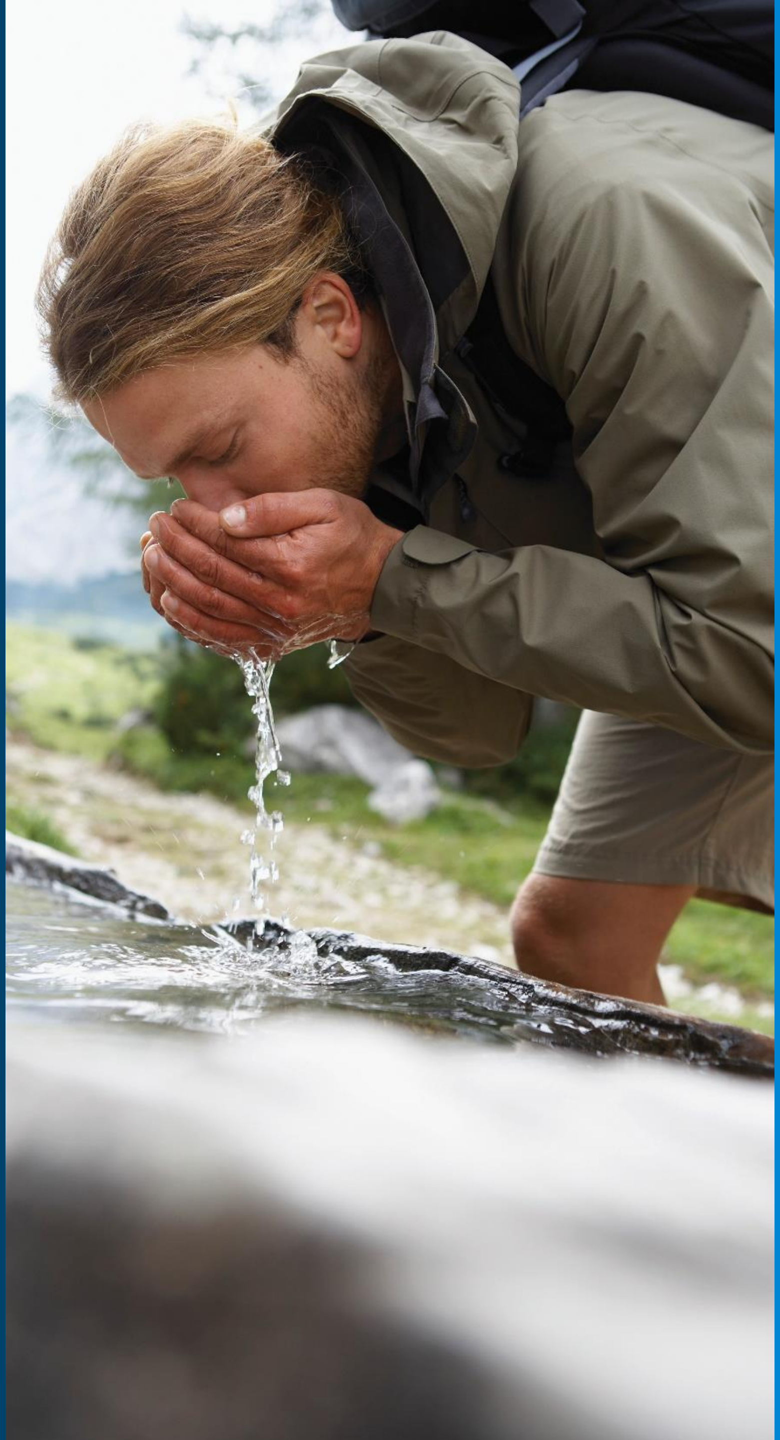
PFAS Analysis in the Environment

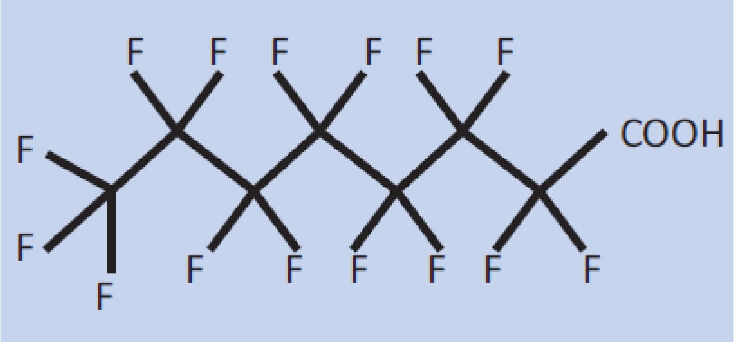
Agilent solutions to improve productivity & robustness



Tarun Anumol, Ph.D.
Global Environment Industry Manager
Agilent Technologies Inc.
February 2019

Terminology

Perfluoroalkyl substance

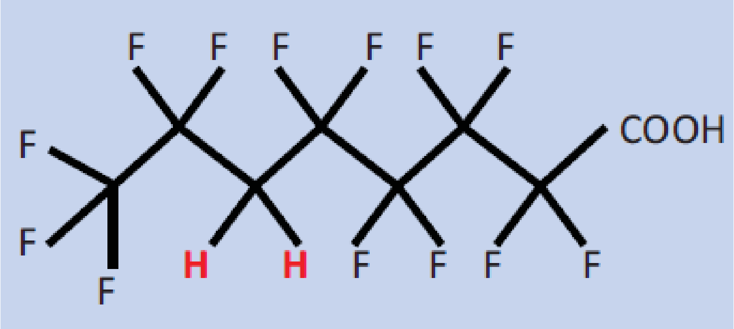


ALL H atoms linked to C in alkyl chain are substituted with F

PFOS

PFOA

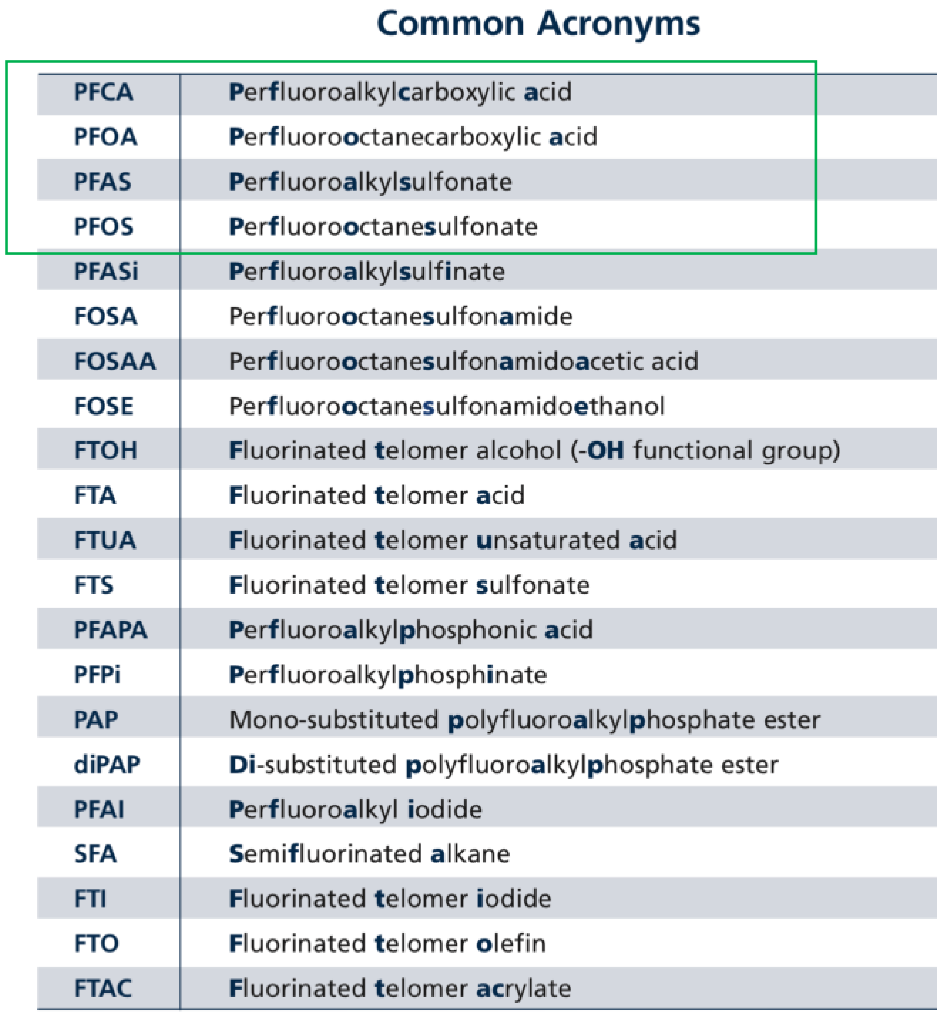
Polyfluoroalkyl substance



SOME *(but not all)* H atoms linked to C in alkyl chain are substituted with F

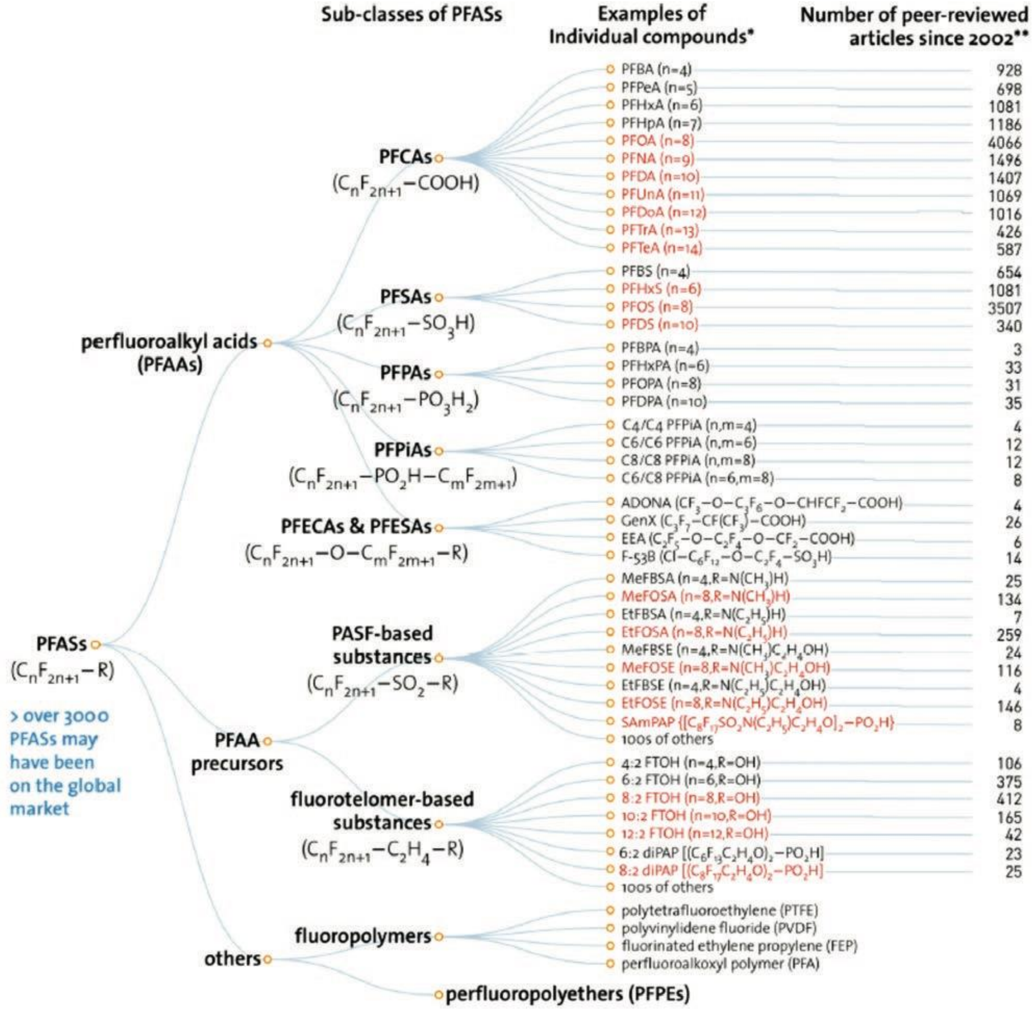
PFAS Classifications and Terminology

>4000 PFAS compounds in commerce



Common Acronyms

PFCA	**P**er**f**luoroalkyl**c**arboxylic **a**cid
PFOA	**P**er**f**luoro**o**ctanecarboxylic **a**cid
PFAS	**P**er**f**luoro**a**lkyl**s**ulfonate
PFOS	**P**er**f**luoro**o**ctane**s**ulfonate
PFASi	**P**er**f**luoro**a**lkyl**s**ul**fi**nate
FOSA	Per**f**luoro**o**ctane**s**ulfon**a**mide
FOSAA	Per**f**luoro**o**ctane**s**ulfon**a**mido**a**cetic acid
FOSE	Per**f**luoro**o**ctane**s**ulfonamido**e**thanol
FTOH	**F**luorinated **t**elomer alcohol (-**OH** functional group)
FTA	**F**luorinated **t**elomer **a**cid
FTUA	**F**luorinated **t**elomer **u**nsaturated **a**cid
FTS	**F**luorinated **t**elomer **s**ulfonate
PFAPA	**P**er**f**luoro**a**lkyl**p**hosphonic **a**cid
PFPi	**P**er**f**luoroalkyl**p**hosph**i**nate
PAP	Mono-substituted **p**olyfluoro**a**lkyl**p**hosphate ester
diPAP	**Di**-substituted **p**olyfluoro**a**lkyl**p**hosphate ester
PFAI	**P**er**f**luoro**a**lkyl **i**odide
SFA	**S**emi**f**luorinated **a**lkane
FTI	**F**luorinated **t**elomer **i**odide
FTO	**F**luorinated **t**elomer **o**lefin
FTAC	**F**luorinated **t**elomer **ac**rylate

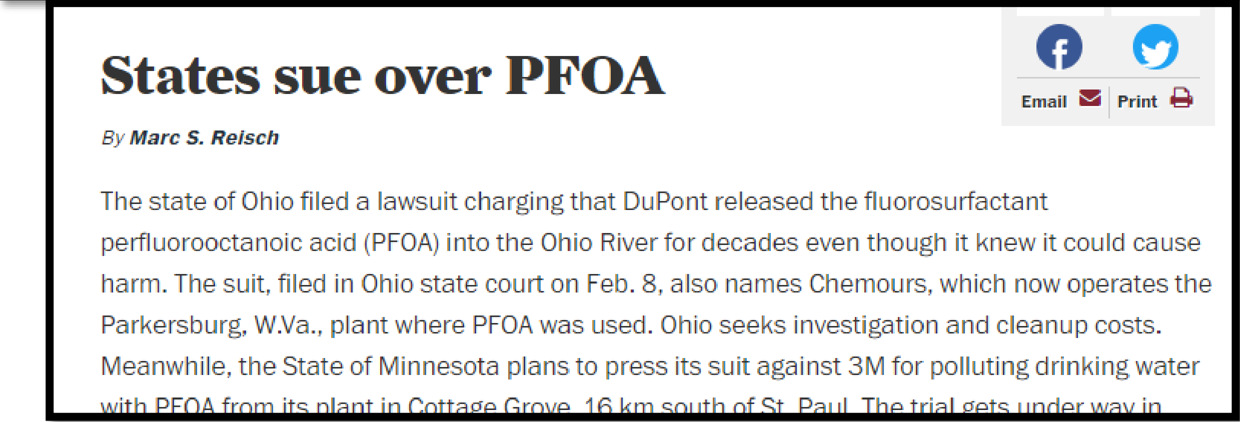


Wang, Z *et al.* (2017). *Environ. Sci. Technol.* 51, 2508-2518.

Per/Polyfluoroalkyl substances (PFAS)
Unique Properties

- Thermal & Chemical stability: grease-proof food packaging, stain repellents
- Zwitterionic properties: surfactants
- Surface-tension lowering: fire-fighting foams



States sue over PFOA

By **Marc S. Reisch**

The state of Ohio filed a lawsuit charging that DuPont released the fluorosurfactant perfluorooctanoic acid (PFOA) into the Ohio River for decades even though it knew it could cause harm. The suit, filed in Ohio state court on Feb. 8, also names Chemours, which now operates the Parkersburg, W.Va., plant where PFOA was used. Ohio seeks investigation and cleanup costs. Meanwhile, the State of Minnesota plans to press its suit against 3M for polluting drinking water with PFOA from its plant in Cottage Grove, 16 km south of St. Paul. The trial gets under way in

Michigan declares state of emergency in town with high PFOS, PFOA levels in drinking water

Source of perfluorocarbon pollution as yet unknown, state says

The New York Times Magazine

NOTEBOOK

The Story Behind the E.P.A.'s Contaminated Water Revelation

TUESDAY, MAY 22, 2018

By David Andrews, Senior Scientist

REPORT: UP TO 110 MILLION AMERICANS COULD HAVE PFAS-CONTAMINATED DRINKING WATER

PFAS Tap Water Data Was Funded By Taxpayers But Kept Secret

Regulatory Updates
What is going on?

Who are the agencies involved in regulating/monitoring PFAS in the US?

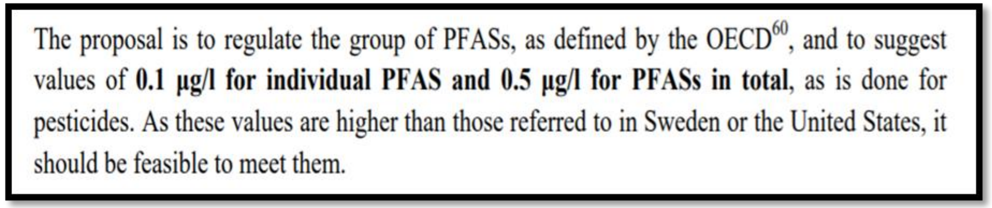
US Environmental Protection Agency (U.S. EPA) – for federal compliance

State EPA's & Department of Environmental Protection (DEP) – for State compliance

Department of Defense – for Military sites

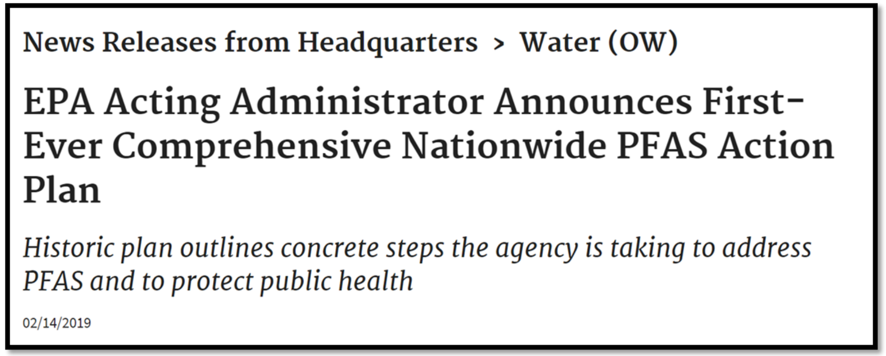
Industrial companies – for individual discharge & remediation sites

Water Utilities – to meet discharge permits



The proposal is to regulate the group of PFASs, as defined by the OECD[60], and to suggest values of **0.1 µg/l for individual PFAS and 0.5 µg/l for PFASs in total**, as is done for pesticides. As these values are higher than those referred to in Sweden or the United States, it should be feasible to meet them.

EU Drinking Water Directive guidelines



News Releases from Headquarters > Water (OW)

EPA Acting Administrator Announces First-Ever Comprehensive Nationwide PFAS Action Plan

Historic plan outlines concrete steps the agency is taking to address PFAS and to protect public health

02/14/2019

This relates to federal status as a contaminant in drinking water only.

Bill would declare PFAS chemicals hazardous substances under Superfund law

Melissa Nann Burke, The Detroit News Published 7:26 p.m. ET Jan. 14, 2019 | Updated 11:05 a.m. ET Jan. 15, 2019

Equipment used to test for PFAS (per- and polyfluoroalkyl chemicals) in drinking water at Trident Laboratories in Holland, Mich., pictured on Monday, June 18, 2018. Trident Labs added testing for perfluorinated chemicals, known as PFAS, in March after toxic contamination was identified at a former tannery near Rockford. *(Photo: Cory Morse, Cory Morse,The Grand Rapids Press via AP)*

This bill will require PFAS to be monitored at all superfund sites

Regulatory Guidance for PFAS in Drinking Water

Compound	Agency/State	Concentration (ng/L)	Year
PFOA + PFOS	EPA DWHA	70	2016
PFOA	MN	35	2017
PFOS	MN	27	2017
PFOA	NJ	14 (40)	2017 (2007)
GenX	NC	140	2017
PFOA/PFOS	UK	300 (Reg. 10)	2009
PFOS/PFHxS	AUS	70	2016
PFOS	VIC EPA	0.23	2016 (Proposed)

Available Methods

US EPA

EPA 537/537.1
(Oct 2018)
Drinking Water
ONLY

EPA 533
(expected 2020)

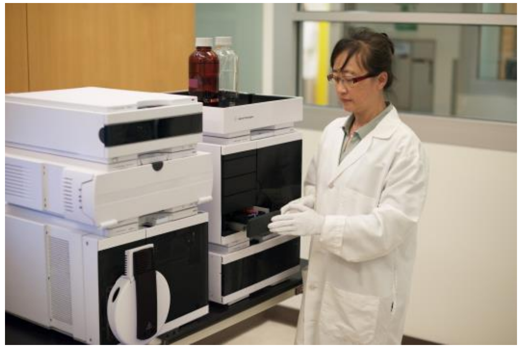
Draft EPA 8327
Non-potable Water (wastewater, groundwater) – 2019

EPA 8328 (proposed)
Soils and solids

Department of Defense – Military Testing
Draft method exp. In 2019 – SPE
Currently: must meet **QSM ver. 5.1** or higher

ASTM INTERNATIONAL

ASTM 7979 (water); **ASTM 7968** (solids)

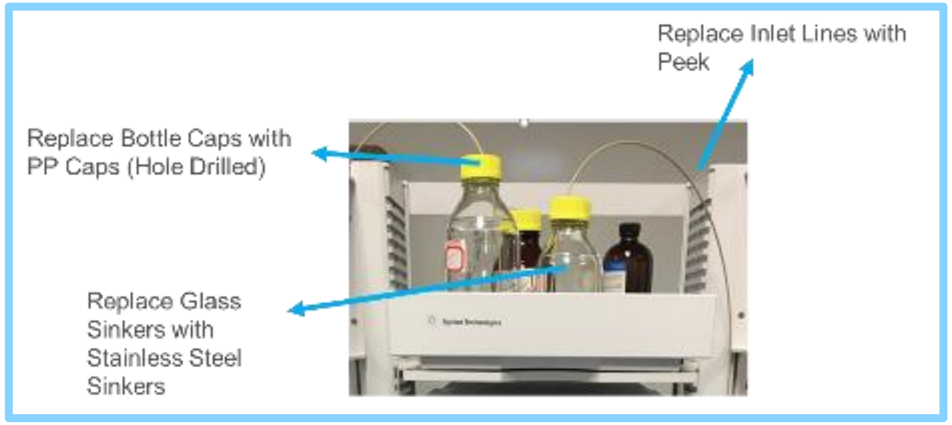


Non-compliance
Research
Academia
Industrial Clients

Ex. Direct injection; online SPE

PFAS Analysis – LC Instrument Setup

Eliminate Background Contamination



Replace Inlet Lines with Peek

Replace Bottle Caps with PP Caps (Hole Drilled)

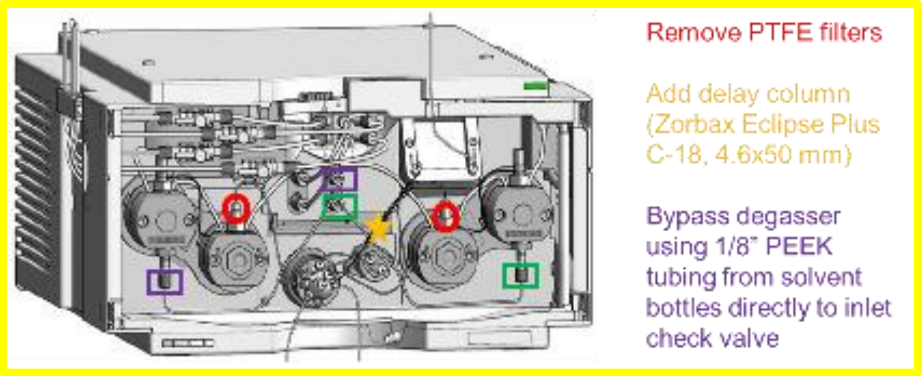
Replace Glass Sinkers with Stainless Steel Sinkers

Potential Contamination Sources

- Solvents
- Filtration apparatus
- Teflon lined tubing

Use snap top polyethylene membrane caps (Septa of regular caps has PTFE)

Replace rotor seal with VESPEL



Remove PTFE filters

Add delay column (Zorbax Eclipse Plus C-18, 4.6x50 mm)

Bypass degasser using 1/8" PEEK tubing from solvent bottles directly to inlet check valve

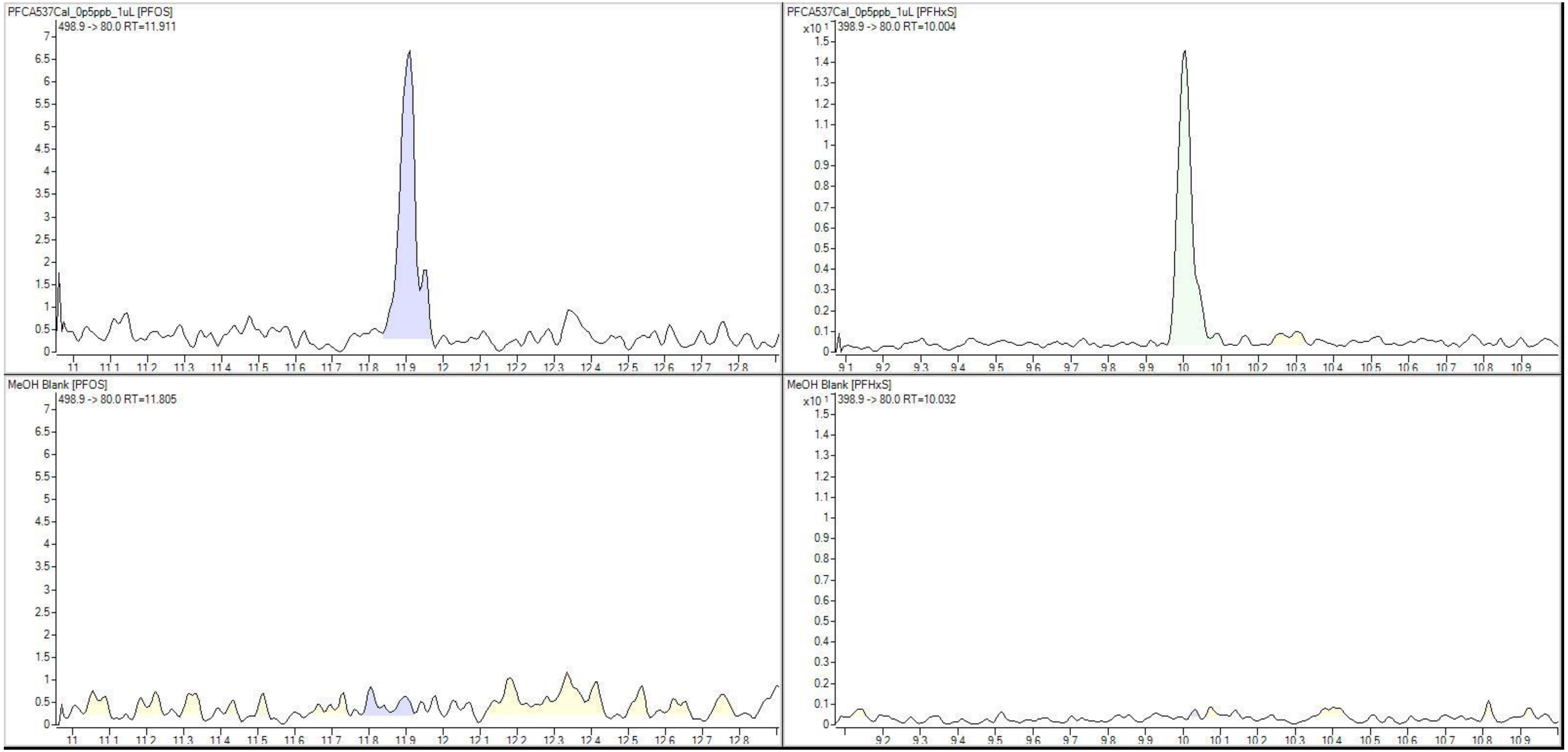
Application Note: Recommended Plumbing Configurations for Reduction in Per/Polyfluoroalkyl Substance Background with Agilent 1260/1290 Infinity (II) LC's, Agilent Application Note (5991-7863EN)

PFAS Analysis – LC Instrument Setup
Eliminate Background Contamination

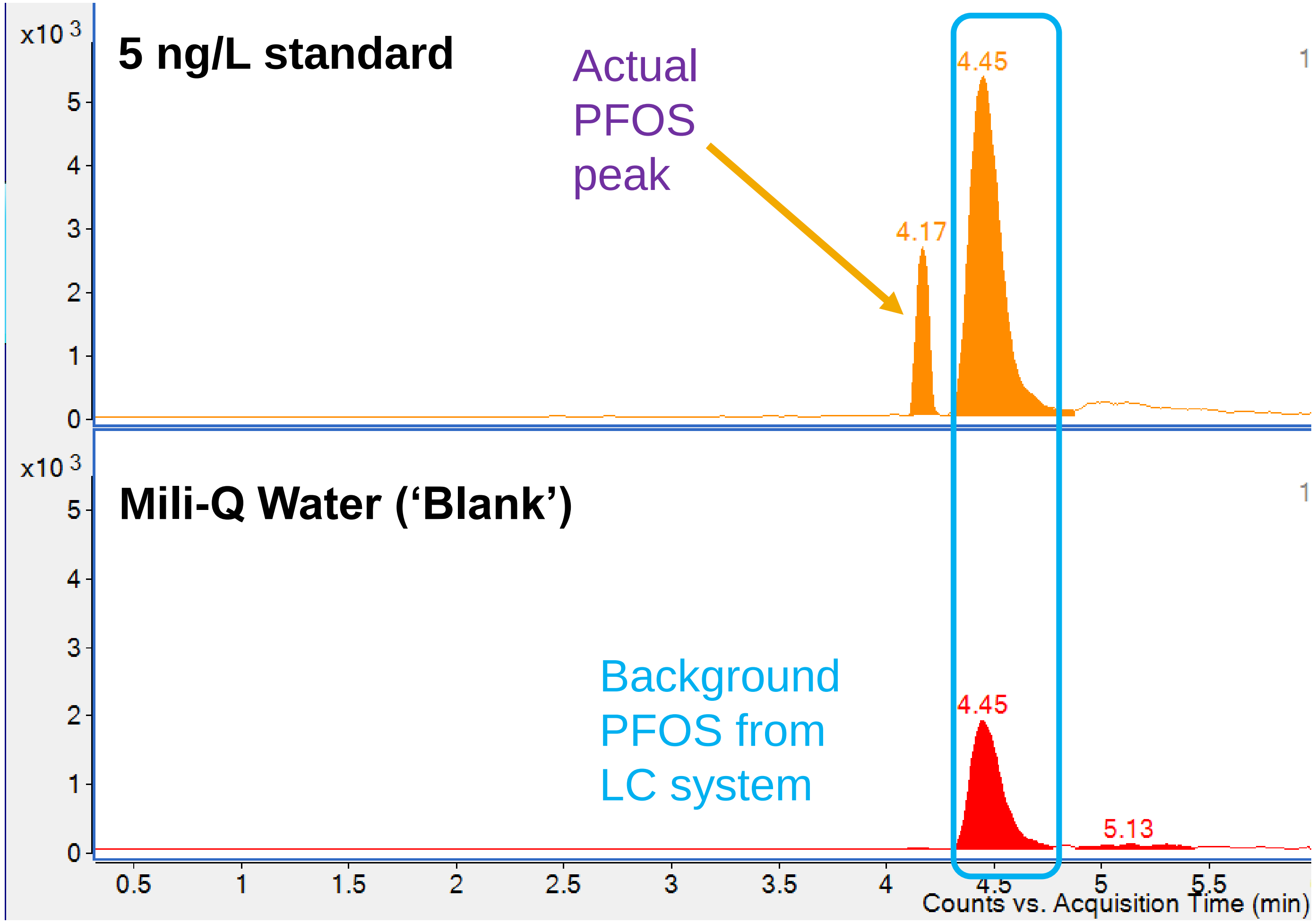
PFOS **PFHxS**

Before Modification

After Modification



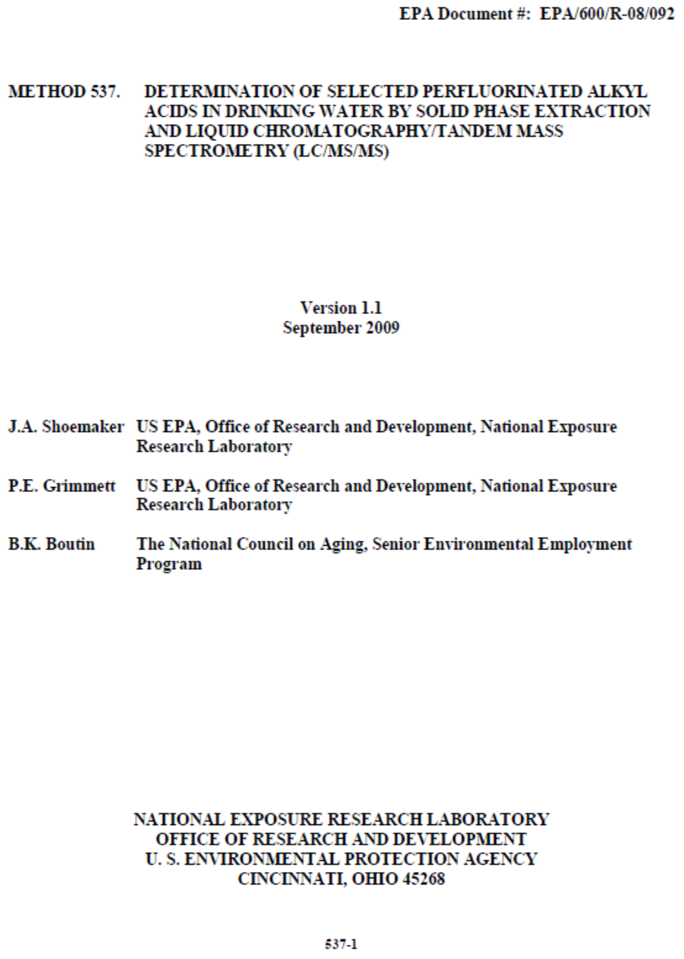
PFAS Instrument Setup
Background Contamination



- **The use of a Delay column is convenient when running multiple methods on the same instrument.**
- **"Delay" column and not a "Trapping" column. I.e. the background peak will be retention time separated but will be present.**
- **The delay column does not account for any contamination after the pump (the autosampler)**

EPA Method 537/537.1
Analysis of PFAS in drinking water

- Method is written ONLY for Drinking Water.
- 18 Analytes in EPA 537.1 (14 analytes in EPA 537)
- Method requires Solid Phase Extraction + LC/MS/MS
- Agilent polystyrenedivinylbenzene (SDVB) SPE cartridge
- 10 µL injection (96/4: MeOH/Water)
- 37 min run time
- MDLs: <1-5 ng/L



EPA Document #: EPA/600/R-08/092

METHOD 537. DETERMINATION OF SELECTED PERFLUORINATED ALKYL ACIDS IN DRINKING WATER BY SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY (LC/MS/MS)

Version 1.1
September 2009

J.A. Shoemaker	US EPA, Office of Research and Development, National Exposure Research Laboratory
P.E. Grimmett	US EPA, Office of Research and Development, National Exposure Research Laboratory
B.K. Boutin	The National Council on Aging, Senior Environmental Employment Program

NATIONAL EXPOSURE RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

537-1

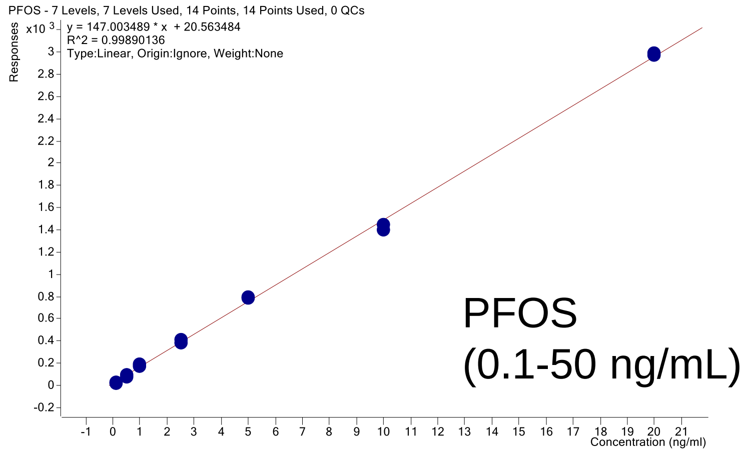
https://cfpub.epa.gov/si/si_public_record_Report.cfm?dirEntryId=343042&Lab=NERL

Analysis of PFAS
EPA 537+ analytes

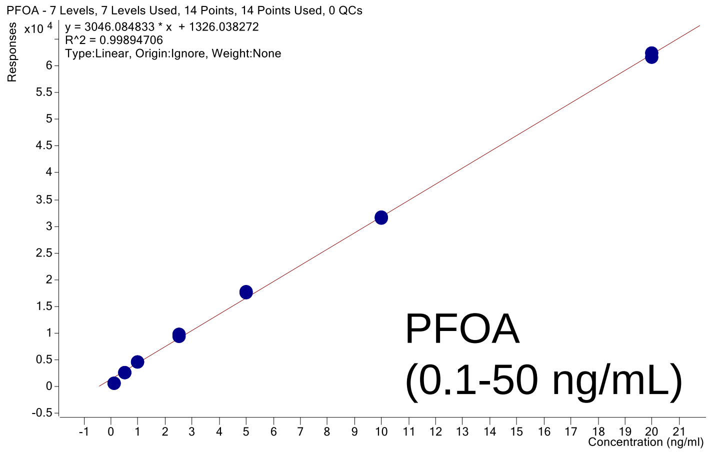
Infinity II
HPLC Stack

Ultivo
Triple Quad

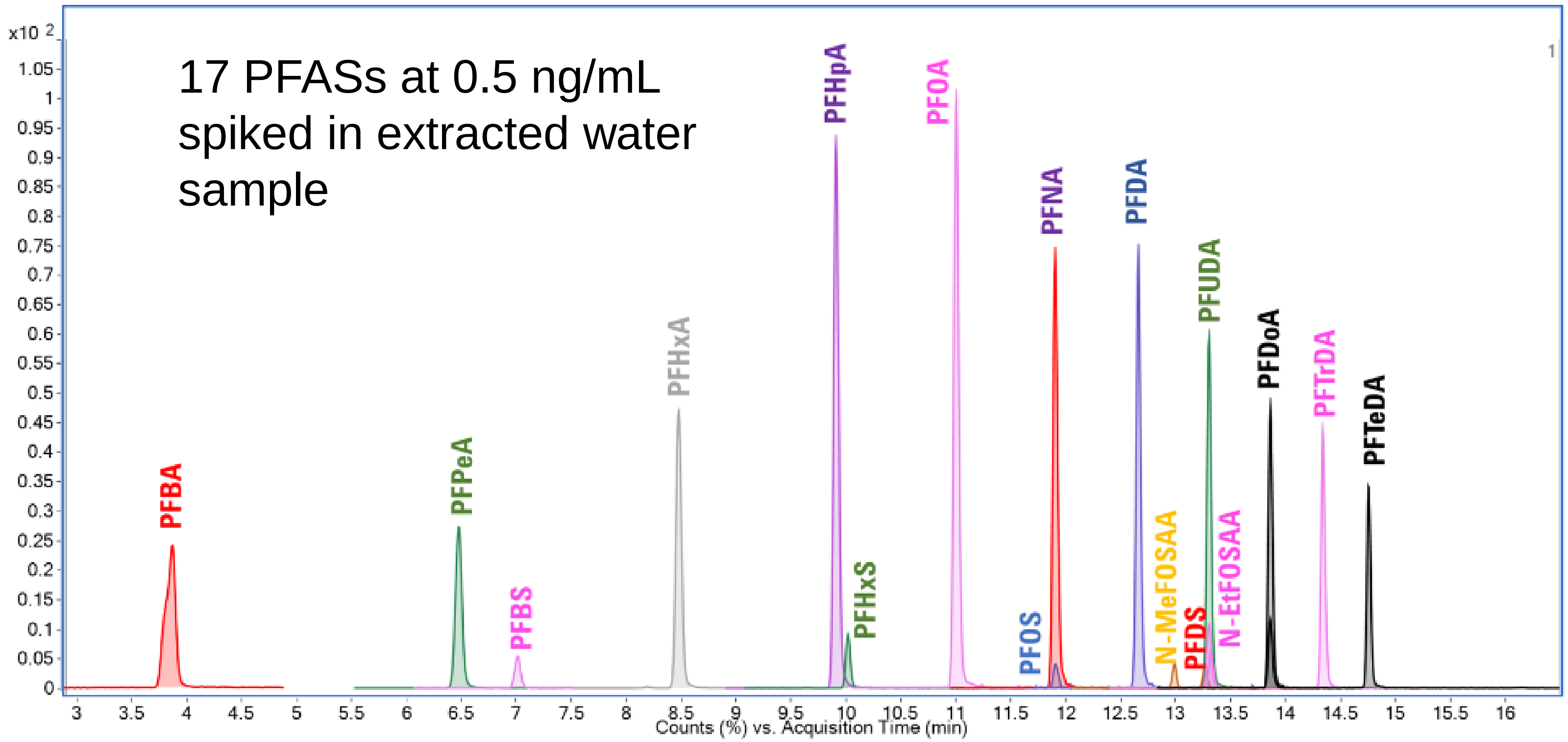
Analysis of per/polyfluoroalkyl substances (PFASs) in drinking water using the Agilent Ultivo triple quadrupole LC/MS; **5991-8969EN**



PFOS
(0.1-50 ng/mL)

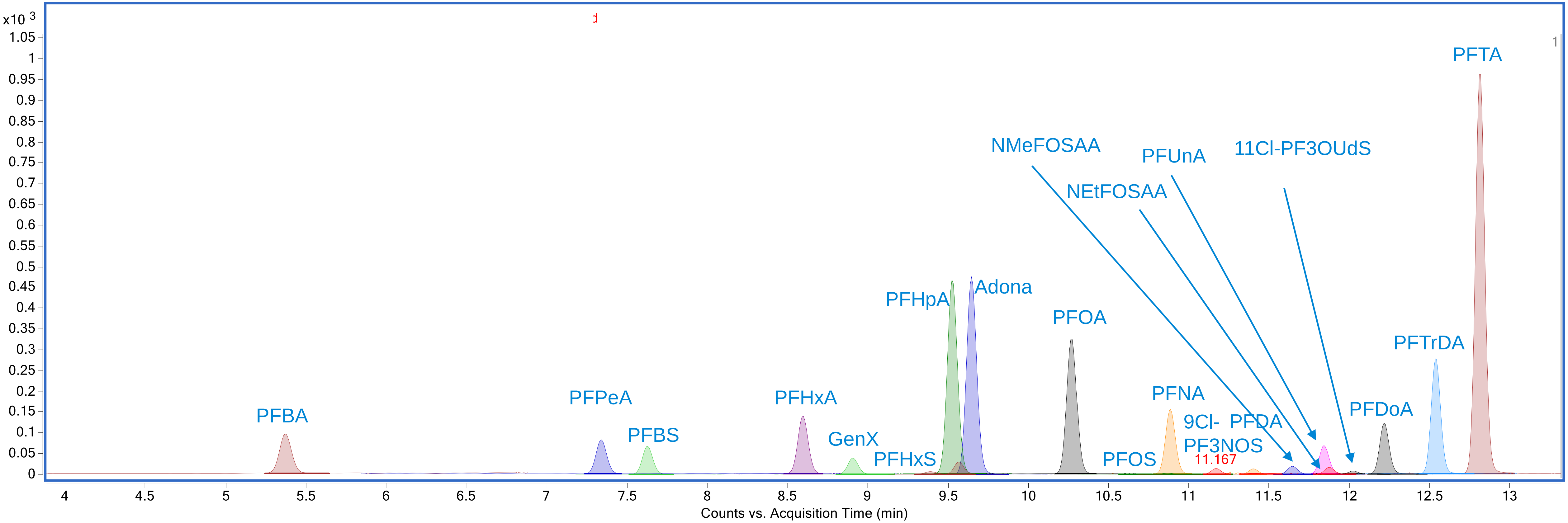


PFOA
(0.1-50 ng/mL)



17 PFASs at 0.5 ng/mL spiked in extracted water sample

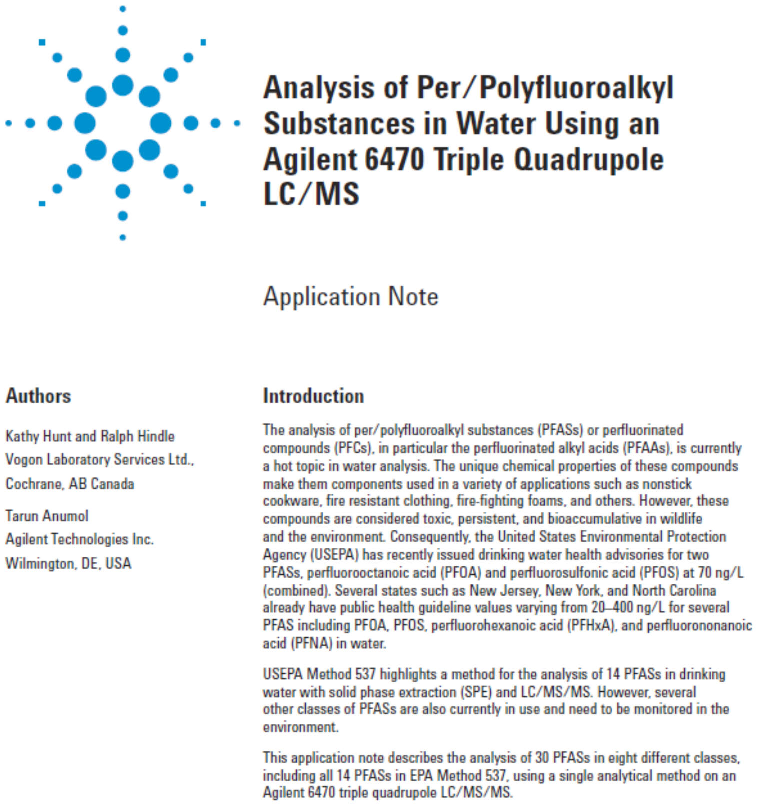
USEPA Method 537.1
Addition of 4 analytes in methods + PFBA & PFPeA with Ultivo LC-MS/MS



Agilent Zorbax Eclipse Plus C18, 3.0 x 50 mm, 1.8 um column

EPA Method 537.1 “Modified”
adding analytes, changes to SPE, lower MRLs etc.

More analytes; Lower DLs



Analysis of Per/Polyfluoroalkyl Substances in Water Using an Agilent 6470 Triple Quadrupole LC/MS

Application Note

Authors

Kathy Hunt and Ralph Hindle
Vogon Laboratory Services Ltd.,
Cochrane, AB Canada

Tarun Anumol
Agilent Technologies Inc.
Wilmington, DE, USA

Introduction

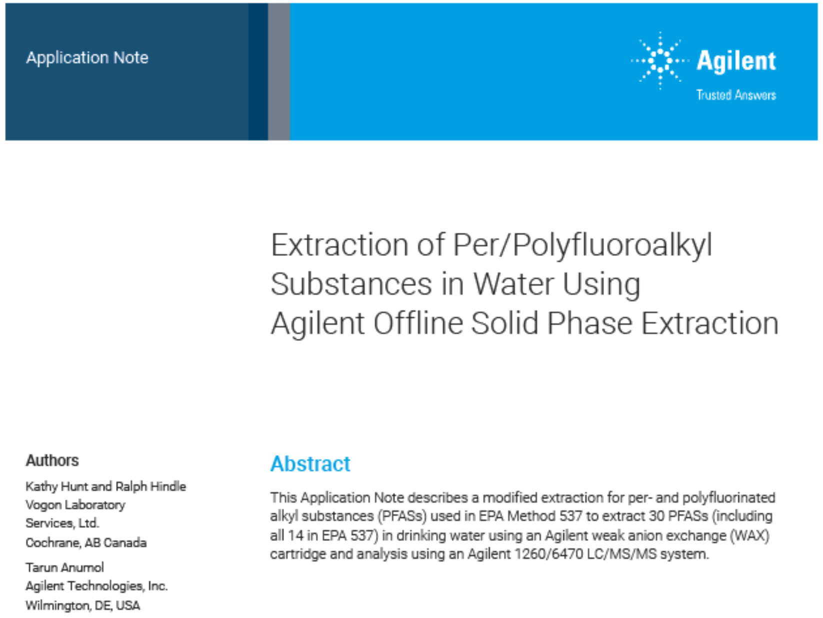
The analysis of per/polyfluoroalkyl substances (PFASs) or perfluorinated compounds (PFCs), in particular the perfluorinated alkyl acids (PFAAs), is currently a hot topic in water analysis. The unique chemical properties of these compounds make them components used in a variety of applications such as nonstick cookware, fire resistant clothing, fire-fighting foams, and others. However, these compounds are considered toxic, persistent, and bioaccumulative in wildlife and the environment. Consequently, the United States Environmental Protection Agency (USEPA) has recently issued drinking water health advisories for two PFASs, perfluorooctanoic acid (PFOA) and perfluorosulfonic acid (PFOS) at 70 ng/L (combined). Several states such as New Jersey, New York, and North Carolina already have public health guideline values varying from 20–400 ng/L for several PFAS including PFOA, PFOS, perfluorohexanoic acid (PFHxA), and perfluorononanoic acid (PFNA) in water.

USEPA Method 537 highlights a method for the analysis of 14 PFASs in drinking water with solid phase extraction (SPE) and LC/MS/MS. However, several other classes of PFASs are also currently in use and need to be monitored in the environment.

This application note describes the analysis of 30 PFASs in eight different classes, including all 14 PFASs in EPA Method 537, using a single analytical method on an Agilent 6470 triple quadrupole LC/MS/MS.

Application note: 5991-7951EN

Different SPE cartridge – better recoveries



Application Note

Agilent
Trusted Answers

Extraction of Per/Polyfluoroalkyl Substances in Water Using Agilent Offline Solid Phase Extraction

Authors

Kathy Hunt and Ralph Hindle
Vogon Laboratory
Services, Ltd.
Cochrane, AB Canada

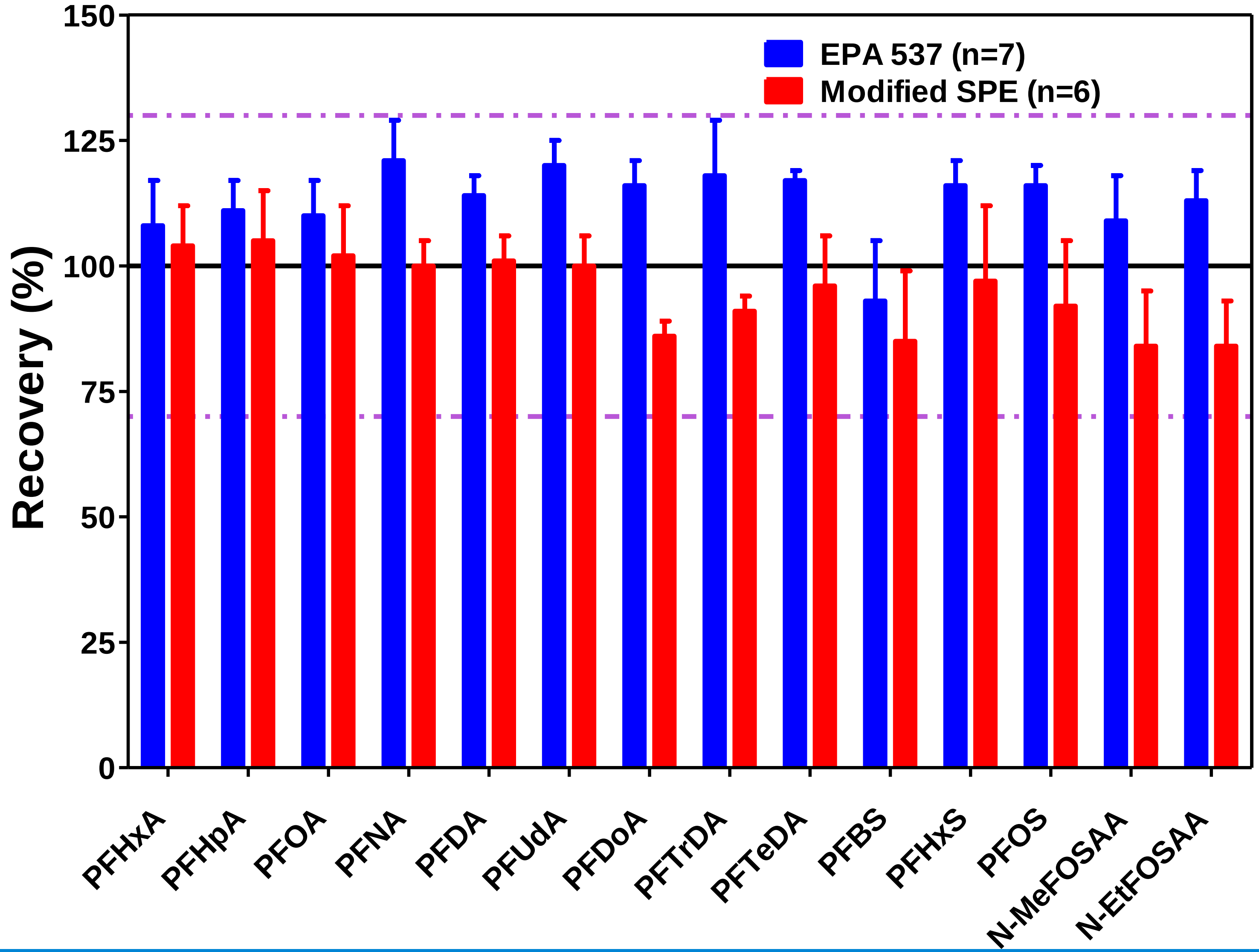
Tarun Anumol
Agilent Technologies, Inc.
Wilmington, DE, USA

Abstract

This Application Note describes a modified extraction for per- and polyfluorinated alkyl substances (PFASs) used in EPA Method 537 to extract 30 PFASs (including all 14 in EPA 537) in drinking water using an Agilent weak anion exchange (WAX) cartridge and analysis using an Agilent 1260/6470 LC/MS/MS system.

Application note: 5994-0250EN

Solid Phase Extraction for Water
USEPA 537 vs Modified



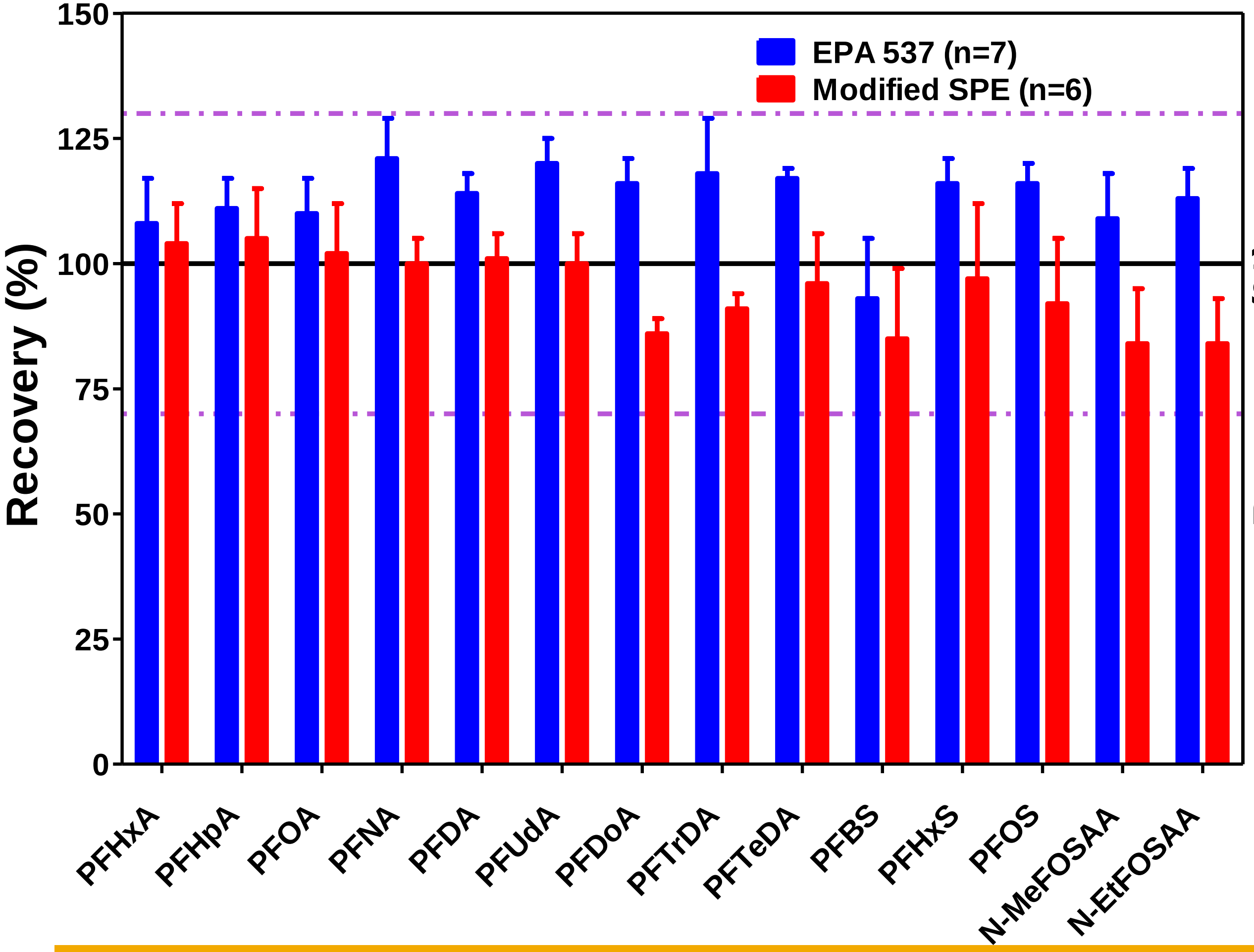
- **Recoveries calculated in Reagent Water**
- **Modified SPE cartridge: SampliQ WAX cartridge (6 cc, 150 mg)**
- **All recoveries between 70-130 %**

Spiking concentrations:

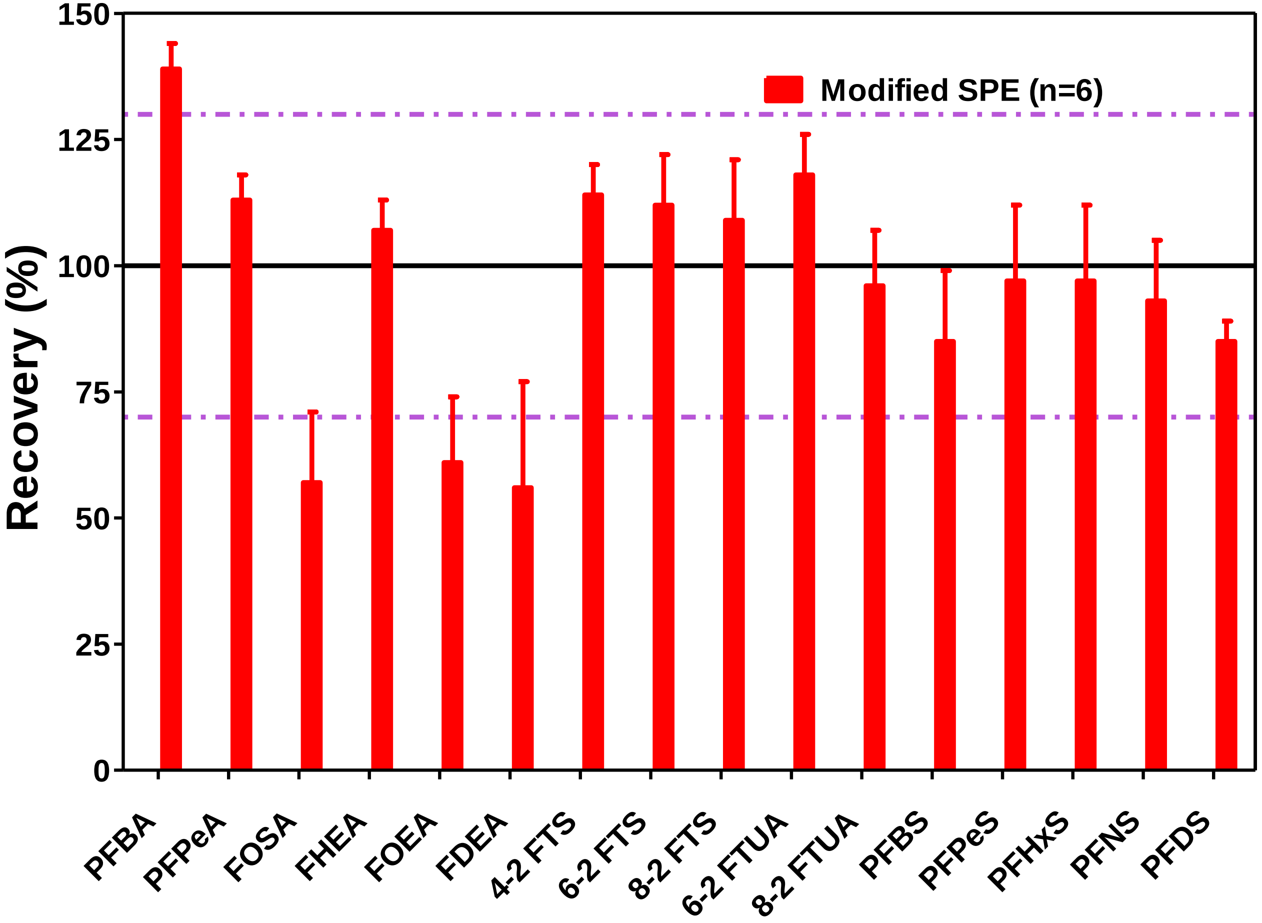
Modified SPE: 4 ng/L in 250 mL
EPA 537: 5-21 ng/L in 250 mL

Final extract: 1 mL ~96% MeOH

Solid Phase Extraction
USEPA 537 vs Modified



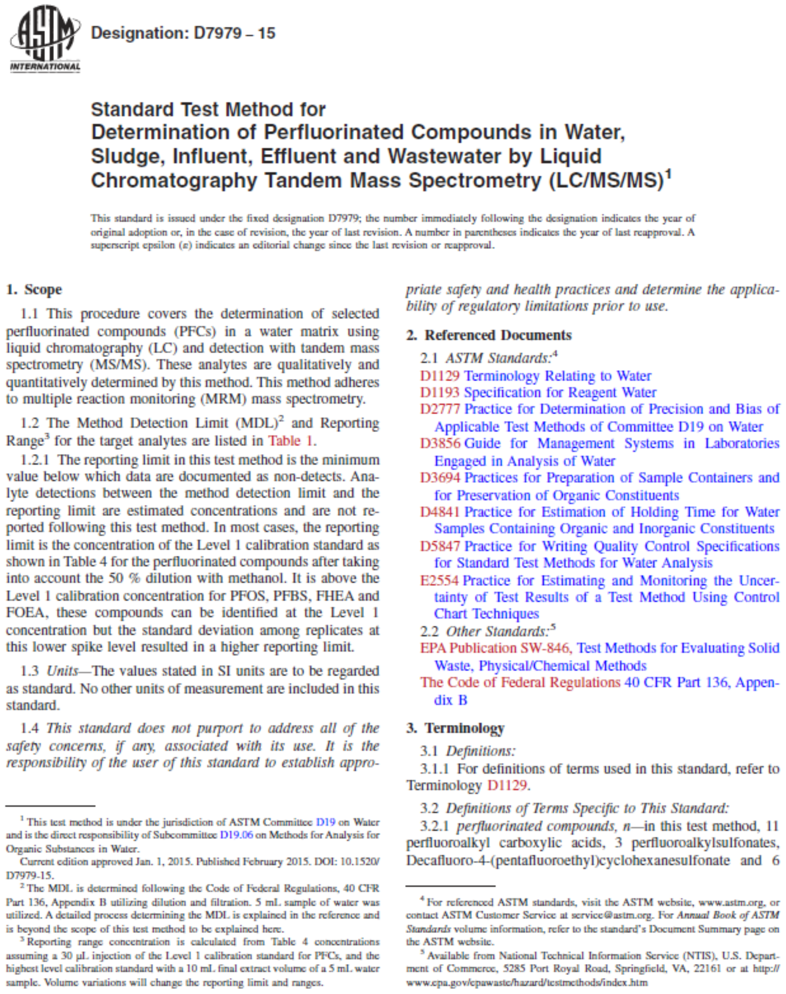
EPA 537 Analytes



Additional PFAS including ASTM

EPA 8327 (draft) & ASTM 7979
Analysis of PFAS in ground, surface and wastewater

- Method is for non-potable waters – surface water, groundwater, wastewater
- EPA 8327 is proposed for release to public in Feb. It is similar as ASTM 7979
- 28 Analytes
- Meant for high throughput; very simple and quick sample prep.
- Method using simple dilution & acidification before large volume injection
- **30** µL injection (50/50: MeOH/Water)
- 21 min run time
- MRLs: 10 ng/L (range: 10-400 ng/L)



ASTM INTERNATIONAL

Designation: D7979 – 15

Standard Test Method for
Determination of Perfluorinated Compounds in Water, Sludge, Influent, Effluent and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)[1]

This standard is issued under the fixed designation D7979; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This procedure covers the determination of selected perfluorinated compounds (PFCs) in a water matrix using liquid chromatography (LC) and detection with tandem mass spectrometry (MS/MS). These analytes are qualitatively and quantitatively determined by this method. This method adheres to multiple reaction monitoring (MRM) mass spectrometry.

1.2 The Method Detection Limit (MDL)[2] and Reporting Range[3] for the target analytes are listed in Table 1.

1.2.1 The reporting limit in this test method is the minimum value below which data are documented as non-detects. Analyte detections between the method detection limit and the reporting limit are estimated concentrations and are not reported following this test method. In most cases, the reporting limit is the concentration of the Level 1 calibration standard as shown in Table 4 for the perfluorinated compounds after taking into account the 50 % dilution with methanol. It is above the Level 1 calibration concentration for PFOS, PFBS, FHEA and FOEA, these compounds can be identified at the Level 1 concentration but the standard deviation among replicates at this lower spike level resulted in a higher reporting limit.

1.3 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[4]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
E2554 Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques

2.2 *Other Standards:*[5]

EPA Publication SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods
The Code of Federal Regulations 40 CFR Part 136, Appendix B

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *perfluorinated compounds, n*—in this test method, 11 perfluoroalkyl carboxylic acids, 3 perfluoroalkylsulfonates, Decafluoro-4-(pentafluoroethyl)cyclohexanesulfonate and 6

---

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

Current edition approved Jan. 1, 2015. Published February 2015. DOI: 10.1520/D7979-15.

[2] The MDL is determined following the Code of Federal Regulations, 40 CFR Part 136, Appendix B utilizing dilution and filtration. 5 mL sample of water was utilized. A detailed process determining the MDL is explained in the reference and is beyond the scope of this test method to be explained here.

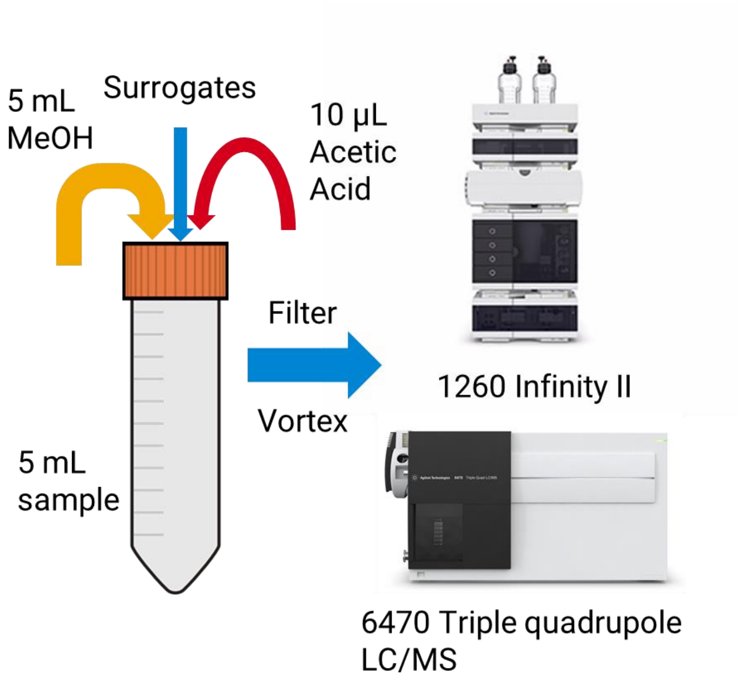
[3] Reporting range concentration is calculated from Table 4 concentrations assuming a 30 µL injection of the Level 1 calibration standard for PFCs, and the highest level calibration standard with a 10 mL final extract volume of a 5 mL water sample. Volume variations will change the reporting limit and ranges.

[4] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[5] Available from National Technical Information Service (NTIS), U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA, 22161 or at http://www.epa.gov/epawaste/hazard/testmethods/index.htm

Sample Preparation Protocol

- ASTM 7979
- EPA draft method 8327



5 mL water sample

Add surrogate (internal standard) mix solution

Add 5 mL MeOH, mix

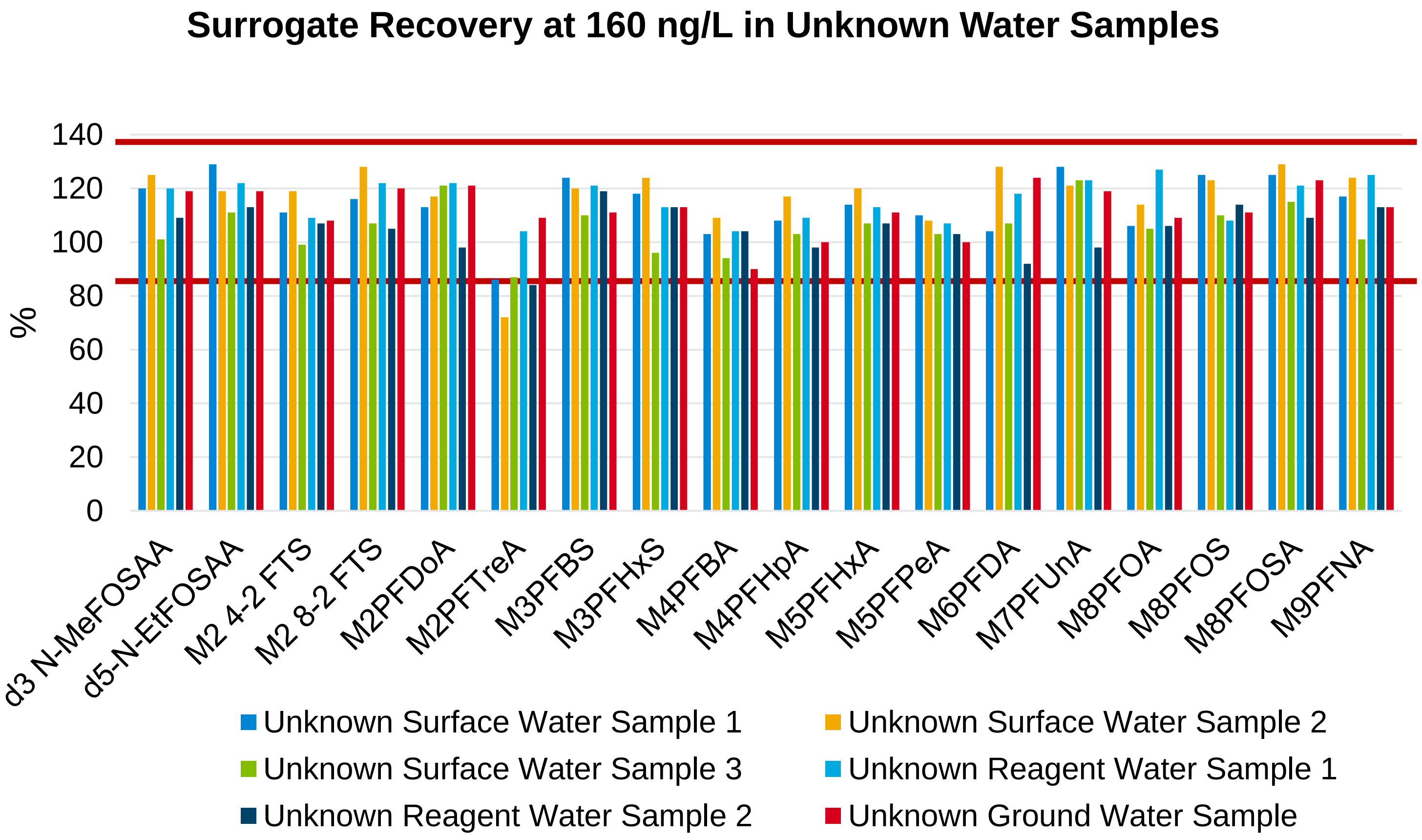
Filter through Acrodisc GxF/0.2µm GHP

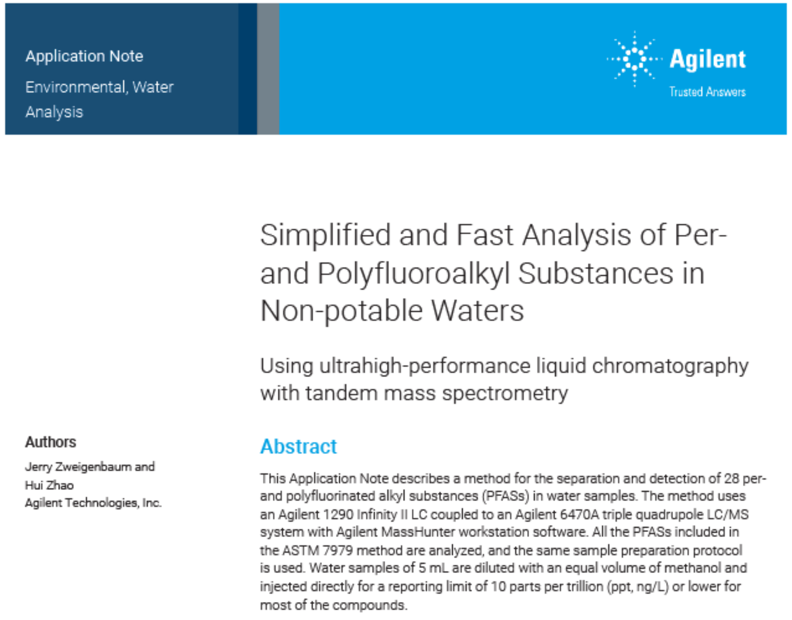
Adjust pH to acidic with 10 µL acetic acid

LC-MS/MS analysis

EPA 8327 (draft)
Agilent data from the inter-lab validation for this method

ALL THE ANALYTES DETECTED < REPORTING LIMIT
SURROGATES RECOVERIES BETWEEN 70-130% IN ALL SAMPLES





Application Note
Environmental, Water Analysis

Agilent
Trusted Answers

Simplified and Fast Analysis of Per- and Polyfluoroalkyl Substances in Non-potable Waters

Using ultrahigh-performance liquid chromatography with tandem mass spectrometry

Authors

Jerry Zweigenbaum and Hui Zhao
Agilent Technologies, Inc.

Abstract

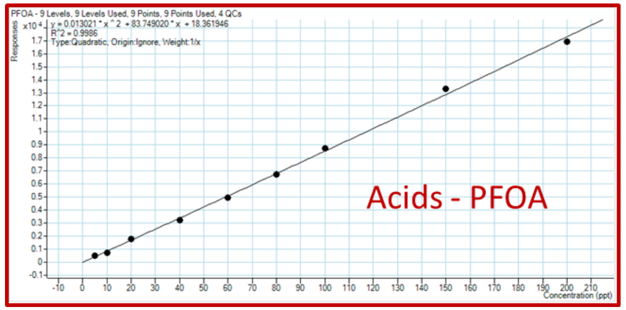
This Application Note describes a method for the separation and detection of 28 per- and polyfluorinated alkyl substances (PFASs) in water samples. The method uses an Agilent 1290 Infinity II LC coupled to an Agilent 6470A triple quadrupole LC/MS system with Agilent MassHunter workstation software. All the PFASs included in the ASTM 7979 method are analyzed, and the same sample preparation protocol is used. Water samples of 5 mL are diluted with an equal volume of methanol and injected directly for a reporting limit of 10 parts per trillion (ppt, ng/L) or lower for most of the compounds.

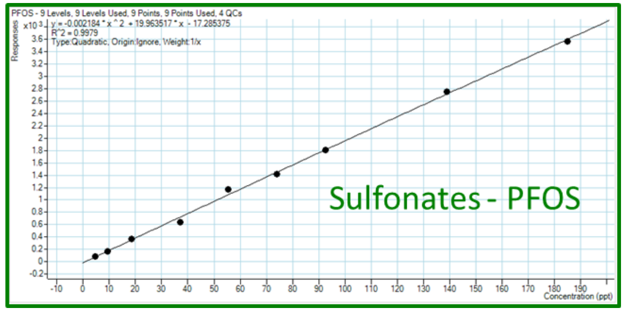
Application: 5994-0678EN

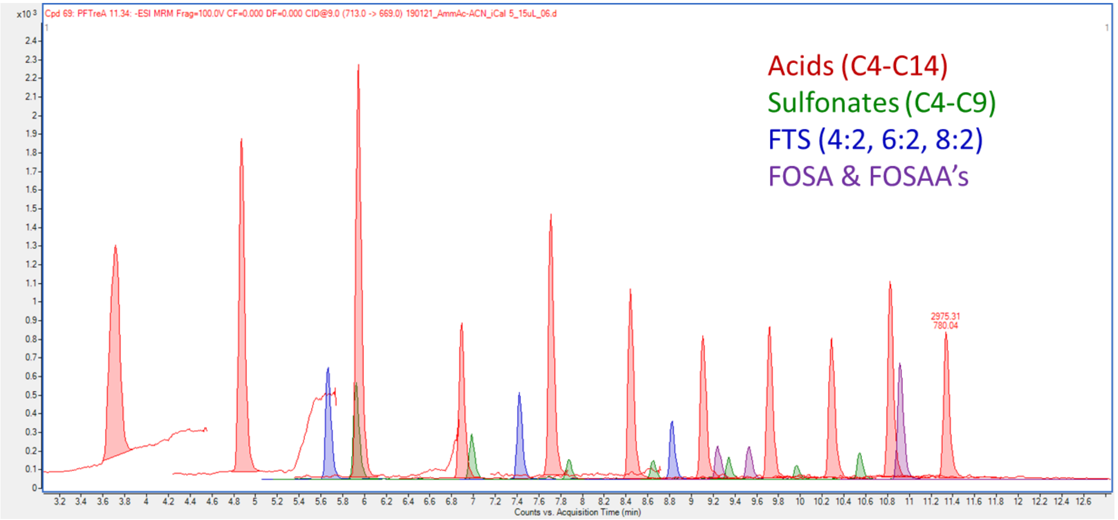
ASTM 7968/EPA method expected based on this PFAS analysis in soil and solid matrices

- Method is for soil and solid matrices
- EPA method expected to be based on ASTM 7968.
- 21 Analytes
- Method using simple dilution & acidification before large volume injection
- **30** µL injection (50/50: MeOH/Water)
- 21 min run time
- MRLs: 25 ng/kg (range: 25-1000 ng/L for most)

ASTM 7968
PFAS analysis in soil and solid matrices







2g Soil Sample

Extract with 10 mL methanol : water at pH 9-10

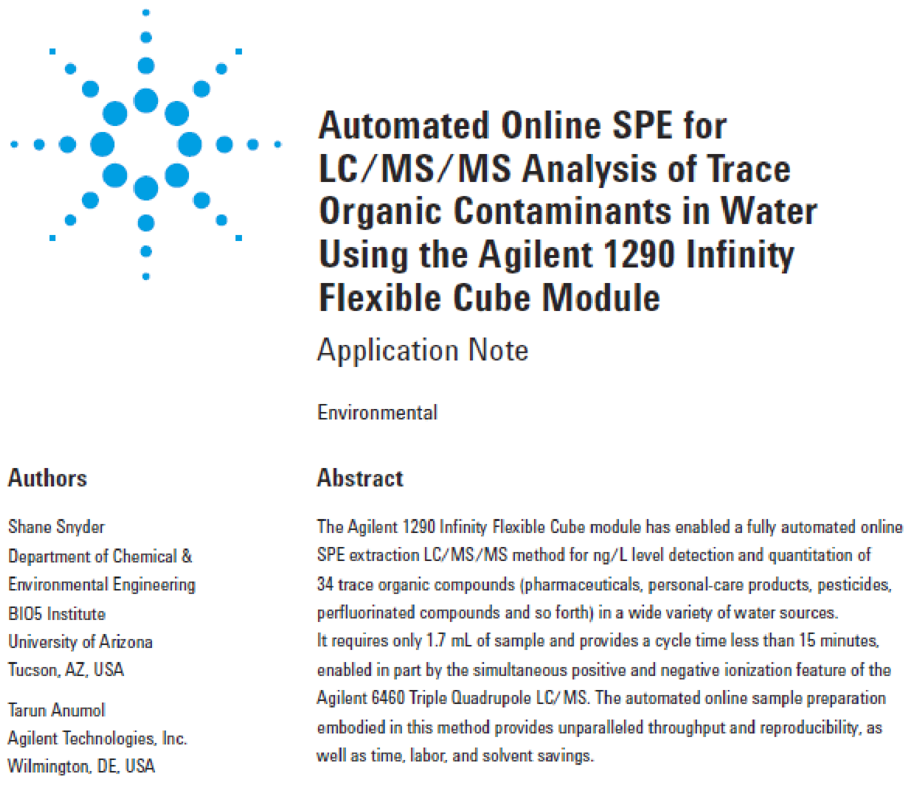
Tumble on rotator for 1 hour, centrifuge

Syringe Filter

Acidify

Analyze by LC/MS/MS

Analysis of PFOA & PFOS in Water by Online SPE



Automated Online SPE for LC/MS/MS Analysis of Trace Organic Contaminants in Water Using the Agilent 1290 Infinity Flexible Cube Module

Application Note

Environmental

Authors

Shane Snyder
Department of Chemical &
Environmental Engineering
BIO5 Institute
University of Arizona
Tucson, AZ, USA

Tarun Anumol
Agilent Technologies, Inc.
Wilmington, DE, USA

Abstract

The Agilent 1290 Infinity Flexible Cube module has enabled a fully automated online SPE extraction LC/MS/MS method for ng/L level detection and quantitation of 34 trace organic compounds (pharmaceuticals, personal-care products, pesticides, perfluorinated compounds and so forth) in a wide variety of water sources. It requires only 1.7 mL of sample and provides a cycle time less than 15 minutes, enabled in part by the simultaneous positive and negative ionization feature of the Agilent 6460 Triple Quadrupole LC/MS. The automated online sample preparation embodied in this method provides unparalleled throughput and reproducibility, as well as time, labor, and solvent savings.

Application note: 5991-6115EN

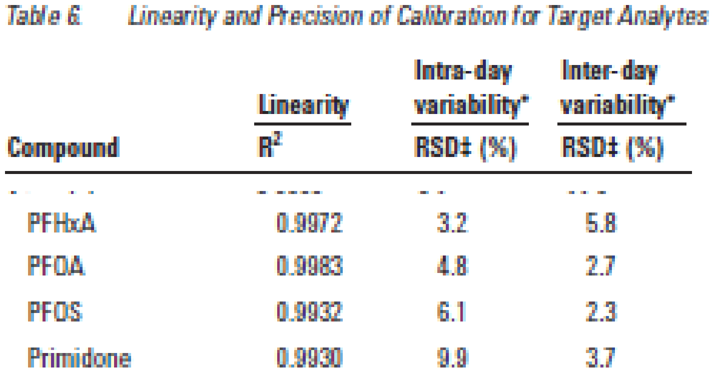
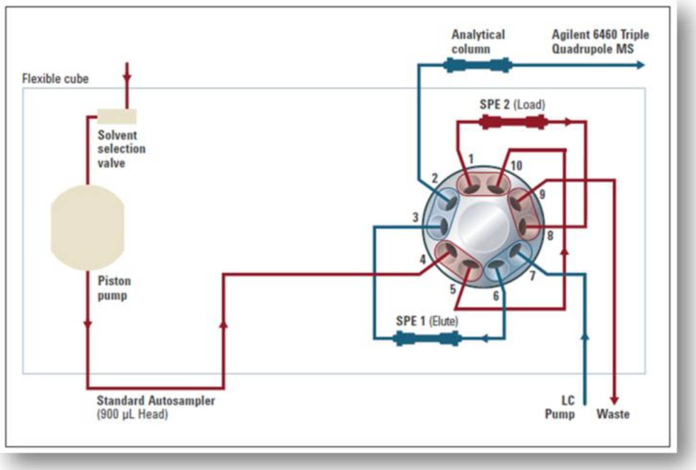


Table 6 Linearity and Precision of Calibration for Target Analytes

	Linearity	Intra-day variability*	Inter-day variability*
Compound	R^2	RSD‡ (%)	RSD‡ (%)
PFHxA	0.9972	3.2	5.8
PFOA	0.9983	4.8	2.7
PFOS	0.9932	6.1	2.3
Primidone	0.9930	9.9	3.7



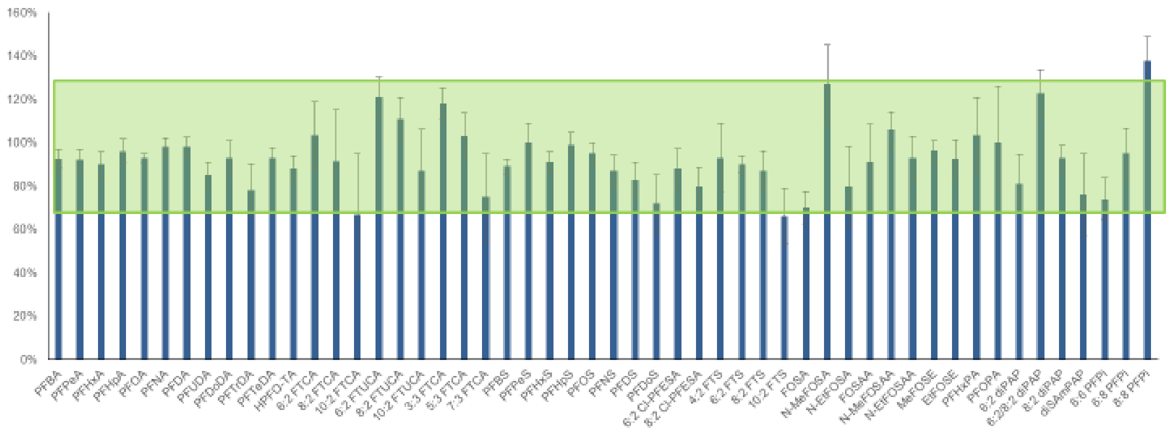
Agilent Flexcube
Online SPE

Quantification of expanded list of Emerging PFAS

Analysis with 6495 in Water & Soil

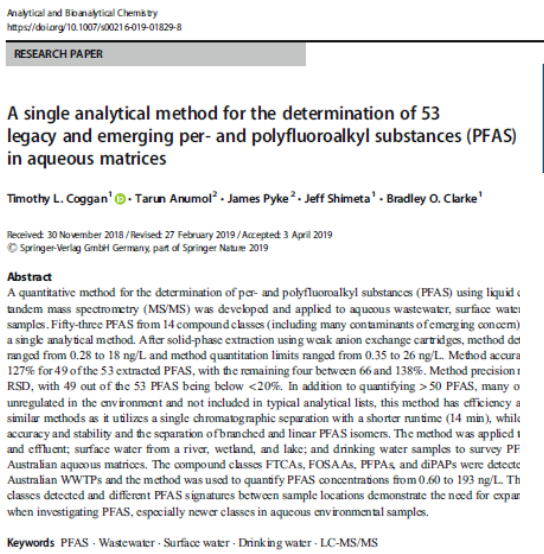
Bradley Clarke – RMIT University (>50 PFAS in 1 method)

SPE Method accuracy – 5 ng/L spike* (n=7)



Accuracy:
49 of 52 between 70 – 130 %
*n:2 FTCAs and FOSEs spike 20 ng/L

MDL (US EPA 40 CFR part 136, rev 2):
Between 0.28 – 17 ng/L



Analytical and Bioanalytical Chemistry
https://doi.org/10.1007/s00216-019-01829-8

RESEARCH PAPER

A single analytical method for the determination of 53 legacy and emerging per- and polyfluoroalkyl substances (PFAS) in aqueous matrices

Timothy L. Coggan[1] · Tarun Anumol[2] · James Pyke[2] · Jeff Shimeta[1] · Bradley O. Clarke[1]

Received: 30 November 2018 / Revised: 27 February 2019 / Accepted: 3 April 2019
© Springer-Verlag GmbH Germany, part of Springer Nature 2019

Abstract

A quantitative method for the determination of per- and polyfluoroalkyl substances (PFAS) using liquid
tandem mass spectrometry (MS/MS) was developed and applied to aqueous wastewater, surface wate
samples. Fifty-three PFAS from 14 compound classes (including many contaminants of emerging concern)
a single analytical method. After solid-phase extraction using weak anion exchange cartridges, method de
ranged from 0.28 to 18 ng/L and method quantitation limits ranged from 0.35 to 26 ng/L. Method accura
127% for 49 of the 53 extracted PFAS, with the remaining four between 66 and 138%. Method precision
RSD, with 49 out of the 53 PFAS being below <20%. In addition to quantifying >50 PFAS, many o
unregulated in the environment and not included in typical analytical lists, this method has efficiency
similar methods as it utilizes a single chromatographic separation with a shorter runtime (14 min), whil
accuracy and stability and the separation of branched and linear PFAS isomers. The method was applied
and effluent; surface water from a river, wetland, and lake; and drinking water samples to survey PF
Australian aqueous matrices. The compound classes FTCAs, FOSAAs, PFPAs, and diPAPs were detect
Australian WWTPs and the method was used to quantify PFAS concentrations from 0.60 to 193 ng/L. Th
classes detected and different PFAS signatures between sample locations demonstrate the need for expa
when investigating PFAS, especially newer classes in aqueous environmental samples.

Keywords PFAS · Wastewater · Surface water · Drinking water · LC-MS/MS

Application Note
Environmental

Agilent
Trusted Answers

Analysis of >50 Legacy and Emerging PFAS in Water Using the Agilent 6495B Triple Quadrupole LC/MS

Authors

Timothy L. Coggan,
Jeff Shimeta, and
Bradley O. Clarke
RMIT University,
Melbourne, VIC, Australia

Tarun Anumol and
James Pyke
Agilent Technologies, Inc.

Abstract

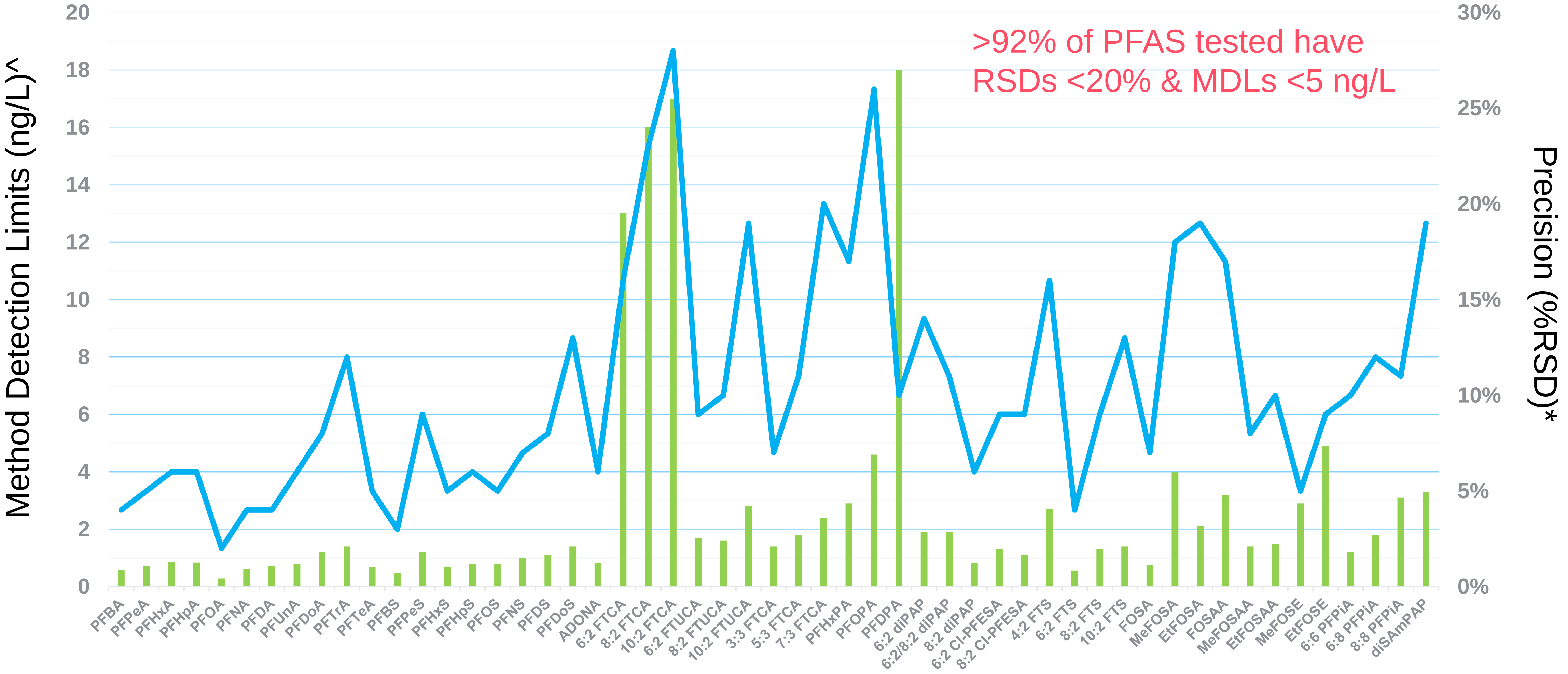
The contamination of the environment with per- and polyfluoroalkyl substances (PFAS) is a serious concern to regulators, scientists, and the public worldwide; due to their ubiquitous presence, persistence, and toxicity.[1-3] Robust analytical techniques that can accurately and precisely quantify these pollutants at trace levels are necessary for understanding their environmental fate, ecological impacts, and impacts on public health. Appropriate analytical techniques and the fundamental data they generate allow scientists and regulators to make informed assessments of PFAS use in modern society.

This Application Note describes a sensitive and reliable method for the simultaneous quantitation of 53 legacy and emerging PFAS from 14 compounds classes. The method uses isotope dilution on an Agilent 1290 Infinity II LC coupled to an Agilent 6495B triple quadrupole LC/MS.[4]

Webinar: www.chromatographyonline.com/lcgc_p/treatment

Application: 5994-0919EN

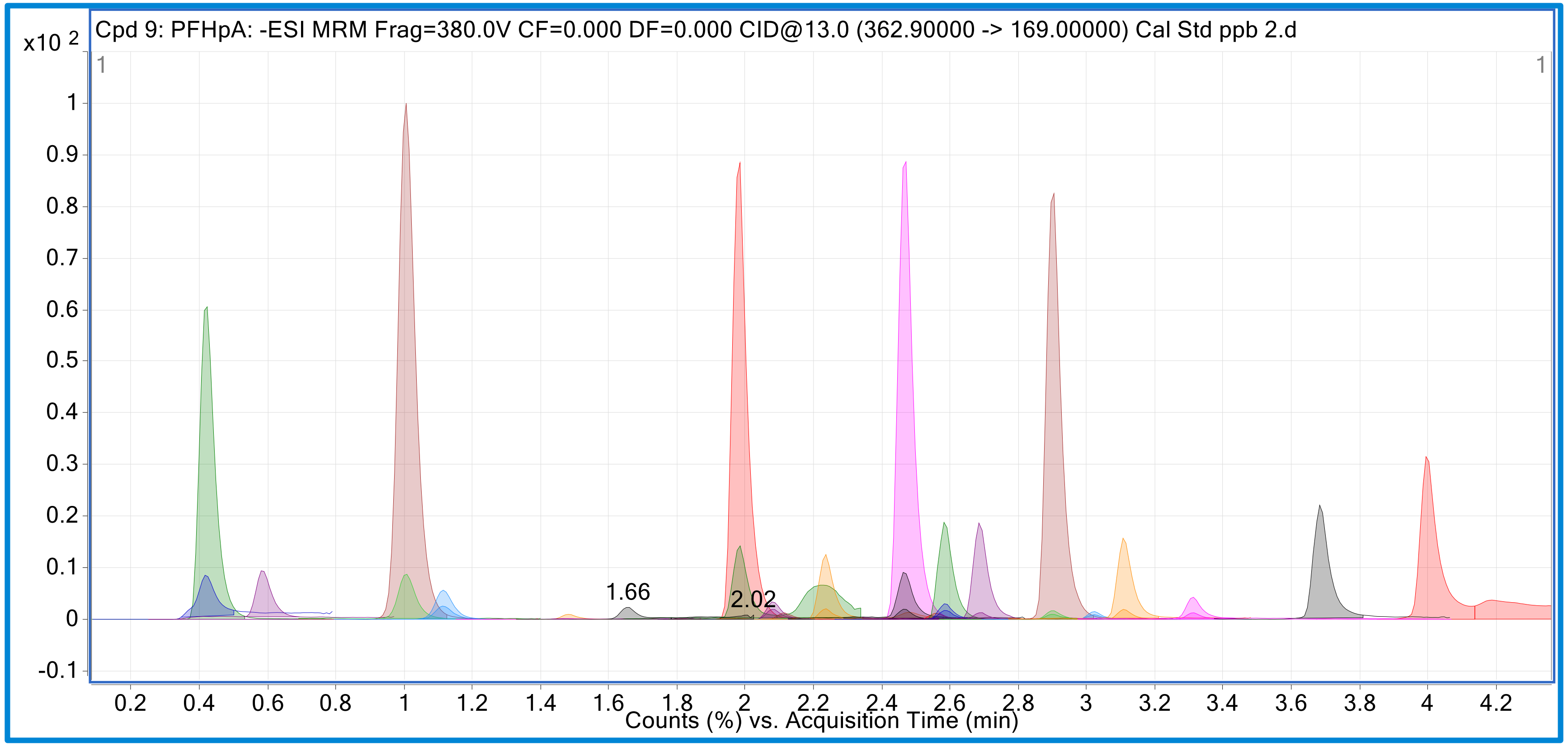
Analysis of >50 PFAS in Water
Method Performance (1 uL injection of extract)



>92% of PFAS tested have RSDs <20% & MDLs <5 ng/L

** Seven replicates at 5 ng/L spiked into 250 mL water samples; followed by SPE and injection of 1 uL onto 6495 LC-MS/MS; ^ based on USEPA 40 CFR Part 136 Appendix B Revision 2*

Perfluorinated Alkyl Acids in Drinking Water by LC/TQ Direct Aqueous Injection with Agilent 6495 LC MS/MS



System

- 1290 Infinity LC coupled to a 6495 LC-MS/MS
- 14 PFAAs in 6 min

MDLs:

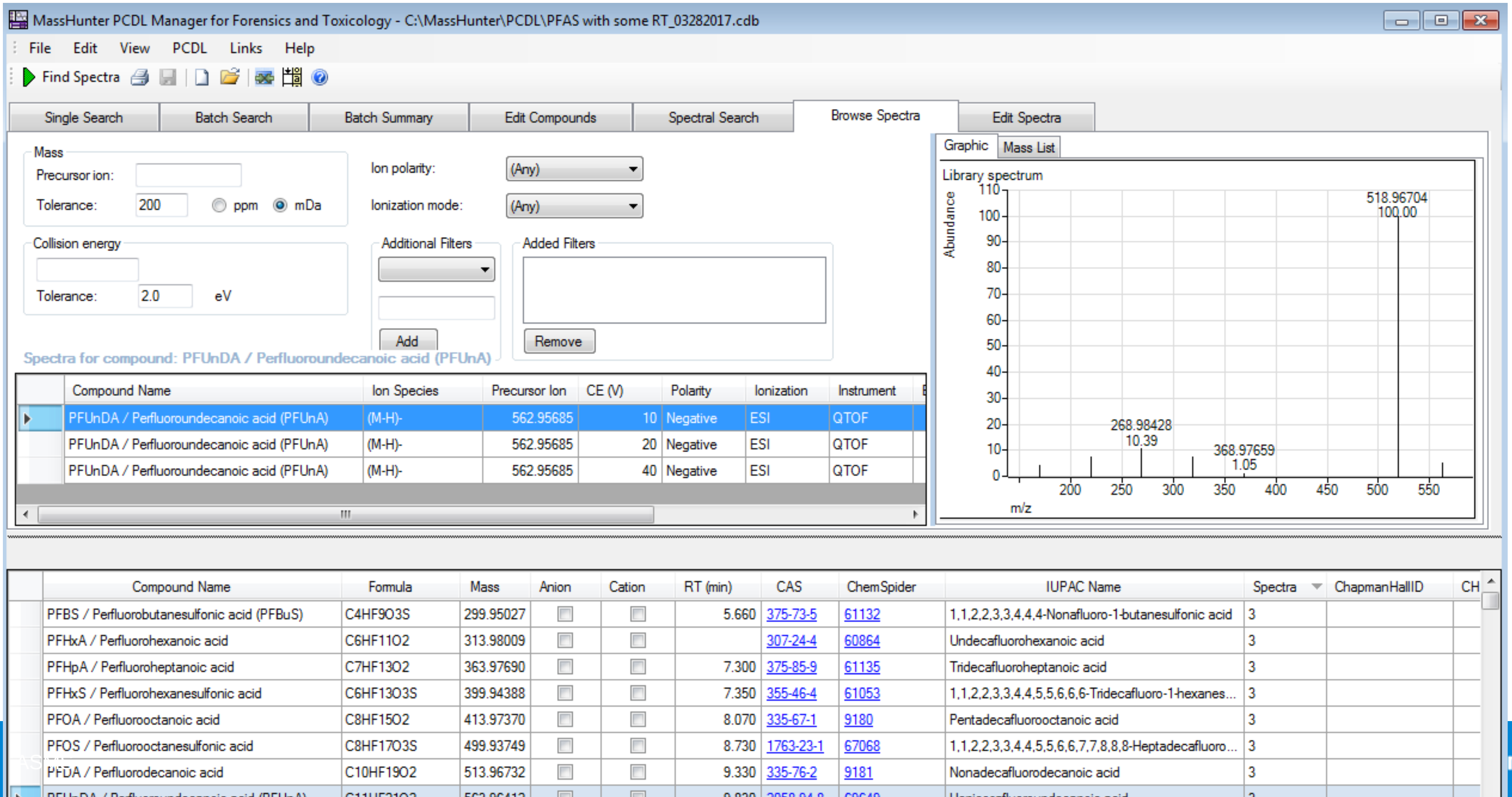
- PFOA, PFOS: <1 ng/L
- Others: 1-5 ng/L
- 75 µL aqueous injection

Matrices:

- Drinking Water
- Surface Water
- Ground Water

Suspect Screening and Untargeted Analysis

- Agilent 6545 LC/Q-TOF
- Custom PFAS database
- MS/MS spectra and retention time data available for a subset of compounds


MassHunter PCDL Manager for Forensics and Toxicology - C:\MassHunter\PCDL\PFAS with some RT_03282017.cdb

Mass
Precursor ion:
Tolerance: 200 ○ ppm ● mDa
Ion polarity: (Any)
Ionization mode: (Any)
Collision energy
Tolerance: 2.0 eV
Additional Filters
Added Filters

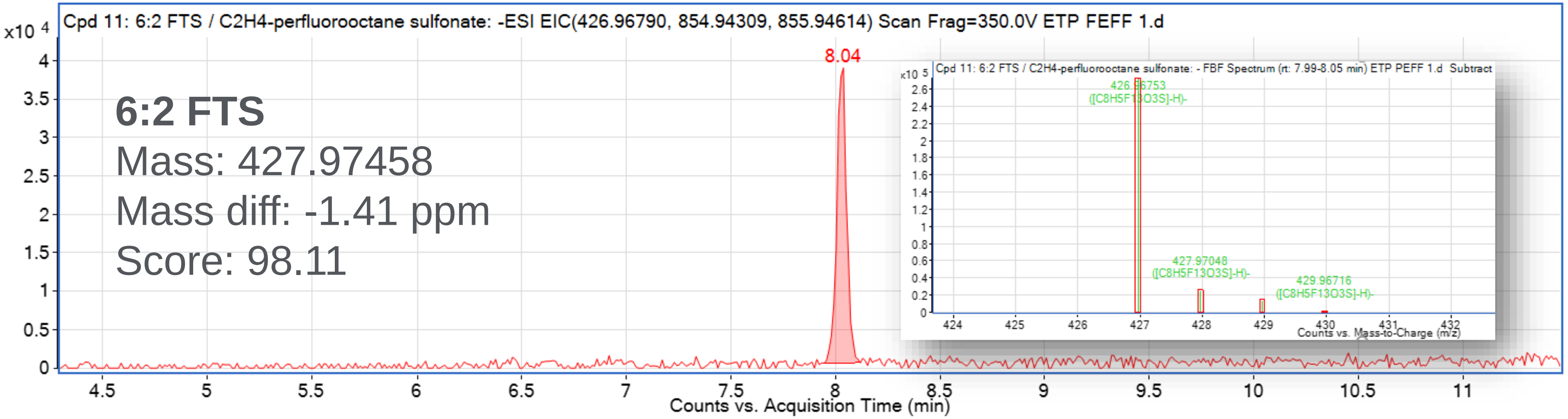
Spectra for compound: PFUnDA / Perfluoroundecanoic acid (PFUnA)

Compound Name	Ion Species	Precursor Ion	CE (V)	Polarity	Ionization	Instrument
PFUnDA / Perfluoroundecanoic acid (PFUnA)	(M-H)-	562.95685	10	Negative	ESI	QTOF
PFUnDA / Perfluoroundecanoic acid (PFUnA)	(M-H)-	562.95685	20	Negative	ESI	QTOF
PFUnDA / Perfluoroundecanoic acid (PFUnA)	(M-H)-	562.95685	40	Negative	ESI	QTOF

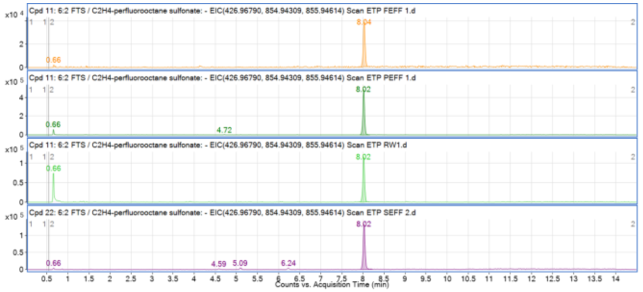
Compound Name	Formula	Mass	Anion	Cation	RT (min)	CAS	ChemSpider	IUPAC Name	Spectra	ChapmanHallID	CH
PFBS / Perfluorobutanesulfonic acid (PFBuS)	C4HF9O3S	299.95027	☐	☐	5.660	375-73-5	61132	1,1,2,2,3,3,4,4,4-Nonafluoro-1-butanesulfonic acid	3		
PFHxA / Perfluorohexanoic acid	C6HF11O2	313.98009	☐	☐		307-24-4	60864	Undecafluorohexanoic acid	3		
PFHpA / Perfluoroheptanoic acid	C7HF13O2	363.97690	☐	☐	7.300	375-85-9	61135	Tridecafluoroheptanoic acid	3		
PFHxS / Perfluorohexanesulfonic acid	C6HF13O3S	399.94388	☐	☐	7.350	355-46-4	61053	1,1,2,2,3,3,4,4,5,5,6,6,6-Tridecafluoro-1-hexanes...	3		
PFOA / Perfluorooctanoic acid	C8HF15O2	413.97370	☐	☐	8.070	335-67-1	9180	Pentadecafluorooctanoic acid	3		
PFOS / Perfluorooctanesulfonic acid	C8HF17O3S	499.93749	☐	☐	8.730	1763-23-1	67068	1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Heptadecafluoro...	3		
PFDA / Perfluorodecanoic acid	C10HF19O2	513.96732	☐	☐	9.330	335-76-2	9181	Nonadecafluorodecanoic acid	3		

Suspect Screening Personal Compounds Database

WWTP1 Final Effluent

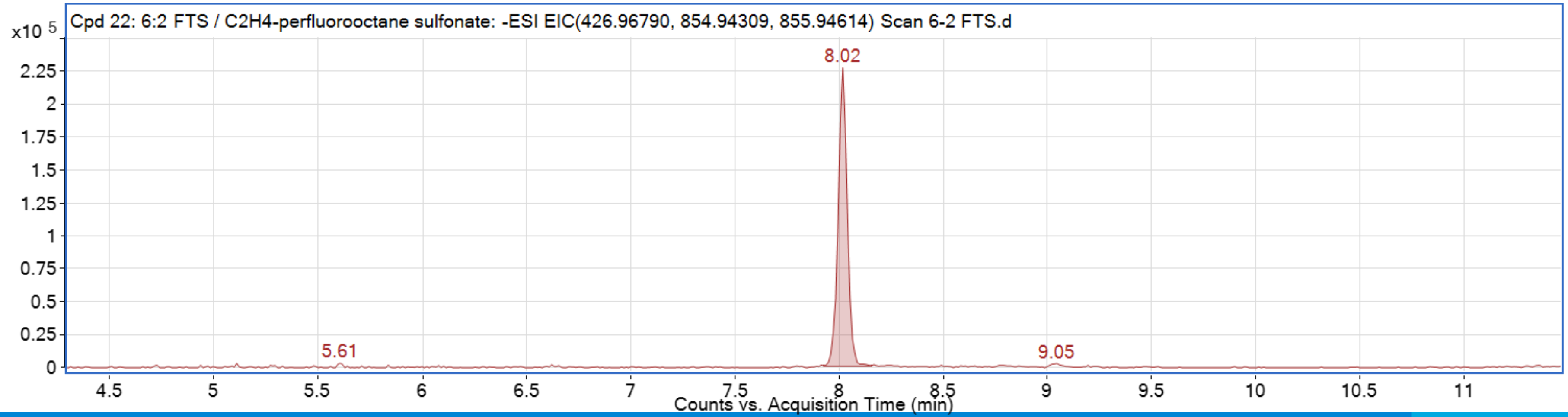


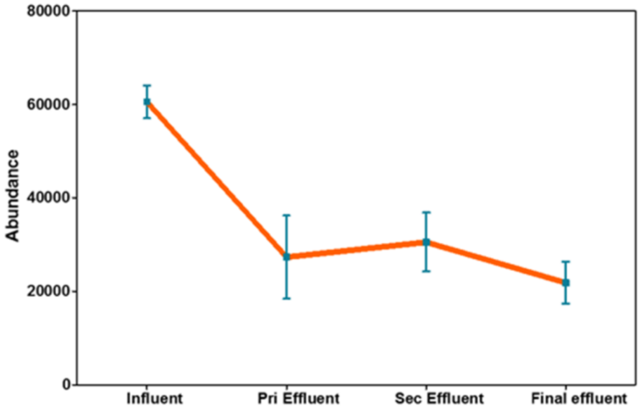
6:2 FTS
Mass: 427.97458
Mass diff: -1.41 ppm
Score: 98.11



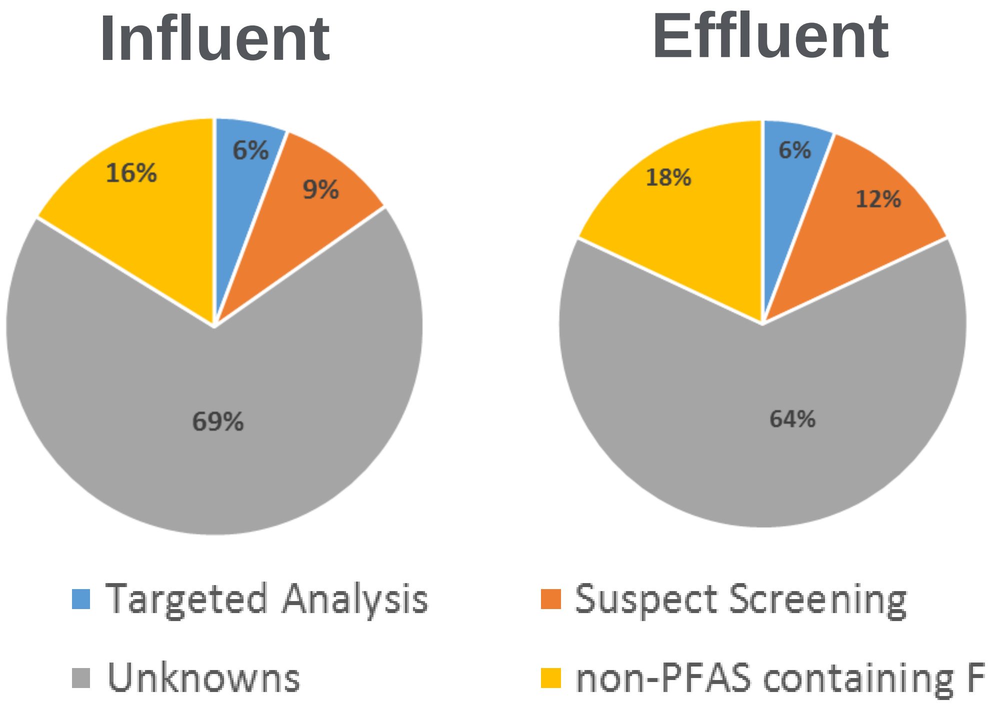
6:2 FTS ID'd in all samples of WWTP

Standard





Unknowns Screening Results

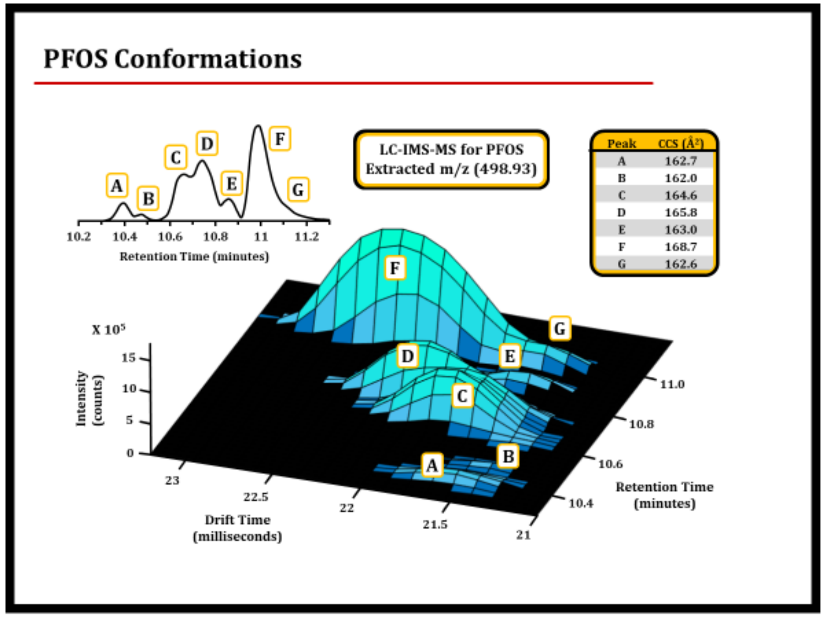


- **Targeted:** Only captured ~6% of compounds
- **Suspects:** 10-16% of fluorinated compounds
- **Unknowns:** 66-81% of fluorinated compounds
- Large portion of fluorinated anionic compounds in sample unknowns

60-70% of fluorine containing molecules in these samples is ‘unknown’

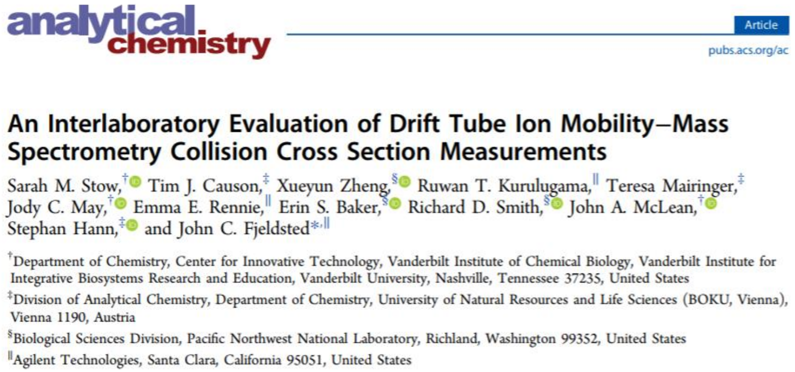
Ion-Mobility MS
The ultimate tool for true PFAS identification

“Rapid Assessment of Isomeric Diversity in PFAS by Ion Mobility Spectrometry-Mass Spectrometry (IMS-MS)”
James Dodds & Erin Baker , NC State
MP 127


PFOS Conformations

LC-IMS-MS for PFOS
Extracted m/z (498.93)

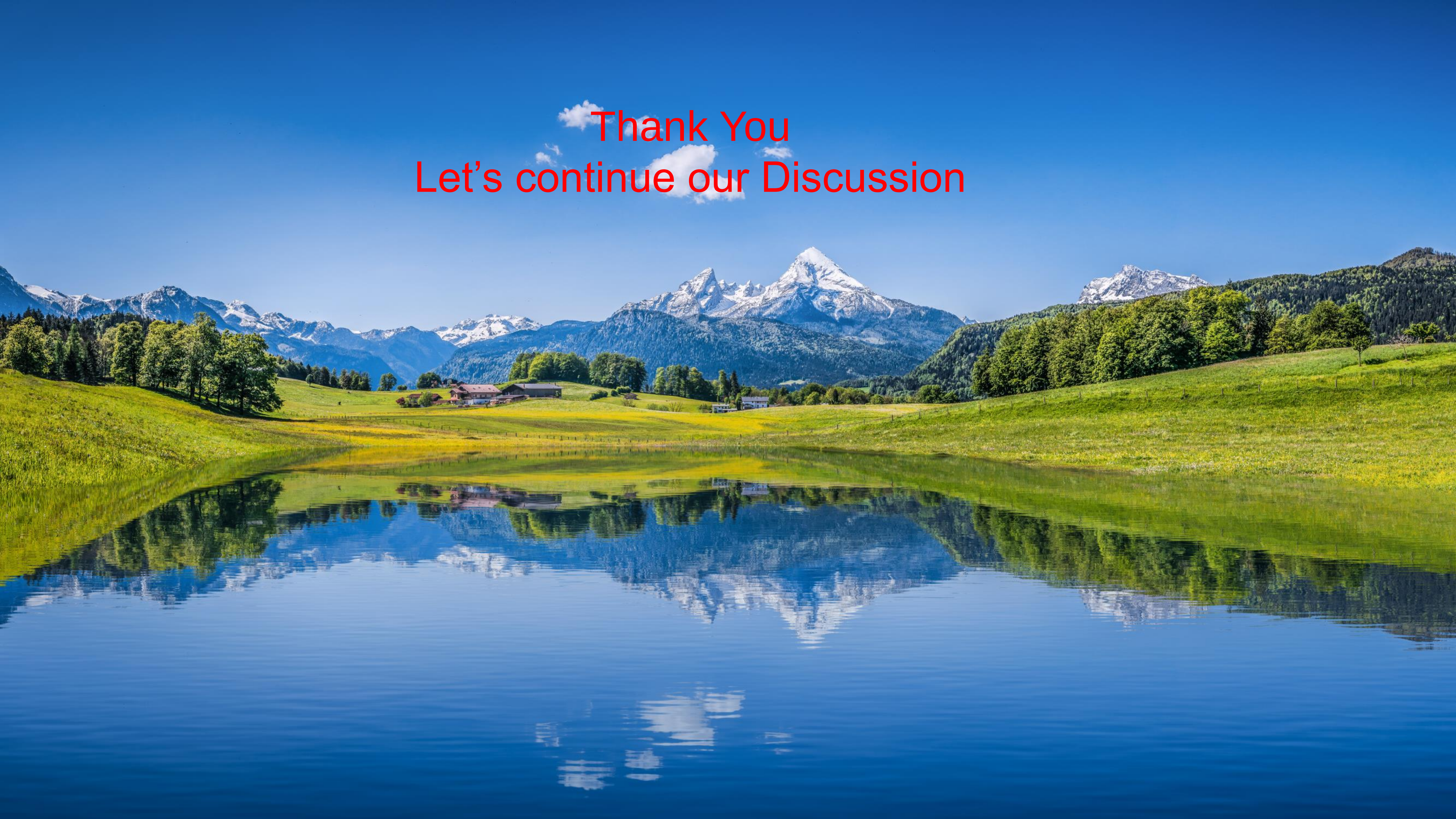
Peak	CCS (Å²)
A	162.7
B	162.0
C	164.6
D	165.8
E	163.0
F	168.7
G	162.6


analytical chemistry
Article
pubs.acs.org/ac

An Interlaboratory Evaluation of Drift Tube Ion Mobility–Mass Spectrometry Collision Cross Section Measurements

Sarah M. Stow,[†] Tim J. Causon,[‡] Xueyun Zheng,[§] Ruwan T. Kurulugama,[‖] Teresa Mairinger,[‡] Jody C. May,[†] Emma E. Rennie,[‖] Erin S. Baker,[§] Richard D. Smith,[§] John A. McLean,[†] Stephan Hann,[‡] and John C. Fjeldsted*[,‖]

[†] Department of Chemistry, Center for Innovative Technology, Vanderbilt Institute of Chemical Biology, Vanderbilt Institute for Integrative Biosystems Research and Education, Vanderbilt University, Nashville, Tennessee 37235, United States
[‡] Division of Analytical Chemistry, Department of Chemistry, University of Natural Resources and Life Sciences (BOKU, Vienna), Vienna 1190, Austria
[§] Biological Sciences Division, Pacific Northwest National Laboratory, Richland, Washington 99352, United States
[‖] Agilent Technologies, Santa Clara, California 95051, United States



Thank You

Let’s continue our Discussion