

# LC-MS/MS analysis using direct injection of legacy and emerging PFAS in soils and sediments

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## INTRODUCTION

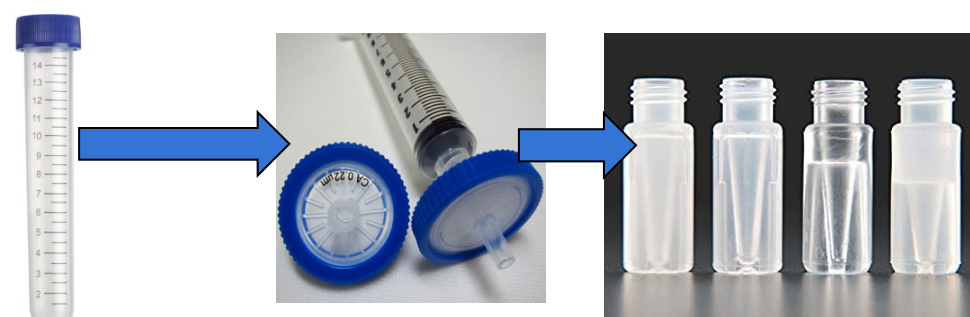
Perfluoroalkyl substances (PFAS) are common, man-made, persistent environmental contaminants that are used in the production of many consumer products as non-stick coatings, surfactants, and for stain and water resistance coatings. PFAS are also a major component of fire fighting foams used for suppression of fuel fires. Global widespread use of these compounds over many decades has led to their release into the environment. Their chemical properties make them bioaccumulative and they are found in all types of environmental samples, including water and soil. Current advisory guidelines around the globe require parts per trillion (ppt) detection of PFAS in various types of environmental samples.

An approach based upon direct injection of a large sample volume was developed for the determination of a wide range of legacy and emerging (e.g. GenX, ADONA, F53-B) PFAS compounds in soils. This approach utilizes little sample preparation and requires a highly sensitive mass spectrometer for detection. By simplifying the sample preparation step, sample throughput can be drastically increased as well as reducing chances for sample contamination from inherent PFAS in typical laboratory supplies. The performance and scope of the method makes it a suitable approach for the testing of soil samples for a wide range of PFAS, legacy and emerging, at relevant concentrations.

## METHODS

### Sample Preparation

Soil samples were provided by the United State Environmental Protection Agency (USEPA). Samples included sand, silt, fat clay, and lean clay spiked with unknown concentrations of PFAS before receiving. 2 g of each sample were provided in a 15 mL Eppendorf tube. Sample preparation was performed in accordance to ASTM 7968, which is described in **Figure 1**.



2 g sample (soil) + 10 mL 1:1  
Water:Methanol  
Adjust pH to ~9-10  
Shake 1 hour

**Figure 1.** Overview of the sample preparation method used for all soil samples.

### Instrumental Conditions

UPLC System: ACQUITY UPLC® I-Class PLUS fitted with PFAS Kit  
Column: CSH Phenyl Hexyl 2.1x100 mm, 1.7µm

Mobile Phase A: 95:5 water:methanol + 2 mM ammonium acetate

Mobile Phase B: Methanol + 2 mM ammonium acetate

Column Temp: 35°C

Sample Temp: 4°C

Strong Needle Wash: 90:10 methanol:water

Week Needle Wash: 50:50 water:methanol

Injection Volume: 30 µl

Gradient:	Time (min)	Flow (mL/min)	% A	% B
	-	0.3	100	0
	1	0.3	80	20
	6	0.3	55	45
	13	0.3	20	80
	14	0.4	5	95
	17	0.4	5	95
	18	0.3	100	0
	22	0.3	100	0

Mass Spectrometer: Xevo TQ-XS

Ionization Mode: ES-

Capillary Voltage: 1.0 kV

Desolvation Temp: 500°C

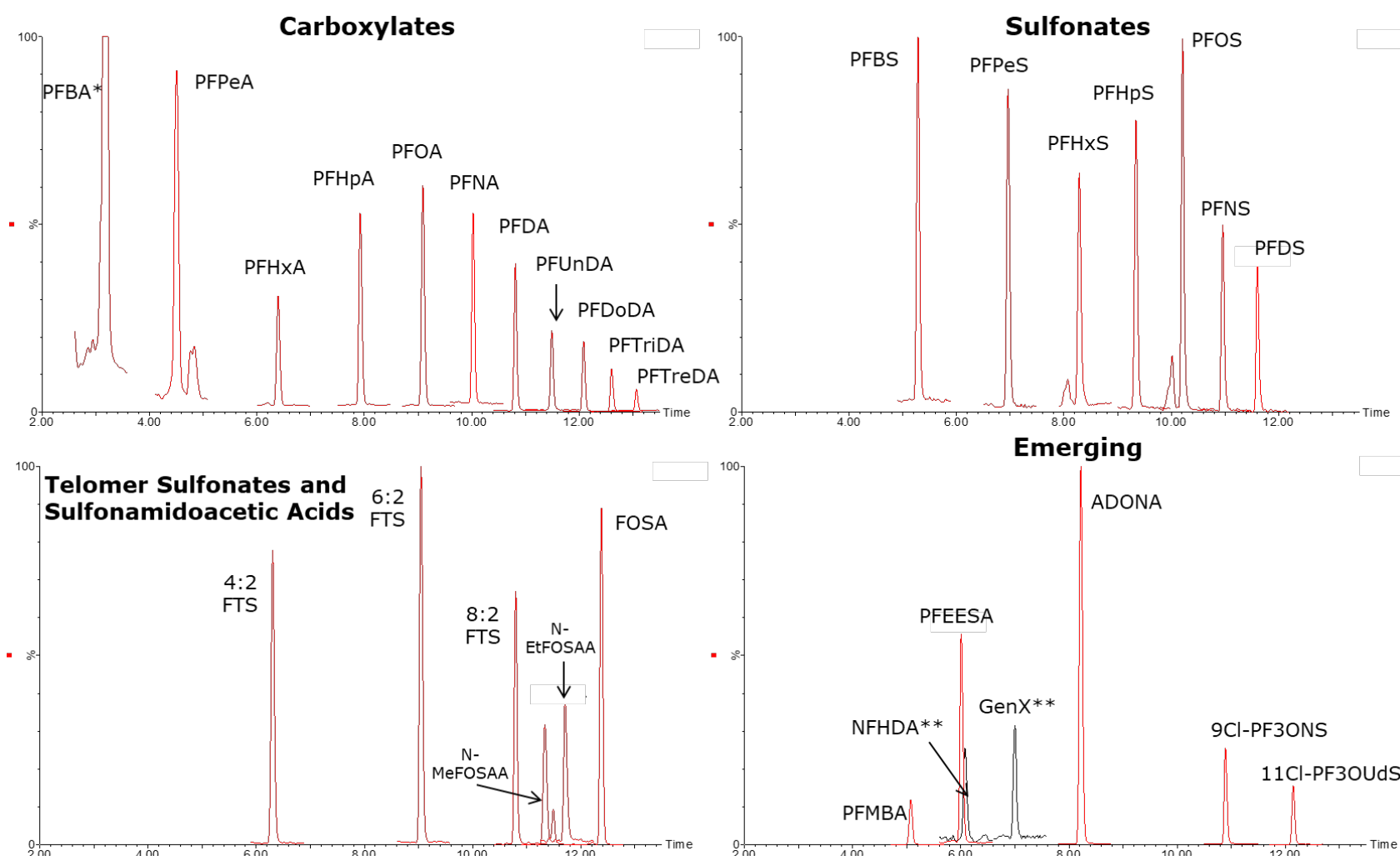
Desolvation Gas Flow: 1100 L/hr

Cone Gas Flow: 150 L/hr

Source Temperature: 100°C

## RESULTS AND DISCUSSION

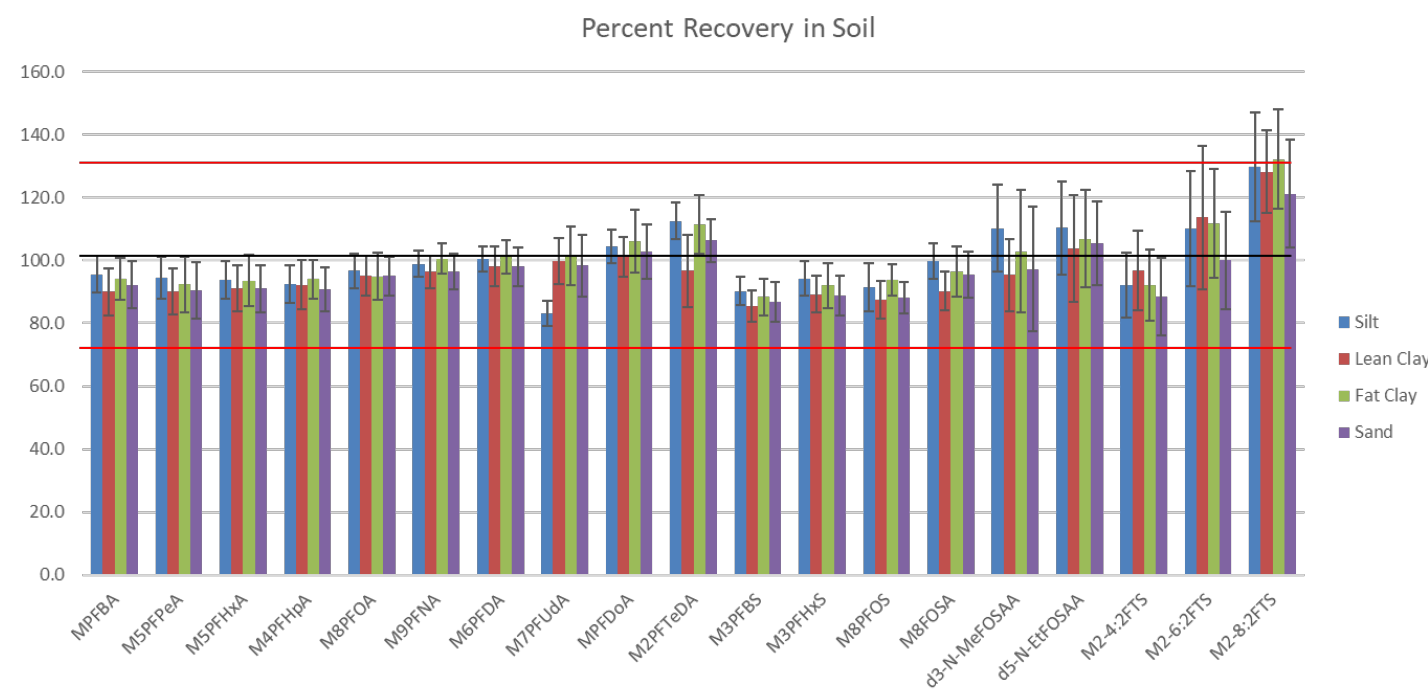
Samples provided were spiked with both a low and high unknown concentration of PFAS prior to receiving them. After completing the analysis and submitting results, it was reported that all PFAS spiked into the samples were detected in both the low and high concentration spikes. **Figure 2** shows an example of all the PFAS detected in the low concentration level spike of a lean clay sample.



**Figure 2.** All PFAS compounds detected in low concentration spiked lean clay sample. (\*\*) these compounds shown zoomed.

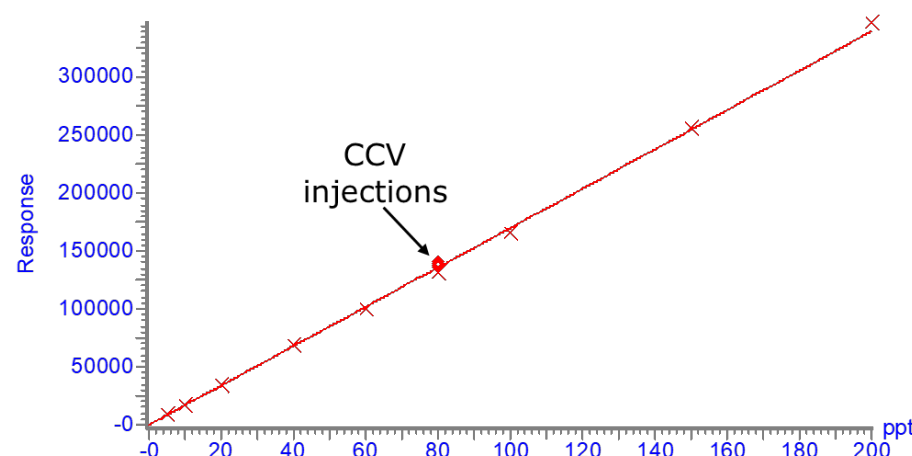
Recovery for the soil samples was assessed using isotope labelled surrogate standards spiked prior to sample preparation. **Figure 3** shows the recovery of each surrogate used in all four soil types evaluated. Overall recoveries were all within the range of 70 - 130%, adhering to the recovery guidelines of the ASTM 7968 method.

Method robustness was assessed using continuing calibration verification (CCV) standards injected after every 10 matrix samples. The CCV was a mid point concentration in the calibration curve. Throughout the 36 hour sample set, six CCV injections were run. These samples are graphed on the calibration curve in **Figure 4**. The CCV samples overlay the mid level calibration point and overlay each other without any shifts in calculated concentration demonstrating the method is robust.



**Figure 3.** Recoveries for each isotope labelled surrogate standard in all four soil types evaluated (n=3).

## CONCLUSIONS



**Figure 4.** Six continuing calibration verification (CCV) injections run over a sample set of approximately 36 hours graphed on the calibration curve to demonstrate the stability and reproducibility of the instrument using this method.

- Direct injection methods, such as ASTM 7968, allow for quick sample turnaround time due to minimal sample preparation.
- The direct injection approach works well for soil matrices.
- Results meet and exceed the ASTM method requirements.
- The large volume direct injection method used on the Xevo TQ-XS was extremely sensitive with method detection limits for most compounds in the low ng/kg range for soils.
- All targeted PFAS compounds were detected in the soil samples analyzed at both low and high concentrations with excellent recovery and reproducibility.
- The direct injection approach is suitable for both legacy and emerging PFAS.

