

# **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



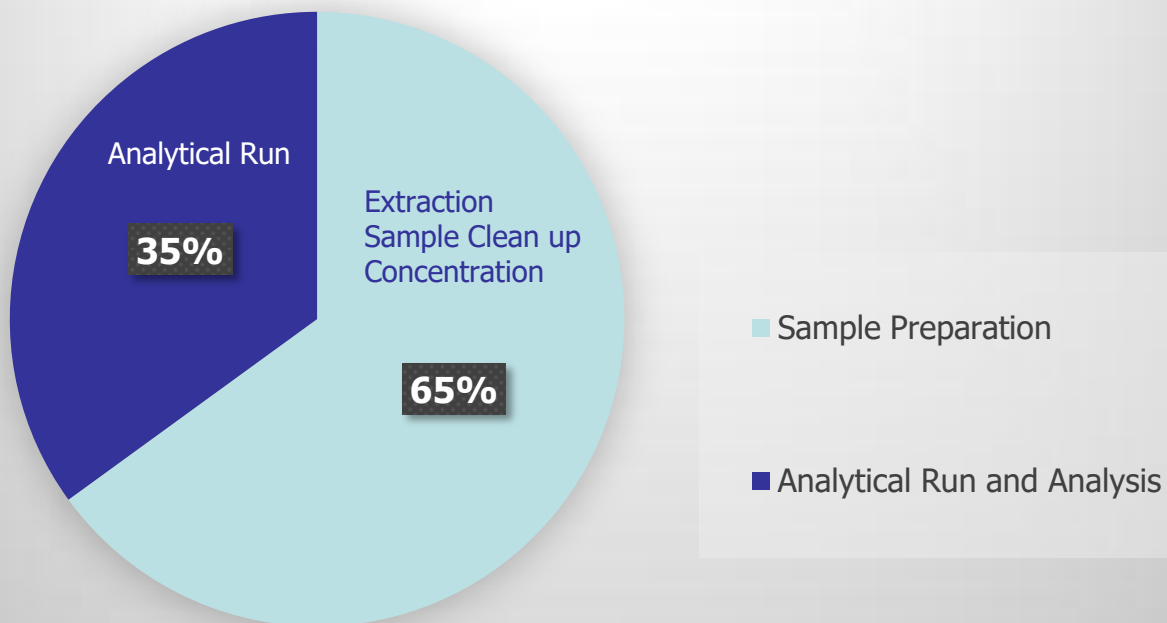
# Optimizing the PFC Analysis Workflow

- **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

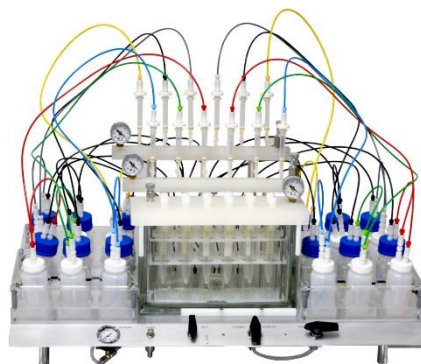
- SuperVap PFC
  - 24 positions
  - 15ml Conical vials



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



**EZSPE**



**EZPFC**



# Sample Analysis Work Flow

## Automated Sample Prep Time

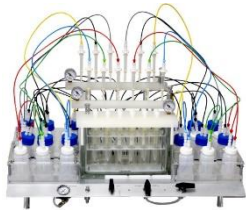
**= 80 Minutes**



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



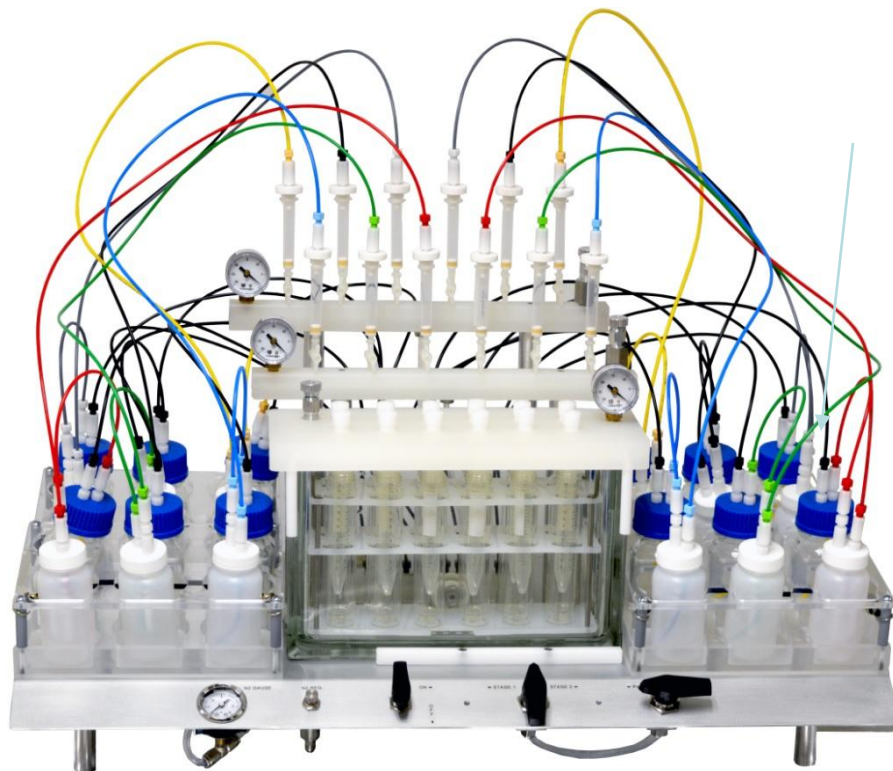
# Goal

- **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



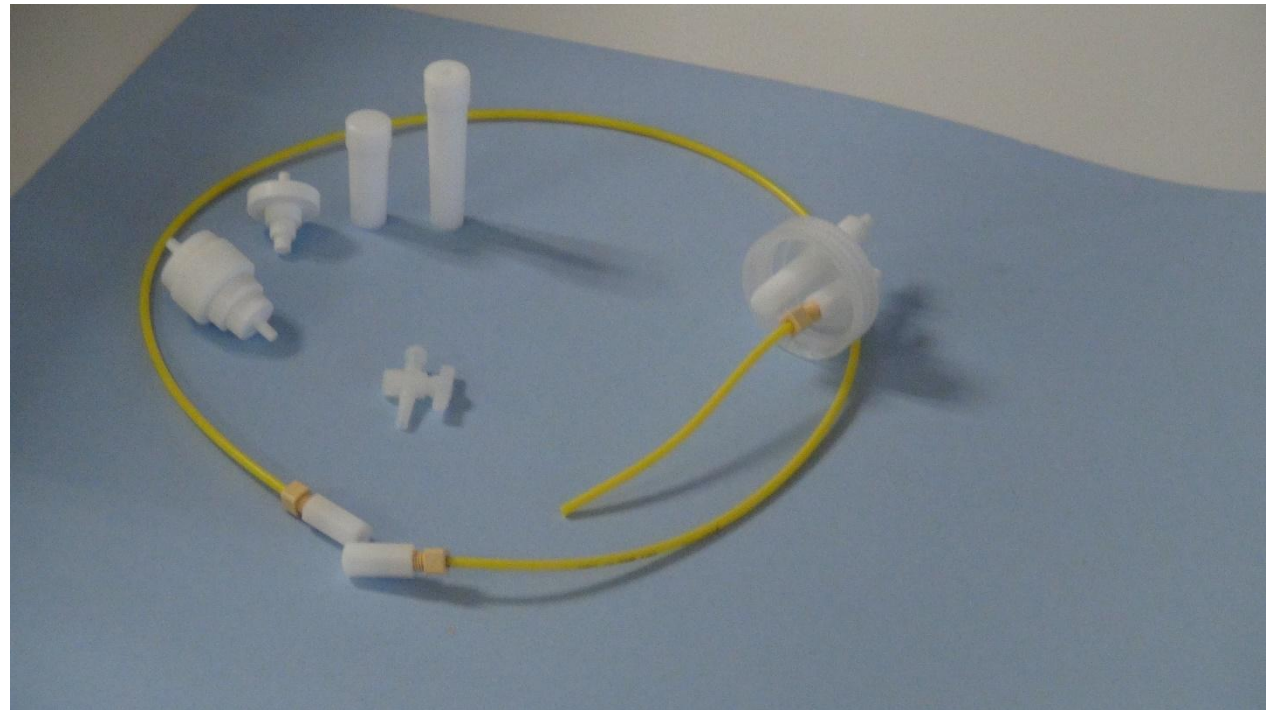
# System Components

**No Teflon**

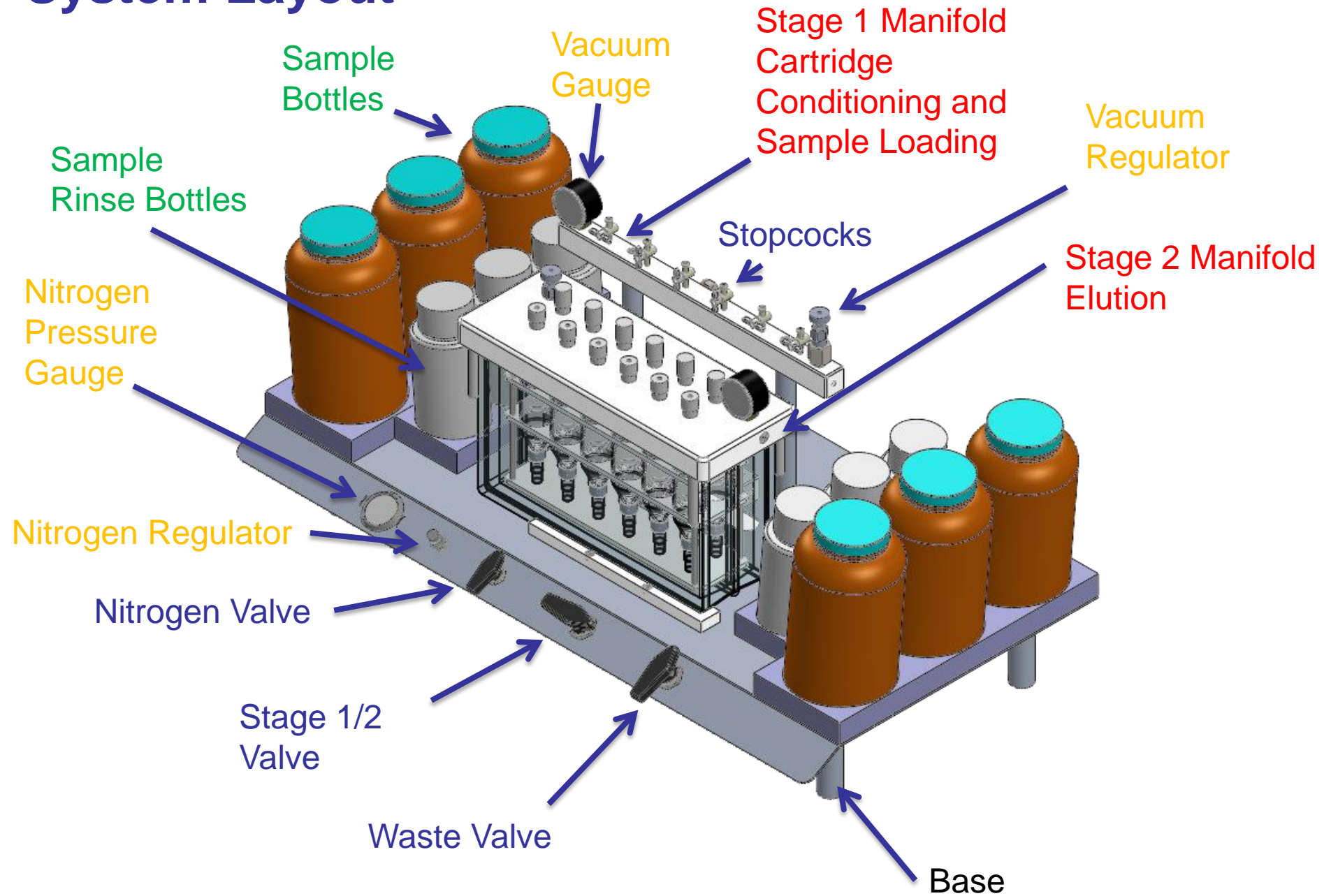
**Tubing - High Density  
Polyethylene**

**Fittings – Delrin**

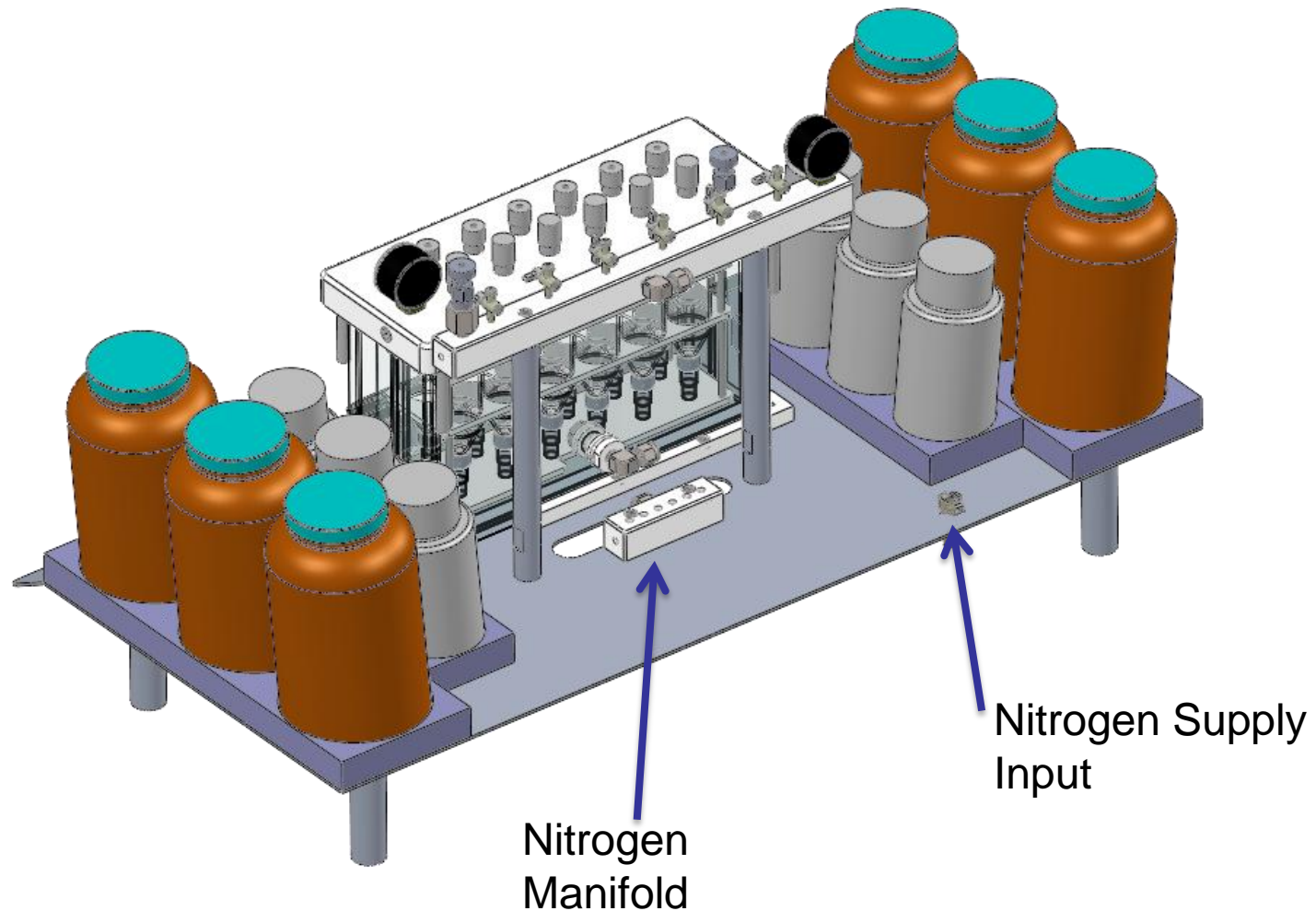
**Cartridge Adapters –  
Medical Grade  
Polypropylene**



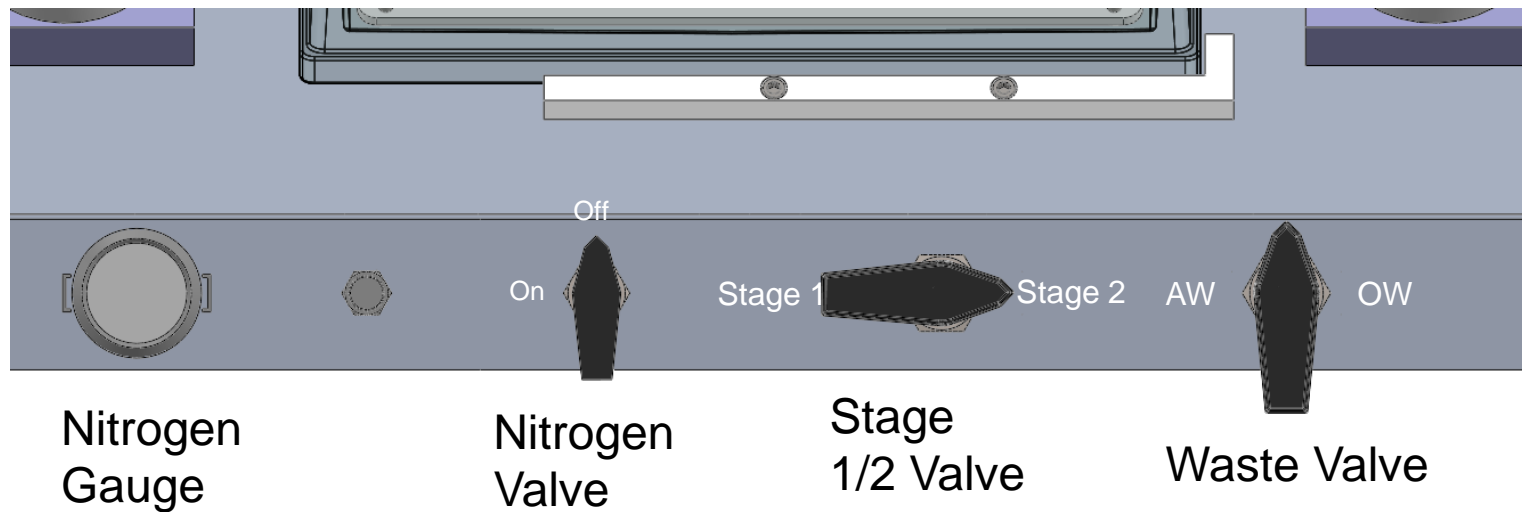
# System Layout



# Nitrogen for Bottle Rinse and Cartridge Drying

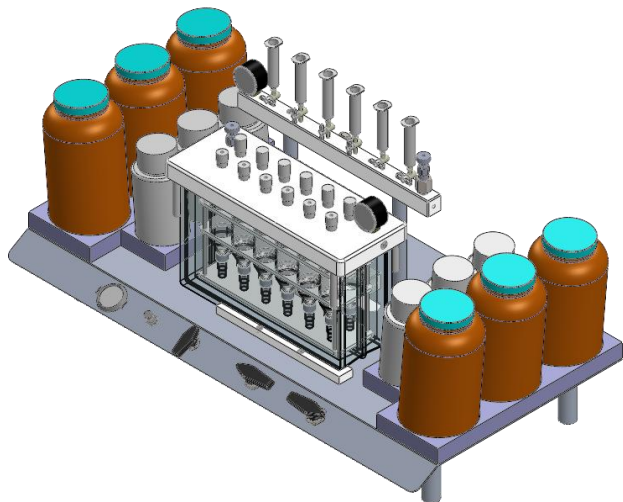


# Control Valve Layout



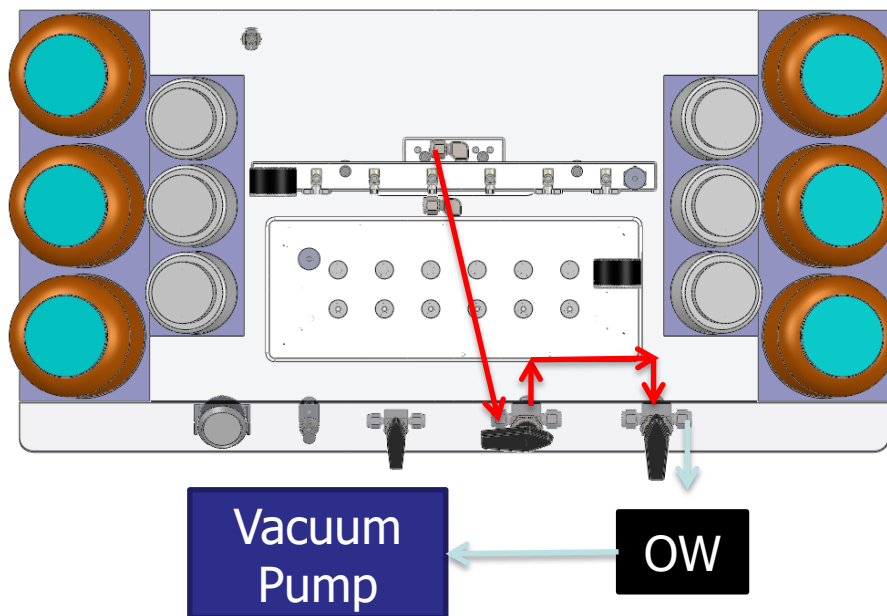
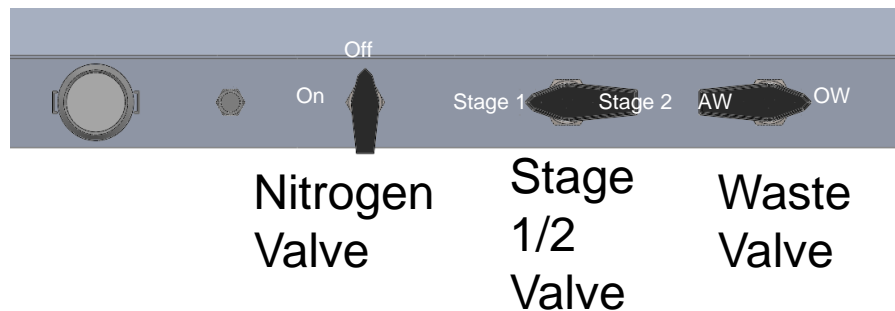


# Cartridge Conditioning (Stage 1, Organic Waste)

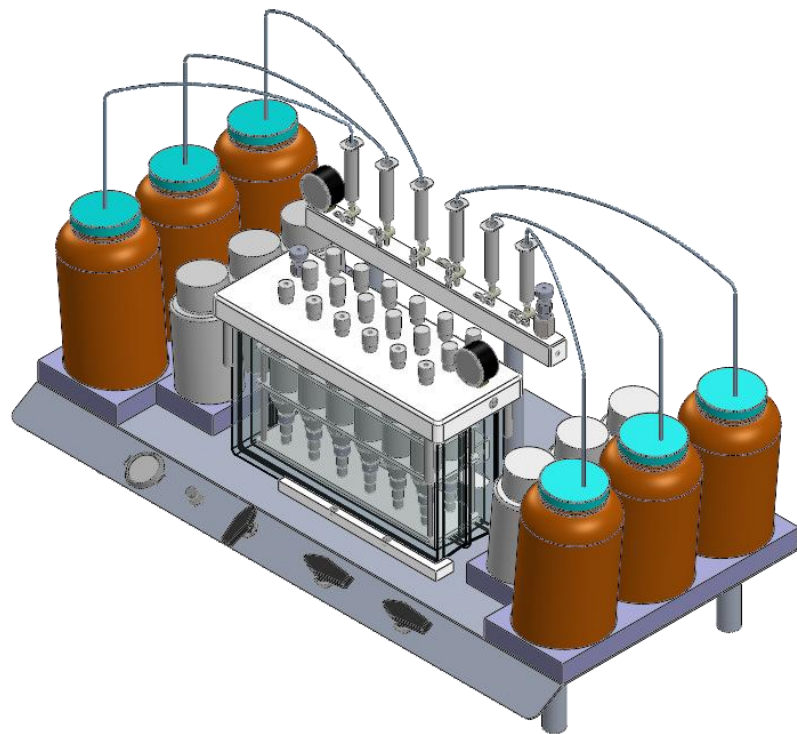


Flow  
Path

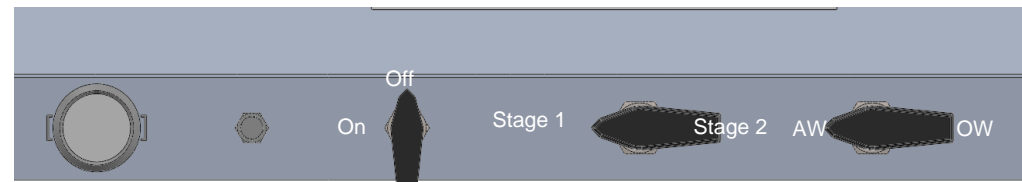
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# Sample Loading (Stage 1, Aqueous Waste)



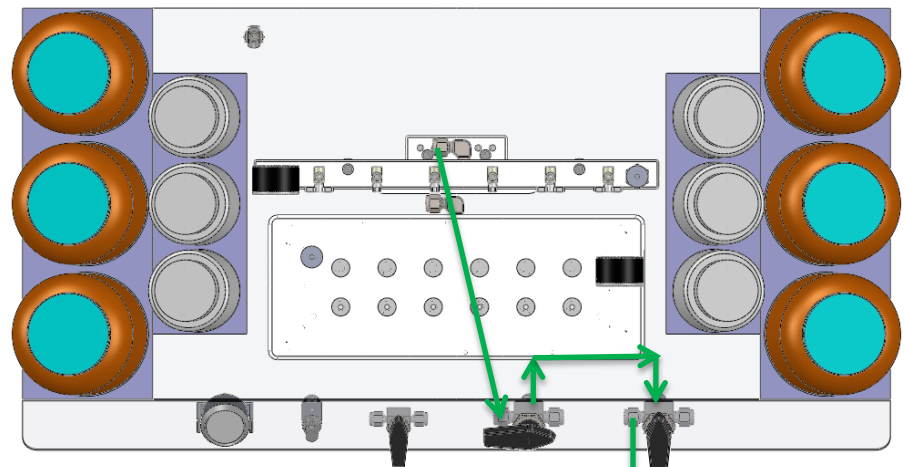
Flow  
Path



Nitrogen  
Valve

Stage  
1/2  
Valve

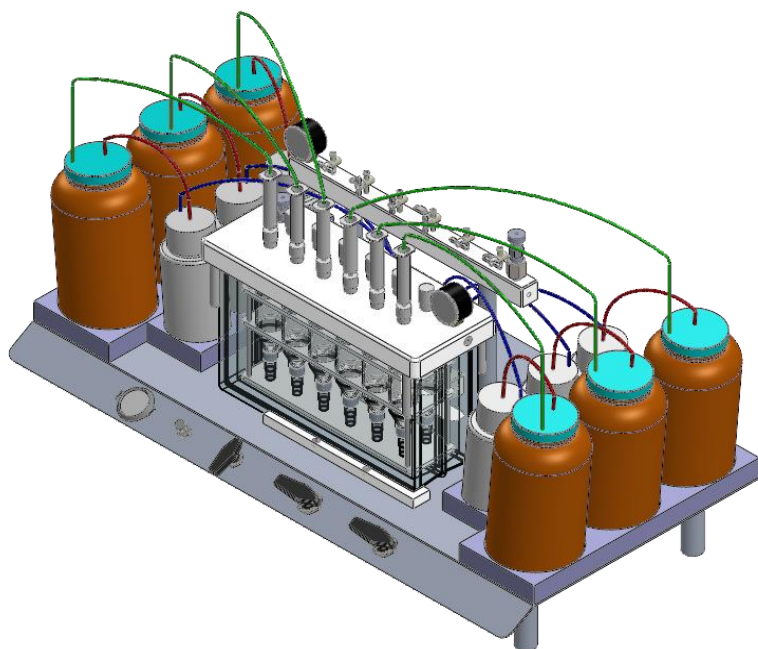
Waste  
Valve



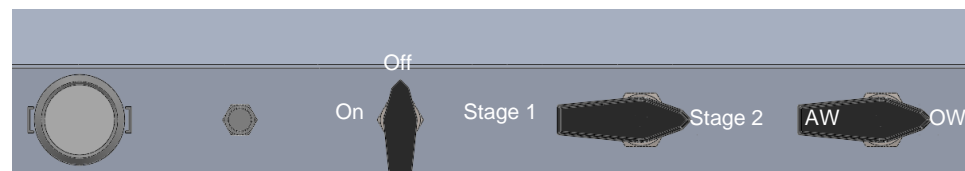
Vacuum  
Pump

AW

# Sample Bottle Rinse (Stage 1)



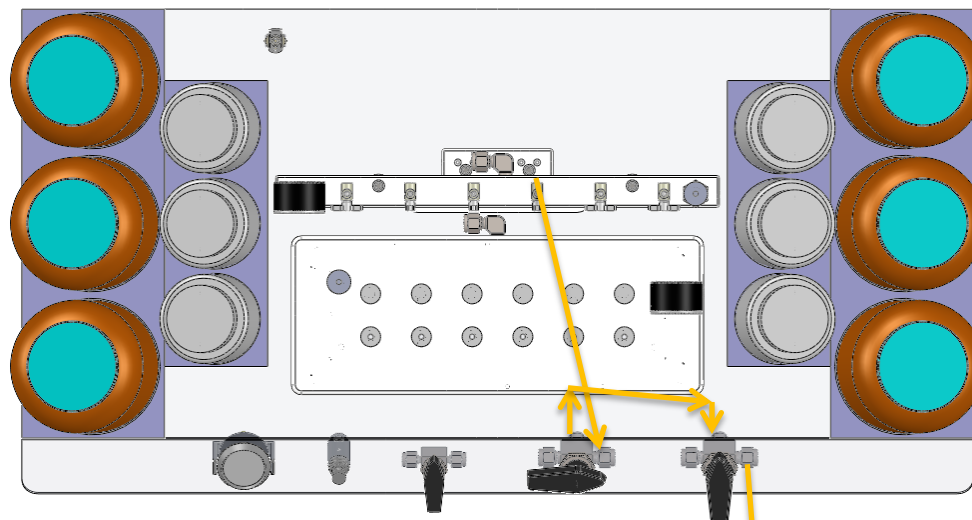
Flow  
Path



Nitrogen  
Valve

Stage  
1/2  
Valve

Waste  
Valve

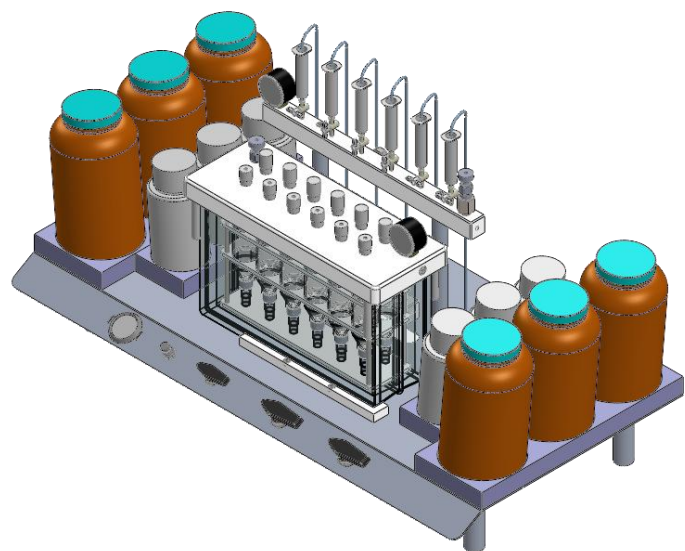


Vacuum  
Pump

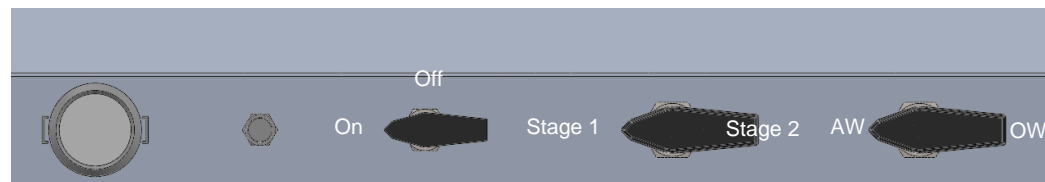
OW



# Cartridge Drying- Nitrogen/Vacuum



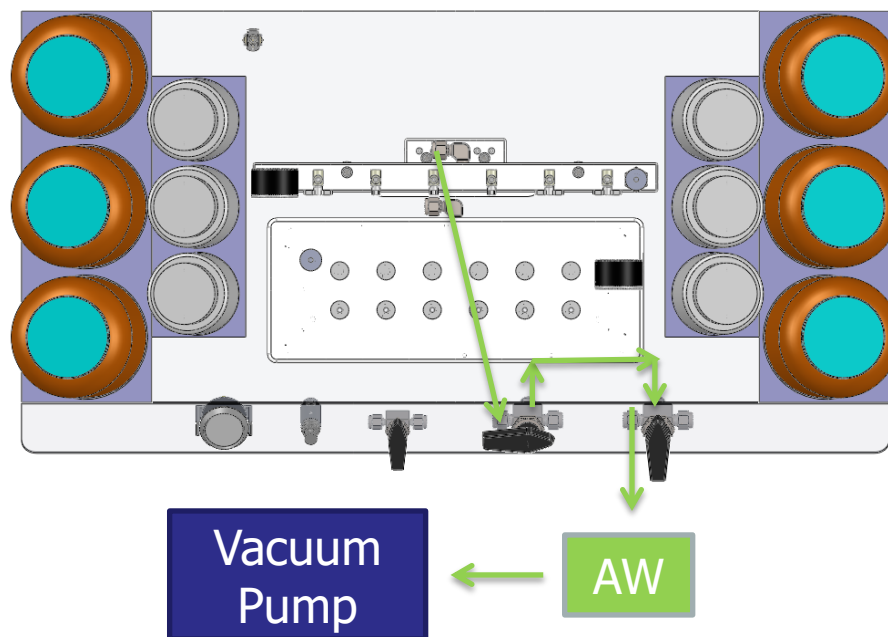
Flow  
Path



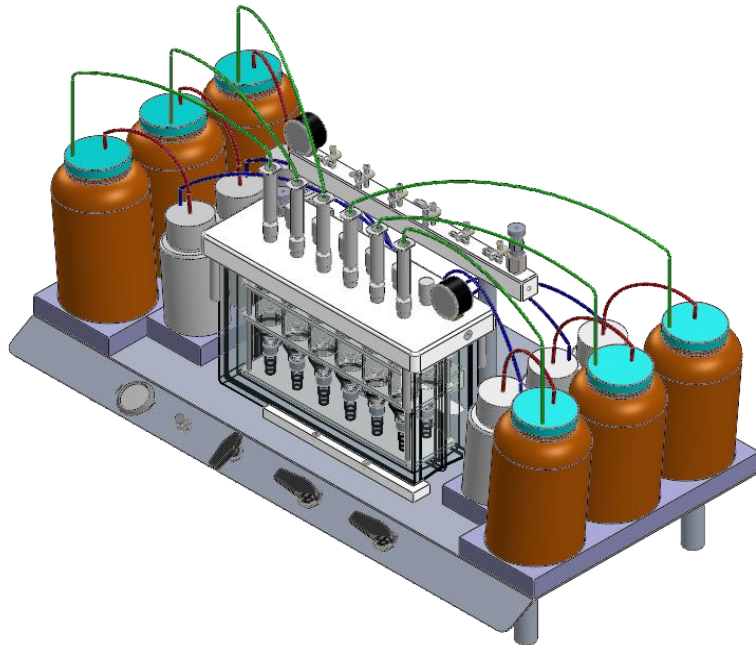
Nitrogen  
Valve

Stage  
1/2  
Valve

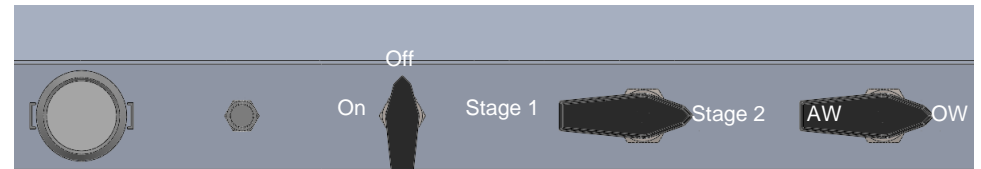
Waste  
Valve



# Sample Elution (Stage 2 )



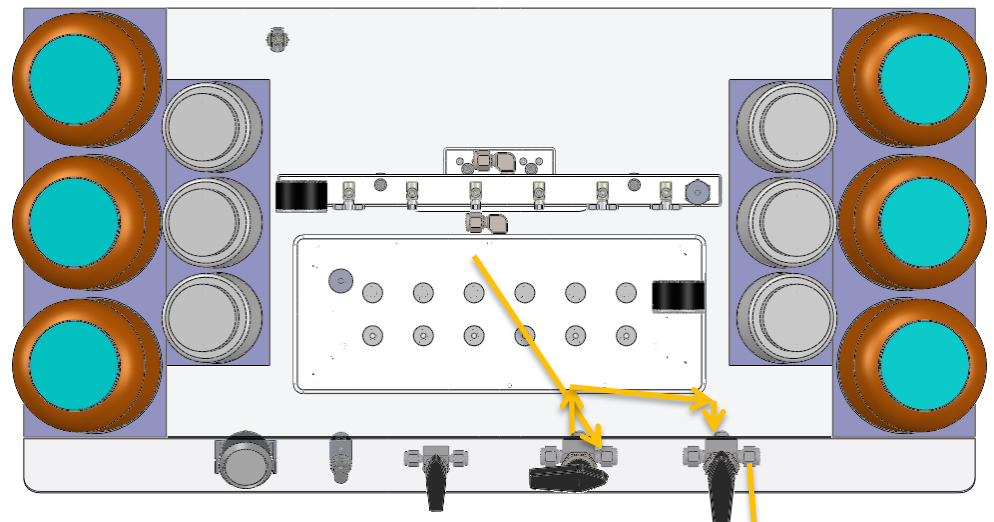
Flow  
Path



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





## **Delrin Plastic Wool**

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



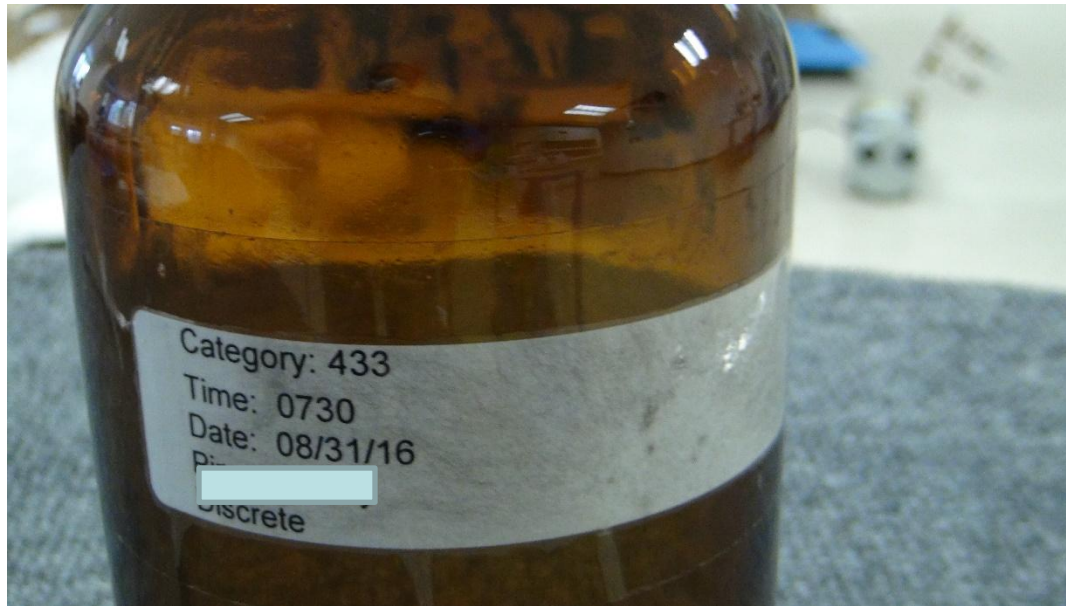
# Prepping the 6ml Cartridge with Plastic Filtration Wool

## 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

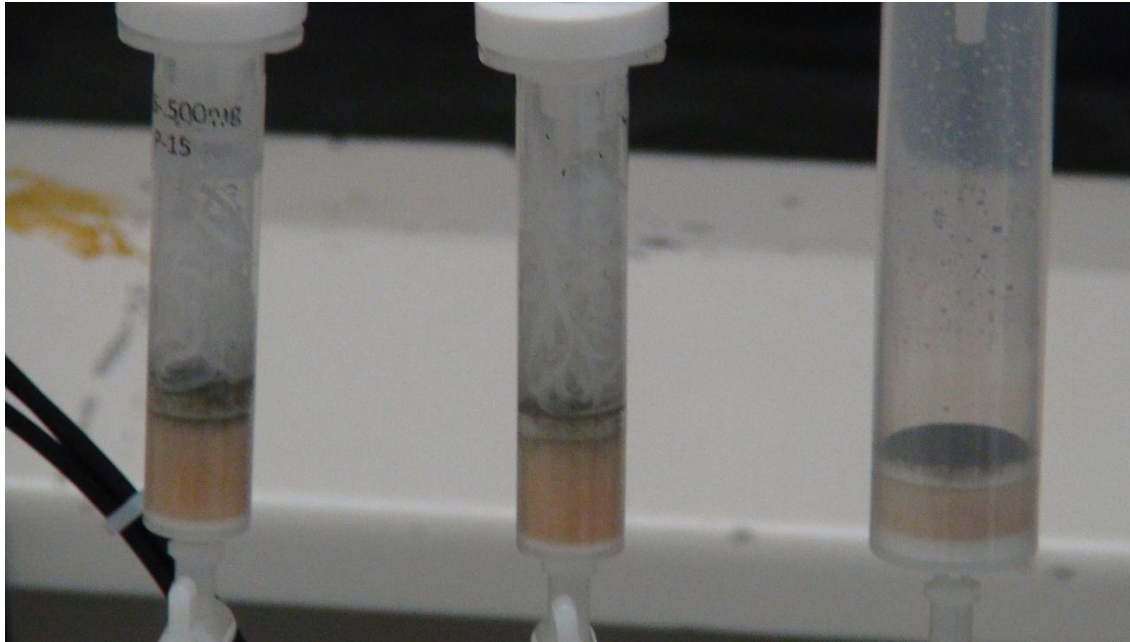




# Industrial 433 Matrix 250ml

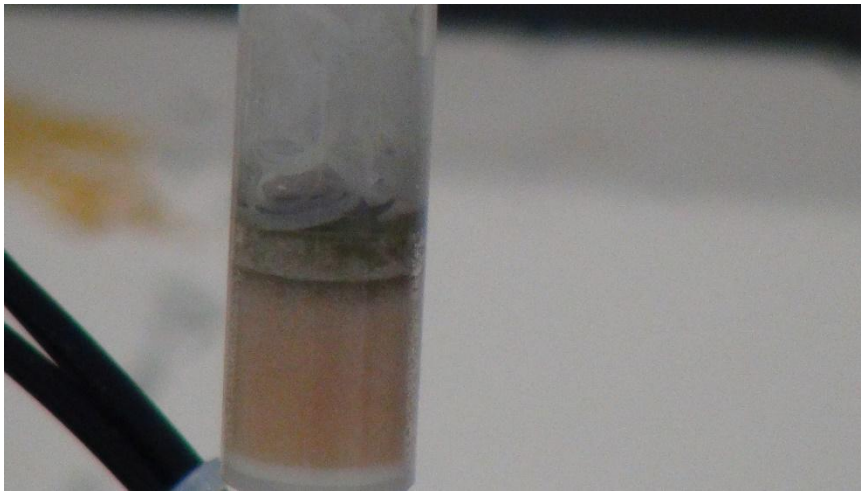


# 6ml and 25ml Cartridges

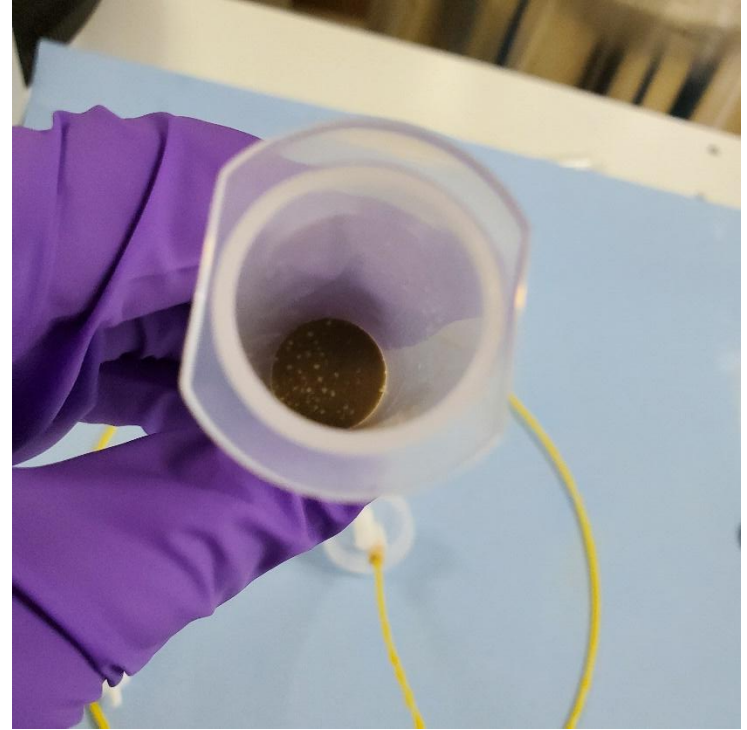
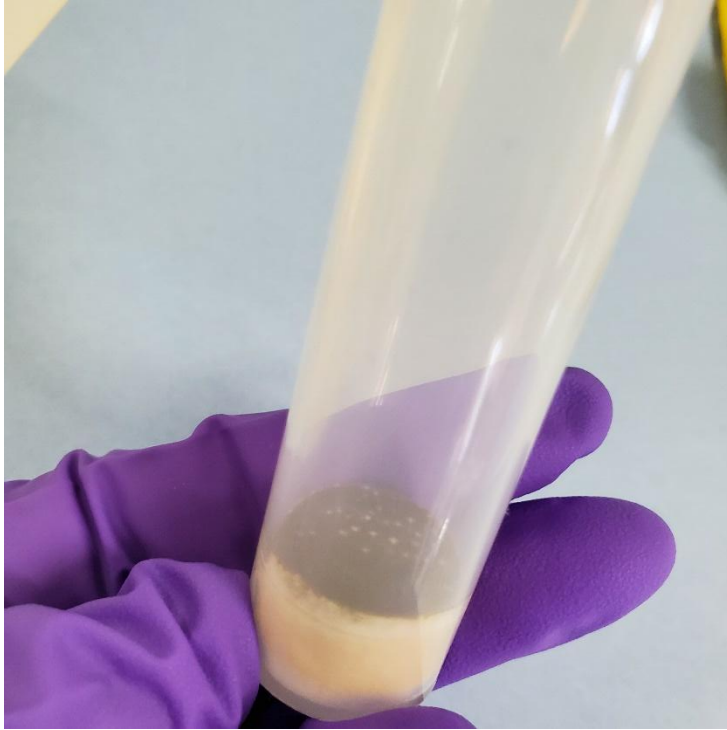




# 250 ml run to completion on 6 ml cartridge with Plastic Wool



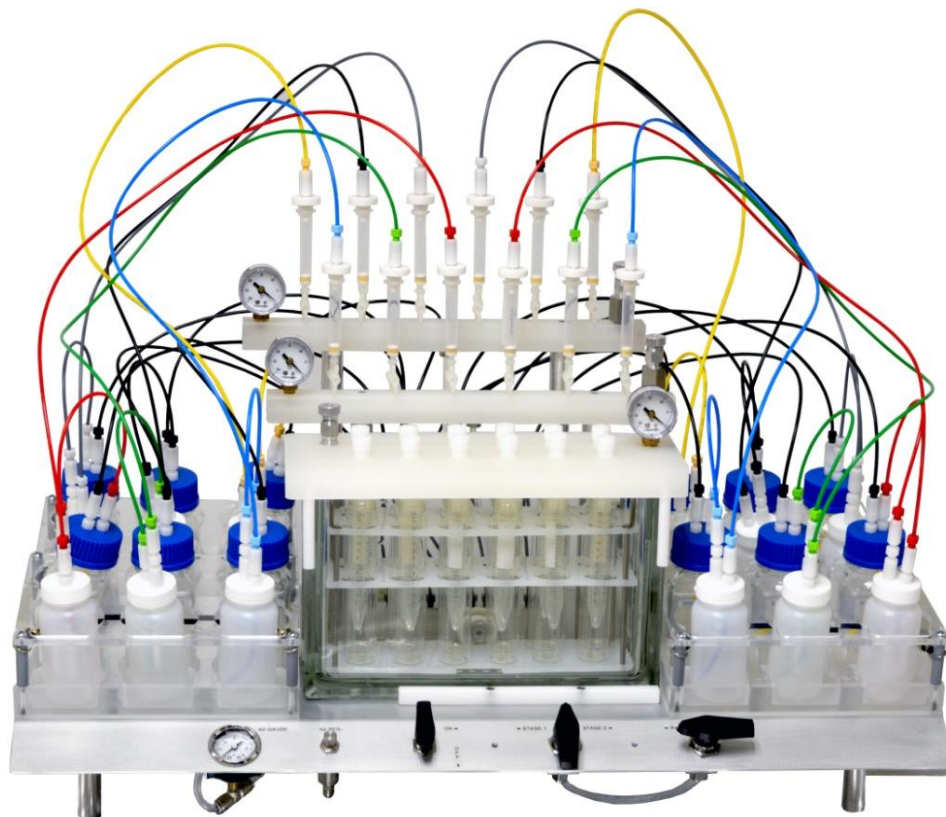
# 250ml run to completion 25ml cartridge



# 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

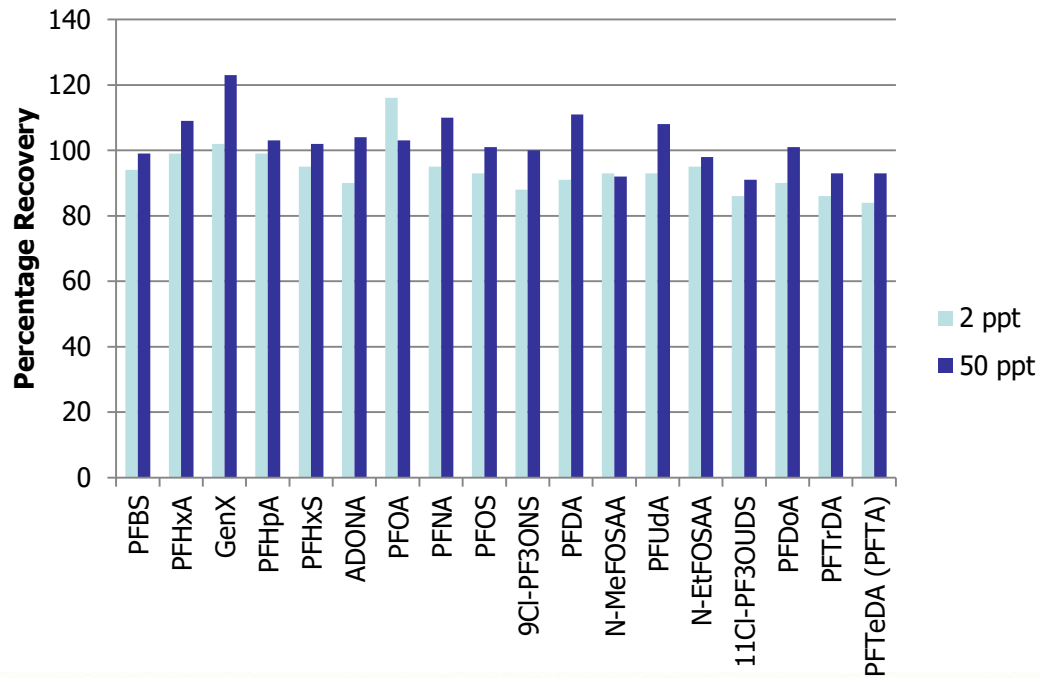
# EZPFC®



EZPFC 12 Sample System

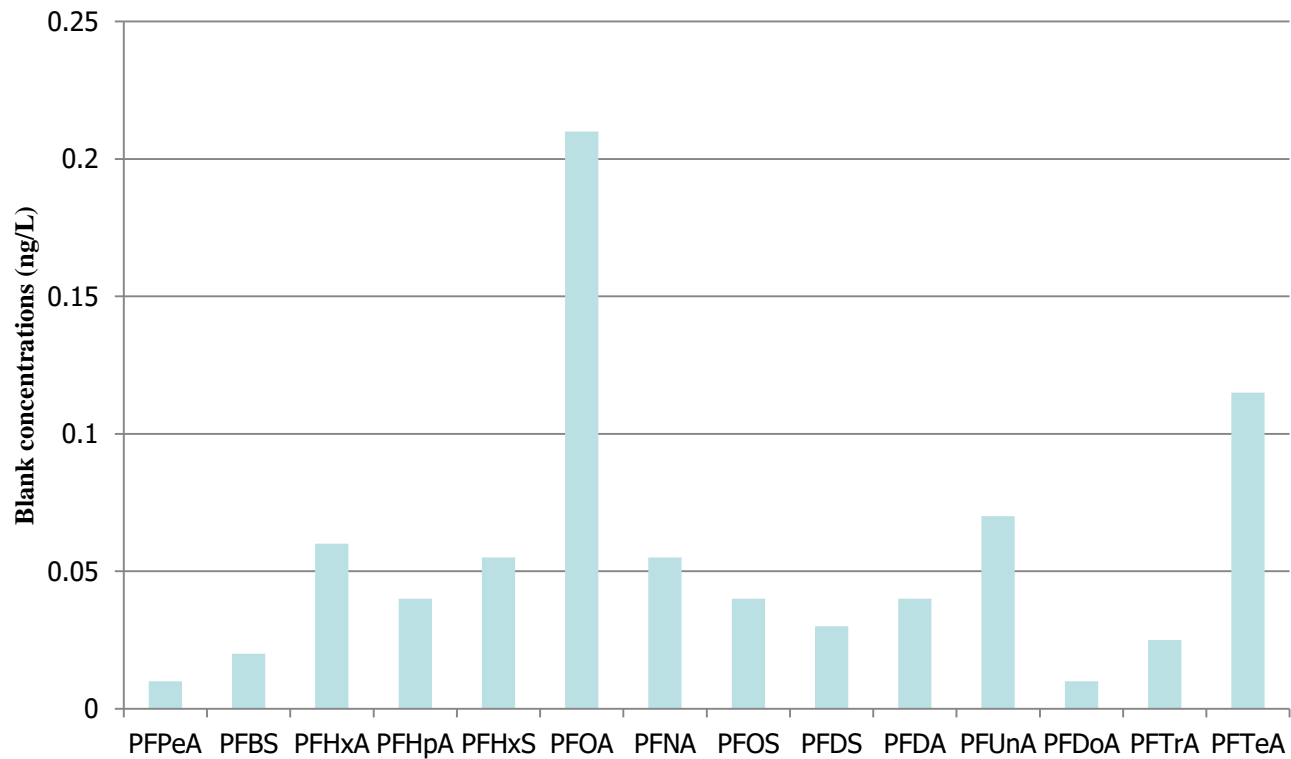


# EPA 537.1

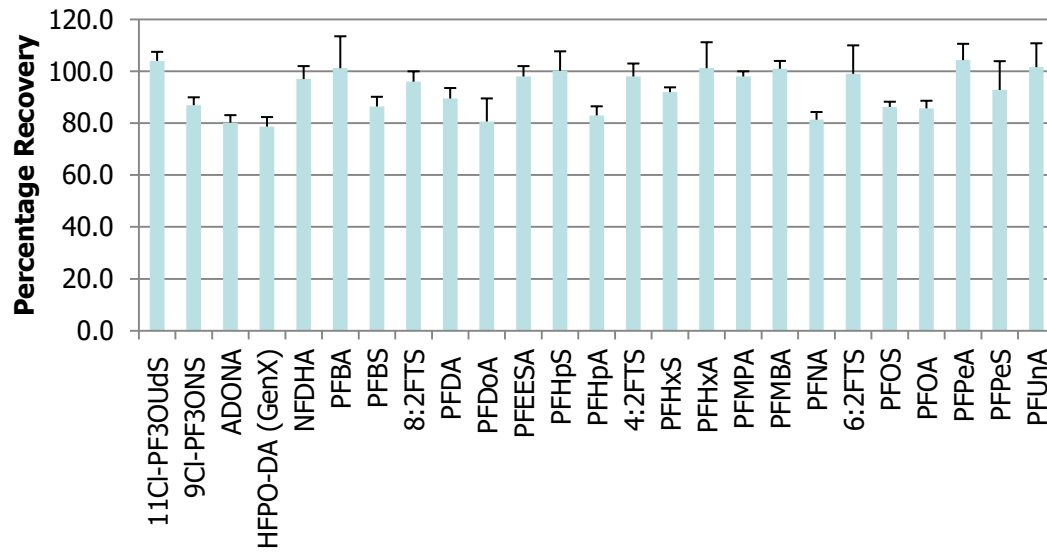




# PFAS Background



# 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?

