



AUTOMATED SOLID PHASE EXTRACTION USING INLINE FILTERS FOR PFAS IN NON-POTABLE WATER FOLLOWING ISO 21675

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ABSTRACT

Before the release of draft EPA Method 1633 in 2021, there were few standardized methods for PFAS in non-potable water. ISO 21675 was published in 2019 to cover a list of 30 PFAS compounds in drinking, natural and waste water containing less than 2 g/L of solids¹. The main challenge of extracting samples with particulates is SPE cartridge clogging, which requires additional steps of dividing a sample between cartridges and pooling the extracts. This application note presents a streamlined extraction of non-potable water samples using PromoChrom's high-capacity inline filters along with the automated SPE-03 system for the 30 compounds of ISO 21675, as well as 3 additional pertinent PFAS compounds.

INTRODUCTION

The Wisconsin Lab of Hygiene has been using the SPE-03 since 2019 for drinking water following EPA Methods 537.1 and 533. In 2021, they introduced the testing of ground, rain and surface water following ISO 21675. This method utilizes isotope dilution and anion-exchange SPE followed by LC-MSMS analysis.

The extraction procedure requires meticulous control of flow rates which becomes a greater challenge when encountering samples with particulates. The multiple conditioning, elution and rinsing steps also call for process automation.

This application note demonstrates the automation of ISO 21675 cartridge extraction using PromoChrom's SPE-03 and high-capacity inline filters. It includes data on background and recovery both with and without inline filters. Field extraction results are also compared between SPE-03 and manual extractions.

MATERIALS

- PromoChrom SPE-03 system with MOD-005 (minimal-Teflon option) and MOD-004 (2019 model without shakers)
- PromoChrom high-capacity inline filters (Cat. No.: F-HC-30)
- Waters OASIS WAX 6 cc SPE Cartridges, 150 mg/30µm
- Reagents and standards following ISO 21675
- SCIEX 5500 QTRAP using Waters Acquity UPLC



METHOD SUMMARY

Solvent 1 = MeOH, **Solvent 2** = H₂O, **Solvent 3** = 60 mM NH₄OH in MeOH (Basic MeOH), **Solvent 4** = 5 mM ammonium acetate

W1 = Aqueous waste, **W2** = Organic waste

Table 1 - ISO 21675 Steps Programmed on SPE-03

Action	Inlet 1	Flow	Volume	Description
Elute W2	Solvent 3	5 mL/min	4 mL	Condition cartridges with 4 mL Basic MeOH
Elute W2	Solvent 1	5 mL/min	4 mL	Condition cartridges with 4 mL MeOH
Elute W1	Solvent 2	5 mL/min	4 mL	Condition cartridges with 4 mL H ₂ O
Add Samp W1	Sample	3 mL/min	275 mL	Load samples at 3 mL/min, using 275 mL to ensure full bottles are loaded
Elute W1	Solvent 2	3 mL/min	4 mL	Wash cartridges with 4 mL H ₂ O
Elute W1	Solvent 4	3 mL/min	4 mL	Wash cartridges with 4 mL ammonium acetate
Air-Purge W1	Air	10 mL/min	20 mL	Purge large water droplets out of cartridges
Blow N2	Time based		10 min	Dry cartridges with nitrogen for 10 mins
Clean	Solvent 1	5 mL/min	5 mL	Deliver 5 mL of MeOH into sample bottles
Wait	Manual Resume			¹ Pause to manually rinse bottles
Collect 1	Sample	0.5 mL/min	6 mL	Collect rinsate and elute cartridges into fraction 1
Collect 1	Solvent 3	0.5 mL/min	4 mL	Elute cartridges with Basic MeOH into fraction 1

1. Full automation of the method can be achieved using the "Rinse" function. Without the newer bottle shakers introduced in 2020, the lab is doing it manually for added assurance. PromoChrom also offers MOD-00P configuration to bypass the inline filter for maximum rinse strength for dirty samples.

The method above is developed by Wisconsin Lab of Hygiene, based on flow rates pre-determined using manual extraction. They have found slower sample loading and elution speeds to improve recoveries on the vacuum manifold. Further flow optimizations can be performed to increase the extraction speed. After extraction, the collected fractions are evaporated to approximately 1 mL, then topped up to 1 mL using MeOH. Fractions are not concentrated to dryness to ensure good recovery of more volatile PFAS compounds. The composition of the final concentrated extract is 10-20% water in Methanol.

RESULTS

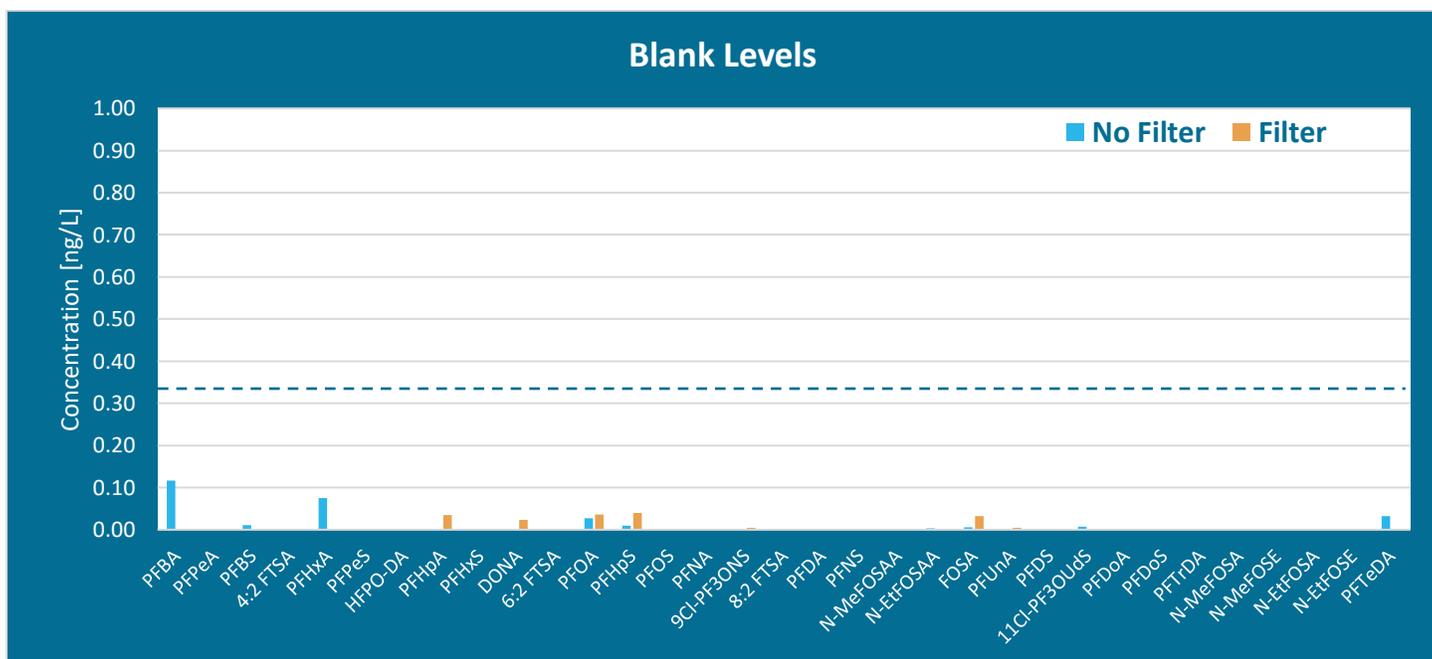
The data was collected from field sample extraction batches over April and May 2022. The Lab Reagent Blanks (LRBs) in these batches are used to assess system background while field samples are used to assess matrix effects. Lab Fortified Blanks (LFBs) between December 2021 and January 2022 demonstrate the recoveries of the SPE-03 with and without the inline filters.

PFAS Background

The Wisconsin lab of Hygiene sets their Minimum Reporting Level (MRL) at 1 ppt for all compounds using this method with the exception of N-MeFOSA and N-EtFOSA which are at 2 ppt. Their SPE-03 comes with the minimal-Teflon option that has all PTFE lines replaced. In order to utilize PromoChrom's SPE-03 and inline filters for ISO 21675, background contamination must be demonstrated to be under 1/3 of the MRL. This was assessed using LRBs from 8 separate field sample extraction batches without the inline filter and 1 with the inline filter.

Based on Figure 1, all background levels were well below the 0.33 ng/L limit and fall within the range that would be susceptible to signal noise. The difference in compounds that were detected with and without the inline filter also suggest external interferences present during different extraction dates rather than background contamination from the SPE-03 or inline filter.

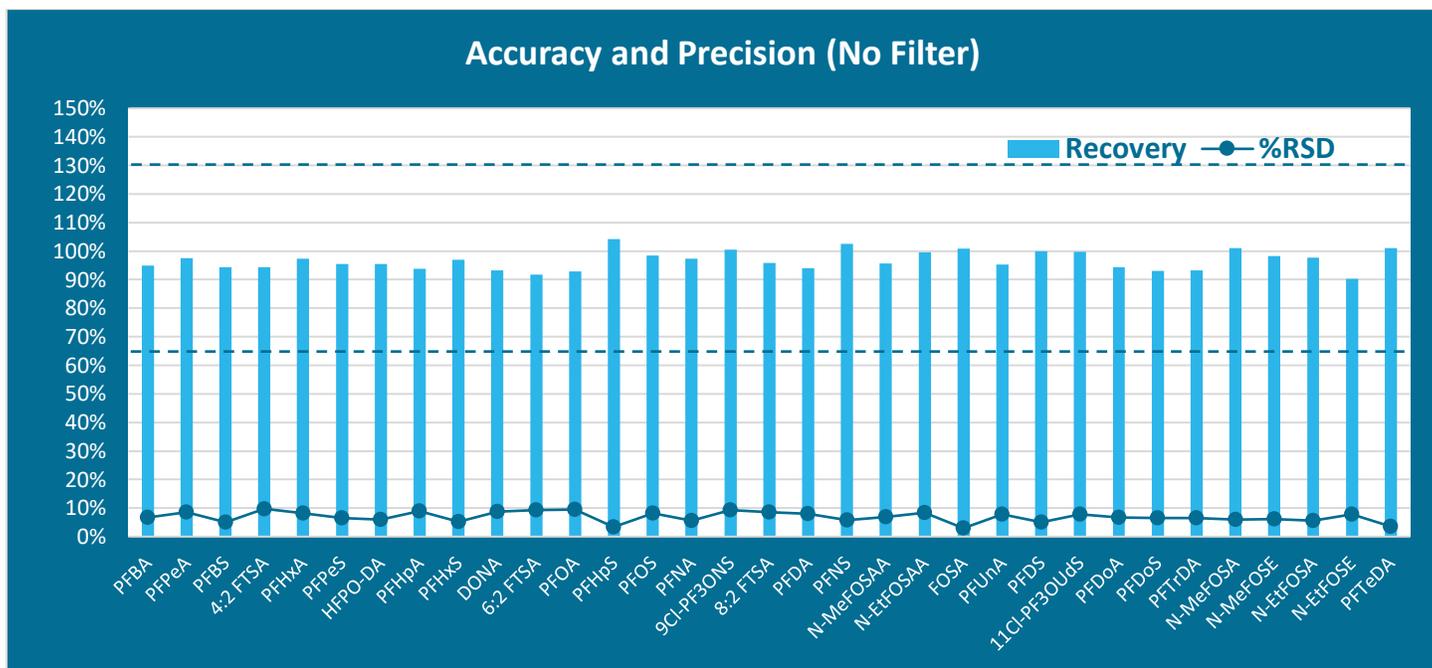
Figure 1 - Background levels with and without inline filters



Accuracy and Precision

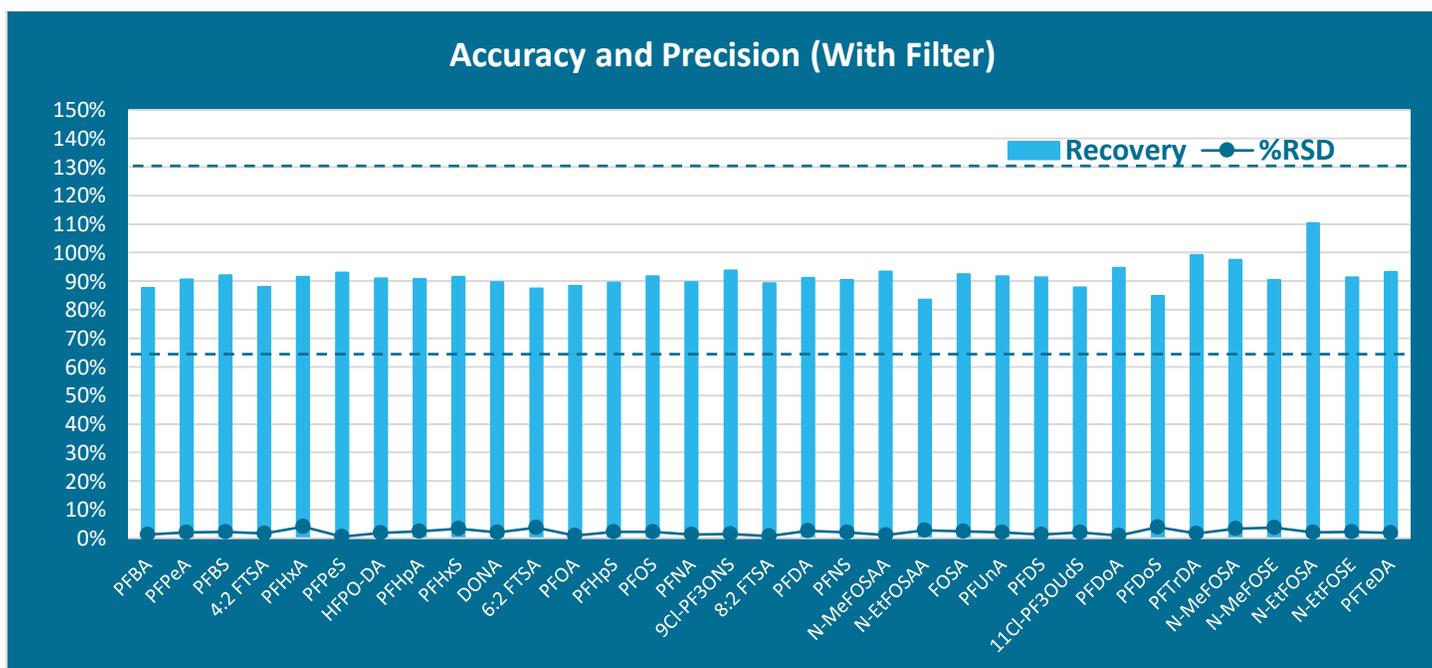
To demonstrate the SPE-03 performance using ISO 21675, 6 LFBs at 8 ng/L were extracted without inline filters. The average recovery was between 90% to 104% which falls well within the limits of 65% to 130% established by the Wisconsin Department of Natural Resources. %RSD was below 10% for each compound, showing good reproducibility.

Figure 2 - Average LFB Recoveries using SPE-03 (no filter)



4 LFBs at 8 ng/L were extracted with the same method and using inline filters. The average recovery was between 84% to 110%. According to the lab, the slightly lower recoveries compared to Figure 1 are within expected batch-to-batch variation. Nevertheless, the levels remained highly accurate. The %RSD was below 5% for each compound which demonstrated excellent consistency when using the inline filters.

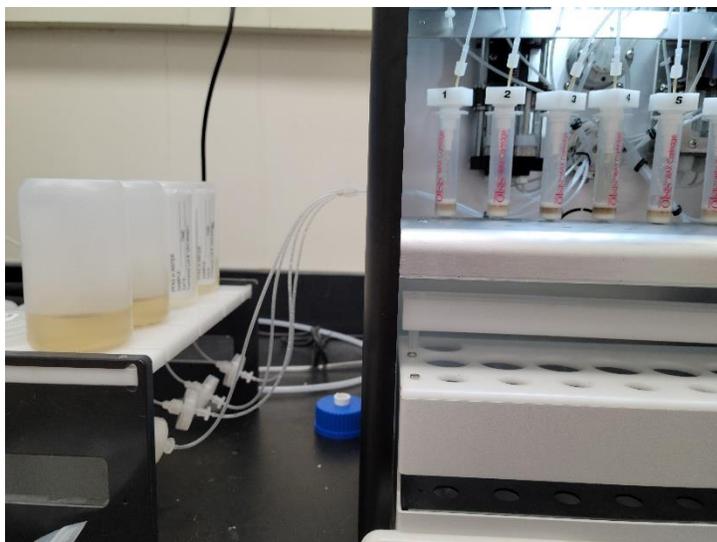
Figure 3 - Average LFB Recoveries using SPE-03 with inline filter



Effect of Field Sample Matrices

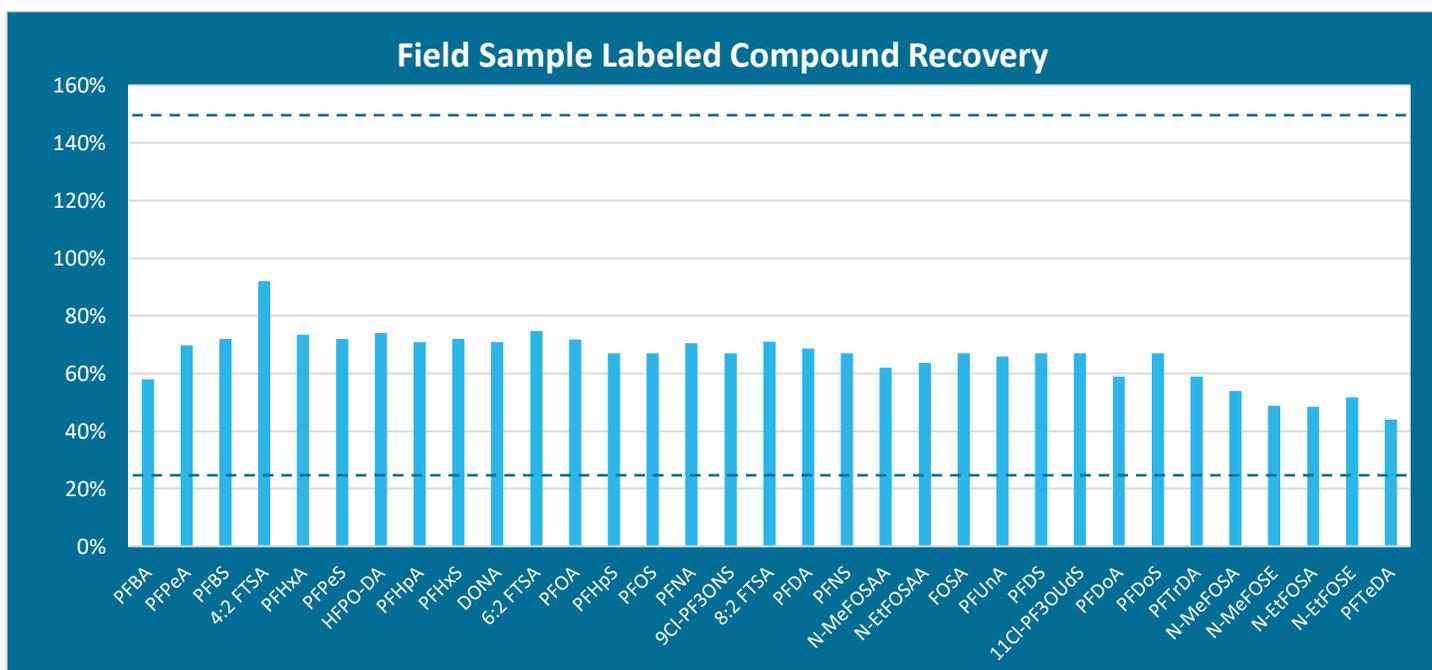
The high-capacity inline filters are connected to the sample lines of the SPE-03 as seen on the right. They serve to trap particulates as the samples are being extracted to prevent SPE cartridge clogging and protect moving parts on the automated extractor. For some applications, they even remove the need for a separate filtration step prior to extraction. During the bottle rinsing step, the elution solvent is pushed through the inline filters and drawn back, which recovers analytes that may be trapped in the filter material.

Below are the average labeled compound recoveries of 4 field samples extracted on 04/22/2022 using inline filters with the SPE-03.



The method limits for labeled compound recovery for field samples is 25% to 150%. The wide range is due to matrix effects that tend to suppress or enhance certain compounds.

Figure 4 - Average Labeled Compound Recovery of Field Samples using Inline Filter with SPE-03



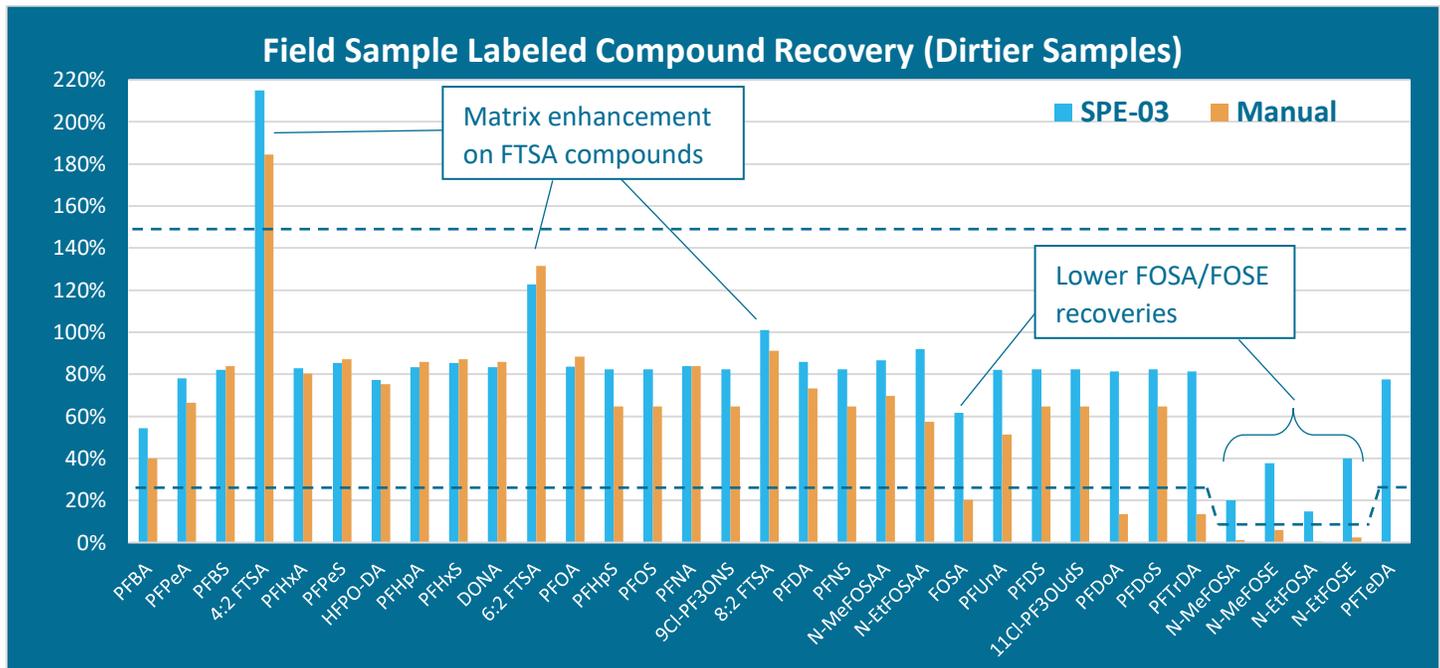
Despite minimal inconsistencies in the extraction procedure, it is observed that dirtier sample matrices can still cause compounds to fall out of range. Figure 5 shows the labeled compound recoveries of two surface water samples from different sources, one extracted on the SPE-03 and another using the vacuum manifold.

The response of all 3 fluorotelomers (4:2 FTSA, 6:2 FTSA and 8:2 FTSA) were enhanced, with increasing effect on shorter chains. This is quite commonly seen in non-potable field samples. In Wellington Labs' reference guide², it mentions that matrix effects can have a considerable impact on the ionization of fluorotelomer sulfonic acids.

The neutral FOSA and FOSE compounds tend to recover lower in dirtier matrices. From experience, these compounds are observed to be very adsorbent, making them difficult to elute or rinse off the sample bottles.

Sample particulates may exacerbate the problem by binding these compounds or retaining additional water in the sorbent material. The Wisconsin Lab of Hygiene sets the limits for these compounds to be 10% to 150%. The slow and controlled elution by the SPE-03 helps to optimize recoveries and the newer bottle shaking feature introduced in 2020 further improves the bottle rinsing.

Figure 5 - Labeled Compound Recovery of Field Samples Extracted on SPE-03 and Manual Manifold



For field sample labeled compound recovery failures, samples are re-injected into the LC-MSMS. The re-injection results are reported if recoveries improve. Otherwise, the original results are reported with comments pertaining to the failed labeled compounds. In the case where more than 5 labeled compounds have failing recoveries, re-extraction may be necessary.

CONCLUSIONS

PromoChrom’s SPE-03 system with high-capacity inline filters provides a simple and streamlined solution for extracting non-potable water samples. Together they have demonstrated clean background, excellent recovery and high reproducibility. Besides ISO 21675, the same solution can be used for the full range of non-potable matrices in draft EPA Method 1633 including soil and tissue extracts. Additionally, drinking water labs use inline filters for occasional samples that contain particulates.

References

1. ISO 21675 <https://www.iso.org/standard/71338.html>
2. Wellington Laboratories https://well-labs.com/docs/pfc_reference_handling_guide.pdf

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