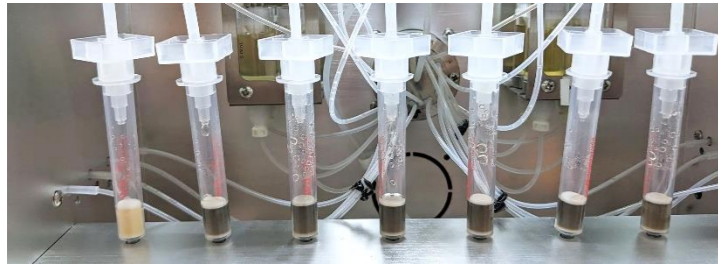


Results and Learnings from Automating the Solid Phase Extraction of draft EPA Method 1633

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KEY HIGHLIGHTS

- **Detection limit, background and recovery** using **automated SPE**
- Factors affecting method performance
- Impact of dispersive SPE (dSPE) **carbon clean up**
- Need for **anti-clogging technologies**



INTRODUCTION

Solid Phase Extraction (SPE) is employed by EPA draft Method 1633 for the extraction of PFAS across 9 different sample matrices. When performed manually, the SPE procedure requires multiple handling steps and constant monitoring of liquid flow. Special requirements for sample preparation, extraction and clean up further adds to the challenges for laboratories when bringing on this method. Automation and optimization of the extraction procedure is critical for achieving good quality results and releasing laboratory workers from labor-intensive routines.

Claros Technologies, an advanced materials company involved in PFAS remediation and testing, currently performs 1633 for waste water and ground leachate. This poster highlights the experience and data obtained while working with Claros and other PFAS labs. It is expected that the learnings will foster wider understanding and discussion of this method.

MATERIALS

- **WAX SPE Cartridge:** Brand A for IPR and field samples, Brand B for MDL
- **Automated SPE system:** SPE-03 8-channel SPE system
- **Instrument for analysis:** Shimadzu 8060 LCMSMS



METHOD DETECTION LIMIT (MDL) AND BACKGROUND

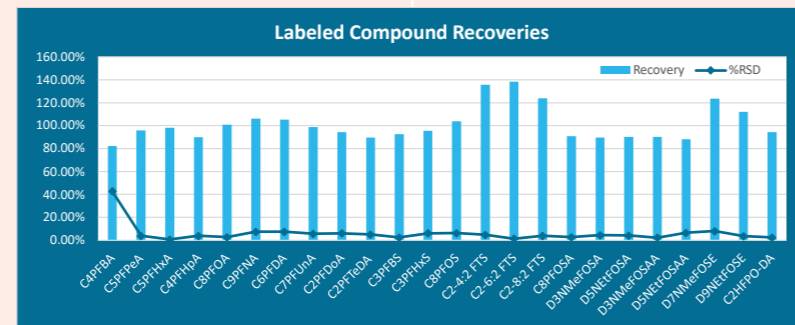
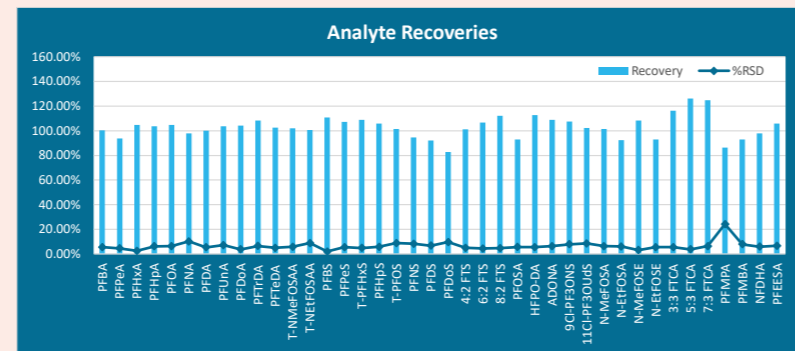
Below are the MDL and corresponding Minimum Level (ML) of each compound. Method Blank (MB) was evaluated based on 1/2 the lowest calibration point.

Analytes	MDL (ppt)	ML (ppt)	MB 1 (ppt)	MB 2 (ppt)
PFBA	2.00	5.00	<1.60	<1.60
PFPeA	0.92	2.00	<0.80	<0.80
PFHxA	0.76	2.00	<0.40	<0.40
PFHpA	0.37	2.00	<0.40	<0.40
PFOA	0.62	2.00	<0.40	<0.40
PFNA	0.59	2.00	<0.40	<0.40
PFDA	0.59	2.00	<0.40	<0.40
PFUnA	0.49	2.00	<0.40	<0.40
PFDoA	0.52	2.00	<0.40	<0.40
PFTriDA	0.83	2.00	<0.40	<0.40
PFTeDA	0.79	2.00	<0.40	<0.40
T-NMeFOSAA	0.70	2.00	<0.40	<0.40
T-NEFOSAA	0.83	2.00	<0.40	<0.40
PFBS	0.79	2.00	<0.35	<0.35
PFPeS	0.71	2.00	<0.38	<0.38
T-PFHs	0.37	2.00	<0.37	<0.37
PFHpS	0.55	2.00	<0.38	<0.38
T-PFOS	0.42	2.00	<0.37	<0.37
PFNS	0.41	2.00	<0.38	<0.38
PFDS	0.39	2.00	<0.39	<0.39
PFDoS	0.34	2.00	<0.39	<0.39
4:2 FTS	2.32	5.00	<1.50	<1.50
6:2 FTS	1.88	5.00	<1.52	<1.52
8:2 FTS	2.43	10.00	<1.54	<1.54
PFOSA	0.75	2.00	<0.40	<0.40
HFPO-DA	1.84	5.00	<0.80	<0.80
ADONA	1.70	5.00	<0.76	<0.76
9Cl-PFOuS	2.23	5.00	<0.75	<0.75
11Cl-PFOuS	1.87	5.00	<0.76	<0.76
N-MeFOSA*	1.47	5.00	<0.80	<0.80
N-EFOSA*	1.16	5.00	<0.80	<0.80
N-MeFOSE*	5.62	20.00	<8.00	<8.00
N-EFOSE*	3.44	10.00	<8.00	<8.00
3:3 FTCA	0.78	2.00	<0.80	<0.80
5:3 FTCA	3.45	10.00	<4.00	<4.00
7:3 FTCA	5.10	20.00	<4.00	<4.00
PFMPA	1.26	5.00	<0.80	<0.80
PFMBA	1.18	5.00	<0.80	<0.80
NFDHA	0.75	2.00	<0.80	<0.80
PFESA	1.22	5.00	<0.71	<0.71

*These 4 compounds were excluded from the lab's accreditation due to variation observed on instrumentation.

INITIAL PRECISION AND RECOVERY (IPR)

4 mid-level lab controlled spikes (LCS) were prepared in 500 mL water and demonstrated good recoveries across analytes and labeled compounds.

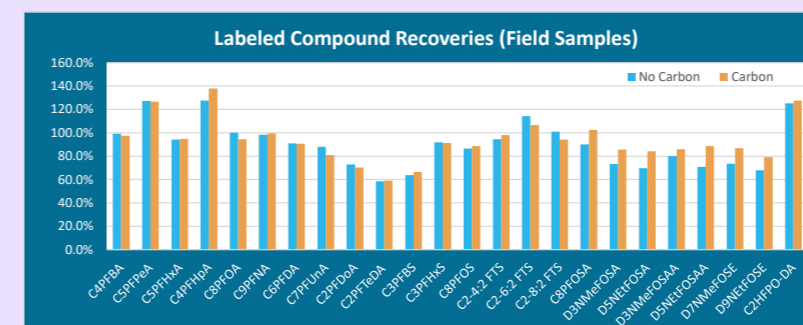
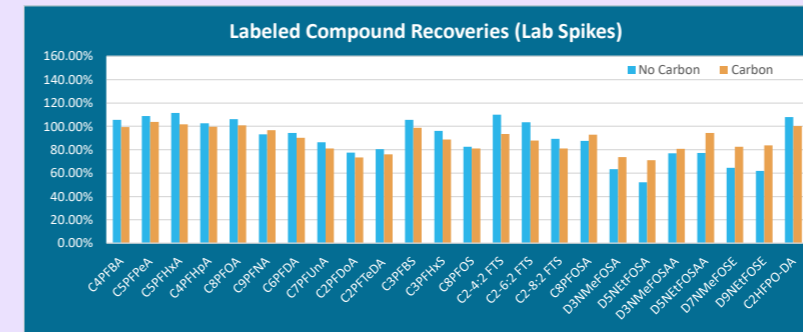


LEARNINGS

1. **C4PFBA Labeled Compound**
 - The higher %RSD for this labeled compound was due to one sample recovering much lower than others. The lab observed that the water rinse step after sample loading can reduce short-chain PFAS recoveries, especially PFBA and sometimes PFPeA and their labeled compounds.
 - The effect also varies across different brands of SPE cartridges.
2. **FOSA and FOSE Labeled Compounds**
 - Recoveries can vary based on brand of instrumentation as these neutral compounds are less readily ionized.
 - Lab temperatures can significantly impact the labeled isotope recoveries on the instrumentation. During the arctic chill in the beginning of 2023, a 2 °C drop in temperature could swing their recoveries beyond 400%. As such, these compounds were excluded from their accreditation.
 - These compounds are highly adsorbent, water in the sample bottles or cartridge during SPE can dilute the elution solvent and reduce recoveries.
3. **Extract Evaporation**
 - This is not required by EPA 1633, but attempting to evaporate the extracts resulted in loss of PFBA, PFPeA and FOSA/FOSE. It is therefore recommended to cap the fractions after the extraction to minimize losses.

CARBON CLEAN UP AND MATRIX EFFECTS

EPA Method 1633 requires carbon clean up of the SPE extracts to remove interfering organic compounds prior to analysis. To investigate the effects of this step, Claros ran 4 lab spikes and 7 field samples with and without carbon clean up. The field samples consist of 100 mL ground leachate samples diluted to 250 mL with water prior to SPE.



LEARNINGS

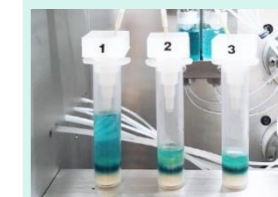
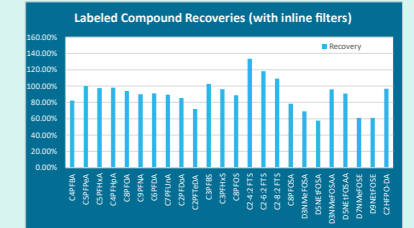
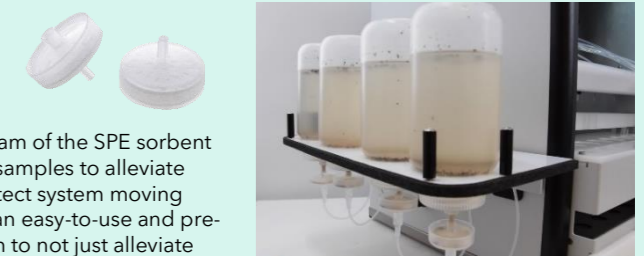
1. The leachate samples tested did not show significant differences using carbon clean up. This clean up may play a bigger role in other types of matrices.
2. In the clean lab spikes, carbon clean up led to a slight decrease in overall labeled compound recoveries but saw noticeable improvements for the FOSA/FOSAA/FOSE compounds. The same compounds also showed slightly better recoveries in the field samples. It is possible that a source of interference was present in the reagents rather than the sample matrix.

ANTI-CLOGGING TECHNOLOGIES

Method Limitations - EPA method 1633 is developed for matrices beyond drinking water, which can contain solids and suspensions that clog SPE cartridges or wear out moving parts in an automated extractor. Although the method limits solids content to <50 mg in aqueous samples, field samples often exceed this level. Using only glass wool suggested by the method is insufficient and does not consider the wide use of automated solutions. The latest draft has not directly addressed the use of new and proven technologies such as inline filters and anti-clogging frits.

Inline Filters -

similar to adding glass wool to SPE cartridges, inline filters are connected upstream of the SPE sorbent and just after the samples to alleviate clogging and protect system moving parts. It presents an easy-to-use and pre-packaged solution to not just alleviate clogging but also protect system moving parts. Since 2021, labs have successfully used inline filters to extract samples with particulates on automated and manual setups. On the right shows acceptable recoveries of 1633 labeled compounds across QC samples from 8 field batches using inline filters.



Anti-clogging Frits - as a secondary measure to further prevent clogging, anti-clogging frits can be placed on SPE cartridges to trap and disperse particulates. The picture on the left shows 3 cartridges, only 2 and 3 have anti-clogging frits. When extracting river water samples, significant build up was only seen in cartridge 1.

LEARNINGS

Given the variety of field samples, it would be beneficial for EPA Method 1633, as a performance-based method, to include clear guidance on allowing such options.

ACKNOWLEDGEMENTS

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