Analyses of Per- and Polyfluoroalkyl Substances in Water Using Ion Exchange Solid-Phase Extraction and LC–MS/MS with an Activated-Carbon Delay Column

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Introduction

The phrase per- and polyfluoroalkyl substances (PFAS) is a general term used for organofluorine compounds. These substances are known to degrade slowly; therefore, they persist in the environment for a long time. Their toxicity and the environmental pollution they cause have attracted worldwide attention, and research to mitigate these effects continues. The methods of solid-phase extraction (SPE) and liquid chromatography–tandem mass spectrometry (LC–MS/MS) have been used to analyze PFAS in drinking water under EPA methods 537.1 and 533. Further, some PFAS are known to elute from the materials of laboratory equipment and can cause contamination to the sample. Therefore, precautions must be taken to accurately quantify PFAS. In particular, care must be taken to minimize the effects of PFAS background and contamination eluting from fluorinated resins such as polytetrafluoroethylene (PTFE), which are commonly used as components in LC systems. A known countermeasure for such effects is to delay the elution time of the blank peak by connecting a delay column packed with a C18 (ODS) material before the autosampler and shift the retention time relative to the peak derived from the sample. However, it is difficult to increase the difference between the two retention times sufficiently using a conventional C18 column. The column sizes are limited because of the relationship between the rise in pressure and the gradient delay time. Therefore, to perform stable PFAS analysis, we have developed a new delay column that is packed with high-purity activated-carbon beads. Furthermore, two SPE cartridges of different sizes, 250 mg and 150 mg, were used and reference standard addition recovery tests were conducted for each cartridge.

Methods

For LC–MS/MS, we used a 4000 QTRAP (AB SCIEX LLC, MA USA) instrument. For the delay column, we packed high-purity, spherical, activated carbon in the LC column hardware and installed in the HPLC system. We used an InertSustain C18–HP 150 mm × 2.1 mm analysis column with 3-µm-particle size (GL Sciences Inc., Tokyo Japan). We prepared a standard sample by diluting a PFAS 21 mixture standard PFAC-MXC (Wellington Laboratories, Ontario, Canada) and adding it to the sample water. We used 13 mixtures of MPFAC-C-ES (Wellington Laboratories, Ontario, Canada) as external standards. For sample preparation, we used SPE cartridge InertSep MA-2 250-mg (GL Sciences, Inc., Tokyo Japan) packed with a methacrylate polymer comprising a weak anion-exchange group (diethyl amine). We performed all the operations—from conditioning of the SPE cartridge to the evaporation of the elution solvent—using the automated SPE instrument AquaTrace ASPE899 (GL Sciences, Inc, Tokyo Japan). We passed a 500-mL sample through the SPE cartridge and then eluted it using 5 mL of 0.1% ammonia methanol. Subsequently, we heated the sample, exposed it to nitrogen gas, and concentrated it to a volume of 0.5 mL. For realizing a rapid SPE method, we used an InertSep MA-2 150-mg cartridge. We passed 30 mL of sample water through the cartridge and then used 1 mL of the eluting solvent. We did not distill off the solvent after elution. We added the mixture of standard MPFAC-C-IS (Wellington Laboratories, Ontario, Canada) to the eluate as an injection standard. To avoid contamination of the PFAS, we used a high-purity polypropylene vial in the autosampler and applied an aluminum foil and silicon septum cap on the vial. Before use, we soaked and washed all the glassware and pipette tips using methanol (Kanto Chemical Co., Inc, Japan). We also automatically washed the AquaTrace sample line tube with methanol.

Table 1 Liquid Chromatograph Conditions

System	Nexera UFLC (Shimadzu Corporation, Japan)
Column	InertSustain C18 (GL Sciences Inc, Japan) 3 µm HP, 150 × 2.1 mm I.D.
Delay Column	Delay Column for PFAS (GL Sciences Inc, Japan) 30 × 3.0 mm I.D.
Mobile Phase A	10 mmol/L Ammonium acetate
Mobile Phase B	Acetonitrile
Flow Rate	0.3 mL/min
Column Temp	40 ℃
Injection Vol	1 µL
Gradient (A/B)	80/20 – 2 min - 80/20 – 13 min - 0/100 – 2 min - 100/0-0.1 min - 80/20 – 6 min - 80/20

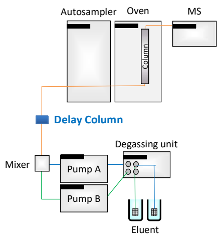

Fig.1 Delay column installation position

Table 2 Compound and Mass Spectrometer Conditions

System	4000 QTRAP (AB SCIEX LLC, MA USA)

Compounds	Transition Q1/Q3	DP	EP	CE	CXP
PFBA	213/169	-45	-10	-14	-9
PFPeA	263/219	-50	-10	-11	-9
PFHxA	313/269	-50	-10	-15	-9
PFHpA	363/319	-55	-10	-14	-9
PFOA	413/369	-45	-10	-14	-9
PFNA	463/419	-65	-10	-16	-9
PFDA	513/469	-65	-10	-14	-9
PFUnDA	563/519	-65	-10	-16	-9
PFDoDA	613/569	-40	-10	-17	-9
PFTrDA	663/619	-50	-10	-19	-9
PFTeDA	713/669	-50	-10	-15	-9
PFHxDA	813/769	-65	-10	-17	-9
PFOcDA	913/869	-65	-10	-17	-12
PFBS	299/80	-80	-10	-62	-3
PFPeS	349/80	-100	-10	-70	-13
PFHxS	399/80	-80	-10	-80	-3
PFHpS	449/80	-100	-10	-104	-15
PFOS	499/80	-90	-10	-95	-3
PFNS	549/80	-105	-10	-116	-13
PFDS	599/80	-80	-10	-80	-3
PFDoS	699/80	-115	-10	-126	-13

Extraction Standard	Transition Q1/Q3	DP	EP	CE	CXP
$^{13}C_4$-PFBA	217/172	-30	-10	-14	-31
$^{13}C_5$-PFPeA	268/223	-25	-10	-12	-11
$^{13}C_5$-PFHxA	318/273	-30	-10	-14	-47
$^{13}C_4$-PFHpA	367/322	-30	-10	-14	-19
$^{13}C_8$-PFOA	421/376	-30	-10	-14	-9
$^{13}C_9$-PFNA	472/427	-30	-10	-14	-11
$^{13}C_6$-PFDA	519/474	-40	-10	-16	-13
$^{13}C_7$-PFUdA	570/525	-60	-10	-16	-7
$^{13}C_2$-PFDoA	615/570	-40	-10	-18	-15
$^{13}C_2$-PFTeDA	715/670	-45	-10	-18	-17
$^{13}C_3$-PFBS	302/80	-75	-10	-70	-13
$^{13}C_3$-PFHxS	402/80	-75	-10	-84	-13
$^{13}C_8$-PFOS	507/80	-110	-10	-90	-13

Injection Standard	Transition Q1/Q3	DP	EP	CE	CXP
$^{13}C_3$-PFBA	216/172	-30	-10	-14	-19
$^{13}C_2$-PFOA	415/370	-30	-10	-14	-9
$^{13}C_2$-PFDA	515/470	-35	-10	-16	-35
$^{13}C_4$-PFOS	503/80	-105	-10	-120	-13

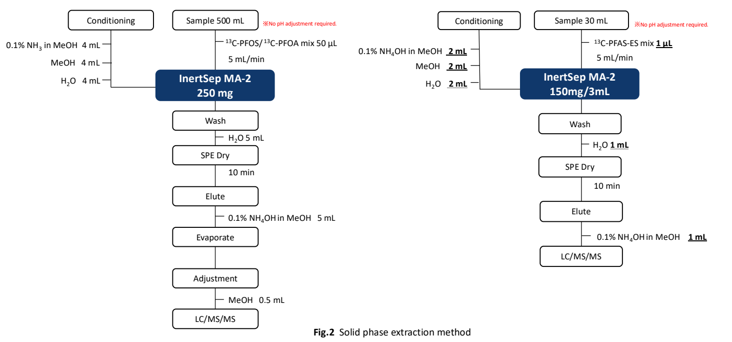

Fig.2 Solid phase extraction method

Results

Using our delay column packed with high-purity activated carbon to analyze the PFAS, we confirmed that the peak to be analyzed and the blank peak were separated sufficiently with respect to the retention time. Further, we confirmed that the PFAS 21 component in water can be extracted using SPE cartridge, InertSep MA-2. As a result of the recovery test and the use of extracted tap-water samples, we found the linearity of the measurements as 0.99 or better in the range 1–20 ng/L and the repeatability at 5 ng/L was ≤16%. When using a 150 mg SPE cartridge, the volume of sample water and the eluting solvent could be reduced, the evaporating operation of the elution solvent could be omitted, and the sample preparation time was shortened.

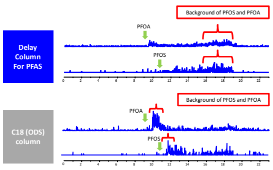

Fig.3 Comparison chromatogram of Delay columns

Table.3 Pressure Comparison of Delay Columns

Analytical column	Delay Column	Pressure
InertSustain C18-HP (150 × 2.1 mm, 3 µm)	None	19.8 MPa
	Delay Column for PFAS (30 × 3.0 mm)	19.8 MPa
	C18 (ODS) column (50 × 2.1 mm, 3 µm)	23 MPa

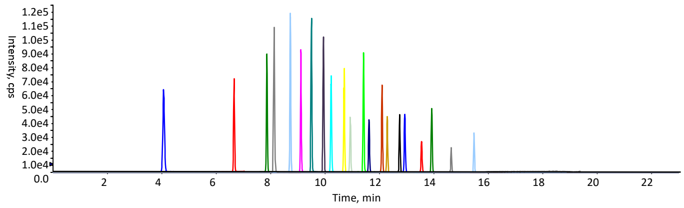

Fig.4 PFAS 21 chromatogram

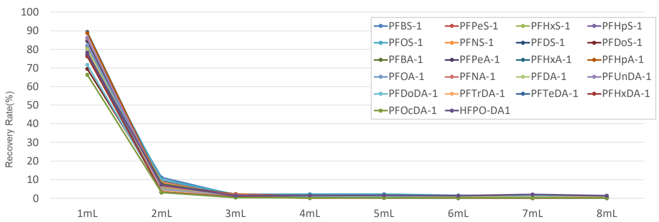

Fig.5 SPE cartridge InertSep MA-2 250mg elution profile

Table.4 Repeatability, Linearity, and Recovery

Compounds	Repeatability (CV %, n = 5)	Calibration Range	Linearity (1 – 20 ng/L)	Recovery Rate (%)	R.T (min)
PFBA	13	1-50	0.9999	80	4.11
PFPeA	8	1-50	0.9999	100	6.69
PFHxA	14	1-50	0.9999	96	7.88
PFHpA	7	1-50	0.9996	107	8.76
PFOA	10	1-50	0.9999	99	9.52
PFNA	10	1-50	0.9999	87	10.25
PFDA	7	1-50	1	101	10.95
PFUdA	7	1-50	0.9997	104	11.65
PFDoA	5	1-50	0.9999	96	12.32
PFTrDA	5	1-50	0.9997	108	12.96
PFTeDA	10	1-50	0.9999	88	13.58
PFHxDA	3	1-50	0.9999	119	14.67
PFODA	8	1-10	0.999	99	15.5
PFBS	12	1-50	0.9998	92	8.15
PFPeS	6	1-50	0.9998	95	9.13
PFHxS	8	1-20	0.9996	97	9.97
PFHpS	9	1-20	0.999	93	10.73
PFOS	16	1-20	0.9995	102	11.45
PFNS	9	1-10	0.996	95	12.13
PFDS	4	1-20	0.9992	86	12.77
PFDoS	10	1-10	0.999	83	13.95

Table.5 Repeatability Using a Small SPE (150 mg)

Compounds	Repeatability (CV %, n = 5)	Recovery Rate (%)
PFBA	8.4	96.2
PFPeA	7.5	96.8
PFHxA	8.7	95.6
PFHpA	9.2	106.1
PFOA	17.5	92.7
PFNA	13	97.6
PFDA	18.2	83.3
PFUnDA	19.9	63
PFDoDA	14	40.1
PFTrDA	10.8	38.8
PFTeDA	8.4	44.4
PFHxDA	12.9	64.8
PFOcDA	10.2	80.1
HFPO-DA	8.8	96.8
PFBS	14.8	103.7
PFPeS	11.9	98.2
PFHxS	16.6	98.3
PFHpS	18.1	90.2
PFOS	18.4	90.4
PFNS	24.3	68.6
PFDS	23.8	52
PFDoS	15.8	39.4

Conclusions

Use of a delay column packed with high-purity, spherical, activated-carbon beads reduced both the system and mobile-phase blanks and the PFAS were analyzed with high accuracy. When we used InertSep MA-2 as the SPE cartridge—which is a weak anion-exchange cartridge—without a reverse-phase mode, we obtained a stable, high recovery rate.

References

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