Analysis of Per- and Polyfluoroalkyl Substances in Drinking Water Using EPA Methods 533 and 537.1 with Semi-automated Solid Phase Extraction

Ruud Addink and Tom Hall
Toxic Report Laboratories
Billerica MA

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Introduction

- Perfluoralkylated compounds contain a perfluorinated or polyfluorinated carbon chain moiety such as $F(CF_2)_n-$ or $F(CF_2)n-(C_2H_4)_n$.

- These make up a large group of persistent chemicals used in industrial processes and consumer applications:
  - Stain-Resistant Coatings for textiles and carpets
  - Grease-Proof Coatings for paper products approved for food contact
  - Firefighting Foams
  - Mining and Oil Well Surfactants
  - Floor Polishes
  - Insecticide formulations

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Origin

- Industrial Sites
- Airport Fire Training Areas
- Wastewater Treatment Facilities
- Widespread use for over 60 years
- Very resistant to degradation
- Ubiquitous Compound in the Environment

Global Health concerns

- **Human exposure is linked to adverse effects**
  - Developmental issues in off-spring
  - Cancer
  - Immune system suppression
  - Endocrine disruption
  - Elevated levels of Cholesterol
  - Obesity

Source concerns

- Many water sources worldwide are found to be contaminated.
- Two compounds most studied:
  - Perfluoroctane sulphonate (PFOS)
  - Perfluoroctannoic acid (PFOA)
- Millions have been exposed through Drinking water supplies in the US and exceed the lifetime advisory of 70ng/L for these compounds

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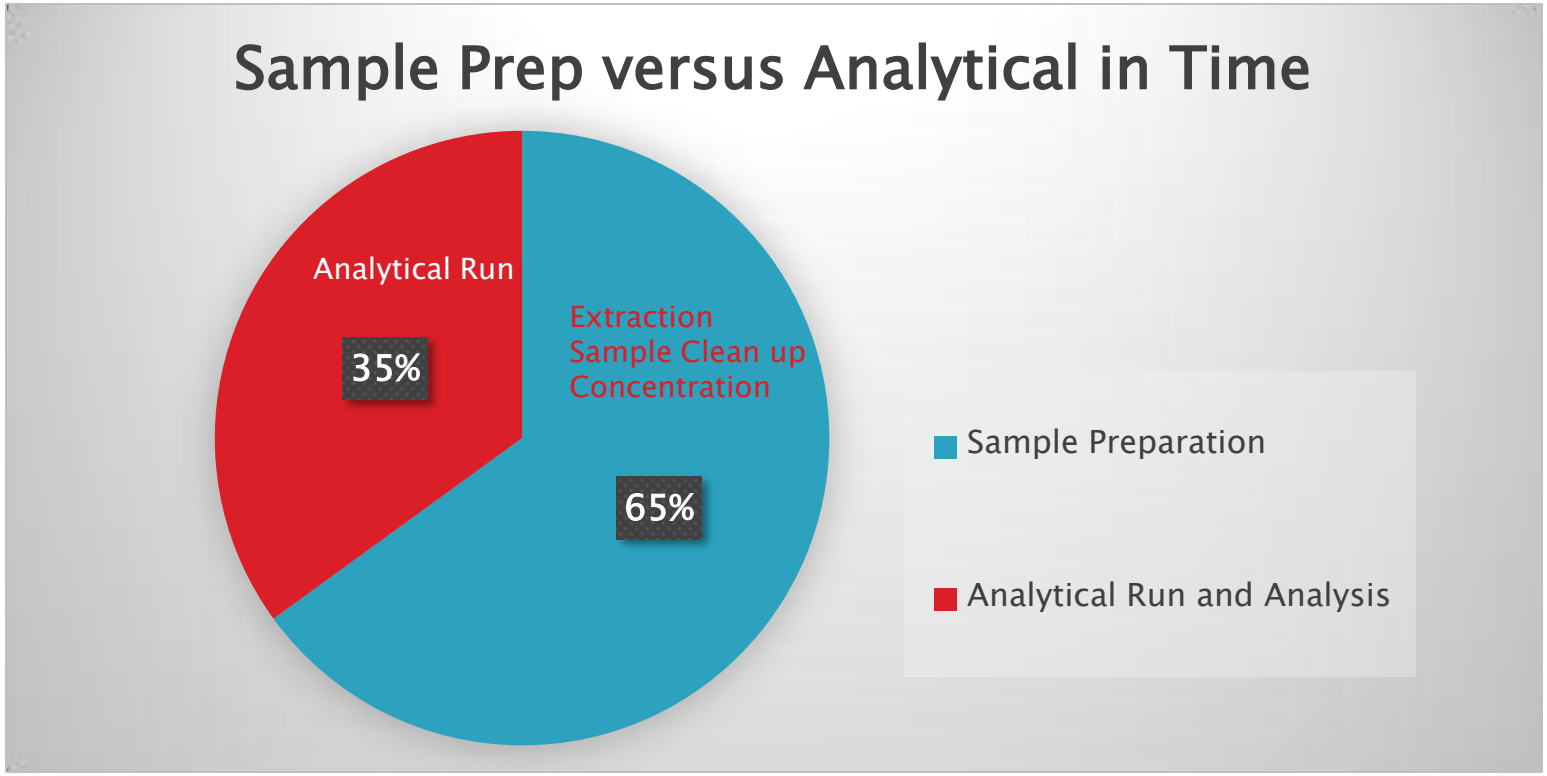
PFAS Analysis

- Many of Thousands Samples are now being analyzed and more areas of concern are starting to be analyzed for PFAS:
  - Drinking Water
  - Waste Water
  - Human Serum
  - Biota
  - Soils

Challenges of Analysis

- The Analytical Systems are expensive
  - UPLC/MS systems
    - Require expertise in a new technology
- Manual Sample Prep processes
  - Inconsistent results
  - Elevated Background issues
  - Labor intensive
  - Extraction can take up to 2 hours
    - Dirty samples
  - Concentration can take up to 2 hours

Laboratory Workflow Breakdown



Reasons for Semi-Automated SPE

- Reduced solvent
- Reduced Actions
- Simplified procedures
- Semi-Automated versus Manual protocols = Reproducibility
- Increased Sample Throughput

Determining Factors

- Ability to load samples by vacuum consistently.
- Ability to dry cartridges by both vacuum and positive gas pressure (N2).
- Easily handle a wide variety of cartridge designs and sizes without cumbersome modifications.
- Simple Sample delivery
- Automated Bottle Rinse

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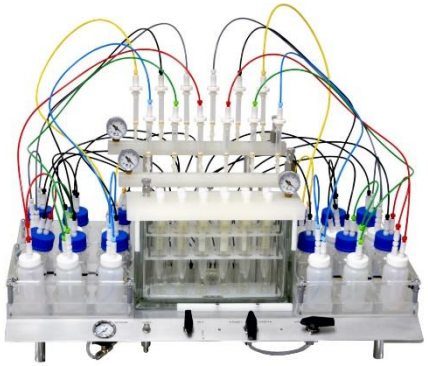
Semi-Automated Solid Phase Extraction front end for GC/MS and LC/MS

EZSPE



EZPFC

Sample Analysis Work Flow

Automated Sample Prep Time

35 Minutes

45 Minutes

= 80 Minutes

Semi Automated Sample Prep Time

35 Minutes

45 Minutes

= 80 Minutes

Objective for Semi Automation

- Use as many features from the FMS Automated systems and implement them into a Semi automated platform
- Develop as many SPE procedures for the testing lab using a single extraction platform.
- Minimize manual steps to lessen error and maximize limited man hours

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Goal

- **Self Installable**
  - Unpacking and Installation/training video
- **Easy to Operate**
  - No Computers or Electronics to fail or maintain
- **Semi – Automated**
  - Hyphenates the entire Solid Phase Extraction Process – Extraction, Bottle Rinse, Inline Drying and Optional Direct to GC Vial Concentration
- **Fast**
  - The fastest sample processing available for SPE
  - Run up to 12 samples simultaneously
  - Vacuum for fast loading of large volume samples
- **Closed system**
  - Eliminate potential outside contamination

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Goal

- **Efficient**
  - Uses all SPE cartridge sizes
  - Dedicated manifold for cartridge conditioning and sample loading
  - Dedicated manifold for extraction and extracts
  - Separates Organic from Aqueous waste
  - Vacuum cartridge drying, Nitrogen cartridge drying or combined
  - Automated Bottle Rinse and Elution
  - Inline Extract Drying
  - Small number of components to clean
- **Low to No Capital Expense**
  - Purchase an FMS Cartridge Contract
  - Receive an EZSpe at No Charge

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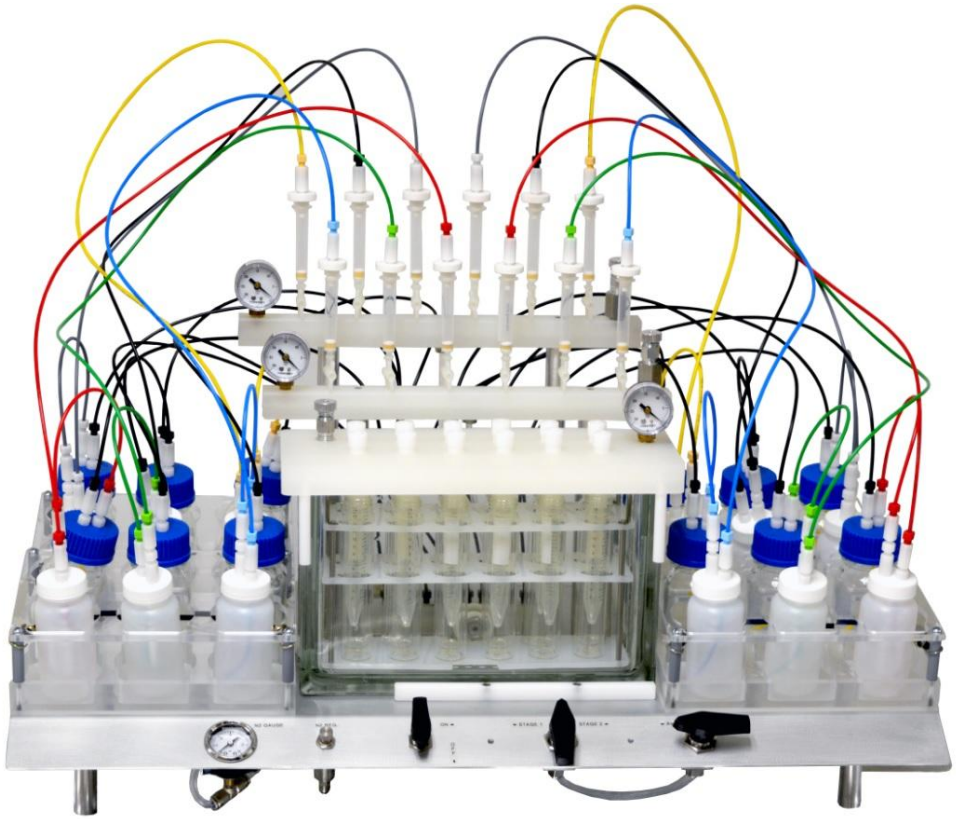
EZPFC®



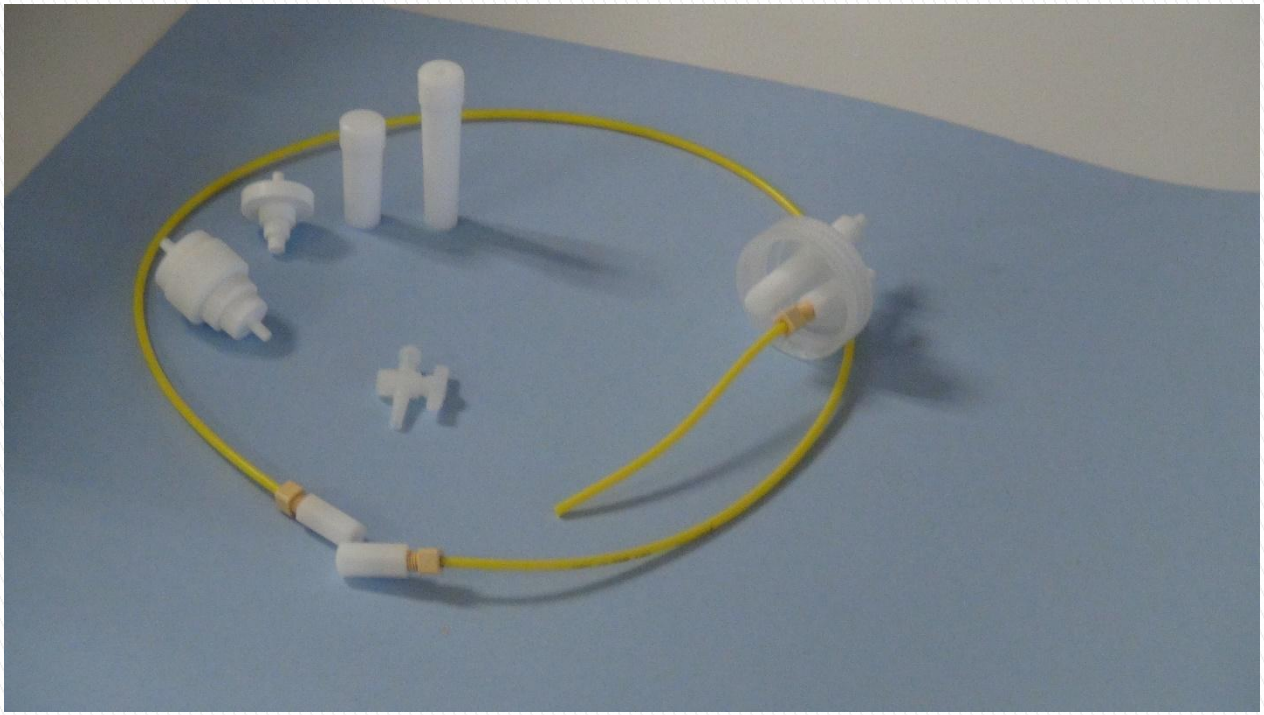
System Components

No Teflon

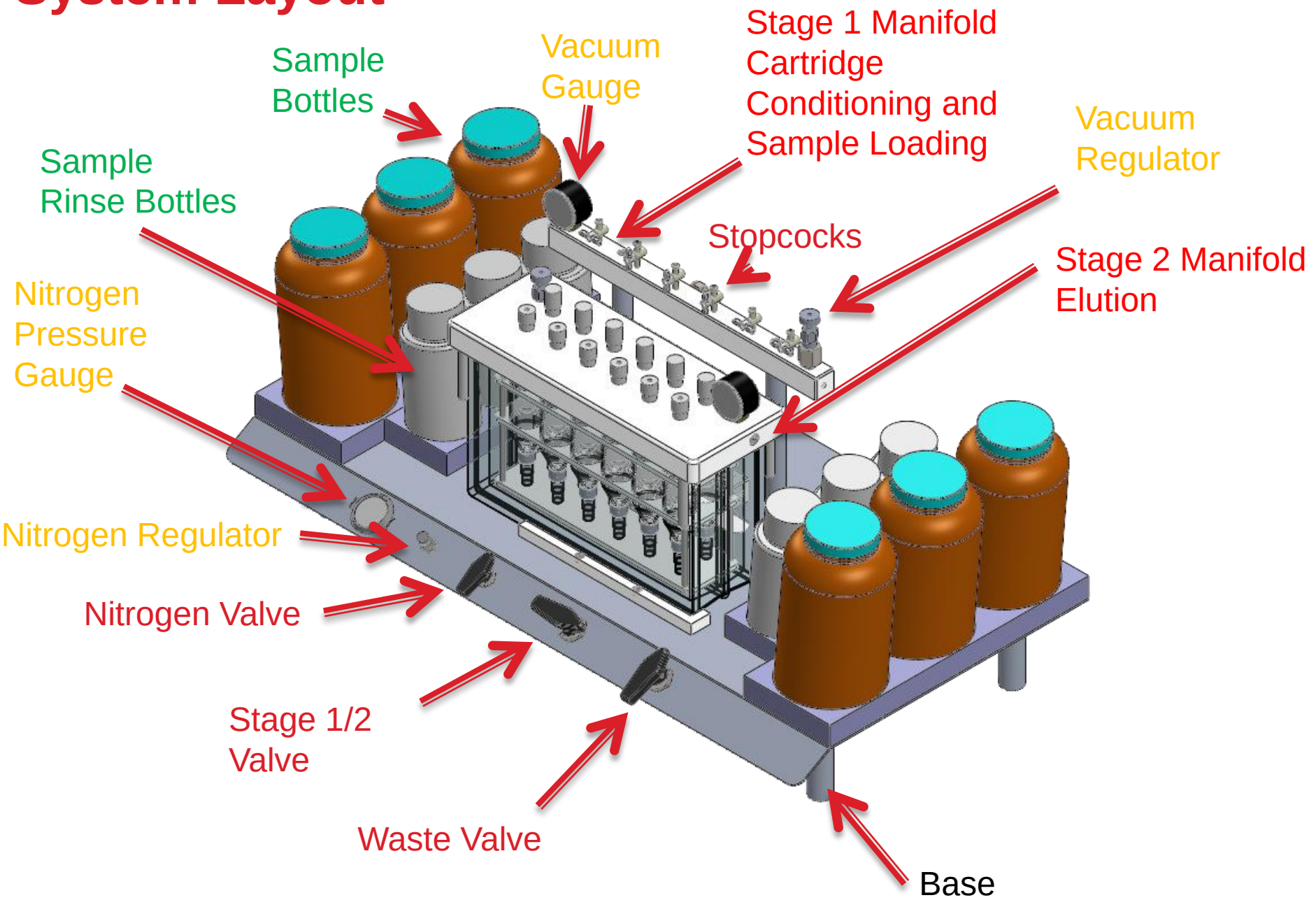
Tubing – High Density Polyethylene

Fittings – Delrin

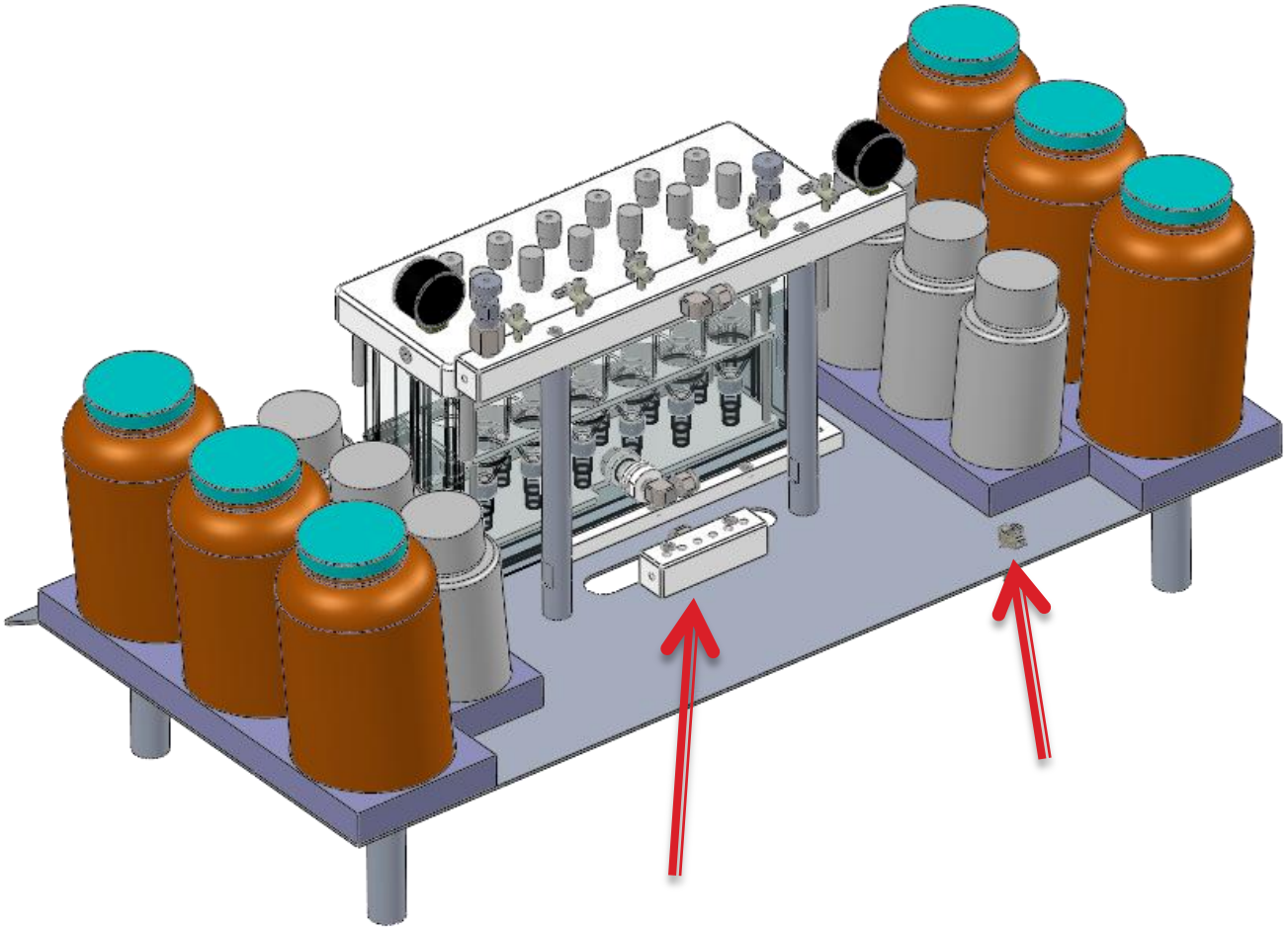
Cartridge Adapters – Medical Grade Polypropylene



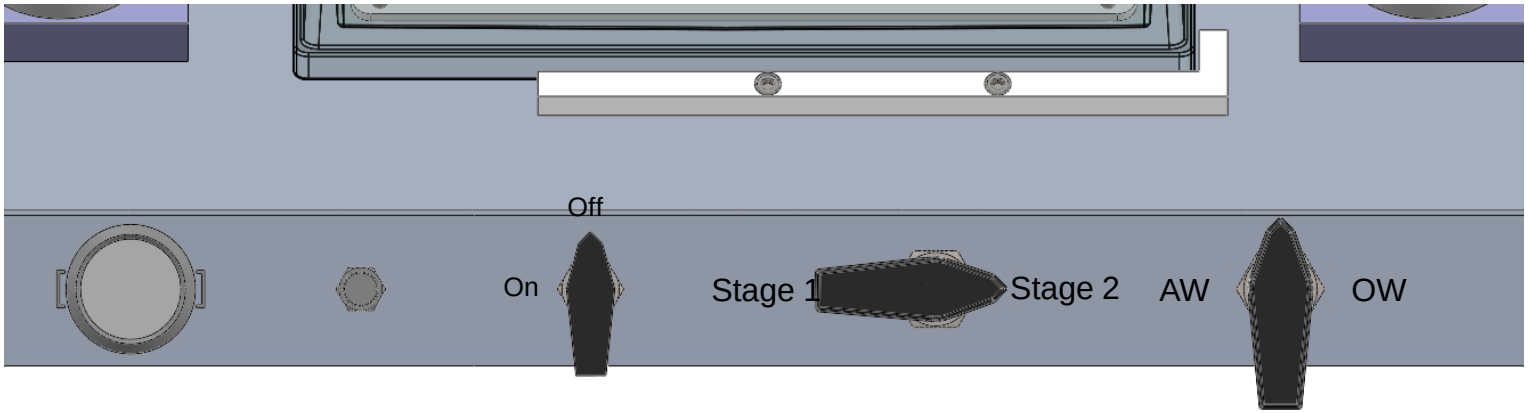
System Layout



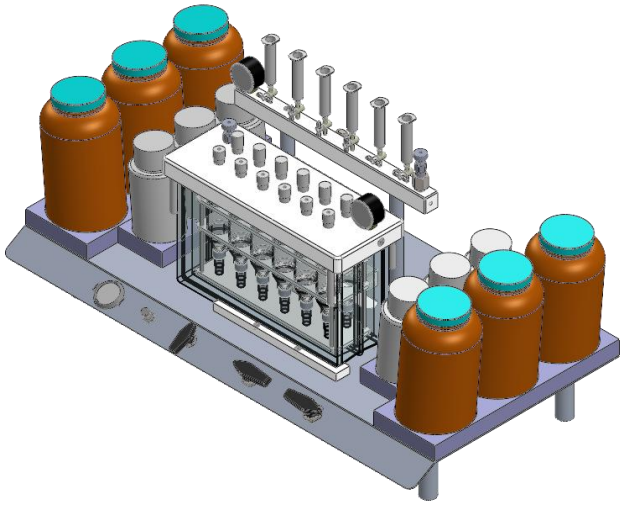
Nitrogen for Bottle Rinse and Cartridge Drying

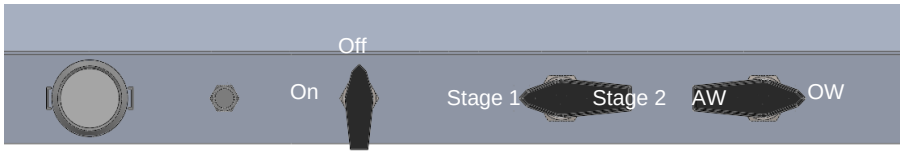


Control Valve Layout



Cartridge Conditioning (Stage 1, Organic Waste)



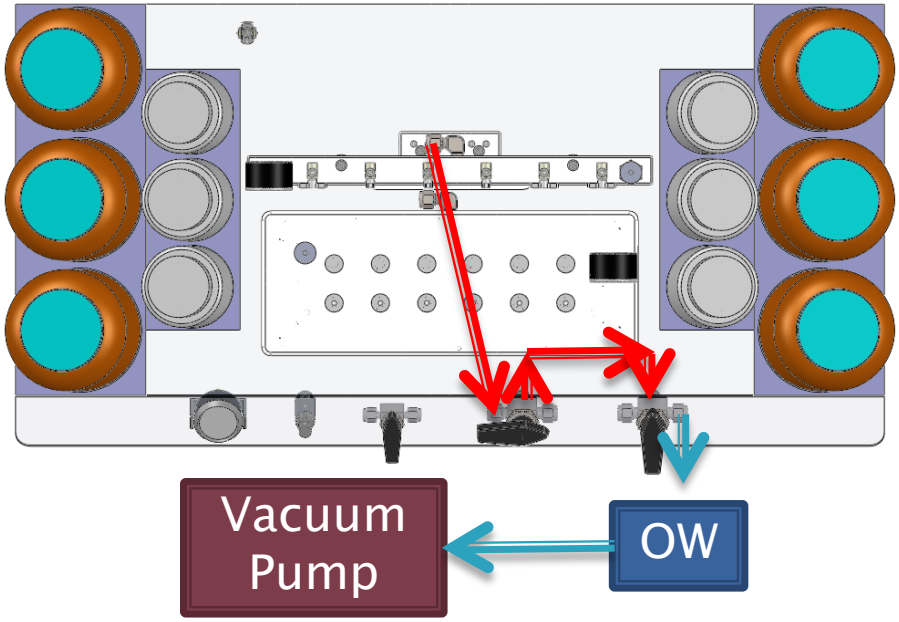


Nitrogen Valve

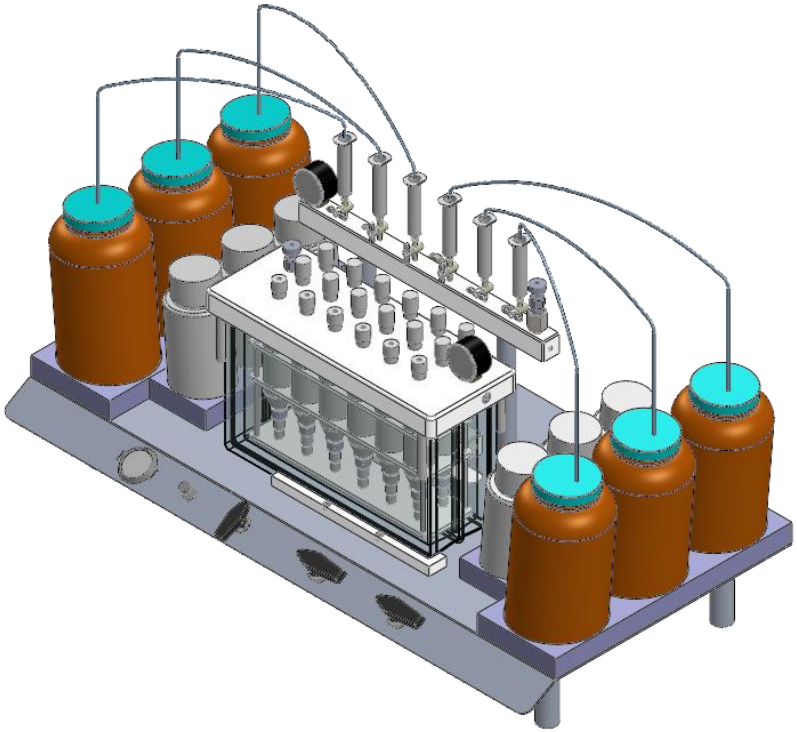
Stage 1/2 Valve

Waste Valve

Flow Path



Sample Loading (Stage 1, Aqueous Waste)

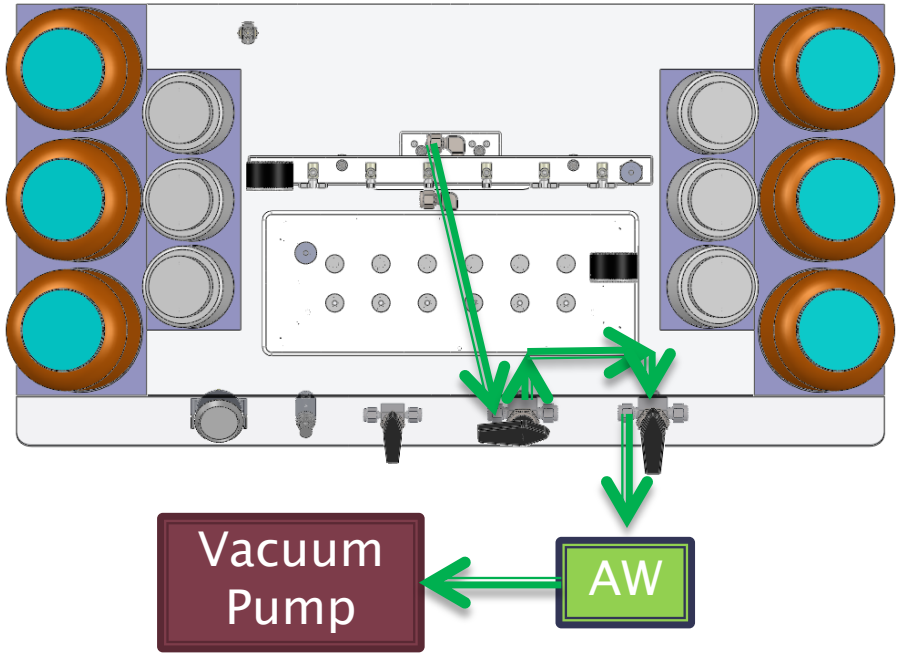


Flow Path

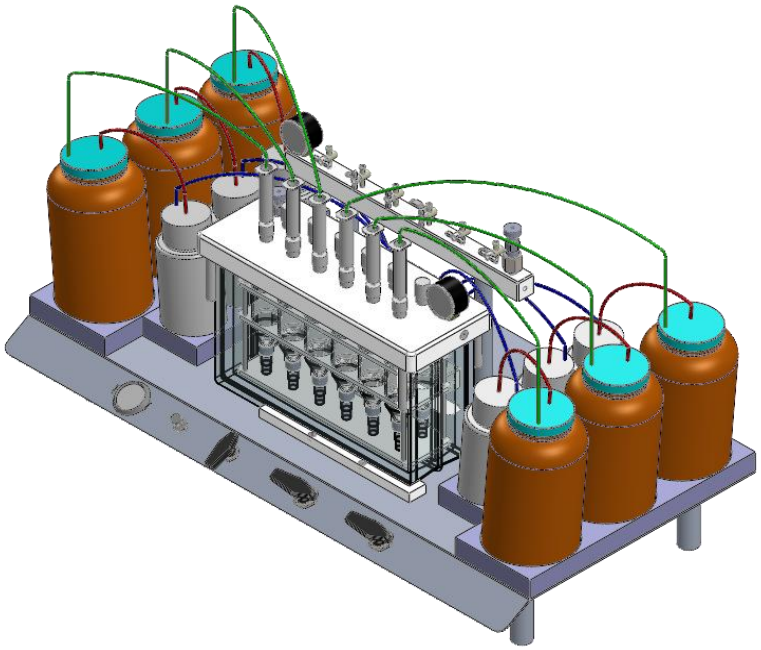
Nitrogen Valve

Stage 1/2 Valve

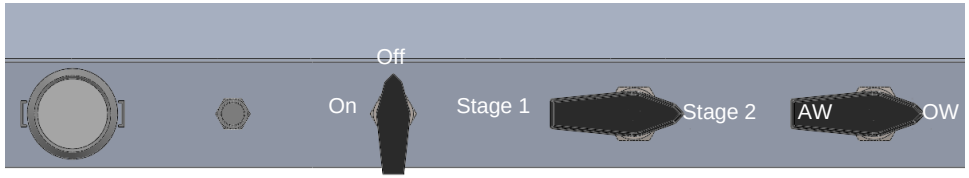
Waste Valve



Sample Bottle Rinse (Stage 1)



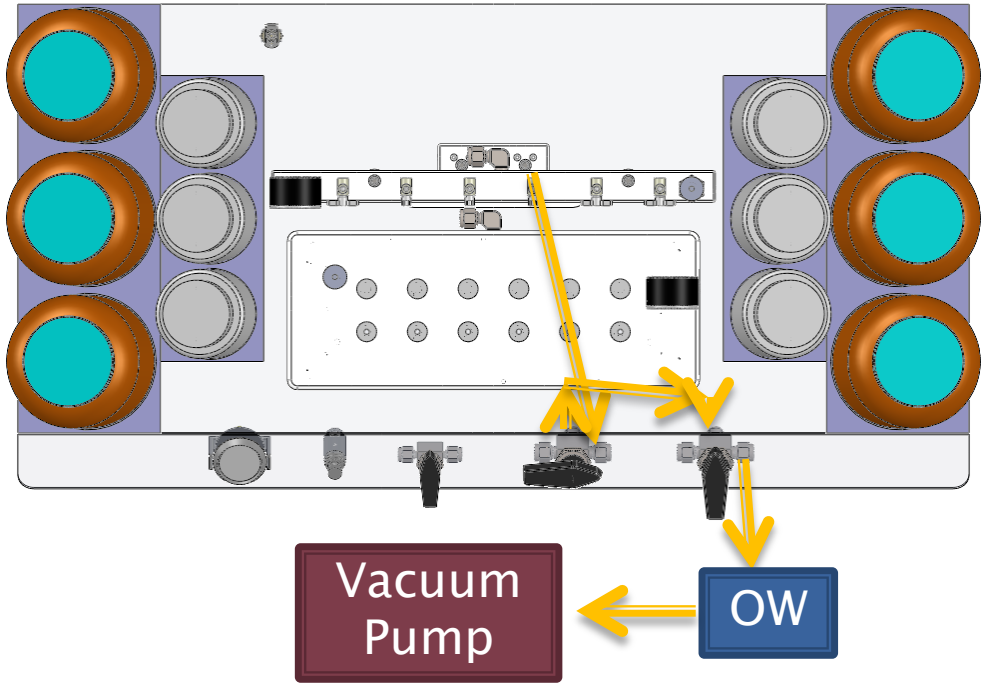
Flow Path



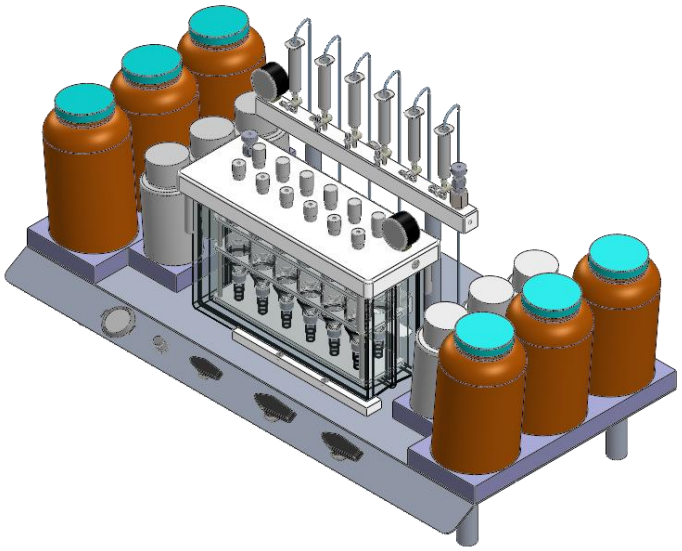
Nitrogen Valve

Stage 1/2 Valve

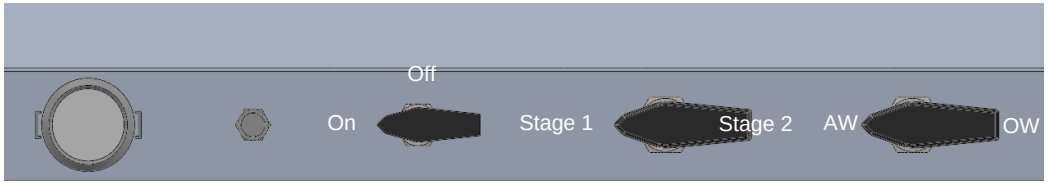
Waste Valve



Cartridge Drying- Nitrogen/Vacuum



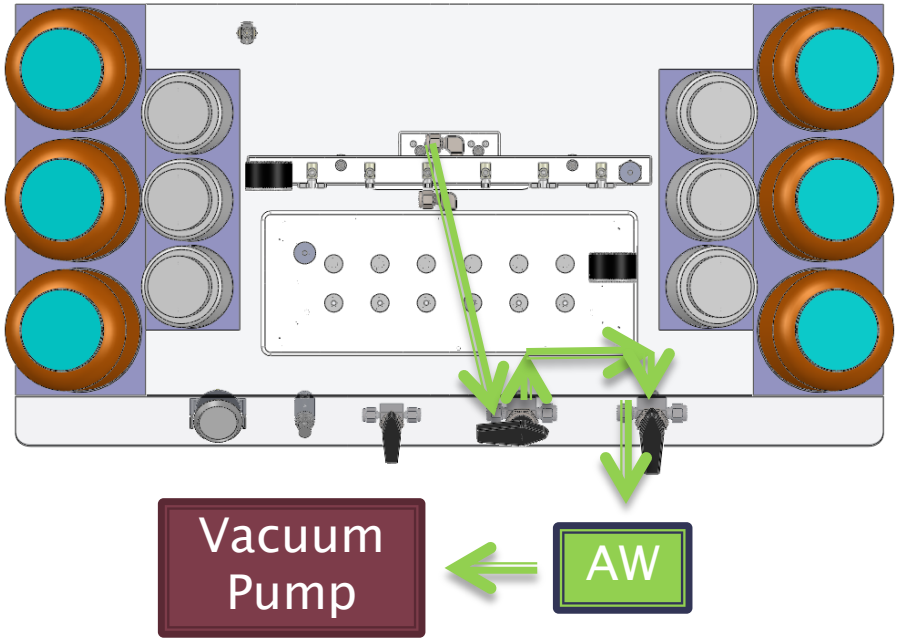
Flow Path



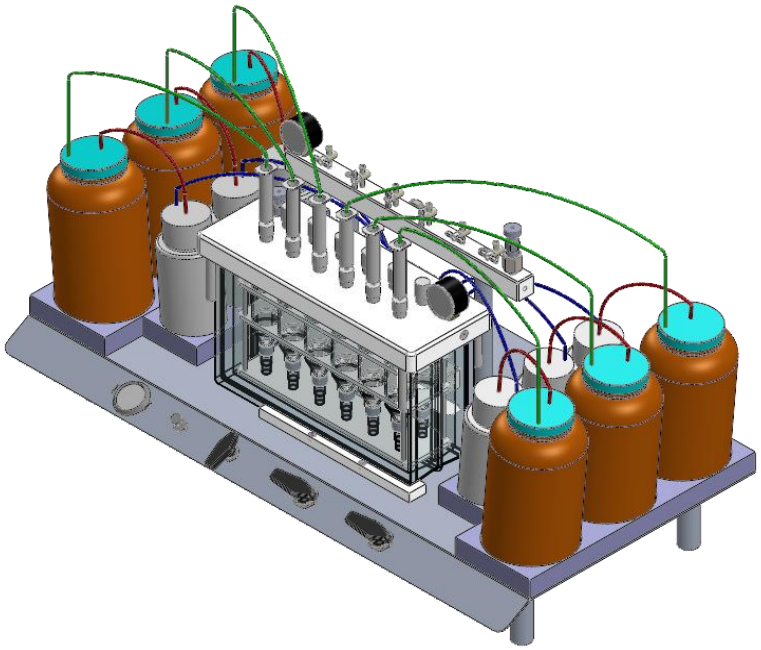
Nitrogen Valve

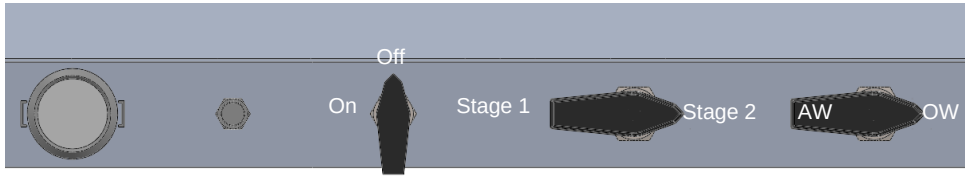
Stage 1/2 Valve

Waste Valve



Sample Elution (Stage 2)

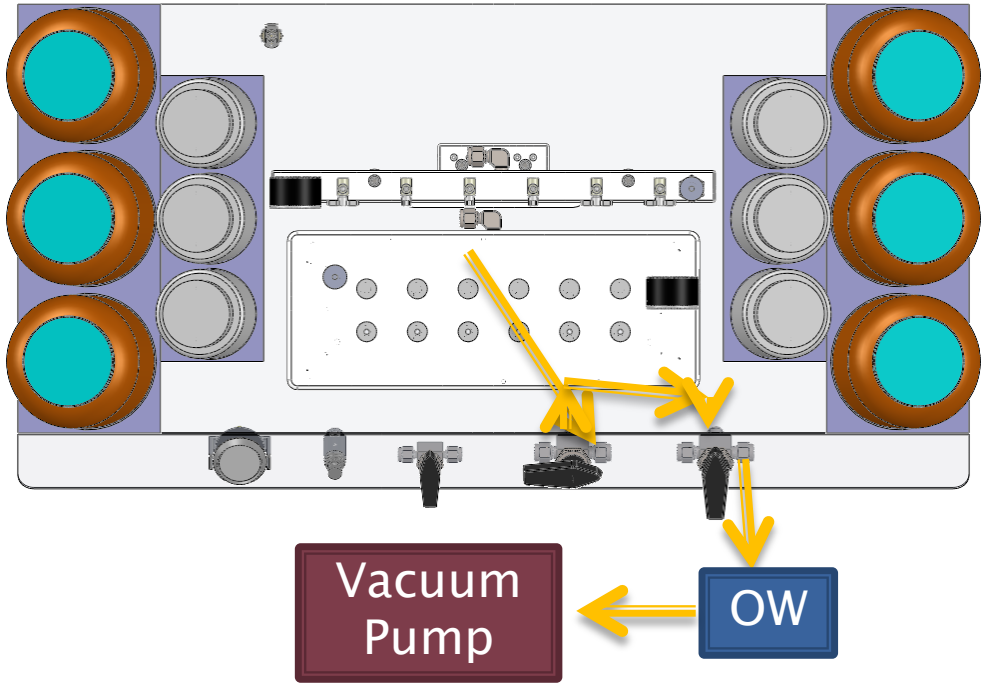




Nitrogen Valve

Stage 1/2 Valve

Waste Valve



Flow Path

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PFAs Methods

- EPA 537.1
- EPA 537 v1.1
- EPA 533
- ISO 25101

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Automated Concentration for PFAs

- SuperVap PFC
  - 24 positions
  - 15ml Conical vials
  - Timed Endpoint

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SuperVap Features

- **Self Installable**
  - **Video unpacking, installation and training video**
- **Preprogrammed with most common temperature settings**
- **6 (250mL) and 12 (50mL) position models for extractions, direct-to-vial connections**
- **Dry bath heating element**
- **Time based endpoint**
- **Savable temperature log**

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Can this Handle Dirty Samples?

Typical Cartridge can have problems!

- 6ml 500mg DVB
  - Doesn't do well
  - Frit Surface Area is to small

Yes, A Cartridge will work

- 25ml 500mg DVB cartridge
  - Does well
  - 3X the Frit Surface Area

FMS, Inc. Plastic Filtration Wool

Delrin Plastic Wool

- Irregular random stranding
- Slows Particles to the Uniform Frit
- Prevents Clogging

Prepping the 6ml Cartridge with Plastic Filtration Wool

6ml 500mg DVB cartridge with Plastic wool

- Take a little and push it into the barrel of the syringe until it touches the cartridge Frit
- The Sample will not clog, it will take longer to process

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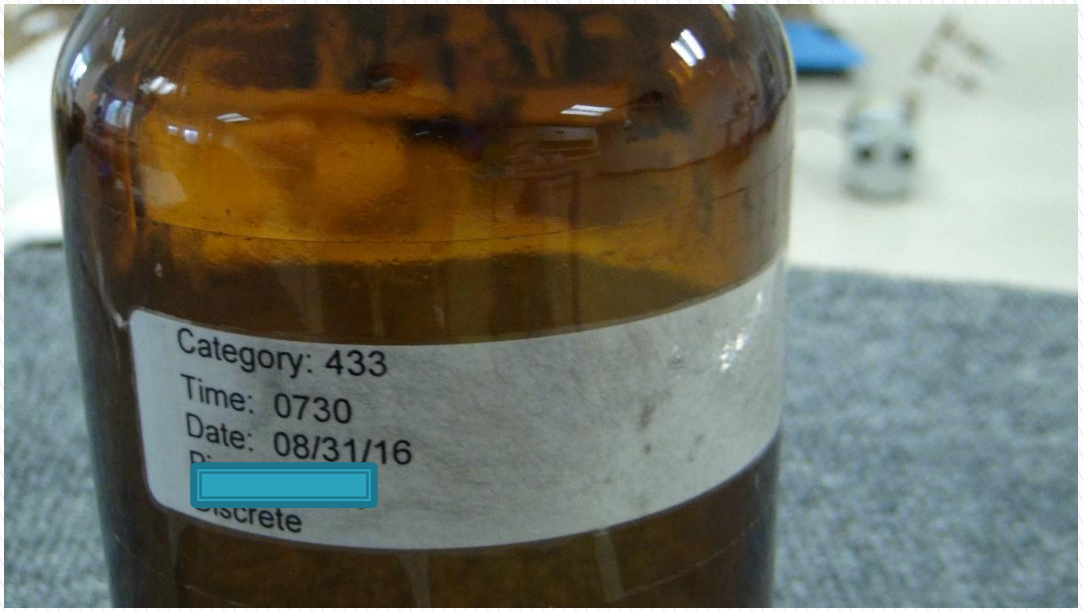
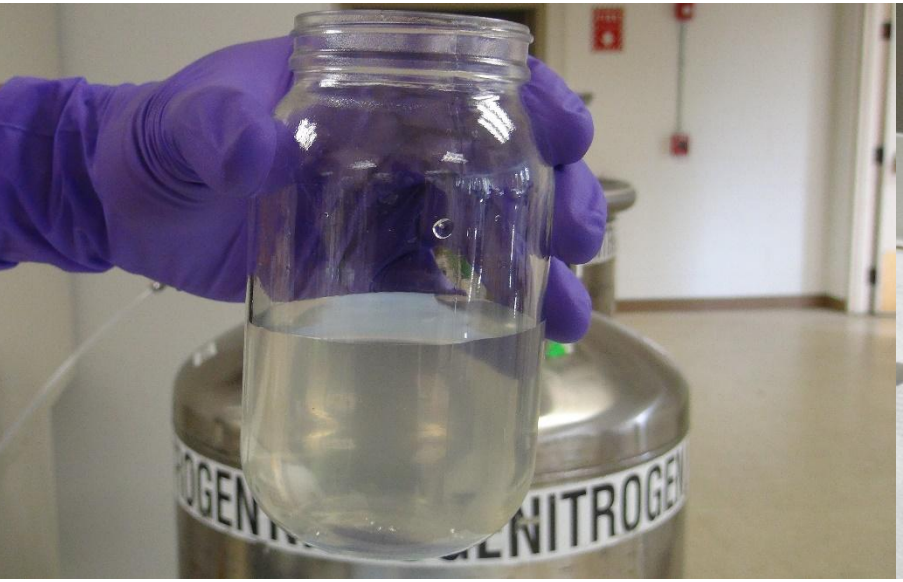
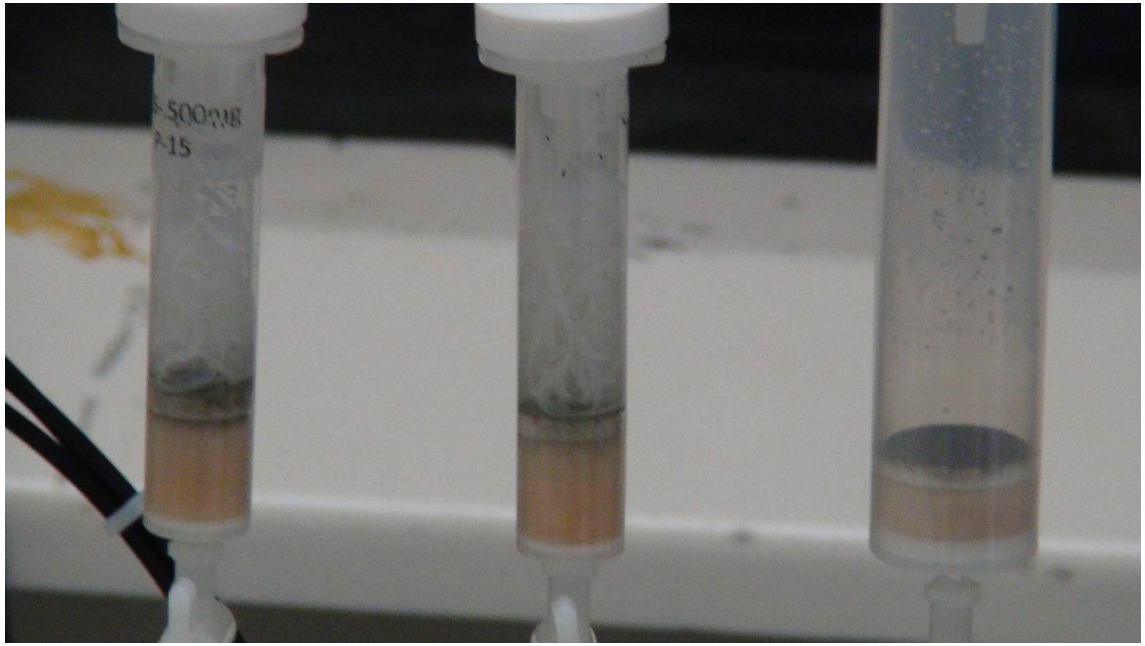
Dirty Sample from a Customer



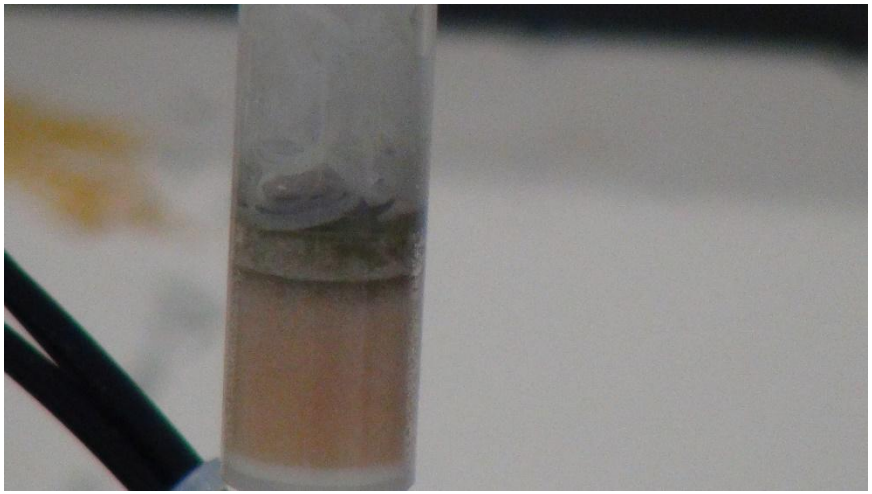
Industrial 433 Matrix 250ml

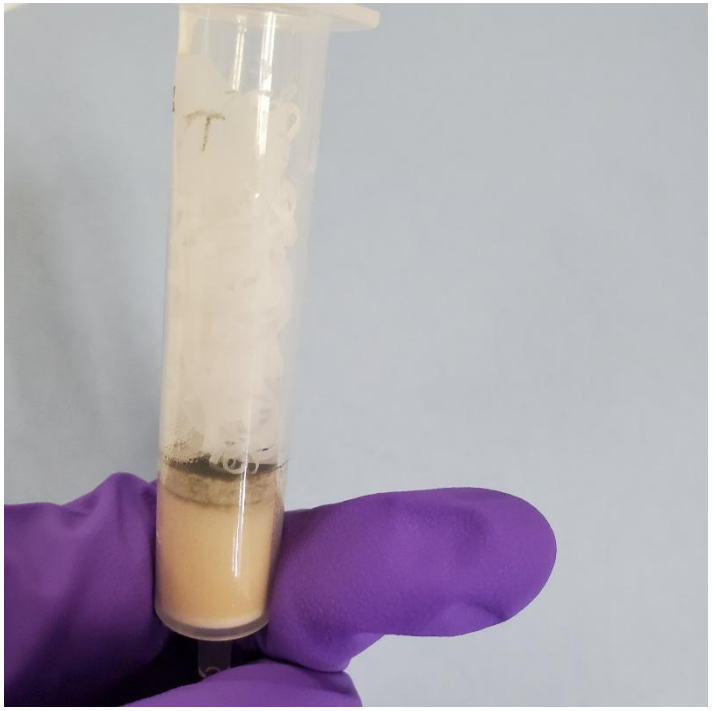


6ml and 25ml Cartridges

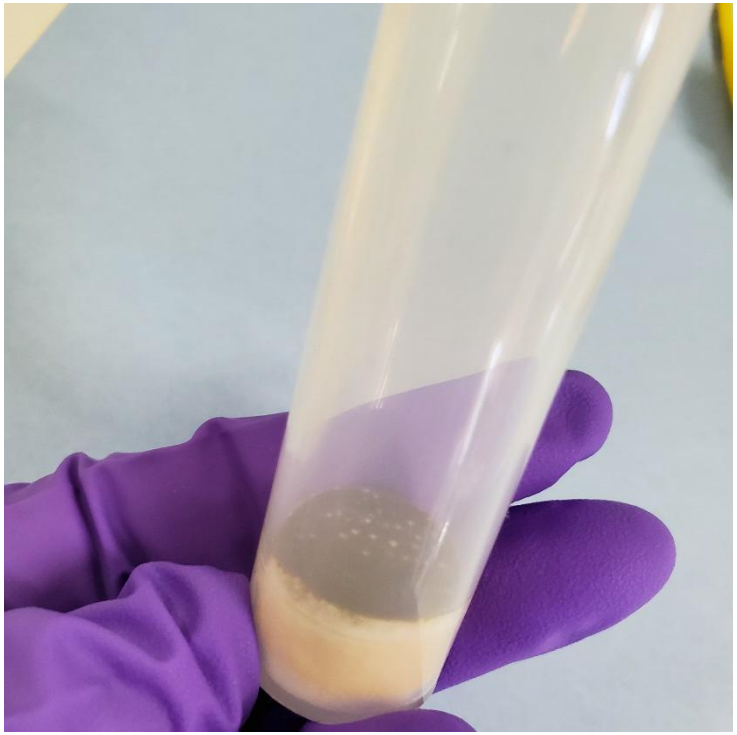


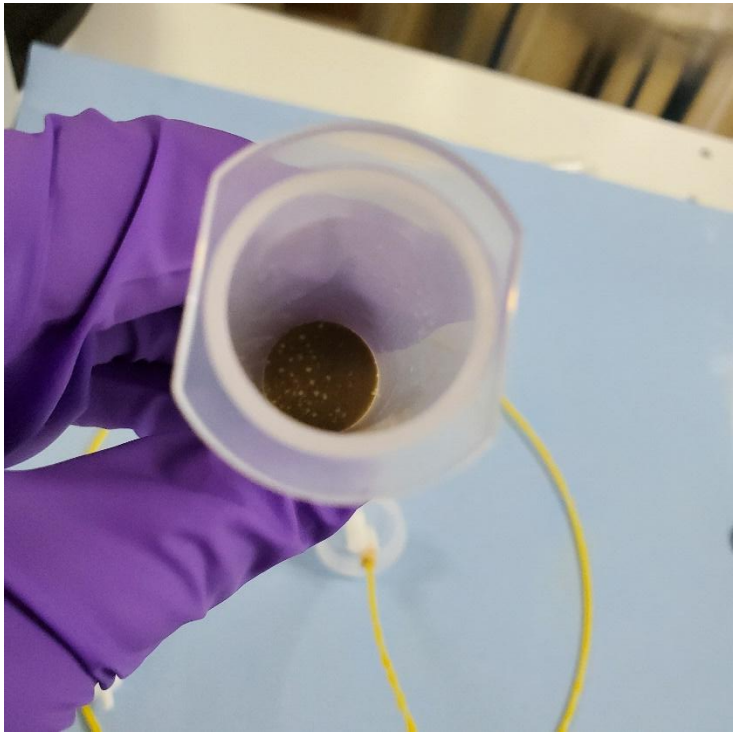
250 ml run to completion on 6 ml cartridge with Plastic Wool





250ml run to completion
25ml cartridge

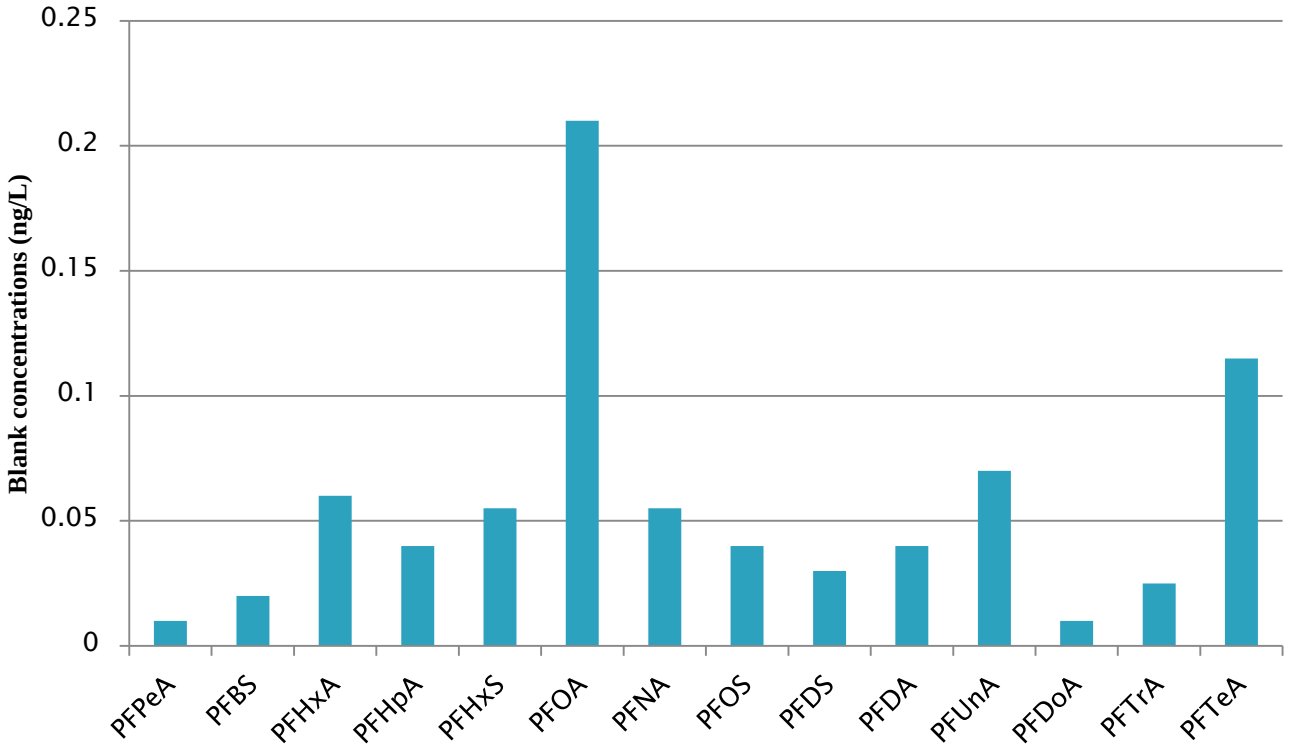




Clean up is easy with no cross contamination

- Back Flush the sample line into the original sample bottle with an IPA non-Teflon squirt bottle.
- Wash the inside of the bottle cap with IPA squirt bottle
- Wash Cartridge Adapters with IPA squirt bottle or sonicate in a beaker
- Ready for the next 12 samples

PFAS Background



Semi-Automated SPE in Summary

- EZPFC and SuperVap systems are easy to use and install
  - Complete Water Sample Prep Workflow
- Low cost, High throughput, Low maintenance solution
- EZPFC Extractions and Concentration
  - Closed System Reduces Contamination
  - Reduces Human error

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Summary (2)

- FMS semi-automated SPE and SuperVap systems deliver consistent, reproducible results
- Handles a wide range of Sample sizes and matrix types
- Uses all SPE Cartridge sizes
- Comply with existing methods that require vacuum, positive pressure and precise delivery of sample and solvents

Summary (3)

- New Solid Phase Extraction Chemistries and Methods are continuously being developed
- EZPFC
  - Designed for Semi-Automated PFAS Extractions
  - SuperVap PFC Concentrator for 24 samples
- Capable of performing in line extract drying and/or Cartridge extract clean-ups