The Analysis of Water for Perfluorinated Compounds Using Automated Solid Phase Extraction

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What are PFCs?

- Perfluorinated chemicals (PFCs) are all manmade and have unique properties such as repelling oil, grease and water.
- PFCs were found to be unreactive and extremely useful and have been used in non-stick coatings, firefighting foams, package material coatings, waterproofing and stain-proof fabrics

Health Concerns

- PFCs persist in the environment and can bioaccumulate
- They pose risks to the developmental, immune, metabolic, and endocrine health of consumers
- PFOA does not break down in the environment; the human half-life is estimated at about 3 years
- Small amounts of PFCs can dissolve in water
- The largest potential source of human exposure is through drinking water

https://www.ncbi.nlm.nih.gov/pmc/articles/PMC2920088/
http://www.cancer.org/cancer/cancercauses/othercarcinogens/athome/teflon-and-perfluorooctanoic-acid--pfoa

Evaluation of Occurrence

- Regulations generally take into account both toxicity and the occurrence or chance of exposure through a medium
- US EPA included six of these chemicals into the third Unregulated Contaminant Monitoring Rule (UCMR 3) in 2012
- UCMR 3 required monitoring for 30 contaminants (28 chemicals and two viruses) between 2013 and 2015 using analytical methods developed by EPA, consensus organizations or both
- The data summary from the extensive study found 0.9% of the public water supplies studied showed concentrations of PFOS greater than the reference level (0.07 µg/L)
- Of the public water supplies studied, 0.3% showed levels of PFOA above the reference level (0.07 µg/L)

https://www.epa.gov/sites/production/files/2016-05/documents/ucmr3-data-summary-april-2016.pdf

Health Advisory Issued

- Water utilities should notify customers if greater than 70 ppt (0.07 µg/L) PFOS or PFOA or a total for the two combined are detected in the water supply

EPA United States Environmental Protection Agency

FACT SHEET
PFOA & PFOS Drinking Water Health Advisories

Overview

EPA has established health advisories for PFOA and PFOS based on the agency's assessment of the latest peer-reviewed science to provide drinking water system operators, and state, tribal and local officials who have the primary responsibility for overseeing these systems, with information on the health risks of these chemicals, so they can take the appropriate actions to protect their residents. EPA is committed to supporting states and public water systems as they determine the appropriate steps to reduce exposure to PFOA and PFOS in drinking water. As science on health effects of these chemicals evolves, EPA will continue to evaluate new evidence.

https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos

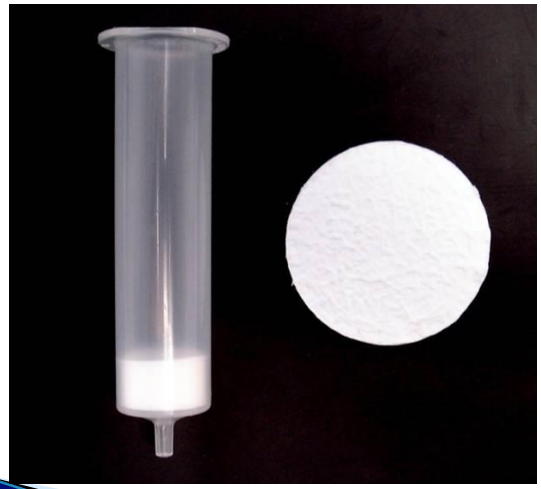
World Wide Concerns

- The twelfth meeting of the United Nations Persistent Organic Pollutants Review Committee was held in Rome in September 2016 to move the consideration of PFCs forward for further regulatory consideration

- Rules developed under this framework will have global impact

Disks vs. Cartridges for SPE

- Disks are excellent when larger volumes of liquid or liquid with particulates need to be extracted
- Cartridges are convenient for smaller volumes and when the samples are relatively free from particulates
- Example shown here is an application for food and although the sample is small it has particulates
- For drinking water, particulates are generally low so depending on the volume, either cartridges or disks will work well



P1-205 Concentrations of Perfluoroalkyl Substances in Foods and Ingestion Exposure among Adults in Taiwan

IAFP 2015 PORTLAND JULY 25-28 OREGON

Sunday, July 26, 2015
Exhibit Hall (Oregon Convention Center)

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Introduction: Perfluoroalkyl substances (PFASs) are persistent, bioaccumulative, and ubiquitous in the environment and may contaminate foods; ingestion is a major route of human exposure.

Purpose: To evaluate human exposure to PFASs, this study quantified six perfluorocarboxylic acids (PFCAs) and two perfluorosulfonic acids (PFSAs) in fourteen majorly consumed foods (total 140 samples) in Taiwan using UPLC-MS/MS with isotope-dilution techniques.

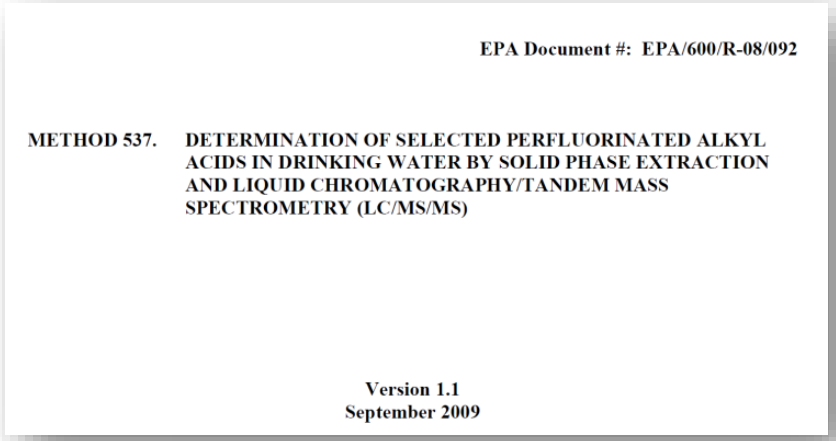
Methods: One-gram homogenized wet samples were digested with 10 ml of 0.5 N potassium hydroxide (KOH) in methanol, and 5-ml supernatant of the samples after centrifugation were diluted with 500-ml Milli-Q water, adjusted to pH 3.5, and were extracted with Atlantic HLB disk by automated solid-phase extraction. Analytes were eluted with 20-ml methanol containing 0.1% ammonium hydroxide (v/v); the eluent were concentrated to 1 ml by a SpeedVac and were analyzed by ultra-high performance liquid chromatography/tandem mass spectrometry at negative electrospray ionization.

Results: The long-chained PFCAs with 10 - 12 carbons were detected in all of the samples with the geometric means ranged from 0.04 to 12.3 ng/g, which were higher than previous reports. Perfluorooctane sulfonate (PFOS) was not detected as frequently as demonstrated in other studies and the measured concentrations ranged from 0.11 ng/g (clam) to 9.91 ng/g (pork liver) in average. Rice and pork liver were rarely studied but some considerable concentrations, such as up to 283 ng/g of perfluorooctanoic acid (PFOA) in liver, were observed in this study.

Significance: Although the daily intake of PFOA (85.1 ng/kg b.w./day) and PFOS (0.46 ng/kg b.w./day) did not exceed the tolerable daily intake suggested by the European Union, Germany, and the U.K., people in Taiwan exposed to more perfluorohexanoic acid, PFOA, perfluorodecanoic acid, and perfluoroundecanoic acid (11.2, 85.1, 44.2, and 4.45 ng/kg b.w./day, respectively) than in western countries, demonstrating that the distribution of PFASs and the dietary habits are crucial to the exposure.

Analytical Methods for PFCs in Drinking Water

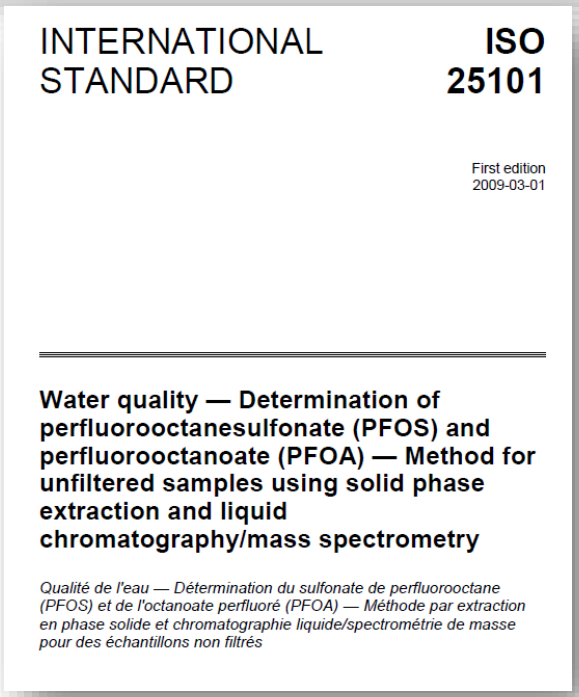
- US EPA Method 537, Rev 1.1
  - SPE using a PSDVB cartridge to extract 250 mL of water for a suite of PFCs
  - Analysis: HPLC/MS/MS
- ISO 25101:2009
  - SPE for extraction of PFOS and PFOA from water
  - SPE Sorbents: HLB/WAX, HLB, C18, PSDVB
  - Analysis: HPLC/MS/MS
  - The method is applicable to a concentration range of 2,0 ng/L to 10 000 ng/l for PFOS and 10 ng/L to 10 000 ng/L for PFOA.



EPA Document #: EPA/600/R-08/092

METHOD 537. DETERMINATION OF SELECTED PERFLUORINATED ALKYL ACIDS IN DRINKING WATER BY SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY (LC/MS/MS)

Version 1.1
September 2009



INTERNATIONAL STANDARD **ISO 25101**

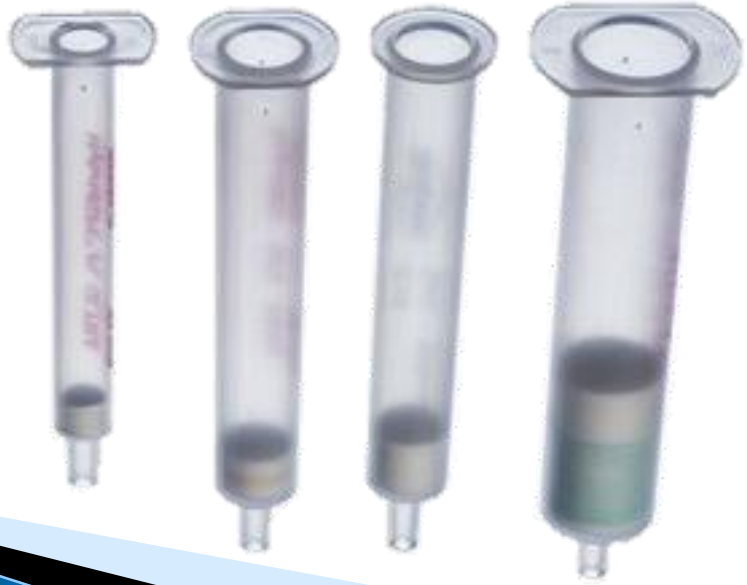
First edition
2009-03-01

Water quality — Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) — Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry

Qualité de l'eau — Détermination du sulfonate de perfluorooctane (PFOS) et de l'octanoate perfluoré (PFOA) — Méthode par extraction en phase solide et chromatographie liquide/spectrométrie de masse pour des échantillons non filtrés

SPE Cartridges

- SPE Cartridges were used for this work
- When cartridges are used, inconsistent flow rates or flow rates faster than specified can affect the recovery and precision. Performance using an automated system can provide more consistent recovery than manual efforts on a manifold



SmartPrep Cartridge Extractor II

- Positive pressure for consistent liquid flow
- All FEP tubing to eliminate sample contact with any contamination
- Segregated waste to dispose of solvent properly
- Fully automates the extraction process
- Precise flow rate control gives better recoveries and consistency
- More efficient method development
  - Multiple methods
  - Fraction collection to screen load, wash and elution steps to determine breakthrough and optimal elution volumes

Experimental

- SmartPrep Extractor II (Horizon Technology)
- Strata® SDBL 100 µm Styrene-divinylbenzene, 6-mL cartridge (Phenomenex)
- N-Evap 112 (Organomation)
- Prominence HPLC System (Shimadzu)
- Atlantis® dc18, 5 µm, 2.1 x 150 mm HPLC column (Waters).
- API4000 LC/MS/MS (SCIEX)

SmartPrep Extractor Procedure

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- Condition cartridge with methanol and reagent water
- Load 250 mL sample onto cartridge
- Rinse sample bottle with multiple water rinse steps
- Load rinse water onto cartridge and purge with N2
- Rinse sample bottle with multiple methanol rinse steps
- Elute sample from cartridge with methanol

Method Summary

1. Collect samples (250 mL) in polypropylene bottles and caps. (A preservative, Trizma® buffering agent, is added to bottle prior to collection.)
2. Add all appropriate standards and surrogates, then cap and invert sample bottle to mix.
3. Load each sample into a position on the SmartPrep extractor with sample sip tube and rinse cap.
4. Load the sample method and sample name in the sequence for each sample to be extracted.
5. Start the sequence.
   - All the appropriate conditioning, air-dry, rinsing and elution steps started are fully automated.
6. The finished extracts are then concentrated to dryness under a gentle stream of nitrogen to remove the water/MeOH mixture.
7. Internal standard is added to the dried extracts and brought to a 1 mL volume with 96:4% (vol/vol) MeOH:water).
8. Follow procedures (EPA method 537, in this case) for the storage of extracts.
9. Analyze by LC/MS/MS.

Method Quality Control (QC)

- US EPA Methods generally require a demonstration of capability before a method can be used for samples and QC tests continuing throughout the analysis. Method 537 is very rigorous
- Some flexibility in how the method is performed is allowed, but the results must still meet quality control requirements
- Initial Demonstration of Capability
  - Generate calibration curve, meeting the criteria specified for forced through zero, peak symmetry factor and validation with initial checks and continuing calibration check samples from a different source
  - Initial demonstrations are performed to show:
    - Low background
    - Adequate precision
    - Adequate accuracy
    - Method detection limit (MDL) determination
    - Evaluation and confirmation of the minimum reporting level (MRL)

Method Quality Control (QC)

- On-Going QC Requirements
  - Laboratory Reagent Blank (LRB)
  - Continuing Calibration Check (CCC)
  - Laboratory Fortified Blank (LFB)
  - Internal standard and Surrogate requirements help to ensure the sample preparation is characterized and under control
  - Laboratory Fortified Sample Matrix (LFSM)
  - Field Duplicate or Laboratory Fortified Sample Matrix Duplicate
  - Field Reagent Blank
  - Quality Control Sample

Six PFCs from UCMR 3

	EPA Method 537 Analyte List	Acronym	CAS
	N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	NA
	N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	NA
1	**Perfluorobutanesulfonic acid**	**PFBS**	**375-73-5**
	Perfluorodecanoic acid	PFDA	335-76-2
	Perfluorododecanoic acid	PFDoA	307-55-1
2	**Perfluoroheptanoic acid**	**PFHpA**	**375-85-9**
3	**Perfluorohexanesulfonic acid**	**PFHxS**	**355-46-4**
	Perfluorohexanoic acid	PFHxA	307-24-4
4	**Perfluorononanoic acid**	**PFNA**	**375-95-1**
5	**Perfluorooctanesulfonic acid**	**PFOS**	**1763-23-1**
6	**Perfluorooctanoic acid**	**PFOA**	**335-67-1**
	Perfluorotetradecanoic acid	PFTA	376-06-7
	Perfluorotridecanoic acid	PFTrDA	72629-94-8
	Perfluoroundecanoic acid	PFUnA	2058-94-8

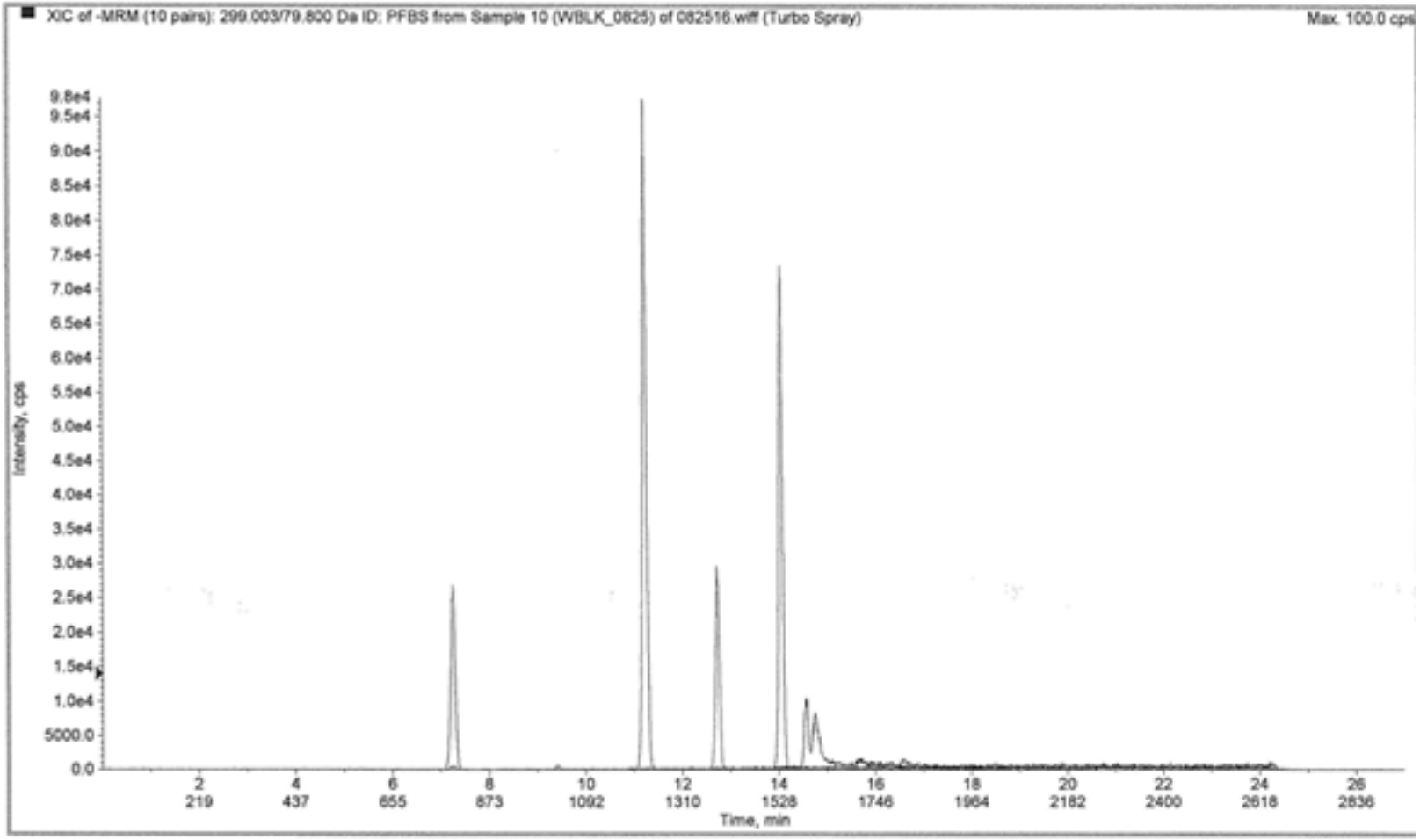
Unregulated contaminant monitoring rule

Demonstration of Low System Background

Compound	Area	INST (µg/L)	Final Conc. (µg/L)
PFBS	0.00	0	0
PFHpA	0.00	0	0
PFHxS	0.00	0	0
PFOA	0.00	0	0
PFNA	0.00	0	0
PFOS	1177	0.072	0.0003
SUR C13-PFHxA	176007	10.1	101%
SUR C13-PFDA	404135	9.42	94.2%
C13-PFOS-(ISTD)	166900	10.0	0.0400
C13-PFOA-(ISTD)	561125	10.0	0.0400

Low background and good surrogate recovery seen
LRB laboratory reagent blank

Low Background Chromatogram



The chromatogram is very clean and the small amount of PFOS detected is well below the reportable limit

IDC Study, Measure of Precision and Accuracy (Spikes are in ng/L)

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									Acceptance Range		
Compound	1	2	3	4	AVG	CONC.	% Rec	Std Dev	-30%	+30%	%RSD
PFBS	160	168	165	157	163	180	90.3	4.78	126	234	2.94
PFHpA	19.9	20.4	19.6	19.1	19.8	20.0	98.8	0.538	14.0	26.0	2.72
PFHxS	52.0	54.4	52.6	51.5	52.6	54.7	96.2	1.28	38.3	71.1	2.43
PFOA	38.0	38.9	38.3	38.2	38.4	40.0	95.9	0.359	28.0	52.0	0.937
PFNA	39.9	42.6	41.1	39.5	40.8	40.0	102	1.39	28.0	52.0	3.41
PFOS	69.6	71.9	68.5	67.4	69.3	74.3	93.3	1.92	52.0	96.6	2.77
SUR C13-PFHxA	8.69	9.07	9.19	8.64	8.90	10.0	89.0	0.272	7.00	13.0	3.06
SUR C13-PFDA	10.4	10.6	10.8	10.2	10.5	10.0	105	0.230	7.00	13.0	2.19

The Initial Demonstration of Precision (IDP) must meet a RSD of less than 20% and the Initial Demonstration of Accuracy (IDA) must meet an average recovery of ± 30% of the compounds true value. Each of the compounds pass the criteria for the IDP by demonstrating a range from 0.94%-3.41% RSD. The IDA is within the method requirement of ± 30% for determining accuracy of the spiked amounts for each of the six PFCs.

MDL Study

Compound	MDL 1	MDL 2	MDL 3	MDL 4	MDL 5	MDL 6	MDL 7	MDL 8	AVG	SDev	CONC.	MDL (µg/L)	LOQ (µg/L)	CONC/ MDL
PFBS	0.036	0.039	0.029	0.039	0.041	0.037	0.041	0.039	0.0375	0.0037	0.0450	0.0111	0.0371	4.05
PFHpA	0.004	0.004	0.003	0.004	0.004	0.004	0.004	0.004	0.0041	0.0003	0.0050	0.00099	0.00331	5.04
PFHxS	0.013	0.013	0.010	0.013	0.013	0.012	0.012	0.013	0.0124	0.0013	0.0137	0.00385	0.0128	3.55
PFOA	0.008	0.009	0.007	0.009	0.009	0.008	0.009	0.008	0.0084	0.0008	0.0100	0.00229	0.00764	4.37
PFNA	0.009	0.010	0.007	0.009	0.010	0.009	0.009	0.009	0.0090	0.0008	0.0100	0.00231	0.00772	4.32
PFOS	0.016	0.016	0.013	0.016	0.017	0.016	0.017	0.016	0.0157	0.0013	0.0186	0.00376	0.0126	4.94

The MDL values for this method with this sample size and equipment are extremely low. They will be able to measure water samples at the US Health Advisory level of 0.07 µg/L for PFOS or PFOA with MDLs of 0.004 and 0.002 µg/L respectively. The limit of quantitation (LOQ) is 0.013 µg/L for PFOS and 0.0076 µg/L for PFOA, which is acceptable for very low level determinations.

Minimum Reporting Limit (MRL) Confirmation (ng/L)

Compound	1	2	3	4	5	6	7	AVG	SD	HR for PIR	Upper PIR Limit	Lower PIR Limit	CONC
PFBS	16.2	18.4	16.2	17.6	17.7	18.2	17.1	17.4	0.895	3.55	92.9%	61.4%	22.5
PFHpA	1.99	2.29	2.00	2.29	2.27	2.19	2.11	2.16	0.133	0.527	108%	65.4%	2.50
PFHxS	5.46	6.30	5.49	6.40	6.57	6.39	6.24	6.12	0.451	1.79	116%	63.4%	6.83
PFOA	4.03	4.55	4.08	4.58	4.62	4.46	4.22	4.36	0.247	0.978	107%	67.7%	5.00
PFNA	4.21	4.56	4.26	4.95	4.92	4.75	4.67	4.62	0.296	1.17	116%	68.8%	5.00
PFOS	6.97	7.65	7.05	8.31	8.02	8.16	8.13	7.76	0.547	2.17	107%	60.2%	9.29

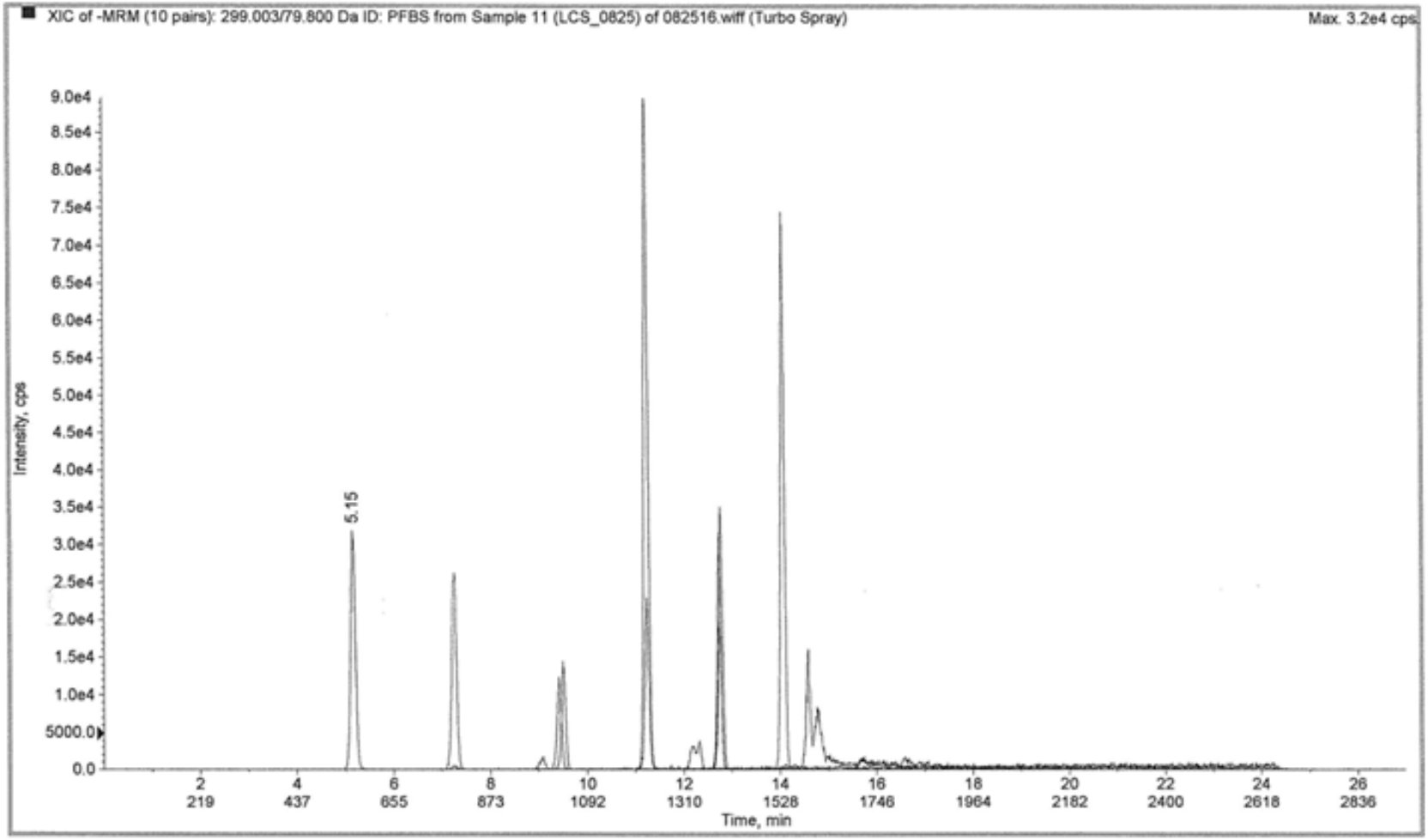
The Upper PIR Limit must be ≤150% recovery
The Lower PIR Limit must be ≥ 50% recovery
Prediction Interval of Result (PIR)

Laboratory Control Sample (LCS)

Compound	Result (ng/L)	Spike Amount (ng/L)	Spike Recovery (%)	Acceptable Range (%)
PFBS	24.9	22.5	111	(50-150)
PFHpA	2.64	2.50	106	(50-150)
PFHxS	7.73	6.83	113	(50-150)
PFOA	5.14	5.00	103	(50-150)
PFNA	5.65	5.00	113	(50-150)
PFOS	9.82	9.29	106	(50-150)

The sample is representative of a drinking water matrix and spiked at a low to mid-range concentration. The LCS spike recoveries are well within the acceptable range specified by the method of 50-150%.

Laboratory Control Sample



Laboratory Fortified Sample Matrix and Duplicate (LFSM and LFSMD)

Compound	Spike Amount (ng/L)	Field Sample Result	LFSM (ng/L)	LFSMD (ng/L)	LFSM Recovery (%)	LFSMD Recovery (%)	RPD
PFBS	22.5	ND	25.4	28.9	113	128	12.7
PFHpA	2.50	ND	2.25	2.62	89.8	105	15.5
PFHxS	6.83	ND	7.12	8.43	104	123	16.8
PFOA	5.00	ND	4.66	5.24	93.3	105	11.8
PFNA	5.00	ND	5.12	5.45	102	109	6.20
PFOS	9.29	ND	9.28	9.74	99.9	105	4.80

The agreement of the duplicates is well within the $\leq$ 30% criteria for concentrations spiked near native concentrations.

Summary

- Although US Method 537 and ISO Method 25101:2009 are both available to guide analysis of PFCs, Method 537 was used here
- Method 537 addresses a larger suite of compounds than PFOA and PFOS, the compounds of most concern
- The quality control requirements before samples are run and during the analysis are clearly described and rigorous in Method 537
- The work done here involved full application of the Method 537 criteria, including calibration requirements, initial demonstration of compliance and on-going quality control and were performed successfully

Conclusion

- Perfluorinated chemicals are of increasing concern in the environment and since drinking water provides a large source of exposure, sensitive and reliable analytical methods for drinking water are essential
- Solid Phase Extraction (SPE) is an excellent mechanism to extract and concentrate PFCs from drinking water and isolate the compounds of interest from interferences and is a standard part of the method
- Automation for the SPE step provides a number of advantages in this analysis including improving reproducibility and reducing the chance of contamination
- This work demonstrated compliance with quality control requirements of method 537 and overall excellent results

Acknowledgment

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Northern Lake Service, Inc., Crandon, WI, USA

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