SHIMADZU
Excellence in Science

Where are my PFAS coming from?

Ruth Marfil-Vega, PhD

Senior Market Manager - Environmental

In today’s presentation

1. Why PFAS?
2. Experimental plan
3. Results
4. Conclusions
5. Q&A

Why PFAS?

Why PFAS?

A systematic evaluation of the sources of PFAS in the laboratory

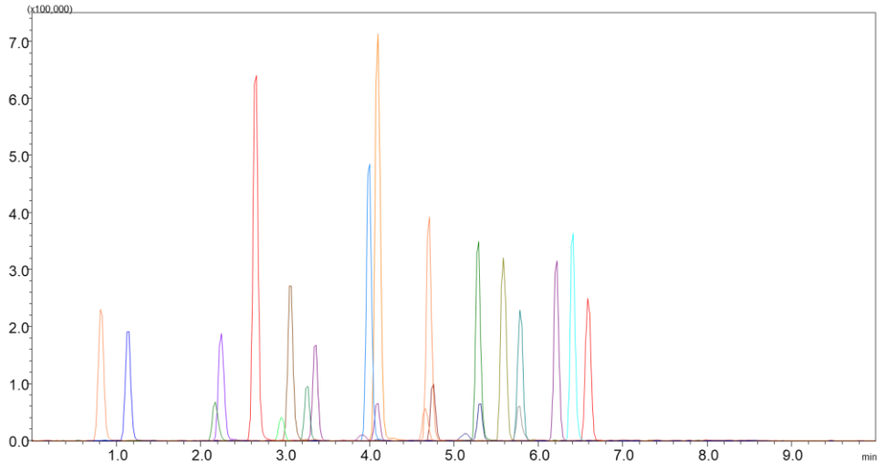
Experimental Plan

Tubing Type	With Degasser		Without Degasser	
	Without Delay Column	With Delay Column	Without Delay Column	With Delay Column
PEEK			✓	✓
FEP	✓	✓		
LLDPE	✓	✓	✓	

FEP: Fluorinated Ethylene Propylene

Experimental Plan

- **Targets – EPA 533.**
- **LC and MS conditions – listed in Table.**
  - ✓ Initial LC conditions: 5%, 10%, 20%, 30% B.
- **Equilibration times/sequence:**
  - ✓ Standard operation.
  - ✓ 30 min delay.
  - ✓ 120 min delay.

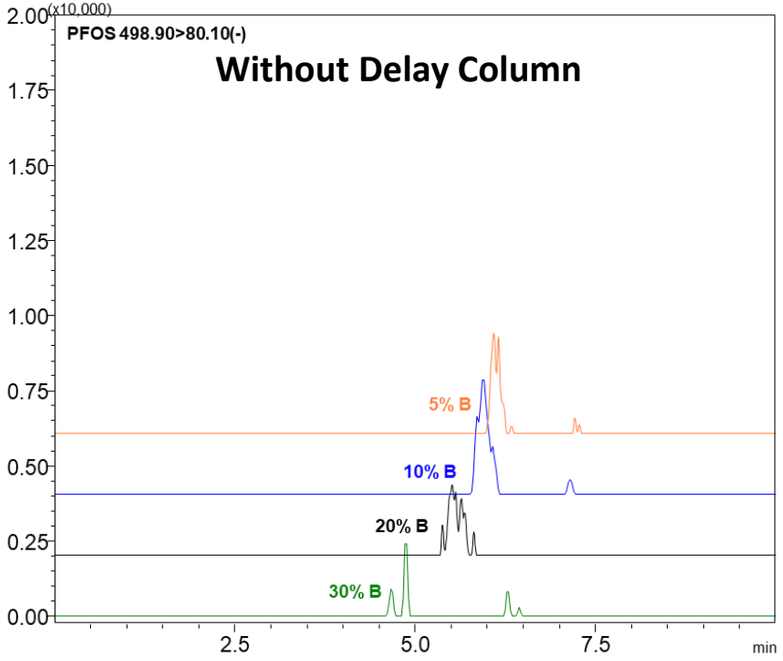


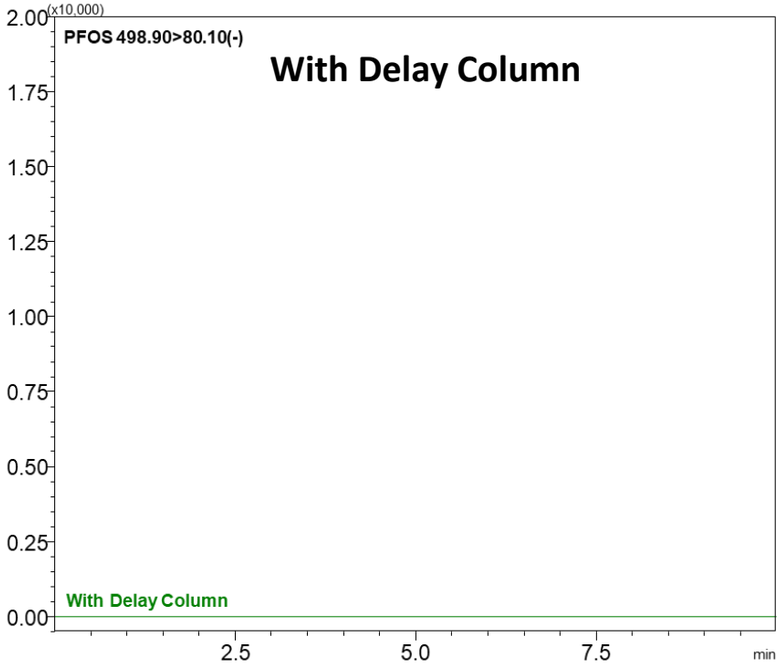
Shimadzu LCMS 8060	
Mobile Phase A	20 mM Ammonium Acetate in Water
Mobile Phase B	Methanol
Ionization Mode	ESI Negative
Analytical Column	Shim-pack Velox C18 (50 x 2.1, 1.8 µM)
Delay Column	Shimadzu Nexcol C18 (50 x 3.0, 5 µM)
Column Temperature	40 °C
Injection Volume	2 µL
Sample Temperature	8 °C
Interface Temperature	100 °C
Desolvation Temperature	160 °C

Specific results

- ✓ Blanks (80:20 MeOH:H2O):
  - ✓ 120 min equilibration time.
- ✓ LC conditions:
  5 %B, **10 %B**, **20 %B**, **30 %B**.

Tubing Type	With Degasser		Without Degasser	
	Without Delay Column	With Delay Column	Without Delay Column	With Delay Column
PEEK			✓	✓
FEP	✓	✓		
LLDPE	✓	✓	✓	

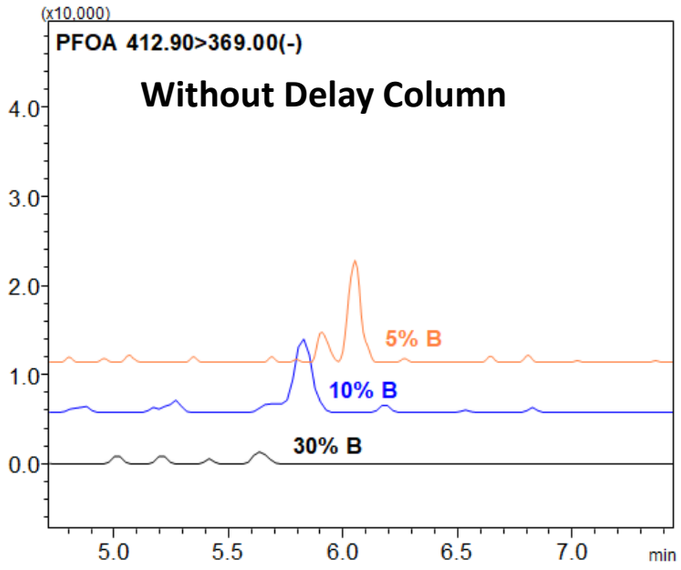


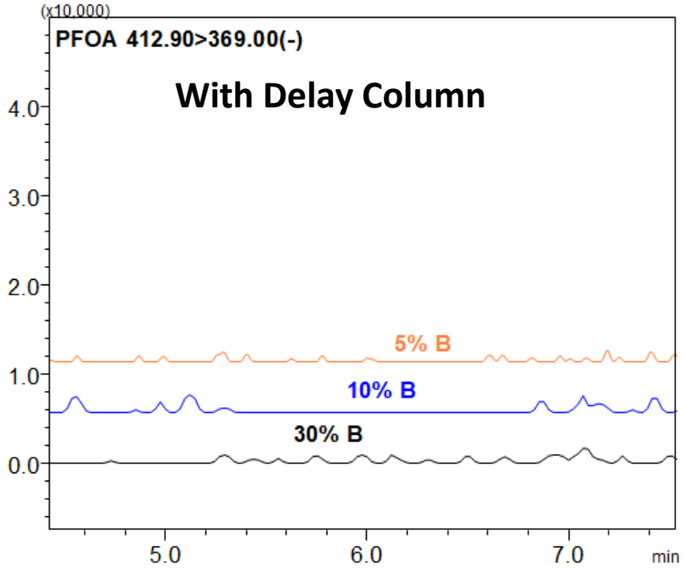


Specific results

- ✓ Blanks (80:20 MeOH:H2O) with 120 min equilibration time.
- ✓ LC conditions: **5 %B**, **10 %B**, **30 %B.**

Tubing Type	With Degasser		Without Degasser	
	Without Delay Column	With Delay Column	Without Delay Column	With Delay Column
PEEK			✓	✓
FEP	✓	✓		
LLDPE	✓	✓	✓	

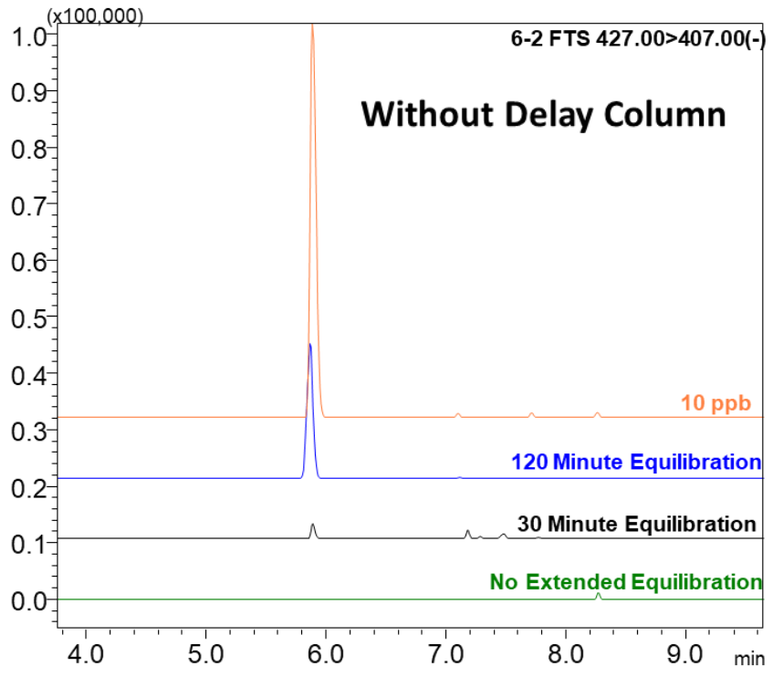


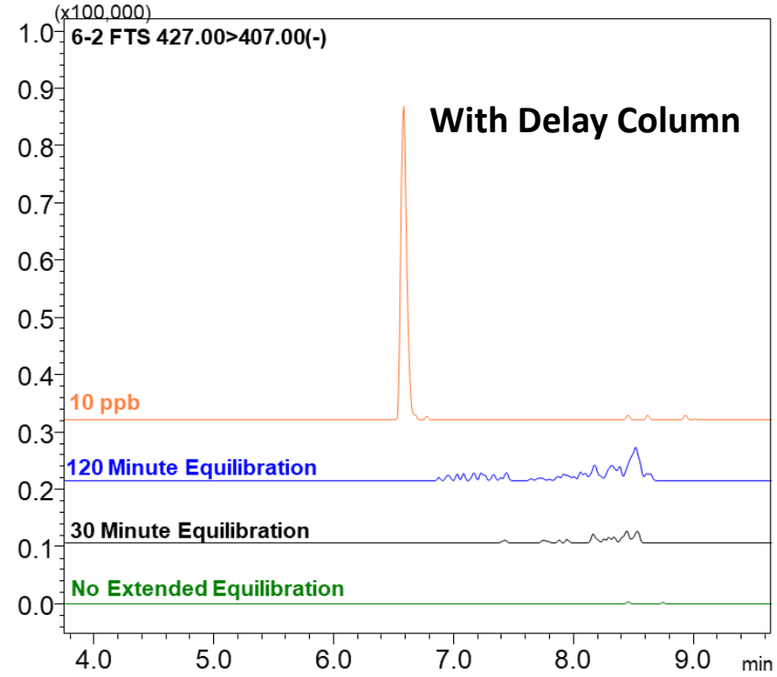


Specific results

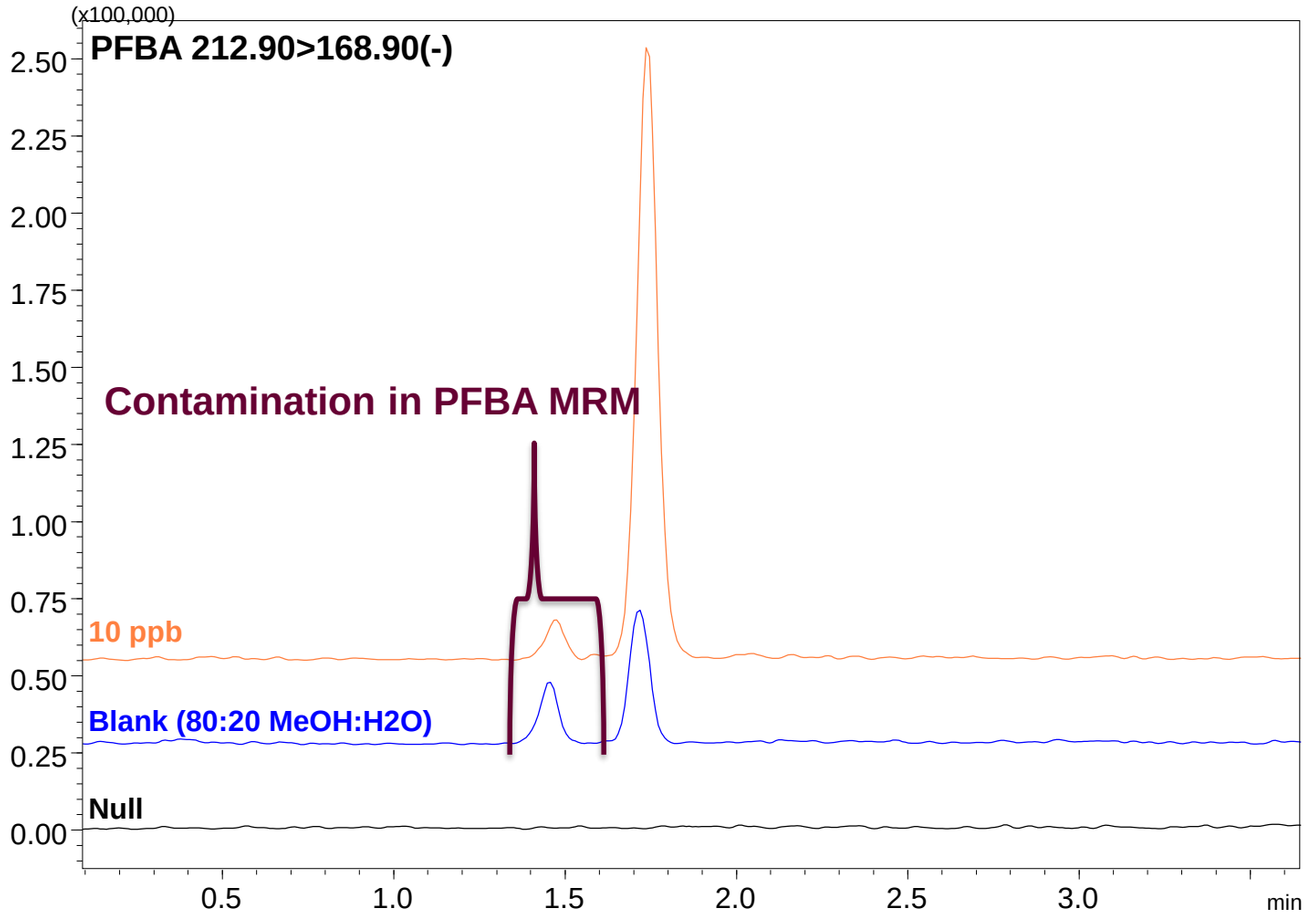
- ✓ Blanks (80:20 MeOH:H2O)
  - 120 min equilibration time
  - 30 min equilibration time
  - No extended equilibration time
- ✓ LC condition: **5%B**

Tubing Type	With Degasser		Without Degasser	
	Without Delay Column	With Delay Column	Without Delay Column	With Delay Column
PEEK			✓	✓
FEP	✓	✓		
LLDPE	✓	✓	✓	





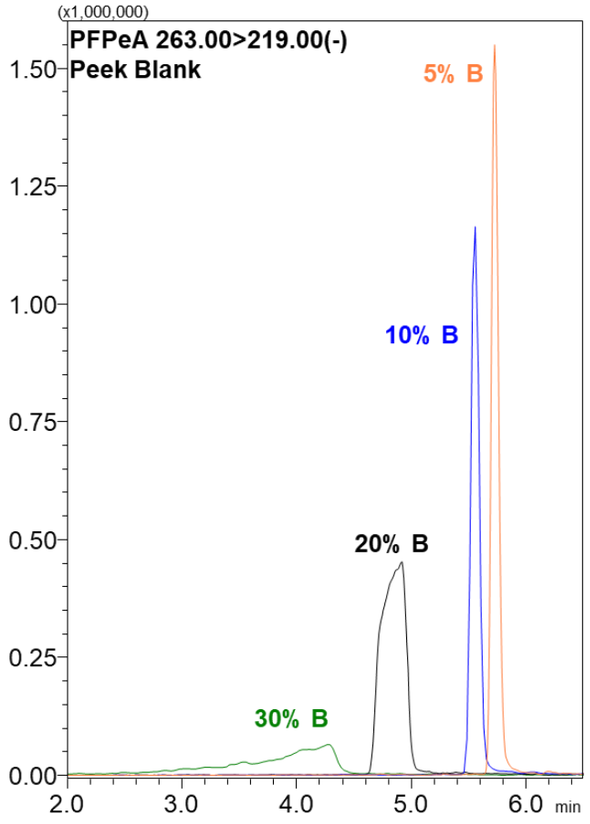
Overall results

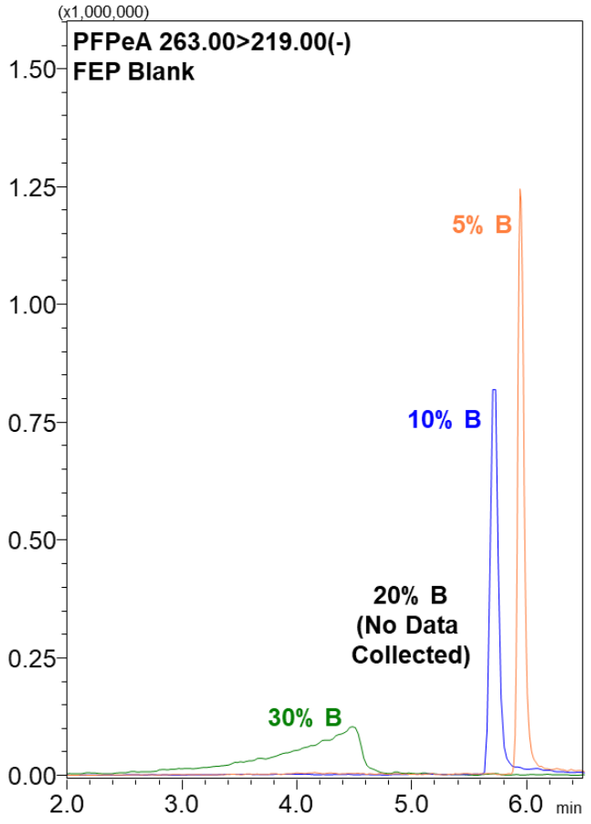


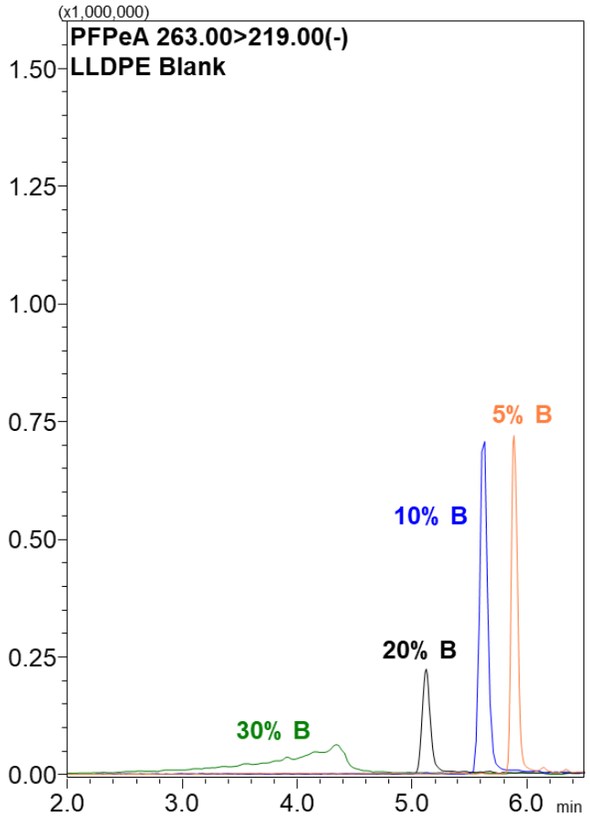
Contamination from PFBA comes from other sources different from LCMS or mobile phase.

Overall results

- Different tubing, no degasser, no delay column; blanks injected after 120 minutes of equilibration.



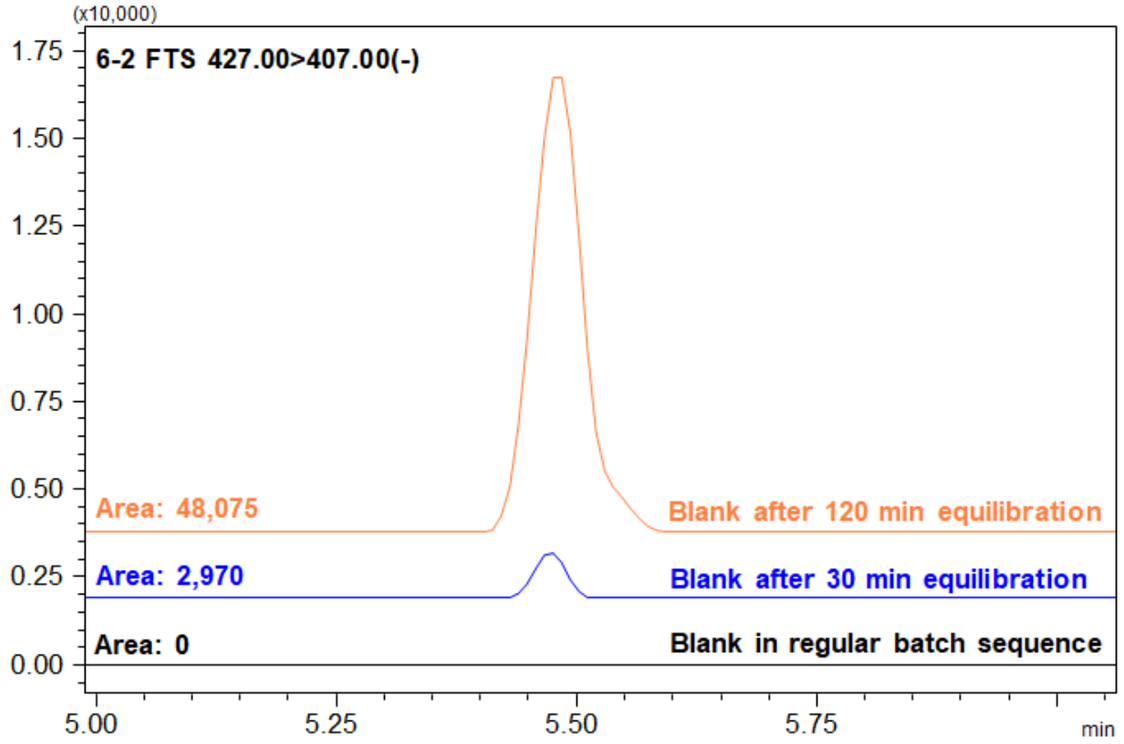




Contamination in PFPeA MRM in blank injections with three types of tubing tested.

Overall results

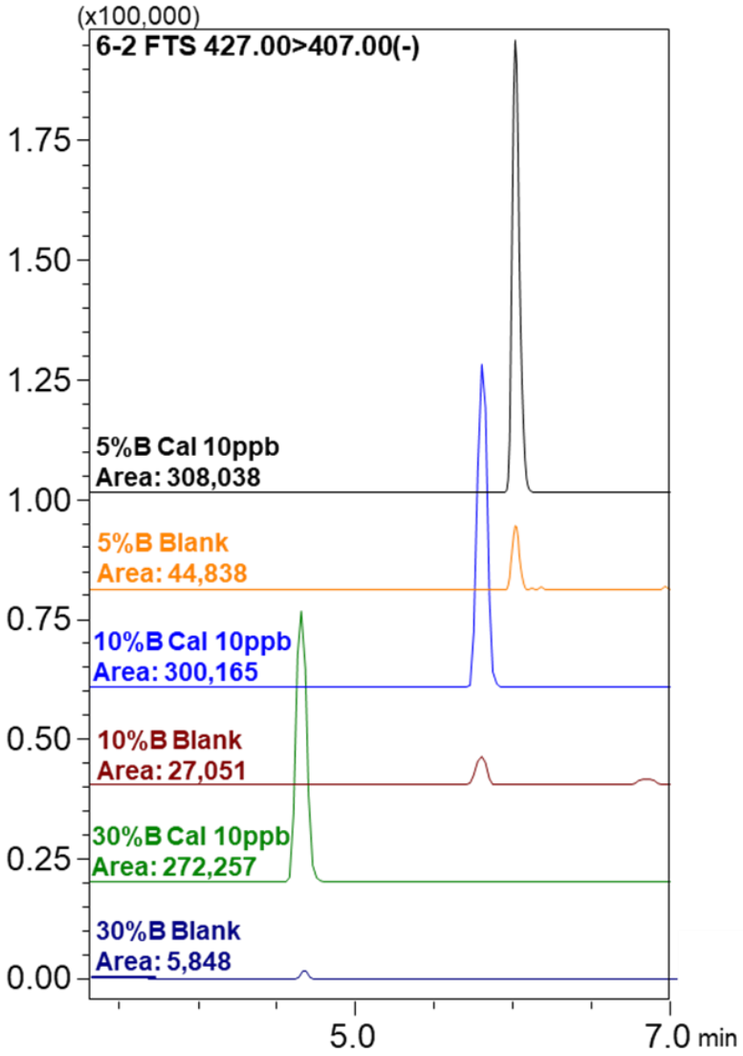
- Effect of LC equilibration time.



- ✓ Blanks (80:20 MeOH:H2O).
- ✓ FEP tubing, degasser, no delay column.

Area of background peaks increases with longer equilibration time before injection.

Overall results



- ✓ Standard (10 ppb in vial) with no equilibration time.
- ✓ FEP tubing, degasser, no delay column.
- ✓ LC conditions: **5 %B**, **10 %B**, **30 %B.**

Percent of organic reduces PFAS background without sensitivity loss.

- ✓ Blanks (80:20 MeOH:H2O) with 120 min equilibration time.
- ✓ FEP tubing, degasser, no delay column.
- ✓ LC conditions: **5 %B**, **10 %B**, **30 %B.**

Summary results

Compounds meeting identification criteria(*) in blanks after 120 min equilibration time, without delay column.

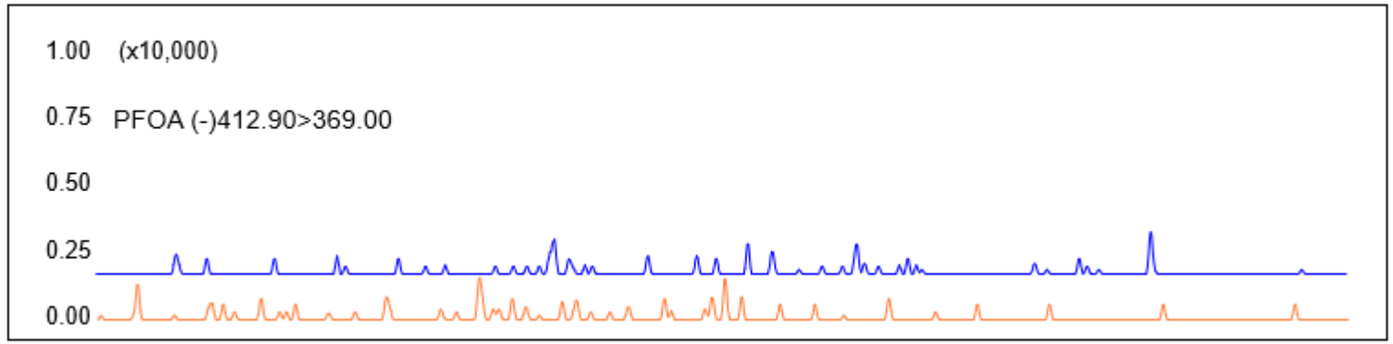
Tubing	PEEK (no degasser)				FEP (degasser)			LLDPE (no degasser)		
LC initial	5 %B	10 %B	20 %B	30 %B	5 %B	10 %B	30 %B	5 %B	20 %B	30 %B
PFHpA					X	X		X		
6-2 FTS	X	X	X		X	X		X	X	
PFOA	X	X			X	X		X	X	
PFNA	X	X	X		X	X	X	X	X	X
PFOS	X	X	X	X	X	X	X	X	X	X
PFDA	X	X	X	X	X	X	X	X	X	X
PFUnA	X				X	X	X	X	X	X
PFDoA	X				X	X		X	X	X

(*) Presence of primary MRM and RT within established window.

Targets included in EPA 533 NOT listed in this table: do not meet both identification criteria.

Future work

- Systematic evaluation of vials and caps, in combination with different LC configurations.



Comparisons of a polypropylene cap and vial (blue) to PTFE cap with silanized glass vial (orange).
Chromatogram from 30th consecutive injection of blank.

Conclusions

- ✓ All types of tested tubing (PEEK, FEP, and LLDPE) displayed PFAS compounds (targets from EPA 533).
- ✓ Presence or absence of in-line degasser did not significantly contribute to PFAS background in samples.
- ✓ Contamination was more severe with longer equilibration times before injection.
- ✓ Initial LC conditions can reduce PFAS background without significant loss in signal.
- ✓ Installation of delay column eliminates measurable PFAS background from all types of tubing tested (Non fluorinated tubing is not essential!).

Acknowledgments

Elizabeth Barnabe
& Christopher Gilles

Ruth Marfil-Vega, PhD
rmmarfilvega@shimadzu.com

Visit OneLabOneEarth.com