

Using a Compact Single Quadrupole LC-MS for PFAS Analysis

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1. Introduction

◆ There is a growing concern in measuring and removing per- and polyfluoroalkyl substances (PFAS) in the environment. Most PFAS applications require the sensitivity and specificity of a triple quadrupole mass spectrometer. However, using a triple quadrupole mass spectrometer presents higher maintenance costs and more laboratory space. Single quadrupole mass spectrometers can also measure PFAS and their small footprint integrates easily into active HPLC systems. Single quadrupole mass spectrometers can be used in many PFAS-related applications, such as evaluating PFAS removal by novel treatments, monitoring remediation, or adding capability to detect emerging contaminants.

◆ This study demonstrates the use of a compact single quadrupole mass spectrometer for PFAS analysis where adherence to regulated methods is not required.

2. Methods

The 28 PFAS standards were purchased through Wellington Laboratories using two mixes (PFAC-MXJ and PFAC-MXH) at concentrations ranging from 1 to 20 $\mu\text{g/mL}$. The standards were further diluted in 50:50 methanol:water with 0.1% acetic acid to create the calibration standards. Acidified diluent has shown to improve PFAS peak shape.

The Shimadzu Nexera LC and the LCMS-2050 were set up for PFAS analysis using a delay column (Fig. 1). The delay column was important for the prevention of native PFAS in the system and mobile phases from interfering with the sample analysis. Chromatography and LCMS-2050 source parameters are provided in Table 1. A DUIS ionization, combining ESI and APCI techniques, was used for the analysis.

A scan event with a m/z range of 50 - 750 was established to monitor the targeted standards. In the same acquisition, selected ion monitoring (SIM) channels were also set up for each PFAS analyte for the ease of quantitation. The $[\text{M}-\text{H}]^-$ ions were automatically generated based on the chemical formula in the acquisition method.

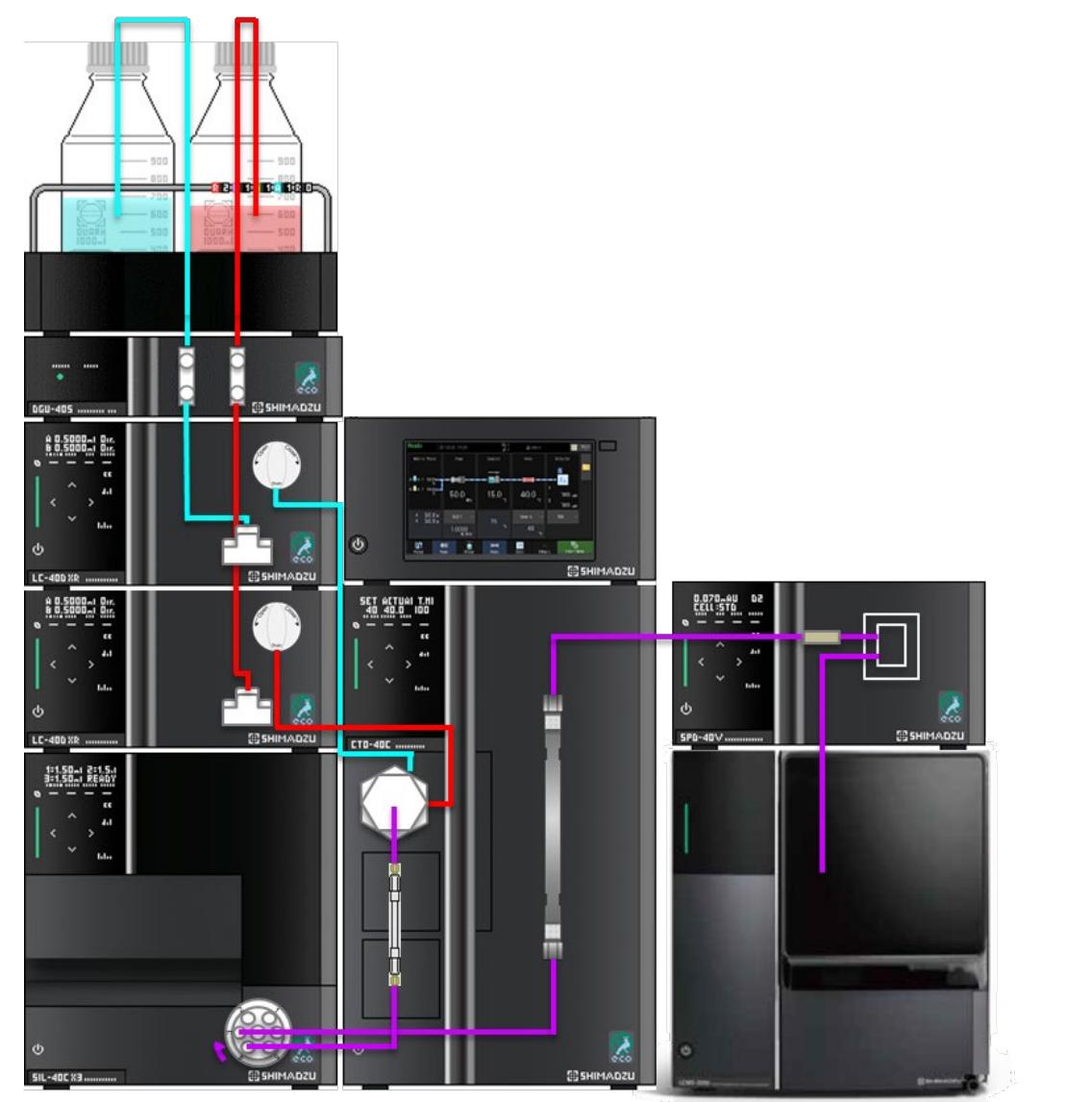


Fig. 1 Illustration of the delay column set up on the compact single quadrupole LC-MS.

Table. 1 Chromatography and optimized LCMS-2050 source parameters used.

Nexera LC		LCMS-2050	
Flow Rate:	0.4 mL/min	Nebulizing Gas:	2 L/min
Oven Temp.:	40 °C	Drying Gas:	5 L/min
Injection Vol.:	1 μL	Heating Gas:	7 L/min
Mobile Phase:	A: 5 mM Ammonium acetate in water B: Methanol	Desolvation Temp.:	350 °C
Delay Column:	Shim-pack GIST C18, 5 μm , 3.0 \times 50 mm	DL Temp.:	200 °C
Analytical Column:	Shim-pack Velox C18 50 \times 2.1mm	Ionization Source:	DUIS

3. Results

◆ A total of 28 components were detected using LC/MS (Fig. 2). The linear calibration range is reported in Table 2 with %accuracy between 80 – 120%. The %RSD area for the lowest calibrator were below 12% ($n = 4$).

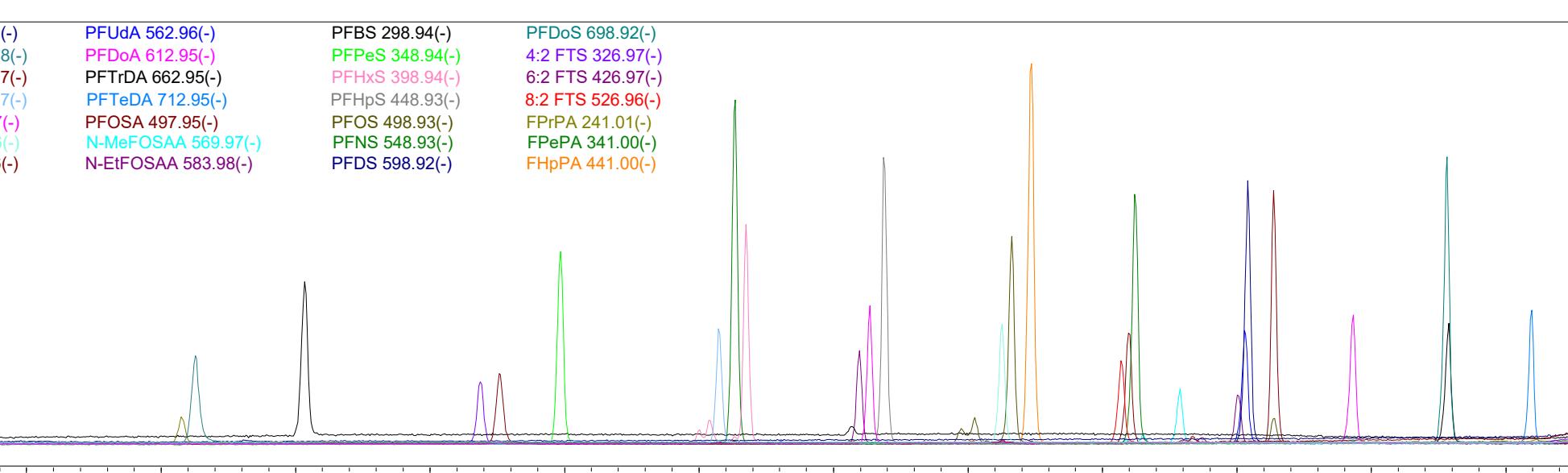


Fig. 2 Representative chromatogram of the 28 PFAS targets at 200 ng/mL using SIM acquisition.

◆ Representative LOQ chromatograms of each analyte are shown in Figure 3. The LOQ is defined as the lowest end of the linear range with S/N greater than 10. Quantitative analysis was done with SIM acquisition. The hardware allowed simultaneous acquisition of multiple SIM and Scan events without sacrificing data quality. The inclusion of the scan event did not hinder the separation and quantitation of the PFAS, which demonstrates the additional benefit of scanning for degradation products and obtaining additional mass information which can only be achieved by a mass spectrometer.

Table. 2 Calibration curve of the 28 PFAS analytes with the reported linear range, %accuracy, and the %RSD area of the lowest calibrator.

PFAS	[M-H] ⁻	Linear Range (ng/mL)	R ²	Accuracy (%)	LOQ %RSD (Area)
PFBA	212.98	2.0 - 80	0.998	85.5 - 108.6	7.5
PFPeA	262.98	1.0 - 40	0.999	88.0 - 109.3	2.1
PFHxA	312.97	0.5 - 20	0.999	90.2 - 107.6	6.6
PFHpA	362.97	0.5 - 20	0.999	84.0 - 115.1	6.9
PFOA	412.97	0.5 - 20	0.999	85.5 - 111.2	7.7
PFNA	462.96	0.5 - 20	0.999	87.8 - 111.1	3.4
PFDA	512.96	0.5 - 20	0.999	86.1 - 108.5	4.3
PFUdA	562.96	0.5 - 20	0.999	85.0 - 109.6	7.6
PFDoA	612.95	0.5 - 20	0.999	91.4 - 113.0	2.2
PFTrDA	662.95	0.5 - 20	0.999	86.3 - 111.7	8.4
PFTeDA	712.95	0.5 - 20	0.999	86.6 - 112.3	7.7
PFOSA	497.95	0.2 - 20	0.999	87.3 - 114.2	7.5
N-MeFOSAA	569.97	1.0 - 20	0.998	81.9 - 116.0	3.2
N-EtFOSAA	583.98	1.0 - 20	0.999	90.4 - 113.4	5.6
PFBS	298.94	0.5 - 20	0.999	89.0 - 112.6	6.0
PFPeS	348.94	0.2 - 20	0.999	85.7 - 109.1	8.1
PFHxS	398.94	0.2 - 20	0.999	84.6 - 109.3	6.5
PFHpS	448.93	0.1 - 20	0.999	82.0 - 113.1	5.7
PFOS	498.93	0.5 - 20	0.999	87.0 - 115.7	8.1
PFNS	548.93	0.2 - 20	0.999	85.5 - 111.2	4.7
PFDS	598.92	0.2 - 20	0.999	82.5 - 115.1	4.8
PFDs	698.92	0.2 - 20	0.999	81.1 - 109.8	5.4
4:2 FTS	326.97	2.0 - 80	0.999	85.9 - 111.6	2.6
6:2 FTS	426.97	2.0 - 80	0.994	90.0 - 119.0	3.3
8:2 FTS	526.96	2.0 - 80	0.999	81.5 - 116.0	5.9
FPrPA	241.01	2.0 - 40	0.999	88.2 - 111.3	8.8
FPePA	341.00	1.0 - 200	0.999	83.3 - 112.4	8.9
FHpPA	441.00	1.0 - 200	0.999	86.5 - 114.5	4.8

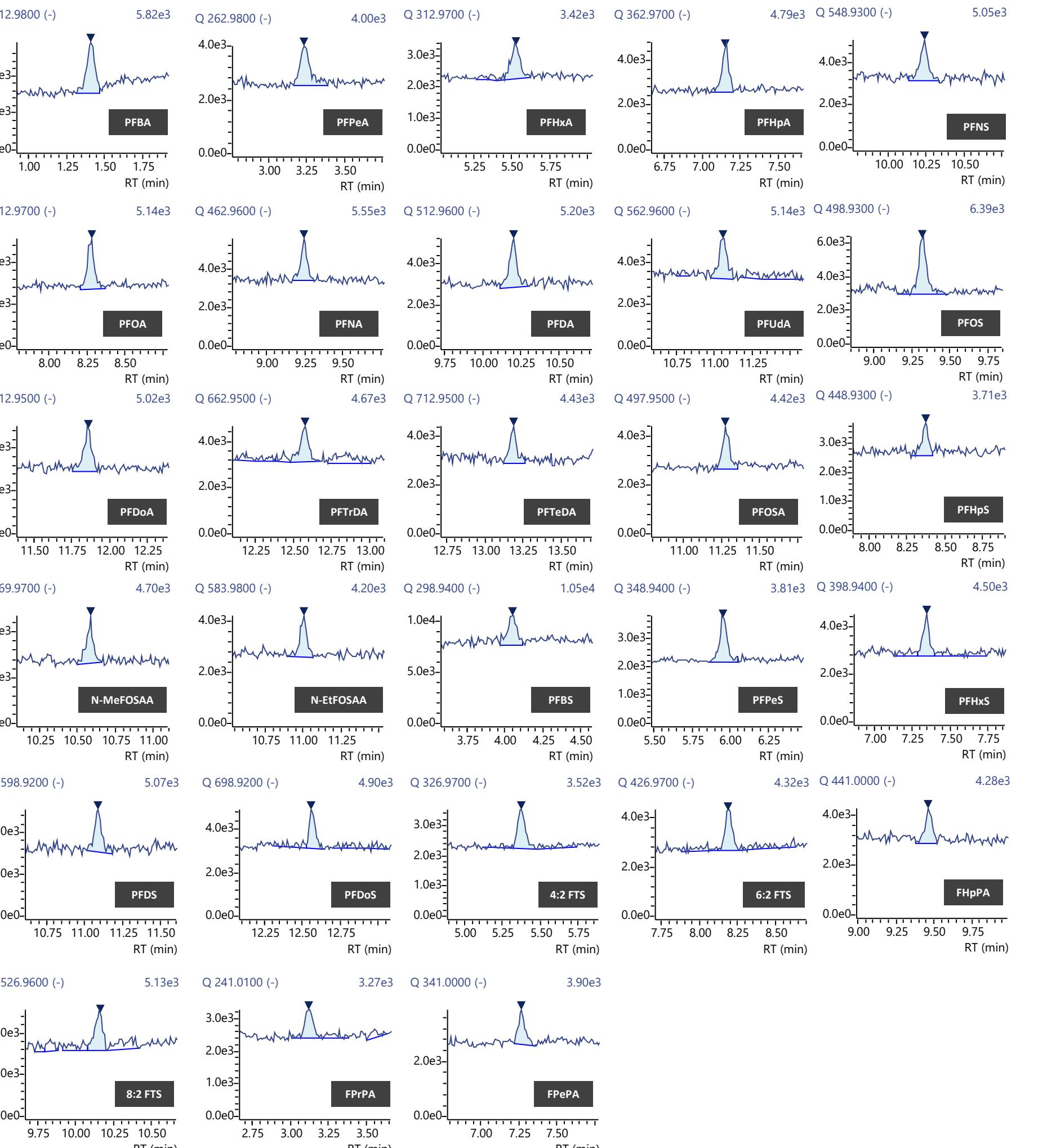


Fig. 3 Representative chromatograph at LOQ for each PFAS analyte. The LOQ concentration can be found in Table 2.

4. Conclusion

◆ The Shimadzu LCMS-2050 compact single quadrupole mass spectrometer was successfully employed for the accurate separation and quantitation of 28 commonly studied PFAS. These results demonstrate the accessible, effective, and cost-effective Shimadzu LCMS-2050 for measuring PFAS for applications such as determining PFAS removal by current and novel treatment technologies.

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