Are there PFAS in my water? A detailed look into bottled water.

Ruth Marfil-Vega[1] , Eberhardt Kuhn[1], Brahm Prakash[(*)]

1.Shimadzu Scientific Instruments, Inc. 7102 Riverwood Drive, Columbia, MD 21046

Introduction

The presence of Per- and Polyfluorinated Alkyl Substances (PFAS) in drinking water is being thoroughly studied due to the persistence of these compounds in the environment and their potential health effects. However, there is limited knowledge about the occurrence of these chemicals in bottled water, despite the increasing concerns about PFAS in the food supply. This poster shows results from a fast and simple direct injection method similar to EPA method 8237, using the Shimadzu LCMS-8050 to analyze seven commercially available samples of bottled water for 24 PFAS. The results demonstrate that the instrument's performance exceeds the requirements in FDA draft method C-010.01 for other matrices, including milk (which is the most similar to water), as well as the limits established by the EPA for drinking water.

While the origin of the water itself maybe the source of PFAS in bottled water, we also wanted to investigate the importance of the type of materials. Migration of PFAS from Food Contact Materials (FCM) is known to occur in all kinds of food containers. In this study, we procured bottled water in several different bottle materials, as well as two types of water source. These included spring and purified water, and bottles made from 5 different kinds of container materials: plastic (virgin and recycled), glass, metal, and cardboard. Preliminary results indicate that observed PFAS levels seem to depend on both the bottle material and the water source.

Instrument Operating Conditions

Table 1: Chromatography and mass spectrometer conditions

Parameter	Value	
LCMS	Shimadzu LCMS-8050	
Analytical Column	Restek Raptor C18 2.1 mm ID. x 150 mm L., 2.7 µm) Part No 9304A62	
Solvent Delay Column	Restek PFAS Delay Column (2.1 mm ID. x 50 mm L) Part No. 27854	
Column Oven Temperature	40 ° C	
Injection Volume	30 µL	
Mobile Phase	A: 20 mmol Ammonium Acetate in 5 % (v/v) Acetonitrile in reagent water B: 10 mmol Ammonium Acetate in 95 % (v/v) Acetonitrile in reagent water	
Gradient Flow rate	0.3 mL/ Min	
Gradient	Time (minutes)	% B
	0	0
	1	20
	6	50
	14	100
	17	100
	18	0
	21	0
Run time	21 minutes	
Nebulizing gas flow	5 L/min	
Heating gas flow	15 L /Min	
Interface temperature	300 °C	
Desolvation Line temperature	100 °C	
Heat Block temperature	200 °C	
Drying gas flow	5 L /min	
Acquisition cycle time	21 min	
Total MRMs	66	

Experimental

We analyzed 24 target PFAS compounds and 19 surrogates in various types of water. The analysis of PFAS was performed using a Shimadzu Nexera X2 SIL-30AC autosampler and a LCMS-8050 triple quadrupole mass spectrometer. An injection volume of 30 µL was used in this study. A detailed description of the LC/MS/MS parameters is included in Table 1.

Chromatography was adjusted to obtain maximum resolution between peaks in the shortest time possible with minimum co-elution of isomers. The total run time of 21 minutes includes a final wash out with concentrated acetonitrile to flush the column, remove background residuals contaminants and restore column performance before starting the next run. The method could easily be modified to include isotopic dilution or internal calibration if needed for quantifying the concentrations.

Calibration Standards

Standards available from Wellington Laboratories were used for these studies (Catalog no. PFAC-24PAR and MPFAC-24ES). These standards were then diluted to working standards using 95:5 acetonitrile:water as the diluent. The working standards were used to create a calibration curve ranging from 5-200 ppt with the injection solvent consisting of 50:50 water:methanol with 0.1% acetic acid in order to match the injection solvent for the extracted samples. Filtration was not performed on the calibration standards.

Sample Preparation

Seven types of bottled water as sample matrices were tested using reagent water as the blank. Each sample was diluted 50:50 with MeOH and 0.1% acetic acid, spiked with isotopically labeled surrogates and vortexed for 2 min. The samples were then filtered through 0.2 µm syringe filters and analyzed by LC/MS/MS.

All compound parameters, including precursor ion, product ion, and collision energies, were optimized. There are at least two multiple reaction monitoring (MRM) transitions for most of the analytes.

Results and Discussion

It is known that PFAS can be present in reagents, glassware, pipettes, tubing, degassers and other parts from the LC-MS/MS instruments. PFAS contamination coming from the LC system is eliminated using a delay column placed between the reagents and the sample valve. This separates PFAS in the sample from the PFAS in the LC system. All supplies used to conduct the study were free from PFAS contamination. To monitor the lack of contamination two blanks were injected at the beginning of each batch: system null injection (air injection) and reagent blank (0.1% acetic acid in high purity water:methanol (50:50)). Figure 1 shows the schematic of the delay column set up, and Figure 2 shows the importance of having a delay column and its impact on data quality.

Fig. 1: Schematic of Delay Column System

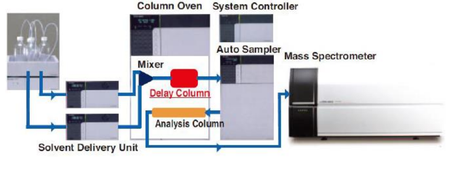
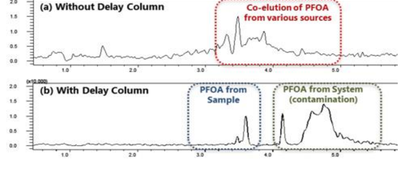


Fig. 2: Comparison of Chromatograms with and without a Delay Column



Recoveries of an 80 ppt standard are shown in Table 2. The data represent an average of 3 individual runs.

This demonstrates the accuracy and reproducibility of the measurements. Recoveries ranged from 87.6% to 129.5%, and %RSD was below 10% for most compounds.

The LOQ was determined at 10 ppt in the sample.

Our method screened for 24 PFAS compounds, but only two were found in any of the samples – PFBA (perfluoro butanoic acid) and 6-2 FTS (fluorotelomer sulfonate). The highest levels were found in plastic bottles. Much of the attention in PFAS analysis has been on the longer chain analogs, especially PFOS and PFOA. We did not see either one of these in the samples tested. There is little information about the ones that we did see regarding their effect on human health.

Table 3 shows a summary of the PFAS residues in each water sample. The sample "Plastic 2" was labelled as "purified water" on the bottle, while all other bottles claimed "spring water" as their water source. Only two of the samples had no detectable PFAS concentration – the glass bottle and the cardboard container. The other containers had at least one PFAS above the levels recommended by The International Bottled Water Association (IBWA). This organization has guidelines for its members of 5 ppt for any individual PFAS, and 10 ppt for total PFAS concentration. The EPA has set guidelines of total PFAS concentration below 70 ppt, while the FDA is currently testing many types of foods for PFAS contamination and will use this data to set exposure limits.

Table 2: Recoveries and Reproducibility of 80 ppt Standard

	Average	%Rec	%RSD
PFBA	103.64	129.55	21.17
MPFBA	81.87	102.34	2.33
PFPeA	79.29	99.12	2.52
M5PFPeA	83.49	104.36	1.39
4-2 FTS	85.54	106.92	6.39
M2-4-2 FTS	86.33	107.91	9.36
PFHxA	78.06	97.58	3.69
M5PFHxA	80.45	100.56	2.83
PFBS	79.55	99.44	3.38
M3PFBS	79.86	99.83	1.25
PFHpA	81.40	101.75	3.39
M4PFHpA	82.34	102.92	2.96
PFHxS	79.85	99.82	3.85
PFPeS	76.30	95.38	8.26
6-2 FTS	80.89	101.12	10.79
M2-6-2 FTS	77.43	96.78	22.96
PFOA	76.72	95.90	6.58
M8PFOA	82.68	103.35	4.87
M3PFHxS	77.67	97.09	5.21
PFOS	83.92	104.90	15.63
PFNA	76.42	95.53	2.82
M9PFNA	82.38	102.98	1.66
PFHpS	82.99	103.74	12.33
8-2 FTS	70.05	87.57	14.64
M2-8-2 FTS	74.27	92.83	3.76
N-EtFOSAA	73.15	91.44	2.87
N-MeFOSAA	79.25	99.06	2.75
PFDA	80.00	100.00	4.15
M6PFDA	76.99	96.23	2.86
d3-NMeFOSAA	73.57	91.96	6.99
M8PFOS	79.76	99.70	7.75
d5-NEtFOSAA	81.58	101.97	15.65
PFUnA	78.98	98.73	4.58
M7PFUnA	77.83	97.28	3.79
PFNS	80.60	100.75	19.61
PFDoA	76.57	95.72	4.70
M2PFDoA	74.04	92.55	2.81
PFDS	84.19	105.24	9.99
PFTriA	73.30	91.63	1.88
FOSA	80.25	100.31	6.54
M8FOSA	73.51	91.89	4.03
PFTreA	76.45	95.57	3.85
M2PFTeA	73.54	91.92	4.97
HFPO-DA	82.41	103.01	4.22
13C-HFPO-DA SURR	79.29	99.12	5.91
ADONA	79.94	99.92	3.23
9Cl-PF3ONS	77.92	97.40	3.74
11Cl-PF3OUdS	79.39	99.24	9.23

There are two data points that stand out:

1. by far the highest level of PFAS was measured in the bottle made from recycled plastic (highlighted in yellow) (it was stated on the label that the bottle was made with 50% recycled plastic). Taken at face value, this would imply that the recycling process introduces additional PFAS into the produced plastic bottles.
2. The bottle labeled "Plastic 3" contained by far the highest amount of PFBA (highlighted in blue). Since the water source was identified as "Spring Water", it could indicate local PFAS contamination near the source of that water.

However, we only have one data point each so far, so it is too early to come to any meaningful conclusions. The data does warrant further investigation, though, on both the source of the water and the bottle material.

Table 3: PFAS Data by Water Bottle Material

PFAS	Blank	Glass	Cardboard	Metal	Plastic 1	Plastic 2	Plastic 3	Recycled Plastic
PFBA	NQ	NQ	NQ	23.8	NQ	15.3	104.3	18.1
PFPeA	ND	ND	ND	ND	ND	ND	ND	ND
4-2 FTS	ND	NQ	NQ	NQ	NQ	NQ	NQ	NQ
PFHxA	ND	ND	ND	ND	ND	ND	ND	ND
PFBS	NQ	ND	ND	NQ	ND	ND	ND	ND
PFHpA	ND	NQ	NQ	ND	NQ	NQ	ND	ND
PFHxS	ND	ND	ND	ND	ND	ND	ND	ND
PFPeS	ND	ND	ND	ND	ND	ND	ND	ND
6-2 FTS	NQ	NQ	ND	NQ	81.5	NQ	ND	253.9
PFOA	ND	NQ	NQ	NQ	NQ	NQ	NQ	NQ
PFOS	ND	ND	ND	ND	ND	ND	ND	ND
PFNA	ND	NQ	NQ	NQ	NQ	NQ	ND	NQ
PFHpS	ND	ND	ND	ND	ND	ND	ND	ND
8-2 FTS	NQ	ND	ND	ND	ND	ND	ND	ND
N-EtFOSAA	ND	ND	ND	ND	ND	ND	ND	ND
N-MeFOSAA	ND	ND	ND	ND	ND	ND	ND	ND
PFDA	NQ	ND	NQ	NQ	ND	NQ	NQ	NQ
PFUnA	ND	ND	ND	ND	ND	ND	ND	ND
PFNS	ND	ND	ND	ND	ND	ND	ND	ND
PFDoA	NQ	NQ	NQ	ND	NQ	ND	ND	NQ
PFDS	ND	ND	ND	ND	ND	ND	ND	ND
PFTriA	ND	ND	ND	ND	ND	ND	ND	ND
FOSA	ND	ND	ND	ND	ND	ND	ND	ND
PFTreA	ND	ND	ND	ND	ND	ND	ND	ND
HFPO-DA	ND	ND	ND	NQ	ND	ND	ND	ND
ADONA	ND	ND	ND	ND	ND	ND	ND	ND
9Cl-PF3ONS	ND	ND	ND	ND	ND	ND	ND	ND
11Cl-PF3OUdS	ND	ND	ND	ND	ND	ND	ND	ND

ND = not detected; NQ = not quantitated

Summary and Conclusions

This study evaluated the direct injection analysis of 24 PFASs and 19 mass-labeled surrogates in bottled water using Shimadzu UFMS™ LCMS-8050. The data shows excellent performance of the LCMS-8050 for PFAS analysis in bottled water matrices with minimal sample preparation. Of the seven types of bottled water containers tested, plastic had the highest amount of PFAS present. In particular, the bottle made from recycled plastic showed by far the highest amount of PFAS. Glass and cardboard bottles had no detectable PFAS levels. While this data would suggest that the plastic recycling process introduces additional PFAS into the water bottles, it is too early to draw that conclusion with any certainty. The data also suggests that the source of the water can contribute PFAS to the bottled water. More experiments are necessary to confirm these preliminary results.

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(*)Brahm Prakash is not currently affiliated with Shimadzu Scientific Instruments