

Unwanted ingredients - Highly specific and sensitive method for the extraction and quantification of PFAS in everyday foods

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Abstract

Perfluorinated alkyl substances (PFAS) are anthropogenic substances and can only come from polluted sources. There are many classes of PFAS which can be transformed to perfluoroalkyl carboxylic acids and perfluoroalkyl sulfonic acids in the environment. Once they are in this form they are environmentally mobile and extremely stable with half lives of decades. These compounds are not innocuous and are implicated in causing many different diseases.

In this publication a method for the extraction and quantitation of perfluorocarboxylic acids and perfluorosulfonic acids, using high resolution liquid chromatography mass spectrometry (HRMS), is evaluated. The linearity, recovery and matrix effect are described and the method tested on tomato, strawberry and milk purchased from different locations. The C₈ PFAS – perfluorooctanoic acid and perfluorooctane sulfonic acid which were added to the Stockholm Convention list for restricted use in 2008 were not determined. However, the C₄ version – perfluorobutanoic acid was determined at different concentrations in all 3 matrices. The samples were sourced from different locations and had different packaging and therefore it is likely the contamination was from environmental sources such as bio-accumulation from groundwater or airborne particles.

Introduction

Perfluorinated alkyl substances (PFAS) substances are manmade fluorinated organic compounds which are ubiquitous in the environment. They were first manufactured in the 1940s and have many industrial and domestic uses from fire-fighting foams to grease repellents in fast food boxes. They have exceptional chemical stability which means that conventional waste treatment processes such as biodegradation are ineffective. They are also known to bioaccumulate. Human exposure to PFAS can be through multiple routes including drinking water, food and indoor air and dust. It is estimated that most humans have PFAS in their bloodstream. Exposure to PFAS has been associated with health problems such as kidney, testicular and pancreatic cancer as well as reproductive and developmental effects.

According to the Organisation for Economic Development and Development (OECD) in 2018 there were over 4700 PFAS worldwide from 42 different chemical families (OECD 2018). Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are two most commonly found PFAS in ground water and drinking water. Campo (Campo et al. 2014) analysed influent, effluent and sludge samples from 16 waste water treatment plants from different locations in Spain for 21 PFAS. Over two years only 2 of the samples were free from PFAS and it was estimated this contributed between 16 and 67 gday⁻¹ of PFAS to the receiving rivers. In an extreme case Eschauzier (Eschauzier et al. 2013) reported a combined total PFAS of 4400 ngL⁻¹ in landfill leachate and Busch (Busch et al. 2010) reported 8060 ngL⁻¹ and 12819 ngL⁻¹ in treated leachate and untreated leachate respectively.

Increasing concern about PFAS led to the U.S. EPA to work with chemical companies to reduce the production of PFOA and PFOS and in 2016, set a combined PFOA and PFOS drinking water advisory level of 70 ngL⁻¹ (US EPA 2016). In Europe, PFOA and PFOS were added to the Stockholm convention on Persistent Organic Pollutants in 2017 (UN Environment 2017). However, the industry response was to manufacture structurally similar PFAS by varying the carbon chain length. This is legitimate business practice but did nothing to reduce the amount of PFAS in the environment and only exacerbated the problem by increasing the number of different PFAS making them more difficult to analyse and quantify. Precursor compounds can potentially breakdown to more persistent PFAS which due to their extreme stability, will recirculate in the environment for decades to come. The perfluoroalkyl carboxylic acids (PFCA) and perfluoroalkyl sulfonic acids (PFSA) are often the ultimate degradation product for these precursor contaminants and their presence can be used as markers of PFAS contamination.

Although dietary intake is considered a major source of human exposure to PFAS, there are no universally recognised standards or regulations to routinely measure PFAS in food. In September 2020 the European Food Safety Authority (EFSA) recommended a maximum intake of 4.4 ng of PFAS per kg body weight per week (European Food Safety Authority 2020). Similarly, there are current regulations for PFOA and PFOS which apply to drinking water and if the concentration of either exceeds 0.3 ugL⁻¹ monitoring is put in place (DWQRS 2009).

Although a maximum intake has been specified, there are no regulations to routinely measure PFAS in food or drinking water. However, there is growing evidence of PFAS in food, probably from bio-accumulation of contaminants present in fertilisers or ground water, but this is still unclear (Stahl et al. 2009). There is also evidence to suggest that this contamination could be from sewage sludge treated agricultural soil (Johnson 2022; Pepper et al. 2021).

The PFCA and PFSA transformation products with a carbon chain length of 6 or less are regarded as short chain PFAS, C₇ and greater are long chain PFAS. A study by Higgins (Higgins and Luthy 2006) demonstrated the longer chain PFAS were more likely to adsorb to the soil

and therefore less likely to be taken up by the plant. However, the C₈ chain lengths were the lowest C chain length in the study.

The short chain PFAS are more easily taken up by plants from the soil but have a shorter metabolic half-life in humans ranging from a few days to a month and are excreted unchanged, whereas the longer chain versions can persist in the human body for years (European Food safety Authority 2020). Food matrices are very varied, and PFAS content is also expected to vary depending on the fat or water content of the product as well as growing conditions. PFAS have been previously detected in cows' milk and dairy products (Hill, Becanova, and Lohmann 2022; Young et al. 2012). Processing and packaging are possible sources of PFAS contamination as well as animal feed or grass fertilized using sewage sludge. Milk could be a significant contributor of dietary PFAS especially to young children. Food with a high water content, e.g. strawberries and tomatoes, is likely to accumulate PFAS from groundwater irrigation as well as fertilizers. The aim of this study is to quantify various end-point PFCAs and PFSAs in tomato, strawberry and milk.

Liquid chromatography mass spectrometry (LCMS) has become the method of choice for determination of trace pollutants in complex matrices. It is highly specific as detection is based on the chemical composition of the analyte of interest. Therefore, for quantitative methods the analyte can be determined by retention time, precursor ion and product ion reducing the risk of false positives. This makes it capable of quantifying multiple analytes in one sample providing more comprehensive information about the occurrence of contaminants in an individual sample. The analysis is further enhanced by the development of low cost and efficient extraction techniques, e.g. QuEChERS (quick, easy, cheap, effective, rugged, and safe) method, to enrich the analyte in the sample and remove extraneous material which might affect the analysis. However, even when the sample is extracted, interferences can still remain. This is called matrix effect and can be a problem especially when using an electrospray ion-source (Nasiri et al. 2021). Although a specific analyte ion is used for the analysis there are still background ions which can adversely affect the analyte signal. Matrix effect can cause an artificial decrease or increase in the signal known as ion suppression or ion enhancement respectively. There is a need to demonstrate the effect the matrix has on the different analytes. Although PFAS described in this paper are from two homologous series and may be considered to behave in a similar manner in the mass spectrometer, they each elute at a different retention time and have the potential to co-elute with different contaminants thereby causing different matrix effects. The matrix effect, along with the recovery efficiency of the target analytes using a QuEChERS method, will be determined.

Experimental

Materials

Perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid PFHxA, perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUdA), perfluorododecanoic acid (PFDoA), perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonic acid (PFHxS), Sodium chloride and magnesium sulphate were purchased from Sigma Aldrich. PFOS and the internal standards ¹³C PFBA, ¹³C PFHxA, ¹³C PFOA and ¹³C PFOS were purchased from LGC. Optima acetonitrile and Optima methanol were from Fisher Scientific.

The tomatoes, strawberries and milk were purchased from two different supermarkets and one independent shop in separate locations on different days. The tomatoes were wrapped in plastic, the milk was in a plastic carton and the strawberries had no wrapping.

Instrumentation and LCMS Conditions

The mass spectrum used was a Thermo Scientific Q-exactive Orbitrap mass, connected to a Dionex Ultimate 3000 RS Pump, Dionex Ultimate 3000 RS Autosampler (temperature controlled at 10 °C) and Dionex Ultimate 3000 RS Column Compartment (temperature controlled at 30 °C). The LC column was a Waters Xselect HSS T3 2.5 µm 2.1 x 150 mm Column XP fitted with a C18 guard cartridge. The flow rate was set to 0.2 mLmin⁻¹ and the injection volume was 10 µL. Gradient elution was chosen: solution (A) was methanol. Solution (B) was 10 mM ammonium formate and formic acid at pH 3.5 in 18 MΩ water. 95% of (B) was run for 1 minute, then up to 95% (A) over 7 minutes, and held for 5 minutes. It was then returned to initial conditions in 1 min and equilibrated with 95% of (B) for 7 minutes. A Raptor PFAS Delay column (50 x 2.1 mm) was fitted after the LC pumps and before the injection system in order to remove PFAS from the solvent system. Stainless steel tubing was used throughout.

The mass spectrometer was operated in negative ion mode. The electrospray conditions were set with a sheath gas of 45 arbitrary units, auxiliary gas 10 arbitrary units, capillary and auxiliary gas temperature 300°C. The spray voltage was -4.5 kV and the mass resolution 17,500.

Calibration Line

The 10 point calibration line was prepared in acetonitrile/water (20/80) over the range 0.1 – 50 ngmL⁻¹. The internal standards, ¹³C PFBA, ¹³C PFHxA, ¹³C PFOA and ¹³C PFOS, were added to the calibration standards and the samples at a concentration of 10 ngmL⁻¹. The peak area for the internal standard should be the same throughout the analysis unless there are interferences. The response is calculated as a ratio of analyte peak area/internal standard peak area and is called the response ratio. The calibration line is created using the response ratio at the different concentrations and the concentration of the unknown determined from it.

Recovery Experiment

A simple QuEChERS method was developed to extract PFAS from the food matrices. The recoveries were performed on tomato and milk. Tomato was emulsified using a stick blender until homogeneous and the milk was taken straight from the carton. In a centrifuge tube, the matrix (5g) was spiked with the PFAS mixture to a concentration of 10 ngmL⁻¹ for all the analytes except for PFOS which was spiked at 1 ngmL⁻¹, followed by 5mL of acetonitrile + 1g of NaCl. The mixture was vortexed for 5 minutes then centrifuged for 20 minutes at 400 rpm. The organic (upper) layer (4 mL) was collected, dried at 40°C then reconstituted in 0.8 mL of acetonitrile/water 20/80 with sonication for 15 minutes. The samples were filtered through a Whatman 0.45 µm nylon filter before analysis.

Matrix Effect Experiment and Quantitation

The QuEChERS method was scaled up to 200g of matrix for tomato, milk and strawberry. Different volumes of acetonitrile were collected due to scale up issues with the different matrices. The volume of acetonitrile collected was measured, the batch dried down as described above and reconstituted in the appropriate amount of acetonitrile/water 20/80. The batch of extracted matrix was filtered through a Whatman 0.45 µm nylon filter. The blanks had no further treatment. Aliquots were spiked to a concentration of 5, 10 and 25 ng mL⁻¹ except for PFOS which was spiked at 0.5, 1 and 2.5 ngmL⁻¹.

The matrix effect was calculated using the equation below.

Matrix effect = $\frac{\text{Concentration in Matrix}}{\text{Concentration in Solvent}} \times 100$

Where matrix is the concentration determined in the spiked matrix and solvent is the same concentration spiked into acetonitrile/water 20/80.

Results

Specificity

The risk of false positives using HRMS is greatly reduced as each analyte is quantified based on retention time, precursor and product ion. Table I describes the retention time and transitions used for each of the PFAS analysed.

Table I. Retention time mass spectrometry transition and calibration range for each analyte. PRM = Parallel reaction monitoring.

Abbreviation	Name	Molecular Formula	Retention Time (Minutes)	PRM transition	Calibration Range (ngmL ⁻¹)	Internal Standard
PFBS	Perfluorobutane sulfonic acid	C ₄ HF ₉ O ₃ S	9.1	298.94 → 79.9558	0.25 - 10	¹³ C PFBA
PFBA	Perfluorobutanoic acid	C ₄ HF ₇ O ₂	8.2	212.98 → 168.9877	0.25 - 100	¹³ C PFBA
PFPeA	Perfluoropentanoic acid	C ₅ HF ₉ O ₂	9.1	262.9757	0.1 - 50	¹³ C PFHxA
PFHxA	Perfluorohexanoic acid	C ₆ HF ₁₁ O ₂	9.6	312.97 → 118.9911	0.1 - 100	¹³ C PFHxA
PFHxS	Perfluorohexane sulfonic acid	C ₆ HF ₁₃ O ₃ S	10	398.94 → 79.9558	0.1 - 10	¹³ C PFOS
PFHpA	Perfluoroheptanoic acid	C ₇ HF ₁₃ O ₂	9.9	362.97 → 168.9877	0.25 - 100	¹³ C PFOA
PFOA	Perfluorooctanoic acid	C ₈ HF ₁₅ O ₂	10.3	412.97 → 168.9877	0.1 - 100	¹³ C PFOA
PFOS	Perfluorooctane sulfonic acid	C ₈ HF ₁₇ O ₃ S	10.6	498.93 → 79.9558	0.025 - 100	¹³ C PFOS
PFNA	Perfluorononanoic acid	C ₉ HF ₁₉ O ₂	10.6	462.96 → 168.9877	0.1 - 100	¹³ C PFOA
PFDA	Perfluorodecanoic acid	C ₁₀ HF ₂₁ O ₂	10.8	512.96 → 168.9877	0.25 - 100	¹³ C PFOA
PFUdA	Perfluoroundecanoic acid	C ₁₁ HF ₂₃ O ₂	10.9	562.96 → 168.9877	0.25 - 100	¹³ C PFOA
PFDoDA	Perfluorododecanoic acid	C ₁₂ HF ₂₅ O ₂	11.1	612.95 → 168.9877	0.1 - 100	¹³ C PFOA

Instrument performance

Before implementation of the delay column PFBA was determined in most samples and blanks. This was not a consistent amount and varied greatly between samples with no discernable pattern. Once the delay column was in place the results were consistent and blanks were free from PFBA. The overall chromatography was improved when ammonium formate was included in the mobile phase as it removed the peak tailing and improved the peak shape (Figure I).

Calibration Data

Table II shows the inter-day calibration data for the PFAS for a 10 point calibration. The data was processed using a 1/X² regression (excluding the origin) and a % relative error of +/- 30 for the points as acceptance criteria for better accuracy at low concentration. The limit of quantitation was set at the lowest calibration standard concentration which fitted this criterion. The average inter-day relative error was from 7 calibration sets run over 4 days.

Table II. Calibration and system performance average inter-day relative error.

Nominal Concentration (ngmL ⁻¹)	Inter-day % Relative Error for Calibration Data											
	PFBA	PFBS	PFPeA	PFHxA	PFHxS	PFHpA	PFOA	PFOS	PFNA	PFDA	PFUdA	PFDodA
0.1	234.71	-72.71	-11.05	-10.86	-14.1	-65.65	2.59	-4.53	-13.08	111.97	34.4	-1.37
0.25	-14.12	-6.17	12.6	-9.42	7.27	-5.33	3.78	-6.78	-1.11	6.56	21.38	-7.33
0.5	23.32	21.49	29.35	5.51	13.17	27.15	14.93	7	34.47	7.58	-0.97	18.6
1	0.9	17.17	13.52	-12.35	13.24	11.17	-1.86	-1.32	6.48	-11.51	-12	-6.12
2.5	-3.72	8.84	7.38	-1.28	10.21	11.82	5.19	1.09	12.64	-3.85	-5.67	-1.8
5	6.83	-0.81	5.54	11.55	-0.42	5.95	8.5	5.7	9.36	7.43	-1.11	8.66
10	0.45	-22.85	-9.19	-5.39	-19.65	-12.22	-1.72	13.89	-4.5	2.1	-6.76	-2.89
25	-0.31	-45.69	-21.58	4.95	-39.87	-21	-0.24	6.28	-6.69	6.04	-1.57	2.5
50	0.96		-27.81	6.99	-54.17	-19.72	2.79	4.22	-5.27	4.32	1.86	-5.15
100	-0.26		-31.35	-2.69	-63.61	-18.3	-1.2	-3.21	-13.75	6.61	-5.61	-19.01

Limit of Detection and Quantitation

The limit of detection (LOD) and limit of quantitation (LOQ) can be calculated by using $3xS/N$ (LOD) and $10 \times SN(LOQ)$. However, this proved unsatisfactory as even at the lowest calibration standard for most of the analytes the signal/noise was infinity. Therefore, to achieve an LOQ value, the most reliable and lowest (Evard, Krueve, and Leito 2016; Miller and Miller 2010; Analytical Methods Committee 2001; B. Magnusson and U. Örnemark (eds.) 2014) concentration in the calibration line was used. Samples designated <LOQ had a value between zero and the lowest acceptable calibration standard. If no peak was determined this was not detected (ND). Due to the sample preparation concentration factor, the data was quantified based on the LOQ from the calibration line and divided by 5.

The data is summarized for each analyte in Table I. The calibration range is also reported where the LOQ is the lowest calibration concentration.

Recovery

The recovery data from milk is over 2 days with 9 extractions each day and for tomato is over 3 days and 9 extractions each day. Most of the recoveries are between 80 and 120%, only PFOS was slightly lower (Figure II). Due to PFBA in the blank samples the recovery was calculated by subtracting the amount of PFBA in the sample from the spiked recovery sample and comparing to the solvent. For milk the recovery for PFBA was 112.6% and for tomato the average recovery was 114.8%.

Results Matrix effect

A matrix effect between 80 and 120% is regarded as no effect. If the matrix is below 80% there is ion suppression and above 120% ion enhancement.

Table III. Matrix effect with and without internal standard. *The analyte had a matched stable isotope internal standard, the others were a surrogate internal standard. S = Suppressed.

Analyte	Matrix Effect with Internal Standard			Matrix Effect no Internal Standard		
	Milk	Tomato	Strawberry	Milk	Tomato	Strawberry
PFBA*	208	136	125	NA	NA	NA
PFBA* - blank	116	114	115	67	133	58
PFHxA*	105	ND	ND	159	ND	ND
PFOA*	118	69	105	182	50	69
PFOS*	96	89	94	139	24	61
PFBS	115	75	35	138	75	35
PFPeA	115	104	39	167	104	19
PFHxS	86	80	64	125	79	65
PFHpA	109	205	227	160	152	149
PFNA	133	75	132	203	55	132
PFDA	104	81	58	158	61	38
PFUdA	120	23	S	182	15	20
PFDODA	83	S	S	127	S	S
Internal Standard	Milk	Tomato	Strawberry	Milk	Tomato	Strawberry
13C PFBA	NA	NA	NA	121	117	51
13C PFHxA	NA	NA	NA	151	49	33
13C PFOA	NA	NA	NA	154	74	66
13C PFOS	NA	NA	NA	145	43	68

PFAS in food

The amount of PFAS determined in each of the foods is summarized in Table IV where the data has been corrected for the concentration factor. Most analytes were not detected (ND) in the samples. In some cases, analyte was detected but was below the limit of quantitation (<LOQ) which is specified in Table I.

Table IV. PFAS concentration in food. Data has been corrected for the five-fold concentration factor.

	Concentration in ng g ⁻¹		
	Milk	Strawberry	Tomato
PFBS	ND	ND	ND
PFBA	0.58	0.20	0.36
PFPeA	0.04	ND	ND
PFHxS	ND	ND	ND
PFHxA	ND	ND	ND
PFHpA	0.03	ND	ND
PFOA	<LOQ	ND	ND
PFOS	ND	ND	ND
PFNA	ND	ND	ND
PFDA	0.03	ND	ND
PFUdA	ND	ND	ND
PFDaA	ND	ND	ND
Σ PFAS	0.68	0.20	0.36

Discussion

Recovery

The recovery data for tomato and milk was generally good and between 80 and 120%. This was with the exception of PFOS in tomato which was low at 69.3%. For the other analytes the recovery from milk is consistently lower which may be due to protein binding (Forsthuber et al. 2020) of the PFAS. Although it is lower the recoveries are still acceptable.

Matrix Effect

In milk, signal enhancement is observed for most of the analytes without the internal standard, this is well compensated when the internal standard is included even when it is not the matched stable isotope. In tomato and strawberry matrix suppression is observed. In tomato, inclusion of the internal standard compensates for the ion suppression effects, including some of those which are not matched. However, in strawberry only the data with the matched internal standards compensate well. The analytes elute between 8 and 12 minutes (Figure I) and this is the noisiest part of the matrix for tomato and strawberry. Strawberry shows most contamination across the analyte peak area despite having the QuEChERS extraction. Although the extraction method removed much of the extraneous matter and gave good recoveries for tomato and strawberry, further cleanup is required, for example using solid phase extraction. The lower recoveries for milk are possibly due to protein binding of the PFAS. The full scan chromatogram for milk shows less contamination across the same retention time. This might explain why there is no suppression but does not explain the signal enhancement. There is less interference in the tomato matrix for PFBA and PFBS which is reflected in the matrix effect results (Zhou, Yang, and Wang 2017).

The current EFSA recommended maximum intake for PFAS is 4.4 ngkg⁻¹ body weight per day. The average weight for a UK man and woman is 83.6 kg and 70.2 kg respectively and therefore a maximum Σ PFAS intake of 368 ng and 309 ng for each. Based on the concentration determined in food stuffs described in Table 4, consuming in excess of 542 g milk, 1840 g strawberry and 1023 g tomato would exceed the intake for a man and 453 g milk, 1540 g strawberry and 856 g tomato for a woman. Although this might seem a lot to consume, only 3 foods were tested and if other foods have similar concentrations of PFAS there will be an accumulative effect throughout the day. The daily maximum intake for an average 3 year old 14 kg child weighing 14 kg() is 61.6 ng. As little as 100g of milk would contribute 68 ng of PFAS alone and a helping of 308 g strawberry and 171 g tomato would also pass the maximum daily intake. The half-life of PFBA in humans is less than longer chain PFAS. However, they are still excreted unchanged and will continue to circulate in the environment for decades with the potential to be re-consumed.

Conclusion

This study describes a cheap and easy method to extract PFAS from food matrices. The method has demonstrated the requirement for a delay column to remove unwanted PFAS contamination which greatly affects the quantitation. Although good intra-day calibration data and recoveries were achieved the data demonstrates the variation of signal by the different matrix. In some cases a surrogate stable isotope internal standard can suffice. This was successful for milk and partially successful for tomato. However, it was only the analytes with the matched internal standards in strawberry which compensated for matrix effect. This demonstrates that although the described QuEChERS method is useful to enrich the analyte, it does not adequately remove interferences in some for example in strawberry, and requires further sample treatment for the long chain PFAS.

PFBA had a matched internal standard, good recovery, minimal matrix effect and was found in all the test substances. This demonstrates even with a ban on the use of C8 PFAS the problem of these substances in food is still an issue and should be monitored on a more regular basis, especially for the shorter chain length versions which are becoming more common.

Declarations

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Author Contribution

Joanne Roberts was responsible for the conceptualization and funding acquisition. Joanne Roberts and Moyra McNaughtan wrote the main text. Hector de las Heras Prieto contributed to most of the practical work with some participation from Joanne Roberts. Hector de las Heras Prieto and Joanne Roberts were responsible for the data analysis.

Table I, II and Figure III were prepared by Hector de las Heras Prieto. Table III, IV and Figure II were prepared by Joanne Roberts.

All three authors reviewed the manuscript before submission.

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Author Declaration

The authors have no relevant financial or non-financial interests to disclose.

Data availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Ethics Approval: This study does not contain experiments involving animals or humans.

Informed Consent: Not Applicable.

Conflict of Interest: Joanne Roberts declares she has no conflict of interest, Moyra McNaughtan declares she has no conflict of interest, Hector de las Heras Prieto declares he has no conflict of interest.

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Figures

Figure 1

extracted ion chromatograms for the PFAS and the matrices over the scan range $m/z = 120 - 1800$ amu.

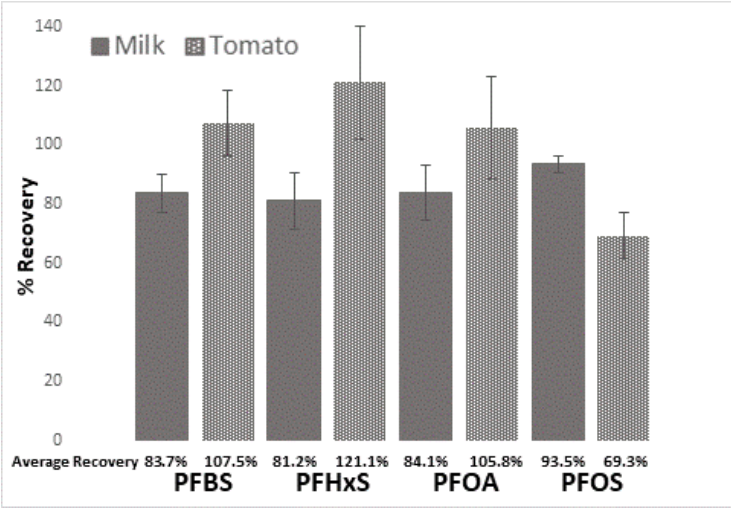


Figure 2

Recovery of PFAS from tomato and milk.