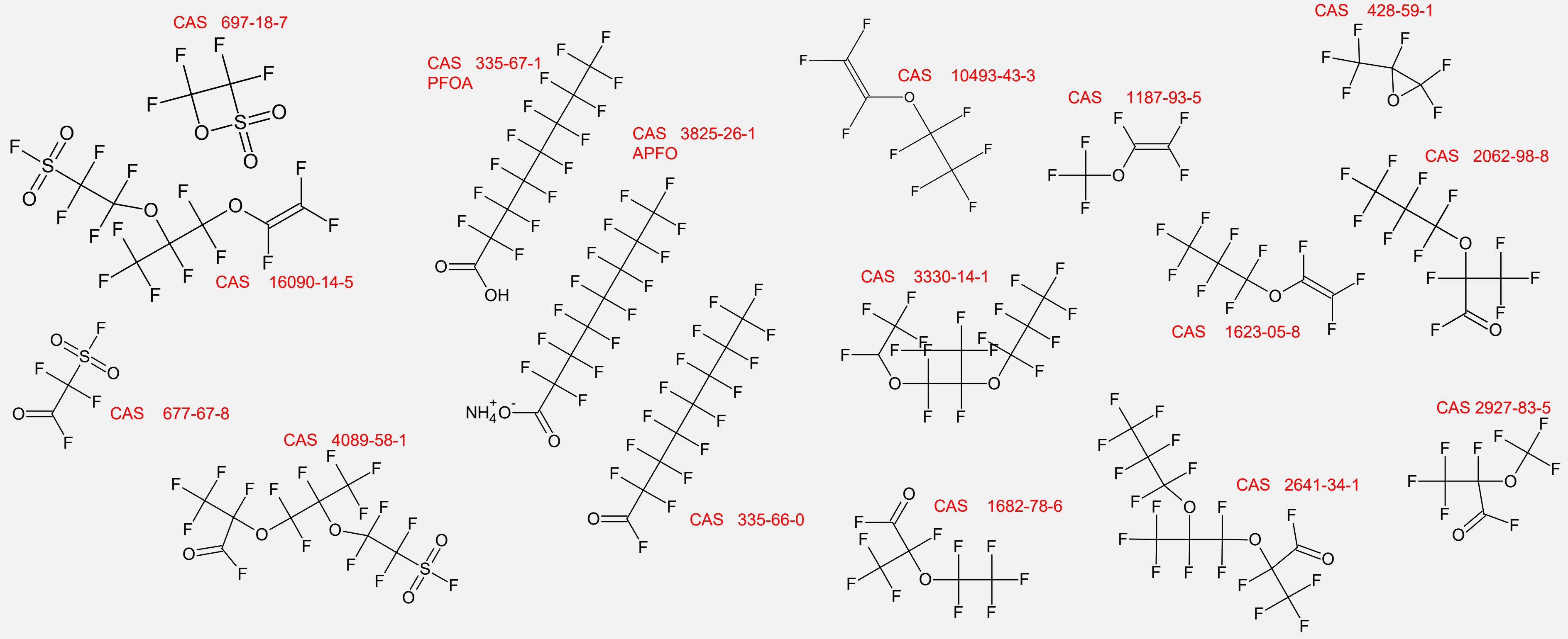
PFAS Emissions Measurement and Incineration Research

Lara Phelps
US EPA Office of Research and Development, Center for Environmental Measurement and Modeling

National Association of Clean Air Agencies
October 15, 2020

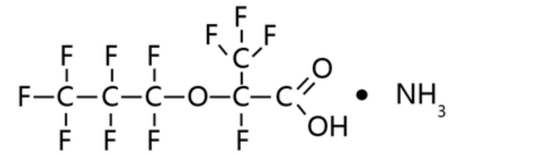
United States Environmental Protection Agency

So many PFAS compounds!



How do we measure them?

How do we destroy them?



GenX Chemical Structure

Potential Sources of PFAS in the Environment

- Direct release of PFAS or PFAS products into the environment
  - Use of aqueous film forming foam (AFFF) in training and emergency response
  - Industrial facilities
  - Incineration/thermal treatment facilities
- Landfills and leachates from disposal of consumer and industrial products containing PFAS
- Wastewater treatment effluent and land application of biosolids

Thousands of chemicals can potentially become air sources during production, use, and disposal of PFAS-contaminated materials

PFAS

- **Non-polymers**
  - **Perfluoroalkyl acids (PFAAs)** $C_nF_{2n+1}R$
    - Perfluoroalkyl carboxylic acids (PFCAs)
    - Perfluoroalkane sulfonic acids (PFSAs)
    - Perfluoroalkyl phosphonic acids (PFPAs)
    - Perfluoroalkyl phosphinic acids (PFPIAs)
  - **Perfluoroalkane sulfonyl fluoride (PASF)** $C_nF_{2n+1}SO_2F$ → **PASF-based derivatives** $C_nF_{2n+1}SO_2\text{-}R$, R = NH, $NHCH_2CH_2OH$, etc.
  - **Perfluoroalkyl iodides (PFAIs)** $C_nF_{2n+1}I$ → **Fluorotelomer iodides (FTIs)** $C_nF_{2n+1}CH_2CH_2I$ → **FT-based derivatives** $C_nF_{2n+1}CH_2CH_2\text{-}R$, R = NH, $NHCH_2CH_2OH$, etc.
  - **Per- and polyfluoroalkyl ethers (PFPEs)-based derivatives**
    - Polyfluoroalkyl ether carboxylic acids
- **Polymers**
  - **Fluoropolymers**
    - Polytetrafluoroethylene (PTFE)
    - Polyvinylidene fluoride (PVDF)
    - Fluorinated ethylene propylene (FEP)
    - Perfluoroalkoxyl polymer (PFA)
    - Others
  - **Side-chain fluorinated polymers**
    - Fluorinated (meth)acrylate polymers
    - Fluorinated urethane polymers
    - Fluorinated oxetane polymers
  - **Perfluoropolyethers**

EPA PFAS Air-Related Research

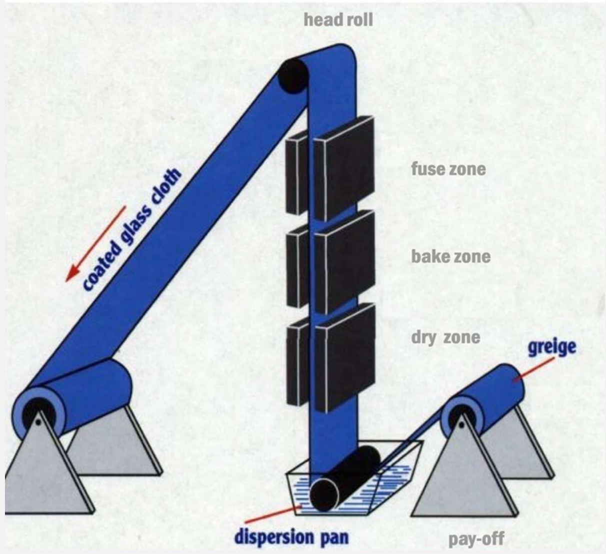
- **Analytical Methods** to detect, identify and quantify PFAS in emissions and ambient air

- **Dispersion Modeling** to predict air transport and deposition associated with air sources

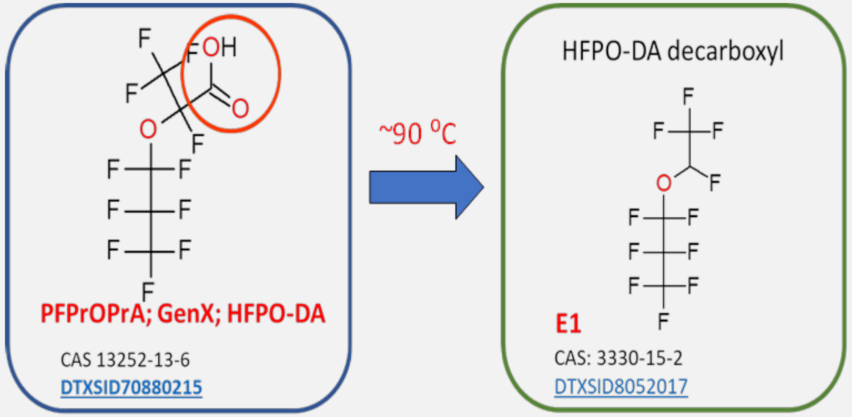
- **Effectiveness of Thermal Treatments** for destroying PFAS materials

Emissions Measurement Considerations/Challenges

- Emission sources are diverse:
  - PFAS chemical manufacturers
  - PFAS used in commercial applications
  - PFAS emitted during thermal treatment of waste (e.g., AFFF, biosolids, municipal)
  - Products of Incomplete Combustion (PICs)
- Process can alter emission composition
- Validated source and ambient air methods for PFAS do not exist, but some research methods are available
- Current emissions tests often target only a small number of PFAS compounds for analysis while significantly more may be present



Example Coating Process

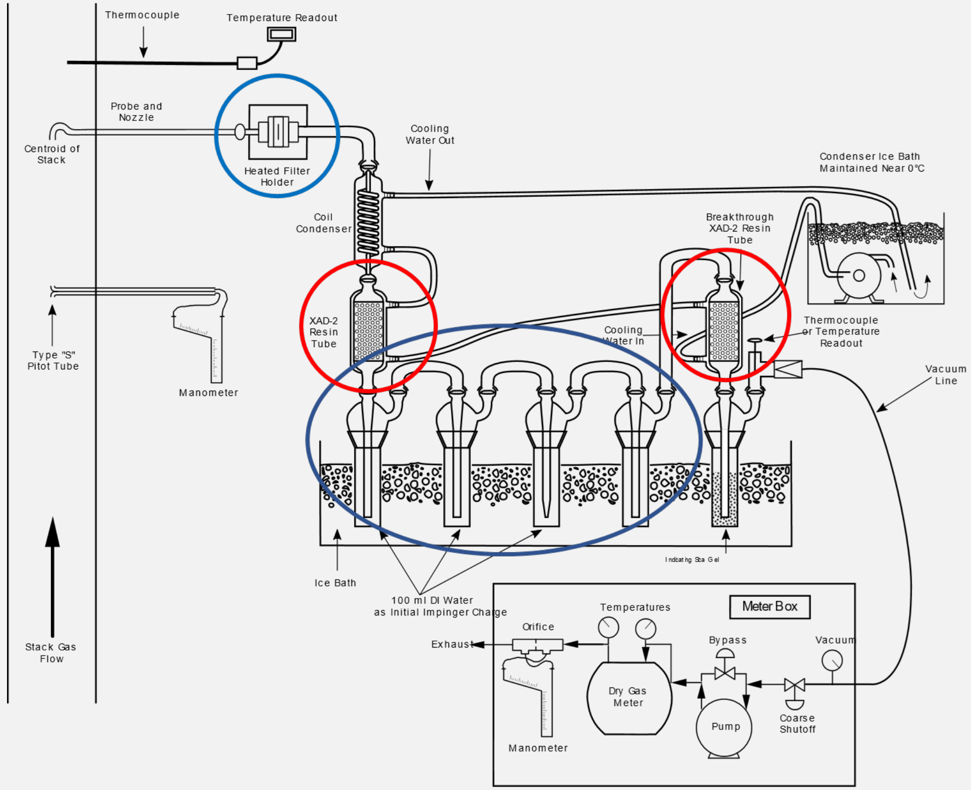


ORD PFAS Emissions Measurement Activities

- Supporting multiple State emissions testing campaigns
  - States and Regions are those most concerned and looking to EPA for guidance
  - ORD collaborating to provide technical guidance and measurement assistance
  - Providing options for more comprehensive emissions characterizations
  - Analysis of industrial emissions samples for non-targeted PFAS compounds
  - Actively participating or leading field emissions tests
- Supporting EPA Program Offices
  - Office of Air Quality Planning and Standards (OAQPS)
  - Office of Land and Emergency Management (OLEM)
- Methods development research and field evaluations
- Conducting combined methods development and source characterization field testing where possible

Semivolatile/Nonvolatile Sampling Methods

- Modified SW-846 Method 0010 (MM5) Train for polar and nonpolar PFAS compounds
  - Extra XAD-2 trap for breakthrough
  - Modified glassware rinses
  - Separate solvent extractions for polar and nonpolar compounds
  - Four (4) separate fractions for analysis
- Primary approach for targeted and non-targeted analyses
  - Isotope dilution for targeted analyses
  - Use of internal and pre-sampling surrogate standards (limited by availability of isotopically labeled standards)
  - High resolution mass spec nontargeted analyses
- Other Test Method (OTM)-45 underway for polar PFAS compounds
- Expanding to include fluorotelomer alcohols (FTOHs)



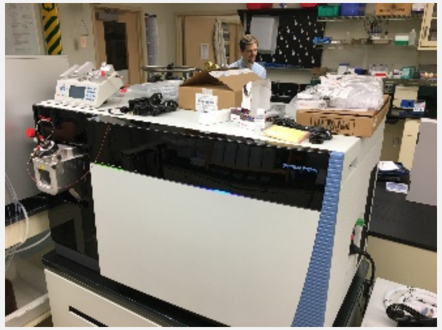
Volatile Sampling Methods

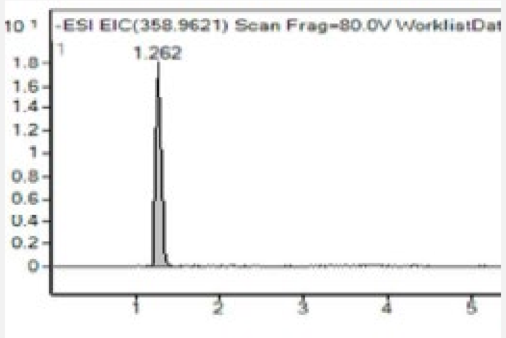
- Using SUMMA canisters (limits use to nonpolars)
- Sorbent traps (suitable for polars and nonpolars)
- Moisture and acid gases a problem for both approaches
- GC/MS analysis for targeted and non-targeted compounds
  - C1-C3 targets
    (e.g., CF_4, CHF_3, C_2F_4,C_2F_6, C_3F_6, C_3F_8, etc)
  - Industrial PFAS
    (e.g., E1, HFPO, FTOHs)
  - High resolution mass spec nontargeted analyses

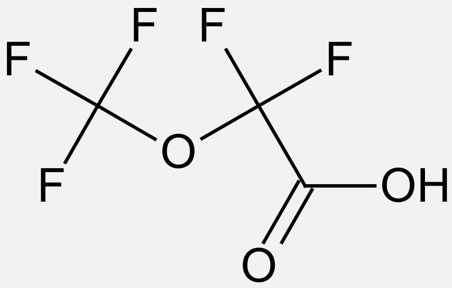
EPA
United States
Environmental Protection
Agency

Non-Targeted Analysis

- High resolution mass spectrometry
- Software calculates exact number and type of atoms needed to achieve measured mass, e.g. $C_3HF_5O_3$
- Software and fragmentation inform most likely structure
- With mass, formula, structure known, potential identities determined by database search





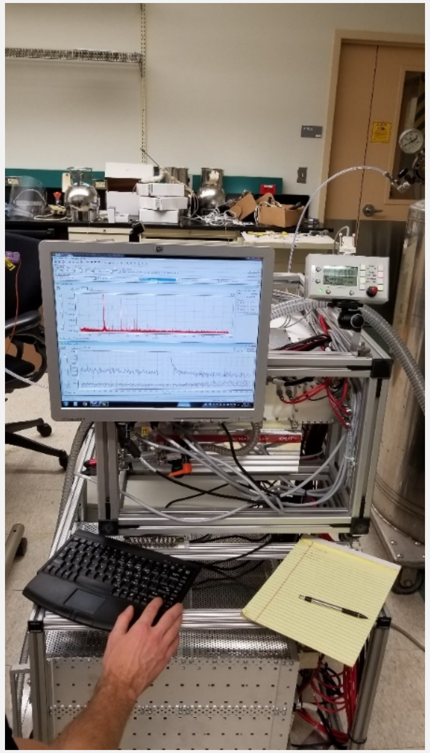


Molecular Formula: $C_3HF_5O_3$
Monoisotopic Mass: 179.984585 Da
[M-H]-: 178.977308 Da

Source: Strynar et al. 2015; Sun et al. 2016

EPA
United States
Environmental Protection
Agency

Innovative Measurements Research



Field Deployable, Time of Flight-Chemical Ionization Mass Spectrometer (ToF–CIMS)

- Real-time measurement of polyfluorinated carboxylic acids (PFAS) and FTOHs
- Super sensitive (ppt measurement levels)
- Currently being evaluated as a process emissions analyzer

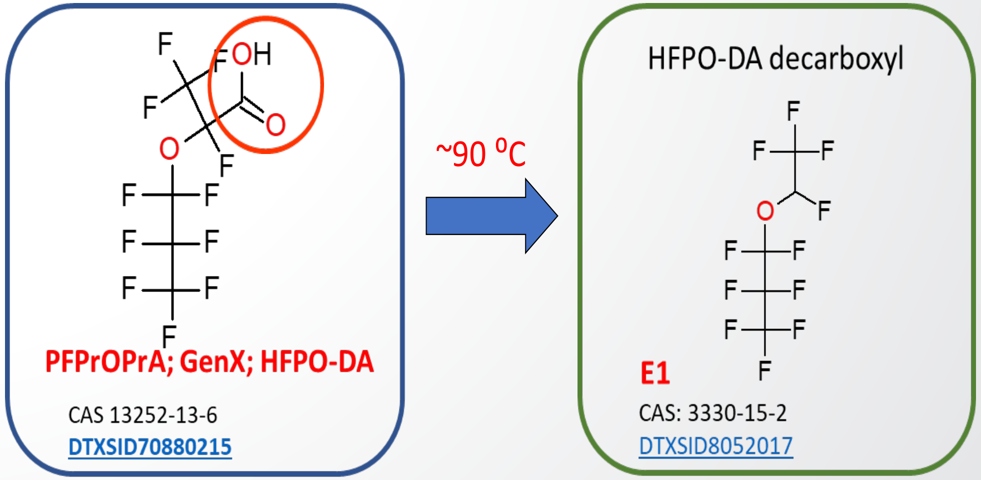
Total Organic Fluorine

- Combustion/Ion Chromatography?
- Potential technique
- Sample collection an important aspect

Thermal Treatment of PFAS

- Highly electronegative fluorine (F) makes carbon/fluorine (C-F) bonds particularly strong, require high temperatures for destruction
  - Unimolecular thermal destruction calculations suggest that CF_4 requires 1,440 °C for >1 second to achieve 99.99% destruction (Tsang et al., 1998)
  - Sufficient temperatures, times and turbulence are required

- Functional group relatively easy to remove/oxidize
  - Low temperature decarboxylation is an example
  - Information regarding potential products of incomplete combustion (PICs) is lacking



Products of Incomplete Combustion (PICs)

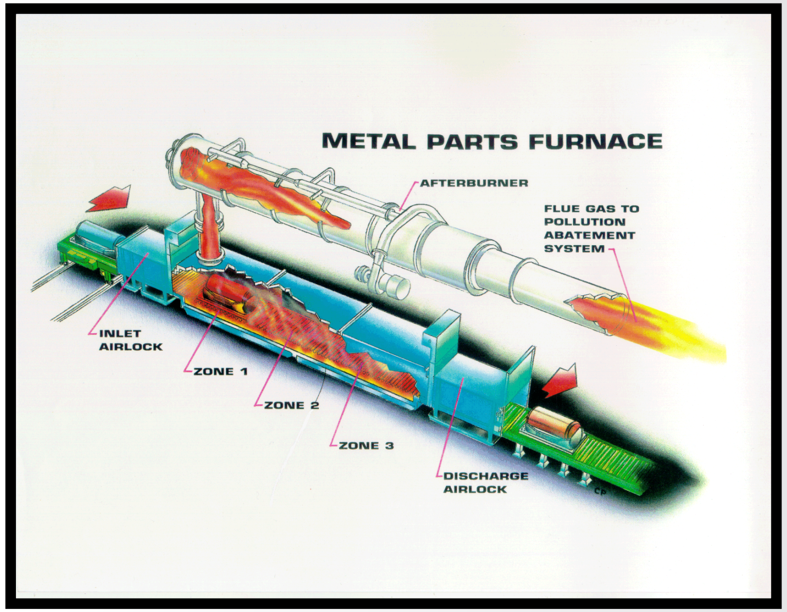
- When formed in flames, F radicals quickly terminate chain branching reactions to act as an extremely efficient flame retardant, inhibiting flame propagation
- PICs are more likely formed with F radicals than other halogens such as chlorine (Cl)
- PICs may be larger or smaller than the original fluorinated Principal Organic Hazardous Constituents (POHC) of concern
  - CF_2 radicals preferred and relatively stable, suggesting the possibility of reforming fluorinated alkyl chains
  - Remaining C-F fragments may recombine to produce a wide variety of fluorinated PICs with no analytical method or calibration standards
  - May result in adequate PFAS destruction but unmeasured and unquantified PICs
- Very little information is published on PFAS destruction
  - Fluorine chemistry sufficiently different than Cl that we cannot extrapolate
  - Analytical methods and PFAS standards are minimal with more needed
  - Measurements focusing on POHC destruction may miss the formation of PICs
- Hazardous waste incinerators and cement kilns may well be effective, but what about municipal waste combustors and sewage sludge incinerators (i.e., lower temperatures)?

Incinerability & Mitigation Research

- Explore minimum conditions (temperature, time, fuel H_2 or hydrogen gas) for adequate PFAS destruction
- Investigate relative difficulties in removing PFAS functional groups (POHC destruction) vs. full defluorination (PIC destruction)
- Effects of incineration conditions (temperature, time and H_2) on PIC emissions
- Examine relative differences in the incinerability of fluorinated and well studied corresponding chlorinated alkyl species

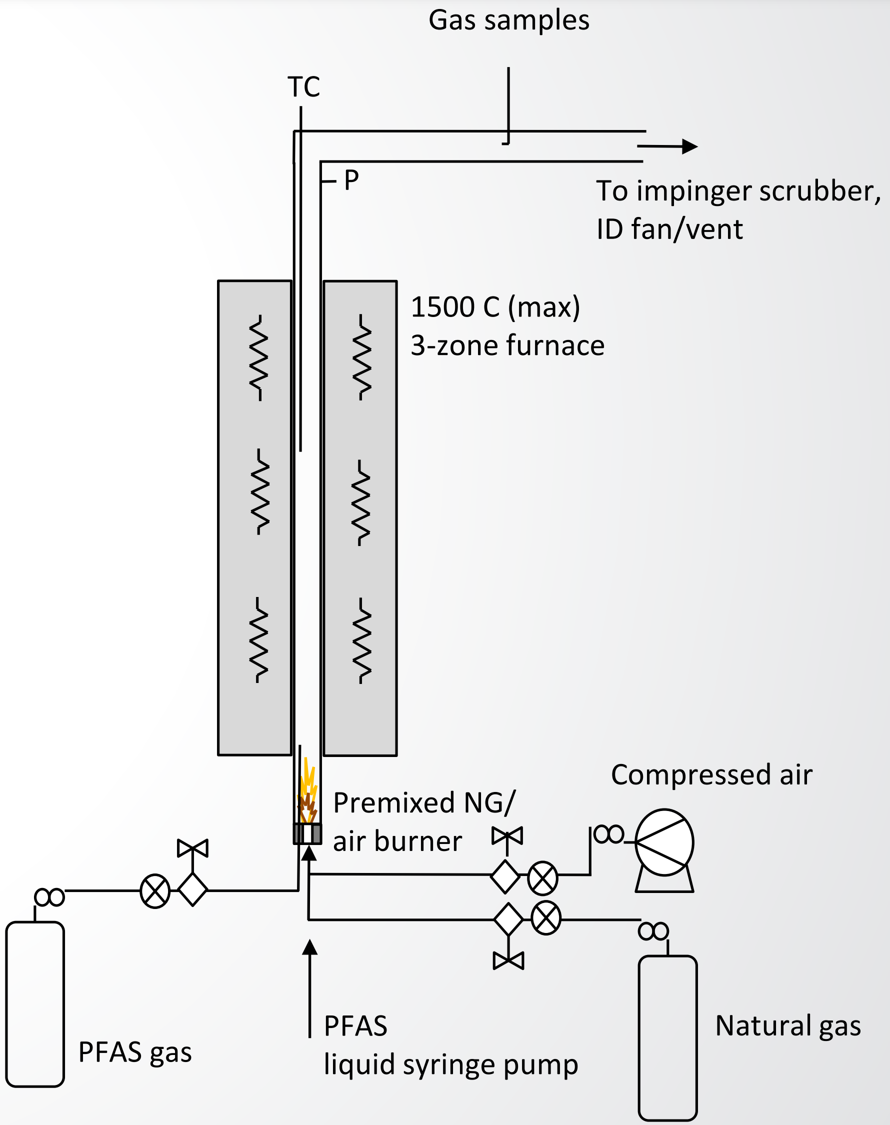
CFS Software for EPA
Reaction Engineering International (REI)

- The **Configured Fireside Simulator (CFS)**
  - Developed for the Department of Defense to evaluate operations of the chemical demilitarization incinerators processing the US chemical warfare agent stockpile
- Destruction kinetics developed
- Adapted to provide for the ability to run "what if" scenarios of waste streams contaminated with chemical and biological warfare agents
  - EPA's pilot-scale Rotary Kiln Incinerator Simulator (RKIS)
  - Three commercial incinerators based on design criteria for actual operating facilities
    - Medical/Pathological Waste Incinerator
    - Hazardous Waste Burning Rotary Kiln
    - Waste-to-Energy Stoker type combustor
- CFS uses chemical kinetic data for destruction derived from bench- and pilot-scale experiments at EPA's Research Triangle Park, NC facility



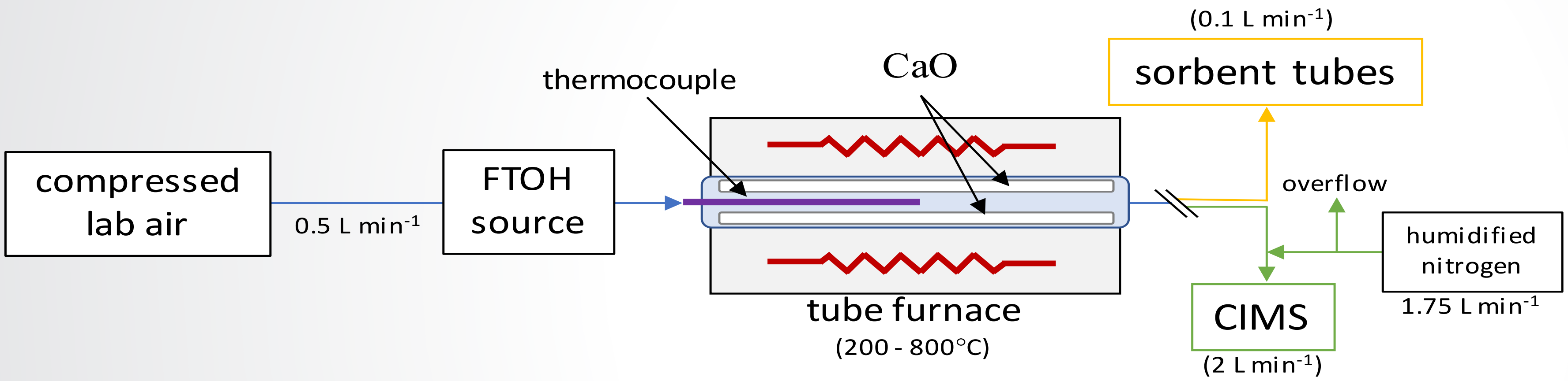
Bench-scale Incineration Experiments

- Repurpose existing equipment (i.e., formerly used for oxy-coal)
- Small scale (L/min & g/min)
- Full control of post-flame temperature & time (2-3 sec)
- Able to add either gas or liquid PFAS through or bypassing flame
- Premixed or diffusion flames possible
- Platform for measurement methods development (e.g., SUMMA, sorbent, total F, Gas Chromatography – Electron Capture Detector (GC/ECD), real-time instruments)

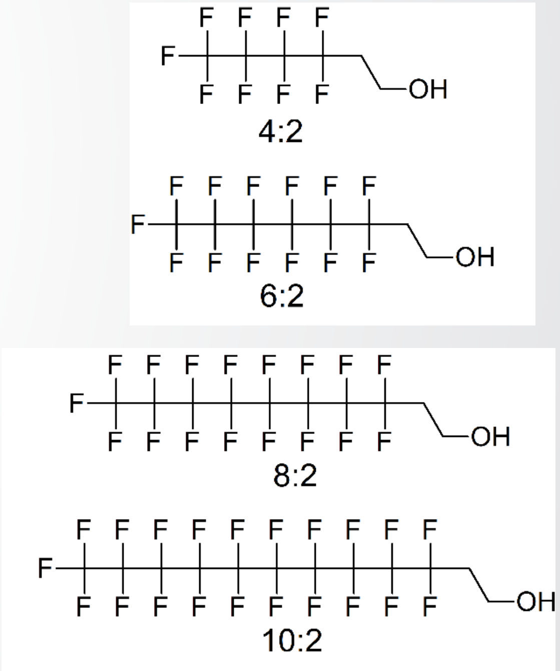


Tube Furnace Experiments

Experimental Setup



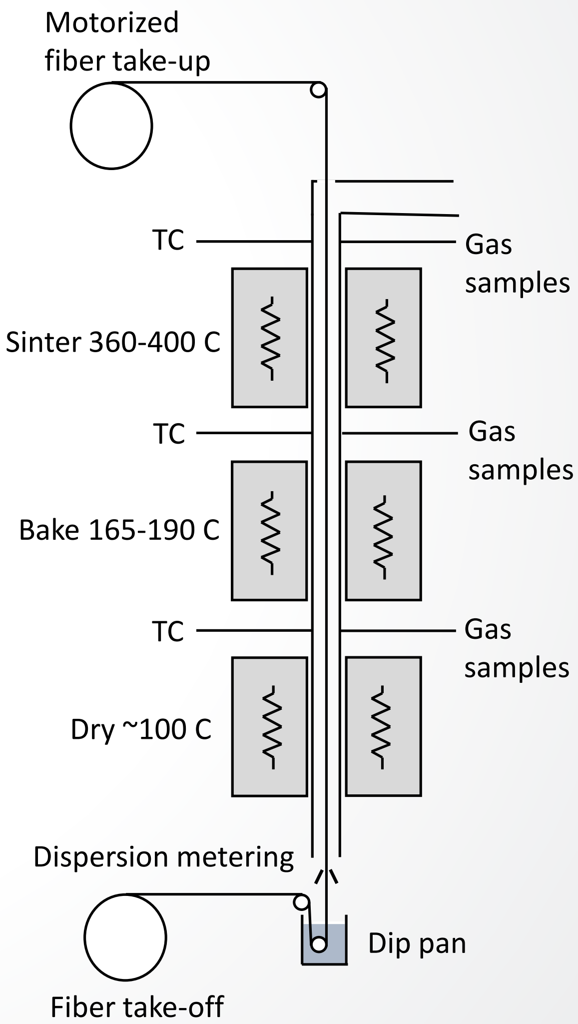
PFAS Fluorotelomer Alcohols Tested:

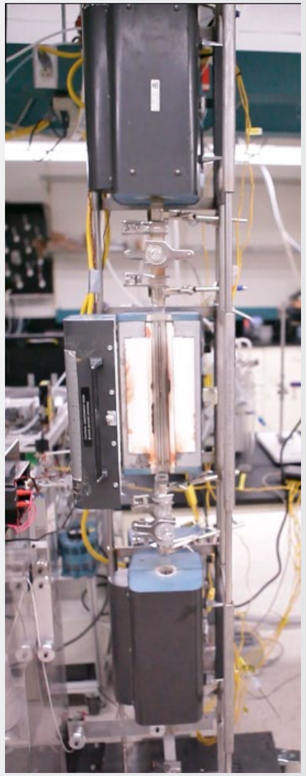


- Thermal treatment with calcium oxide (CaO) from 250 to 800 °C
- Observe destruction of parent compound using two techniques: CIMS and sorbent tube analysis by thermal desorption–gas chromatography–mass spectrometry (TD-GC/MS)
- TD-GC/MS analyses show the presence of degradation products from fluorotelomer alcohols (FTOH) destruction

String Reactor Experiments

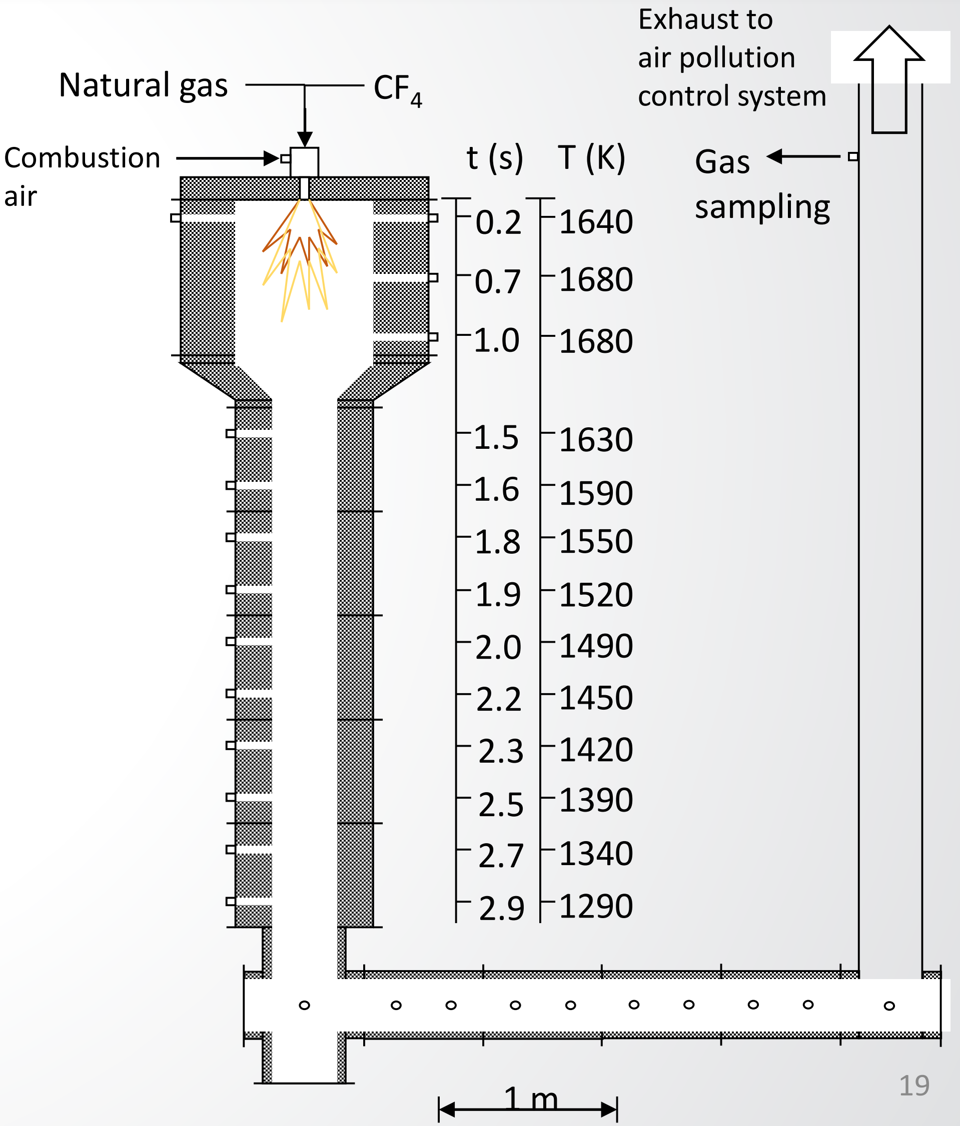
- **New experiment that simulates industrial PFAS coating facilities**
  - Built from 3 existing furnaces
  - Applies commercial dispersions to fiber (string)
  - Full control of flows, times, temperatures, application rates
  - Small scale (L/min & g/min)
  - Located in lab w/ real-time instruments
- **Investigates key research questions:**
  - What PFAS & additives are present in different commercial dispersions?
  - What PFAS (and other species) are vaporized during application processes?
  - How do vapor phase PFAS emissions compare to dispersion compositions?
    - Are surfactants (GenX, telomer alcohols) included in the vapor emissions?
  - Are processing temperatures sufficient to transform PFAS?
    - Cleave functional groups to produce new PFAS?
    - Are processing temperatures sufficient to cleave C-F bonds and produce fluorine (F_2) and hydrogen fluoride (HF)?
  - How do processing temperatures and times affect vapor and aerosol emissions (mass and composition)?





Pilot-scale Incineration Experiments

- 65 kW refractory lined furnace (aka Rainbow Furnace) with peak temperatures at ~1400 ºC, and >1000 ºC for ~3 sec
- Combustor connected to facility air pollution controls
  - Afterburner, baghouse, NaOH (sodium hydroxide) scrubber
- Introduce C1 and C2 fluorinated compounds with fuel, air, post flame to measure POHC destruction and PIC formation
  - FTIR (Fourier-transform infrared spectroscopy) and other real-time and extractive methods
- Add modeling component using REI's Configured Fireside Simulator (CFS) CFD/kinetic model to include C1 & C2
  - F chemistry from literature (Burgess et al. [1996])



Planned Products

- **ORD Products on Fundamental Understanding of Thermal Treatment**
  - Thermogravimetric Analysis/Mass Spectrometry (TGA/MS)Thermal Destruction Temperature Points with Off Gas Measurements on Potential Defluorination
  - PFAS Model Incorporation of Published C1 and C2 Fluorocarbon Kinetics to Predict Simple PFAS Behavior in Incineration Environments
  - Low Temperature Interactions of PFAS with Sorbents from Bench-Scale Experiments
  - Thermal Destruction of PFAS from Pilot-Scale Experiments

- **ORD Measurement Methods for PFAS**
  - Quantitative Assessment of Modified Method 5 Train for Targeted PFAS
  - PFAS Method OTM 45
  - Total Organic Fluorine Methods
  - Non-targeted Measurement Approaches to Identify PFAS

- **Other Contributions**
  - Supporting Incineration Guidance as part of the National Defense Authorization Act

EPA United States Environmental Protection Agency

Take Home Messages

- Reliable and comprehensive PFAS and PFAS-related emissions measurement methods are needed for multiple purposes
- Application to thermal treatment/incineration/combustion sources a major focus amongst a host of methods for all media
- Identifying what compounds need to be targeted for measurement is the hard part
- Non-targeted analyses are critical to knowing what compounds are present because you don’t find what you don’t look for
- Surrogate approaches are needed to know exactly what goes in and what comes out
- Need to have access to actual sources to evaluate methods and conduct comprehensive source characterizations
- ORD collaboration/partnership is integral

For More Information

- The research discussed in this presentation is part of EPA's overall efforts to rapidly expand the scientific foundation for understanding and managing risk from PFAS.

- For more information on EPA's efforts to address PFAS, please visit the following websites
  - EPA PFAS Action Plan - https://www.epa.gov/pfas/epas-pfas-action-plan
  - EPA PFAS Research - https://www.epa.gov/chemical-research/research-and-polyfluoroalkyl-substances-pfas

Contact

Lara Phelps
Director
Air Methods and Characterization Division
Center for Environmental Measurement and Modeling
US EPA Office of Research and Development
919-541-5544
Phelps.Lara@epa.gov