SHIMADZU
Excellence in Science

High Performance Liquid Chromatograph Mass Spectrometer

Application News

Analysis of PFAS in Water Samples Containing Insolubles Using Triple Quadrupole LC/MS/MS

Nami Iwasa

User Benefits

- Per- and polyfluoroalkyl substances (PFAS) in water samples containing insolubles can be analyzed in accordance with the newly developed PFAS analytical manual[1].
- 30 different PFAS in environmental water, agricultural water, and other water samples containing insolubles can be measured with good recovery rates.

■ Introduction

Because of their outstanding heat-resistance and water-repelling properties, PFAS are used in a wide range of consumable products and industrial applications. While they confer useful properties, they also contaminate surface water, groundwater, soil, and air. Due to their potential negative effect on human health and other living organisms, there is a global trend toward more stringent regulations. Significant progress has been made in developing regulations and analytical methods for PFAS in drinking water, but these methods are not directly applicable to environmental water, agricultural water, and other water samples that contain large amounts of suspended solids. This is due to concerns such as the need to remove suspended solids and the potential decrease in recovery rates caused by these solids.

The National Agriculture and Food Research Organization (NARO) recently developed a manual with a method for determining PFAS in water samples that contain insolubles.[1] The method employs a sample preparation technique capable of efficiently extracting trace-level, multi-component PFAS from small-volume water samples containing various types of suspended solids. Simultaneous analysis of PFAS is performed by liquid chromatography tandem mass spectrometry (LC/MS/MS).

This article describes the use of the LCMS-8060RX (Fig. 1) to analyze PFAS in a water sample that contained insolubles.

Fig. 1 LCMS- 8060RX

■ Sample Preparation

Samples were prepared in accordance with the method described in the manual. The sample preparation workflow is shown in Fig. 2. Further information about this sample preparation method can be found in the manual.

Water samples that do not contain any insoluble materials, such as drinking water, can be directly applied to a solid-phase column without pretreatment. However, samples containing large amounts of suspended solids, such as environmental water and agricultural water, may cause clogging if applied directly to a solid-phase column. Therefore, these impurities must be removed from the water samples prior to analysis. Impurities are typically removed by filtration; however, this method may result in reduced recovery of target compounds due to adsorption onto the filter or residual impurities. In contrast, the method described in NARO's manual employs centrifugation to remove impurities, followed by purification using an extract derived from the impurity fraction combined with water. This approach allows for effective pretreatment of water samples containing impurities at the milligram level without clogging the solid-phase extraction column.

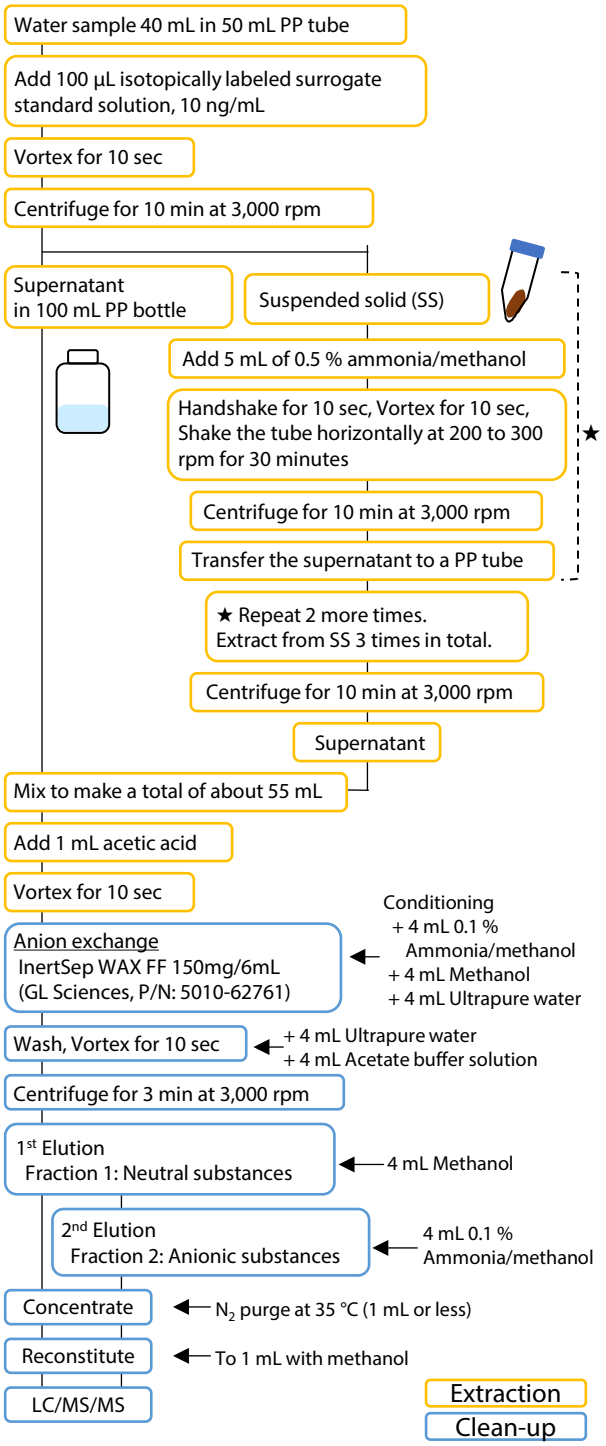

Fig. 2 Sample Preparation Workflow

■ Analysis Conditions and Target Compounds

The HPLC and MS analysis conditions used are shown in Table 1, and the PFAS compounds measured are listed in Table 2. MRM chromatograms of the mixed standard solution of PFAS (0.2 ng/mL) are shown in Fig. 3.

Table 1 Analysis Conditions

[HPLC Conditions] Nexera X3	
Analytical Column:	Shim-pack Scepter C18-120 (100 mm × 2.1 mm I.D., 1.9 µm, P/N: 227-31012-05)
Guard Column*1:	Shim-pack Scepter C18-120 (5 mm × 2.1 mm I.D., 1.9 µm, P/N: 227-31120-01)
Delay Column:	Delay column for PFAS (GL Sciences, P/N: 5020-90005)
Mobile Phases:	A) 2 mmol/L Ammonium Acetate in H_2O B) Methanol
Gradient Program:	B conc. 5 % (0 min) → 50 % (2 min) → 100 % (19.0–23.0 min) → 5 % (23.01–28.0 min)
Flowrate:	0.3 mL/min (0–19.0 min) → 0.6 mL/min (19.01–23.00 min) → 0.3 mL/min (23.01–28.00 min)
Column Temp.:	40 °C
Injection Volume:	5 µL

[MS Conditions] LCMS-8060RX	
Ionization:	ESI (Negative mode)
Interface Temp.:	250 °C
Interface Voltage:	-1.0 kV
Focus Voltage:	-2.0 kV
ESI Probe Position:	+3 mm
Nebulizing Gas:	3 L/min
Drying Gas:	5 L/min
Heating Gas:	15 L/min
DL Temp.:	200 °C
Heat Block Temp.:	300 °C

*1 Shim-pack EXP Guard Column Holder (P/N: 227-32041-01)

Table 2 PFAS Target Compound List

	Target				Surrogate		
	Compound Name	Molecular Formula	Retention Time (min)	*m/z*	Compound Name	Retention Time (min)	*m/z*
Sulfonate	PFBS	$C_4HF_9O_3S$	5.458	298.95 > 79.95	$^{13}C_3$-PFBS	5.458	301.95 > 79.95
	PFHxS	$C_6HF_{13}O_3S$	8.115	398.95 > 79.95	$^{13}C_3$-PFHxS	8.114	401.95 > 79.95
	PFHpS	$C_7HF_{15}O_3S$	9.535	448.95 > 79.95	$^{13}C_8$-PFOS	10.868	506.95 > 79.95
	PFOS	$C_8HF_{17}O_3S$	10.868	498.95 > 79.95			
	PFDS	$C_{10}HF_{21}O_3S$	13.135	598.90 > 79.95			
	FOSA	$C_8H_2F_{17}NO_2S$	13.365	497.95 > 77.95	$^{13}C_8$-FOSA	13.363	505.95 > 77.95
	N-MeFOSA	$C_9H_4F_{17}NO_2S$	15.319	511.95 > 169.00	d_3-N-MeFOSA	15.307	515.00 > 168.90
	N-EtFOSA	$C_{10}H_6F_{17}NO_2S$	15.942	526.00 > 169.00	d_5-N-EtFOSA	15.918	531.00 > 168.90
	N-MeFOSAA	$C_{11}H_6F_{17}NO_4S$	12.62	569.95 > 418.95	d_3-N-MeFOSAA	12.608	573.00 > 418.95
	N-EtFOSAA	$C_{12}H_8F_{17}NO_4S$	13.165	584.00 > 418.95	d_5-N-EtFOSAA	13.143	589.00 > 418.95
	6:2FTSA	$C_8H_5F_{13}O_3S$	9.356	426.95 > 406.95	$^{13}C_2$-6:2FTSA	9.356	428.95 > 409.00
	8:2FTSA	$C_{10}H_5F_{17}O_3S$	12.032	526.95 > 506.95	$^{13}C_2$-8:2FTSA	12.03	528.95 > 509.00
	9Cl-PF3ONS	$C_8HClF_{16}O_4S$	11.587	530.90 > 350.95	$^{13}C_8$-PFOS	10.868	506.95 > 79.95
Carboxylate	PFBA	$C_4HF_7O_2$	4.154	213.00 > 169.00	$^{13}C_4$-PFBA	4.153	217.00 > 172.00
	PFPeA	$C_5HF_9O_2$	5.254	263.00 > 219.00	$^{13}C_5$-PFPeA	5.252	268.00 > 223.00
	PFHxA	$C_6HF_{11}O_2$	6.543	312.95 > 269.00	$^{13}C_5$-PFHxA	6.543	318.00 > 273.00
	PFHpA	$C_7HF_{13}O_2$	7.995	362.95 > 319.00	$^{13}C_4$-PFHpA	7.994	367.00 > 322.00
	PFOA	$C_8HF_{15}O_2$	9.454	412.95 > 369.00	$^{13}C_8$-PFOA	9.452	421.00 > 376.00
	PFNA	$C_9HF_{17}O_2$	10.829	462.95 > 418.95	$^{13}C_9$-PFNA	10.826	472.00 > 427.00
	PFDA	$C_{10}HF_{19}O_2$	12.067	512.95 > 468.95	$^{13}C_6$-PFDA	12.066	519.00 > 474.00
	PFUnA	$C_{11}HF_{21}O_2$	13.155	562.95 > 518.95	$^{13}C_7$-PFUnA	13.153	570.00 > 525.00
	PFDoA	$C_{12}HF_{23}O_2$	14.114	612.95 > 568.95	$^{13}C_2$-PFDoA	14.114	615.00 > 569.95
	PFTrDA	$C_{13}HF_{25}O_2$	14.946	662.95 > 618.95			
	PFTeDA	$C_{14}HF_{27}O_2$	15.676	712.95 > 668.95	$^{13}C_2$-PFTeDA	15.676	714.95 > 669.95
	PFHxDA	$C_{16}HF_{31}O_2$	16.87	813.00 > 768.80	$^{13}C_2$-PFHxDA	16.87	815.00 > 769.75
	PFOcDA	$C_{18}HF_{35}O_2$	17.8	913.00 > 868.65			
	8:2 FTUCA	$C_{10}H_2F_{16}O_2$	11.186	456.95 > 393.00	$^{13}C_2$-8:2 FTUCA	11.185	459.00 > 393.90
	8:2 diPAP	$C_{20}H_9F_{34}O_4P$	17.26	989.00 > 97.00	$^{13}C_4$-8:2 diPAP	17.26	993.00 > 97.00
	HFPO-DA	$C_6HF_{11}O_3$	6.957	285.00 > 169.00	$^{13}C_3$-HFPO-DA	6.957	287.00 > 169.00
	DONA	$C_7H_2F_{12}O_4$	8.16	376.95 > 251.00	$^{13}C_4$-PFHpA	7.994	367.00 > 322.00

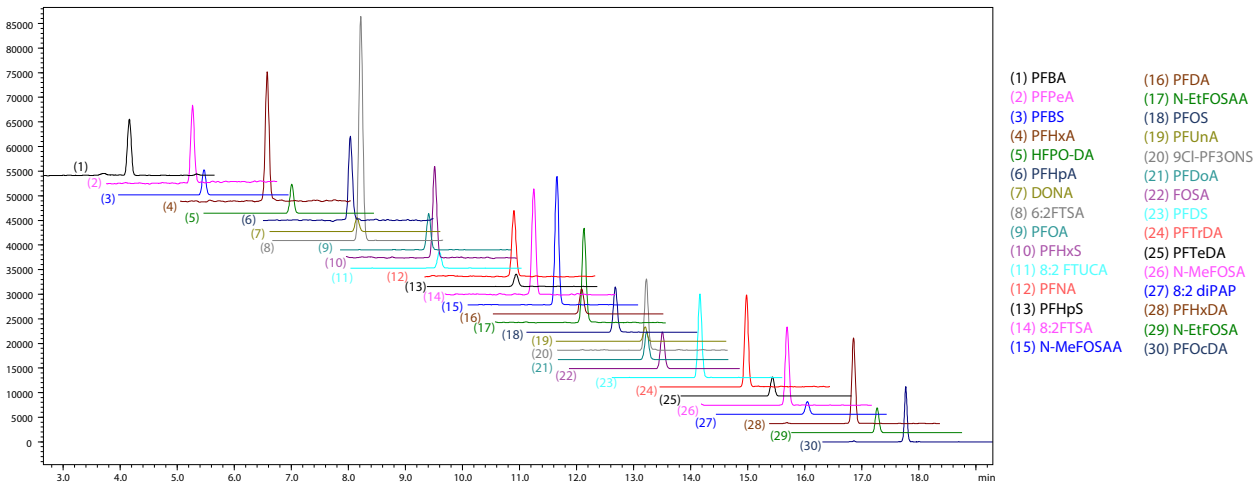

Fig. 3 MRM Chromatograms of Mixed Standard Solution of PFAS (0.2 ng/mL in Solution)

■ Measuring Standard Solutions

A standard mixture of 30 PFAS (Cat. No. ISO 21675-NSS, Wellington Laboratories) and an internal standard mixture (Cat. No. ISO 21675-LSS, Wellington Laboratories) were diluted with methanol to prepare calibration standards at 0.002, 0.01, 0.05, 0.2, 1, 5, and 10 ng/mL (internal standard concentration: 1 ng/mL).

The linear range and correlation coefficient (R) of the calibration curves created for each PFAS are shown in Table 3. Examples of calibration curves are also shown (Fig. 4) for four compounds identified as group 1 PFAS in NARO's manual (PFHxS, PFOS, PFOA, and PFNA).

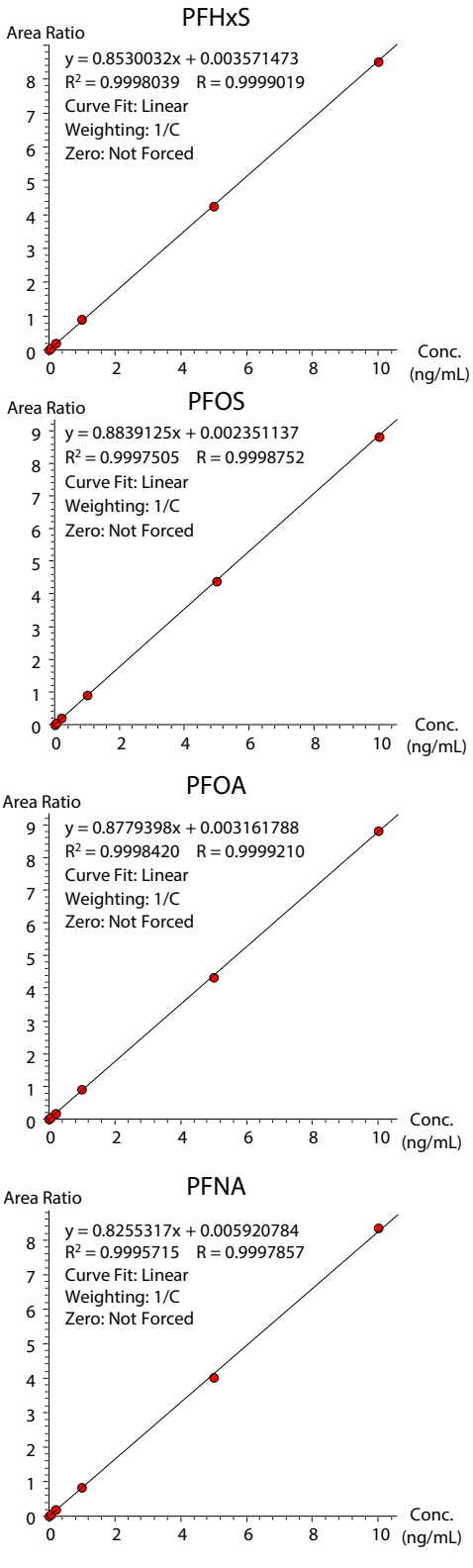

Fig. 4 Calibration Curves for PFHxS, PFOS, PFOA, and PFNA

Table 3 Linear Range and Correlation Coefficient of PFAS Calibration Curves

	Compound Name	Calibration Range (ng/mL in solution)	Correlation Coefficient R
Sulfonate	PFBS	0.01 - 10	0.99975
	PFHxS	0.01 - 10	0.99990
	PFHpS	0.01 - 10	0.99994
	PFOS	0.01 - 10	0.99988
	PFDS	0.01 - 10	0.99988
	FOSA	0.002 - 10	0.99989
	N-MeFOSA	0.01 - 10	0.99967
	N-EtFOSA	0.01 - 10	0.99987
	N-MeFOSAA	0.01 - 10	0.99966
	N-EtFOSAA	0.01 - 10	0.99985
	6:2FTSA	0.05 - 5	0.99847
	8:2FTSA	0.05 - 5	0.99800
	9Cl-PF3ONS	0.002 - 10	0.99993
Carboxylate	PFBA	0.01 - 10	0.99986
	PFPeA	0.01 - 10	0.99987
	PFHxA	0.01 - 10	0.99984
	PFHpA	0.01 - 10	0.99978
	PFOA	0.002 - 10	0.99992
	PFNA	0.01 - 10	0.99979
	PFDA	0.01 - 10	0.99987
	PFUnDA	0.01 - 10	0.99998
	PFDoDA	0.01 - 10	0.99993
	PFTrDA	0.01 - 10	0.99973
	PFTeDA	0.01 - 10	0.99962
	PFHxDA	0.01 - 10	0.99981
	PFOcDA	0.01 - 10	0.99973
	8:2FTUCA	0.01 - 10	0.99991
	8:2diPAP	0.01 - 10	0.99979
	HFPO-DA	0.01 - 10	0.99949
	DONA	0.002 - 10	0.99976

■ Procedure Blank Test and Spike Recovery Test

Procedure blank testing of the sample preparation method was performed using 40 mL of ultrapure water, and spike recovery testing was performed using 40 mL of ultrapure water spiked with 100 µL of 10 ng/mL PFAS standard solution for recovery testing (final concentration: 25 ng/L in water). Samples for each test were prepared by the method shown in Fig. 2. The results from the procedure blank and spike recovery tests are shown in Table 4.

The spike recovery test yielded recovery rates ranging from 91 to 141 %. According to previous findings, 6:2 FTSA, the compound with the highest recovery, is easily contaminated during sample preparation, and the recovery tends to vary depending on the timing of sample preparation and other factors. Excluding 6:2 FTSA, the remaining 29 compounds showed good performance with recoveries ranging from 91 to 107 %.

Table 4 Procedure Blank and Spike Recovery Results

	Compound Name	Concentration (ng/L in water)		Recovery Rate*2 (%)
		Blank Test	Spiked at 25 ng/L	
Sulfonate	PFBS	-	25.9	104
	PFHxS	-	27.4	110
	PFHpS	-	24.6	99
	PFOS	-	24.0	96
	PFDS	-	22.8	91
	FOSA	-	24.7	99
	N-MeFOSA	-	25.1	101
	N-EtFOSA	-	24.5	98
	N-MeFOSAA	-	24.1	96
	N-EtFOSAA	-	24.0	96
	6:2FTSA	-	35.4	141
	8:2FTSA	-	26.8	107
	9Cl-PF3ONS	-	24.2	97
Carboxylate	PFBA	0.5	25.3	101
	PFPeA	0.4	26.9	108
	PFHxA	0.6	25.3	101
	PFHpA	0.6	24.0	96
	PFOA	0.6	23.8	95
	PFNA	0.5	24.6	98
	PFDA	0.2	23.5	94
	PFUnDA	0.3	25.5	102
	PFDoDA	0.0	26.1	104
	PFTrDA	0.1	26.6	107
	PFTeDA	0.0	24.5	98
	PFHxDA	-	23.6	94
	PFOcDA	-	25.0	100
	8:2FTUCA	-	24.5	98
	8:2diPAP	-	24.6	98
	HFPO-DA	-	23.7	95
	DONA	-	22.9	92

*2 According to the manual, the recovery rate was calculated without considering the operation blank.

■ Quantitative Levels in Agricultural Water

The agricultural water for PFAS analysis (rice field water obtained from NARO) contained several mg of suspended solids per 40 mL of sample. Three independent pretreatments (Fig. 2) were performed under identical conditions and samples were analyzed by LC/MS/MS. Table 5 shows the quantitative results and intra-day repeatability for these samples.

Excluding 6:2 FTSA, the results show good repeatability with %RSD (n = 3) below 6 for all compounds. As mentioned earlier, results from 6:2 FTSA are subject to variability. In this case, the variability is believed to have been caused by differences in contamination levels, depending on which line was used for solid-phase extraction and nitrogen concentrations.

Table 5 Quantitative Levels in Agricultural Water for PFAS Analysis

	Compound Name	Concentration (ng/L in water)			Intra-day Repeatability (n = 3, %RSD)
		Sample 1	Sample 2	Sample 3	
Sulfonate	PFBS	11.7	11.9	11.7	0.9
	PFHxS	11.3	11.6	10.9	2.9
	PFHpS	10.5	11.2	10.8	3.0
	PFOS	11.5	11.4	11.4	0.4
	PFDS	10.5	10.3	10.2	1.7
	FOSA	10.6	10.5	9.9	3.6
	N-MeFOSA	11.3	10.6	10.6	3.3
	N-EtFOSA	10.7	10.2	11.4	5.6
	N-MeFOSAA	10.9	11.0	10.8	1.1
	N-EtFOSAA	11.4	11.5	10.7	3.9
	6:2FTSA	16.8	42.1	36.6	41.8
	8:2FTSA	12.3	12.6	11.5	4.4
	9ClPF3ONS	11.3	10.9	11.2	1.9
Carboxylate	PFBA	27.9	27.8	28.5	1.2
	PFPeA	21.0	22.9	21.4	4.4
	PFHxA	15.9	16.3	15.6	2.4
	PFHpA	13.3	13.1	12.8	1.8
	PFOA	12.6	13.0	12.8	1.6
	PFNA	12.1	12.1	12.0	0.4
	PFDA	11.4	10.8	11.3	2.8
	PFUnDA	11.1	11.2	11.3	0.6
	PFDoDA	11.7	11.0	11.1	3.3
	PFTrDA	11.2	11.3	10.9	1.9
	PFTeDA	11.1	11.0	11.3	1.2
	PFHxDA	10.9	11.0	10.0	4.8
	PFOcDA	9.3	10.0	9.6	3.6
	8:2FTUCA	10.3	10.7	10.1	3.1
	8:2diPAP	11.3	11.1	10.4	4.1
	HFPO-DA	15.2	14.9	14.9	1.3
	DONA	9.6	9.7	9.6	0.6

■ Internal Standard Recovery Rates

For the internal standards, a single-point calibration curve (n = 3) was constructed using data from 1 ng/mL QC samples. The recovery rates of the internal standards measured in the procedure blank test, the spike recovery test, and the quantitative analysis of agricultural water were then evaluated. As shown in Table 6, the recovery rates of neutral PFAS internal standards such as d_3-N-MeFOSA and d_5-N-EtFOSA tended to be low, ranging from approximately 49 to 73 %. In contrast, $^{13}C_4$-8:2 diPAP showed a relatively high recovery rate of 146 %, indicating some variability among compounds. However, the recovery of the other compounds was 77 to 115 %. This was within the range in NARO's manual (70 to 125 %) and was a very favorable result.

Table 6 Internal Standard Recovery Rates

Compound Name	Recovery Rate of internal Standards (%)				
	Blank Test	Spiked at 25 ng/L	Sample 1	Sample 2	Sample 3
$^{13}C_3$-PFBS	95	94	95	95	103
$^{13}C_3$-PFHxS	103	97	98	101	108
$^{13}C_8$-PFOS	96	99	92	95	102
$^{13}C_8$-FOSA	89	96	99	91	106
d_3-N-MeFOSA	62	64	70	66	73
d_5-N-EtFOSA	49	54	60	60	63
d_3-N-MeFOSAA	88	90	91	91	99
d_5-N-EtFOSAA	88	93	91	92	103
$^{13}C_2$-6:2FTSA	80	86	82	77	96
$^{13}C_2$-8:2FTSA	84	97	94	96	115
$^{13}C_4$-PFBA	92	99	98	96	102
$^{13}C_5$-PFPeA	98	97	99	90	105
$^{13}C_5$-PFHxA	95	99	100	97	108
$^{13}C_4$-PFHpA	99	100	100	104	110
$^{13}C_8$-PFOA	96	100	97	98	106
$^{13}C_9$-PFNA	98	99	97	100	108
$^{13}C_6$-PFDA	98	98	97	102	106
$^{13}C_7$-PFUnA	98	93	98	97	106
$^{13}C_2$-PFDoA	91	91	97	97	109
$^{13}C_2$-PFTeDA	87	94	99	96	103
$^{13}C_2$-PFHxDA	92	93	93	95	104
$^{13}C_2$-8:2 FTUCA	85	92	85	84	90
$^{13}C_4$-8:2 diPAP	102	108	127	111	146
$^{13}C_3$-HFPO-DA	97	106	97	100	104

■ Conclusion

PFAS analysis in water containing insolubles was conducted using the LCMS-8060RX, in accordance with the analytical manual developed by NARO for such matrices.

The analysis of standard solutions produced good calibration curve linearity for each of the 30 PFAS compounds. The spike recovery test also produced good recovery and repeatability results for 29 of the 30 compounds (excluding 6:2 FTSA). For 6:2 FTSA, appropriate blank control measures were considered essential.

Stable analysis was shown to be feasible even in water containing various impurities, such as agricultural water.

This analysis was performed by referring to the preliminary manual. Please note that the latest version of the manual may contain updated procedures, including pretreatment steps, so it is recommended to consult the most recent manual when conducting measurements.

<Acknowledgments>
This study was conducted under the research project on "Regulatory research projects for food safety, animal health and plant protection (JPJ008617.23812803)" funded by the Ministry of Agriculture, Forestry and Fisheries of Japan.

<References>
1) Determination of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in Water — From Sample Collection to Measurement — Version 1.0 (National Agriculture and Food Research Organization)

01-00992-EN First Edition: Jul. 2026

SHIMADZU
Shimadzu Corporation
www.shimadzu.com/an/

› Please fill out the survey

Related Products Some products may be updated to newer models.

› LCMS-TQ RX Series Triple Quadrupole LC-MS/MS

Triple Quadrupole LC-MS/MS

› Nexera Series Ultra High Performance Liquid C···

Ultra High Performance Liquid Chromatograph

› Shim-pack Scepter LC Columns

HPLC Column

Related Solutions

› Environment

› Water

› PFAS

› Price Inquiry

› Product Inquiry

› Technical Service / Support Inquiry

› Other Inquiry