Results and Learnings from **Automating** the Solid Phase Extraction of **EPA Method 1633**

Authors: Ian Wan (ian_wan@promochrom.com)

PROMOCHROM

KEY HIGHLIGHTS

- ✓ **EPA Method 1633 Performance and Learnings**
- ✓ **Anti-Clogging Solutions**
- ✓ **Accelerating extraction using the new Presto system**

INTRODUCTION

Solid Phase Extraction (SPE) is employed by EPA Method 1633 for the extraction of PFAS across a range of matrices. Since 2021, PromoChrom has helped laboratories automate this method through its draft stages. Understanding the method potential and practical needs can help laboratories successfully implement this method with minimal cost and hassle. This poster shares our learnings, anti-clogging solutions, and the significant time savings using the new Presto accelerated 8-Channel system.

EPA METHOD 1633 PERFORMANCE

Results from this section are obtained from Claros Technologies who performs EPA Method 1633 on wastewater samples using:

- SPE Cartridge: 6 mL WAX SPE Cartridge
- Automated SPE system: SPE-03 8-channel SPE system
- Instrument for analysis: LCMSMS

Method Detection Limit (MDL)

Below are the MDL and Minimum Level (ML) of the analytes with 500 mL samples.

***Figure 1** – MDL and ML for EPA Method 1633 using SPE-03*

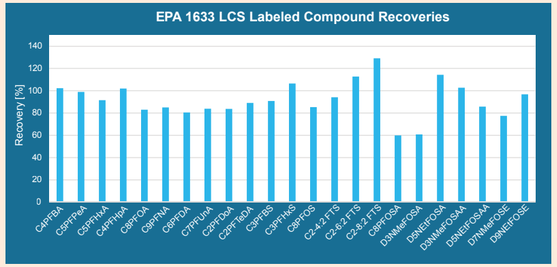
Analytes	MDL (ppt)	ML (ppt)	Analytes	MDL (ppt)	ML (ppt)
PFBA	2.00	5.00	PFDoS	0.34	2.00
PFPeA	0.92	2.00	4:2 FTS	2.32	5.00
PFHxA	0.76	2.00	6:2 FTS	1.88	5.00
PFHpA	0.37	2.00	8:2 FTS	2.43	10.00
PFOA	0.62	2.00	PFOSA	0.75	2.00
PFNA	0.59	2.00	HFPO-DA	1.84	5.00
PFDA	0.59	2.00	ADONA	1.70	5.00
PFUnA	0.49	2.00	9Cl-PF3ONS	2.23	5.00
PFDoA	0.52	2.00	11Cl-PF3OUdS	1.87	5.00
PFTrDA	0.83	2.00	N-MeFOSA	1.47	5.00
PFTeDA	0.79	2.00	N-EtFOSA	1.16	5.00
T-NMeFOSAA	0.70	2.00	N-MeFOSE	5.62	20.00
T-NEtFOSAA	0.83	2.00	N-EtFOSE	3.44	10.00
PFBS	0.79	2.00	3:3 FTCA	0.78	2.00
PFPeS	0.71	2.00	5:3 FTCA	3.45	10.00
T-PFHxS	0.37	2.00	7:3 FTCA	5.10	20.00
PFHpS	0.55	2.00	PFMPA	1.26	5.00
T-PFOS	0.42	2.00	PFMBA	1.18	5.00
PFNS	0.41	2.00	NFDHA	0.75	2.00
PFDS	0.39	2.00	PFEESA	1.22	5.00

Learnings: It was found that attempting to evaporate the sample extracts to achieve lower detection limits can lead to the loss of PFBA, PFPeA and FOSA/FOSE. Precise temperature and timing control are required to minimize recovery losses.

Labeled Compound Performance

Since EPA Method 1633 uses isotope dilution, the analyte recoveries are corrected. To assess true performance, the labeled compound (isotope) recoveries from an SPE-03 extraction batch consisting of 8 x 500 mL lab spikes are shown in ***Figure 2***.

***Figure 2** - Average LCS Labeled Recovery across 8 samples using SPE-03*



Learnings: Stickier labeled isotopes - PFTeDA (although not observed at Claros), NEtFOSA, NMeFOSA, NEtFOSE and NMeFOSE have lower recoveries as they tend to adsorb to the SPE sorbent, bottle and tubing walls. Other labs that include longer chain compounds like PFHxDA in their analyte list have observed similar effects. The following approaches can help improve the recovery of these compounds:

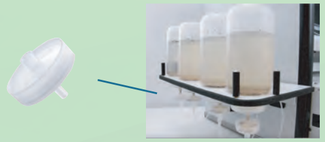
1. Increasing the drying time or air flow through the SPE cartridges during drying to minimize water content in the SPE sorbent prior to final elution.
2. Increasing the bottle rinsing flow rate and bottle shaking magnitude.
3. Using the SPE-03's new "Boost" function that oscillates the elution solvent back and forth within the SPE cartridge, to further promote solvent interaction.

ANTI-CLOGGING SOLUTIONS

EPA method 1633 is developed for matrices beyond drinking water, which can contain significant solids and suspensions that clog SPE cartridges sample lines. Although the method suggests using a 2nd SPE cartridge when total suspended solids (TSS) is >50 mg in aqueous samples, this adds further complexity and challenges. PromoChrom's anti-clogging solutions can help achieve smooth extraction while meeting the recovery criteria of this performance-based method.

High-Capacity Inline Filters

Similar to adding glass wool to SPE cartridges, PromoChrom's high-capacity inline filters are connected upstream of the SPE sorbent and just after the samples to alleviate clogging and protect system moving parts.

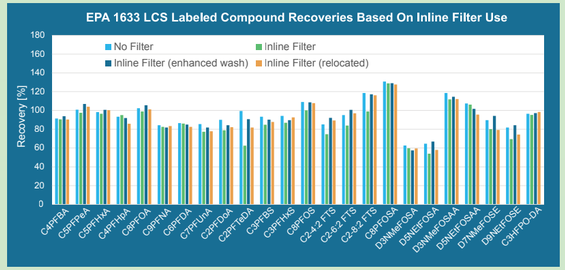


The batch of 8 samples previously from ***Figure 2*** consists of 4 different conditions to determine the effects of using the inline filter, with 2 samples subject to each:

- **No Filter** – Extraction performed with no inline filter on the sample lines
- **Inline Filter** – Extraction performed with inline filter on the sample lines
- **Inline Filter (Enhanced wash)** – The 5 mL of 1% Basic MeOH used for bottle rinsing is reused to wash the inline filter 3 times, keeping solvent use unchanged while maximizing analyte recovery
- **Inline filter (Relocated)** – Simulating the extreme case where the high-capacity filter becomes fully clogged. The filter is then relocated above the SPE cartridge after sample loading to continue extraction

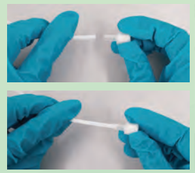
The individual performance of each condition is plotted below in ***Figure 3***. Majority of the compounds recovered similarly across all 4 conditions. Some lower recoveries were seen on the stickier compounds such as PFTeDA, NMeFOSE and NEtFOSE and the fluorotelomer sulfonates using inline filter only. While the results are still within method limits, the enhanced wash was explored on the inline filters which demonstrated results closely matching the scenario with no filters. Relocating the inline filters during extraction also had insignificant effect on recoveries.

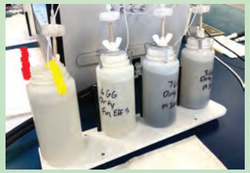
***Figure 3** - Average LCS Labeled Recovery based on Inline Filter conditions*



Anti-Clogging Tips

When handling samples with significant sediment or floating debris such as influent wastewater, PromoChrom's Anti-Clogging Tips serve as the primary defence against sample line and filter blockages. Below shows the simple attachment of anti-clogging tips to the sample lines, and combined use with inline filters to successfully extract influent wastewater samples with more than 800 mg of TSS.





Learnings: Extracting matrices outside of drinking water calls for practical implementations to alleviate sample line and SPE cartridge clogging. PromoChrom has developed a suite of inline anti-clogging solutions based on experience working with customers that run the most challenging samples. The inline filters, anti-clogging tips and other anti-clogging features on PromoChrom's automated extractor serve to promote seamless extraction while preserving recoveries.

ACCELERATING EPA METHOD 1633

While reducing sample volume can decrease extraction time, it is subject to instrumentation sensitivity and matrix complexity. Labs that work with older equipment or wastewater samples may not be able to go below 250 or 500 mL. To address this, PromoChrom developed the **Presto SPE system** that offers significant time savings on larger volume samples and improved handling of clogging. This is achieved by:

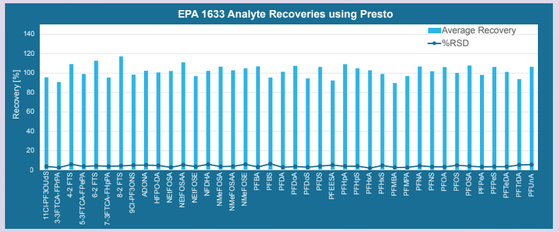
Continuous pumps for sample loading. Compared to syringe pumps on the SPE-03, 1 hr can be saved on 1 L extractions running at the same flow rate.

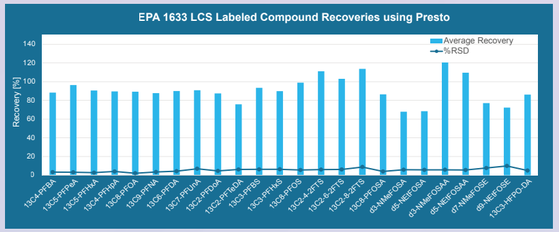
Built-in **liquid detection** to stop individual sample channels that complete loading. This minimizes time when extracting field samples with varying volumes.

Pressure and flow monitoring algorithm to regulate the pump to match desired flow rate when loading samples with high particulate content. This operates within a safe pressure ceiling to ensure maximum efficiency without putting stress on the hardware.

Below are the results from Maryland DOH who Beta-Tested the Presto for EPA 1633, showcasing excellent analyte recoveries, comparable labeled compound recoveries to the SPE-03 and low RSD. By running the extraction at 15 mL/min, it was able to reduce the extraction of 8 x 250 mL samples **from 105 minutes to just 50 minutes**.

***Figure 4** – Analyte and Labeled Compound Recoveries using Presto for EPA 1633*





Learnings: The use of continuous pumps and higher flow rates can achieve more than 50% time savings for 250 mL samples when running EPA Method 1633.