

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

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Introduction

- ▶ Perfluoralkylated compounds contain a perfluorinated or polyfluorinated carbon chain moiety such as $\text{F}(\text{CF}_2)_n-$ or $\text{F}(\text{CF}_2)_n-(\text{C}_2\text{H}_4)_n$.
- ▶ 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

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:
 - Perfluorooctane sulphonate (PFOS)
 - Perfluorooctanoic acid (PFOA)
- ▶ Millions have been exposed through Drinking water supplies in the US and exceed the lifetime advisory of 70ng/L for these compounds

PFAS Analysis

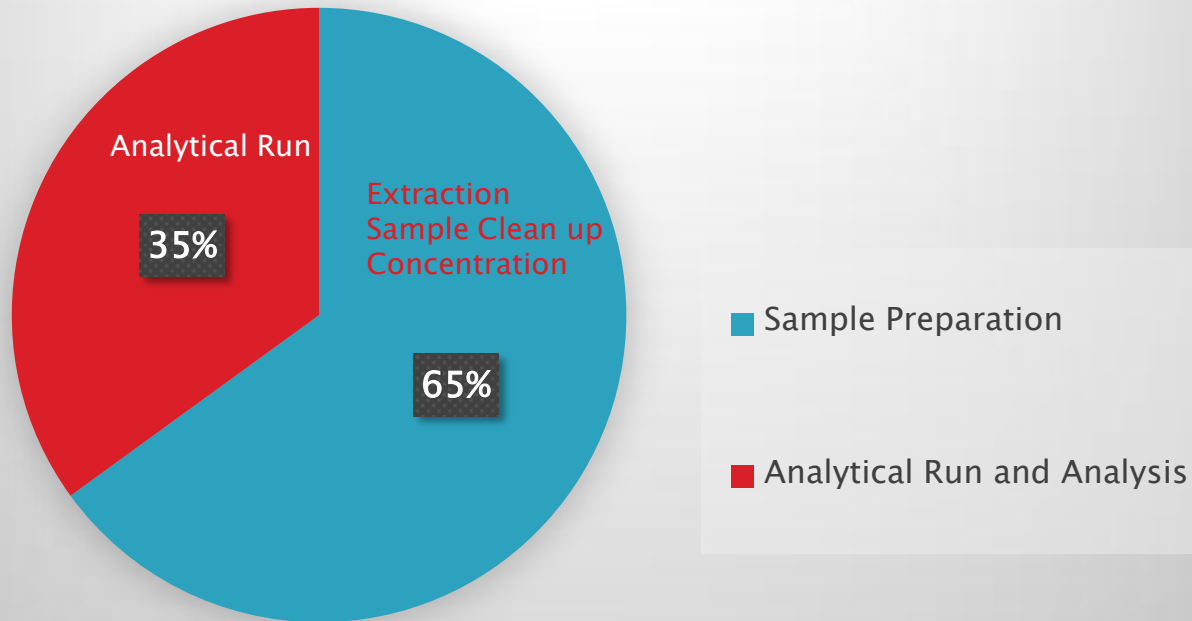
- ▶ Many of Thousands Samples are now being analyzed and more areas of concern are starting to be analyzed for PFAS:
 - Drinking Water
 - Waste Water
 - Human Serum
 - Biota
 - Soils

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

Sample Prep versus Analytical in Time



Reasons for Semi-Automated SPE

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

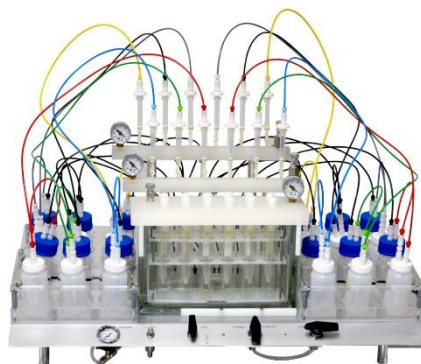
Determining Factors

- ▶ 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

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



EZSPE



EZPFC



Sample Analysis Work Flow

Automated Sample Prep Time

= 80 Minutes



35 Minutes



45 Minutes

Semi Automated Sample Prep Time

= 80 Minutes

35 Minutes



45 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

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

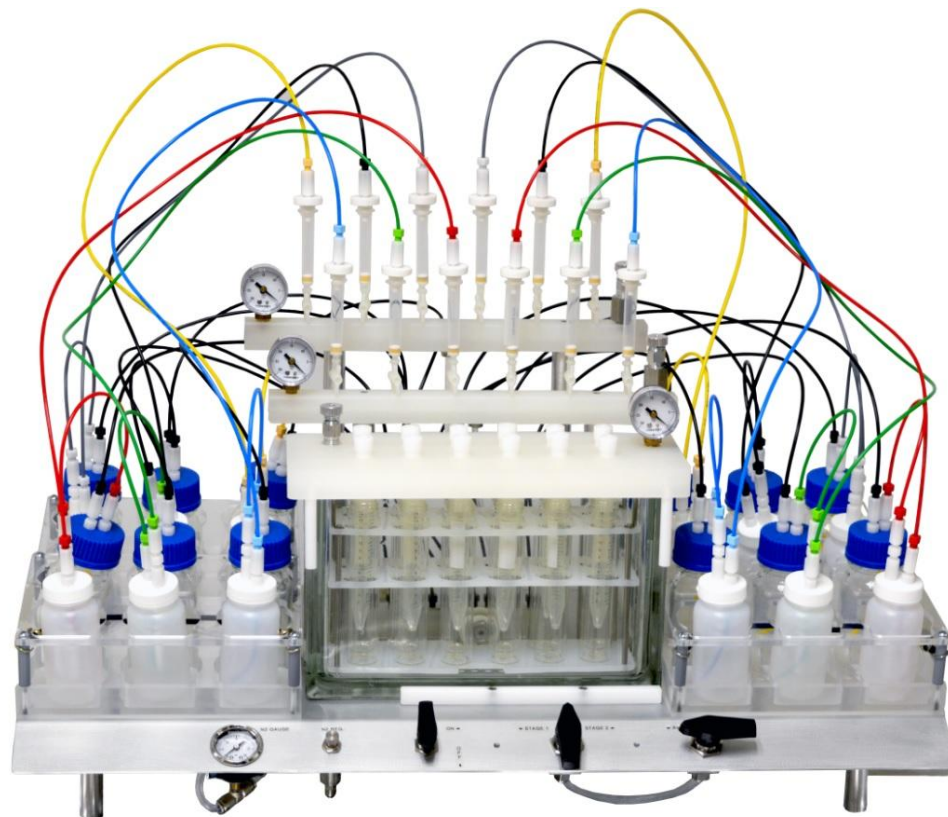
Goal

▶ **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



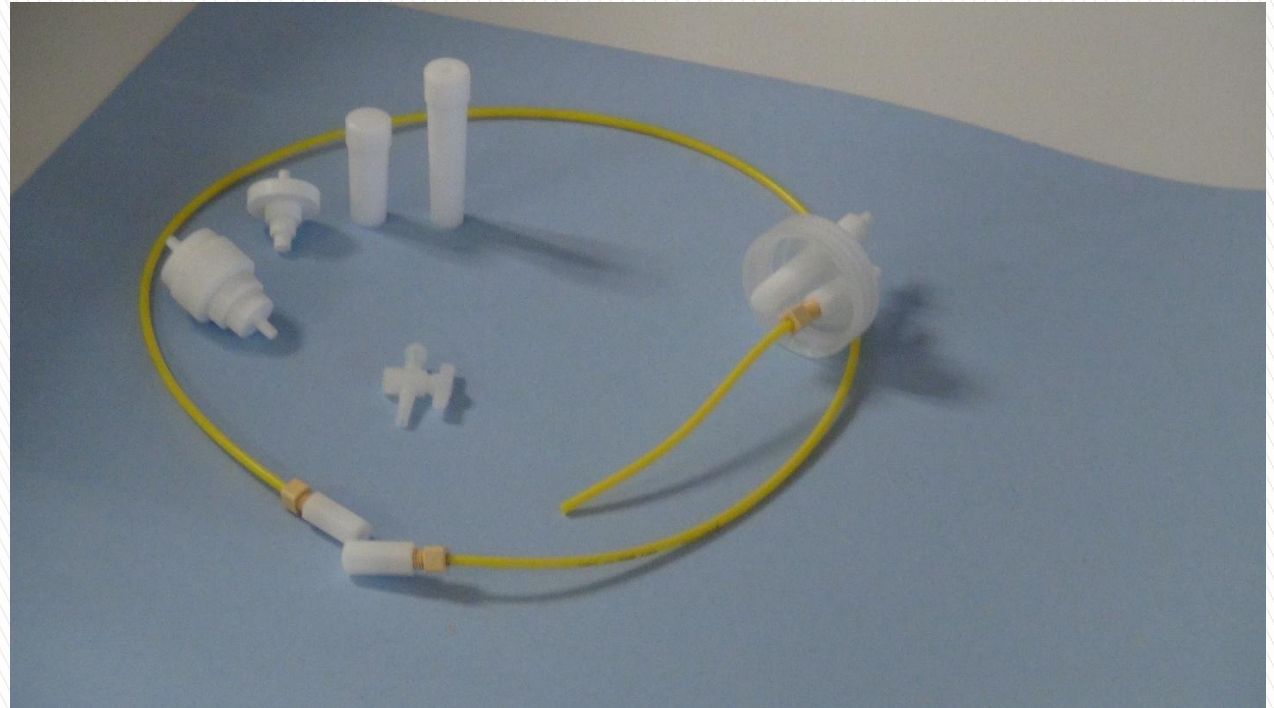
System Components

No Teflon

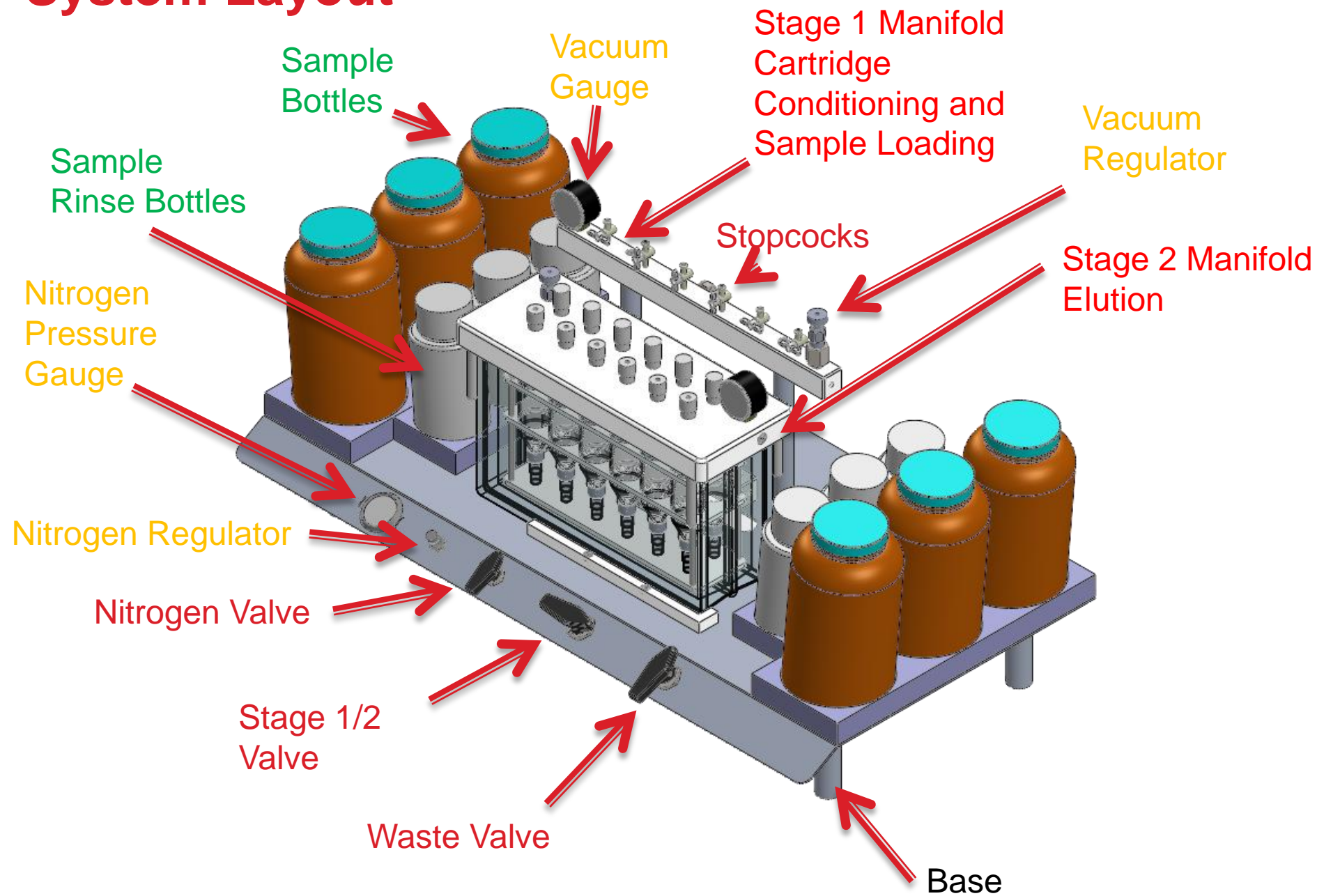
Tubing – High
Density Polyethylene

Fittings – Delrin

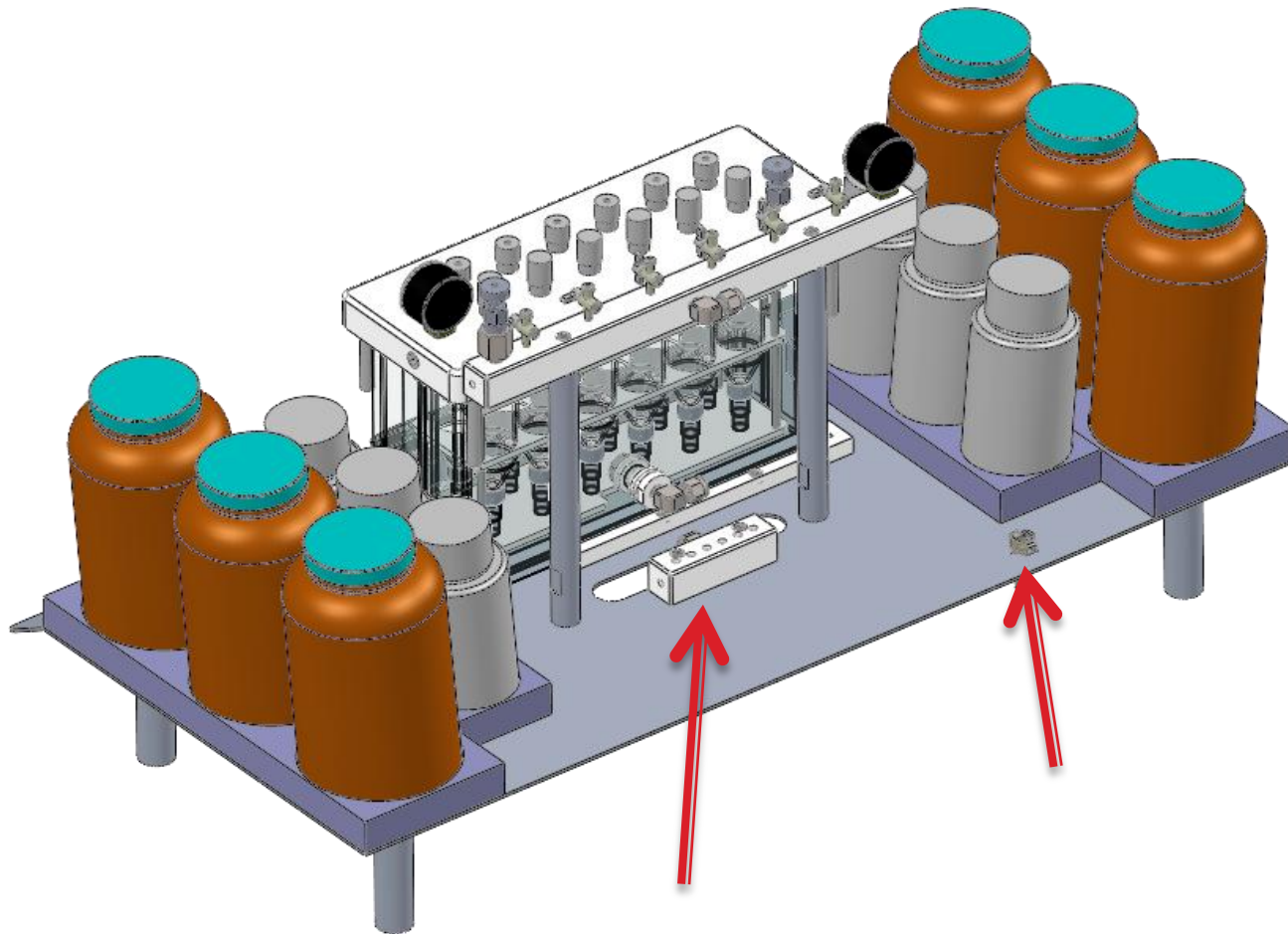
Cartridge Adapters –
Medical Grade
Polypropylene



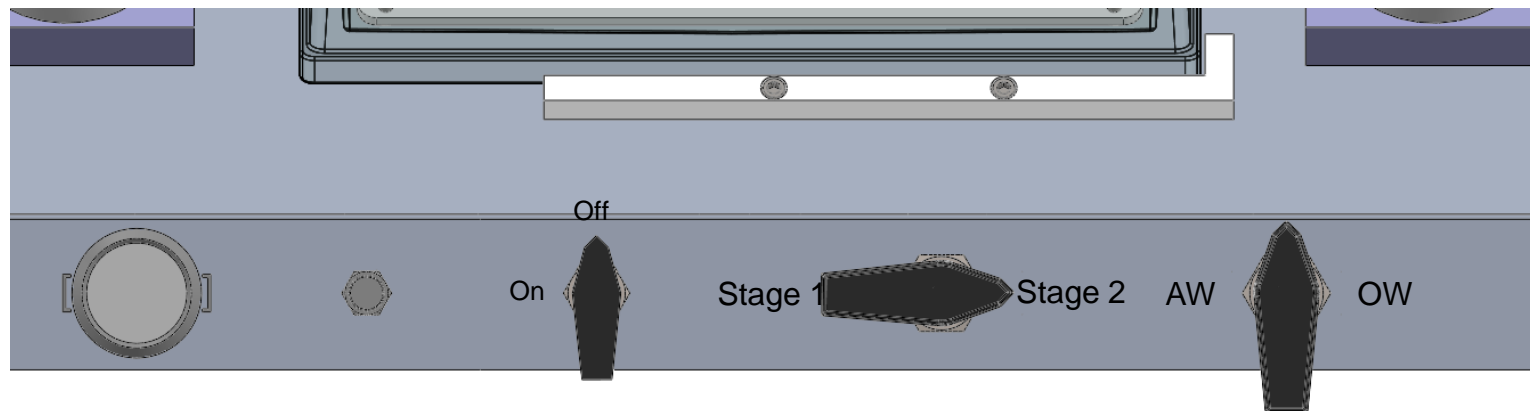
System Layout



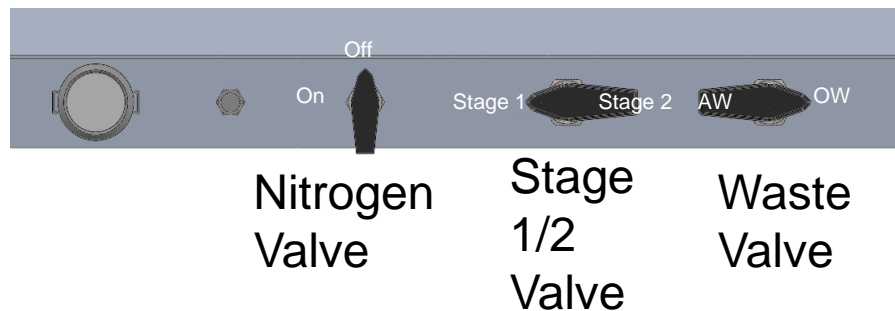
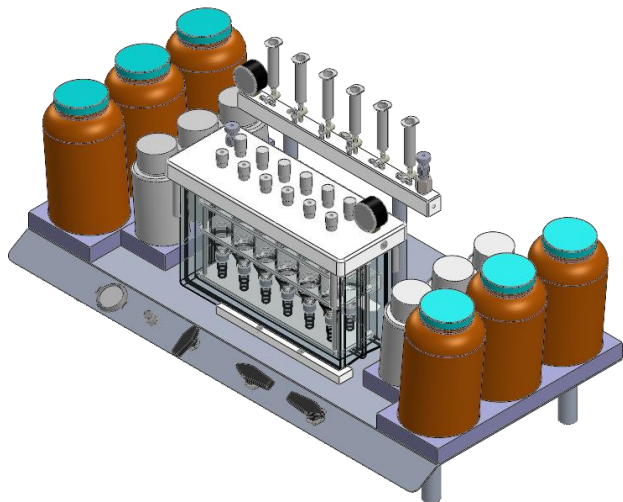
Nitrogen for Bottle Rinse and Cartridge Drying



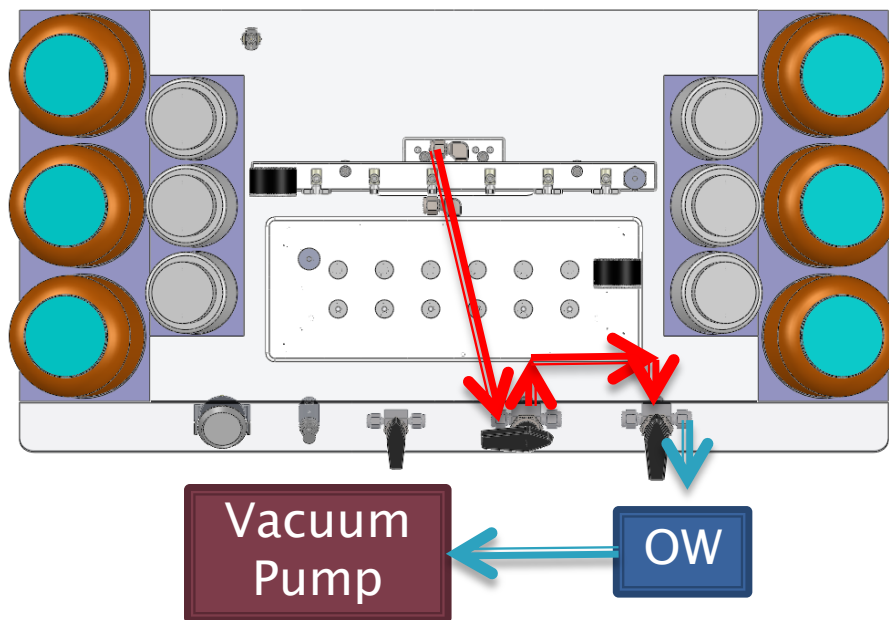
Control Valve Layout



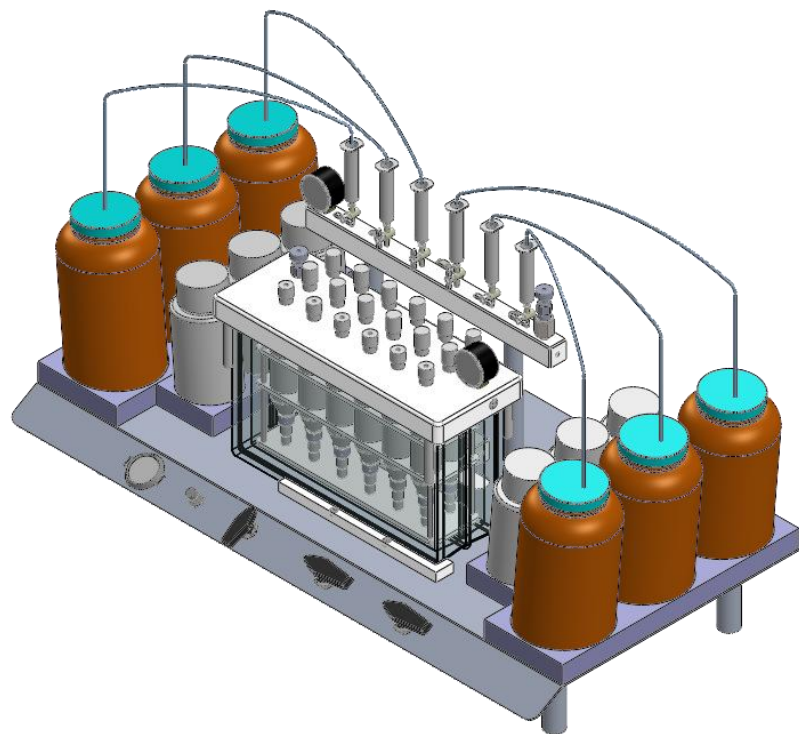
Cartridge Conditioning (Stage 1, Organic Waste)



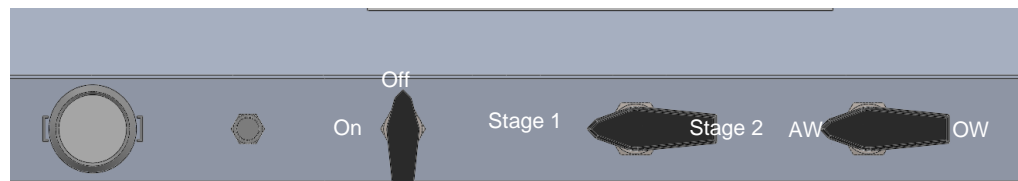
Flow Path



Sample Loading (Stage 1, Aqueous Waste)



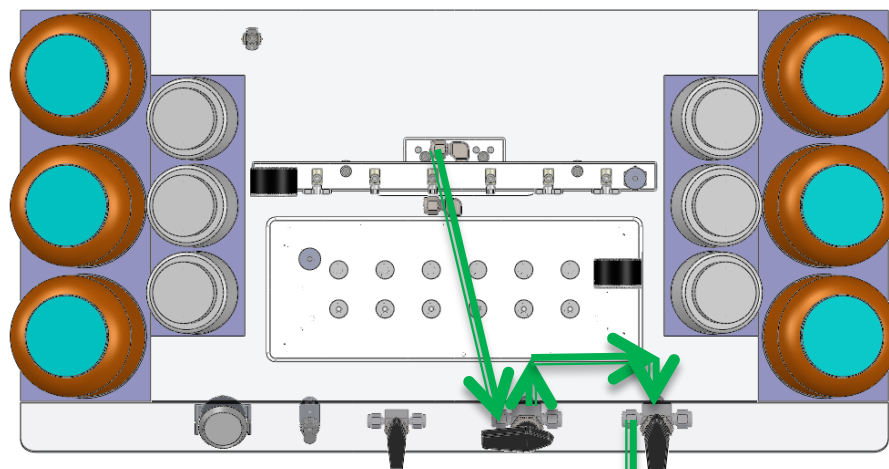
Flow
Path



Nitrogen
Valve

Stage
1/2
Valve

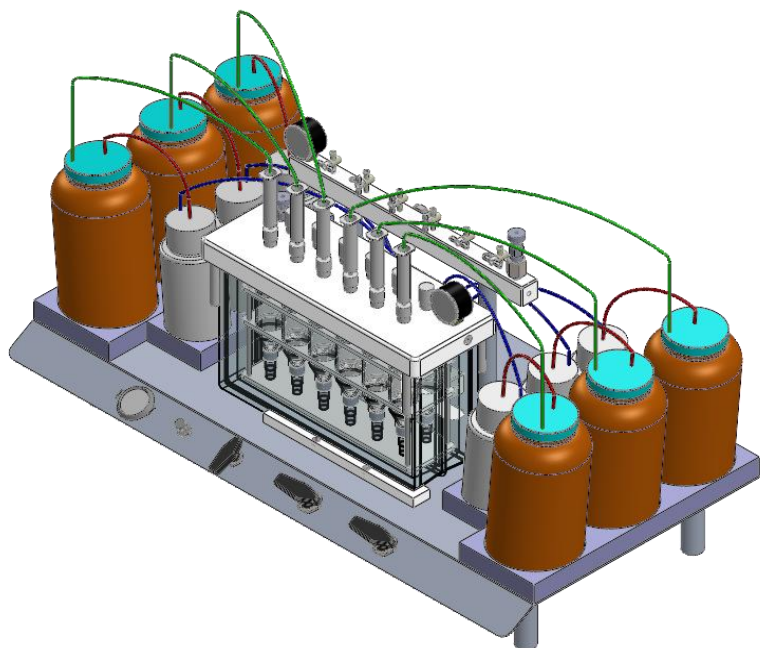
Waste
Valve



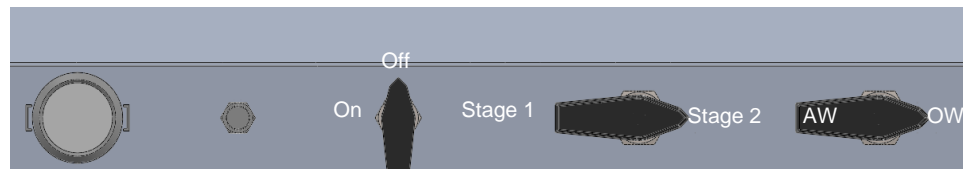
Vacuum
Pump

AW

Sample Bottle Rinse (Stage 1)



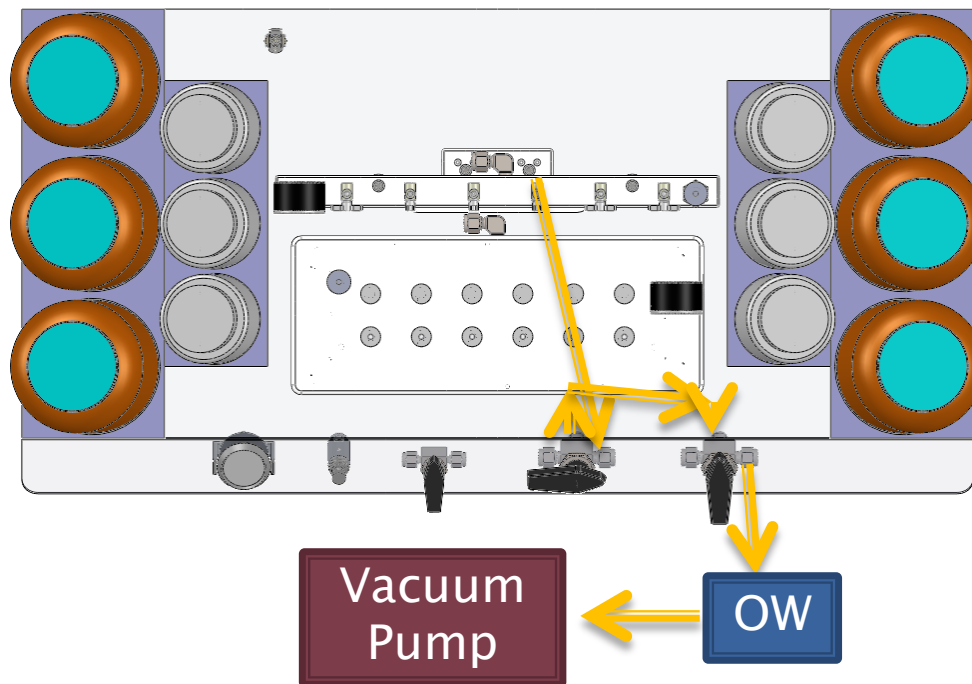
Flow
Path



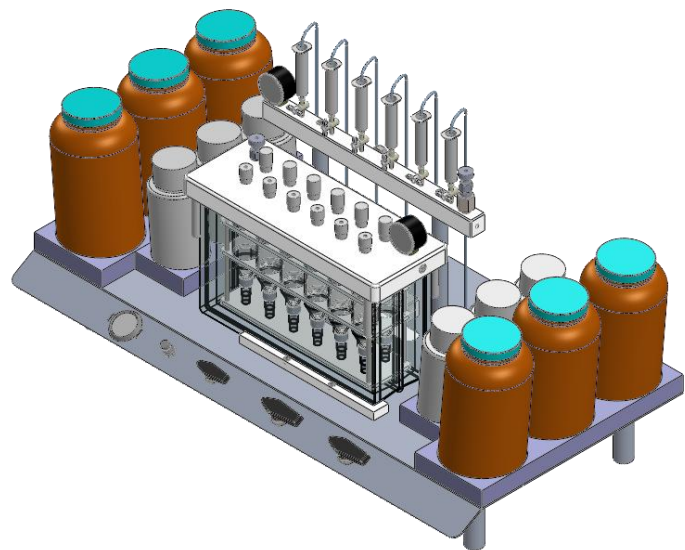
Nitrogen
Valve

Stage
1/2
Valve

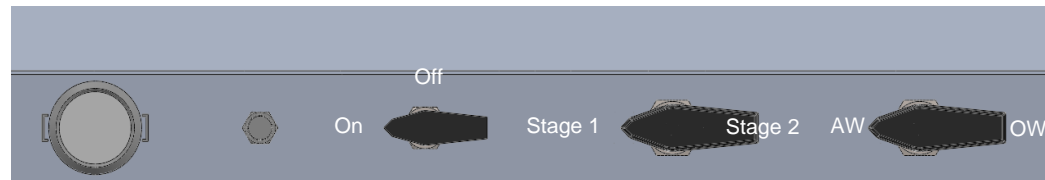
Waste
Valve



Cartridge Drying- Nitrogen/Vacuum



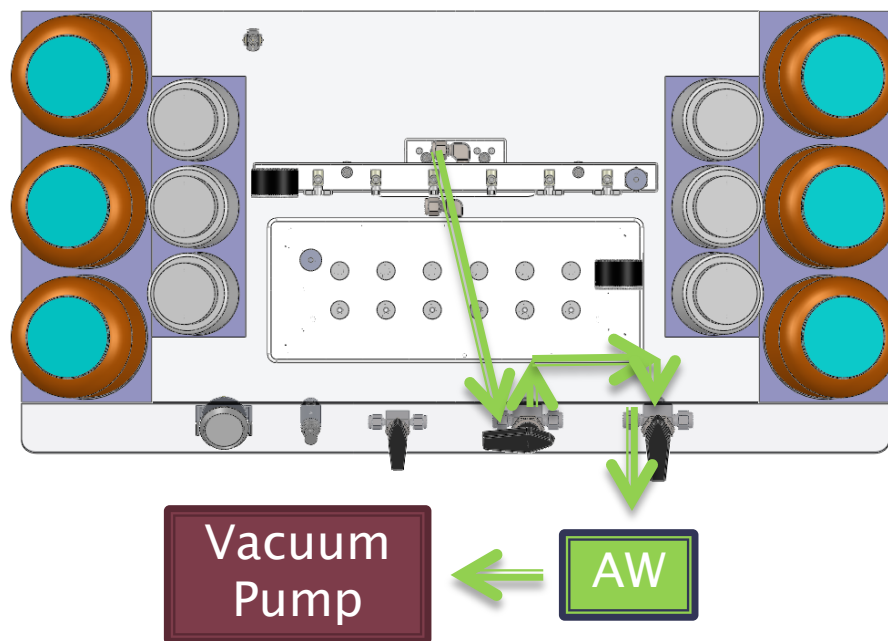
Flow
Path



Nitrogen
Valve

Stage
1/2
Valve

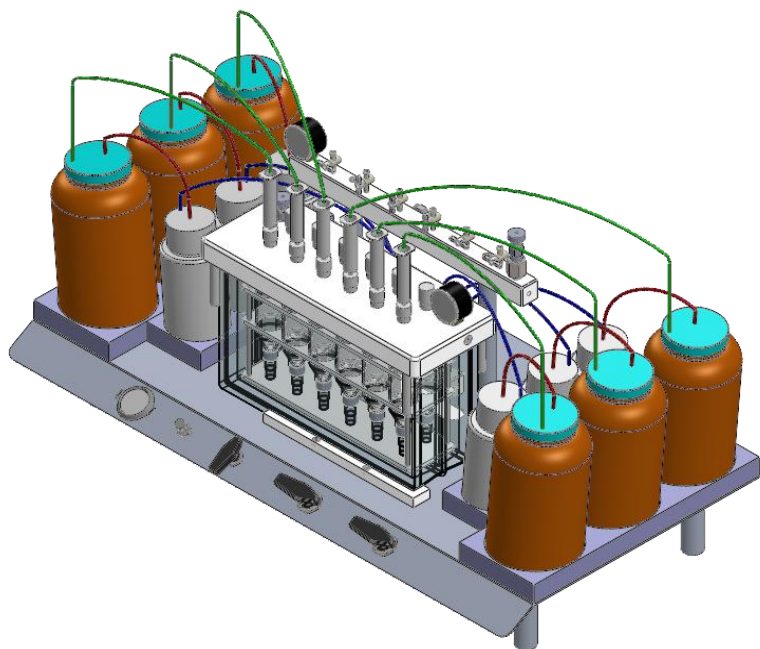
Waste
Valve



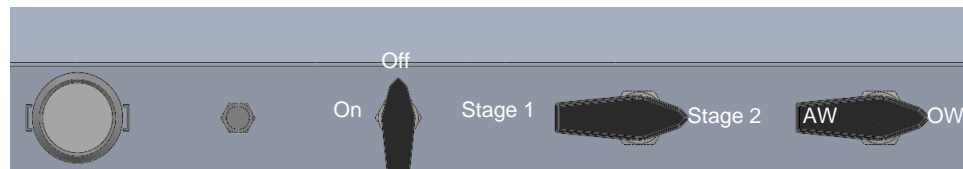
Vacuum
Pump

AW

Sample Elution (Stage 2)



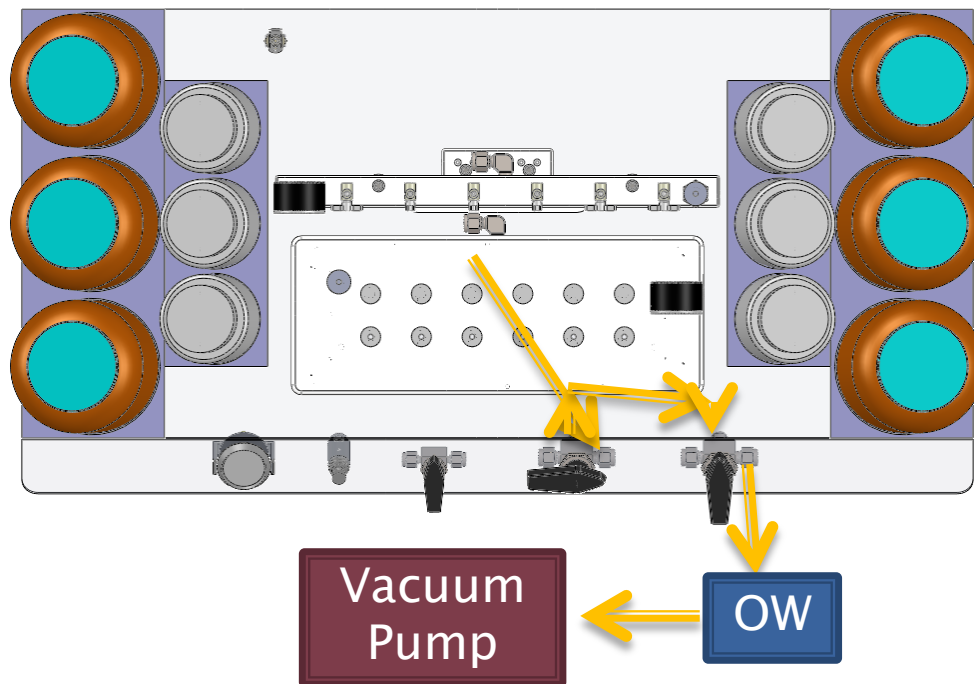
Flow
Path



Nitrogen
Valve

Stage
1/2
Valve

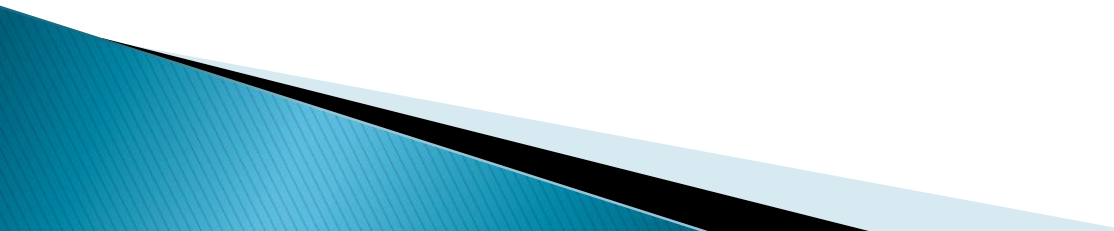
Waste
Valve



Vacuum
Pump

OW

PFAs Methods

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

Automated Concentration for PFAs

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



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**

Can this Handle Dirty Samples?

Typical Cartridge can have problems!

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



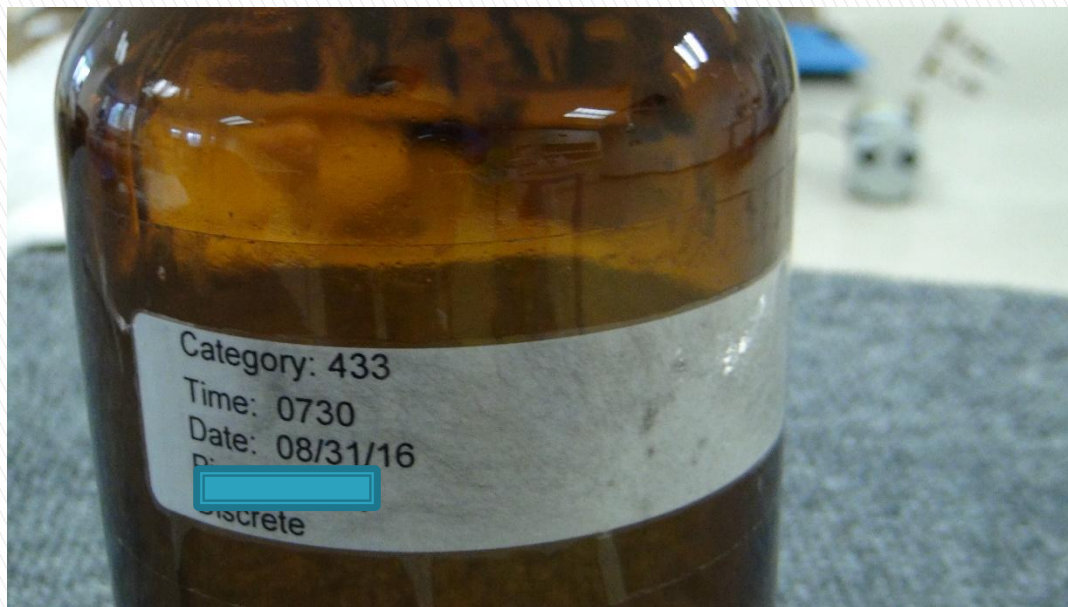
Prepping the 6ml Cartridge with Plastic Filtration Wool

**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



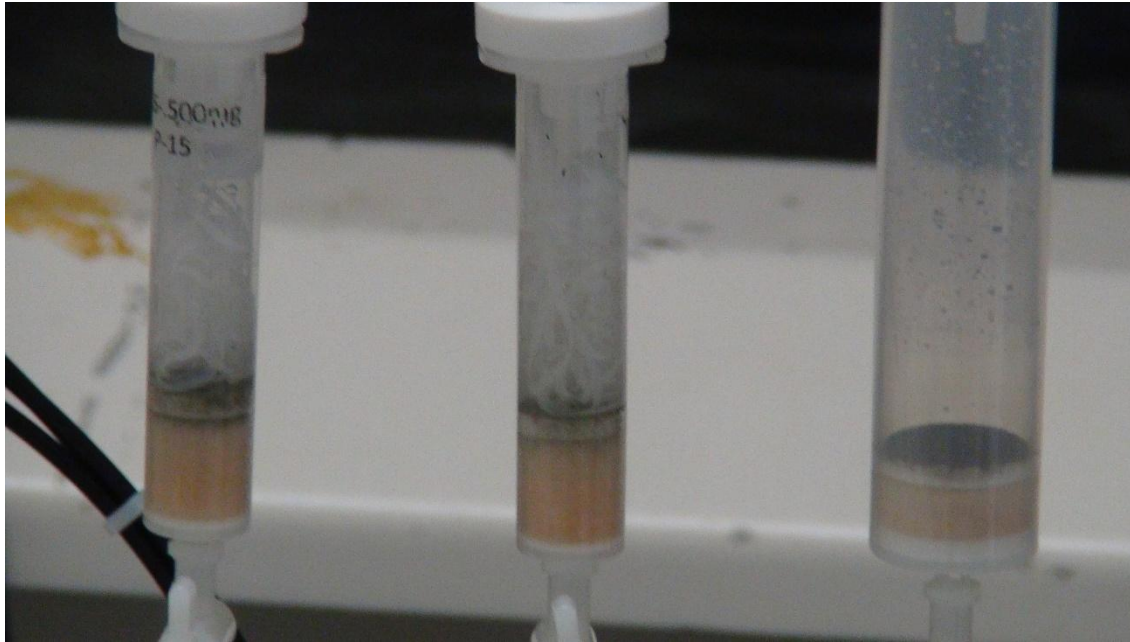
Dirty Sample from a Customer



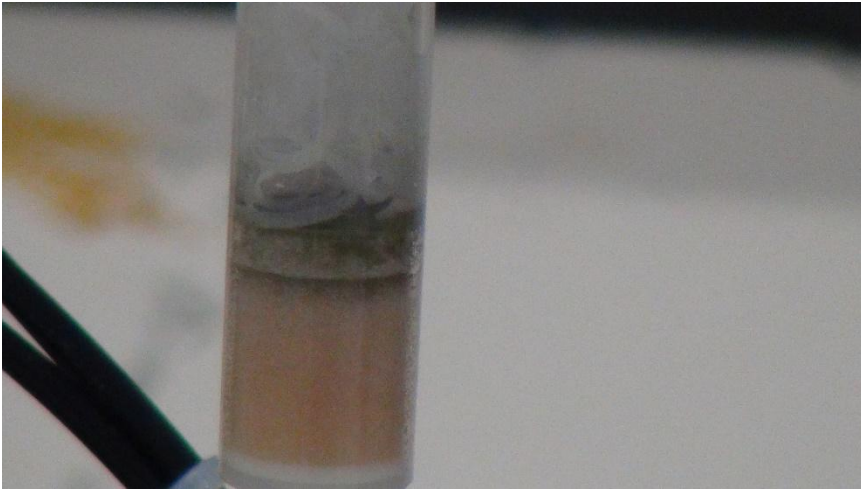
Industrial 433 Matrix 250ml



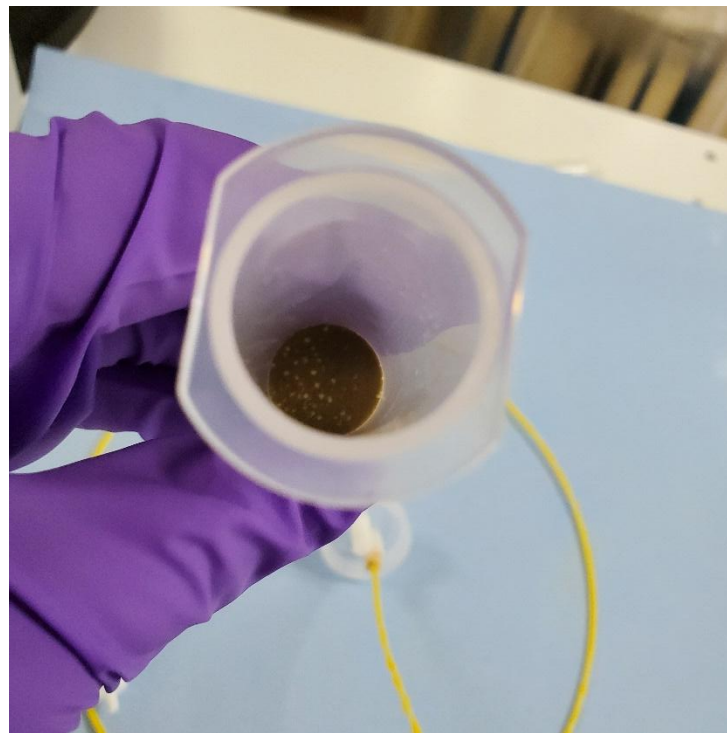
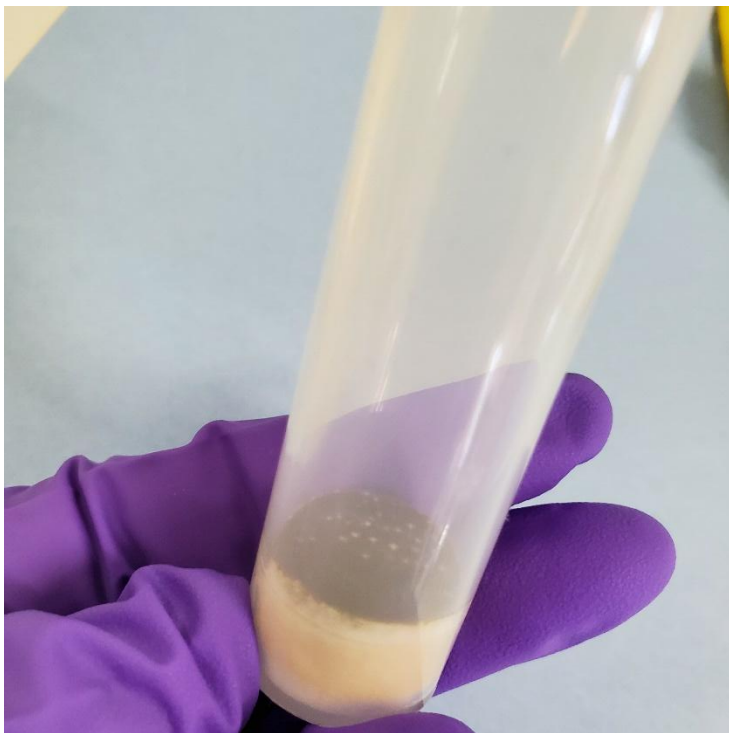
6ml and 25ml Cartridges



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



250ml run to completion 25ml cartridge

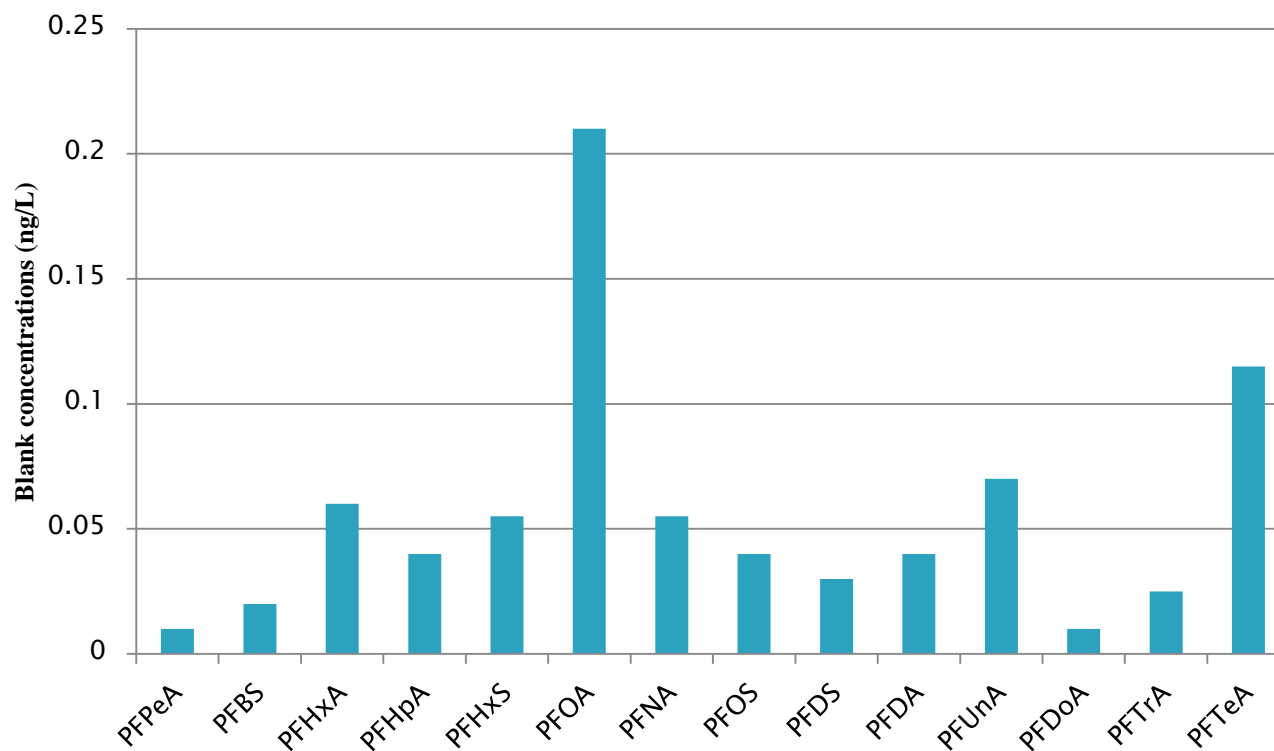


Clean up is easy with no cross contamination

- ▶ 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

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**

Contact information

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