Automated Solid Phase Extraction of 40 native PFAS Compounds in Wastewater Using Vacuum and Positive Pressure

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Purpose

- Sample Preparation Workflows and tools for EPA method 1633 (draft)
- Comparison of Automated and Semi-Automated Solid Phase Extraction for PFAS applications
- EPA Method 1633 applications

Target Analytes

Method	533	537.1	1633	ISO21675
PFBA	x		x	x
PFPeA	x		x	x
PFHxA	x	x	x	x
PFHpA	x	x	x	x
PFOA	x	x	x	x
PFNA	x	x	x	x
PFDA	x	x	x	x
PFUnA	x	x	x	x
PFDoA	x	x	x	x
PFTrDA		x	x	x
PFTeDA		x	x	x
PFBS	x	x	x	x
PFPeS	x		x	
PFHxS	x	x	x	x

Target Analytes

Method	533	537.1	1633	ISO21675
PFHpS	x		x	x
PFOS	x	x	x	x
PFNS			x	
PFDS			x	x
PFDoS			x	
4:2FTS	x		x	
6:2FTS	x		x	x
8:2FTS	x		x	x
PFOSA			x	x
NMeFOSA			x	x
NEtFOSA			x	x
NMeFOSAA		x	x	x
NEtFOSAA		x	x	x
NMeFOSE			x	

Target Analytes

Method	533	537.1	1633	ISO21675
NEtFOSE			x	
HFPO-DA	x	x	x	x
ADONA	x	x	x	x
PFMPA	x		x	
PFMBA	x		x	
NFDHA	x		x	
9Cl-PF3ONS	x	x	x	x
11Cl-PF3OUdS	x	x	x	
PFEESA	x		x	
3:3 FTCA			x	
5:3 FTCA			x	
7:3 FTCA			x	
PFOcDA				x
PFHxDA				x
8:2 FTUCA				x
8:2 diPAP				x

Optimizing the PFAS 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 and background**
  - **Reduces Solvent Usage**
  - **Reduces Labor**

- **Use SPE solutions to deliver consistent, reproducible results**
- **Different configurations to handle Matrix type and Budget**
- **No Teflon Components**

Comparison of Manual SPE vs. Automated SPE Methods

Manual SPE	Automated/Semi-Auto SPE
Manually Separate Waste	Separates Aqueous and Organic Waste
<10 mls solvent evaporate	<10 mls solvent to evaporate
Run times are ~ 30 to 90 minutes	Run times are ~20 to 50 minutes or less
Technician Time 25 minutes	Technician time 5 minutes
Physical transfer and Concentration steps	Automatic and Direct to Concentration delivery and completion
Concentration steps 70 to 200 minutes	Concentration step 70 minutes ready for injection

Determining Factors

- **Closed System**
- **Ability to load samples by vacuum or positive pressure consistently.**
- **Handle difficult Matrices**
- **Ability to dry cartridges by vacuum and positive Nitrogen gas pressure.**
- **Easily handle various cartridge designs and sizes without cumbersome modifications.**
- **Easy, Simple Sample delivery**
- **Bottle Rinse**

Automated Solid Phase Extraction front end for LC/MS

EconoTrace® PFC

TurboTrace® PFC

TurboTrace®
Parallel
Sequential

LC/MS

Can this Handle Dirty Samples?

Typical Cartridge can have problems!

- **6ml cartridge**
  - **Doesn't do well**
  - **Frit Surface Area is to small**

Yes, A Cartridge will work

- **25ml cartridge**
  - **Does well**
  - **3X the Frit Surface Area**

FMS, Inc. Plastic Filtration Wool

Glass/Plastic Wool

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

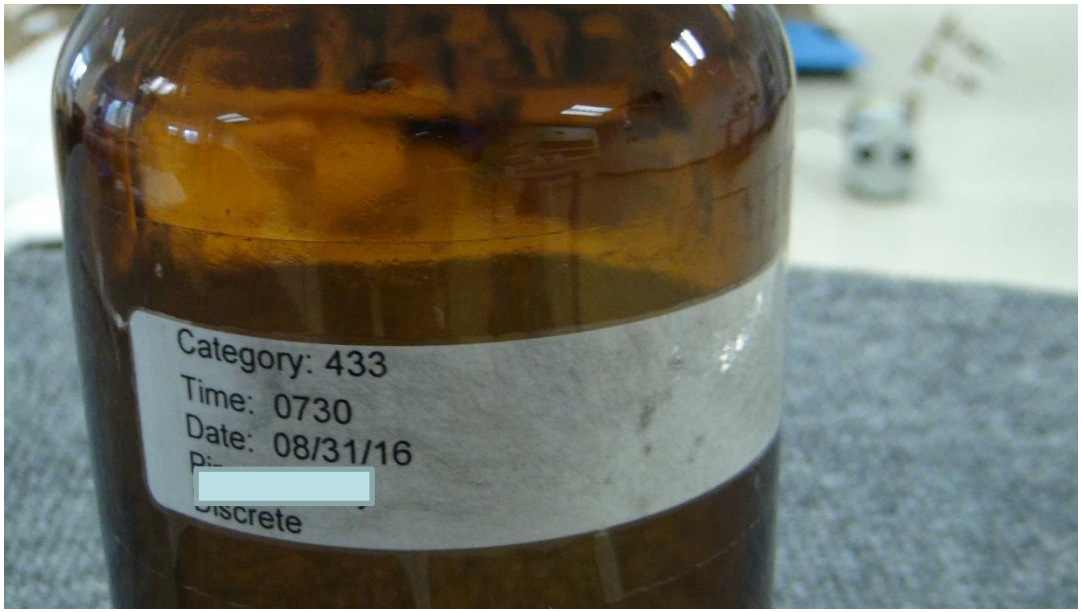
Prepping the 6ml Cartridge with Plastic Filtration Wool

6ml cartridge with Plastic wool

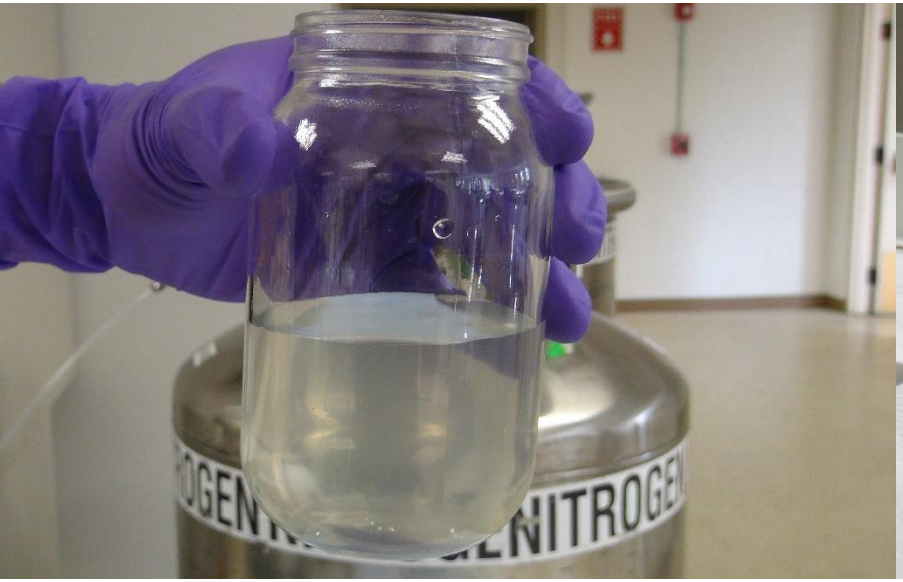
- Take a little and push it into the barrel of the syringe until it touches the cartridge Frit

- The Sample will not clog, it will take longer to process

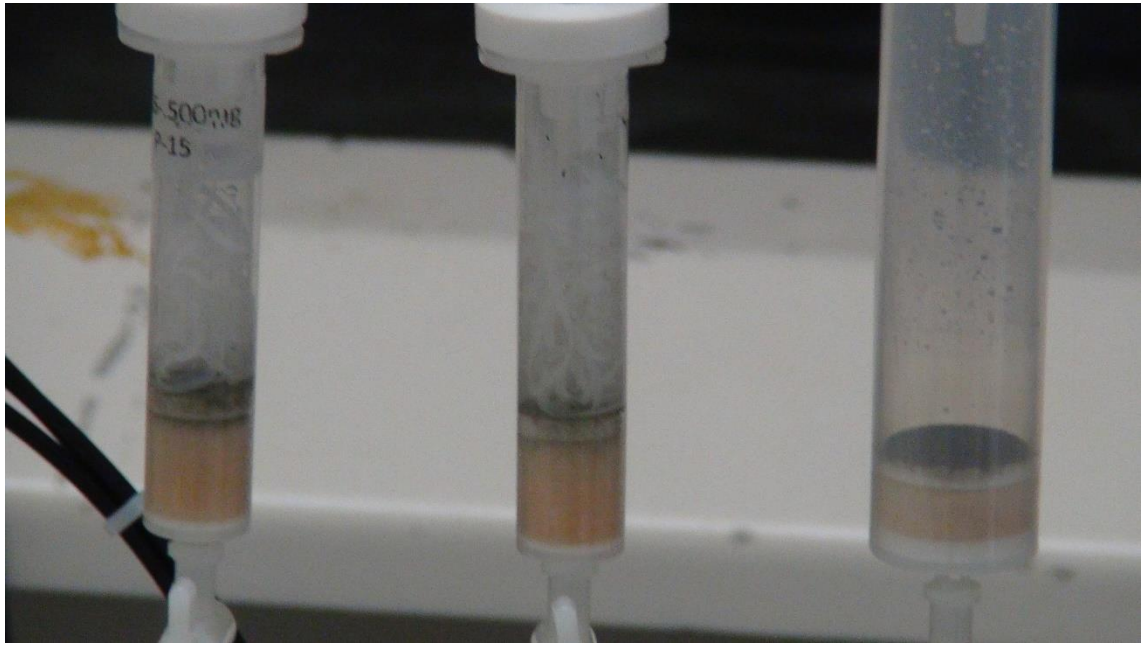
Dirty Sample from a Customer



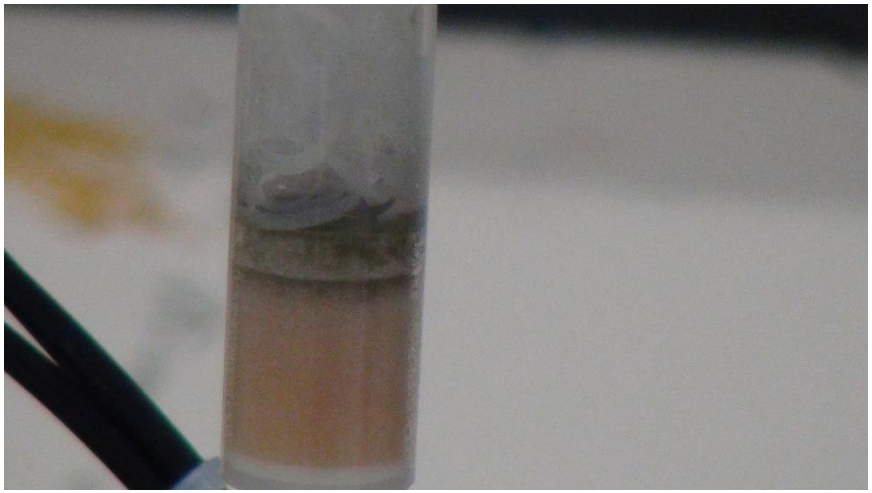
Industrial 433 Matrix 250ml

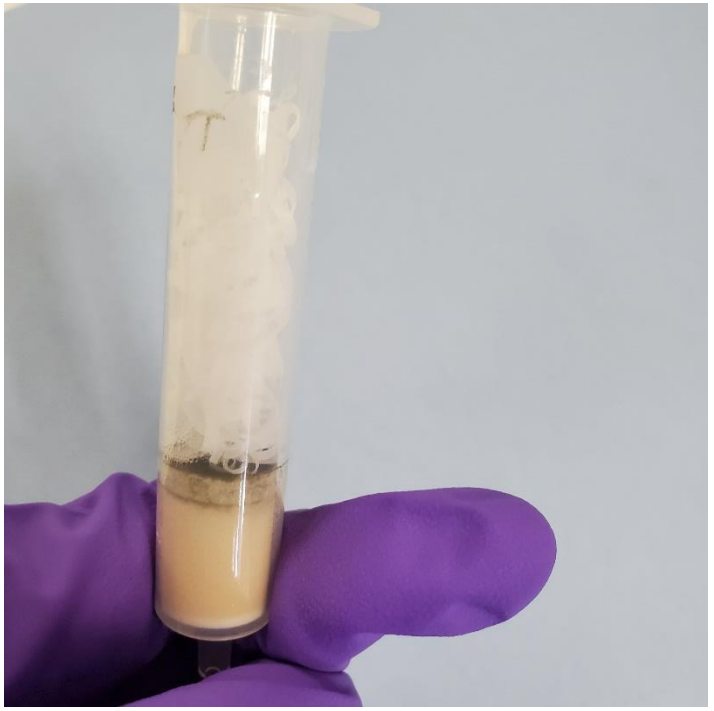


6ml and 25ml Cartridges

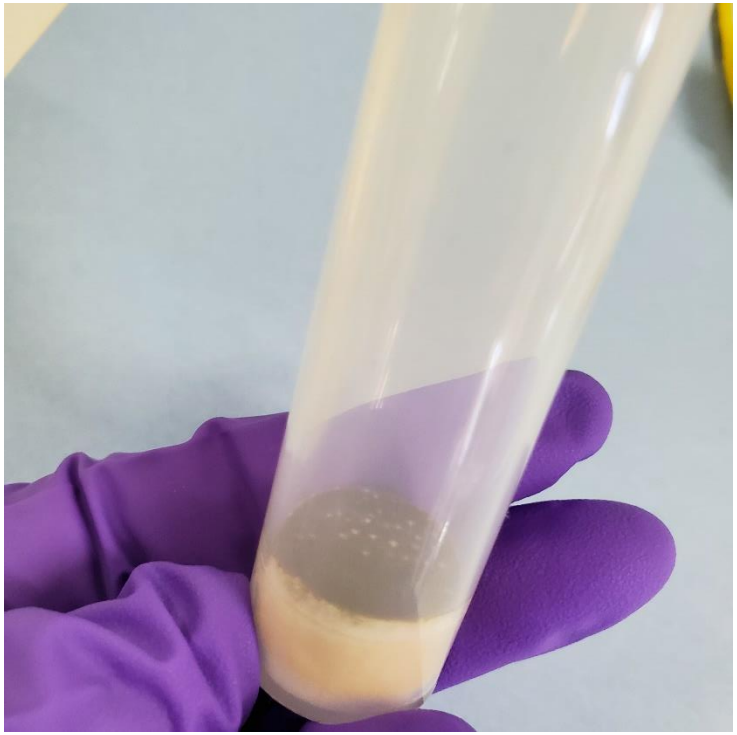


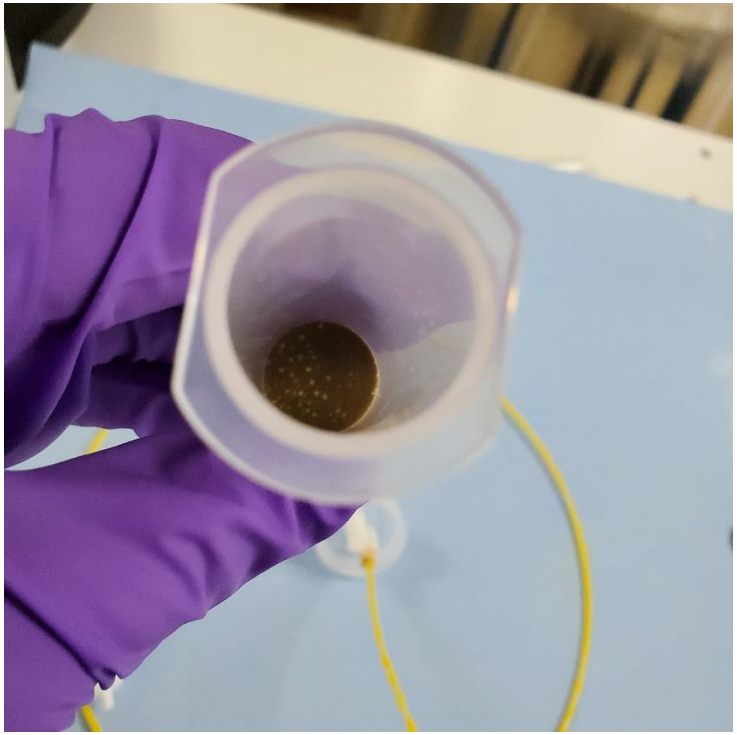
250 ml run to completion on 6 ml cartridge with Plastic Wool





250ml run to completion
25ml cartridge





Automated Extraction and Concentration for PFAS/PFOS in Drinking Water

EconoTrace® PFC

Drinking Water, Serum and samples minimal particulate
Positive Pressure Pumping

LC/MS

EconoTrace for Extraction and Concentration of PFAS/PFOS in Drinking Water

Fluid Management Systems

Fully Automated

Modular and expandable from 1 to 4 Modules

High Throughput Runs
2 to 8 Sample Extractions in Parallel

Uses Positive Pressure Pumping only for Precise delivery of Conditioning Solvent, Sample, Bottle Rinse and Elution Solvent

Automatic Bottle Rinse

Delivers extract directly to SuperVap Concentrator for final blowdown

TurboTrace PFC Automated Extraction and Concentration for PFAS/PFOS in WasteWater

TurboTrace® PFC

LC/MS

Wastewater, Particulate Laden Samples
Drinking water Samples
Vacuum Pump for loading samples
Positive Pressure Pumping for conditioning, rinsing and elution

TurboTrace for Extraction and Concentration of PFAS/PFOS in Waste Water

Fluid Management Systems

- Fully Automated
- Modular and expandable from 1 to 6 Modules
- High Throughput Runs Sample Extraction in Parallel
- Uses Positive Pressure Pumping for Precise delivery of Elution and Wash Solvent
- Uses Vacuum or Positive Pressure Pumping to Load Samples
- Direct delivery to Concentrator for Evaporation

Automated Concentration for PFAs

- SuperVap PFC
  - 24 positions
  - 15ml Conical vials
  - Dry Bath

Concentration Functionality

- **Self Installable**
  - **Video unpacking, installation and training video**
- **Preprogrammed with most common temperature settings**
- **Direct to 15ml Centrifuge Tubes**
- **Dry bath heating element**
- **Time based endpoint**
- **Savable temperature log**
- **No Teflon Components**

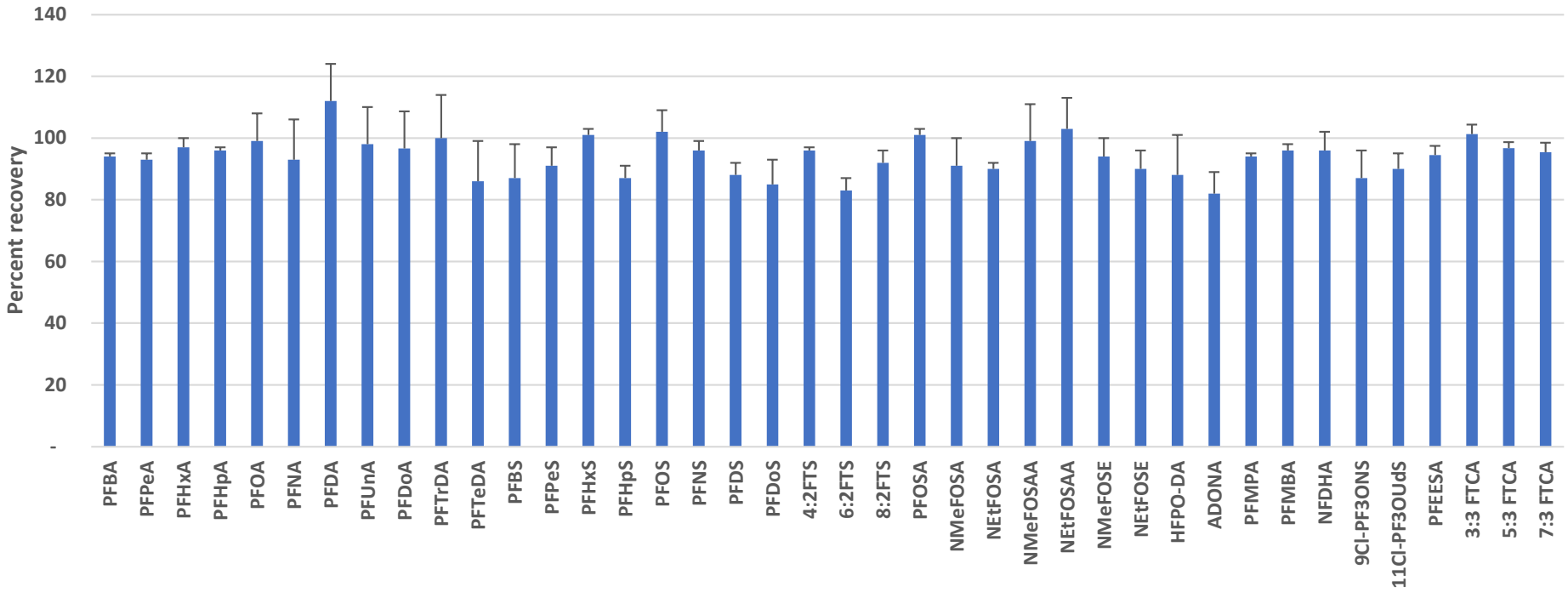
TurboTrace Parallel Sequential PFC Automated Extraction and Concentration for PFAS/PFOS in Drinking Water and WasteWater

TurboTrace® PFC Parallel Sequential

LC/MS

Wastewater, Particulate Laden Samples
Drinking water Samples
Vacuum Pump or Positive Pressure for loading samples
Positive Pressure Pumping for conditioning, rinsing and elution
Direct to SuperVap Concentrator

EPA 1633
Turbo Trace Parallel/Sequential



Various Blanks EPA 1633

	ch.1	ch.2	ch.3	ch.4	ch.5	stopcock	sample bottle
Name	Calc. Conc.	Calc. Conc.	Calc. Conc.	Calc. Conc.	Calc. Conc.	Calc. Conc.	Calc. Conc.
3-3 FTCA	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PFBA	0.00	0.00	0.00	0.00	0.02	0.00	0.91
PFMPA	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PFPeA	0.00	0.04	0.03	0.00	0.00	0.13	0.01
PFMBA	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HFPO-DA	0.01	0.00	0.00	0.00	0.00	0.00	0.12
4-2 FTS	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NFDHA	0.00	0.00	0.00	0.00	0.00	0.00	0.01
PFHxA	0.03	0.04	0.02	0.00	0.00	0.00	0.00
PFBS	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5-3 FTCA	0.03	0.00	0.00	0.00	0.00	0.00	0.00
PFHpA	0.00	0.02	0.00	0.02	0.01	0.00	0.00
PFEESA	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Various Blanks EPA 1633

	ch.1	ch.2	ch.3	ch.4	ch.5	stopcock	sample bottle
Name	Calc. Conc.	Calc. Conc.	Calc. Conc.	Calc. Conc.	Calc. Conc.	Calc. Conc.	Calc. Conc.
ADONA	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PFPeS	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PFOA	0.03	0.01	0.02	0.02	0.00	0.28	0.01
PFNA	0.02	0.03	0.01	0.03	0.05	0.00	0.01
8-2 FTS	0.01	0.00	0.00	0.02	0.01	0.00	0.00
PFDA	0.02	0.02	0.03	0.01	0.02	0.04	0.00
PFDoS	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PFOS	0.03	0.02	0.04	0.02	0.01	0.03	0.05
6-2 FTS	0.01	0.00	0.00	0.00	0.00	0.00	0.02
PFHxS	0.00	0.00	0.01	0.03	0.03	0.05	0.06
PFTrDA	0.01	0.00	0.00	0.04	0.04	0.00	0.03
N-EtFOSAA	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PFHpS	0.00	0.00	0.02	0.03	0.03	0.00	0.00

Various Blanks EPA 1633

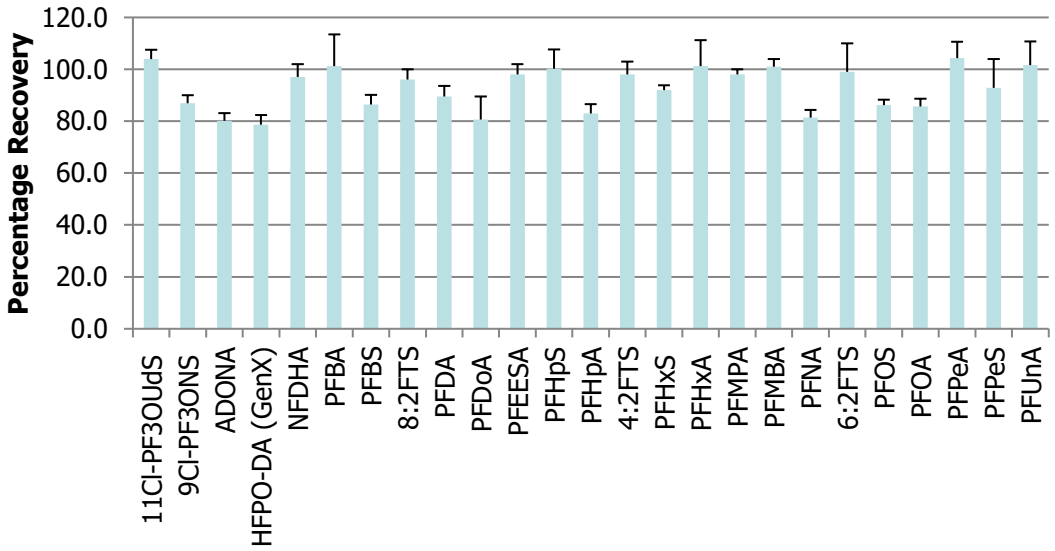
	ch.1	ch.2	ch.3	ch.4	ch.5	stopcock	sample bottle
Name	Calc. Conc.	Calc. Conc.	Calc. Conc.	Calc. Conc.	Calc. Conc.	Calc. Conc.	Calc. Conc.
N-MeFOSAA	0.00	0.00	0.00	0.02	0.00	0.00	0.00
PFNS	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7-3 FTCA	0.00	0.00	0.00	0.00	0.01	0.00	0.01
9Cl-PF3ONS	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11Cl-PF3OUdS	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PFDoA	0.01	0.00	0.00	0.03	0.02	0.03	0.00
PFUnA	0.00	0.00	0.00	0.00	0.04	0.00	0.04
PFTDA	0.00	0.01	0.00	0.01	0.00	0.04	0.00
PFDS	0.00	0.00	0.00	0.00	0.00	0.00	0.01
PFOSA	0.02	0.00	0.00	0.02	0.03	0.01	0.00
MeFOSE	0.00	0.00	0.00	0.00	0.00	0.01	0.00
EtFOSE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N-MeFOSA	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N-EtFOSA	0.00	0.00	0.00	0.00	0.00	0.00	0.00

TurboTrace for Extraction and Concentration of PFAS/PFOS in Drinking/WasteWater

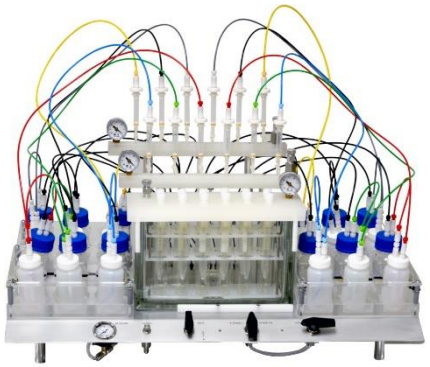
Fluid Management Systems

- **Fully Automated**
- **Modular and Scalable expandable from 1 to 6 Modules**
- **Run 1 to 6 samples simultaneously, up to 30 sequentially**
- **Each Module can Run 5 Samples in a Sequence**
- **Uses Positive Pressure Pumping for Precise delivery of Elution and Wash Solvent**
- **Uses Vacuum with liquid sensor to Load Dirty Samples**
- **Direct Extract delivery to Concentrator for Evaporation**

EPA 533


Percentage Recovery
120.0
100.0
80.0
60.0
40.0
20.0
0.0
11Cl-PF3OUdS
9Cl-PF3ONS
ADONA
HFPO-DA (GenX)
NFDHA
PFBA
PFBS
8:2FTS
PFDA
PFDoA
PFEESA
PFHpS
PFHpA
4:2FTS
PFHxS
PFHxA
PFMPA
PFMBA
PFNA
6:2FTS
PFOS
PFOA
PFPeA
PFPeS
PFUnA

Semi-Automated Solid Phase Extraction front end LC/MS



EZPFC

LC/MS

Sample Analysis Work Flow

Automated Sample Prep Time = 80 Minutes

Solid Phase Extraction

35 Minutes

Concentration

45 Minutes

Semi Automated Sample Prep Time = 80 Minutes

Solid Phase Extraction

35 Minutes

Reasons for Semi-Automated SPE

- **Closed System**
- **12 samples in parallel**
- **Reduced Actions / Easy to Use**
- **Simplified procedures**
- **Semi-Automated versus Manual protocols = Reproducibility**
- **Increased Sample Throughput**
- **Low cost compared to Automated solutions**

Objective for Semi Automation

- **Incorporate automated system capabilities to the semi-automated platform.**
- **Our goal is to establish several Standard Operating Procedures (SOPs) for the testing lab through the utilization of a solitary extraction platform.**
- **In order to optimize time and minimize mistakes, it is crucial to decrease the amount of manual steps involved.**

FMS
Fluid Management Systems

Goal

- **Low Cost**
  - Extract and Concentrate a batch of 24 samples 2 to 3 hours
- **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 Direct to 15ml Centrifuge tube for easy Concentration
- **Fast**
  - The fastest sample processing available for SPE
  - Run up to 12 samples simultaneously
  - Vacuum for fast loading of large volume samples
  - Unattended Sample loading walkaway time
- **Closed system**
  - Eliminate potential outside contamination

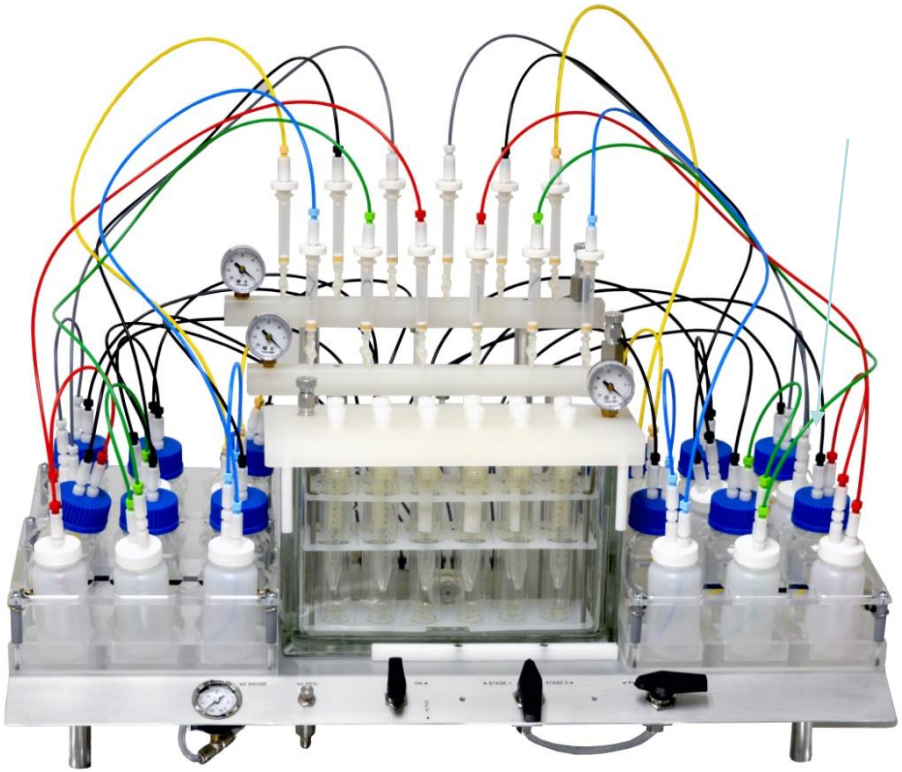
Goal

- **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 Capital Expense**

EZPFC®

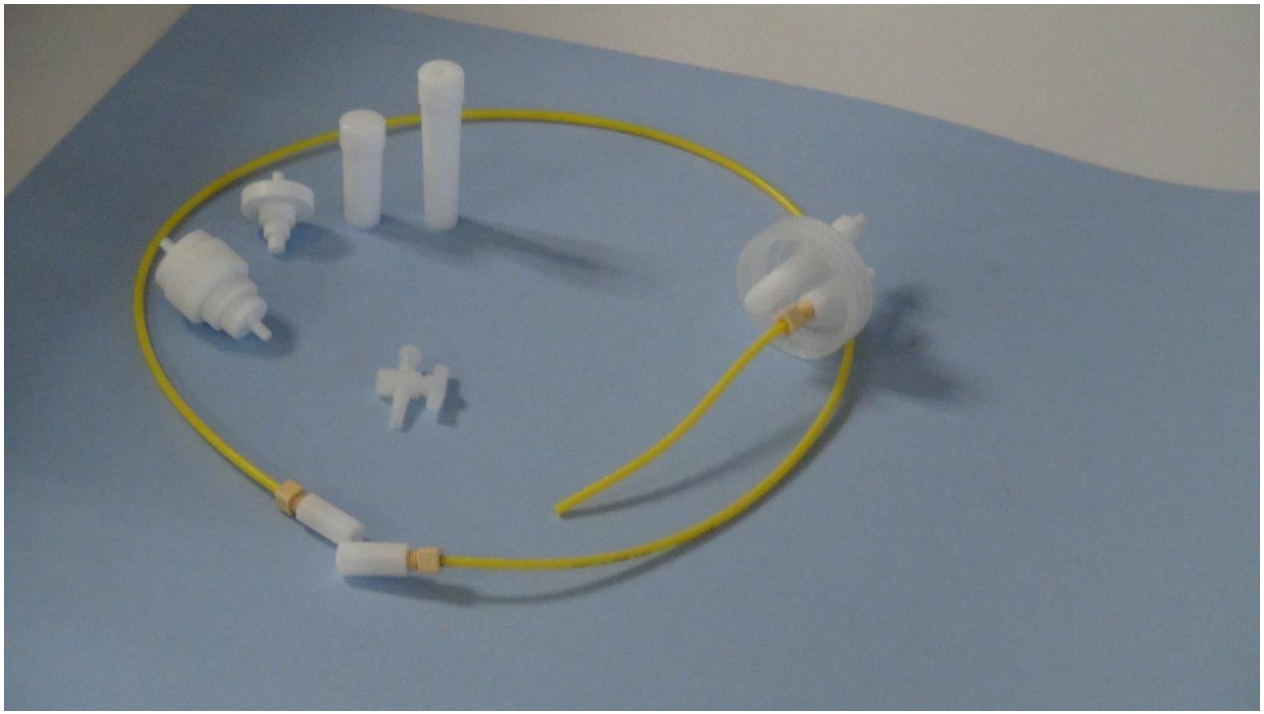
Drinking Water,
Wastewater,
Particulate laden samples



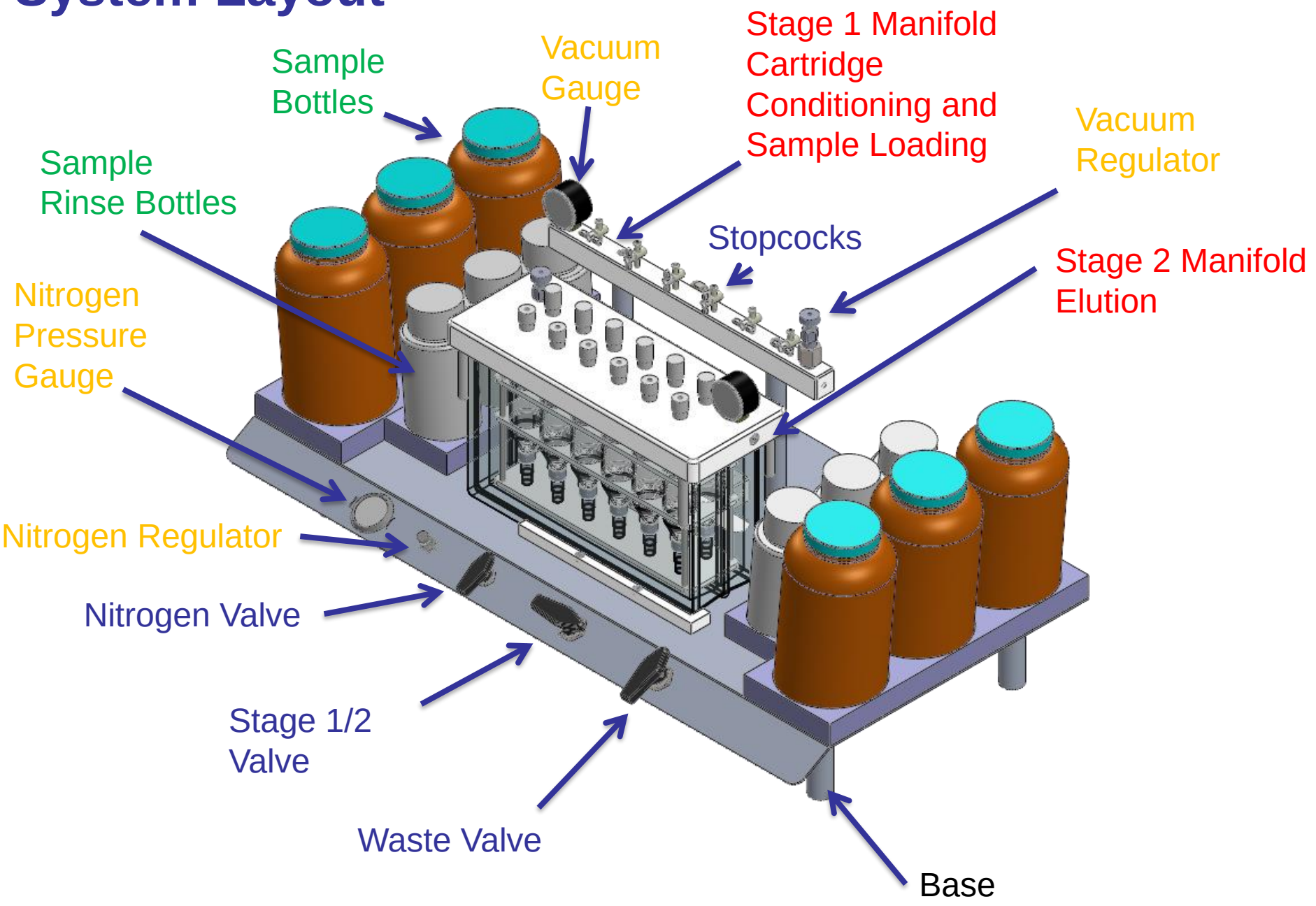
EZPFC 12 sample

System Components

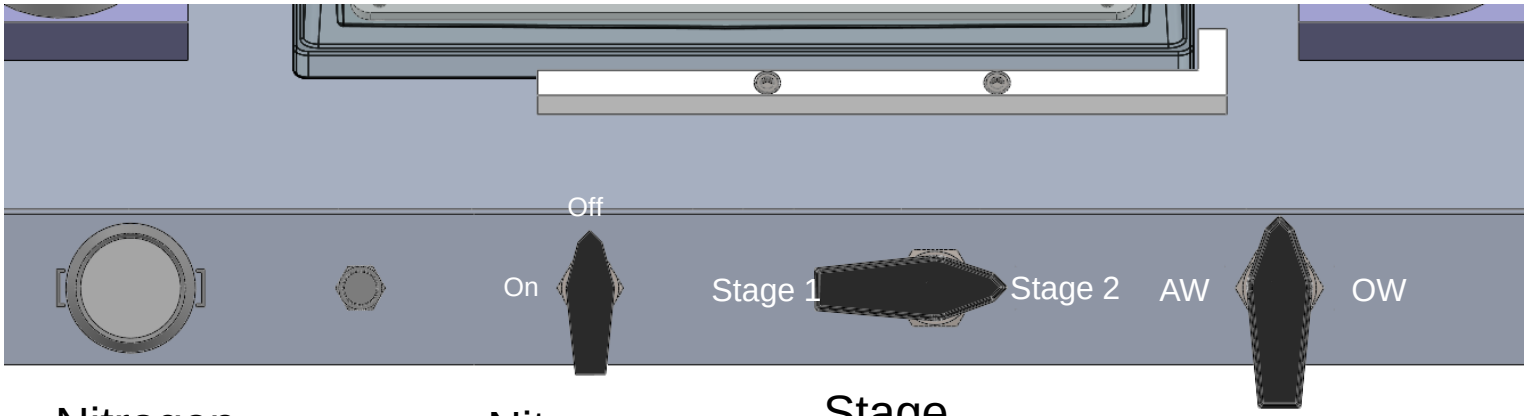
- No Teflon
- Tubing - High Density Polyethylene
- Fittings – Delrin
- Cartridge Adapters – Medical Grade Polypropylene



System Layout



Control Valve Layout



Nitrogen Gauge

Nitrogen Valve

Stage 1/2 Valve

Waste Valve

Automated Concentration for PFAs

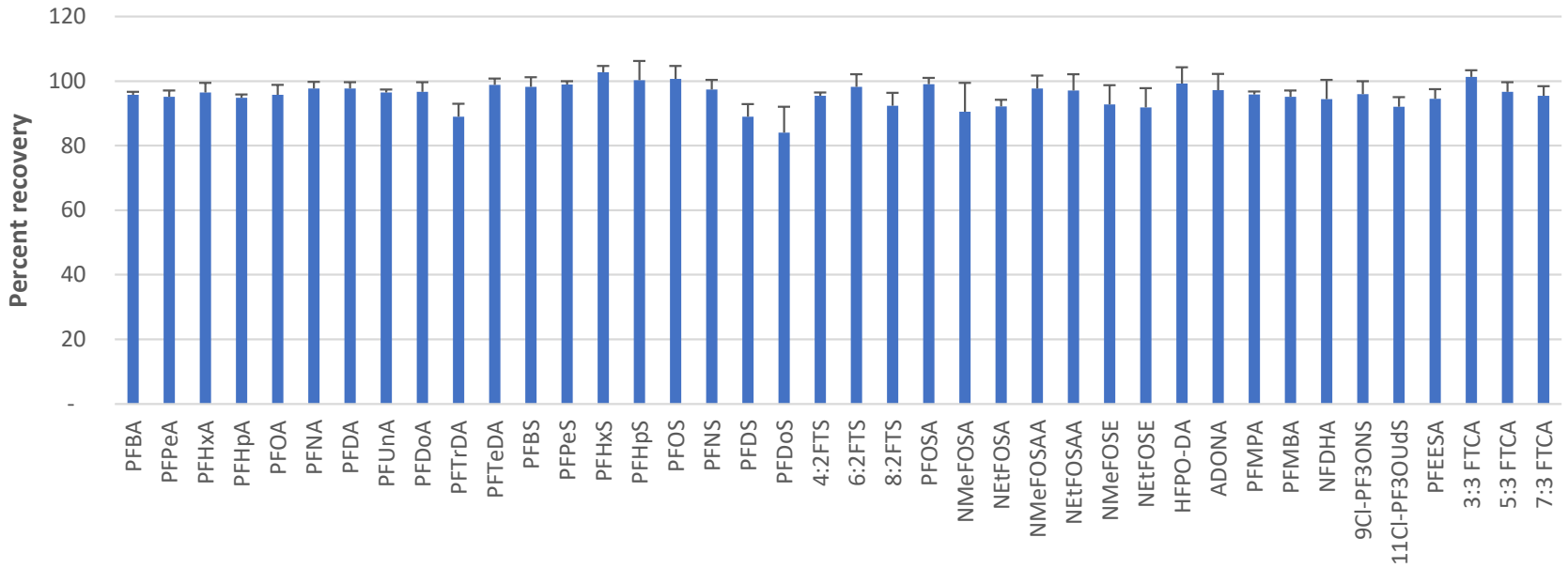
- SuperVap PFC
  - 24 positions
  - 15ml Conical vials
  - Timed Endpoint

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

EPA 1633

EZPFC



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

Automated SPE for PFAS

- **EconoTrace**
  - Fully automated, positive pressure system, automated bottle rinse, direct delivery to SuperVap Concentrator
  - Designed for cleaner samples

- **TurboTrace**
  - Fully automated, Vacuum pump for loading "dirty samples", automated bottle rinse,
  - Direct delivery to SuperVap Concentrator

Semi Automated SPE for PFAS

- **EZPFC**
  - 2 EZPFC 12 position systems and the SuperVap PFC Concentrator for 24 samples
  - Run a batch of 24 in 2 hours