Per- and PolyFluorinated Alkyl Substances (PFAS)

PRESENTED BY

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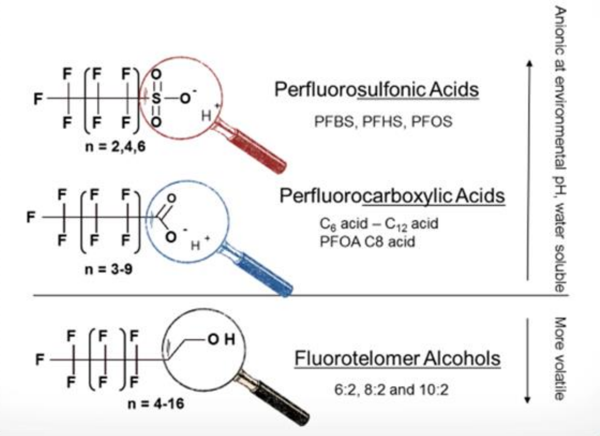
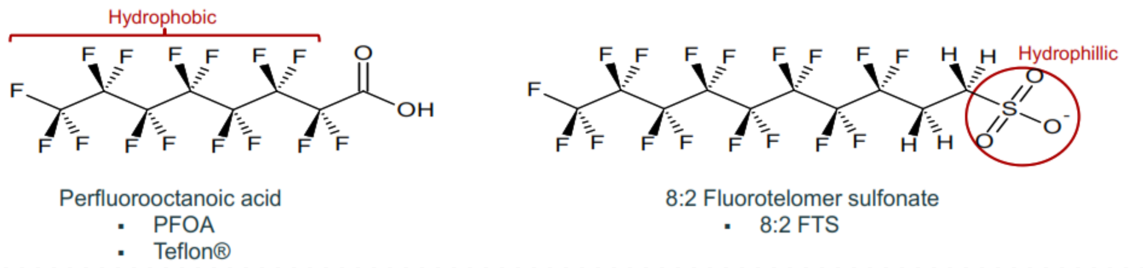
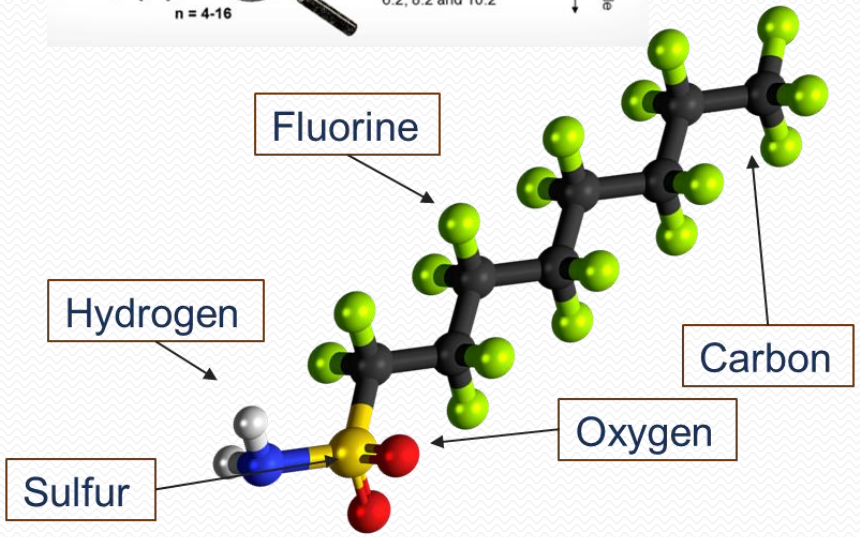
Background – What are PFAS compounds?

aka - “Forever Chemicals”



- PFASs are **P**er- and **P**oly**F**luorinated **A**lkyl **S**ubstances. Exclusively anthropogenic.
- Structures contain a hydrophobic perfluoroalkyl backbone and a hydrophilic end group
- Include a diverse range of compounds with a variety of chain lengths and end groups





Persistent in the environment

C-F bonds are very strong and do not break down

Health Concerns* https://www.atsdr.cdc.gov/pfas/health-effects.html

- Affect growth, learning, and behavior of infants and children
- Endocrine disruption
- Increase cholesterol levels
- Affect the immune system
- Increase risk of cancer
- Infertility

Background – What are PFAS compounds?

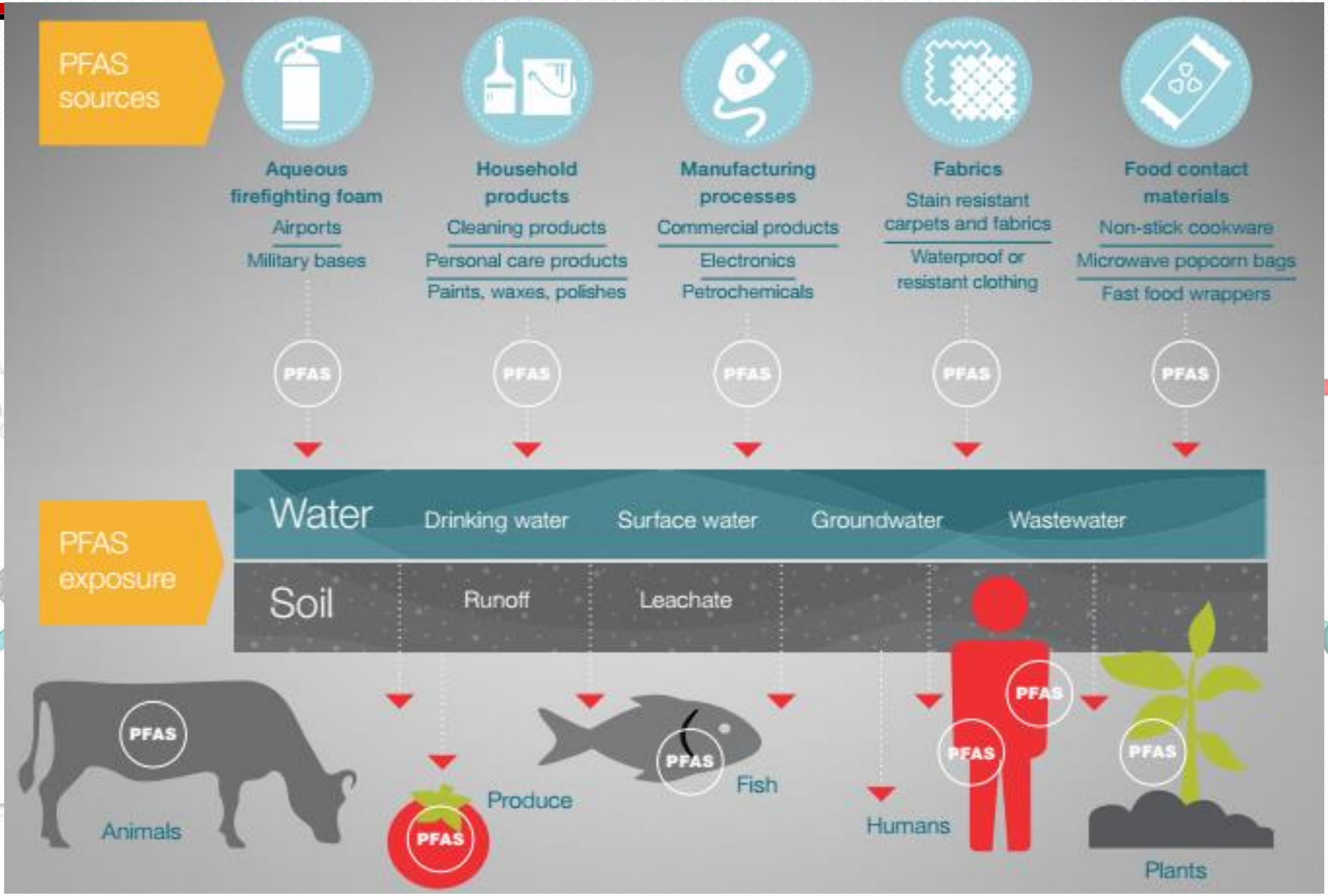
Table 2-1. Discovery and manufacturing history of select PFAS

PFAS[1]	Development Time Period							https://pfas-1.itrcweb.org/
	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s
PTFE	Invented	Non-Stick Coatings			Waterproof Fabrics			
PFOS		Initial Production	Stain & Water Resistant Products	Firefighting foam				U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS[2])
PFOA		Initial Production	Protective Coatings					
PFNA					Initial Production	Architectural Resins		
Fluoro-telomers					Initial Production	Firefighting Foams		Predominant form of firefighting foam
Dominant Process[3]		Electrochemical Fluorination (ECF)						Fluoro-telomerization (shorter chain ECF)
Pre-Invention of Chemistry /			Initial Chemical Synthesis / Production			Commercial Products Introduced and Used		

- Drinking water
- Food chain – found in food, feed
- Most people have been exposed => found in blood

Bioaccumulation => PFAS compounds build up in biological systems over time

PFAS: Source and Exposure



PFAS: Source and Exposure

It's Literally Raining 'Forever Chemicals', And The Storm Could Last For Decades

ENVIRONMENT 03 August 2022 By CARLY CASSELLA

https://www.sciencealert.com/

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PRESS ROOM

100% of breast milk samples tested positive for toxic “forever chemicals”

May 13, 2021

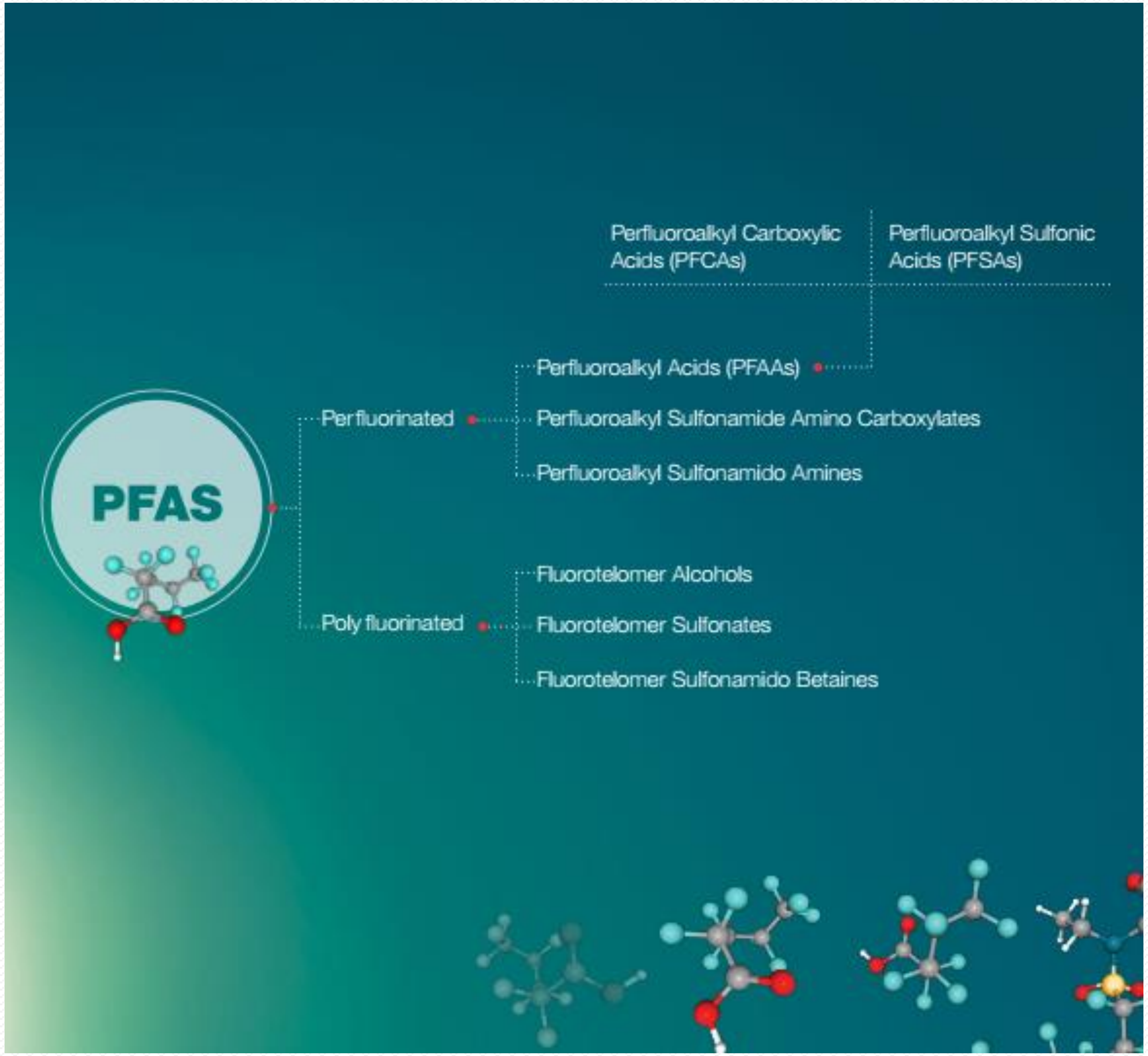
New study finds that newer PFAS chemicals build up in people, despite opposite claims made by the chemical industry

Press Contact

Stephanie Stohler,
sstohler@toxicfreefuture.org

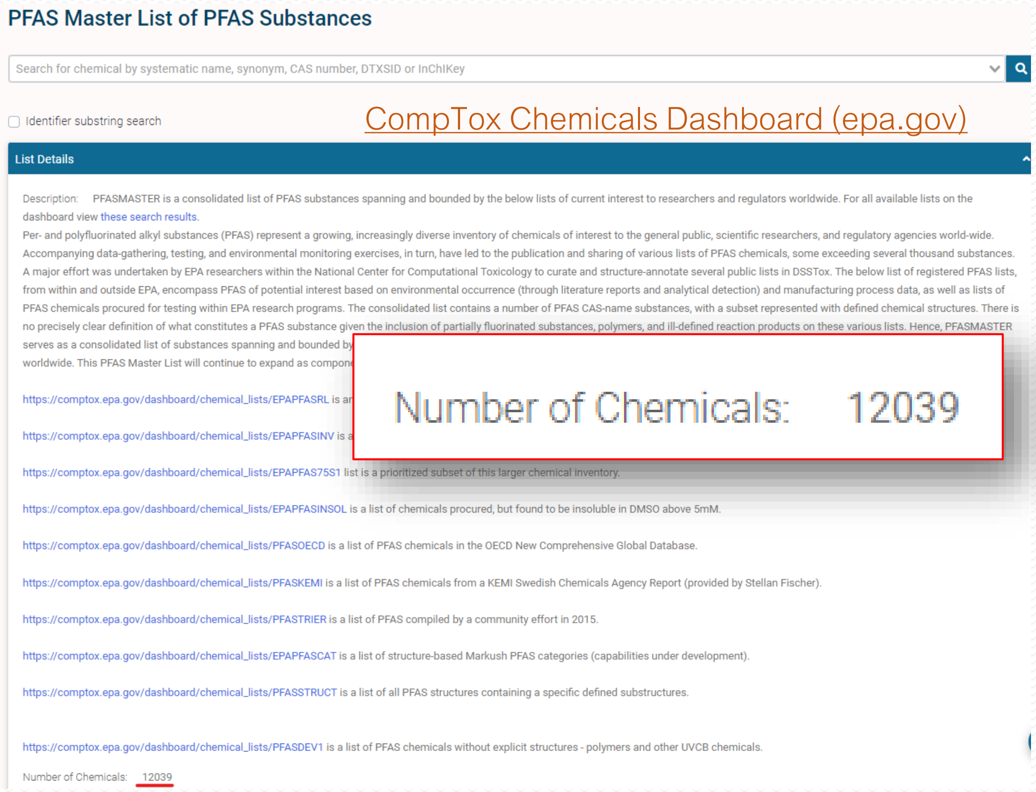
https://toxicfreefuture.org/

Challenge to laboratory work



EPA United States Environmental Protection Agency

- Need related standards from supplier to quantify


PFAS Master List of PFAS Substances

Search for chemical by systematic name, synonym, CAS number, DTXSID or InChIKey

Identifier substring search

CompTox Chemicals Dashboard (epa.gov)

List Details

Description: PFASMASTER is a consolidated list of PFAS substances spanning and bounded by the below lists of current interest to researchers and regulators worldwide. For all available lists on the dashboard view these search results.
Per- and polyfluorinated alkyl substances (PFAS) represent a growing, increasingly diverse inventory of chemicals of interest to the general public, scientific researchers, and regulatory agencies world-wide. Accompanying data-gathering, testing, and environmental monitoring exercises, in turn, have led to the publication and sharing of various lists of PFAS chemicals, some exceeding several thousand substances. A major effort was undertaken by EPA researchers within the National Center for Computational Toxicology to curate and structure-annotate several public lists in DSSTox. The below list of registered PFAS lists, from within and outside EPA, encompass PFAS of potential interest based on environmental occurrence (through literature reports and analytical detection) and manufacturing process data, as well as lists of PFAS chemicals procured for testing within EPA research programs. The consolidated list contains a number of PFAS CAS-name substances, with a subset represented with defined chemical structures. There is no precisely clear definition of what constitutes a PFAS substance given the inclusion of partially fluorinated substances, polymers, and ill-defined reaction products on these various lists. Hence, PFASMASTER serves as a consolidated list of substances spanning and bounded by [...] worldwide. This PFAS Master List will continue to expand as compone[...]

https://comptox.epa.gov/dashboard/chemical_lists/EPAPFASRL is ar[...]

https://comptox.epa.gov/dashboard/chemical_lists/EPAPFASINV is a[...]

Number of Chemicals: 12039

https://comptox.epa.gov/dashboard/chemical_lists/EPAPFAS75S1 list is a prioritized subset of this larger chemical inventory.

https://comptox.epa.gov/dashboard/chemical_lists/EPAPFASINSOL is a list of chemicals procured, but found to be insoluble in DMSO above 5mM.

https://comptox.epa.gov/dashboard/chemical_lists/PFASOECD is a list of PFAS chemicals in the OECD New Comprehensive Global Database.

https://comptox.epa.gov/dashboard/chemical_lists/PFASKEMI is a list of PFAS chemicals from a KEMI Swedish Chemicals Agency Report (provided by Stellan Fischer).

https://comptox.epa.gov/dashboard/chemical_lists/PFASTRIER is a list of PFAS compiled by a community effort in 2015.

https://comptox.epa.gov/dashboard/chemical_lists/EPAPFASCAT is a list of structure-based Markush PFAS categories (capabilities under development).

https://comptox.epa.gov/dashboard/chemical_lists/PFASSTRUCT is a list of all PFAS structures containing a specific defined substructures.

https://comptox.epa.gov/dashboard/chemical_lists/PFASDEV1 is a list of PFAS chemicals without explicit structures - polymers and other UVCB chemicals.

Number of Chemicals: 12039

Targeted analysis

LC-MS/MS Methods for Quantitation of PFAS

Method Name	PFAS Targets	Sample Preparation	Reporting Limits
EPA Method 537.1	18	SPE (250 mL drinking water); reconstitute 1 mL 96% MeOH	0.53-6.3 ng/L
EPA Method 533	25	SPE (100-250 mL drinking water); reconstitute 1 mL 80% MeOH	1.4-16 ng/L
EPA 8327	24	5 mL water sample + 5 mL MeOH; filter; add 10 uL HOAc	10-50 ng/L
ASTM D7979-16	21	5 mL water sample + 5 mL MeOH; filter	1.5-107 ng/L
ASTM D7968-14	21	2 g Soil + 10 mL 50% MeOH + 0.1% HOAc; filter	2.4-258 ng/kg

PFAS workflow and analytical instrument

Sample | **Sample Preparation** | **Analytical method**

Soil sample

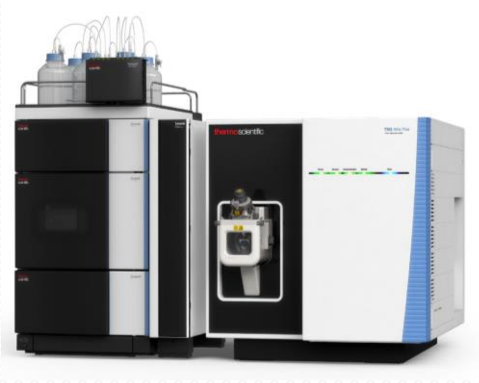
X-TRACTION® PFAS (PFE*) or MIX-TRACTION
For Extraction

D-EVA Concentration
For the sensor controlled evaporation of extracts

FREESTYLE™ SPE PFAS
For clean-up up to 50 mL (e.g. Dual SPE)

EluCLEAN® PFAS
SPE columns

D-EVA Concentration
For the sensor controlled evaporation to a few µL



LC-MS/MS Triple quad mass spectrometer

Aqueous sample

FREESTYLE™ XANA PFAS
For clean-up of up to 4 L

or

FREESTYLE™ XANA PFAS TableTop
For clean-up of up to 250 mL

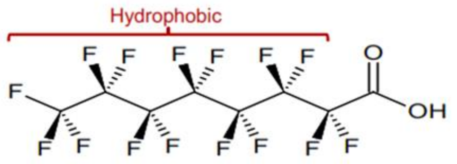
EluCLEAN® PFAS
SPE columns

D-EVA Concentration
For the sensor controlled evaporation to a few µL

LC-HRAM High resolution accurate mass Q-orbitrap mass spectrometer

PFAS Analysis Kit

Thermo Scientific™ PFC-free kit (P/N 80100-62142)



Perfluorooctanoic acid
- PFOA
- Teflon®

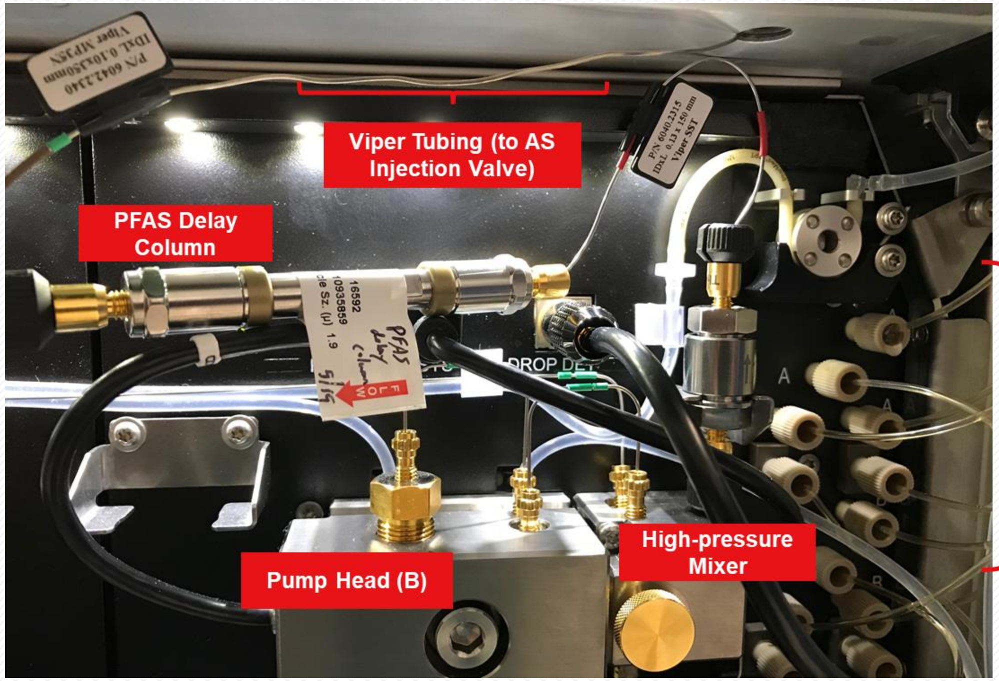
Replacing the wetted Teflon™ surfaces with comparable PEEK components and installing a PFOA trapping column.

solvent bottle cap

HPLC vials to do PFAS analysis

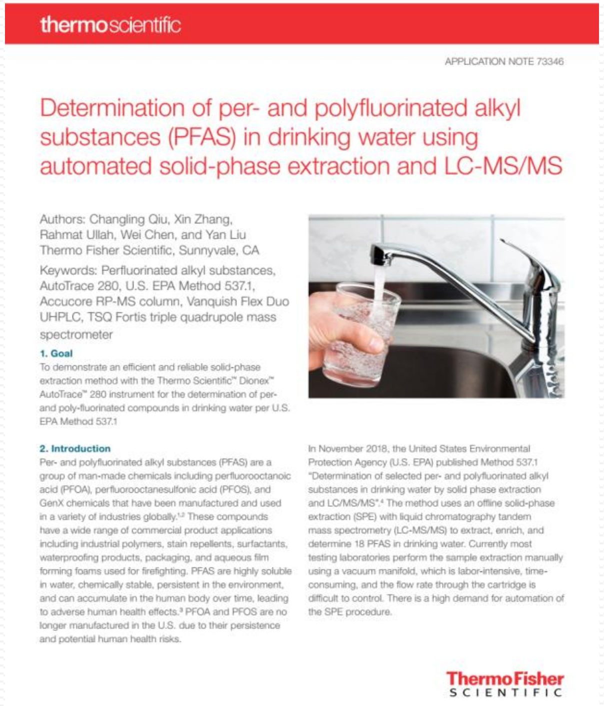
PEEK tubing assemblies

PEEK tubing assemblies and the trap column



Application note for PFAS analysis

Drinking water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APPLICATION NOTE 73346

Determination of per- and polyfluorinated alkyl substances (PFAS) in drinking water using automated solid-phase extraction and LC-MS/MS

Authors: Changling Qiu, Xin Zhang, Rahmat Ullah, Wei Chen, and Yan Liu
Thermo Fisher Scientific, Sunnyvale, CA

Keywords: Perfluorinated alkyl substances, AutoTrace 280, U.S. EPA Method 537.1, Accucore RP-MS column, Vanquish Flex Duo UHPLC, TSQ Fortis triple quadrupole mass spectrometer

1. Goal
To demonstrate an efficient and reliable solid-phase extraction method with the Thermo Scientific™ Dionex™ AutoTrace™ 280 instrument for the determination of per- and poly-fluorinated compounds in drinking water per U.S. EPA Method 537.1

2. Introduction
Per- and polyfluorinated alkyl substances (PFAS) are a group of man-made chemicals including perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), and GenX chemicals that have been manufactured and used in a variety of industries globally.[1,2] These compounds have a wide range of commercial product applications including industrial polymers, stain repellents, surfactants, waterproofing products, packaging, and aqueous film forming foams used for firefighting. PFAS are highly soluble in water, chemically stable, persistent in the environment, and can accumulate in the human body over time, leading to adverse human health effects.[3] PFOA and PFOS are no longer manufactured in the U.S. due to their persistence and potential human health risks.

In November 2018, the United States Environmental Protection Agency (U.S. EPA) published Method 537.1 "Determination of selected per- and polyfluorinated alkyl substances in drinking water by solid phase extraction and LC/MS/MS".[4] The method uses an offline solid-phase extraction (SPE) with liquid chromatography tandem mass spectrometry (LC-MS/MS) to extract, enrich, and determine 18 PFAS in drinking water. Currently most testing laboratories perform the sample extraction manually using a vacuum manifold, which is labor-intensive, time-consuming, and the flow rate through the cartridge is difficult to control. There is a high demand for automation of the SPE procedure.

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APPLICATION NOTE 73883

Determination of per- and polyfluorinated alkyl substances (PFAS) in drinking water

Using automated solid phase extraction and LC-MS/MS for U.S. EPA Method 533

Authors: Xin Zhang, Changling Qiu, Rahmat Ullah, and Yan Liu

Thermo Fisher Scientific, Sunnyvale, CA

Keywords: Perfluorinated and polyfluorinated alkyl substances, AutoTrace 280 PFAS, U.S. EPA Method 533, Acclaim 120 C18 column, Vanquish Flex UHPLC, TSQ Fortis triple quadrupole mass spectrometer

Goal
To demonstrate an efficient and reliable solid phase extraction method with a Thermo Scientific™ Dionex™ AutoTrace™ PFAS, an automated solid-phase extraction (SPE) system, for the determination of per- and poly-fluorinated compounds in drinking water per U.S. EPA Method 533

1. Introduction
Drinking water perfluorinated and polyfluorinated alkyl substances (collectively referred to as PFAS) occurrence studies have typically targeted perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), and as a result, these two are the most commonly detected compounds. This discussion focuses primarily on PFOS and PFOA. However, other compounds including PFBA, PFHxA, PFHpA, PFNA, PFUnDA, and PFHxS have also been detected in drinking water. In December 2019, the United States Environmental Protection Agency (U.S. EPA) took a key step in implementing the PFAS Action Plan by announcing a new validated method for testing PFAS in drinking water. This new validated test method complements other actions the agency is taking under the Action Plan to help communities address PFAS nationwide. It focuses on "short chain" PFAS, those PFAS with carbon chain lengths of four to twelve, and covers PFOS, PFOA, and other common PFAS that have been detected and reported. Currently most testing laboratories are

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Non-drinking water


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APPLICATION NOTE 65397

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

Authors
Cristina C. Jacob, Claudia P.B. Martins, Alan R. Atkins, Richard F. Jack
Thermo Fisher Scientific, San Jose, CA, USA

Keywords
Perfluorinated organic compounds, PFAA, PFOS, PFOA, GenX, PFCs, environmental contaminants, emerging contaminants, EPA 8327, EPA 537, EPA 537.1

Goal
To demonstrate method performance for the PFAS analysis at low levels (ng/L) in a wide variety of non-drinking water matrices by direct analysis and submit data package for EPA 8327 interlaboratory method validation.

Introduction
Per- and polyfluoroalkyl substances (PFAS) are a group of man-made chemicals that includes perfluorooctanoic (PFOA), perfluorooctyl sulfonic acid (PFOS), and hexafluoropropylene oxide dimer acid (HFPO-DA, which is part of GenX process). PFAS compounds have been manufactured since the 1940s. The most well-known PFAS compounds, PFOA and PFOS, have been the most extensively produced and studied for chemical properties and toxicological effects. Both chemicals are very persistent in the environment and accumulate in the human body over time. It is well documented that exposure to PFAS can lead to adverse human health effects[1-3] and are found in food packaging material as well as food processing equipment. Plants can accumulate PFAS when grown in PFAS-containing soil and/or water. These compounds are also found in a wide variety of consumer products such as

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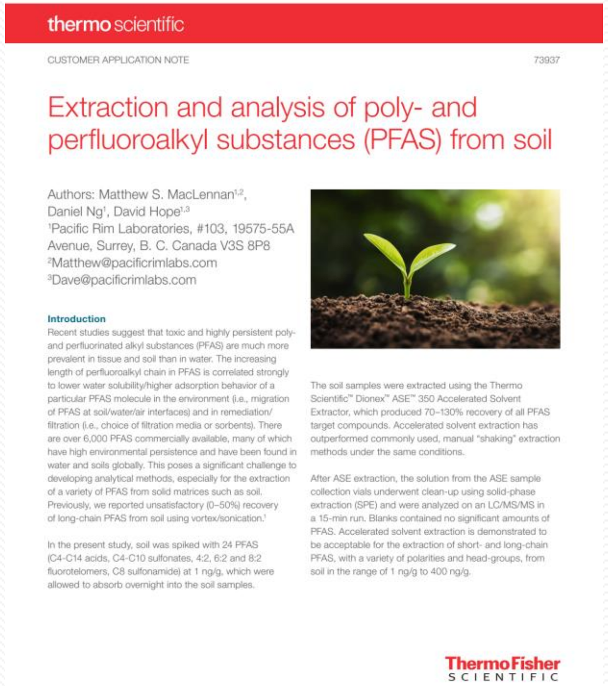
Soil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CUSTOMER APPLICATION NOTE 73937

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

Authors: Matthew S. MacLennan[1,2], Daniel Ng[1], David Hope[1,3]
[1]Pacific Rim Laboratories, #103, 19575-55A Avenue, Surrey, B. C. Canada V3S 8P8
[2]Matthew@pacificrimlabs.com
[3]Dave@pacificrimlabs.com

Introduction
Recent studies suggest that toxic and highly persistent poly- and perfluoroalkyl substances (PFAS) are much more prevalent in tissue and soil than in water. The increasing length of perfluoroalkyl chain in PFAS is correlated strongly to lower water solubility/higher adsorption behavior of a particular PFAS molecule in the environment (i.e., migration of PFAS at soil/water/air interfaces) and in remediation/filtration (i.e., choice of filtration media or sorbents). There are over 6,000 PFAS commercially available, many of which have high environmental persistence and have been found in water and soils globally. This poses a significant challenge to developing analytical methods, especially for the extraction of a variety of PFAS from solid matrices such as soil. Previously, we reported unsatisfactory (0–50%) recovery of long-chain PFAS from soil using vortex/sonication.[1]

In the present study, soil was spiked with 24 PFAS (C4-C14 acids, C4-C10 sulfonates, 4:2, 6:2 and 8:2 fluorotelomers, C8 sulfonamide) at 1 ng/g, which were allowed to absorb overnight into the soil samples.

The soil samples were extracted using the Thermo Scientific™ Dionex™ ASE™ 350 Accelerated Solvent Extractor, which produced 70–130% recovery of all PFAS target compounds. Accelerated solvent extraction has outperformed commonly used, manual "shaking" extraction methods under the same conditions.

After ASE extraction, the solution from the ASE sample collection vials underwent clean-up using solid-phase extraction (SPE) and were analyzed on an LC/MS/MS in a 15-min run. Blanks contained no significant amounts of PFAS. Accelerated solvent extraction is demonstrated to be acceptable for the extraction of short- and long-chain PFAS, with a variety of polarities and head-groups, from soil in the range of 1 ng/g to 400 ng/g.

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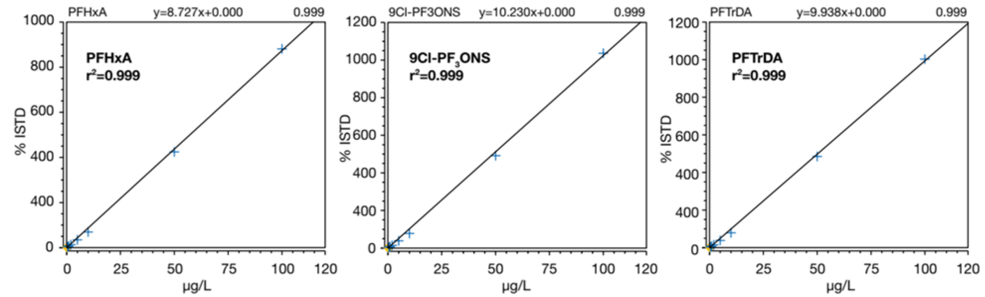
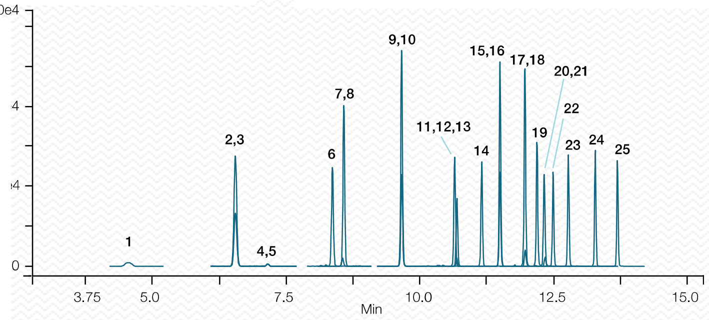
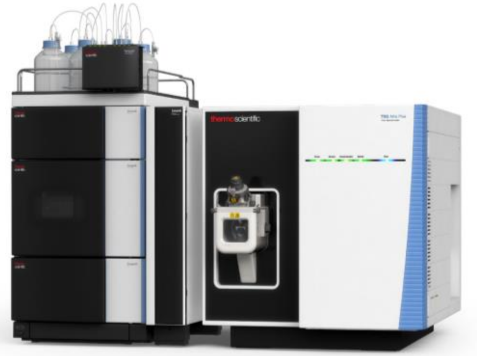






LC-MS/MS

Triple quadrupole mass spectrometer

PFAS: Source and Exposure

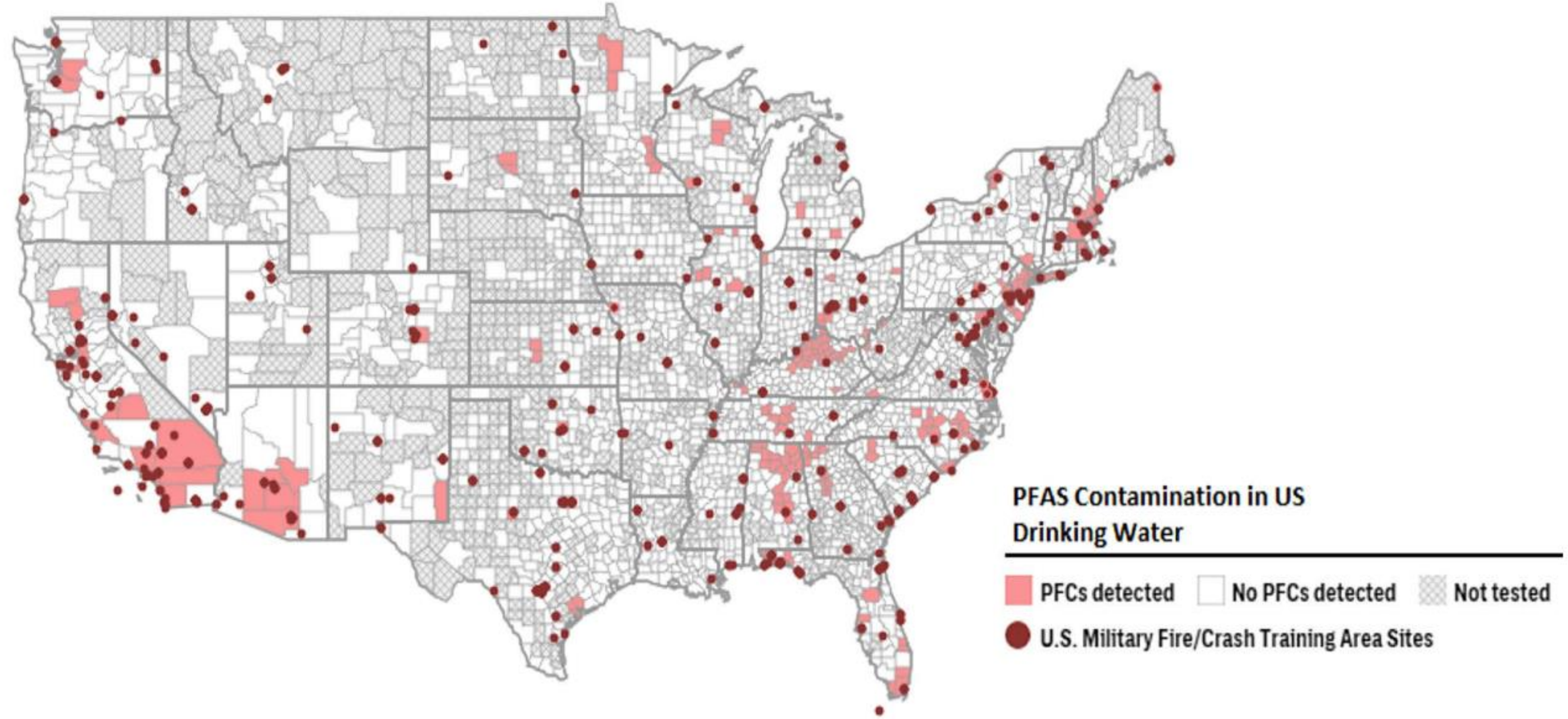
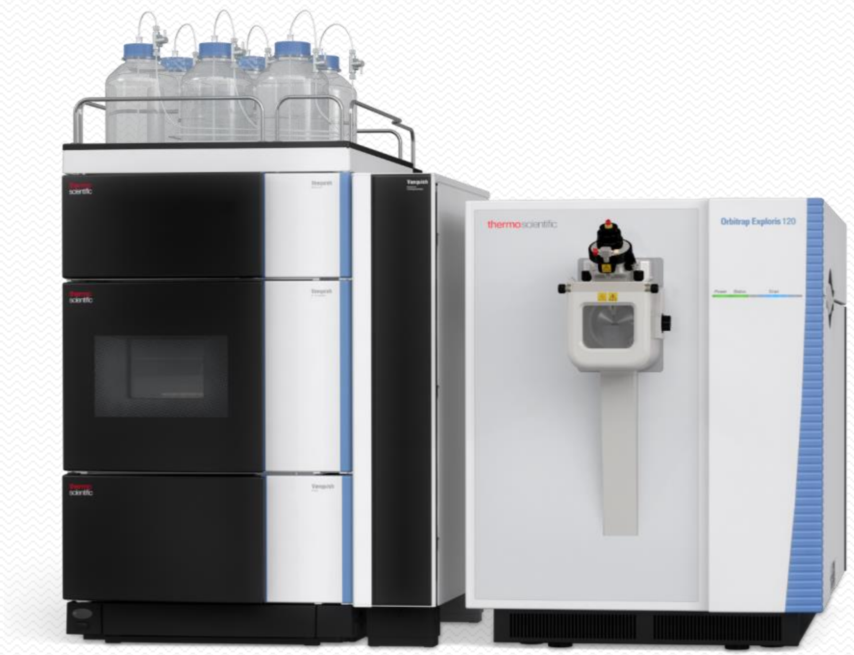


Figure 2. PFAS occurrence data released by EPA for UCMR 3, using EPA Method 537 and monitoring six PFAS compounds. Data visualization by Moiz Syed. Sources: EPA and Departmennt of Defense. https://theintercept.com/2015/12/16/toxic-firefighting-foam-has-contaminated-u-s-drinking-water-with-pfcs/

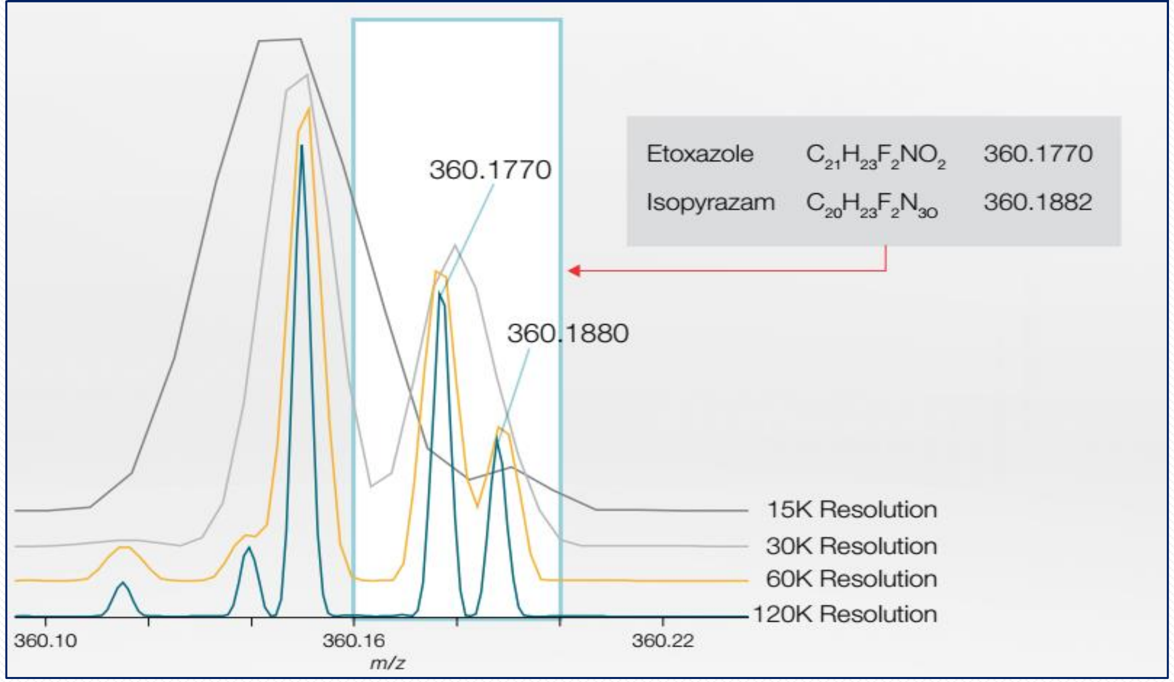
- the United States Environmental Protection Agency (EPA) developed EPA Method 5374 for the Unregulated Contaminant Monitoring Rule (UCMR 3) program, which collects data for contaminants suspected to be present in drinking water but that do not currently have health-based standards set under the Safe Drinking Water Act (SDWA).5
- In 2012, six PFASs were added to the UCMR 3 list to be monitored, including PFOS and PFOA using EPA Method 537.
- In October 2015, occurrence data from the study was released. It is important to note that this is only a small fraction of the hundreds of compounds that can potentially exist in the environment, such as the multiple branched and polyfluorinated PFASs breakdown products that have been known to be in environmental waters.

Screening for untargeted PFAS



Thermo Scientific™ Orbitrap Exploris™ 120 High Resolution, Accurate-Mass (HRAM) Quadrupole Orbitrap MS

High Resolution & High Accuracy



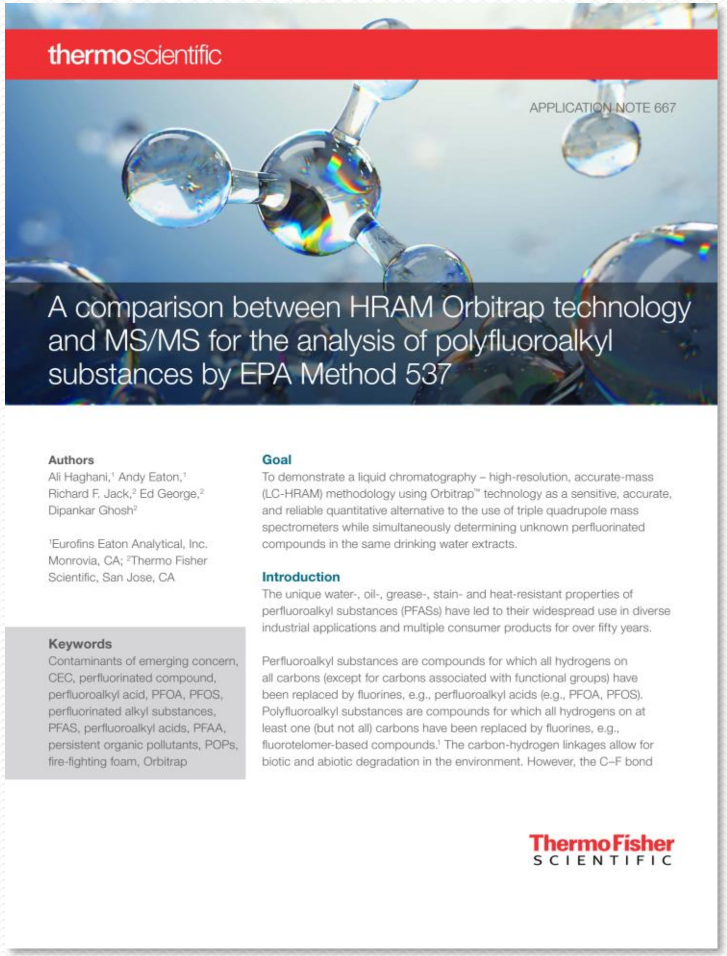
Full scan quantitation of target PFASs

+ MS/MS confirmation

+ Screening for other contaminants

Routine quantitative workflows and non-targeted analysis can be performed in a single analysis.

Targeted quantitation & untargeted screening of PFASs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APPLICATION NOTE 667

A comparison between HRAM Orbitrap technology and MS/MS for the analysis of polyfluoroalkyl substances by EPA Method 537

Authors
Ali Haghani,[1] Andy Eaton,[1] Richard F. Jack,[2] Ed George,[2] Dipankar Ghosh[2]

[1]Eurofins Eaton Analytical, Inc. Monrovia, CA; [2]Thermo Fisher Scientific, San Jose, CA

Keywords
Contaminants of emerging concern, CEC, perfluorinated compound, perfluoroalkyl acid, PFOA, PFOS, perfluorinated alkyl substances, PFAS, perfluoroalkyl acids, PFAA, persistent organic pollutants, POPs, fire-fighting foam, Orbitrap

Goal
To demonstrate a liquid chromatography – high-resolution, accurate-mass (LC-HRAM) methodology using Orbitrap™ technology as a sensitive, accurate, and reliable quantitative alternative to the use of triple quadrupole mass spectrometers while simultaneously determining unknown perfluorinated compounds in the same drinking water extracts.

Introduction
The unique water-, oil-, grease-, stain- and heat-resistant properties of perfluoroalkyl substances (PFASs) have led to their widespread use in diverse industrial applications and multiple consumer products for over fifty years.

Perfluoroalkyl substances are compounds for which all hydrogens on all carbons (except for carbons associated with functional groups) have been replaced by fluorines, e.g., perfluoroalkyl acids (e.g., PFOA, PFOS). Polyfluoroalkyl substances are compounds for which all hydrogens on at least one (but not all) carbons have been replaced by fluorines, e.g., fluorotelomer-based compounds.[1] The carbon-hydrogen linkages allow for biotic and abiotic degradation in the environment. However, the C–F bond

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U.S. EPA Method 537 target list

PFAS compound	Critical Level (ng/L)	DL (ng/L)	LCMRL (ng/L)
PFBS	0.15	0.2	<0.5
PFDA	0.15	0.26	<0.5
PFDoA		0.47	0.73
PFHpA	0.09	0.15	<0.5
PFHxA	0.13	0.19	<0.5
PFHxS		1.7	2.4
PFNA	0.11	0.17	<0.5
PFOA		0.22	0.5
PFOS		0.26	0.5
PFTA	0.15	0.2	<0.5
PFTrDA		0.31	0.55
PFuNA		0.38	1

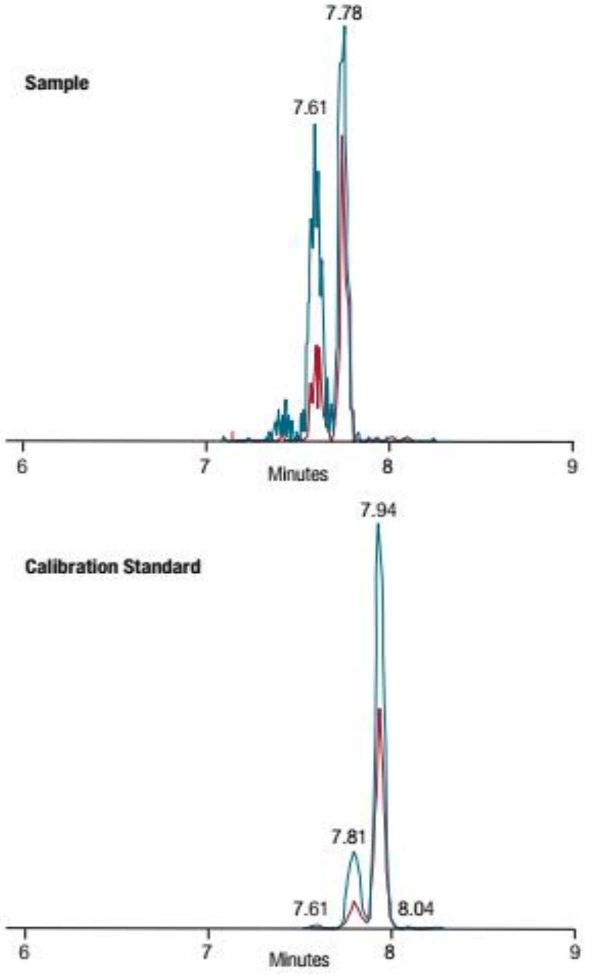


Figure 8. PFOS branch ratio comparison in a sample vs. a calibration standard. These ratios are represented by overlay of the SRM transitions 499→80 (blue trace) and 499→99 (red trace).

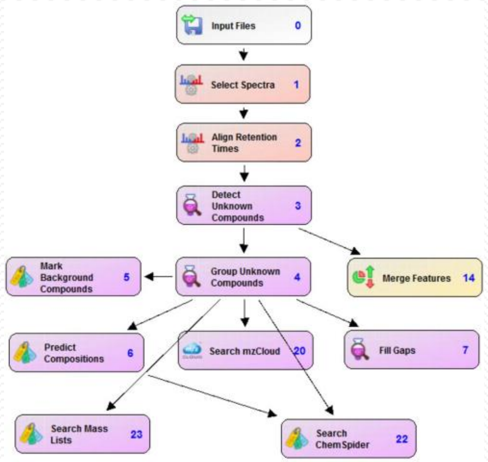
HRAM Orbitrap technology provides equal or better quantitation in full scan as compared to traditional triple quadrupole techniques, with the additional capability to screen for unknown PFASs.

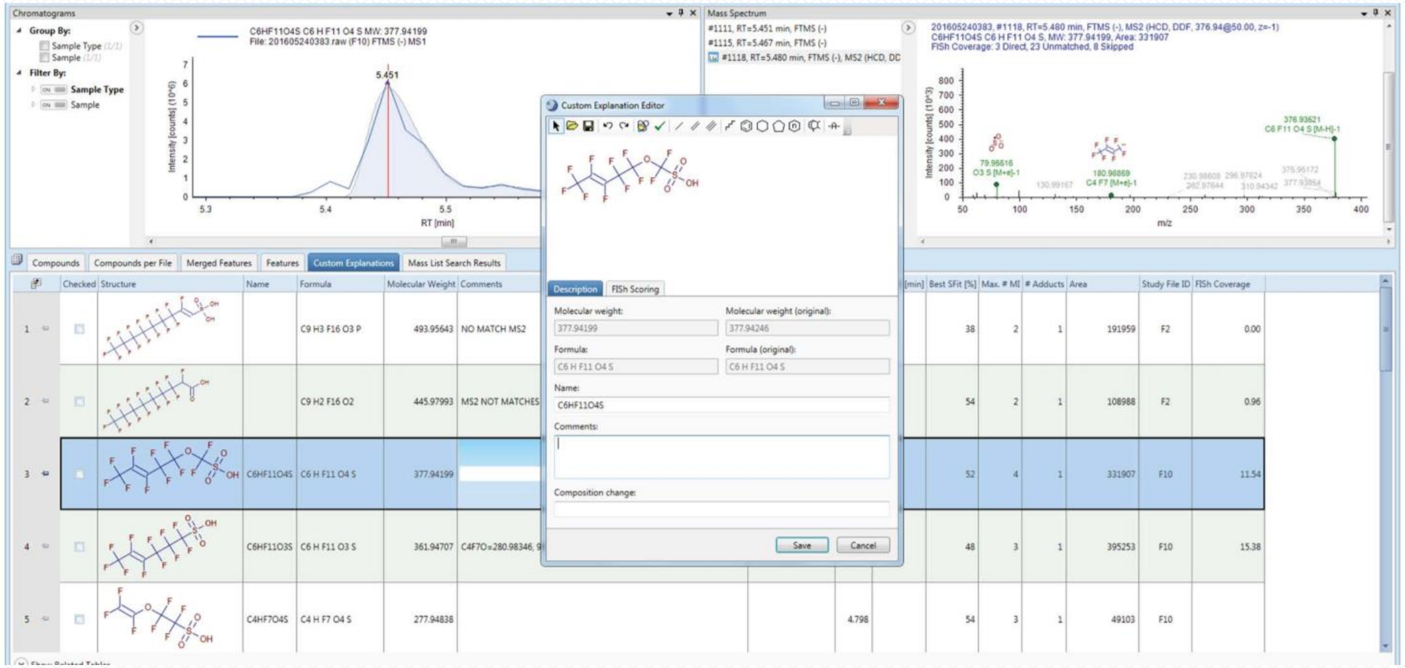
Targeted quantitation & untargeted screening of PFASs

Using a full scan approach, required detection limits or MRLs can be achieved while interrogating for other untargeted PFAS compounds.

The compounds highlighted in blue are additional analytes that are not part of the original U.S. EPA Method 537 list but were found in processed drinking water from the same UCMR3 water extracts.

PFAS compound	Critical Level (ng/L)	DL (ng/L)	LCMRL (ng/L)
PFBA		0.19	0.64
PFODA		0.55	1
PFDS	0.13	0.19	<0.5
PFHxDA		0.12	0.5
PFPA	0.18	0.19	<0.5





Summary

PFAS, a global concern

- The vast uses of PFAS compounds has resulted in a great number of sources for these substances to enter the environment.
- Common modes of transport are runoff, especially with firefighting foams into water, or leachate from landfills, discharge from manufacturing processes or improper disposal.
- Once in the ecosystem, plants, animals and humans are all exposed to PFAS.
- The C-F bonds in the PFAS molecule are very strong,

  which make metabolism of these compounds very difficult.
- PFAS bioaccumulates over time and causes various health concerns
- The detection and quantification of known PFAS and the discovery of unknown PFAS substances are important

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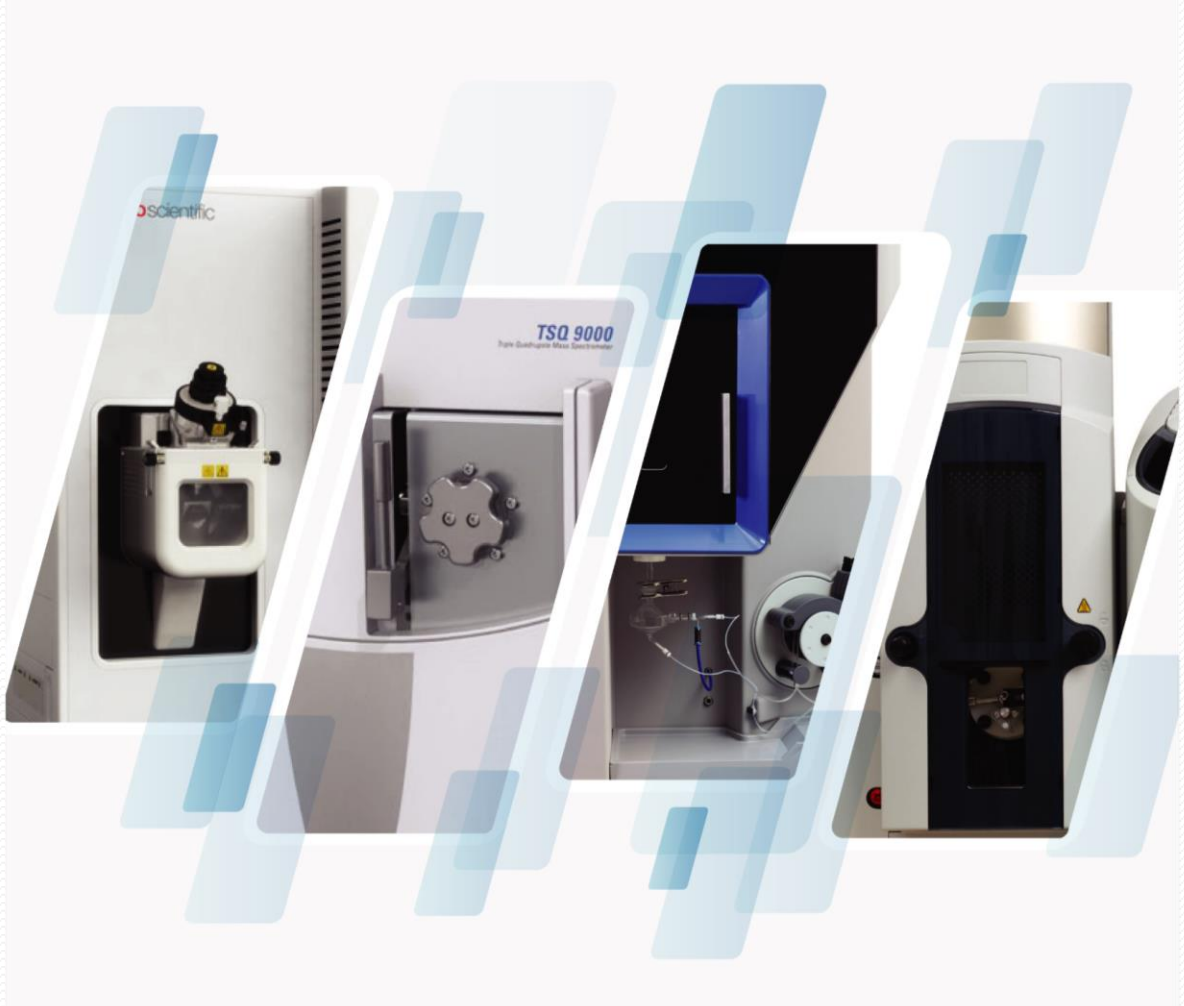

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