

High Throughput, Solid Phase Extraction and Concentration of PFAS/PFOS in Waste Water Using EPA Method 533 and 537.1

Fluid Management Systems
Billerica, MA USA



Introduction

- Perfluoralkylated compounds contain a perfluorinated or polyfluorinated carbon chain moiety such as $\text{F}(\text{CF}_2)_n\text{-}$ or $\text{F}(\text{CF}_2)_n\text{-(C}_2\text{H}_4)_n\text{-}$.
- These make up a large group of persistent chemicals (POPs) 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**



Regulation

- **PFOS is now subject to varying but increasing levels of control in several countries.**
- **PFOA, also a widespread contaminant but with a far lower bioaccumulation potential, is still under evaluation.**



The Analysis of PFCs

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



Challenges in the Analysis of PFCs

- 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



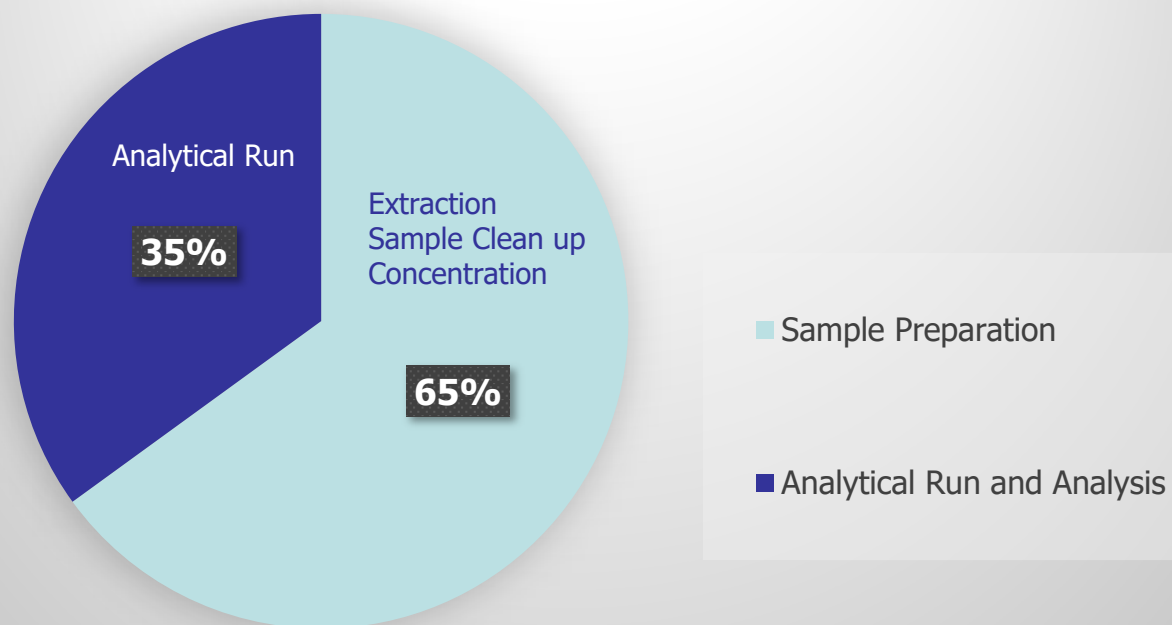
Optimizing the PFC Analysis Workflow

- **Automate the Sample Prep Workflow**
 - **Automate the Solid Phase Extraction Step**
 - **Automate the Concentration/Evaporation Step**
- **Automated, Semi Automated SPE extractions and Concentration**
 - **Reduces Human Error**
 - **Reduces Outside contamination**
 - **Reduces Solvent Usage**
 - **Reduces Labor**
- **Use SPE solutions to deliver consistent, reproducible results**



Laboratory Workflow Breakdown

Sample Prep versus Analytical in Time



Comparison of Manual SPE vs. Automated SPE Methods

Manual

Open to laboratory background

Uses >60mls solvent

Filtration process

No emulsions formed

Wide Selectivity (adsorbent)

Requires water removal

Labor intensive requires monitoring

Automated SPE

Closed system

Uses <60mls solvent

Filtration process

No emulsions formed

Wide Selectivity (adsorbent)

In-line water removal

Fast and Unattended





Comparison of Manual SPE vs. Automated SPE Methods

Manual SPE

Separates Aqueous and Organic Waste

<60mls solvent evaporate

Run times are ~ 45 minutes

Technician Time 25 minutes

Physical transfer and Concentration steps

Concentration steps 45 minutes

Automated/Semi Auto SPE

Separates Aqueous and Organic Waste

<60mls solvent to evaporate

Run times are ~ 35 minutes or less

Technician time 5 minutes

Automatic and Direct to Concentration
delivery and completion

Concentration step 45 minutes ready for
injection



Reasons for Semi-Automated SPE

- **Reduced solvent**
- **Reduced Actions**
- **Simplified procedures**
- **Semi-Automated versus Manual protocols = Reproducibility**
- **Increased Sample Throughput**
- **Low cost compared to Automated solutions**



Determining Factors

- **Ability to load samples by vacuum consistently.**
- **Ability to dry cartridges by both vacuum and positive gas pressure (N2 or CO2).**
- **Easily handle a wide variety of cartridge designs and sizes without cumbersome modifications.**
- **Simple Sample delivery**
- **Bottle Rinse**





Automated Solid Phase Extraction front end for LC/MS



EconoTrace® PFC



TurboTrace® PFC



TurboTrace®
Parallel
Sequential



Automated Concentration for PFAs

- SuperVap PFC
 - 24 positions
 - 15ml Conical vials

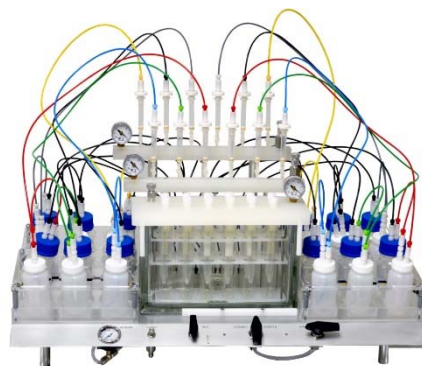




Semi-Automated Solid Phase Extraction front end for GC/MS and LC/MS



EZSPE



EZPFC



Sample Analysis Work Flow

Automated Sample Prep Time

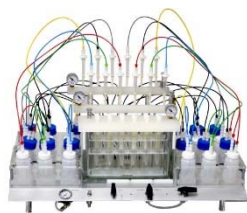
= 80 Minutes



Solid Phase Extraction
35 Minutes



Concentration
45 Minutes



Solid Phase Extraction
35 Minutes



Semi Automated Sample Prep Time

= 80 Minutes



Objective for Semi Automation

- **Use as many features as possible from the 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 six samples simultaneously
 - Vacuum for fast loading of large volume samples
 - Unattended Sample loading walkaway time
- **Closed system**
 - Eliminate potential outside contamination



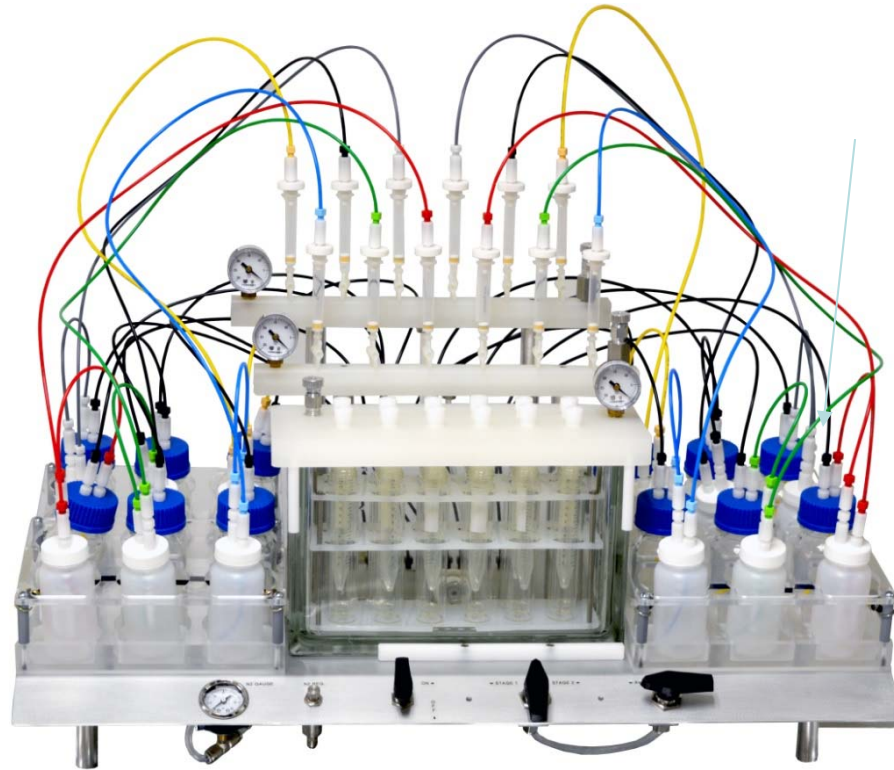
Goal

- **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**





EZPFC 12 sample

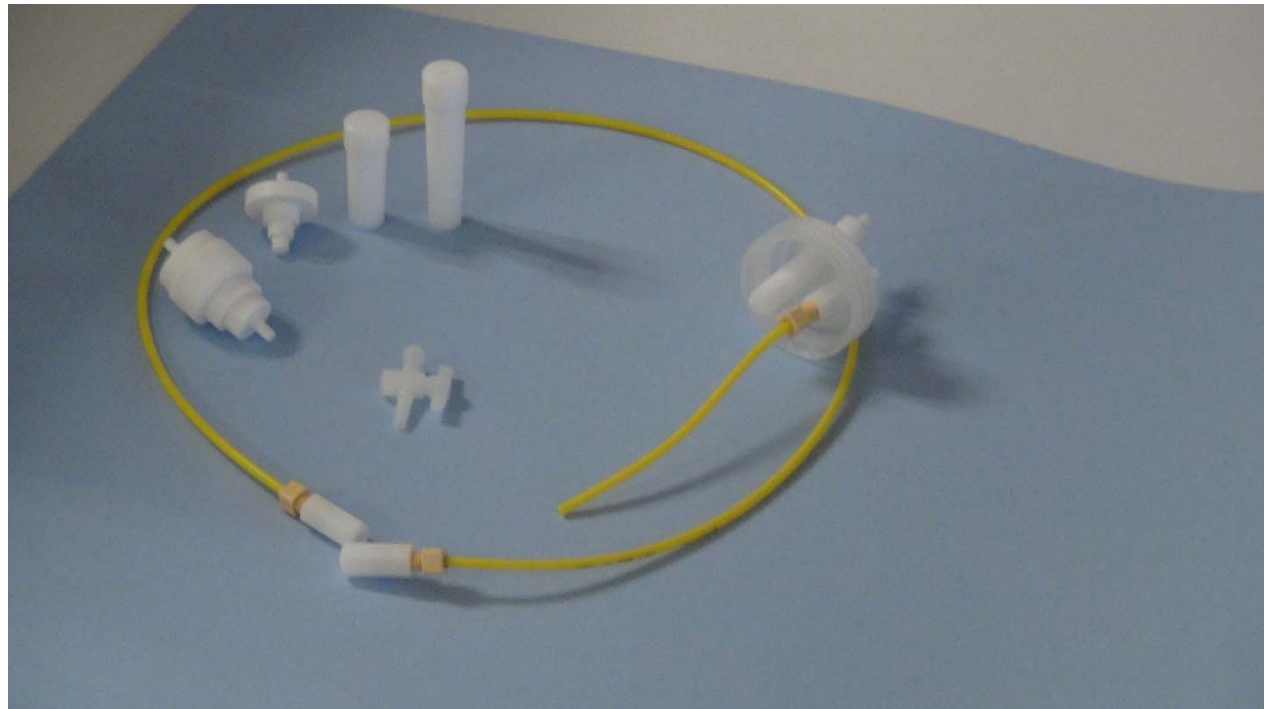
System Components

No Teflon

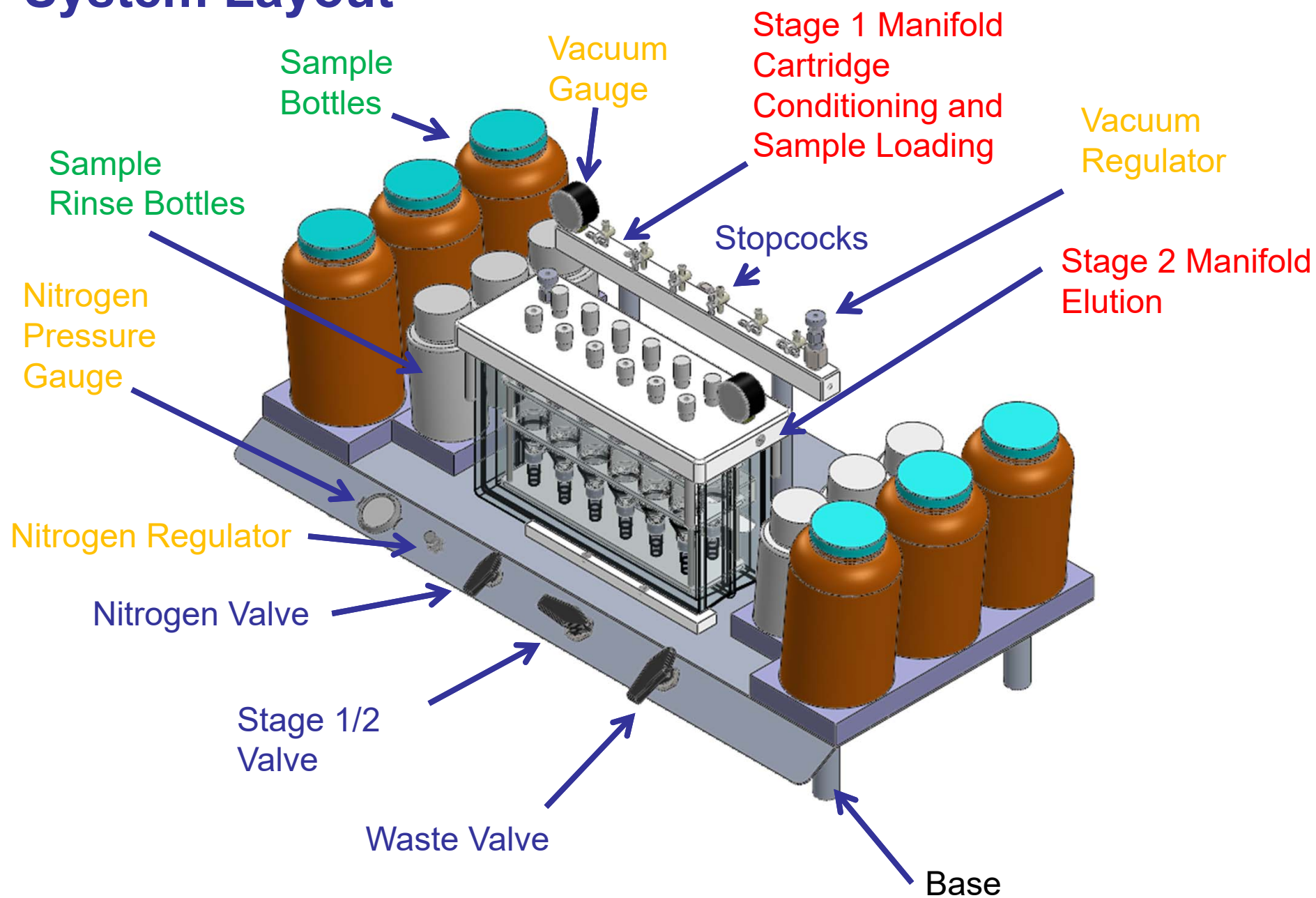
**Tubing - High Density
Polyethylene**

Fittings – Delrin

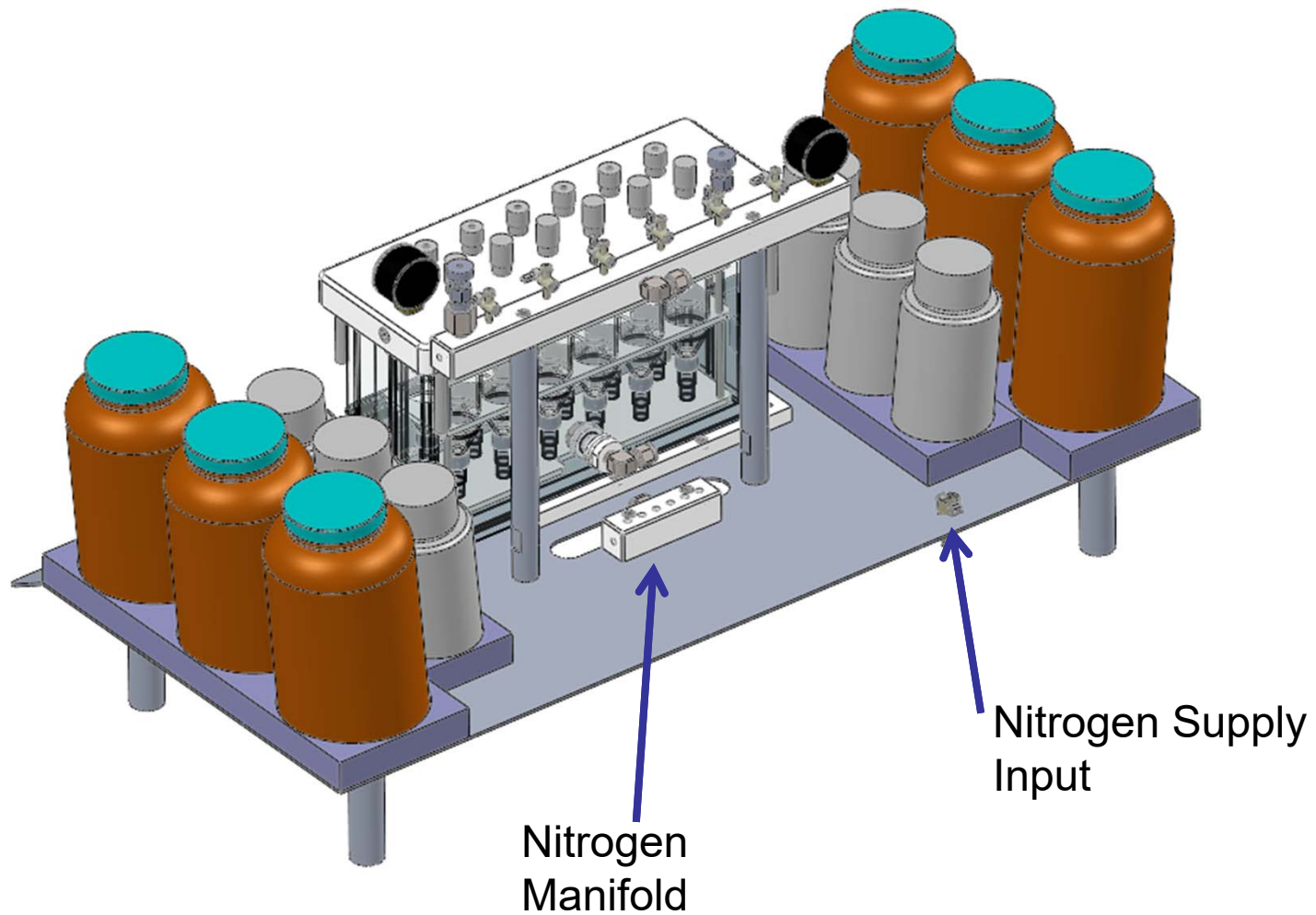
**Cartridge Adapters –
Medical Grade
Polypropylene**



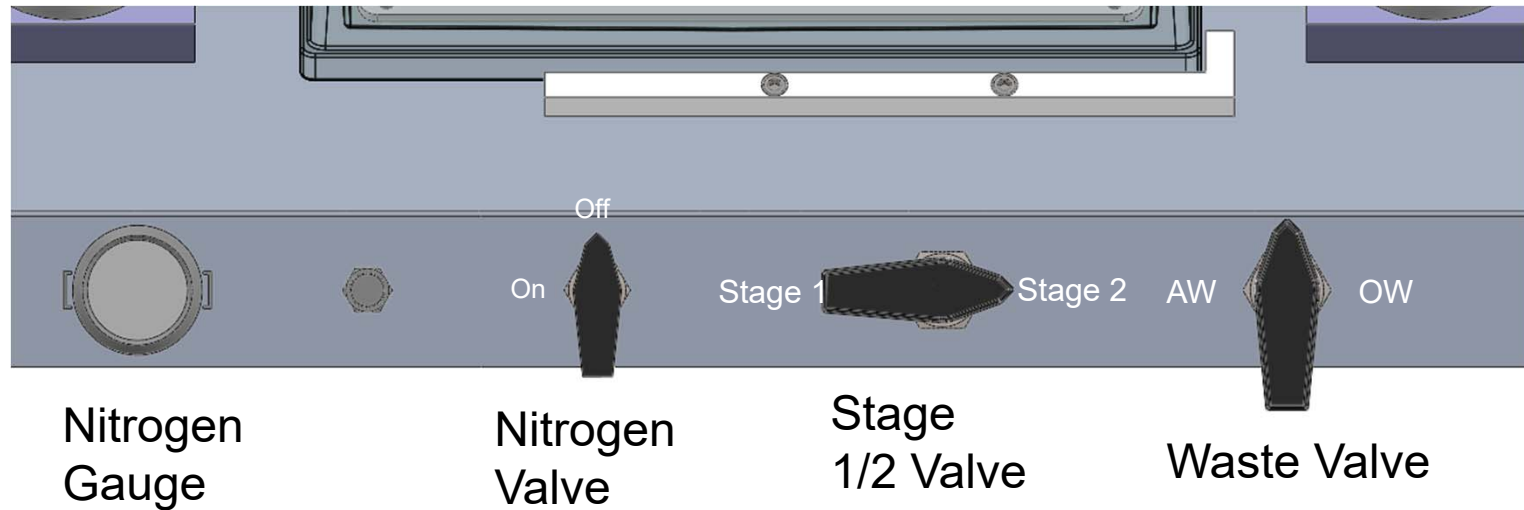
System Layout

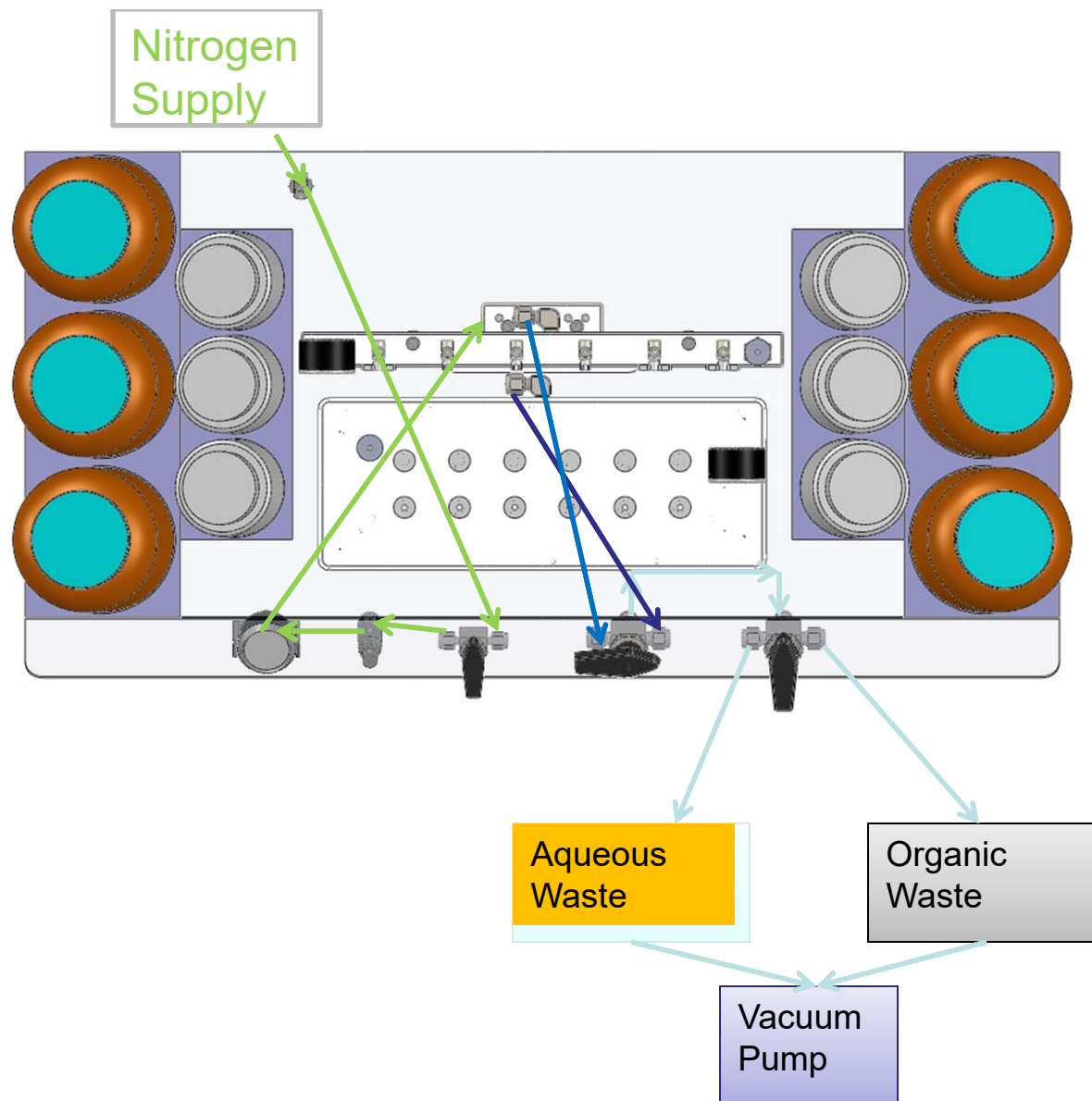


Nitrogen for Bottle Rinse and Cartridge Drying



Control Valve Layout





Plumbing Diagram

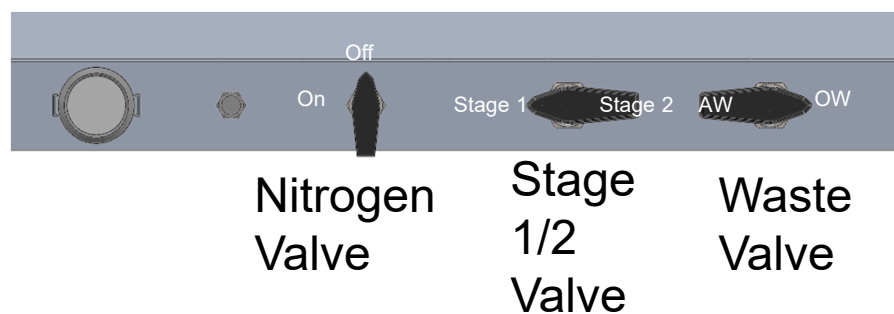
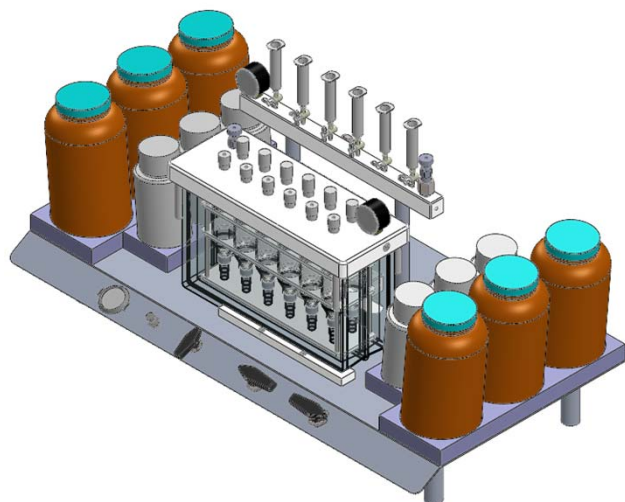
Nitrogen Flow Path ———

Stage 1 Flow Path ———

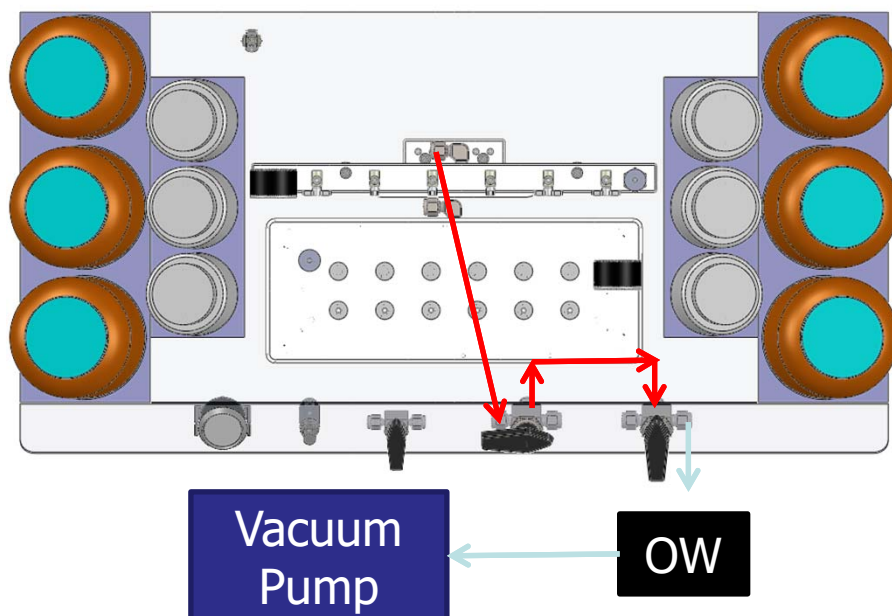
Stage 2 Flow Path ———

Waste Flow Path ———

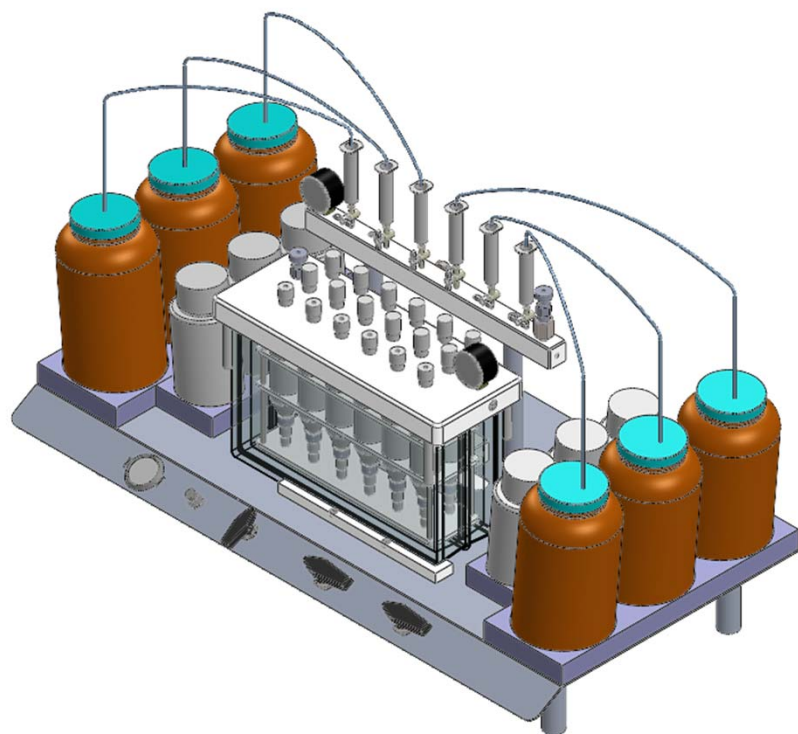
Cartridge Conditioning (Stage 1, Organic Waste)



Flow Path



Sample Loading (Stage 1, Aqueous Waste)



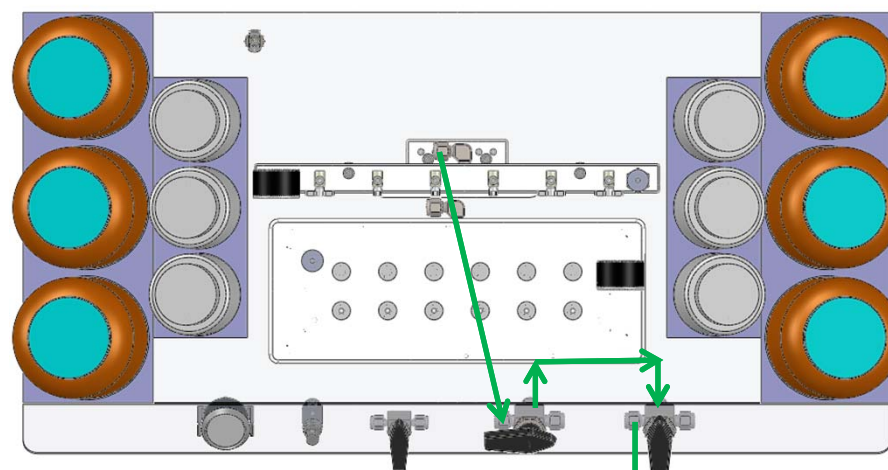
Flow
Path



Nitrogen
Valve

Stage
1/2
Valve

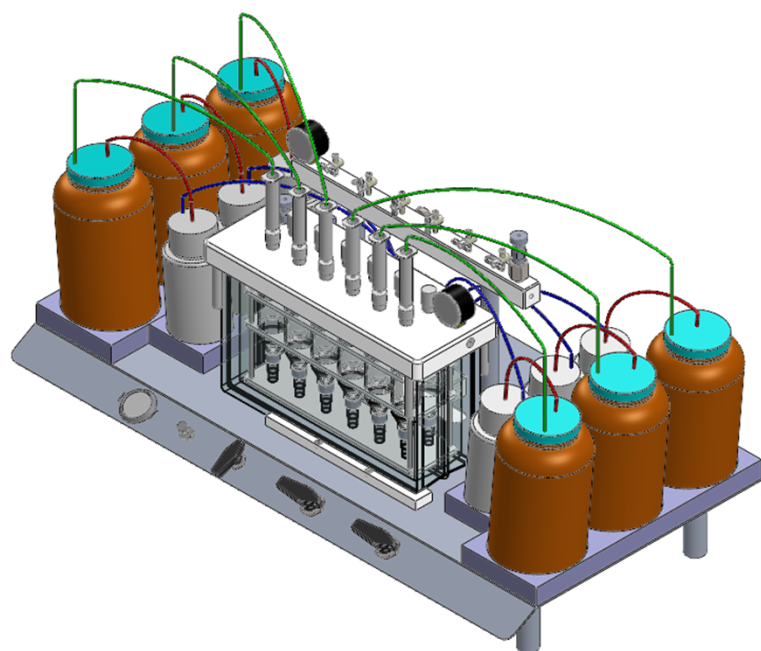
Waste
Valve



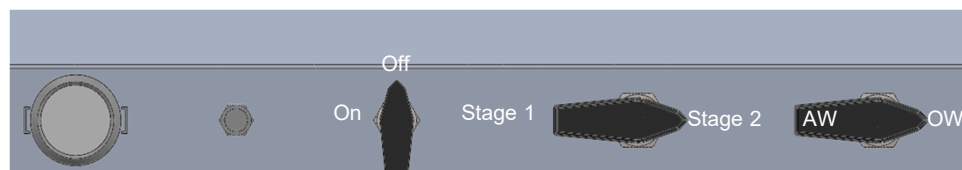
Vacuum
Pump

AW

Sample Bottle Rinse (Stage 1)



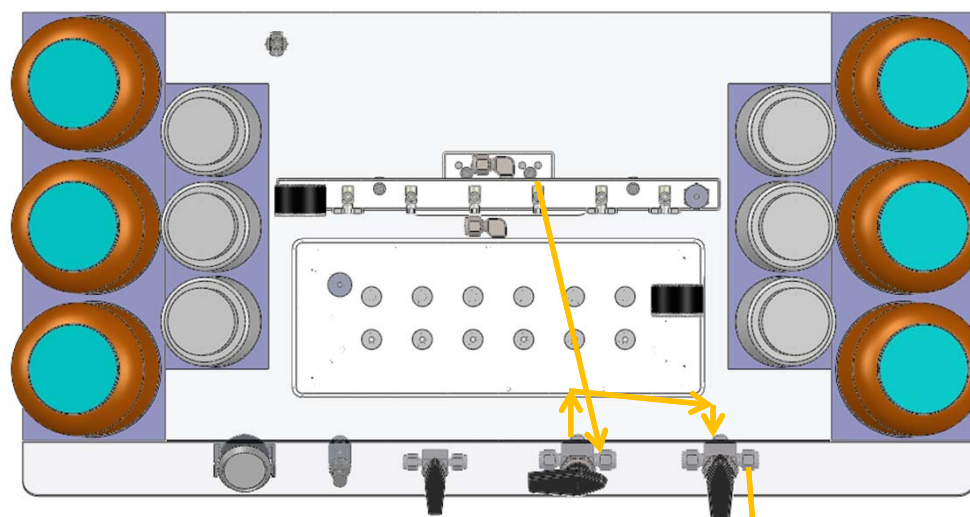
Flow
Path



Nitrogen
Valve

Stage
1/2
Valve

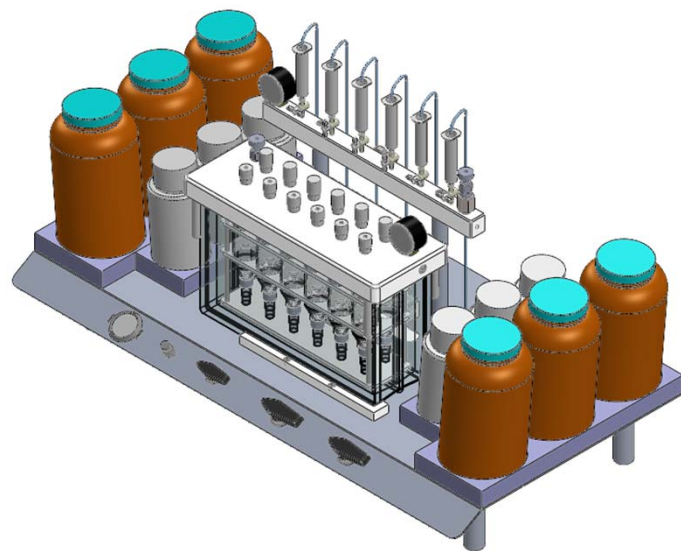
Waste
Valve



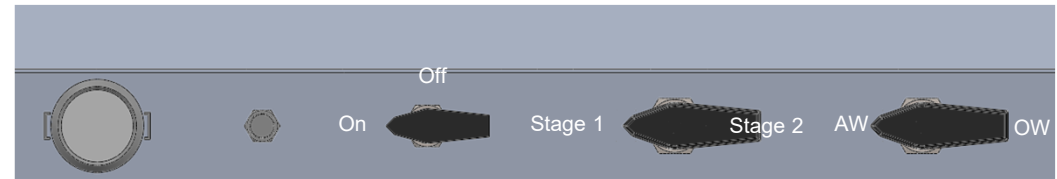
Vacuum
Pump

OW

Cartridge Drying- Nitrogen/Vacuum



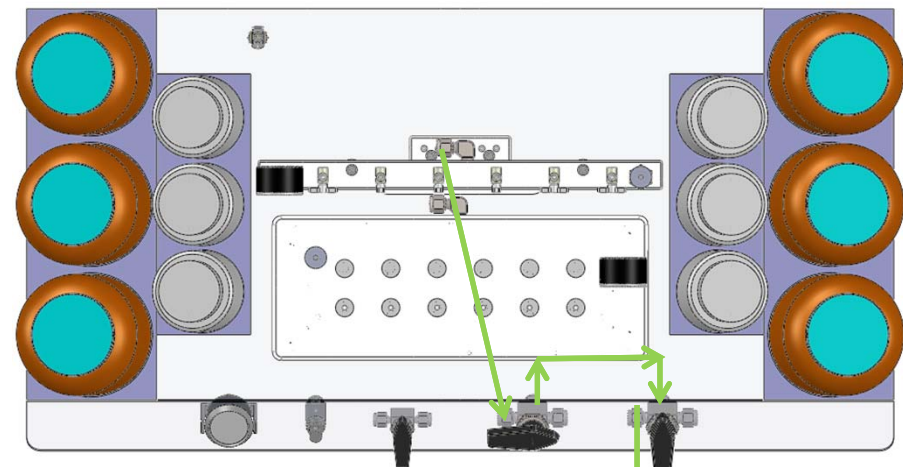
Flow
Path



Nitrogen
Valve

Stage
1/2
Valve

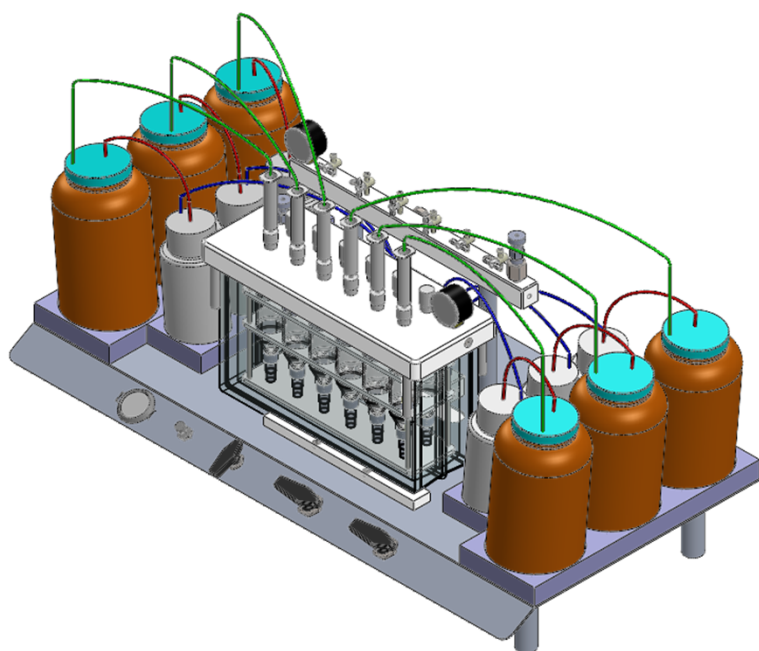
Waste
Valve



Vacuum
Pump

AW

Sample Elution (Stage 2)



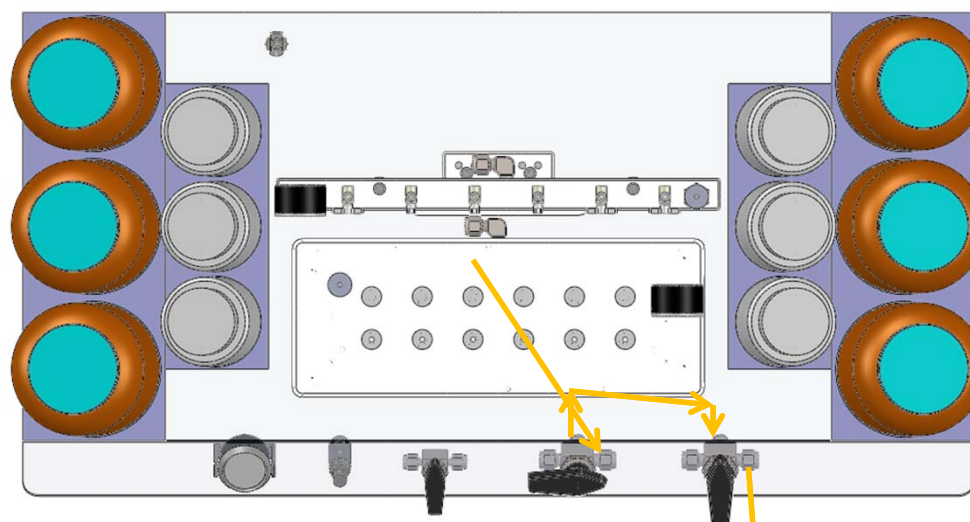
Flow
Path



Nitrogen
Valve

Stage
1/2
Valve

Waste
Valve



Vacuum
Pump

OW

PFAs Methods

- EPA 537.1
- EPA 537 v1.1
- EPA 533
- EPA 8327 with 3512: PFAS in drinking, surface, wastewater 24 compounds; no SPE; mixing 1:1 with solvent and add standards (isotope dilution); filtration; LC/MS/MS
- EPA 8327 also for solids but not specified yet how (method not finalized)



PFAs Methods

- ASTM 7968 is for 21 PFAS mostly sand and soil, solvent extraction and filtration, LC/MS
- ASTM 7979 similar to EPA 8327
- ISO 25101: 2009 this is SPE method with WAX cartridge for non-particulate or low-grade particulate water samples
- DOD QSM 5.3: PFAS in non-drinking water with SPE and isotope dilution, LC/MS/MS



Automated Concentration for PFAs

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



Concentration Functionality

- **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



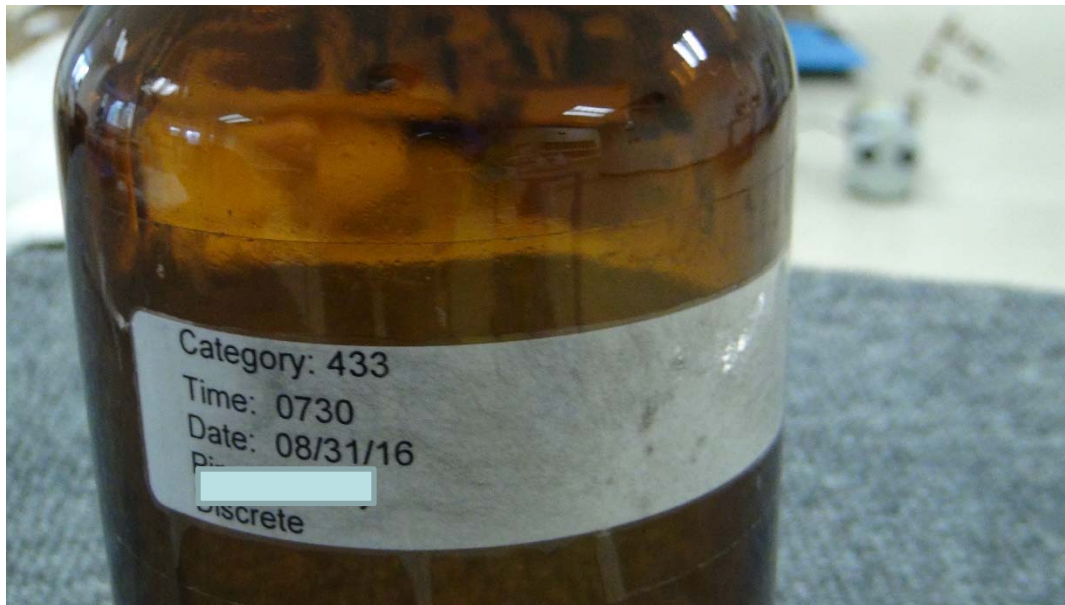
Prepping the 6ml Cartridge with Plastic Filtration Wool

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



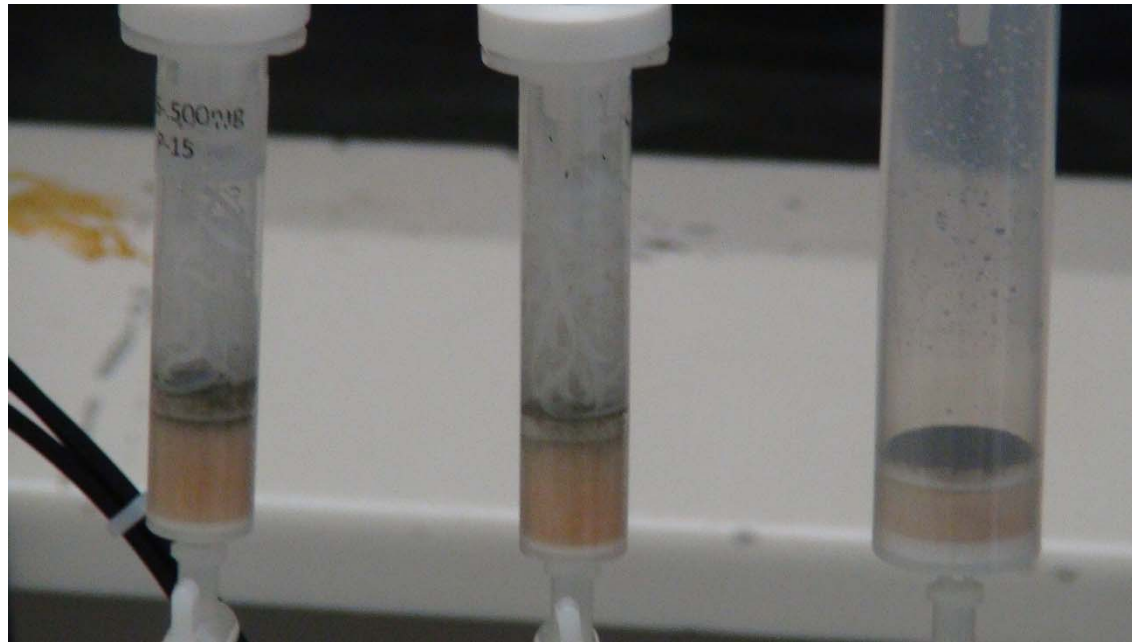


Industrial 433 Matrix 250ml

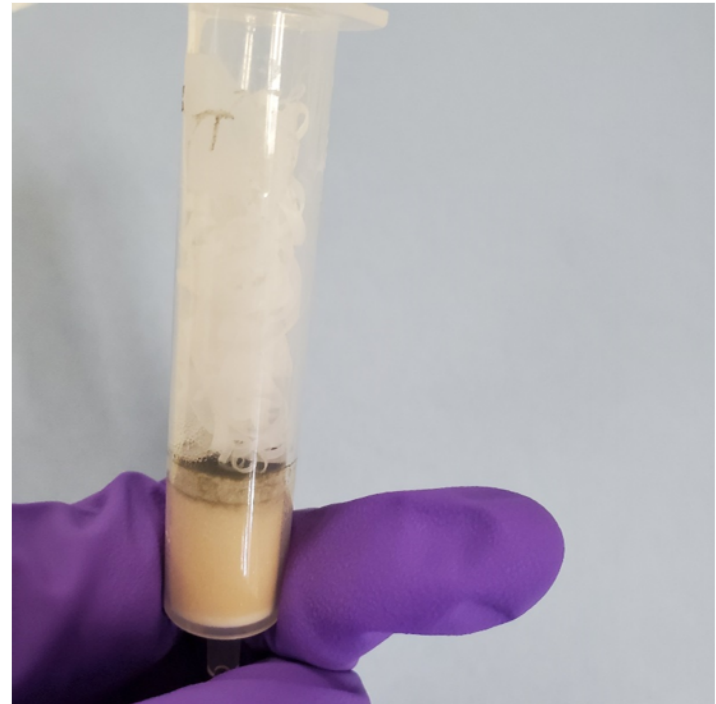
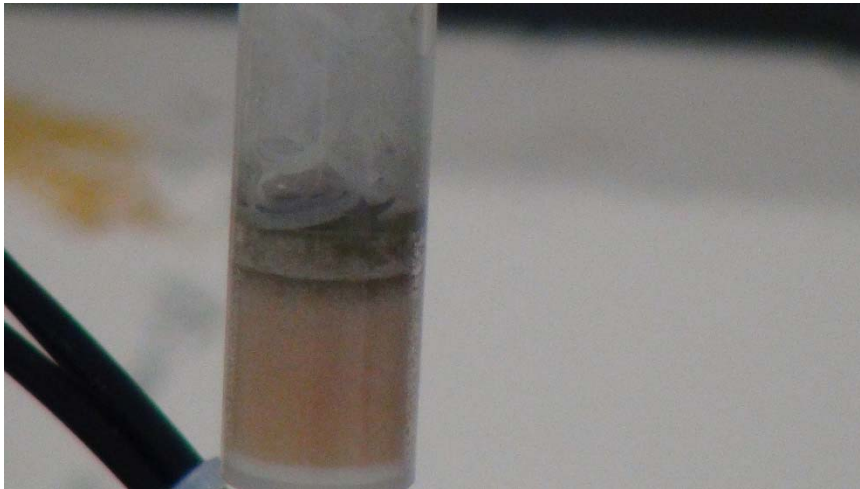




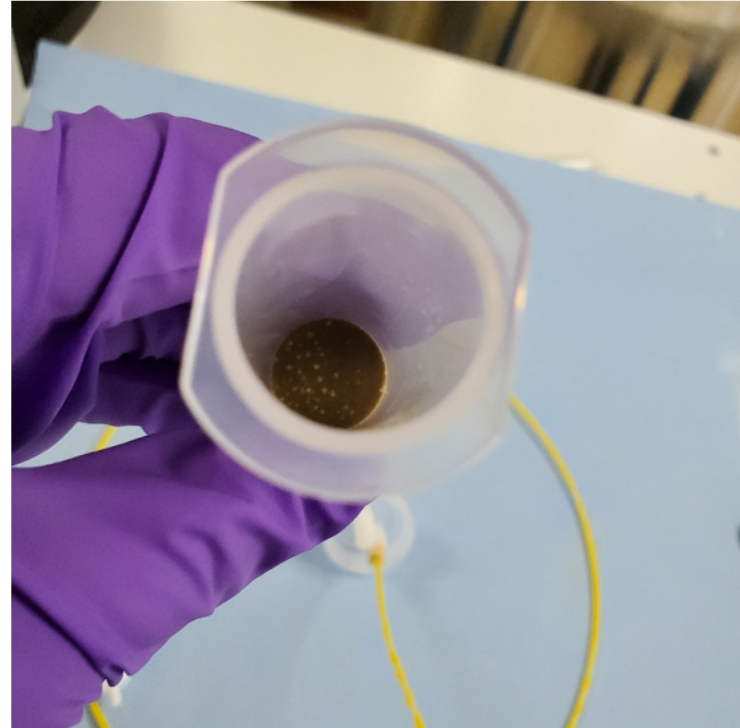
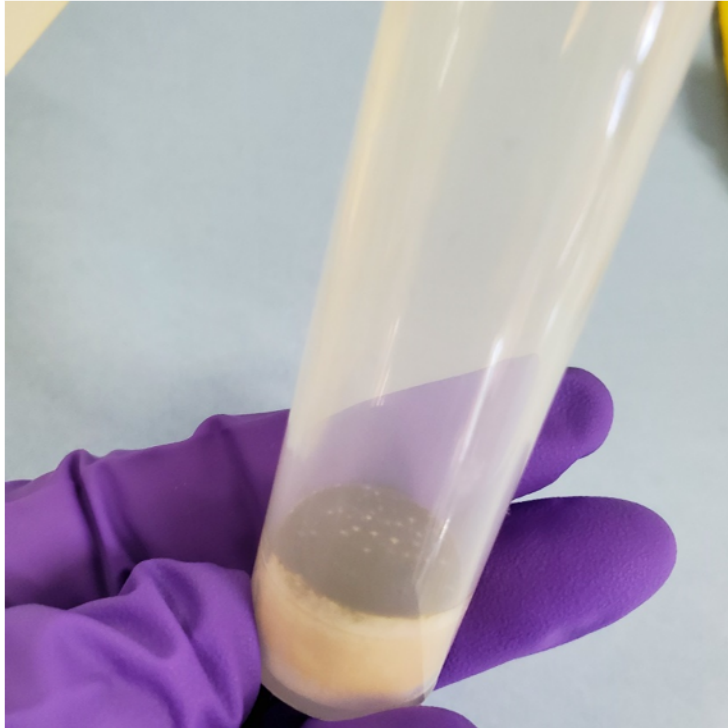
6ml and 25ml Cartridges



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



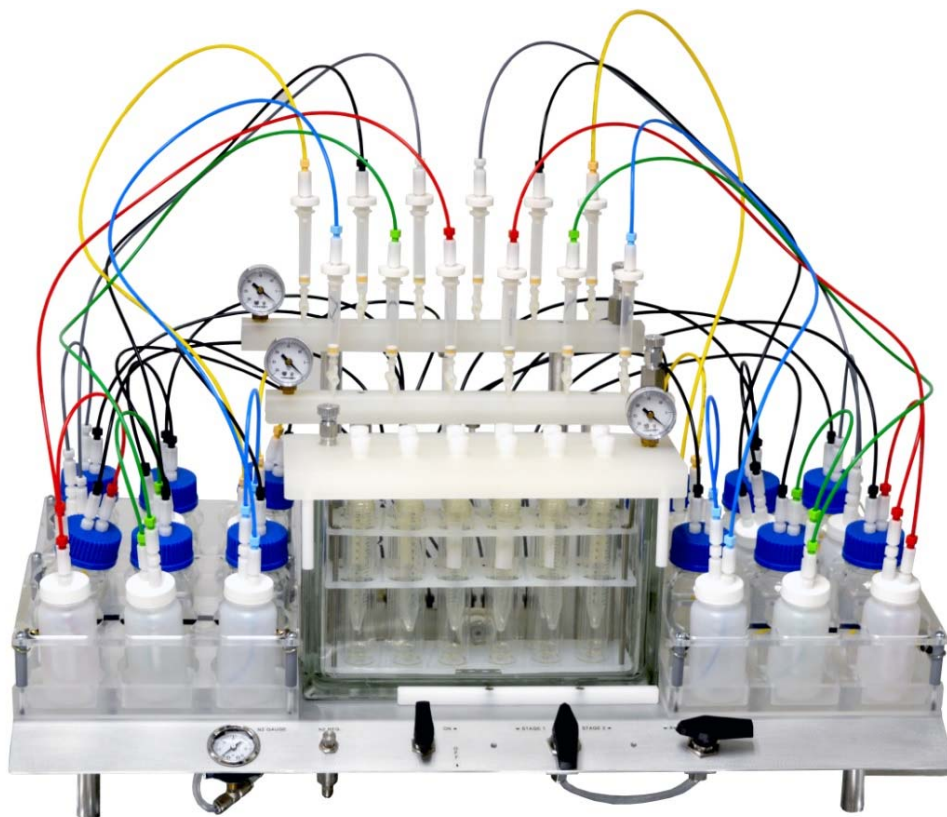
250ml run to completion 25ml cartridge



Clean up is easy with no cross contamination

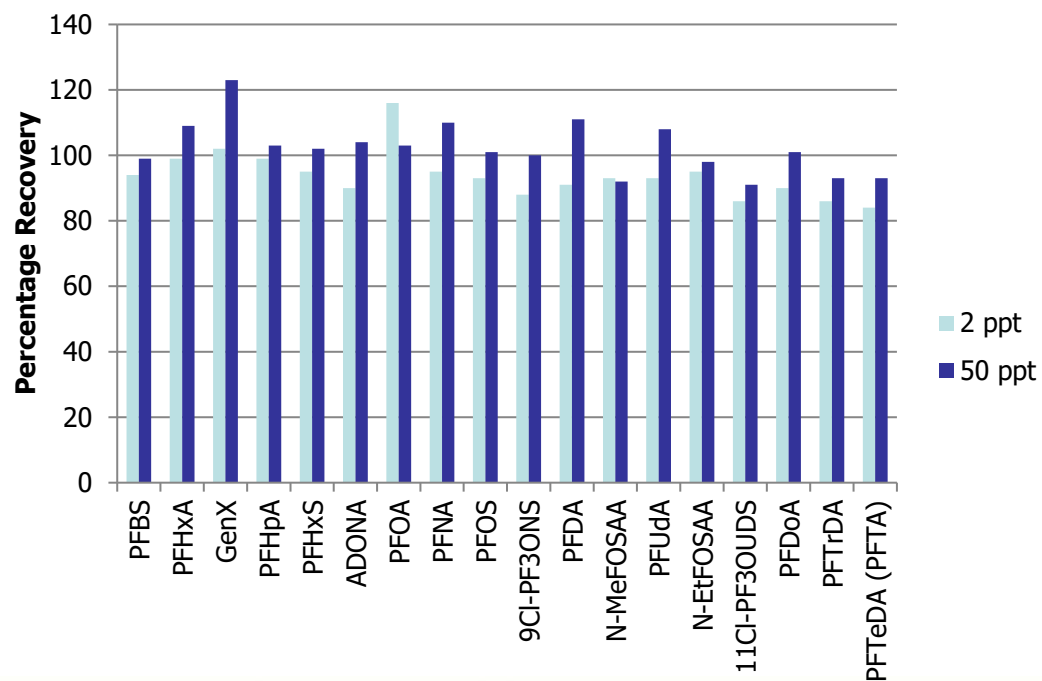
- Back Flush the sample line into the original sample bottle with an IPA non-Teflon squirt bottle.
- Wash the inside of the bottle cap with IPA squirt bottle
- Wash Cartridge Adapters with IPA squirt bottle or sonicate in a beaker
- Ready for the next 12 samples



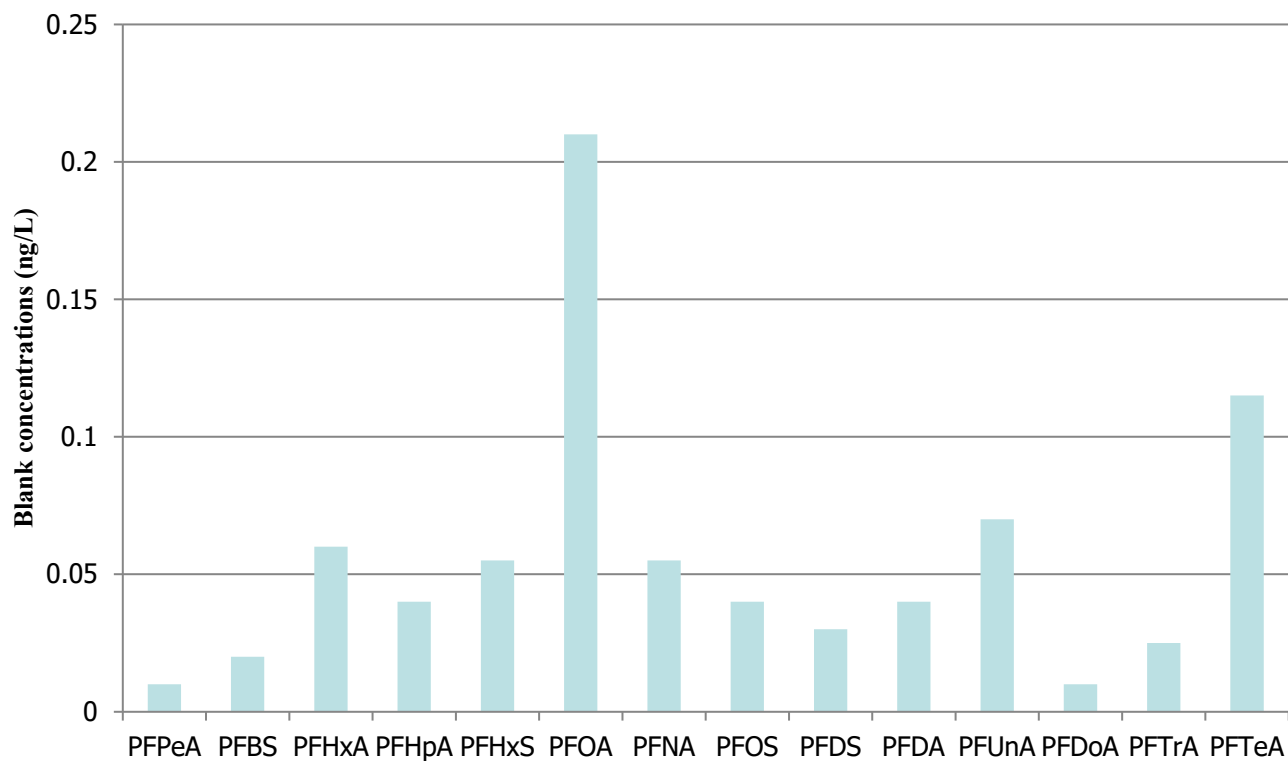


EZPFC 12 Sample System

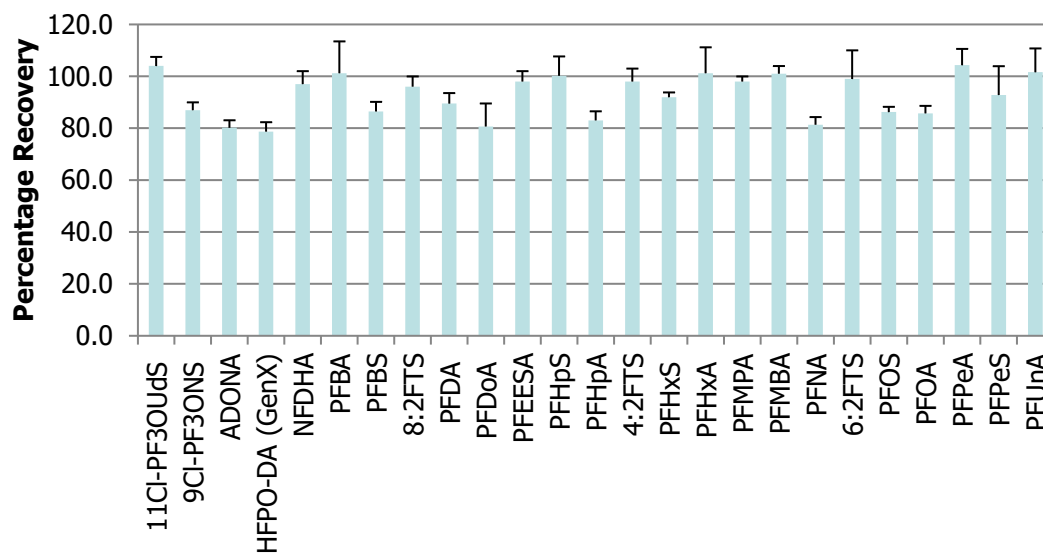
EPA 537.1



PFAS Background



EPA 533



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

- **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

- **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**



Questions?

