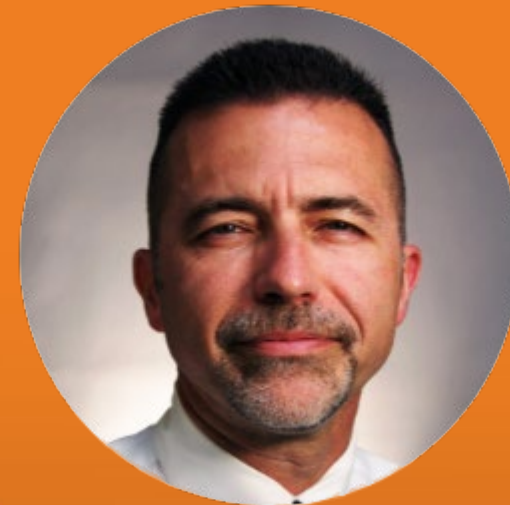


Presentation for:

# What are “Volatile PFAS” and How Do You Analyze for Them in Air?



**Charles Neslund**

*Scientific Officer and PFAS Practice Leader*

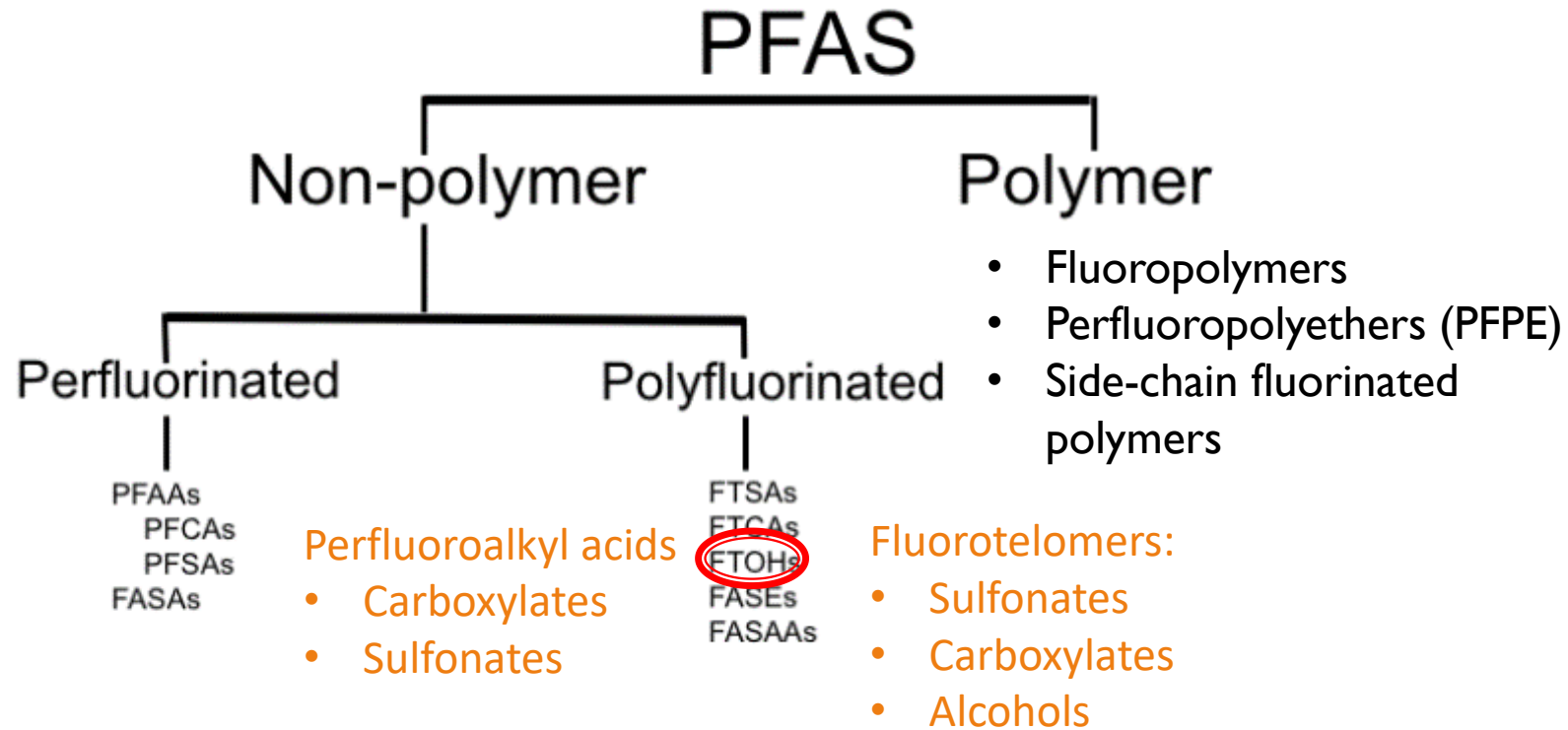


Environment Testing  
America

# WHAT ARE VOLATILE PFAS



# The General Classes of Per- and Polyfluoroalkyl Substances (PFAS)



Source: ITRC Naming Conventions and Physical Chemical Properties fact sheet



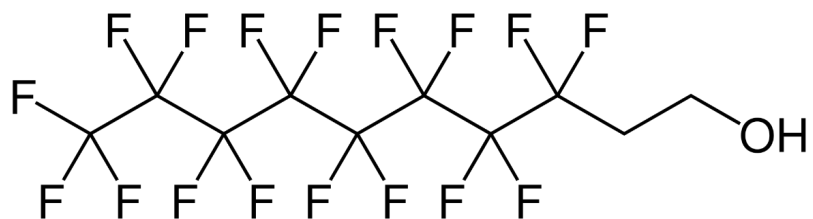
# What are fluorotelomer alcohols (FTOH)?

Fluorotelomer alcohols are polyfluorinated alkyl substances that have been used as precursors in the manufacture of perfluorinated alkyl substances, acrylate polymers and used in the manufacture of some consumer products.

- Paper based food contact material (FCM)
- Waterproofing/Impregnation Agents
- Waxes and cleaning agents
- Textiles
- Clothing
- Carpet
- Commercial AFFF



## 8:2 Fluorotelomer Alcohol

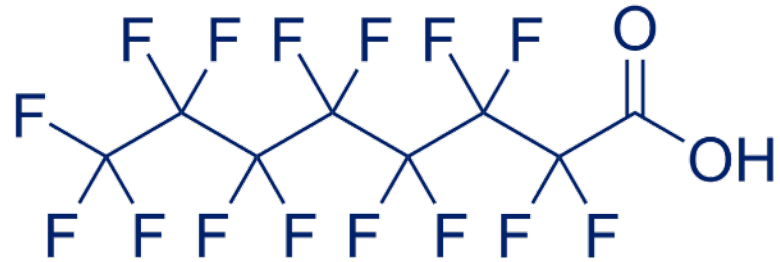


Naming convention is the number of carbons that are fully fluorinated followed by the number of hydrocarbon carbons

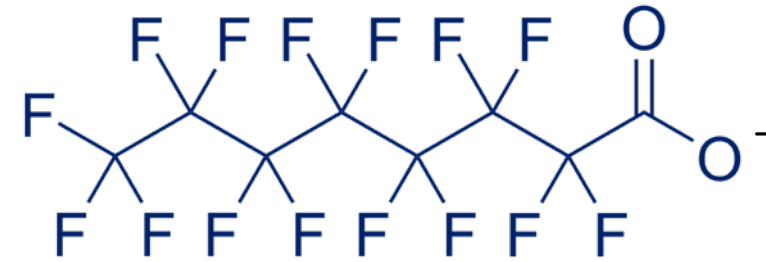
Other fluorotelomer alcohols typically used:

- 4:2 FTOH
- 6:2 FTOH
- 7:2s FTOH
- 8:2 FTOH
- 10:2 FTOH

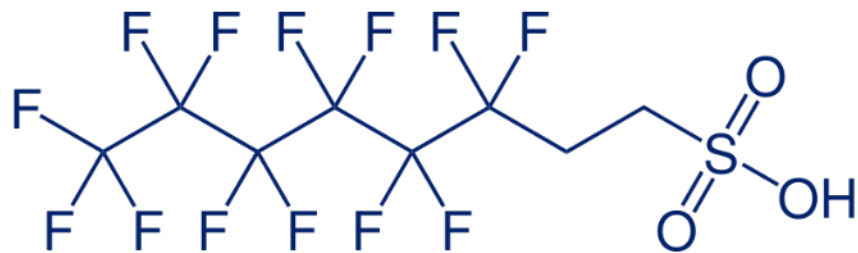
# Examples



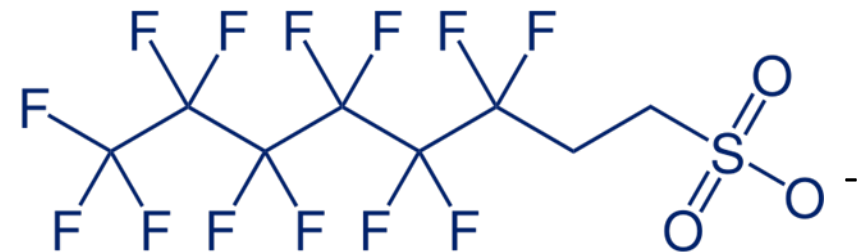
Perfluorooctanoic acid (PFOA)



Perfluorooctanoate (PFOA)



6:2 Fluorotelomer sulfonic acid (6:2 FTS)



6:2 Fluorotelomer sulfonate (6:2 FTS)



# Fluorotelomer Alcohols

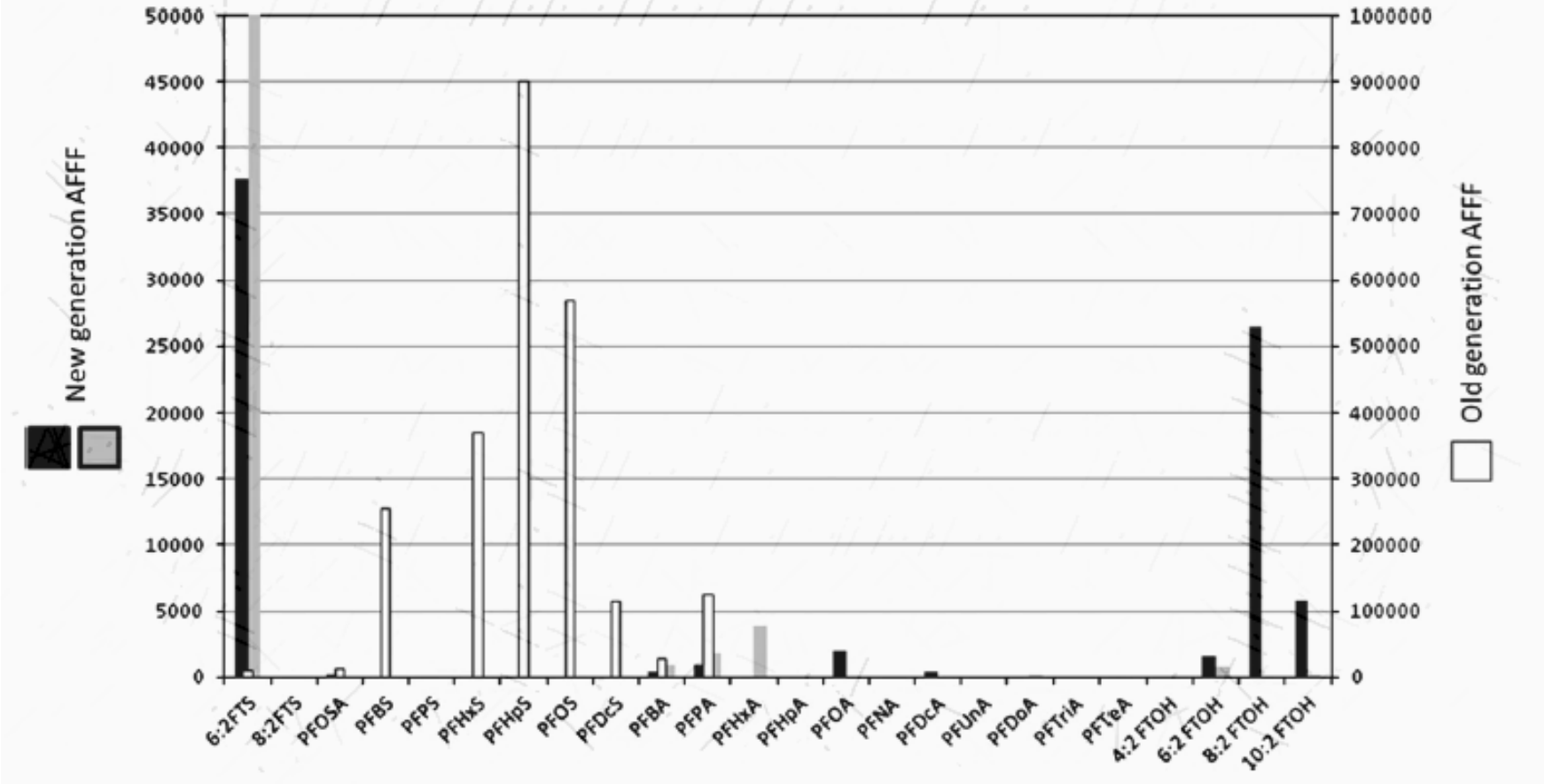
Therefore, fluorotelomer alcohols are volatile meaning that they can be separated and analyzed by gas chromatography.

But are they 8260 type volatile or 8270 type semi-volatile?

We chose 8270 type...

- GC/MS/MS method
- Water and solids
- Instrumental set-up like 8270E
- Extractions like 3510 and 3540/50
- Isotopically labeled analogs available as surrogates

# Chemical Fingerprinting



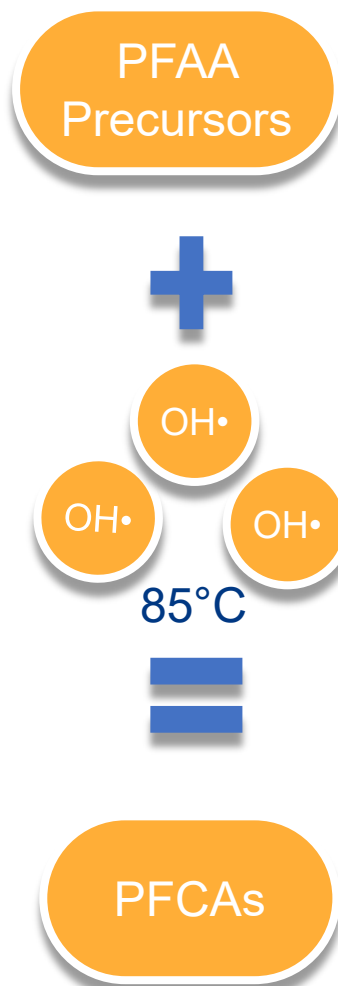
Herzke, et al., 2012, Chemosphere, 88, 980-987



## What is the Total Oxidizable Precursor (TOP) Assay?

- A PFAS sample preparation technique
- Indicates presence of unidentified precursors
- Used in conjunction with standard analysis
- Contrasts pre and post oxidation results

<https://pubs.acs.org/doi/10.1021/es302274g>



## What the TOP Assay is NOT

- A risk assessment tool
- Total PFAS methodology
- Identify Unknown PFAS
- Mass balance PFAS
- Non-target identification

# WHAT IS THE CONCERN





# SOURCES

Where PFAS contamination in air emissions could be coming from

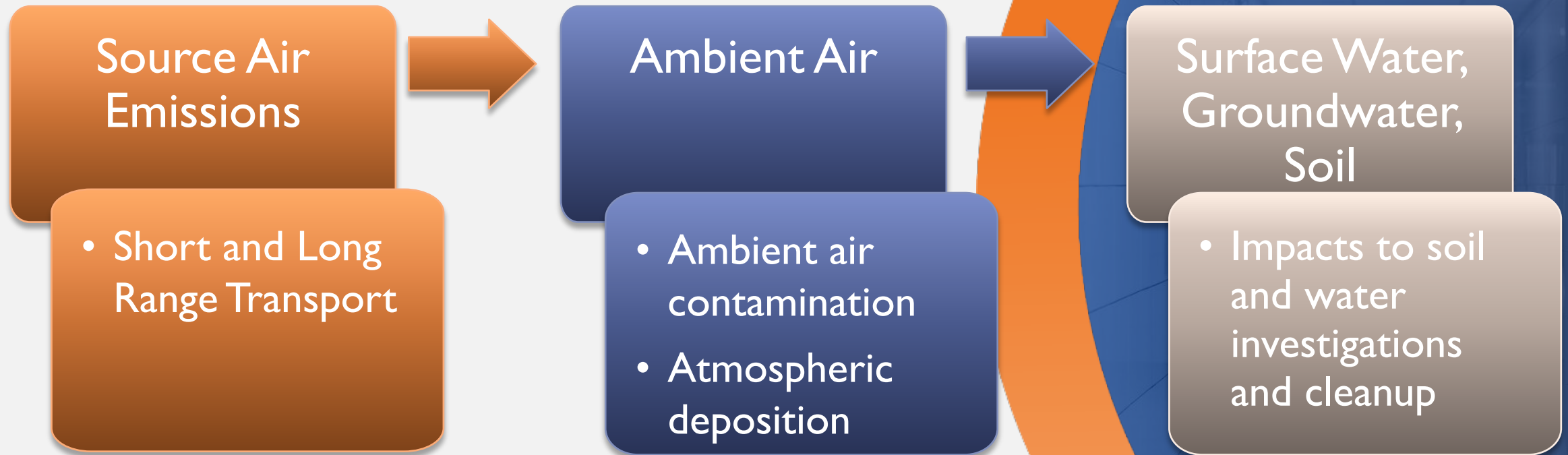
- Hazardous Waste Incinerators
- Sewage Sludge Incinerators
- Thermal Oxidizers
- Thermal Desorbers “Dirt Burners”
- Chemical Plants/Process Vents

- Manufacturing Emissions
- Treatment System Emissions
- Landfill Gas
- Airports/Fire Fighting
- Users/Coating Operations





# WHY IS THIS A PROBLEM



# TYPES OF AIR VOLATILE PFAS ARE FOUND IN



# Source Air

## **EPA OTM 45 / GCMSMS**

Application: Volatile PFAS  
from Source Air Emissions

Collection: by OTM-45 or  
Modified Method 18

Sample Preparation: by  
OTM-45 or MM18

Analysis: FTOHs by GCMSMS  
with Isotope Dilution

# Ambient Air

## **Modified TO-13A / GCMSMS**

Application: Volatile PFAS in  
Ambient Air

Collection: PUF/Resin Cartridge  
based off EPA TO-13A

Sample Preparation: Methanol  
Extraction, user-defined  
method

Analysis: FTOHs by GCMSMS  
with Isotope Dilution

# Vapor

## **Modified TO-17 / GCMSMS**

Application: Volatile PFAS in  
Indoor Air and Soil Vapor

Collection: Thermal Desorption  
(TD) Tube based off EPA TO-17

Sample Preparation: Thermal  
Desorption based off EPA TO-17

Analysis: FTOHs by TD/GCMSMS



# VOLATILE PFAS IN SOURCE AIR



# Targeted PFAS

## TARGETED PFAS

Perfluorobutanoic acid (PFBA)

Perfluoropentanoic acid (PFPeA)

Perfluorohexanoic acid (PFHxA)

Perfluoroheptanoic acid (PFHpA)

Perfluorooctanoic acid (PFOA)

Perfluorononanoic acid (PFNA)

Perfluorodecanoic acid (PFDA)

Perfluoroundecanoic acid (PFUnA)

Perfluorododecanoic acid (PFDoA)

Perfluorotridecanoic Acid (PFTriA)

Perfluorotetradecanoic acid (PFTeA)

Perfluorobutanesulfonic acid (PFBS)

Perfluorohexanesulfonic acid (PFHxS)

Perfluoroheptanesulfonic Acid (PFHpS)

Perfluorooctanesulfonic acid (PFOS)

Perfluorodecanesulfonic acid (PFDS)

Perfluorooctane Sulfonamide (FOSA)

Perfluoro-1-pentanesulfonate (PFPeS)

Perfluoro-1-nonanesulfonate (PFNS)

Perfluorododecanesulfonic acid (PFDoS)

Perfluoro-n-hexadecanoic acid (PFHxDA)

Perfluoro-n-octadecanoic acid (PFODA)

NMeFOSAA

NEtFOSAA

NEtFOSA

NMeFOSA

NMeFOSE

NEtFOSE

4:2FTS

6:2FTS

8:2FTS

10:2FTS

DONA

HFPO-DA (GenX)

11CI-PF3OUdS

9CI-PF3ONS

NFDHA

PFEESA

PFMPA

PFMBA

3:3 FTCA

5:3 FTCA

7:3 FTCA

6:2 FTCA

8:2 FTCA

10:2 FTCA

6:2 FTUCA

8:2 FTUCA

PFECHS

10:2 FTUCA

PFPrS

PFMOAA

PFECA G

FTOHs

PFO4DA

PFO3OA

PFO2HxA

PFO5DA

PMPA

PEPA

MTP

PFPrA

R-EVE

NVHOS

Hydro-EVE Acid

EVE Acid

R-PSDA

Hydrolyzed PSDA

R-PSDCA

PS Acid

Hydro-PS Acid

Fluoroether E-1



# Non-Ionic PFAS Compounds

**4:2 FTOH**

4:2 Fluorotelomer Alcohol



**Fluoroether E-1**

Heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether

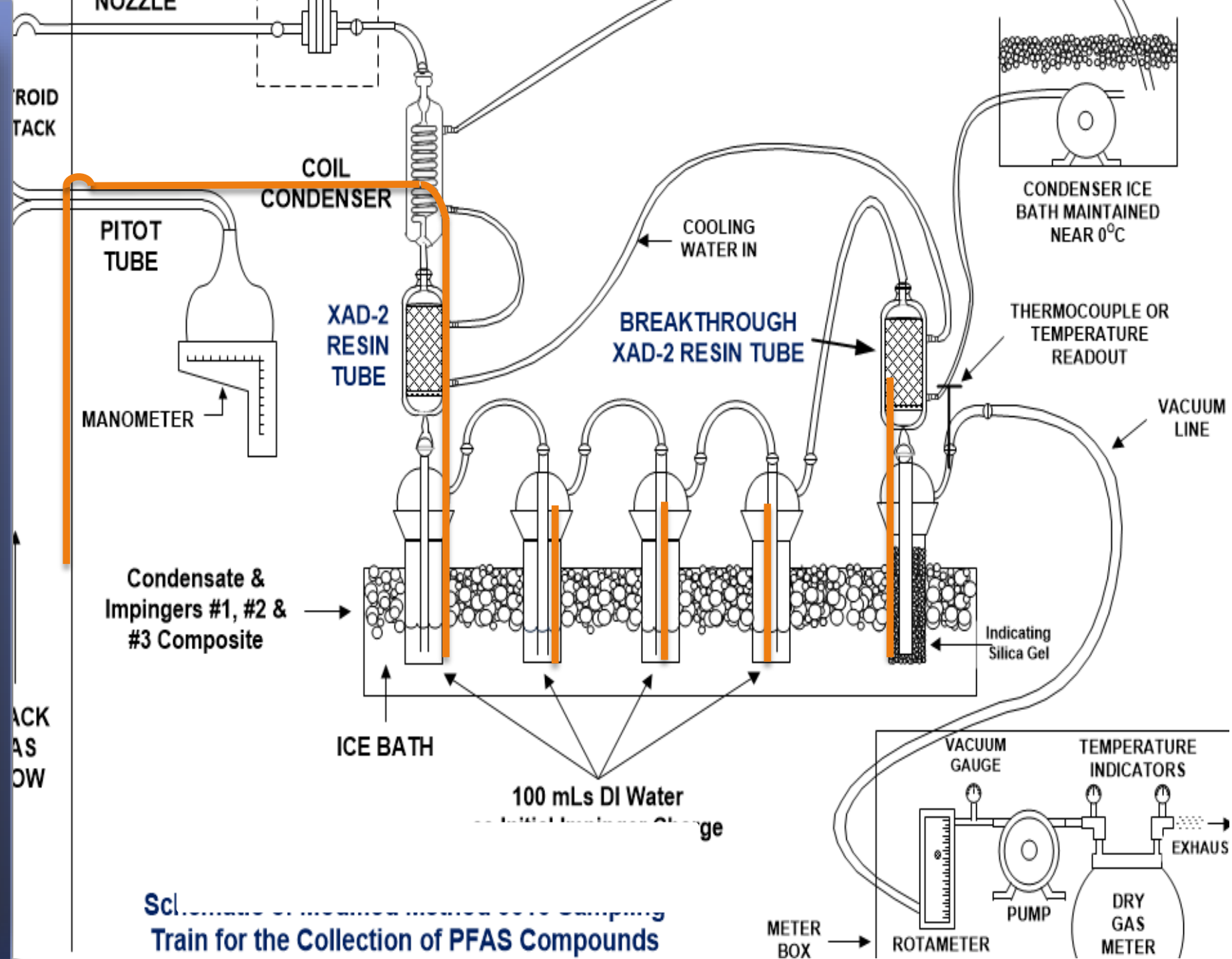


**CF<sub>4</sub>**

Carbon Tetrafluoride







Sci. Train for the Collection of PFAS Compounds



# TESTING FOR PFAS IN AMBIENT AIR



# Vapor Pressure

Compound	Vapor Pressure 20-25C (PA)	Henry's Law Constant
4:2 FTOH	2.1 E+02	2.4 E-02
6:2 FTOH	1.8 E+01	1.5 E-01
7:2s FTOH	-	-
8:2 FTOH	4.0 E+00	5.5 E+00
10:2 FTOH	2.1 E-01	4.2 E+00

Trichloroethene has a vapor pressure of 7.8 E+03 at 20C



# High Volume

~300m<sup>3</sup>



High Volume Sampler

~220L/min

PUF/Resin/Quartz  
Filter, High Volume

~2 pg/m<sup>3</sup> range

# Low Volume

100s to 1000s Liters



Personal Sized Pump

1 L-20L/min

PUF/Resin Cartridge,  
Low Volume

~1 ng/m<sup>3</sup> range

# Ultra-Low Vol

10s to 100s Liters



Multi-sorbent  
Tube

Thermal  
Desorption

Analysis by  
GC/MS/MS

~1 ug/m<sup>3</sup> range

*Currently used for R&D*

# FTOHs in Air by Modified EPA TO-17



## Thermal Desorption (TD) – GC/MS/MS

- Multi-bed sorbent tube
- Concentrates sample to improve sensitivity
- Targets FTOHs
- Accommodates low volume for soil gas and high volume for indoor air
- TD sample introduction
  - Enhanced sensitivity as compared to solvent injection



## FTOHs in Air by Modified EPA TO-17

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- GC/MS/MS
  - Sensitivity and Selectivity demonstrated for FTOHs in representative soil gas and indoor air matrices
- FTOH Reporting Limits
  - Base reporting limits ~0.1 ng/sample
  - Final reporting limits dependent upon sample volume collected with ranges from 1 ng/m<sup>3</sup> to 1 µg/m<sup>3</sup>.



# QUESTIONS?

Charles.Neslund@EurofinsET.com  
717-799-0439



Environment Testing  
America

