Systematic Study of Techniques to Minimize PFAS Background Interferences

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1. Introduction

Public concern over PFAS has spurred efforts by EPA, FDA, etc. to standardize PFAS quantification methods in various environmental samples. However, analyzing these ubiquitous contaminants with LC-MS is challenging due to pervasive lab-based PFAS contamination, compromising accuracy. Common culprits include LC components, solvents, and consumables. Achieving sub-ppt level accuracy requires a combination of measures, including rigorously evaluated consumables and a delay column (like Schematic 1) used with a sensitive LCMS system. While other measures are important, the delay column is crucial for minimizing background PFAS interference. It should: 1) have minimal backpressure, 2) reliably delay PFAS, 3) be stable at high pressures, and 4) offer excellent reproducibility. This research will assess the impact of delay columns and consumables on EPA methods 533, 537.1, and 1633.

2. Method

We used a reversed phase method (**Table 1**) using a gradient coupled with the Shimadzu LCMS-8060NX triple quadrupole mass spectrometer to analyze PFAS. Multiple reaction monitoring (MRM) was employed to quantify PFAS for all analyses. We chose EPA method 1633 to evaluate the various delay columns. (**Table 2**) This EPA method was chosen as it monitors the most PFAS analytes among the EPA regulatory methods. System background and blank injections were used to evaluate the PFAS present from the system and consumables employed in this study. The best delay column was then applied to methods from previous EPA methods 533 and 537.1 to evaluate the suitability of the delay column and consumables specifically selected for these workflows.

Table 1 Method conditions for EPA 1633.

Instrument	LCMS-8060NX	Mobile Phase A	2 mM Amm. Ace.
Anal. Column	Scepter C18-120 (50x2.0mm; 3 µm)	Mobile Phase B	Acetonitrile
Delay Column	Nexcol PFAS Delay (50x3.0mm; 5 µm)	Oven Temp.	40 °C
Flow Rate	0.4 mL/min	Run Time	14 min
Inj. Vol.	2 µL		

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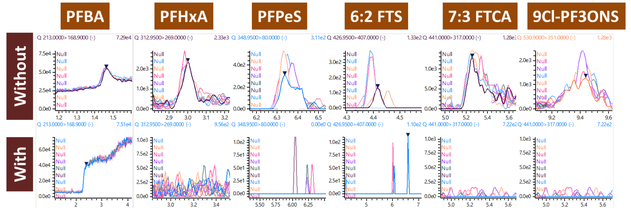
3. Results

For this study, we used EPA method 1633 to evaluate the importance of using a delay column and which type of delay column worked best. System background checks were performed with and without a delay column (**Figure 1**). This highlights the necessity of utilizing a delay column, so that background interferences are pushed outside of the MRM window. It also negates the necessity of employing PFAS-free tubing kits that often require bypassing the degasser, which causes other consequences like poor baseline stabilization due to air bubbles.

Figure 1 Common PFAS from null injections with and without a delay column

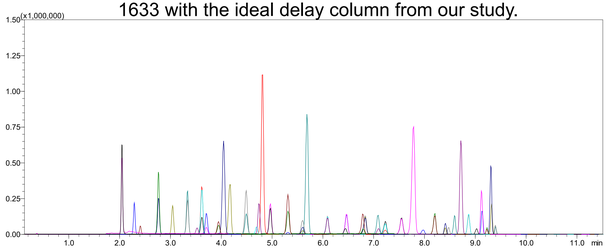


After showing the benefit that came from a utilizing a delay column, we evaluated several different delay columns to optimize our method. We discovered that particle size made little difference in the performance of the delay column. The ideal column contributed minimal back pressure but was able to withstand high pressures so that future method improvements could be employed. It was also crucial for the first eluting PFAS, PFBA, to have good peak shape and have low background. **Table 2** outlines the relative outcomes of our column study. The Nexcol PFAS delay column was the best performer overall. In field tests, the Nexcol PFAS delay column exhibited excellent column lifetime and robustness.

Table 2 Study of five different delay columns.

Delay Column	Dimensions (L x D; particle size)	Frit Housing	Max P	Back P	PFBA asymm	Resilience
Delay 1	100 x 2.1 mm; 3 µm	PEEK	+++	+	+++	+
Delay 2	50 x 2.1 mm; 3 µm	PEEK	+++	++	+	+
Delay 3	50 x 3.0 mm; 3 µm	PEEK	++	+++	+++	++
Delay 4	50 x 3.0 mm; 5 µm	PEEK	+	+++++	+++	+++
Nexcol Delay	50 x 3.0 mm; 5 µm	Stainless	++++	++++	+++	++++

Figure 2 Chromatogram showing good performance for EPA method 1633 with the ideal delay column from our study.

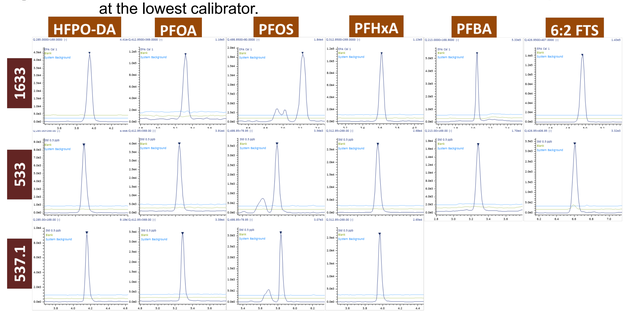


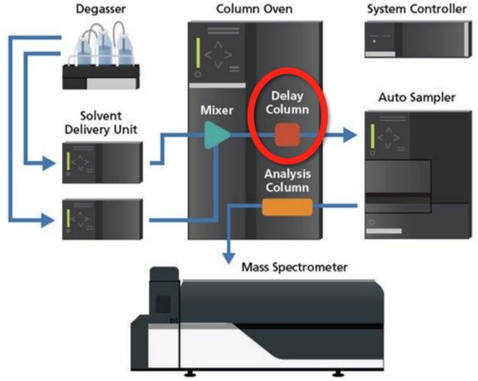
After optimizing the delay column, consumables and method for EPA method 1633 (**Figure 2**) we then investigated whether these consumables would be suitable for EPA methods 533 and 537.1. As part of our optimization, we rigorously evaluated sample vials, vial caps, solvents, additives, glassware and micropipette tips.

Confident in our method improvements of EPA 1633, we applied these optimizations to EPA methods 533 and 537.1 and determined whether they would be suitable for these methods as well. We determined that these consumable choices were also compatible with EPA 533 and 537.1.

This finding meant that we could employ the same delay column and consumables for EPA methods 533, 537.1 and 1633 **(Figure 3).** We do note however, that the analytical columns are still unique for each method.

Figure 3 Common PFAS from EPA 533, 537.1 and 1633 with Nexcol Delay Column at the lowest calibrator.





4. Conclusions

- The best performing delay column we was the Nexcol PFAS delay column (220-91394-09). It was suitable for use in EPA methods 533, 537.1 and 1633. PFBA peak shape was excellent.
- Consumables must be rigorously regularly evaluated for PFAS contamination to ensure that sub-pt levels of sensitivity can be achieved.
- PFAS delay columns negate the necessity for tubing kits.