Addressing PFAS Contamination: Troubleshooting Common Contamination And Instrument Problems

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Introduction

Due to the widespread presence of PFAS throughout the country and with the EPA recently adopting Maximum Contaminant Level's (MCLs) for PFOS, PFOA, PFNA, PFHxS, and HF-PODA. Accurately performing PFAS analyses while minimizing the impact of background contamination is becoming even more important and challenging. In tackling these issues, OCWD has resorted to new practices such as lot testing new consumables and new preventative maintenance schedules. These practices have helped to significantly reduce the amount of re-extraction, re-analysis and system downtime at the OCWD laboratory.

Materials and methods

Instrumentation

- Sample Prep
  - Automated: Promochrom SPE-03
  - Manual: 20-port Manifolds
  - Biotage TurboVap LV
- Analysis
  - SCIEX QTRAP 5500 & 6500+
  - Agilent LC 1260
  - CTC Analytics Pal HTC-xt

Methods

- EPA 537.1 and 533

Routine maintenance

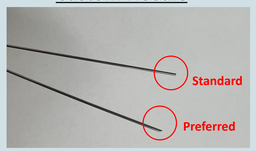
- Routine physical cleaning and solvent rinsing of automated extraction systems and manual SPE manifolds.
- Routine LC flushing and maintenance to reduce major system downtime and system background

Verifying consumable quality control

- Inspect instrument parts prior to installation for QC issues.
- During each extraction verify cartridges fit tightly to SPE-03 cartridge adaptors
- Testing of new solvents and reagents for contamination and issues affecting instrument response.
- Analyze a Reagent Blank and Laboratory Fortified Blank whenever a new lot of cartridges, centrifuge tubes, preservatives, sample bottles, etc. are received to test for contamination and other QC issues.

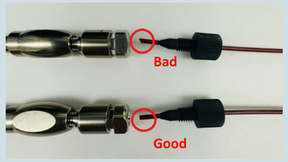
Quality Check Vendor Products

Custom Needle



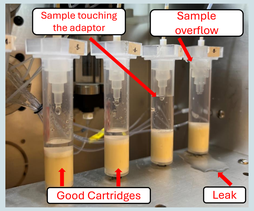
- 45-degree angle cut preferred
- When using standard flat cut, frequent needle clogging or bending was encountered when puncturing polypropylene caps

Peek tubing Connections



- Ensuring good peek tubing cuts and no void volume increased peak response by ~20%

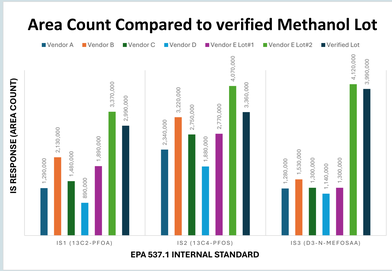
Loose Cartridges



Good Cartridges vs Loose Cartridges

- Some cartridges would not seal properly with the SPE-03 adaptors.
- During sample loading, loose cartridges would overflow or leak, resulting in possible low recovery or contamination.
- The loose cartridges may result in poor drying of the cartridges during the drying step after sample loading, leading to increased concentration time due to excess water.

Evaluating new lots of LCMS Grade Methanol



- New methanol lots were tested by replacing methanol bottle used for LC system with new bottle of test lot.
- Standards were then run on the LCMS system and response was compared to previous verified lot of methanol
- A significant change in internal standard response was observed between Vendor E Lot#1 and Lot#2, which originated from different countries.

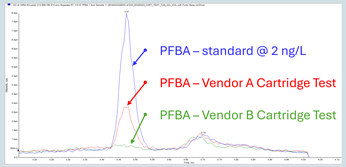
Consumable Contamination

a) EPA 533 mobile phase contamination

- The same ammonium acetate bottle was used to make mobile phase and preserve EPA 533 sample bottles.
- Frequent use of the same ammonium acetate bottle for mobile phase and sample preservation led to contamination.
- Separating the ammonium acetate used for mobile phase prep and sample preservation prevented further issues.

b) Contamination from consumables

- PFBA contamination in Cartridges
- Reagent blanks extracted to identify source of contamination



c) Carboy Water

- Milli-Q water is stored in 20 L Carboy vessels and water is tested using 533 and 537.1 analyses before use for Lab Quality Control samples and Field Reagent Blank.
- Water is replaced every 3 weeks

Preventative Maintenance

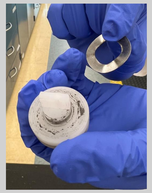
LCMS Maintenance

a) **LC Flush:** Periodically flushing LC system with water, a rinse solution (0.1% formic acid in 25% each of H2O,ACN, IPA, MeOH), and then methanol. This helps reduce high system baseline or background contamination observed after running dirty sample matrix, or from the installation of new LC valves and pump seals.

b) **Column Storage:** Flush mobile phase from column at the end of analysis and store in methanol (shortens equilibration for the next batch).

Symptom	Possible Cause	Recommended Action
Low or no response	Clogged syringe	Replace syringe barrel, plunger or needle.
	Clogged stator	Flush 6-port stator with methanol. Sonicate for stubborn clogs
	Needle penetration is not optimized	Adjust the needle penetration depth
High pressure	Particulates building up in sample flow path	Replace sample flow path PEEK tubing
		Replace column
Excessive carry over	Dirty syringe	Clean or replace the syringe
	Dirty or warped rotor	Replace rotor in injection valve
	LC injector valve failure	Valve that turns rotor can fail over time. Replace valve.
Contamination	TIS probe contamination	Probe needs to be replaced
	Front end contamination in MS	Clean curtain plate with Bar Keepers Friend and wipe with lint free cloth
Retention time shifting	Possible air bubbles in solvents	Prime solvent lines for at least 5 minutes
Tailing or fronting peak	Small leak in the column fitting	Disconnect the column and re-tighten the fitting

Automated SPE-03	
Daily before and after use	Rinse the system and prime solvent lines using extracting solvents
Weekly	Rinse the system using 1% Formic Acid in methanol
Monthly	Replace reagent and solvent bottles
Quarterly	Clean the valves, rotor and plunger
Yearly	PM and parts replacements according to the manufacture's recommendation
Manual Manifold	
Daily before and after use	Soak manifolds in hot soapy (Liquinox) water, then rinse using 10% HCl , DI water and then methanol



Dirty SPE-03 valve

Clogged cartridges

Conclusion

- Ensure all vendor products meet in-house quality standards by analyzing Reagent Blank and Laboratory Fortified Blank for all consumables prior to bulk ordering to avoid contamination, QC issues, supply chain issues, and maintain good response.
- Evaluate **each lot** of consumables because lot to lot performance of critical consumables can vary drastically (ex. Methanol).
- Perform routine SPE-03 maintenance and LC flushing to prevent re-extract and/or re-analysis due to background contamination in QC and samples.
- Inspect and replace high wear parts regularly (needle, syringe barrel, injector rotor, mobile phase frit, etc.) on instruments before they fail.

Acknowledgements

All OCWD Organic Staff

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