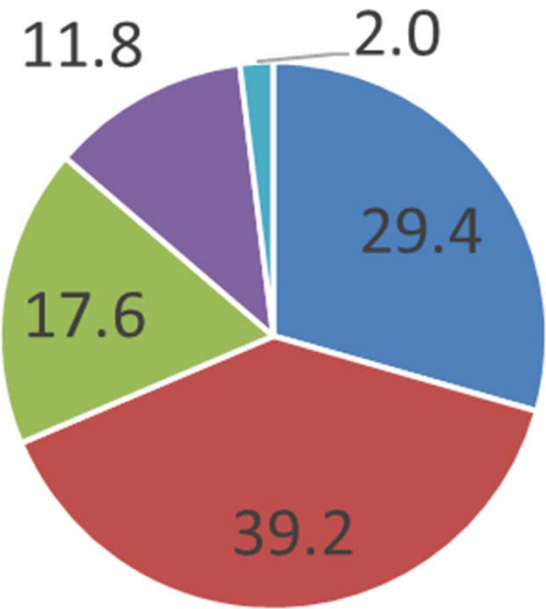
Detection Sensitivity



Distribution of the limits of quantitation for 51 contaminants (accuracy 80-120%)

Analyte	LOQ (ng/L)
PFBS	5
PFDA	20
PFDoA	10
PFHpA	1.25
PFHxA	2.5
PFHxS	2.5
PFNA	2.5
PFOA	1.25
PFPeA	20
PFUdA	50

Detection Precision



%RSD at the lowest concentration for accurate quantitation (n=6)

■ 1-5% ■ 5-10% ■ 10-15% ■ 15-20% ■ >20%

Conclusions

- PFAS compounds included in TOrC method.
- Online SPE is fast, and can streamline your laboratory workflows.
- Only 900ul of sample required.
- Sensitive and reproducible results.
- Quantitation limits below 50 ppt – many in single digit ppt range





UNBELIEVABLY POWERFUL
REMARKABLY SMALL

Ultivo Triple Quad LC/MS

Fit for Purpose!

References

Application Note



Analysis of per/polyfluoroalkyl substances (PFASs) in drinking water using the Agilent Ultivo triple quadrupole LC/MS

5991-8969EN

Application Note



Sensitive Detection of Trace Organic Contaminants in Water

Using Agilent 1290 Infinity FlexCube Online SPE and Agilent Ultivo Triple Quadrupole LC/MS

5991-8767EN

Thank you Tarun Anumol and Dorothy Yang