SHIMADZU

WP 137

Robustness Evaluation of PFAS Analysis in Soil Using LC-MS/MS

Yui Higashi[1]; Nami Iwasa[1]; Kazuhiro Kawakami[1]; Riki Kitano[1]; Evelyn Wang[2]; Ruth Marfil-Vega[2]; Yuka Fujito[1]
(1) Shimadzu Corporation, Kyoto, Japan; (2) Shimadzu Scientific Instruments, Columbia, Maryland

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are widely used in various fields and industries. However, due to their structural stability and resistance to degradation, they accumulate in the environment and are suspected of being harmful to humans. PFAS in soil can accumulate in the human body via agricultural products, thus it is essential to develop sensitive and robust analytical methods for the detection of PFAS in soil with complex matrices.[1]

This study shows a robustness evaluation by adding 30 PFAS to a soil matrix and using the LCMS-8060RX to measure these PFAS in the soil matrix 500 consecutive times.

2. Methods

For this analysis, LC-MS/MS equipped with a newly designed ESI source was used, and a delay column was installed between the mixer and the autosampler to inhibit the effects of PFAS contamination from the LC system. Six points calibration curves were built, and each calibration point was measured 3 times. A soil sample was prepared referring to part of the soil preparation procedures published by the National Agricultural and Food Research Organization.[2] Thirty PFAS compounds were spiked to the soil sample at 0.1 µg/L after pretreatment and 500 soil sample analyses were performed for the robustness evaluation. This sample contains more than 90% soil matrix. QC samples were also analyzed after every 20 injections of the soil samples.

Table 1 Analytical Conditions

UHPLC (Nexera™-X3 System)	
Analytical Column:	Shim-pack Scepter™ C18-120 (100 mm × 2.1 mm I.D., 1.9 µm, P/N: 227-31012-05)
Solvent Delay Column:	Delay column for PFAS (GL Science, P/N 5020-90005)
Mobile Phase A:	2 mM Ammonium Acetate in reagent water
Mobile Phase B:	Methanol
Gradient Program:	B 1 % – 50 % (2.0 min) – 100 % (11.0 – 15.0 min) – 1 % (15.1-20.0 min)
Flowrate:	0.3 mL/min
Column Temp.:	40 ° C
Injection Volume:	5 µL
Run Time:	20 min
MS (LCMS™-8060RX)	
Ionization:	ESI (Negative mode)
Mode:	MRM
Nebulizing Gas:	3 L/min
Drying Gas Flow:	5 L/min
Heating Gas Flow:	15 L/min
DL Temp.:	200 °C
Block Heater Temp.:	300 ° C
Interface Temp.:	250 ° C
Probe Position:	+3 mm

Fig. 1 LCMS™- 8060RX

3. Analysis of Standards

Thirty PFAS, including 5 major PFAS (PFOA, PFOS, PFHxS, PFNA, and HFPO-DA), were successfully separated in about 12 minutes with good peak shape (Fig. 2).The correlation coefficients of the calibration curve were greater than 0.996 in the concentration range of 0.01 - 10 µg/L for most compounds. The accuracies were within 70 to 130 %, and the %RSDs of the area were less than 20 % for all concentrations of the calibration curve. (Fig.3)

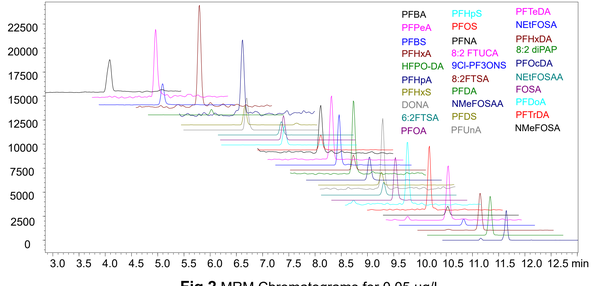

Fig.2 MRM Chromatograms for 0.05 µg/L

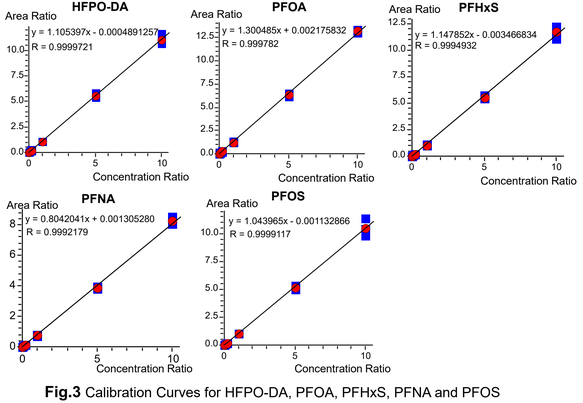

Fig.3 Calibration Curves for HFPO-DA, PFOA, PFHxS, PFNA and PFOS

4. Robustness Evaluation with a Soil Matrix

Fig. 4 shows the normalized peak areas of five major compounds (HFPO-DA, PFOA, PFHxS, PFNA, and PFOS) in the spiked soil sample and peak area repeatability was good. Good peak shapes were obtained at the start and end of the 500 analyses（Fig. 5）. Table 2 shows the %RSD and the detection limit in the soil matrix sample (based on the 500 consecutive injections) for all 30 target PFAS. Peak area repeatability was good with %RSD below 8.5 for all target compounds. Recovery from the QC samples was within 80 to 120 % for all target compounds for the duration of the 500 consecutive injections (Fig. 6).

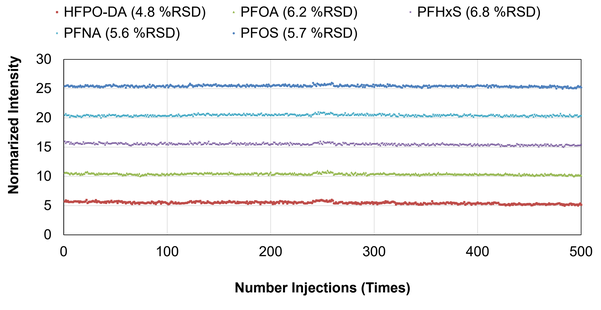

Fig. 4 Peak Area Repeatability (n = 500) for the Soil Sample Spiked to 0.1 µg/L (Concentration in Solution)

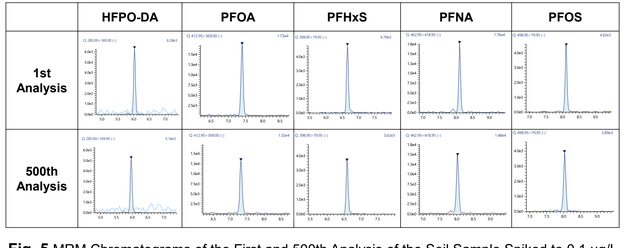

Fig. 5 MRM Chromatograms of the First and 500th Analysis of the Soil Sample Spiked to 0.1 µg/L (Concentration in Solution)

Table 2 Peak Area %RSD, Detection Limit , and Mean Recovery for the Soil Sample Spiked to 0.1 µg/L (Concentration in Solution)

#	Compound	Peak Area %RSD (n = 500)	Detection Limit in the Soil Matrix Sample (µg/L) (n = 500)	#	Compound	Peak Area %RSD (n = 500)	Detection Limit in the Soil Matrix Sample (µg/L) (n = 500)
1	PFBA	5.4 %	0.013	16	PFDA	7.0 %	0.016
2	PFPeA	5.2 %	0.012	17	NEtFOSAA	7.0 %	0.016
3	PFBS	5.0 %	0.012	18	PFOS	5.7 %	0.013
4	PFHxA	5.9 %	0.014	19	PFUnA	7.7 %	0.018
5	HFPO-DA	4.8 %	0.011	20	9Cl-PF3ONS	7.0 %	0.016
6	PFHpA	5.0 %	0.012	21	PFDoA	6.4 %	0.015
7	DONA	4.9 %	0.011	22	FOSA	6.9 %	0.016
8	6:2FTSA	6.8 %	0.016	23	PFDS	6.9 %	0.016
9	PFOA	6.2 %	0.014	24	PFTrDA	5.9 %	0.014
10	PFHxS	6.8 %	0.016	25	PFTeDA	5.9 %	0.014
11	8:2 FTUCA	6.0 %	0.014	26	NMeFOSA	6.7 %	0.016
12	PFNA	5.6 %	0.013	27	8:2 diPAP	7.3 %	0.017
13	PFHpS	7.7 %	0.018	28	PFHxDA	5.5 %	0.013
14	8:2FTSA	8.5 %	0.020	29	NEtFOSA	6.3 %	0.015
15	NMeFOSAA	5.7 %	0.013	30	PFOcDA	8.3 %	0.019

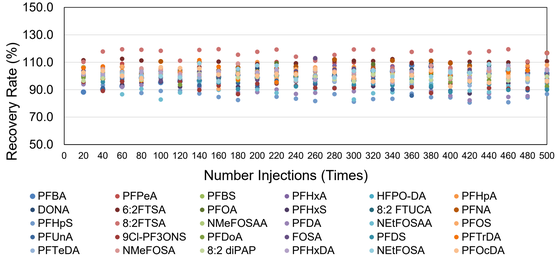

Fig. 6 Mean Recovery from QC Samples at 0.1 µg/L (Concentration in Solution) (n = 3)

5. Conclusion

The LCMS-8060RX performed 500 consecutive measurements of 30 PFAS spiked to a soil matrix sample. The results showed good peak area repeatability, good peak shapes, and good recovery. The newly designed ESI source showed excellent robustness, and stable analysis was achieved over a long period, even for samples with complex matrices.

Reference
1) Basic research on the movement of PFOA, PFOS, and other PFAS from agricultural environments (water, soil, etc.) into agricultural products
2) DRAFT METHOD 202201 Determination of perfluoroalkyl and polyfluoroalkyl substances (PFAS) in soil

The authors are affiliated and funded by Shimadzu Corporation.