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Rapid Quantification of Per- and Polyfluoroalkyl Substances by Combustion Gas Analysis

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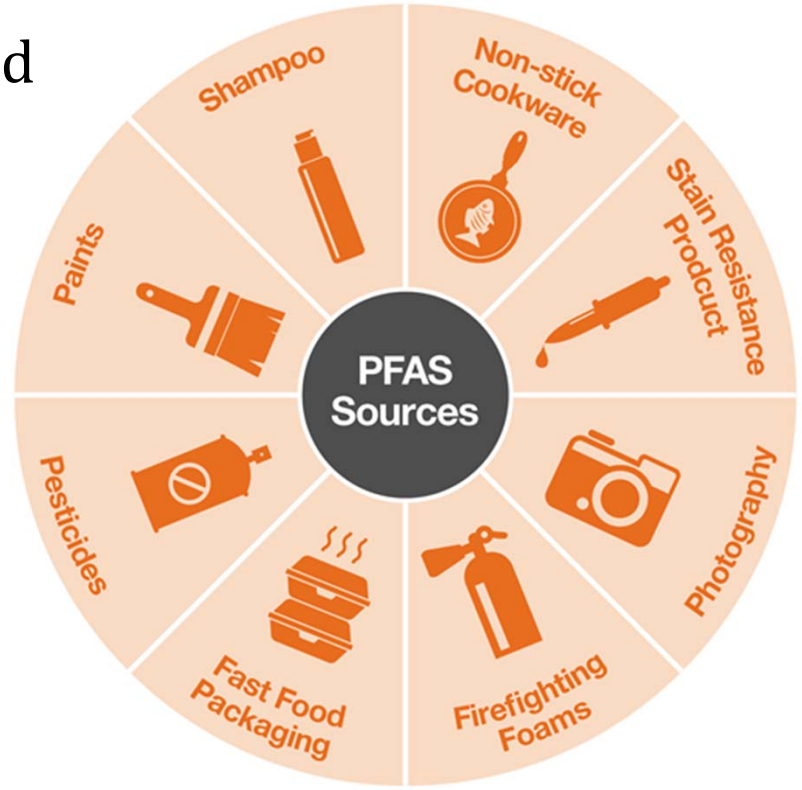
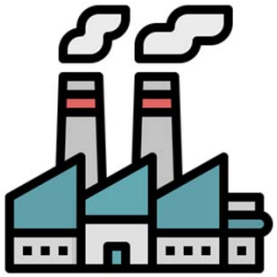
Per- and Polyfluoroalkyl Substances (PFAS)

- PFAS are a collection of manmade fluorinated organic chemicals made popular by their water and oil repellant attributes
- They are also used for firefighting at airfields and in a number of industrial processes
- Due to their wide usage, they have been detected in environment and in human



PFAS in Water



Industrial Production

Wastewater discharge

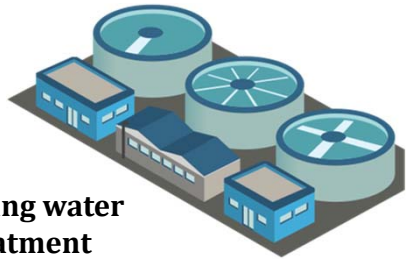
Wastewater Treatment Plant

Sewage

City

Aqueous film-forming foams (AFFFs)

Direct discharge of wastewater



Drinking water Treatment Plant

River

Groundwater

PFAS in Water

- Environmentally persistent
- Most Common PFAS in water are Perfluorooctanoic acid (PFOA) and Perfluorooctanesulfonic acid (PFOS)
- PFAS have been linked to adverse health effects including cancer and many others
- EPA has only issued health advisories for drinking water exposure to PFOA and PFOS at 0.07 part per billion each

Removal of PFAS in Contaminated sites

- There was a need to remediate PFAS-contaminated sites
- Current remediation techniques include granular activated carbon, membranes, anion exchange and others
- ***However, these techniques generate PFAS waste streams and often create new PFAS through transformation of unidentified precursors.*** ***<u>New PFAS might be more toxic than the parent PFAS</u>***
- Thus, its important to measure ***total concentration of PFAS in water*** to protect human and the aquatic ecosystem from the hazardous PFAS.

Measurement of PFAS in Water

- PFAS are generally quantified using liquid chromatography tandem mass spectrometry (LC-MS/MS)

  Limitations:

  - *Measure individual PFAS species with known molecular weight*
  - *Time-intensive*
  - *Difficult to deploy in the field (energy consumption, long startup time, etc.)*
  - *Costly*
  - *Unable to quantify total fluorine mass balance or total organic fluorine (TOF) in water*

LC-MS/MS system

Total Organic Fluorine (TOF) Analysis

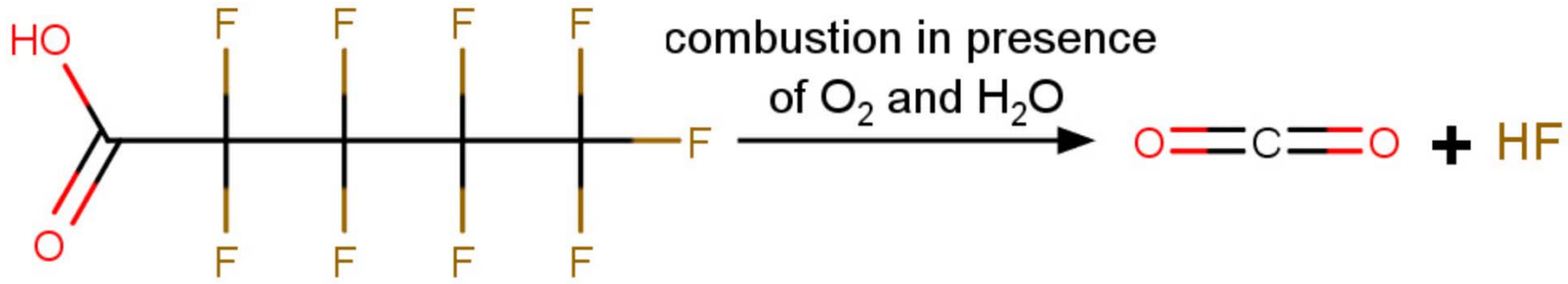
- **TOF analysis**
  - *Measure the total concertation of fluorinated organic compounds in water.*
  - *Account for all individual PFAS compounds and precursors.*
  - *Can be used as an indicator for PFAS toxicity in water.*

Current Measurement Techniques

- Particle-induced gamma ray emission (PIGE)
- Total Oxidizable Precursor (TOP)
- ***Combustion Ion Chromatography (CIC)***

Combustion Ion Chromatography (CIC)

- CIC which combusts TOF to HF gas



- Sparges the gas through a NaOH aqueous trap to produce F^-, and quantifies F^- by ion chromatography

Shortcomings of CIC

- No separation between the inorganic F^- in the initial sample and organic fluorine or TOF
- The method is limited by the instrument detection limit of ion chromatography (~1 µg/L PFOA as F^-)
- Not field-deployable because the instrumentation is designed for lab use
- ***Thus, There is a distinct need for validated, standardized, field-deployable, and robust methods for TOF measurements***

Total Organic Carbon Analyzer (TOC)

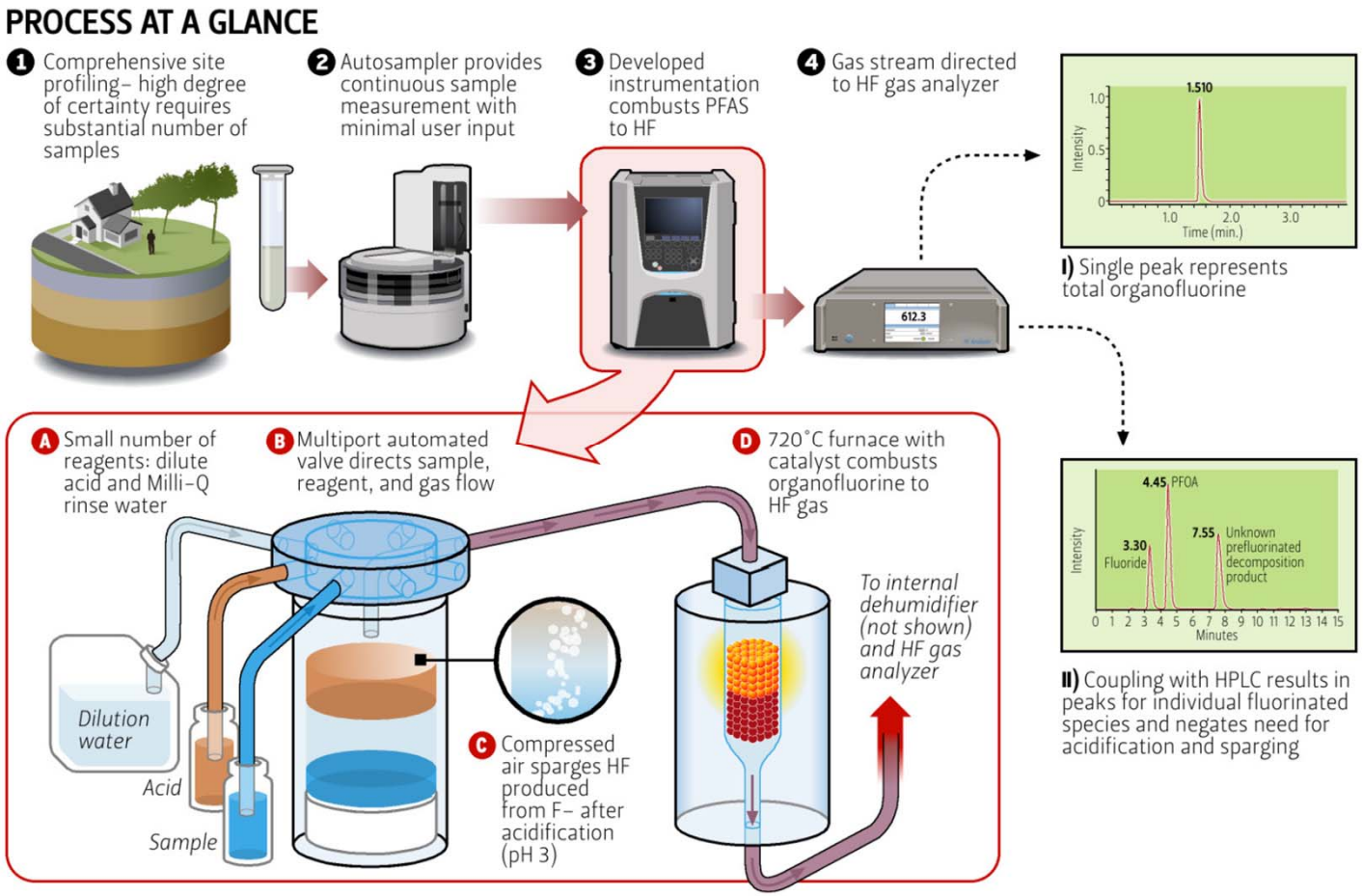
- Use CIC method to measure organic carbon in water samples
- Use an autosampler to introduce an aqueous sample containing organic carbon into a 720ºC furnace filled with a catalyst, which combusts organic carbon to CO_2.
- Very common instrument in labs
- Have been already deployed in fields

Research Objectives

The overarching objective of this study is

To develop and validate robust, field-ready instrumentation and methods to quantify TOF in water using TOC instrument.

Research Approach



Research Approach

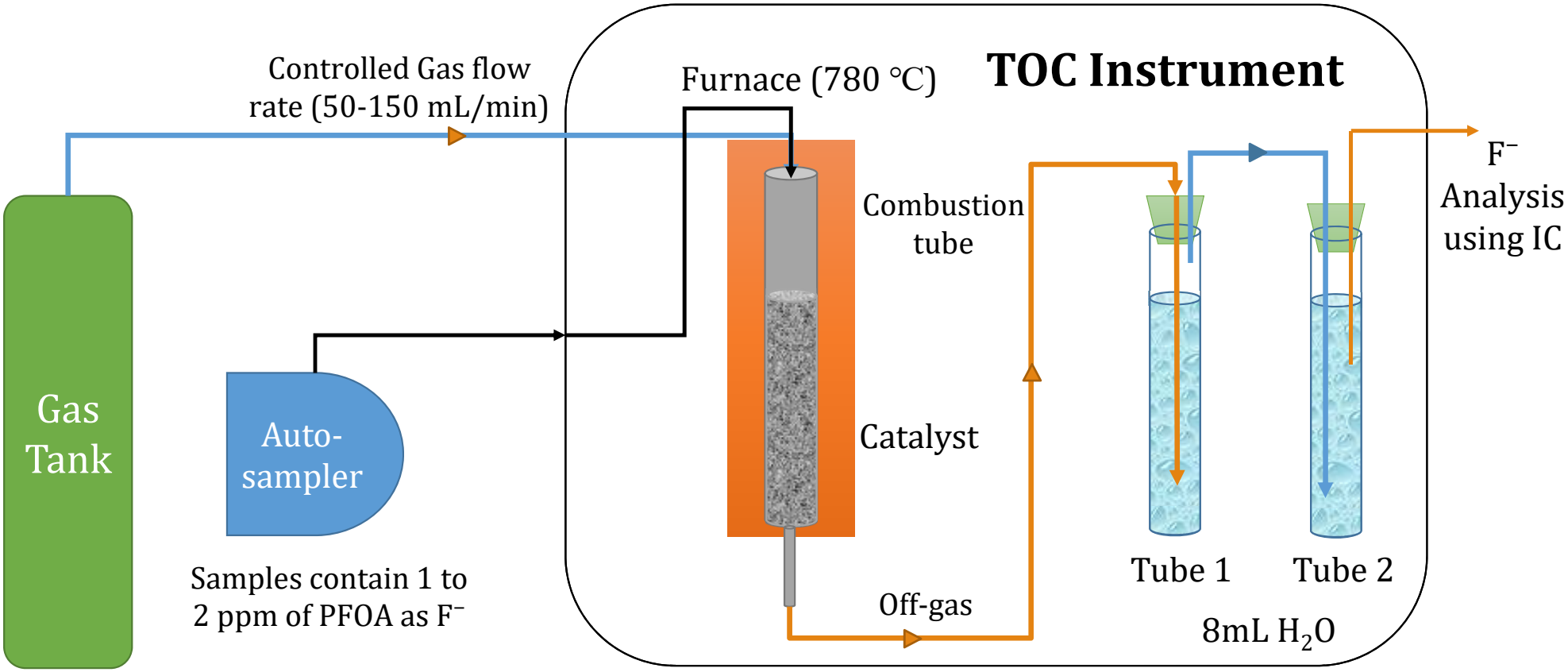
Task 1 – Design, build, and develop combustion laser spectroscopy total fluorine instrumentation

Task 2 – Validate method and compare to other PFAS methodology

Task 3 – Mobilize and field demonstrate the instrumentation

Task 4 – Develop instrumentation that results in species-specific quantitation of PFASs, PFAA precursors, and PFAS decomposition products

Experimental Design

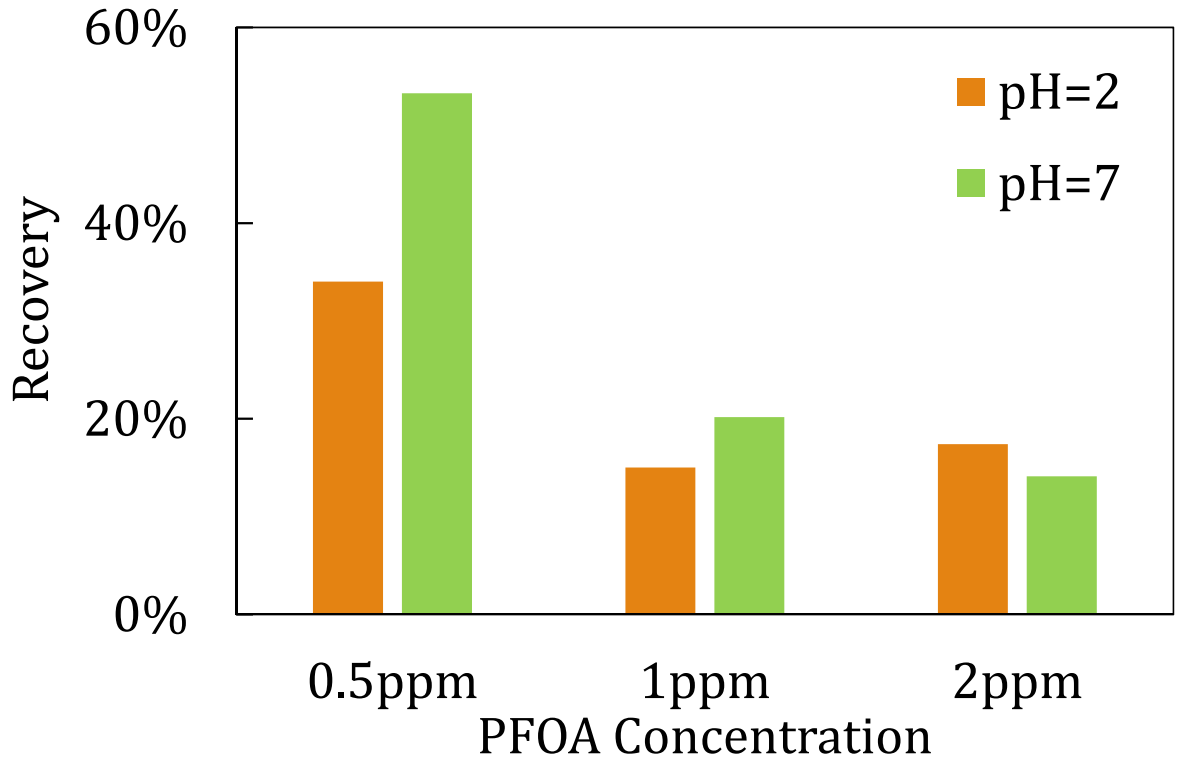


Experimental Design

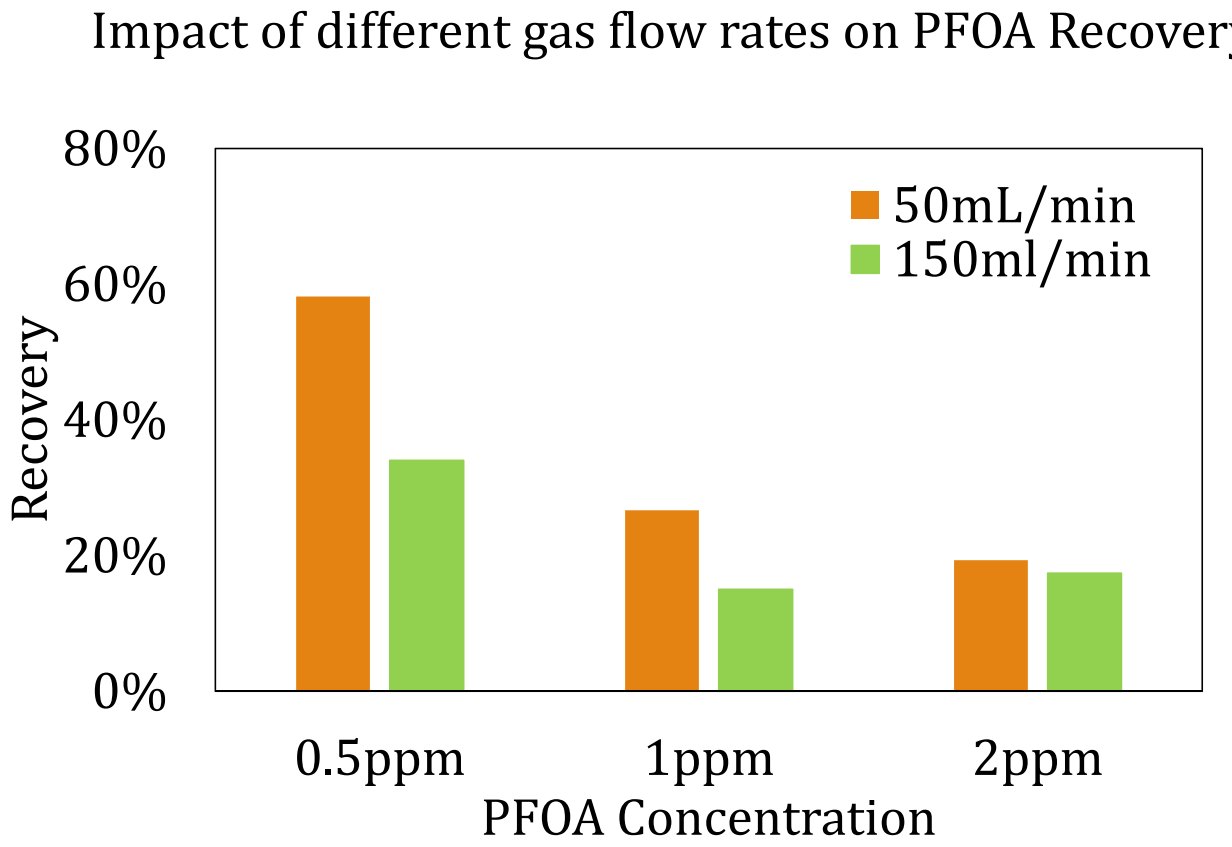
- The furnace temperature was set to 780 ℃;
- PFOA samples pH were adjusted between 2 and 7.
- Sample injection volume was 100 µL;
- Combusted HF gas was pushed using oxygen carrier gas at different flow rates (50-150 mL/min)
- After combustion, samples in both of the tubes were analyzed for fluoride using ion chromatography.

Results to Date

Impact of initial sample pH on PFOA Recovery at 150 mL/min gas flow rate



Results to Date



Future Experiments

- Comparing different combustion oven temperatures (680 ℃, 780 ℃ and 1000 ℃)
- Removal of interference from inorganic fluoride using adsorption material such as hydrated tin dioxide.
- Capturing the combusted fluorine via alkaline impingers
- Routing of gas flow to minimize fluoride losses

Acknowledgments

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