Per- and Polyfluoroalkyl Substances (PFAS) analysis in water using ion exchange SPE-LC-MS/MS with Activated Carbon Delay Column

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Introduction

Per- and Polyfluoroalkyl Substances (PFAS) is a general term for organofluorine compounds. It is known to be low in degradability and persist in the environment for a long time. Their toxicity and environmental pollution have attracted global attention and research continues. The solid-phase extraction-LC/MS/MS method has been used for the analysis of PFAS in drinking-water under EPA Methods 537.1 and 533. Because some countries and regions have low targets, it can be difficult to achieve stable, sensitive and accurate measurements that meet the required levels. Care must be taken to minimize the effects of blanks eluting from fluorinated resins such as PTFE, which are commonly used as components in LC systems. A known countermeasure, is to delay the elution time of the blank peak by connecting a Delay column packed with a C18 material before the autosampler, and to shift the retention time from the peak derived from the sample. However, it is difficult to sufficiently increase the difference between the two retention times with a conventional C18 column. Due to the relationship between the rise in pressure and the gradient delay time, column sizes are limited. Therefore, in order to obtain a stable PFAS analysis, we have developed a new Delay column. Our Delay column is packed with high-purity activated carbon beads. To speed up solid phase extraction, you can also scale down the amount of sample water, the size of the SPE cartridge and the amount of the elution solvent.

Methods

The Delay column is packed with high-purity spherical activated carbon in LC column hardware. The analysis column is a InertSustain C18-HP 150 mm x 2.1 mm, 3 µm (GL Sciences, Inc.). LC-MS/MS uses a 4000 QTRAP (SCIEX). The standard sample was prepared by diluting a PFAS 21 Mixture Standard (PFAC-MXC, Wellington Laboratories) and adding it to the sample water, 13 mixtures of MPFAC-C-ES (Wellington Laboratories) was added as an external standard. Solid phase extraction was used. The SPE column is a InertSep MA-2 250 mg (GL Sciences, Inc.) packed with a methacrylate polymer with a weak anion exchange group (Diethyl amine) was introduced. The operation from conditioning the SPE cartridge to the evaporation of the elution solvent was performed using the automated SPE instrument the AquaTrace ASPE899(GL Sciences, Inc.). A 1000mL sample passed through a SPE cartridge, and then eluted with 5 mL of 0.1% ammonia methanol, after that it is heated and sprayed with nitrogen gas, and concentrated to 0.5 mL. For the Rapid SPE method using an InertSep MA-2 150 mg, 30 mL of the sample water was passed through the cartridge, and then 1 mL of the eluting solvent was used. The solvent was not distilled off after elution. A mixture of standard MPFAC-C-IS (Wellington Laboratories) was added to the eluate as an injection standard. In order to avoid contamination of PFAS, a high-purity polypropylene vial was used as the vial for the autosampler, and an aluminum foil and silicon septum cap was used for the vial. All glassware and pipette tips were soaked in methanol and washed before use.

Table 1 LC Conditions

System	Nexera UFLC (Shimadzu)
Column	InertSustain C18 (3 µm HP, 150 x 2.1 mm I.D.)
Delay Column	Delay Column for PFAS (30 mm x 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 - 2min - 80/20 - 13min - 0/100 - 2min - 100/0-0.1min - 80/20 - 6min - 80/20

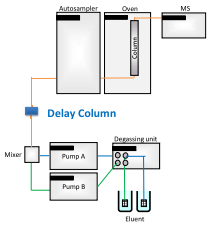


Fig.1 Delay Column installation position

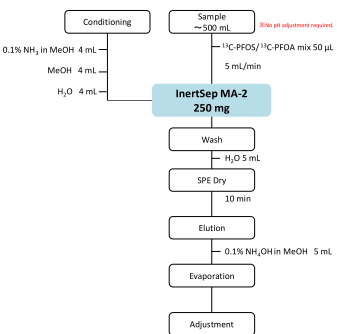
Table 2 Compound and MS Conditions

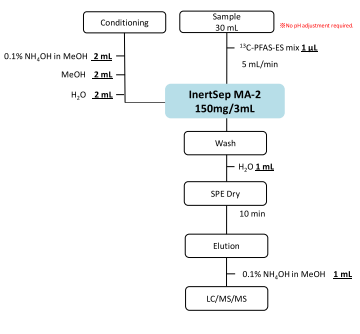
System	4000 QTRAP (SCIEX)

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





Results

By using our Delay Column for PFAS, packed with high-purity activated carbon, it is confirmed that the peak to be analyzed and the blank peak were sufficiently separated. In the concentration, using our SPE column, InertSep MA-2, all of the PFAS 21 components from C4 to C18 were eluted with 5 mL of 0.1% ammonia methanol. As a result of the recovery test and the extracted tap water samples, linearity was 0.99 or more in the range of 1 - 20 ng/L, and repeatability at 5 ng/L was 16% or less.

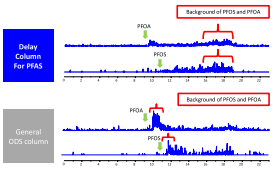


Fig.3 Comparison chromatogram of Delay columns

Table.3 Pressure comparison of Delay columns

Analytical column	Delay Colum	Pressure
InertSustain C18 (2.1 x 150 mm 3 µm-HP)	-	19.8 MPa
	Delay Column for PFAS (3.0 x 30 mm)	19.8 MPa
	General ODS (2.1 x 50 mm 3 µm)	23 MPa

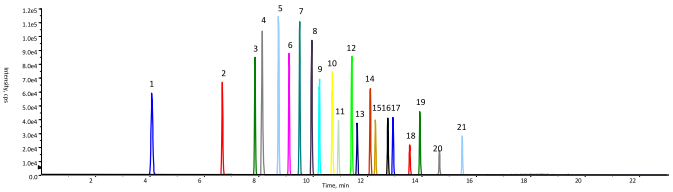


Fig.4 PFAS 21 Chromatogram

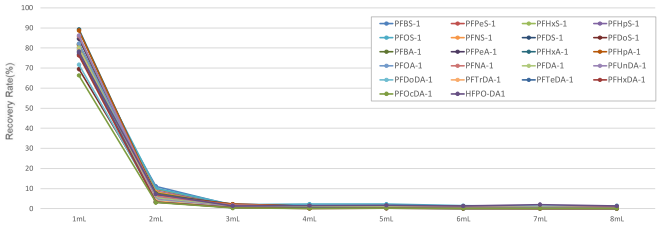


Fig.5 SPE Cartridge InertSep MA-2 250mg elution profile

Table.4 Repeatability Linearity, and Recovery

Compounds	Repeatability (CV%, n=5)	Calibration Range	Linearity (1～20ng/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 small SPE(150mg)

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

Using a Delay Column packed with high-purity spherical activated carbon beads, the system and mobile phase blanks were reduced and PFAS was analyzed with high accuracy. When InertSep MA-2, which is a weak anion exchange column, without a reverse phase mode, was used as the SPE column, a stable high recovery rate was obtained. Lastly, by reducing the SPE procedure and the concentration ratio, rapid extraction is possible.

References

1. Standard test method in water, Ministry of Health, Labor and Welfare, Japan
2. Water Supply Test Method 2011 Edition, Japan Water Works Association
3. EPA METHOD 537.1 DETERMINATION OF SELECTED PER- AND POLYFLUORINATED ALKYL SUBSTANCES IN DRINKING WATER BY SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY (LC/MS/MS)Version 1.0,November 2018
4. EPA METHOD 533: DETERMINATION OF PER- AND POLYFLUOROALKYL SUBSTANCES IN DRINKING WATER BY ISOTOPE DILUTION ANION EXCHANGE SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY

Ordering Information

SPE Cartridge

InertSep MA-2
(Weak Anion Exchange)

Methacrylate polymer with Diethyl amine
Average Particle Size: 70 µm
Ion Capacity Volume: 0.5 meq/g
pH Range: 1 - 14
Remark: Cl^- Ion Pair


Description	Column Dimension	Qty.	Cat.No.
InertSep MA-2	30mg/1mL	100pcs	5010-27324
	60mg/3mL	100pcs	5010-27325
	100mg/3mL	50pcs	5010-27320
	150mg/3mL	50pcs	5010-27319
	250mg/6mL	30pcs	5010-27321
	500mg/6mL	30pcs	5010-27322
	1g/20mL	20pcs	5010-27326
	2g/20mL	20pcs	5010-27327
InertSep Slim-J MA-2 (luer compatible)	280mg	50pcs	5010-65785

InertSep WAX
(Mix of Weak Anion Exchange and Reversed Phase)

SDVB polymer with Diethyl amine
Average Particle Size: 70 µm
pH Range: 1 - 14


Description	Column Dimension	Qty.	Cat.No.
InertSep WAX FF	60mg/3mL	50pcs	5010-62760
	150mg/6mL	30pcs	5010-62761
	500mg/6mL	30pcs	5010-62762
	150mg/12mL	20pcs	5010-62763
	500mg/20mL	20pcs	5010-62764

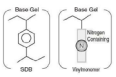
InertSep PLS-2
(Reversed phase)

Styrene-Divinylbenzene copolymer(SDVB)
Average Particle Size: 70 µm
pH Range: 1 - 14


Description	Column Dimension	Qty.	Cat.No.
InertSep PLS-2	265mg/6mL	50pcs	5010-27430
	270mg/6mL	50pcs	5010-25020
	500mg/6mL	30pcs	5010-25025
	1000mg/6mL	20pcs	5010-25030
	265mg/20mL	20pcs	5010-27431
	270mg/20mL	20pcs	5010-25035
	500mg/20mL	20pcs	5010-25036
InertSep Slim-J PLS-2	230mg	50pcs	5010-65720
	265mg	50pcs	5010-65721

InertSep HLB
(Reversed phase)

SDVB polymer with hydrophilic group
Average Particle Size: 60 µm, 30 µm
pH Range: 1 - 14




Description	Column Dimension	Qty.	Cat.No.
InertSep HLB FF 60µm	60mg/3mL	50pcs	5010-27532
	200mg/6mL	30pcs	5010-27533
	500mg/6mL	30pcs	5010-27534
	200mg/20mL	20pcs	5010-27535
	500mg/20mL	20pcs	5010-27536
InertSep HLB 30µm	10mg/1mL	100pcs	5010-27520
	30mg/1mL	100pcs	5010-27521
	60mg/3mL	50pcs	5010-27522
	200mg/6mL	30pcs	5010-27523
	500mg/6mL	30pcs	5010-27524
InertSep HLB 30µm Well plate	10mg	1pc	5010-66440
	30mg	1pc	5010-66441

LC Column

InertSustain C18

Base Material: High Purity ES Silica Gel
Particle Size: 2 µm, 3 µm, 5 µm
Surface Area: 350 m2/g
Pore Size: 100 Å (10 nm)
Pore Volume: 0.85 mL/g
Functional Group: Octadecyl
End-capping: Yes
Carbon Loading: 14.0 %
USP Code: L1
pH Range: 1 - 10

Particle Size	I.D.	Length	Qty.	Cat.No.
3µm HP	2.1mm	150mm	1pc	5020-14415

InertSustain AQ-C18

Base Material: High Purity ES Silica Gel
Particle Size: 1.9 µm, 3 µm, 5 µm
Surface Area: 350 m2/g
Pore Size: 100 Å (10 nm)
Pore Volume: 0.85 mL/g
Functional Group: Octadecyl
End-capping: Yes
Carbon Loading: 13.0 %
USP Code: L1
pH Range: 1 - 10

Particle Size	I.D.	Length	Qty.	Cat.No.
1.9µm	2.1mm	100mm	1pc	5020-89939
1.9µm	2.1mm	150mm	1pc	5020-89940
3µm HP	2.1mm	150mm	1pc	5020-89924

Delay Column

Delay Column for PFAS


Particle	I.D.	Length	Qty.	Cat.No.
Activated carbon	3.0mm	30mm	1pc	5020-90005

Autosampler Vial

High Purity PP Vial (Screw)

Size: 11.6 x 32 mm
Cap size: 9-425
Material: Polypropylene

Volume	Qty.	Cat.No.
0.3mL	100pcs	1030-14000
0.3mL	1000pcs	1030-14004

High Purity PP Vial with Cap(Snap)

Size: 11.6 x 32 mm
Cap size: 11mm
Material: Polypropylene(Vial)
Polyethylene(Cap)

Volume	Qty.	Cat.No.
1 mL	100set	1030-14030
1 mL	1000set	1030-14034

Short Thread Cap with Aluminum/Silicone Septa

Cap size: 9-425
Material: Polypropylene(Cap)
Aluminum Foil / Silicone(Septa)

Cap Color	Qty.	Cat.No.
Green	100pcs	1030-72000
Yellow	100pcs	1030-72001

Automated Solid Phase Extraction System

AquaTrace ASPE899

Channel:	6
Operation:	LCD touch panel
Number of solvent:	7
Number of storage methods:	120 (Inside body) / 120 (USB memory)
Sample water volume:	10-99990 mL
Sample water flow rate:	0.5-100 mL / min
Liquid level sensor:	Yes (optional)
Size:	480 (W) × 560 (D) × 615 (H) mm (excluding protrusions, rubber feet included)
Weight (standard specification):	About 56 kg

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