

TECHNICAL REPORT

TITLE: THE ANALYSIS OF PFAS IN BOTTLED WATER

MARKET SEGMENT: ENVIRONMENTAL

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ABSTRACT

PFAS exposure in humans has been linked to a variety of diseases, including cancer, ulcerative colitis, thyroid disease, and hypercholesterolemia. Since the early 2000's, the EPA has established limits of PFAS chemicals in drinking water at 70 parts per trillion, however there is no federally established limit for PFAS chemicals in bottled water. Bottled water is among the most heavily consumed beverage in the world, with the average person consuming over 40-50 gallons per year. The lack of regulation and testing of bottled water for PFAS is concerning as it is an exposure point for humans. Here we present the HALO® PFAS solution for PFAS analysis of bottled water.

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are chemicals that have been known to have a deleterious environmental impact and are suspected carcinogens. In recent years however, there have been increasing instances of PFAS being detected and transitioning into the food supply.¹ Two common sources of how contamination can be introduced is by food packaging, or through the cooking process.¹ Due to the hydrophobic nature of the fluorocarbon section, these are highly stable compounds, however due to the hydrophilic nature of the carboxylate section, they are soluble and dissolve in water, remaining largely intact due to the stability. As such, high levels of PFAS accumulation in the blood have been seen in both humans and animals. Multiple examples of fish contaminated with PFAS have been reported. Additionally, high levels of PFAS have been reported in birds as well as various other animal tissue.¹

In 2009, the EPA began to establish limits for PFAS in drinking water with the introduction of EPA method 537, which established the maximum limit of PFAS chemicals in drinking water at 70 parts per trillion. This method was revised in 2018 to include 4 additional PFAS compounds and labeled EPA 537.¹ In 2019 EPA method 533 was introduced and focused on "short chain" PFAS: those PFAS with carbon chain lengths between 4 and 12. Also in 2019, the EPA

validated method 8327 for non-potable water testing, which includes the analysis of 24 total PFAS compounds in a variety of aquatic matrices, and in 2021 EPA Method 1633 was introduced and covers more than 40 PFAS species in a variety of matrices as well, including tissue.²⁻⁵

The bottled water industry registers sales of over \$300 billion with an average person consuming between 40-50 gallons of bottled water per year.⁶ Under EPA method 537,¹ the maximum limit of PFAS chemicals in drinking water has been set at 70 parts per trillion, however it has not yet established a limit for bottled water. There are established limits by non-governmental agencies, such as the International Bottled Water Association for PFAS. This association established limits for member company bottled water products at 5 parts per trillion (ppt) for one PFAS, 10 ppt for more than one

KEY WORDS:

PFAS, EPA 1633, bottled water, MRLs

PFAS.⁶ These limits are not tightly regulated however, and since PFASs from fluoropolymers and coatings are ubiquitous in most plastics, and often leach out during analysis, PFAS contamination of bottled water is highly concerning.

In this report, we apply the HALO[®] PFAS solution to the analysis of bottled water. Multiple samples of bottled water from different vendors were screened and quantitated for PFAS. Furthermore, one sample was subjected to long-term storage to see if excessive storage time would result in an increase in PFAS leaching from the bottle into the water.

EXPERIMENTAL

An Agilent 6400 Series Triple Quadrupole (Santa Clara, USA), was coupled to an Agilent 1200 series HPLC system. STRIDE Center for PFAS Solutions (Delaware, USA) prepared bottled water samples following EPA method 1633. A HALO[®] PFAS Delay, 2.7 μ m, 3.0 x 50 mm (Advanced Materials Technology, Wilmington, DE) was used as the delay column, and a HALO[®] PFAS column, 2.7 μ m, 2.1 x 100 mm (Advanced Materials Technology, Wilmington, DE) was used as the analytical column. The delay column was positioned between the mixer and the autosampler.

TEST CONDITIONS

Analytical Column: HALO[®] PFAS, 2.7 μ m, 2.1 x 100 mm

Part Number: 92812-613

Delay Column: HALO[®] PFAS Delay, 2.7 μ m, 3.0 x 50 mm

Part Number: 92113-415

Mobile Phase A: 20 mM Ammonium Acetate

Mobile Phase B: Methanol

Gradient:

Time	%B
0.0	20
15.0	90
20.0	90

Flow Rate: 0.4 mL/min

Pressure: 505 bar

Temperature: 44 °C

Detection: -ESI MS/MS

Injection Volume: 2.0 μ L

Sample Solvent: Methanol (96%) Water (4%)

MS System: Agilent 6400 series

LC System: Agilent 1200 series

MS Source Conditions:

Gas Temp: 130 °C

Nebulizer: 25 psi

Gas Flow: 11 L/min

Sheath Gas Heater: 250 °C

Capillary: 3500 V

RESULTS

Multiple samples (6) of bottled water from different vendors were screened for PFAS and labeled: A, B, C, D, E, F. two separate samples of D were injected, one was stored in the bottle for 3 months and the other was recently purchased and injected immediately.

EPA method 1633 was chosen as the method for the analysis of the bottled water samples because of the wide variety of matrices that it covers, including aqueous, solid, biosolids, and tissue samples.

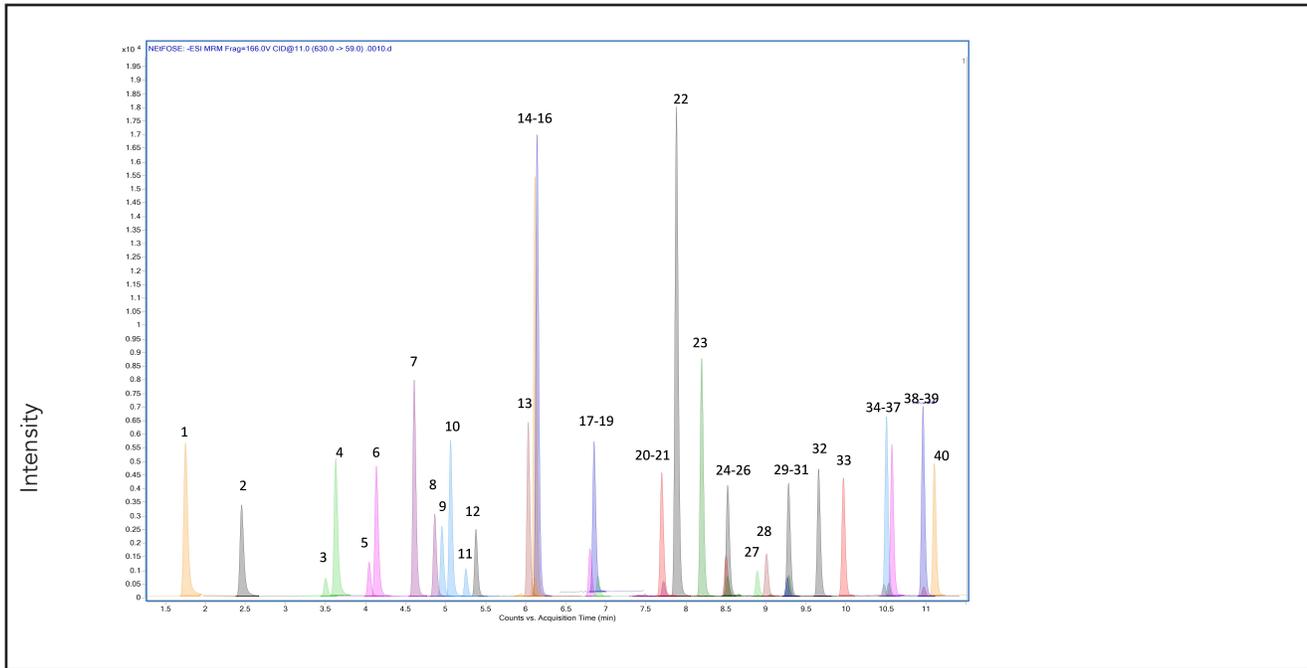


Figure 1. Standards for EPA method 1633

Initial experimentation began with running the standards found in 1633, and Figure 1 shows the separation of the standards in just over 11 minutes.

Peak	Peak ID	RT
1	PFBA	1.75135
2	PFMPA	2.45145
3	3-3 FTCA	3.503417
4	PFPeA	3.627217
5	PFBS	4.047833
6	PFMBA	4.133983
7	PFEESA	4.609983
8	NFDHA	4.8655
9	4-2FTS	4.956233
10	PFHxA	5.061883
11	PFPeS	5.256433
12	HFPO-DA	5.379517
13	PFHpA	6.031417
14	PFHxS	6.114117
15	5-3 FTCA	6.116983
16	ADONA	6.139667
17	6-2FTS	6.8027
18	PFOA	6.85485
19	PFHpS	6.9054
20	PFNA	7.697217

Peak	Peak ID	RT
21	PFOS	7.7258
22	7-3 FTCA	7.88195
23	9Cl-PF3ONS	8.194433
24	8-2FTS	8.498183
25	PFNS	8.5213
26	PFDA	8.51965
27	NMeFOSAA	8.891467
28	PFOSA	9.007333
29	PFDS	9.264283
30	PFUnA	9.28205
31	NEtFOSAA	9.285017
32	11Cl-PF3OUdS	9.659083
33	PFDoA	9.96475
34	NMeFOSA	10.47117
35	NMeFOSE	10.50327
36	PFDoS	10.52672
37	PFTTrA	10.57155
38	NEtFOSE	10.96262
39	NEtFOSA	10.96952
40	PFTeDA	11.09977

Initial experimentation began with running the standards found in 1633, and Figure 1 shows the separation of the standards in just over 11 minutes.

Table 2. PFAS species present in A-E samples

Sample A Analyte	Result ng/L	MRL (LOQ) ng/L
PFOS	<MRL	1
7:3 FTCA	<MRL	20
PFOSA	<MRL	1
NMeFOSE	<MRL	10
NEtFOSE	<MRL	10
Sample B	Result ng/L	MRL (LOQ) ng/L
PFBS	<MRL	1
PFHxA	<MRL	1
PFHxS	<MRL	1
7:3 FTCA	<MRL	20
PFOSA	<MRL	1
NMeFOSE	<MRL	10
NEtFOSE	<MRL	10
Sample C	Result ng/L	MRL (LOQ) ng/L
PFBA	<MRL	4
Sample D	Result ng/L	MRL (LOQ) ng/L
PFOS	<MRL	1
Sample D*	Result ng/L	MRL (LOQ) ng/L
PFOS	<MRL	1
Sample E	Result ng/L	MRL (LOQ) ng/L
PFBS	<MRL	1
PFHpA	<MRL	1
PFHxS	<MRL	1
PFOS	<MRL	1

* D water was aged 3 months before analysis

As seen in Table 2, samples A through E had detectable PFAS species, however they were below the maximum reportable limits. Of note however is Sample D*, which was aged 3 months and showed the same amount of PFAS present as the fresh sample of D. This indicate that there was no evidence that storing bottled water for an extended period of time has an effect on the amount of PFAS that leaches out of the plastic. Additional and more thorough experimentation will need to be done to confirm this result, but the results of our crude storage study showed no increase in PFAS as related to storage time.

Sample F however did show 8 PFAS species detected above the maximum reportable limits. Figure 2 shows the 8 Pfas species found, and Table 3 shows the levels.

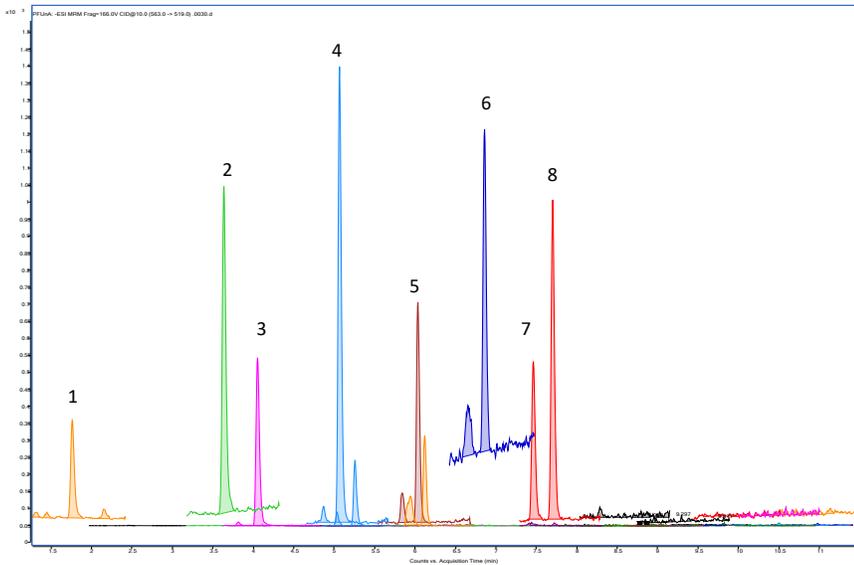


Figure 2. 8 PFAS species detected and quantitated above MRLs in sample F

Peak id	Analyte	Result ng/L	MRL (LOQ) ng/L
1	PFPeA	3.5	2
2	PFBS	3.3	1
3	PFHxA	2.2	1
4	PFPeS	2	1
5	PFHpA	1.1	1
6	PFHxS	4.5	1
7	PFOA	2	1
8	PFNA	2.7	1

Table 3. 8 PFAS species detected and quantitated above MRLs in sample F

The majority of the PFAS species that were detected were 2- 3 times higher than the MRL, of note is PFHxS which was 4.5 times higher than the MRL. This is concerning because in the United States there are no federal limits established for PFAS in bottled water, and therefore very little testing and regulation is being done. The levels of PFAS that were detected in the sample is indicative of a larger problem, as only 6 samples were tested and hundreds of vendors available, there is no clear picture on how much PFAS is being ingested by people every year from drinking bottled water. It is imperative that testing be done in order to ascertain the possible threat, because with the average person consuming up to 50 gallons of bottled water per year, the levels of PFAS ingested could be very significant.

CONCLUSION:

The HALO® PFAS solution was able to detect and quantify PFAS species in bottled water, both above and below the MRL. PFAS was found in all 6 commercial water samples that were tested, and all showed levels below the MRL, with the exception of sample F, which in one case had levels 4.5x higher than the MRL. There was no evidence that excessive storage time leads to an increase in PFAS leaching from the bottle into the water. The high levels of PFAS detected in sample F show that there is a critical need for federal limits to be established in the bottled water industry.

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