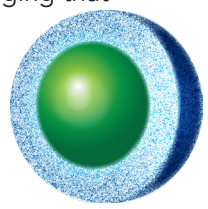
Introducing HALO® PFAS Column Solutions

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are human-made fluorinated compounds that contain carbon-fluorine bonds. With desirable properties such as resistance to heat, stains, and water, they were and some continue to be, used for consumer products such as food packaging, nonstick cookware, food processing equipment, cleaning products, fire-fighting foams, paints, and stain- and water-resistant fabrics and carpeting. These compounds do not break down easily due to the presence of the strong carbon-fluorine bonds, which has earned them the nickname "forever chemicals." There are nearly 5000 PFAS compounds mainly because as some were banned others were created to replace them. Part of the problem with PFAS is that they are found everywhere and have entered water supplies. Another issue with PFAS is that only certain compounds have been extensively studied for their impact on human health. There is worldwide concern about the presence of PFAS in the environment. In the US, the Environmental Protection Agency (EPA) has developed methods for the analysis of drinking water (533 and 537.1) and another method for the analysis of groundwater, surface water, and wastewater samples (8327). The EPA has a health advisory limit of 70 ppt for levels of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) either combined or individually, but it is non-enforceable and non-regulatory. This leaves individual states to determine maximum levels for themselves. In Europe, the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) regulation restricts PFOA and its precursors while PFOS is restricted by the EU persistent organic pollutants (POPs) Regulation. More comprehensive regulations are currently under development in the EU.

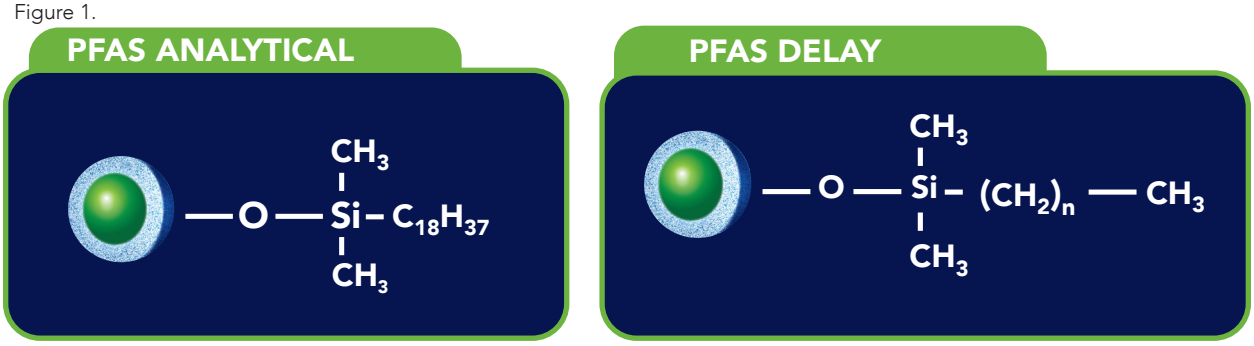
People are exposed to PFAS in several ways. One way is through eating PFAS contaminated food. The food can become contaminated through the soil and water used to grow it, the packaging that contains the food, or through PFAS contaminated equipment that processed the food. Another way people are exposed is through PFAS-containing products, such as nonstick cookware, carpets, clothes, and food packaging. Where water has become contaminated with PFAS, the drinking water can expose people to PFAS. These sites are normally near PFAS production plants or facilities that manufactured PFAS-containing products. Other typical locations are near oil refineries, airports, or military bases where aqueous film forming foam (AFFF) formulations were used to extinguish fires mainly during training exercises.

Since PFAS accumulate in the body, the increased level of these compounds over time may cause health effects. Exposure to PFOA and PFOS can cause increased cholesterol, low birth weights, immune system effects, cancer (PFOA), and thyroid hormone disruption (PFOS). While the health effects of PFOA and PFOS have been studied, the same is not true for all of the 1000's of PFAS compounds. Consequently, research continues to uncover the impact that PFAS have on human health. It was recently reported that 6:2 fluorotelomer alcohol (6:2 FTOH) is more toxic than perfluorohexanoic acid (PFHxA), which had been used to assess the toxicity of 6:2 FTOH. This has prompted the manufacturers of food packaging that contain 6:2 FTOH to voluntarily phase out the sale of these products in the US over a three-year time span beginning in January 2021.



HALO® PFAS and HALO® PFAS Delay columns have been developed specifically for the analysis of PFAS. The densely bonded, extensively endcapped ODS stationary phase of HALO® PFAS provides an application assured and method qualified solution for PFAS analysis. The highly retentive endcapped alkyl silane of the HALO® PFAS Delay column provides high retention of PFAS compounds across various mobile phase conditions and is used to delay background instrument PFAS contamination from coeluting with analyzed samples. Figure 1 shows the HALO® PFAS and HALO® PFAS Delay particle and ligand structures.

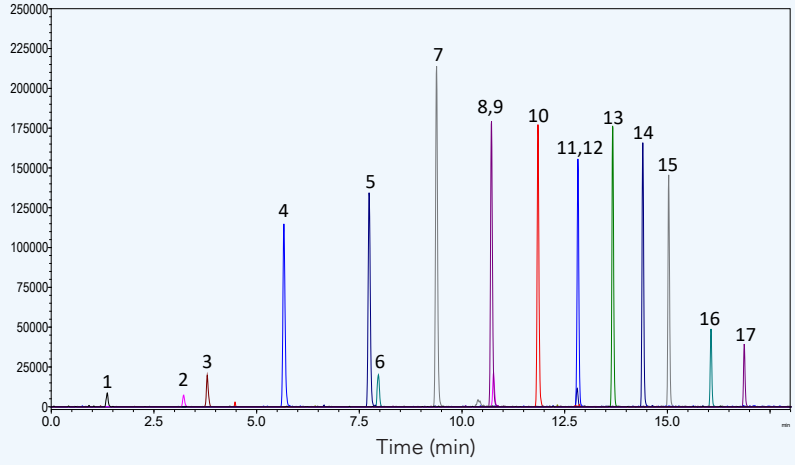
Figure 1.



APPLICATIONS

Every HALO® PFAS lot is quality assurance tested by LC-MS/MS analysis of a mix of 17 PFAS consisting of a broad range of short and long chain compounds. Set specifications ensure reproducible results across multiple lots. An example LC-MS/MS MRM QA separation is shown in Figure 2.

Figure 2. Representative MRM QA chromatogram showing the analysis of 17 PFAS compounds using HALO® PFAS.



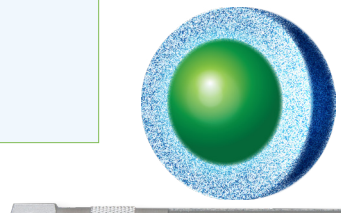
PEAK IDENTITIES

1. PFBA
2. PFPeA
3. PFBS
4. PFHxA
5. PFHpA
6. PFHxS
7. PFOA
8. PFNA
9. PFOS
10. PFDA
11. PFDS
12. PFUnDA
13. PFDoDA
14. PFTrDA
15. PFTeDA
16. PFHxDA
17. PFOcDA

TEST CONDITIONS

Delay Column: HALO® PFAS Delay, 2.7 µm, 3.0 x 50 mm
Analytical Column: HALO® PFAS, 2.7 µm, 2.1 x 100 mm
Mobile Phase: 10 mM Ammonium Acetate [A]; Methanol [B]
Gradient: 33-98% B in 18 min
Flow Rate: 0.4 mL/min
Initial Back Pressure: 420 bar

Temperature: 35 °C
Detection: Negative ESI, MRM
Injection Volume: 1 µL
Sample: PFAC-MXB (Wellington Laboratories)
Concentration: 100 ppb in 96% Methanol



For those just beginning to venture into PFAS analysis, the concept of a delay column may be unfamiliar. PFAS contamination is commonly found in the HPLC equipment used to conduct the experiments. This contamination stems from the solvent bottle caps, PTFE tubing, filters, sample preparation consumables, solvents, and even the laboratory environment itself. While fluorocarbon-free replacements exist, there may still be system contamination which is detrimental for trace analysis. The HALO® PFAS Delay column is meant to trap and delay any PFAS that is unrelated to the sample of interest. Figure 3 shows a null injection (gradient was run, but no sample was injected) and PFOA from the system is clearly visible. The prevalence of PFOA is commonly observed as an instrument materials contaminant.

Figure 3. PFOA found in a null injection run on a HALO® PFAS Delay column and a HALO® PFAS column. (Conditions same as Figure 2.)

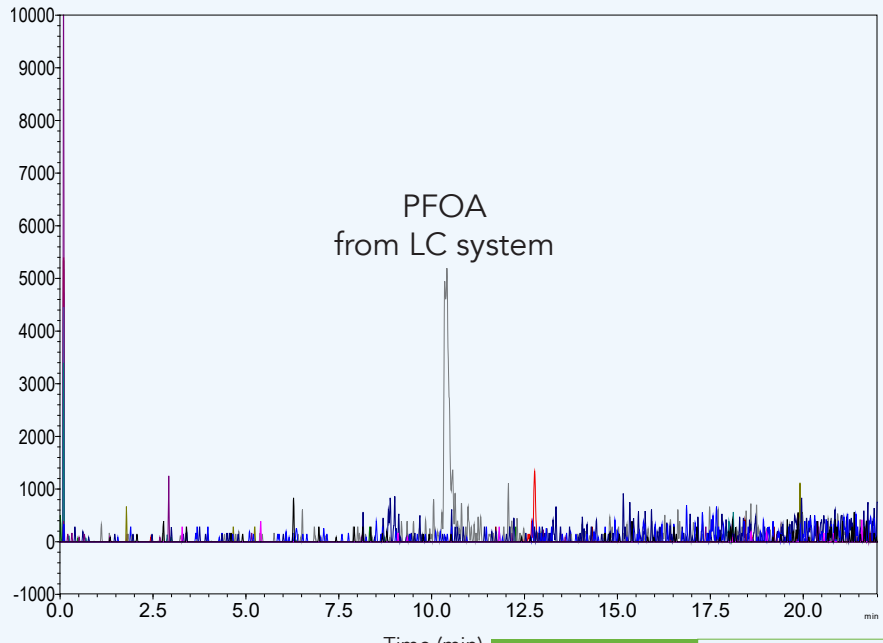
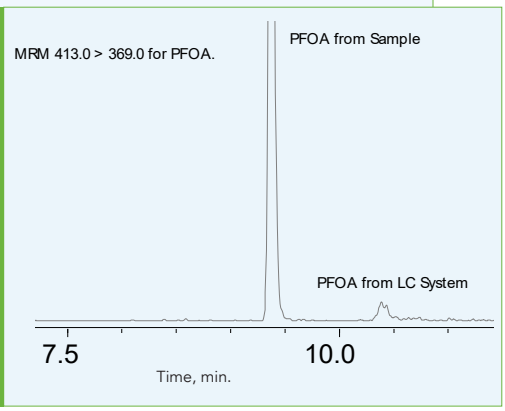
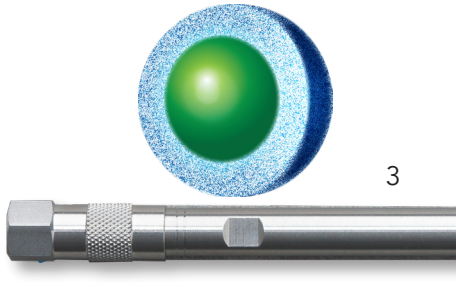


Figure 4. PFOA from sample and LC system run on a HALO® PFAS Delay column and a HALO® PFAS column.

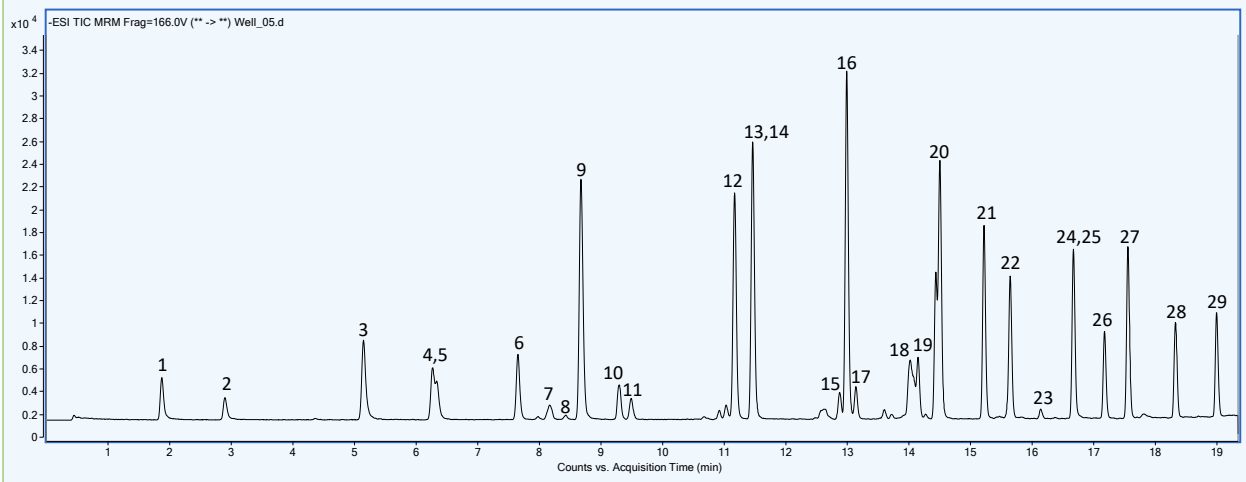


When a sample is run, the PFOA from the LC instrument elutes at a later time compared to the PFOA from the sample. See Figure 4.



One of the challenging aspects to PFAS analysis is the presence of linear and branched isomers. Branched isomers are a byproduct of the process of electrochemical fluorination (ECF) used to manufacture PFAS. Conversely, when telomerization is used, only linear isomers are formed. Branched PFAS isomers, which are more polar, are less retained compared to the linear PFAS isomers. This explains why branched isomers are found in water while linear isomers are found in soil and sediment. In Figure 5, a well water sample is run on a HALO® PFAS column and shows the excellent resolution of the branched and linear isomers of PFHxS.

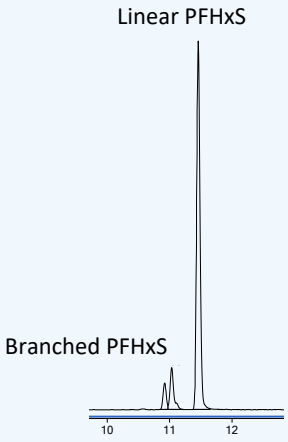
Figure 5. HALO® PFAS separation of branched and linear PFHxS isomers from a well water sample.



PEAK IDENTITIES

1	PFBA
2	PFMPA
3	PFPeA
4	PFBS
5	PFMBA
6	PFEESA
7	NFDHA
8	4:2FTS
9	PFHxA
10	PFPeS
11	HFPO-DA
12	PFHpA
13	PFHxS
14	ADONA
15	6:2FTS
16	PFOA
17	PFHpS
18	PFNA
19	PFOS

20	9Cl-PF3ONS
21	8:2FTS
22	PFDA
23	NMeFOSAA
24	NEtFOSAA
25	PFUnA
26	11Cl-PF3OUdS
27	PFDoA
28	PFTrA
29	PFTA



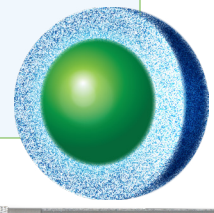
TEST CONDITIONS

Analytical Column: HALO® PFAS, 2.7 µm, 2.1 x 100 mm
Delay Column: HALO® PFAS Delay, 3.0 x 50 mm
Mobile Phase A: 20 mM Ammonium Acetete
B: Methanol
Gradient:

Time	%B
0.0	20
15	90
20	90

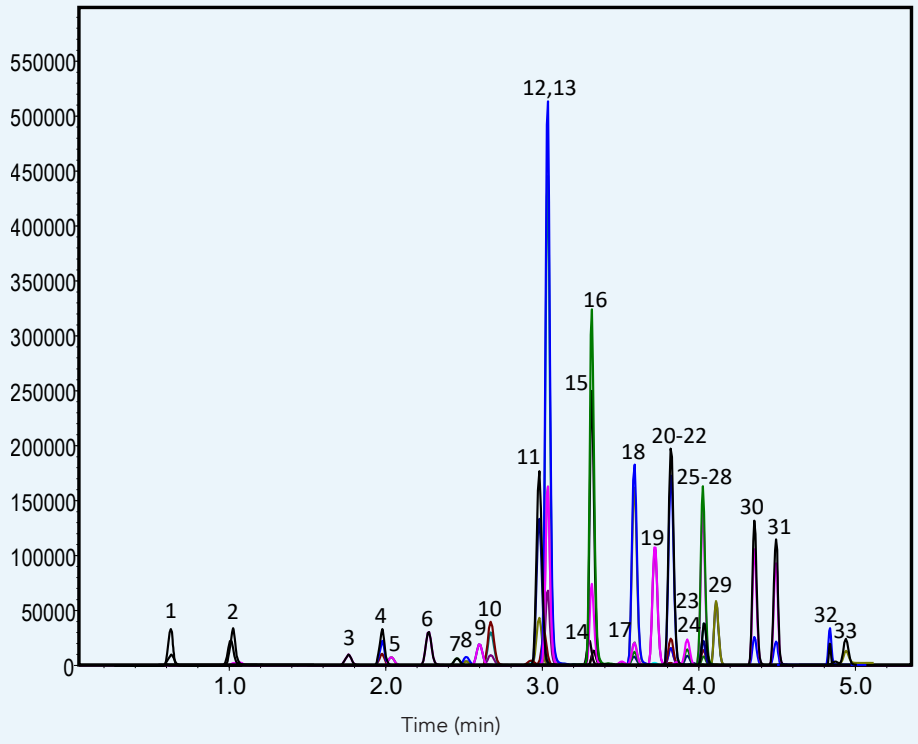
Flow Rate: 0.4 mL/min
Pressure: 505 bar
Temperature: 44 °C

Detection: -ESI MRM
Injection Volume: 2.0 µL
Sample Solvent: Methanol (96%) Water (4%)
LC System: Agilent Triple Quadrupole LC/MS 6400



With all of the research being done on PFAS, a high throughput method is essential for both time and solvent savings. HALO® PFAS which utilizes Fused-Core® technology is well suited for rapid PFAS analysis. Figure 6 shows an efficient analysis of 33 PFAS in less than 5 minutes. These compounds comprise all of the target analytes in EPA methods 533, 537.1, and 8327.

Figure 6. Rapid separation of 33 PFAS in under 5 minutes on a HALO® PFAS column.



TEST CONDITIONS

Analytical Column: HALO® PFAS, 2.7 µm, 2.1 x 100 mm
Delay Column: HALO® PFAS Delay, 3.0 x 50 mm
Mobile Phase A: 10 mM Ammonium Acetete
B: Methanol

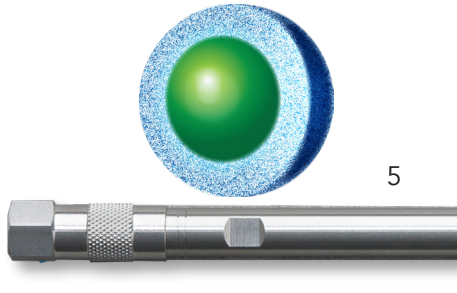
Gradient:

Time	%B
0.0	33
4.0	98
4.10	100
6.00	100
6.10	33
7.50	End

Flow Rate: 0.4 mL/min
Pressure: 479 bar
Temperature: 35 °C
Injection Volume: 2.0 µL
Sample Solvent: Methanol (96%) Water (4%)

PEAK IDENTITIES

1	PFBA
2	4:2FTS
3	PFPeA
4	PFBS
5	PFHpS
6	PFPeS
7	PFMPA
8	PFHxA
9	PFEESA
10	HFPO-DA
11	PFHxS
12	NaDONA
13	ADONA
14	FOSA
15	PFOA
16	PFMBA
17	PFHpA
18	PFOS
19	9Cl-PF3ONS
20	8:2FTS
21	PFNS
22	PFDA
23	N-MeFOSAA
24	PFNA
25	NFDHA
26	PFUnA
27	N-EtFOSAA
28	6:2FTS
29	11Cl-PF3OUdS
30	PFTrDA
31	PFDoA
32	PFTeDA
33	PFDS



CONCLUSION

The combination of HALO® PFAS Delay and HALO® PFAS columns offers a complete solution for PFAS analysis. HALO® PFAS lots are quality assurance tested specifically with a mixture of 17 PFAS compounds. The HALO® PFAS Delay efficiently traps and delays PFAS from the LC system. Whether the goal is high resolution or high speed, HALO® PFAS columns deliver rugged, reproducible performance for the most challenging environmental sample matrices.

ORDERING INFORMATION:

SPECIFICATIONS

Column	Particle Size (µm)	Surface Area (m^2/g)	Low pH/T Limit	High pH/T Limit	Endcapped
PFAS Analytical	2.7	135	9/40 °C	2/60 °C	Yes
PFAS Delay	2.7	90	9/40 °C	2/60 °C	Yes

ANALYTICAL COLUMNS

Dimensions: ID x Length (in mm)	PN
2.1 x 50	92812-413
2.1 x 100	92812-613
2.1 x 150	92812-713
2.1 x 250	92812-913
3.0 x 50	92813-413
3.0 x 100	92813-613
3.0 x 150	92813-713
3.0 x 250	92813-913

DELAY COLUMNS

Dimensions: ID x Length (in mm)	PN
3.0 x 50	92113-415
4.6 x 50	92114-415