Evaluation of LC/MS/MS Method Parameters for High Sensitivity PFAS Analysis

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Introduction

Two methods were developed based on EPA methods 533 and 537.1, which support the analysis of PFAS in drinking water. The EPA methods allow flexibility in the method conditions. A number of parameter settings were evaluated to determine the best sensitivity of the compounds. These settings included MS interface temperatures, MS probe position, and mobile phase additive concentrations. The system and a number of vials and caps were evaluated for PFAS contamination. These included glass and polypropylene vials, as well as polyethylene, polypropylene, silicone, and PTFE lined silicone caps. Identified sources of PFAS contamination will be discussed in more detail.

Method

Final MS interface settings:
Capillary position: +1 mm
Interface Temperature: 100ºC
DL/HB Temperature: 150ºC/250ºC
Mobile Phase A/B: 5 mM Ammonium Acetate in Water/Methanol
Conditions as listed in the Method Package

Capillary positioning experiment

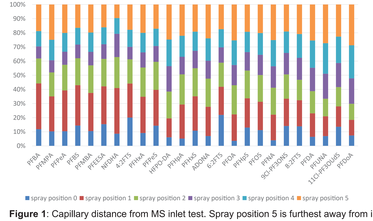


Figure 1: Capillary distance from MS inlet test. Spray position 5 is furthest away from inlet. Compounds arranged according to elution times.

Spray positions of 1 and 5 mm were found to provide the best overall sensitivities. Generally, spray position 1 was optimal for early eluting compounds and spray position 5 was optimal for late eluting compounds. A spray position of 1 was chosen for the analysis since it is a common positioning of the capillary.

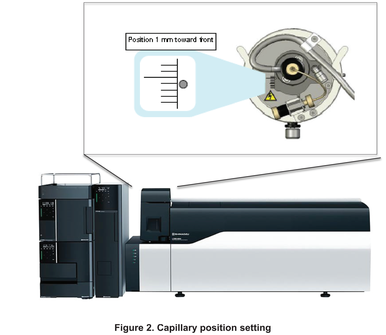


Figure 2. Capillary position setting

Interface Temperature experiment

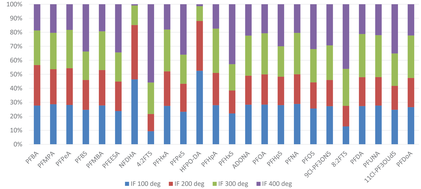


Figure 3. Interface temperature test

There was a variation in sensitivity for the compounds depending on the interface temperature. However, two compounds (HFPO-DA and NFDHA) showed significantly less sensitivity with higher interface temperatures. For that reason, it seems best to keep the MS interface temperature lower (100-200 degrees C).

Desolvation Line/Heat Block experiment

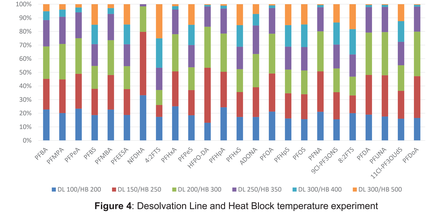


Figure 4: Desolvation Line and Heat Block temperature experiment

Higher DL and HB temperatures had a negative effect on the sensitivity of a number of compounds. It seems best to keep DL/HB temperatures lower, ie 150/250°C respectively.

Mobile Phase additive test

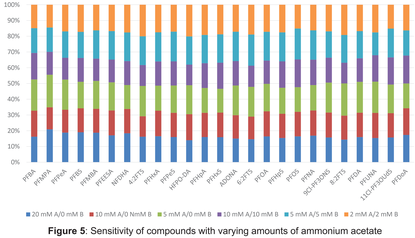


Figure 5: Sensitivity of compounds with varying amounts of ammonium acetate buffer in A:Water and B: Methanol

Large differences in PFAS compound sensitivities were not observed with varying concentrations of buffer. A final concentration of 5 mM was chosen for mobile phase A, and no added buffer was chosen for mobile phase B (methanol)

Contamination

The evaluated system included a delay column and modified tubing to minimize PFAS contamination. A number of glass, silanized glass, and polypropylene vials were tested and showed no PFAS contamination. PFBS contamination was observed with one particular glass vial and PFBS levels would increase with a second injection from the vial. The contamination was traced back to the vial septa. Polypropylene vials are recommended for analysis, but care must be taken regarding sample solvent evaporation.

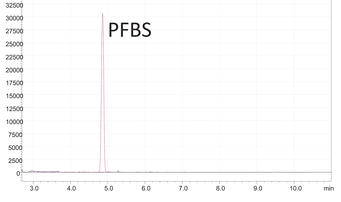


Figure 6: PFBS contamination observed from blank sample.

Carryover

NMeFOSAA and NEtFOSAA, specific to EPA 537.1, showed higher levels of carryover than other compounds. An extended MeOH rinse at the end of the analysis was used to reduce these values.

Crosstalk

Crosstalk occurs when leftover ions pass through the final quadrupole of the next transition that have similar product ions. This can result in reporting incorrect values for the PFAS compounds. Shimadzu uses sweeper technology to prevent this occurrence.

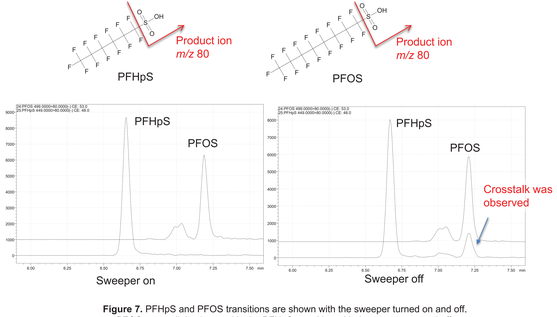
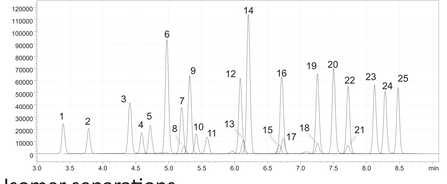


Figure 7. PFHpS and PFOS transitions are shown with the sweeper turned on and off. PFOS crosstalk is observed in the PFHpS transition with the sweeper turned off.

Final Method Chromatograms

After MS optimization, methods were developed based on the found settings. EPA methods 533 and 537.1 allow chromatographic modifications but isomer separations and peak asymmetry requirements must be met. The below chromatograms were obtained with the optimized method conditions.

EPA 533



1	PFBA
2	PFMPA
3	PFPeA
4	PFBS
5	PFMBA
6	PFEESA
7	NFDHA
8	4:2 FTS
9	PFHxA
10	PFPeS
11	HFPO-DA
12	PFHpA
13	PFHxS
14	ADONA
15	6:2 FTS
16	PFOA
17	PFHpS
18	PFOS
19	PFNA
20	9Cl-PF3ONS
21	8:2 FTS
22	PFDA
23	PFUNA
24	11Cl-PF3OUdS
25	PFDoA

Isomer separations

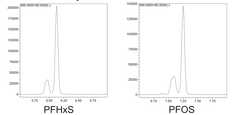
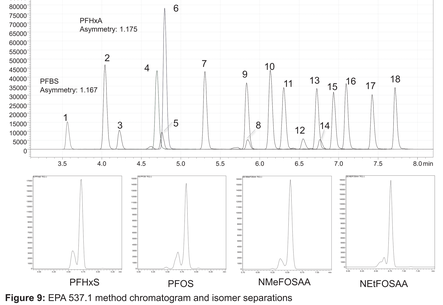


Figure 8: EPA 533 method chromatogram and isomer separations

EPA 537.1



1	PFBS
2	PFHxA
3	HFPO-DA
4	PFHpA
5	PFHxS
6	ADONA
7	PFOA
8	PFNA
9	PFOS
10	9Cl-PF3ONS
11	PFDA
12	NMeFOSAA
13	PFUNA
14	NEtFOSAA
15	11Cl-PF3OUdS
16	PFDoA
17	PFTrDA
18	PFTA

Figure 9: EPA 537.1 method chromatogram and isomer separations

Summary and Conclusions

Optimized parameter settings and issues found in the development of EPA 533/537.1 methods were presented. Method development was performed on an LCMSMS system that included a PFAS delay column and modified tubing to reduce PFAS contamination issues. Low interface temperatures were required to maintain sensitivities of NFDHA and HFPO-DA. Heat block and desolvation line temperatures should also be kept at lower temperatures to maintain sensitivities. Elution times for the final compound were 8.5 minutes for EPA 533 and 7.7 minutes for EPA 537.1. Required isomer separations and EPA 537.1 peak asymmetry requirements of 0.8 to 1.5 were met with the method conditions.