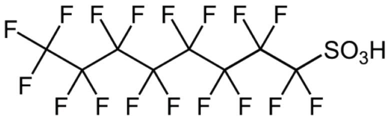
Analyzing PFAS in Wastewater, Solids, & Soils

State of the Science Webinar

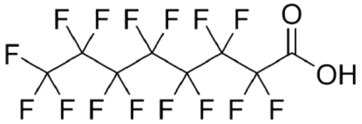
PRODUCED BY nebra North East Biosolids & Residuals Association

PFOS



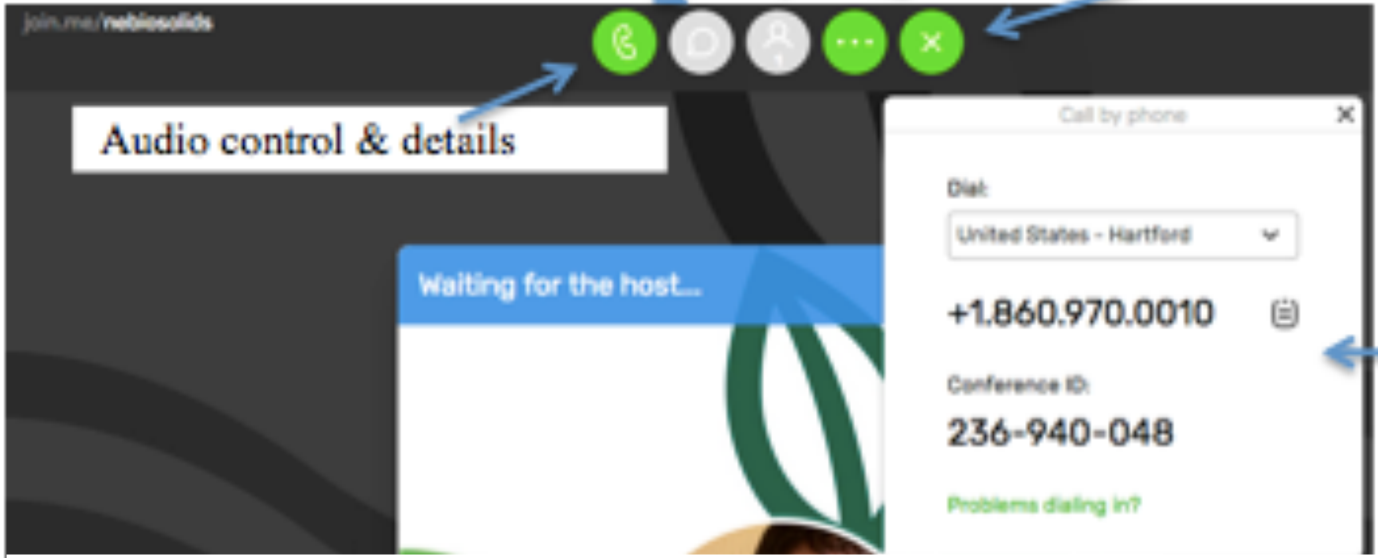
Perfluoro-1-octanesulfoninc acid (PFOS)

PFOA



Perfluoro-n-octanoic acid (PFOA)

INSTRUCTIONS



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Best to use a phone for audio. When prompted, enter the conference ID: 236-940-048 # .

Introduction

- Why are we here?
  - Regulatory agency requests for testing PFAS in wastewater, solids, and soils.
  - Concerns about data quality.
- This webinar is about continual improvement in understanding PFAS in the environment. Analytical methods are critical cornerstones.
- NEBRA is not expert in analytical methods. We are consumers of lab services. We and others in our profession need guidance & quality control.
- We've asked experts for guidance….

NEBRA has resources on PFAS related to solids on our members' page.

Today's Agenda

- **10:00 Welcome**. **This webinar is being recorded.**
- **10:05 EPA Method 537 - Modified** - *Steve DiMattei, EPA Region 1 Laboratory*
- **10:25 Slippery When Wet: Overview and Comparison of Methods 537 and ASTM D7979 and D7968** - *William Lipps, Shimadzu*
- **10:50 Region 5 CRL Methods for the Analysis of Polyfluorinated Compounds (PFAS) Using a Quick Sample Extraction/Preparation Followed by UPLC/MS/MS Analysis** – *Lawrence Zintek, U. S. EPA Region*
- **11:20 Laboratory Perspectives** – *Tim Fitzpatrick, SGS Axys; Charles Neslund, Eurofins*
- **11:35 Facilitated Q & A / Discussion**
  (Please use the chat bubble icon to ask questions.)
- **11:55 Summary & End**

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EPA Method 537 - Modified

Stephen DiMattei
EPA Region 1
New England Regional Laboratory

Disclaimer

What is EPA Method 537?

- Method 537 is a method for analyzing drinking water under the federal drinking water regulations. The drinking water methods must be followed without modification.

- The method is published as EPA Document #: EPA/600/R-08/092 (Version 1.1, September 2009). In addition, there is an EPA Technical Advisory 815-B-16-021 (September 2016).

What Does “Method 537 Modified” Mean?

- In general terms, it means that the “modified” method is different in some way from the published method.
- It could mean anything:
  - Different sample media (other than drinking water)
  - Different sample containers or sample size
  - Different preservation of samples (Trizma versus no preservative)
  - Different compounds of concern (6, 14, 24, or 30 PFAS compounds)
  - Different internal standards or no I.S. (Isotope Dilution)
  - Different surrogates
  - Different extraction and analytical techniques; direct injection, SPE (manual and automated), LC/MS/MS with or without Isotope Dilution)
  - Any combination of the above

Why is Method 537 Modified?

- Programs such as Superfund, Brownfields, and RCRA need to analyze non-drinking water samples for PFAS. Since the matrices are not drinking water, “modified” methods are used.

- Drinking water is relatively free of matrix effects, but that is not true for waste water, semi-solid and solid matrices. Therefore, the method may need to be modified (i.e. different SPE cartridge, different solvent, different preservation, etc.) to resolve potential matrix interferences.

Project Planning

- Project planning is critical (QAPP, SAP, or SOP) to meeting objectives.

- Setting the project objectives before you start collecting data will help to ensure the data collected are the right type, the correct quantity, and the right quality.

- Getting the right people on board as soon as possible, including the laboratory, is important for setting and meeting objectives.
  - Who is the end user of the data? EPA, State, Tribal Nation, local government, or a combination?

Project Planning

- End users of the data help establish the data quality objectives:

  For example:

  - EPA has a drinking water health advisory for PFOA and PFOS (70 ppt single compound or combined)
  - Some states use EPA's Health Advisories (MA)
  - Some states have different limits for PFAS (VT, CT, NH and NJ).
  - Some end users may require use of a "certified" laboratory (NELAP and DOD)
  - There may be other state requirements, such as acceptable and unacceptable method modifications

Project Planning

- Include samplers’ and analysts’ and end users’ input when planning a project.

- Develop or obtain a copy of the sample collection method. It should include, but is not limited to:

  - Sample containers (include any special prep procedures and preservatives added)
  - Precautions taken to prevent contamination
  - The step by step procedure to collect each type of sample (water, sludge, soil)
  - Transportation procedures to get the samples to the lab
  - Chain of custody procedure (include an example of a Chain of Custody)

Project Planning

- List all of the information that will be reported by the lab to the client.(Make sure you're getting the information you need to meet your objectives).

- Obtain a copy of the analytical method (with confidential business information (CBI) redacted if need be). It should include:
  - A compound list including surrogates, internal standards, external standards;
  - Acceptance criteria for calibration curves, surrogates, blanks, spikes, duplicates;
  - An initial demonstration of capability (for each analyst);
  - Analytical reporting limits; and
  - All method modifications.

Questions?

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- Email: dimattei.steve@epa.gov
- Phone: 617-918-8369

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Excellence in science

Overview and Comparison of Methods 537 and ASTM D7979 and D7968

William Lipps, Brahm Prakash
Shimadzu Scientific Instruments, Inc. Columbia MD
September 14, 2017

Contents

- The need for standardized tests
- Overview of current EPA method
- Overview of ASTM method
- Summary and Conclusion

Safe Drinking Water Act

- Primary and Secondary Pollutants List (40 CFR Part 141)
- Disinfection By Products
- UCMR
- Must use approved methods at certified labs

Clean Water Act – Wastewater (aka dirty water)

- Priority Pollutants
- NPDES permits
- All methods <u>must</u> be promulgated at 40 CFR Part 136!

Resource Conservation and Recovery Act (RCRA) – aka Solid Waste

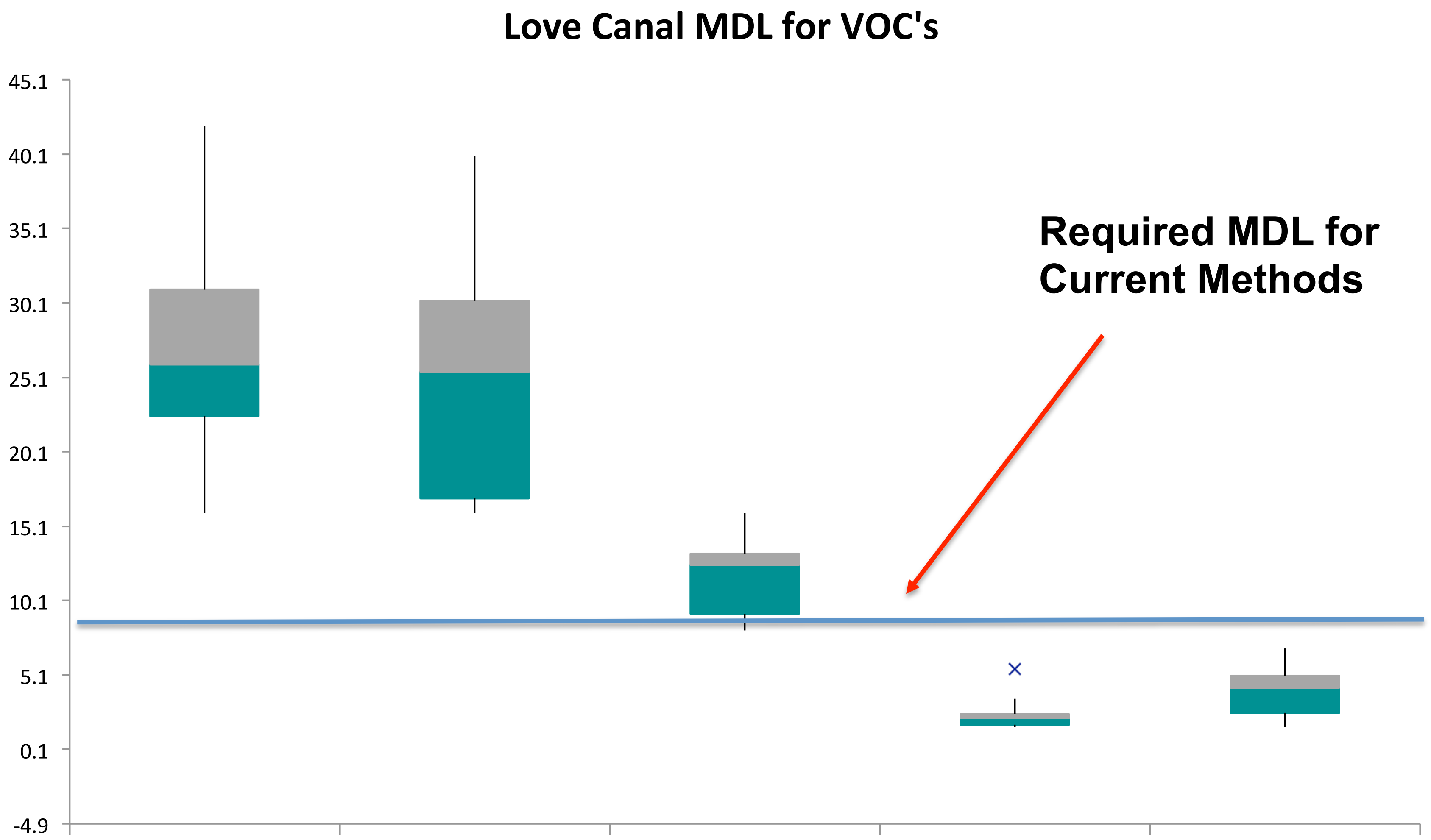
- **Methods are in the SW 846 Manual of Solid Waste**
- **With a few exceptions – Guidance document (performance based)**

What do environmental testing labs do?

- They run methods, not instruments!
- Methods are a **prescription**
- The method defines:
  - MDL
  - Calibration range
  - QC acceptance criteria
  - Extraction
  - Instrument

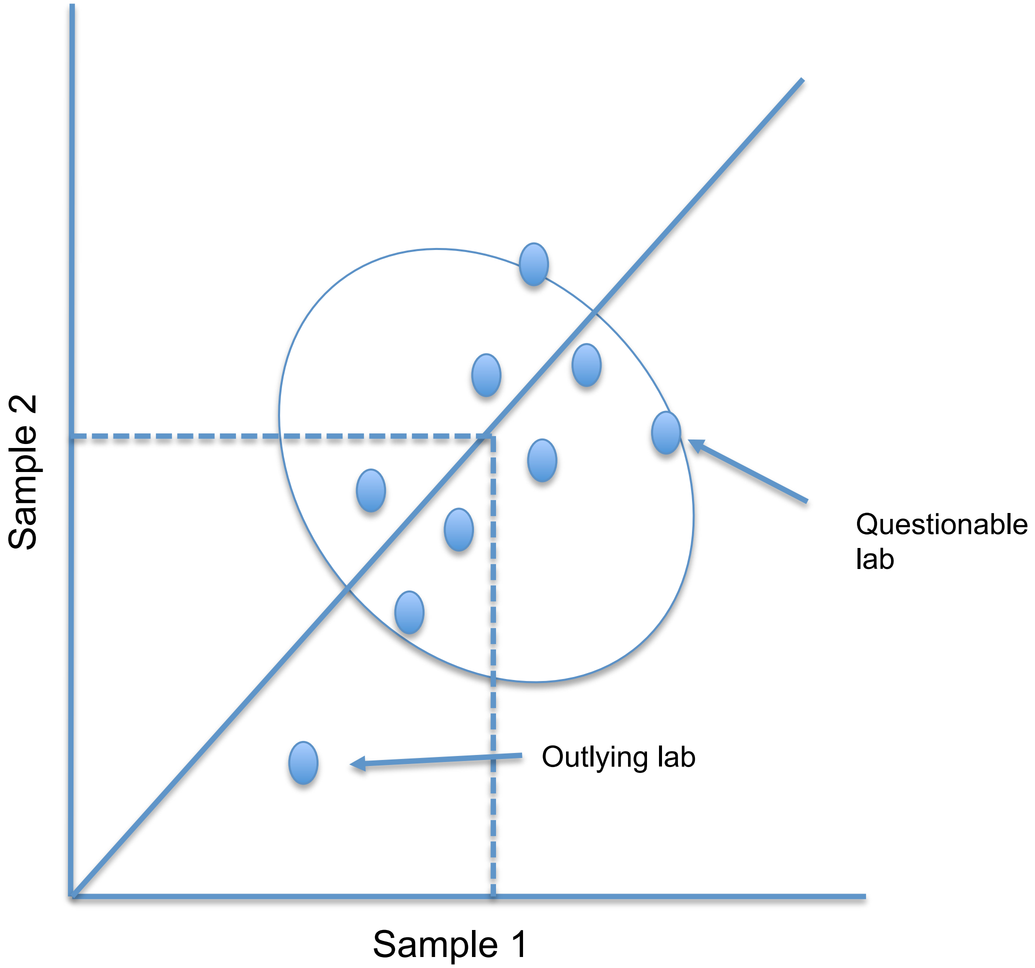
- Limited flexibility to modify methods

We need standard methods for consistency in reporting


Love Canal MDL for VOC's

Required MDL for Current Methods

Following a validated method ensures that multiple lab results are comparable



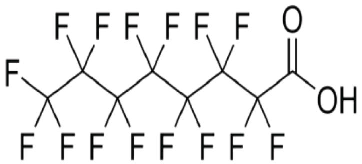
Samples distributed along 45º line

Rarely is there random scatter -

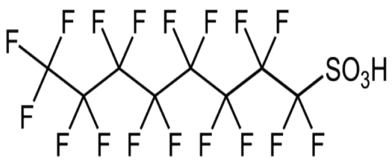
- **Drinking water PFC method**

Health Advisory for Perfluorinated Compounds in Drinking Water

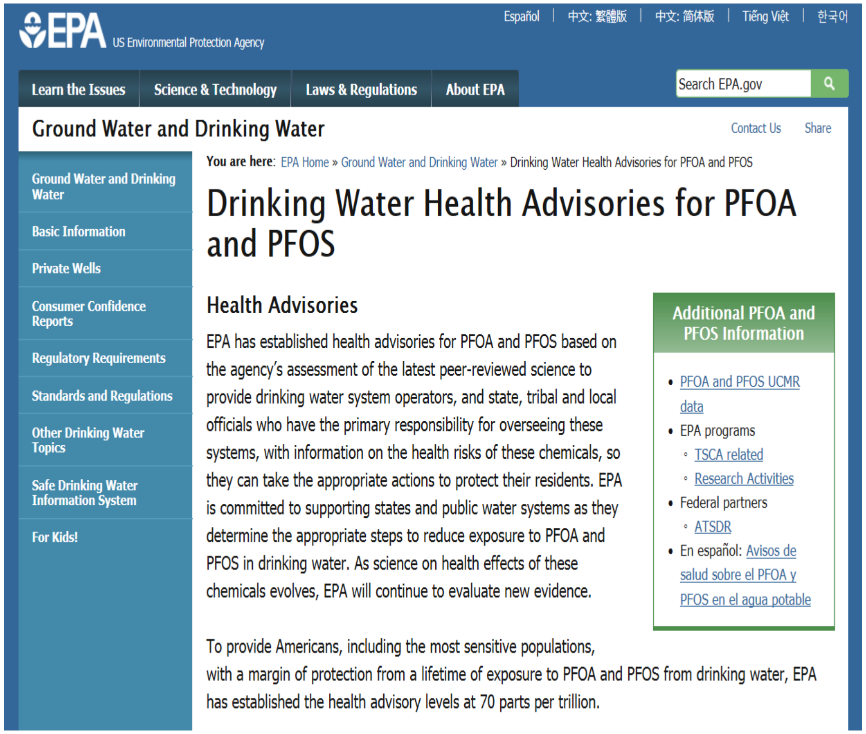
- PFOA
- PFOS


Perfluoro-n-octanoic acid (PFOA)

+


Perfluoro-1-octanesulfoninc acid (PFOS)

< 70 ppt



Ground Water and Drinking Water

You are here: EPA Home » Ground Water and Drinking Water » Drinking Water Health Advisories for PFOA and PFOS

Drinking Water Health Advisories for PFOA and PFOS

Health Advisories

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.

Additional PFOA and PFOS Information

- PFOA and PFOS UCMR data
- EPA programs
  - TSCA related
  - Research Activities
- Federal partners
  - ATSDR
- En español: Avisos de salud sobre el PFOA y PFOS en el agua potable

To provide Americans, including the most sensitive populations, with a margin of protection from a lifetime of exposure to PFOA and PFOS from drinking water, EPA has established the health advisory levels at 70 parts per trillion.

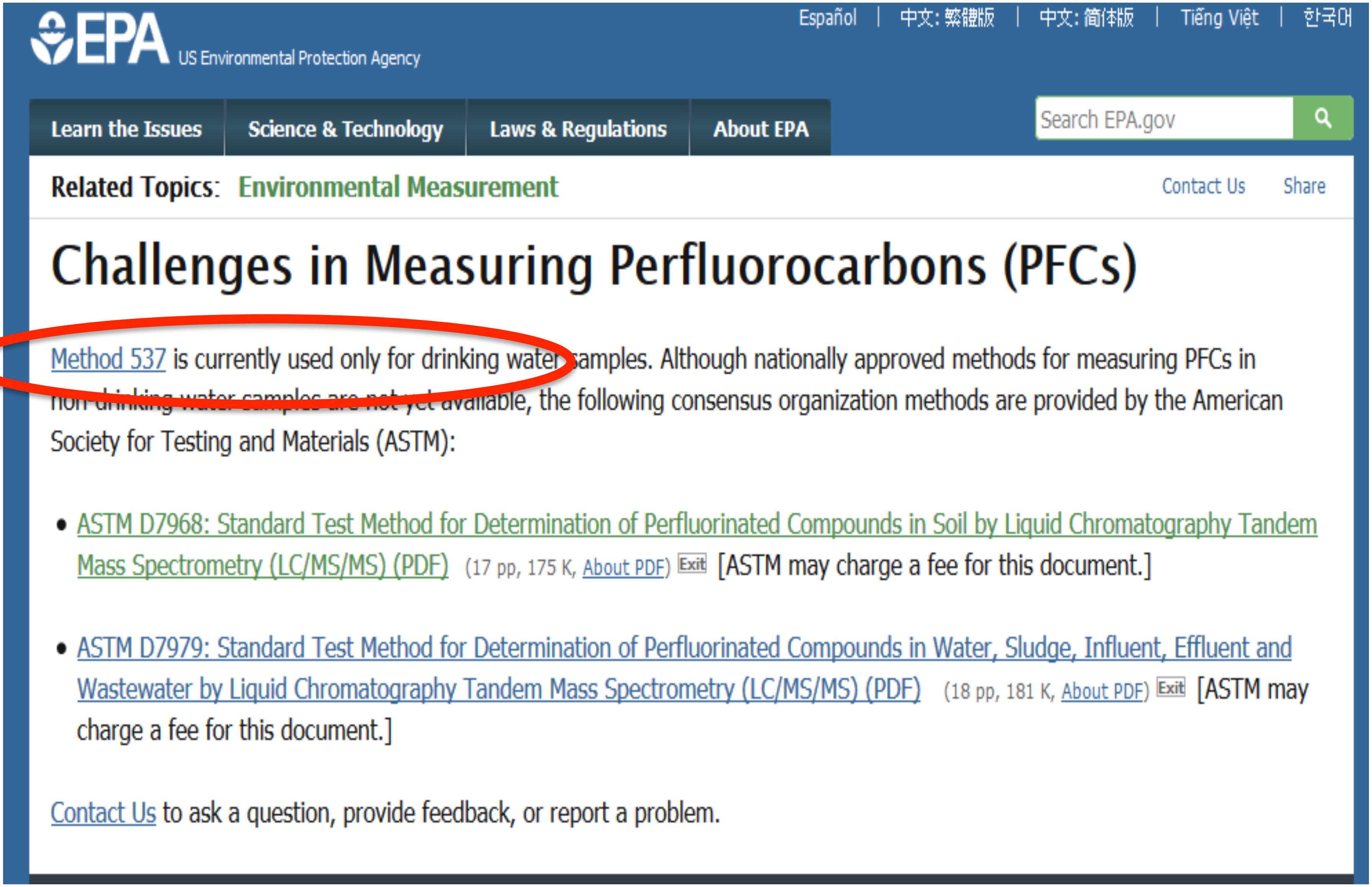
Illustration: The Intercept

WITH NEW EPA ADVISORY, DOZENS OF COMMUNITIES SUDDENLY HAVE DANGEROUS DRINKING WATER

Sharon Lerner

May 19 2016, 2:36 p.m.

Perfluorinated Compounds are measured by HPLC-MSMS using EPA or ASTM methods



Challenges in Measuring Perfluorocarbons (PFCs)

Method 537 is currently used only for drinking water samples. Although nationally approved methods for measuring PFCs in non-drinking water samples are not yet available, the following consensus organization methods are provided by the American Society for Testing and Materials (ASTM):

- ASTM D7968: Standard Test Method for Determination of Perfluorinated Compounds in Soil by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) (PDF) (17 pp, 175 K, About PDF) Exit [ASTM may charge a fee for this document.]
- ASTM D7979: Standard Test Method for Determination of Perfluorinated Compounds in Water, Sludge, Influent, Effluent and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) (PDF) (18 pp, 181 K, About PDF) Exit [ASTM may charge a fee for this document.]

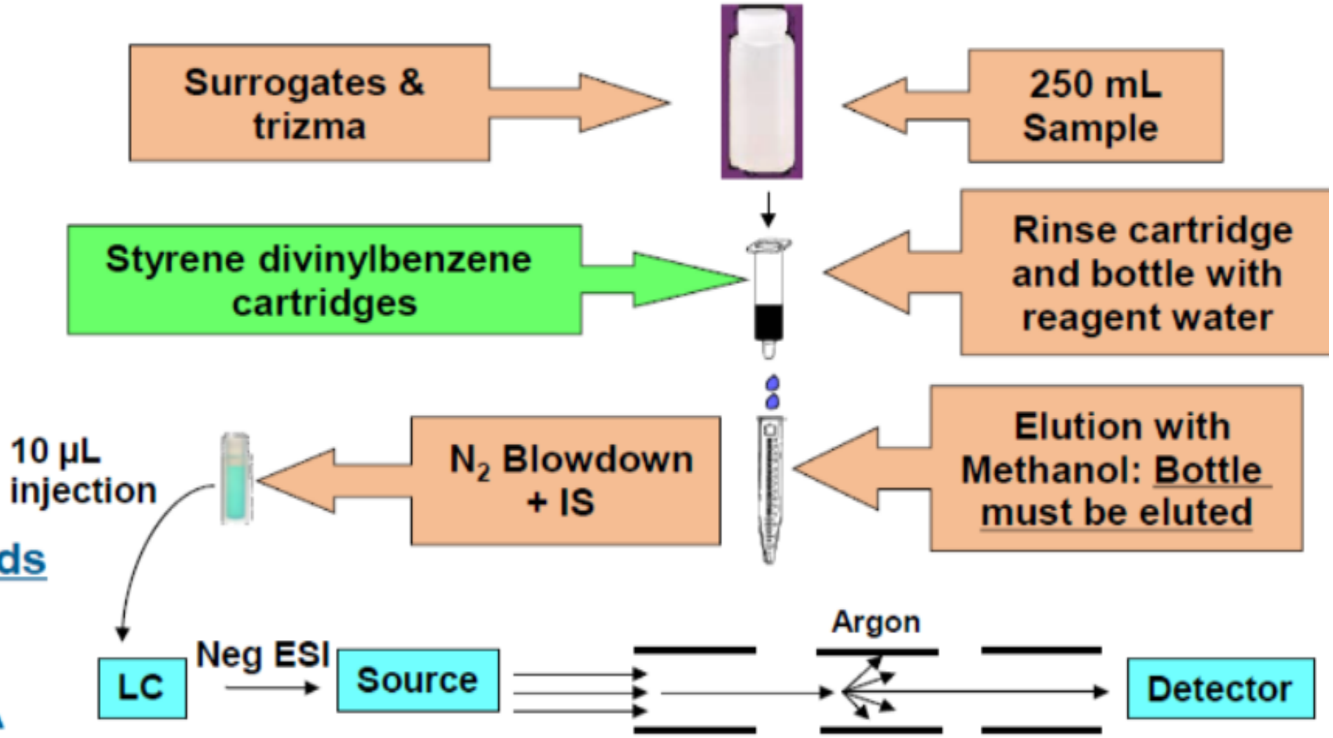
Contact Us to ask a question, provide feedback, or report a problem.

Method 537 Approach

Preservative
trizma

Surrogates
^{13}C-PFHxA
^{13}C-PFDA
d_5-NEtFOSAA

Internal Standards
^{13}C-PFOA
^{13}C-PFOS
d_3-NMeFOSAA



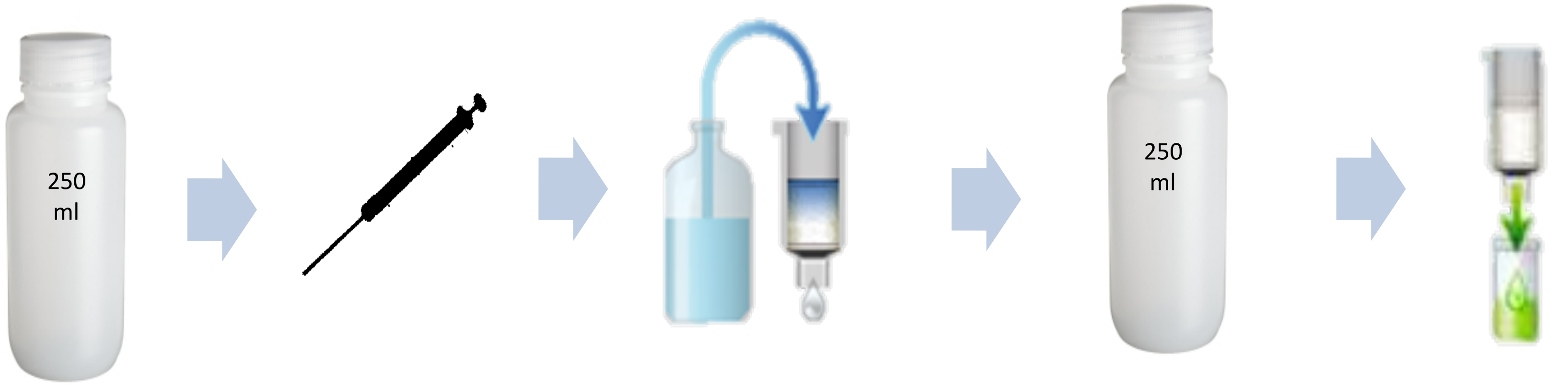
LC/MS/MS - Selected Reaction Monitoring

What Method 537 is:

- **Solid Phase Extraction**
- **DRINKING WATER method**

- **Changes may not be made to sample collection and preservation (Sect. 8), the sample extraction steps (Sect. 11), or to the quality control requirements (Sect. 9).**

EPA 537 Extraction procedure



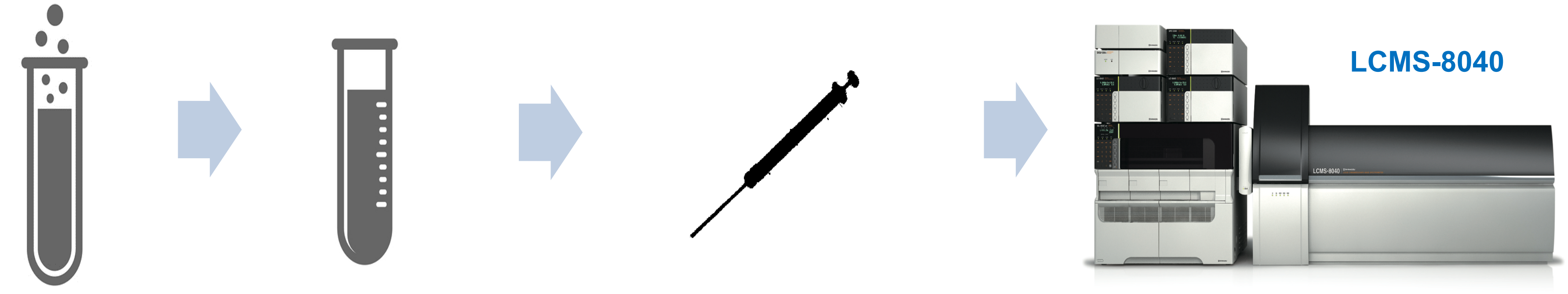
Surrogate

10 ml/
Minute

4 ml MeOH

Elute

EPA 537 Extraction procedure



Evaporate

1 ml 96%
MeOH

Internal
Standard

Method 537: Problems

- Variable, analyte dependent, recovery
- Must rinse sample bottle → must extract entire 250 ml
- Transfer sample like this

Method 537: Problems

- **Laboratory and field blank contamination:**
  - Many lab supplies and equipment can contain PFAAs.

Non- Drinking Water PFCs

Wastewater and wastewater treatment

Land applied bio-solids

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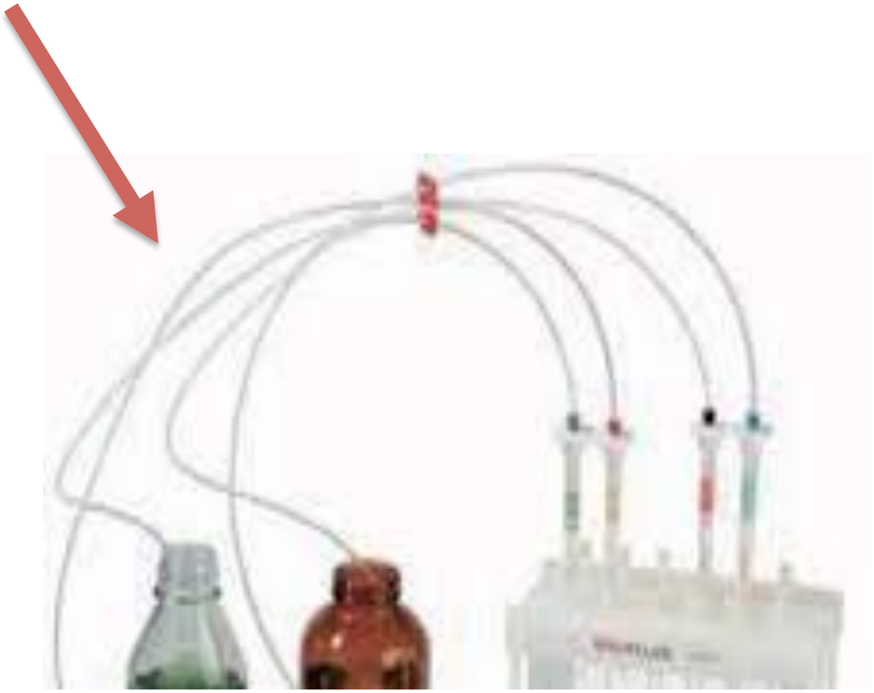
Method 537 as written cannot be used for wastewater or soil, it is a prescription based SDWA method

- How do you extract 250 ml of wastewater or soil?
- Or transfer sample like this?

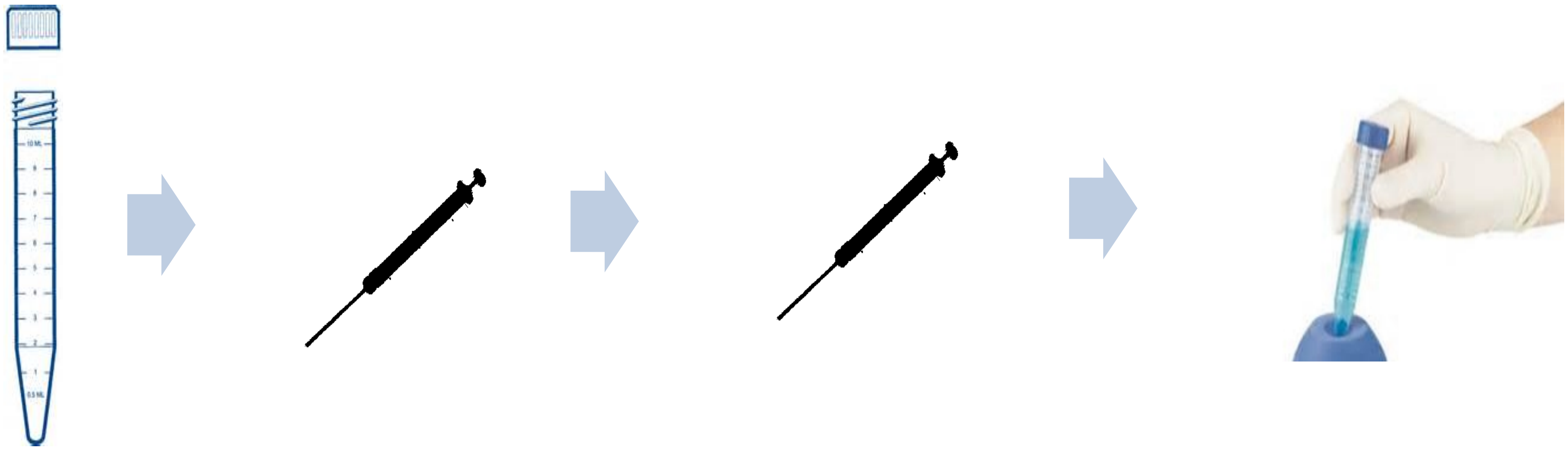


What Method 537 is not:

- Wastewater or Solid Waste Method

Overview of ASTM Methods

ASTM D7979 Extraction procedure



5 ml Sample

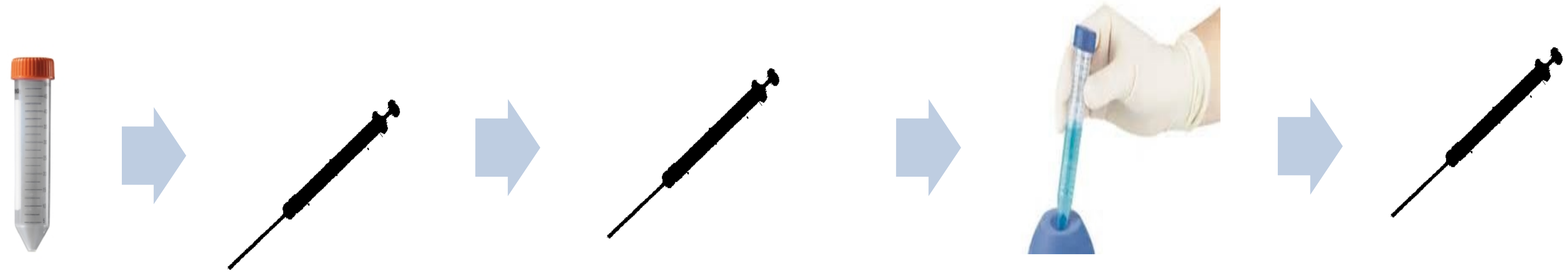
Surrogate

5 ml MeOH

ASTM D7979 Extraction procedure

10 µL Acetic
Acid

ASTM D7968 Extraction procedure



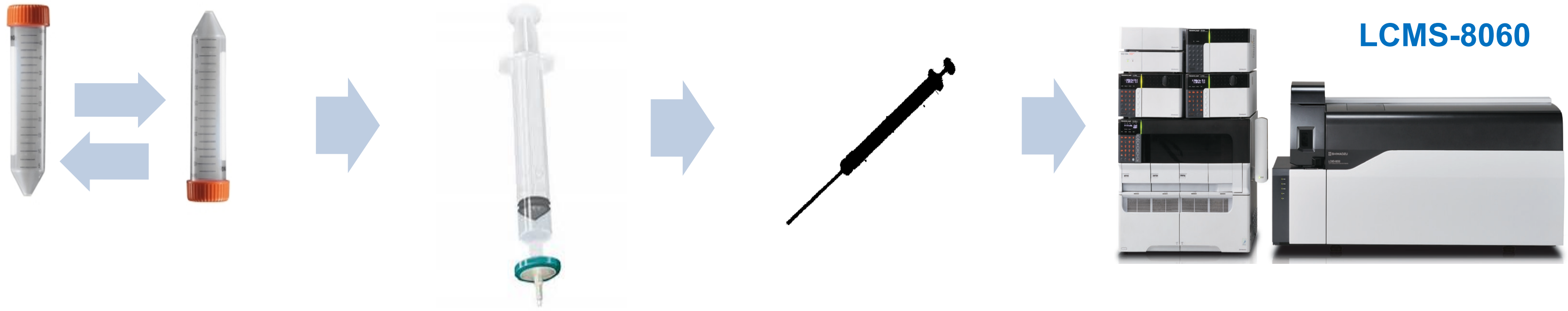
2 g Sample

Surrogate

10 ml (1+1) MeOH

20 µL NH_4OH

ASTM D7968 Extraction procedure

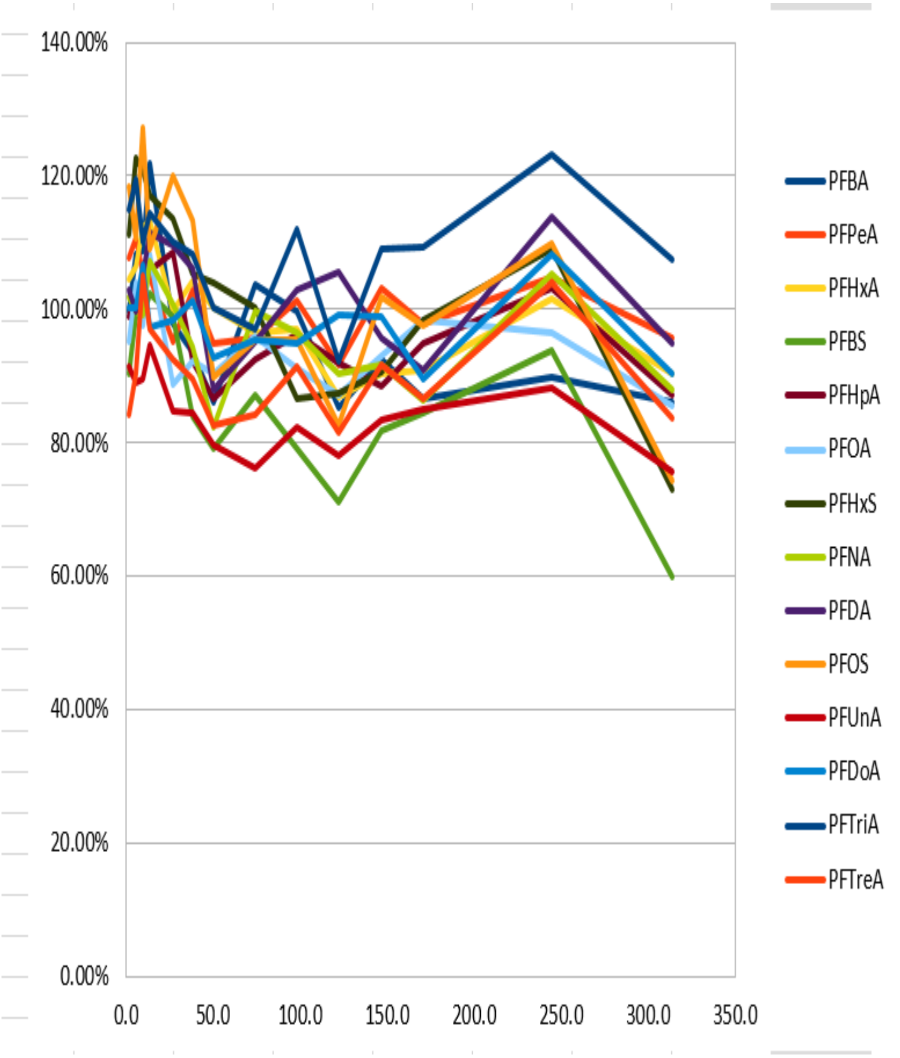


Tumble 1
hour

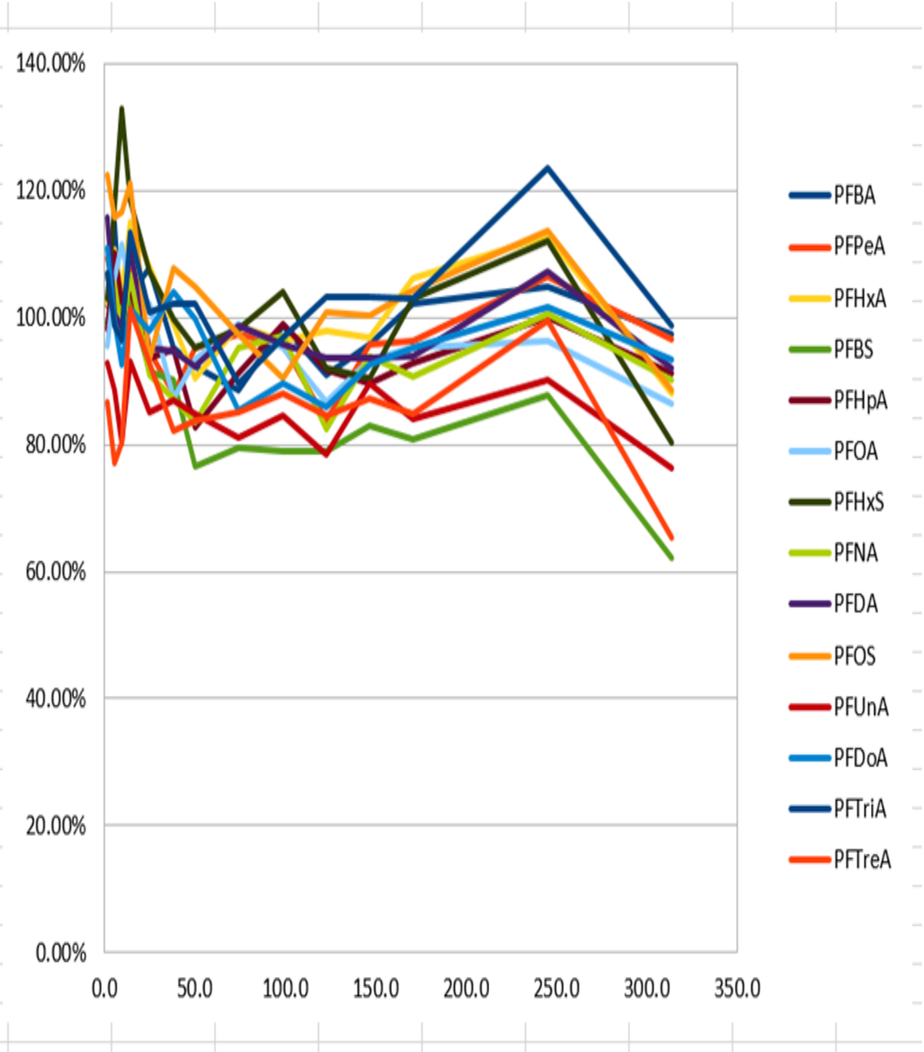
50 µL Acetic
Acid

Standard Stability Study - 50% Methanol 50% water

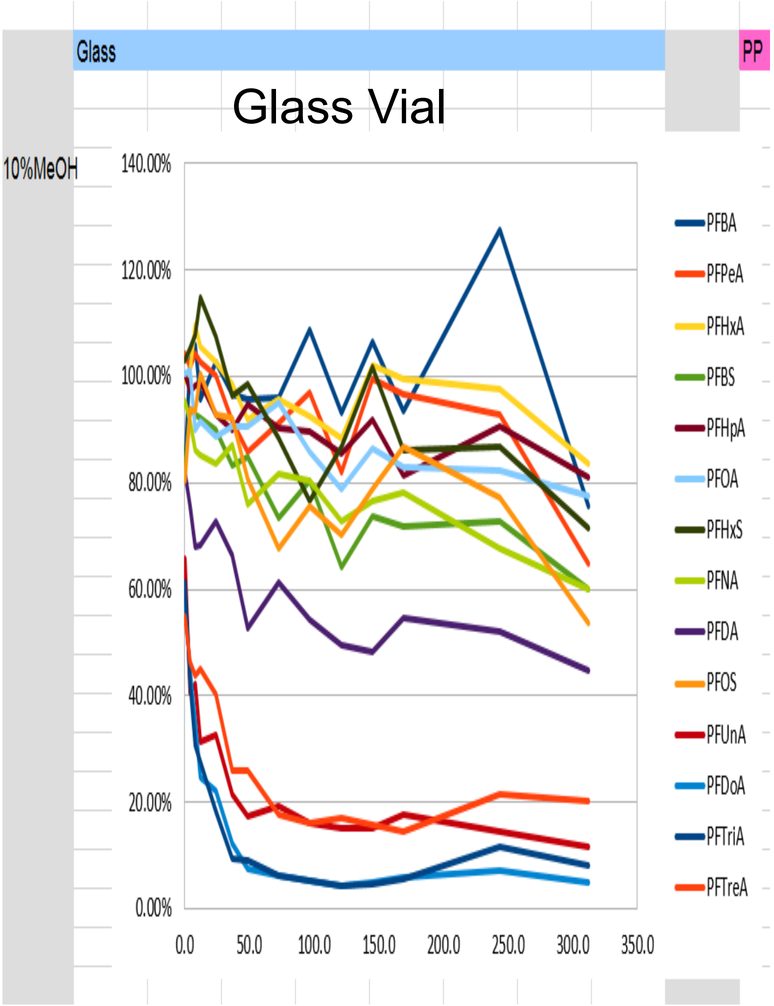
Glass Vials



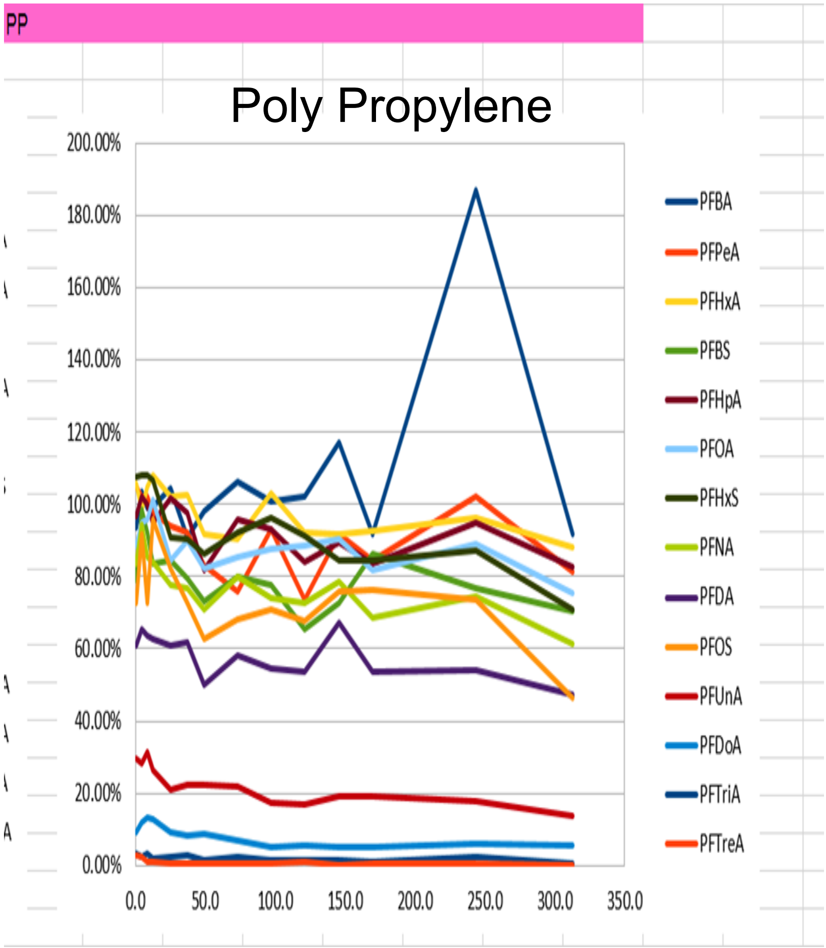
Poly Propylene Vials



Standard Stability Study -10% Methanol 90% water

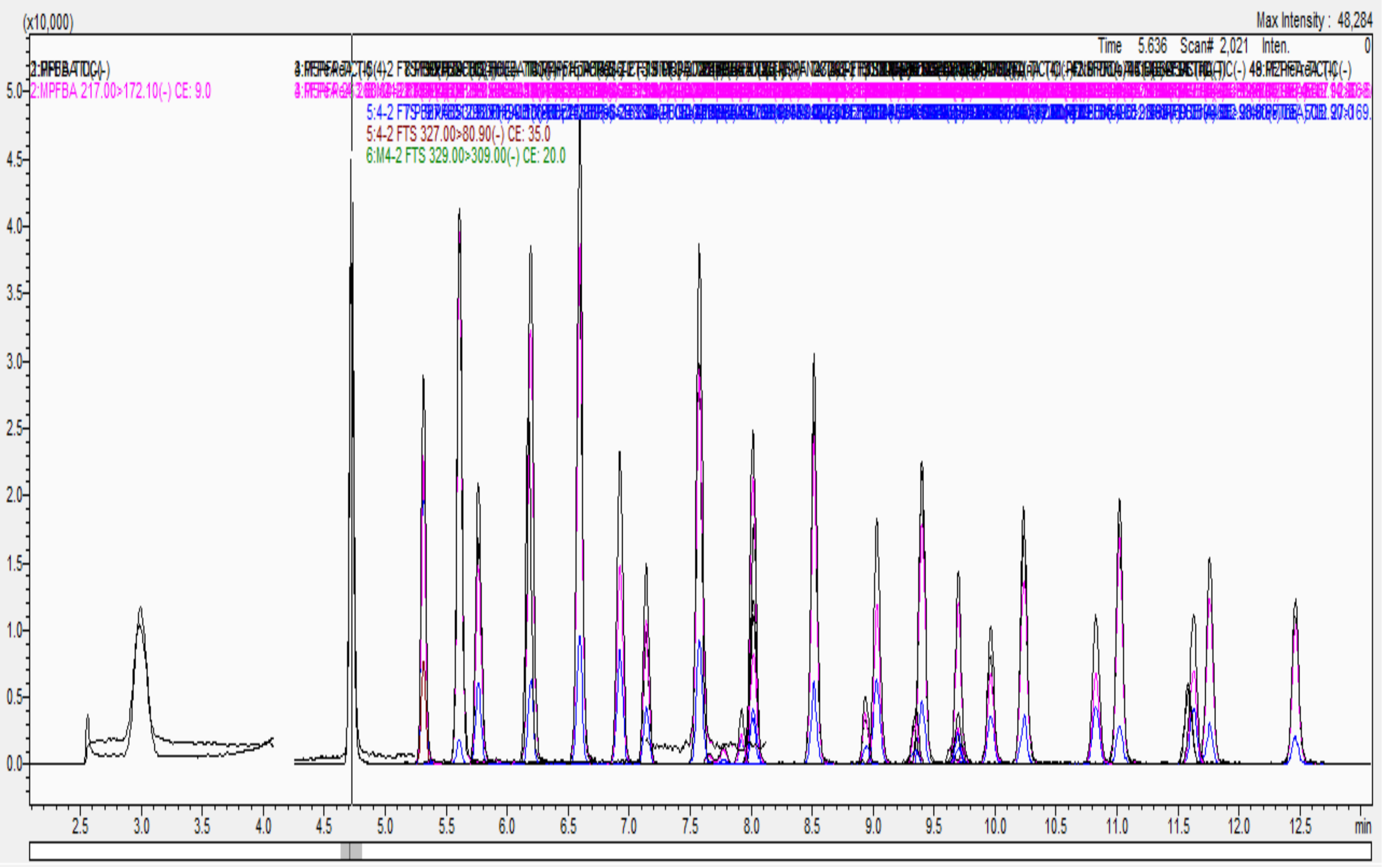


Glass Vial

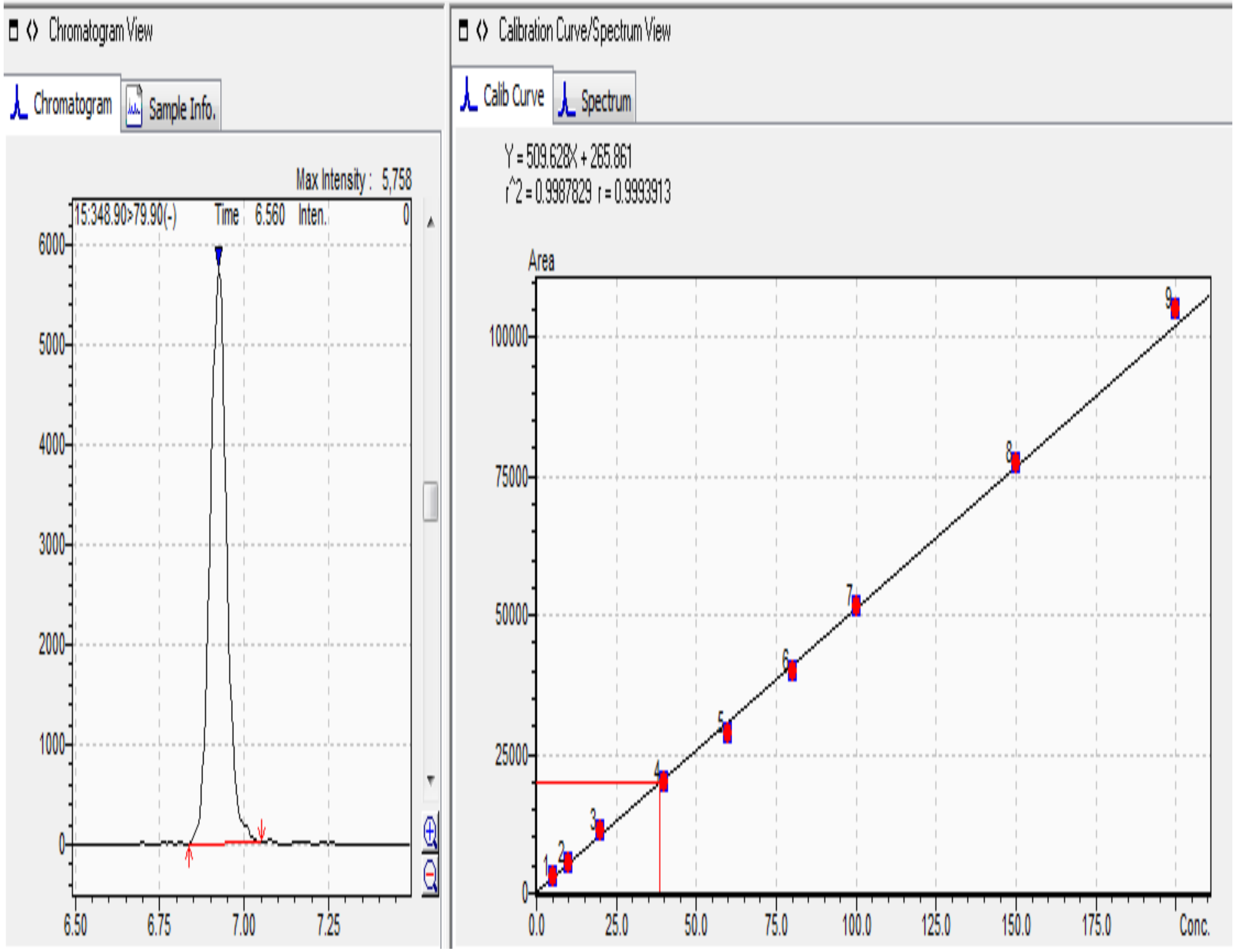


Poly Propylene

Chromatogram at 100 ppt



ASTM D7979 by 10 uL Direct Injection at 40 ppt PFPeS



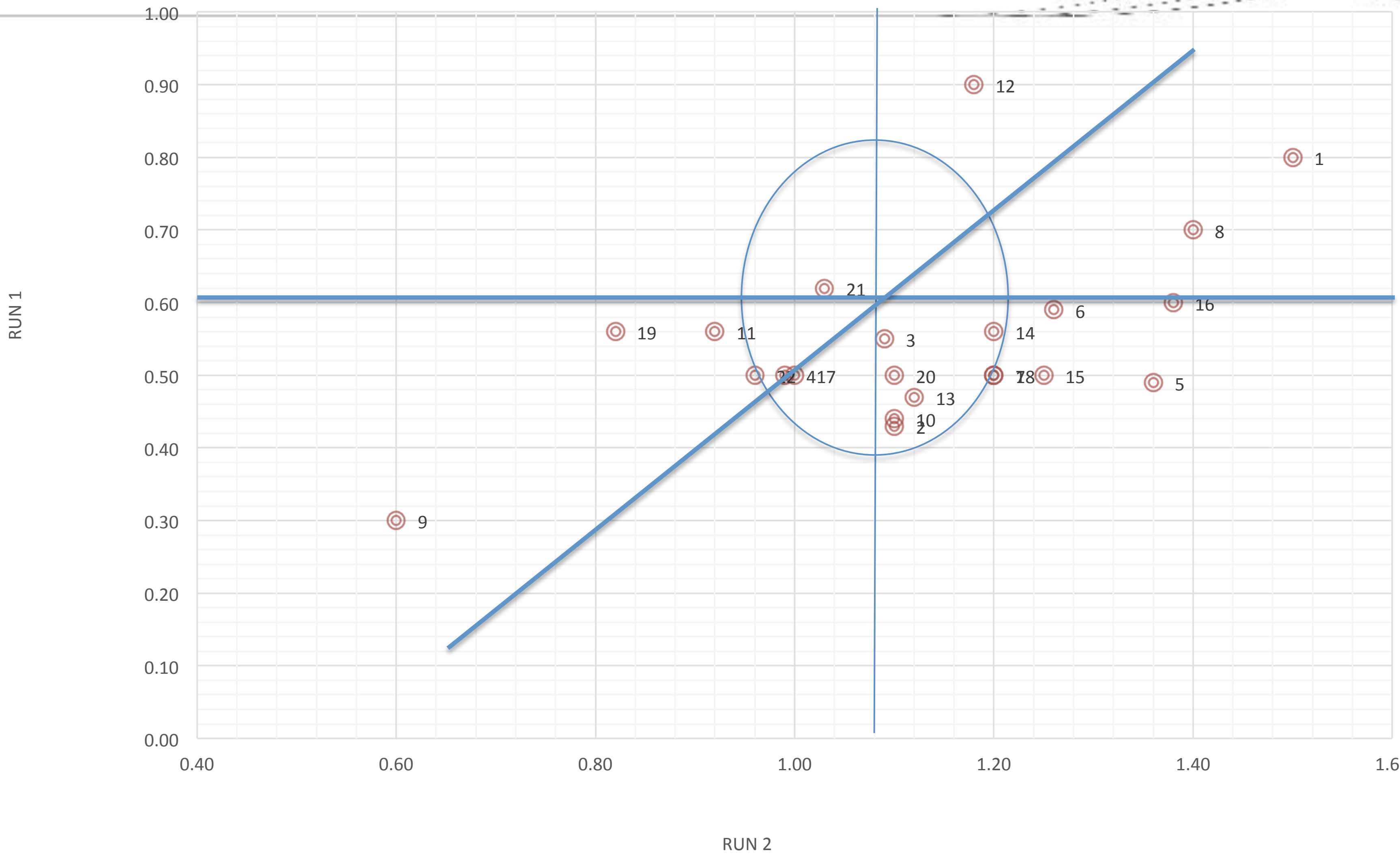
Y = 509.628X + 265.861
r^2 = 0.9987829 r = 0.9993913

Level	Concentration
1	5 ppt
2	10 ppt
3	20 ppt
4	40 ppt
5	60 ppt
6	80 ppt
7	100 ppt
8	150 ppt
9	200 ppt

Comparison of sample specific batch QC criteria

Method	EPA 537	D7979	D7968
MS/MSD recovery	70 – 130 %	70 – 130 %	70 – 130 %
Surrogate Recovery	70 – 130 %	70 – 130 %	70 – 130 %
RPD	≤ 30 %	≤ 30 %	≤ 30 %

How does the ASTM data compare to what others are doing?


RUN 1
RUN 2
1.00
0.90
0.80
0.70
0.60
0.50
0.40
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0.20
0.10
0.00
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0.80
1.00
1.20
1.40
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12
1
8
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6
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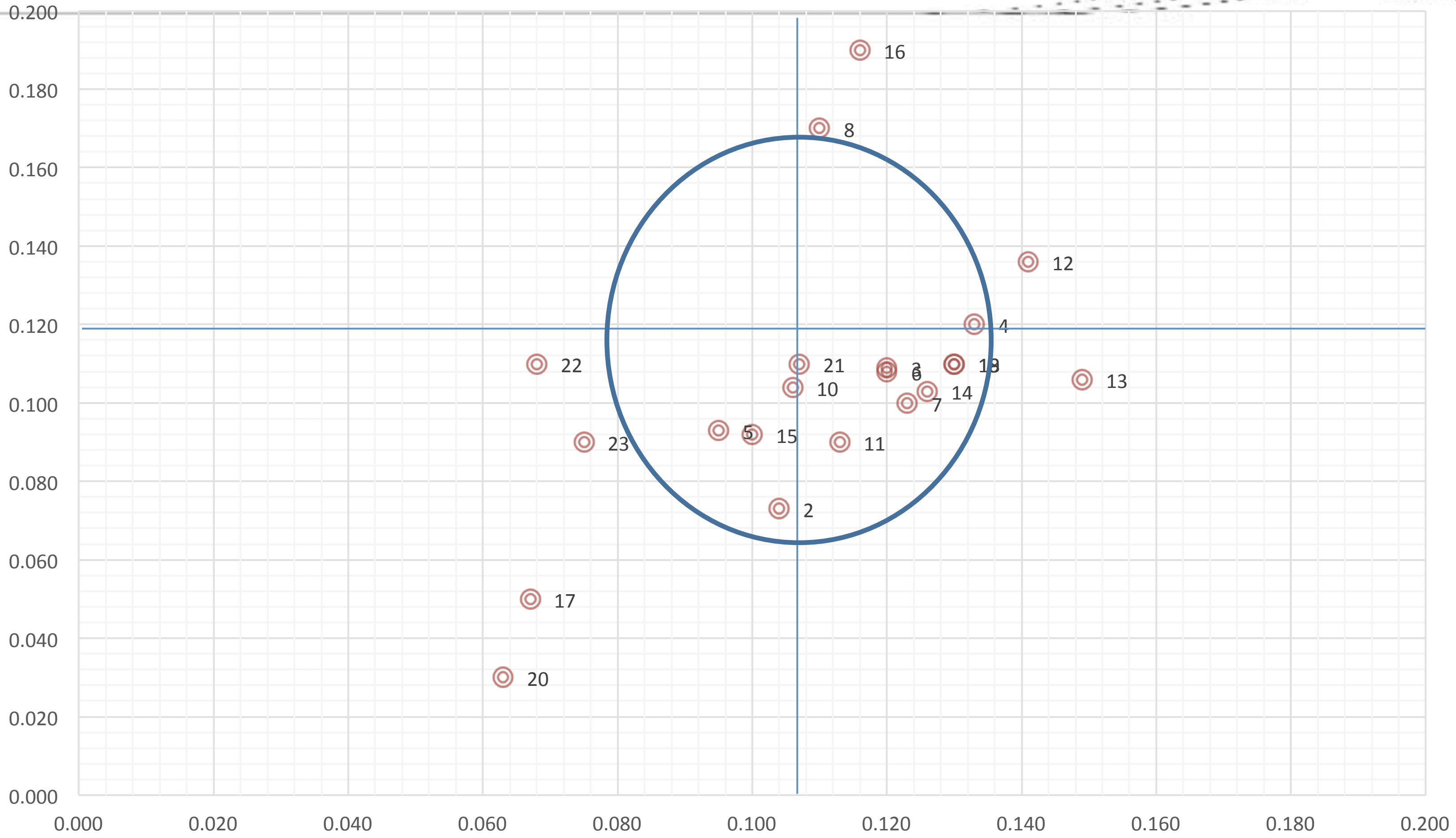
0.200
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17
20

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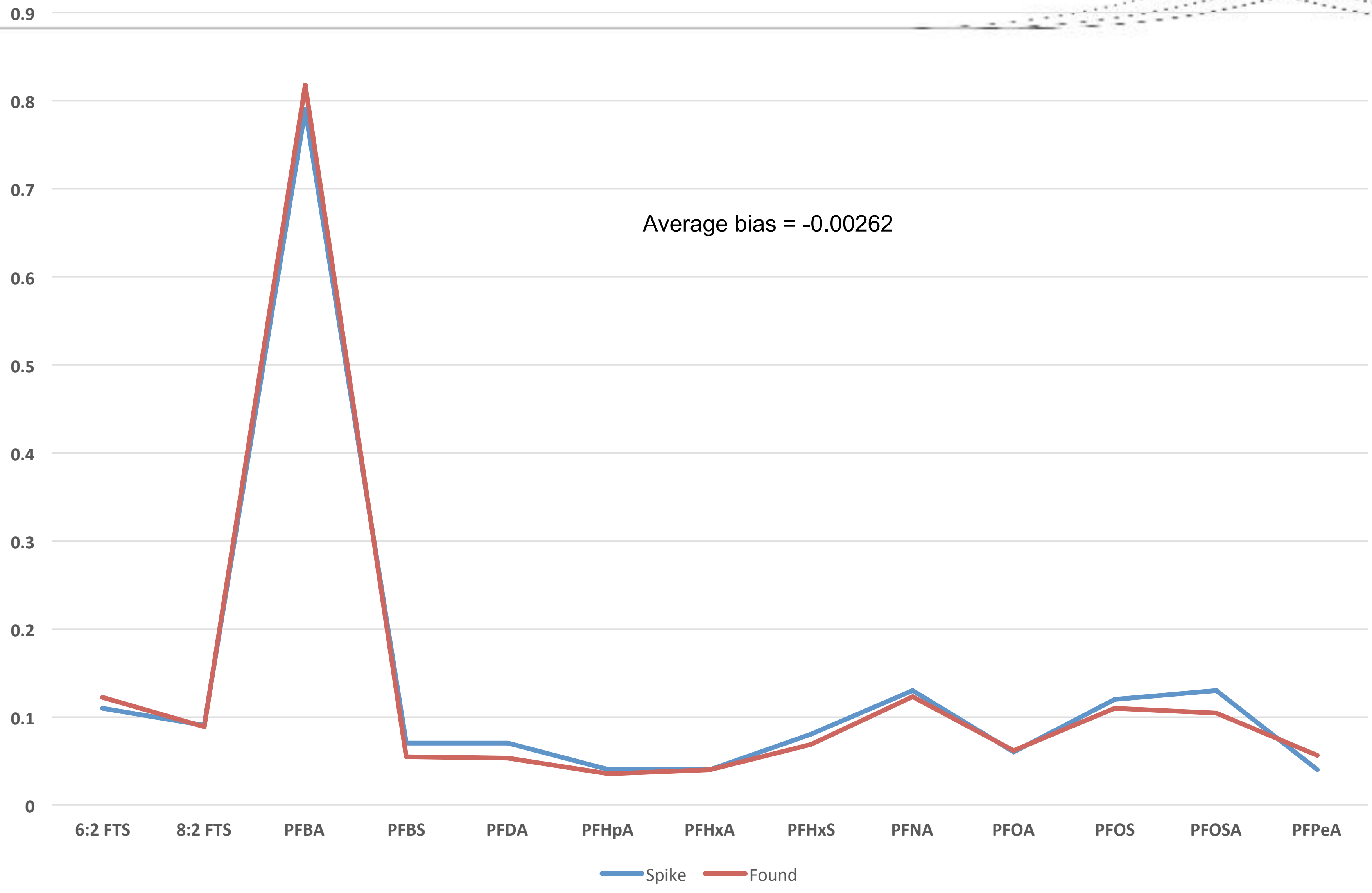
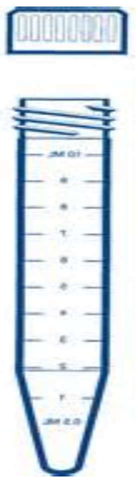
ASTM results compared to known additions



Summary for the three US methods

EPA 537

Drinking Water



ASTM D7979

Wastewater

ASTM D7968

Sludge and Solids

Thank you

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www.ssi.shimadzu.com

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Region 5 CRL Methods for the Analysis of Polyfluorinated Compounds (PFAS) Using a Quick Sample Extraction/Preparation

Followed by UPLC/MS/MS Analysis

Lawrence B. Zintek, Danielle Kleinmaier, Dennis J. Wesolowski,
Solidea Bonina[#] and Carolyn Acheson*
US EPA Region 5 Chicago Regional Laboratory (CRL)
[#]Pegasus Technical Services, Inc.
*US EPA ORD/NRMRL, Cincinnati, OH.

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Topics

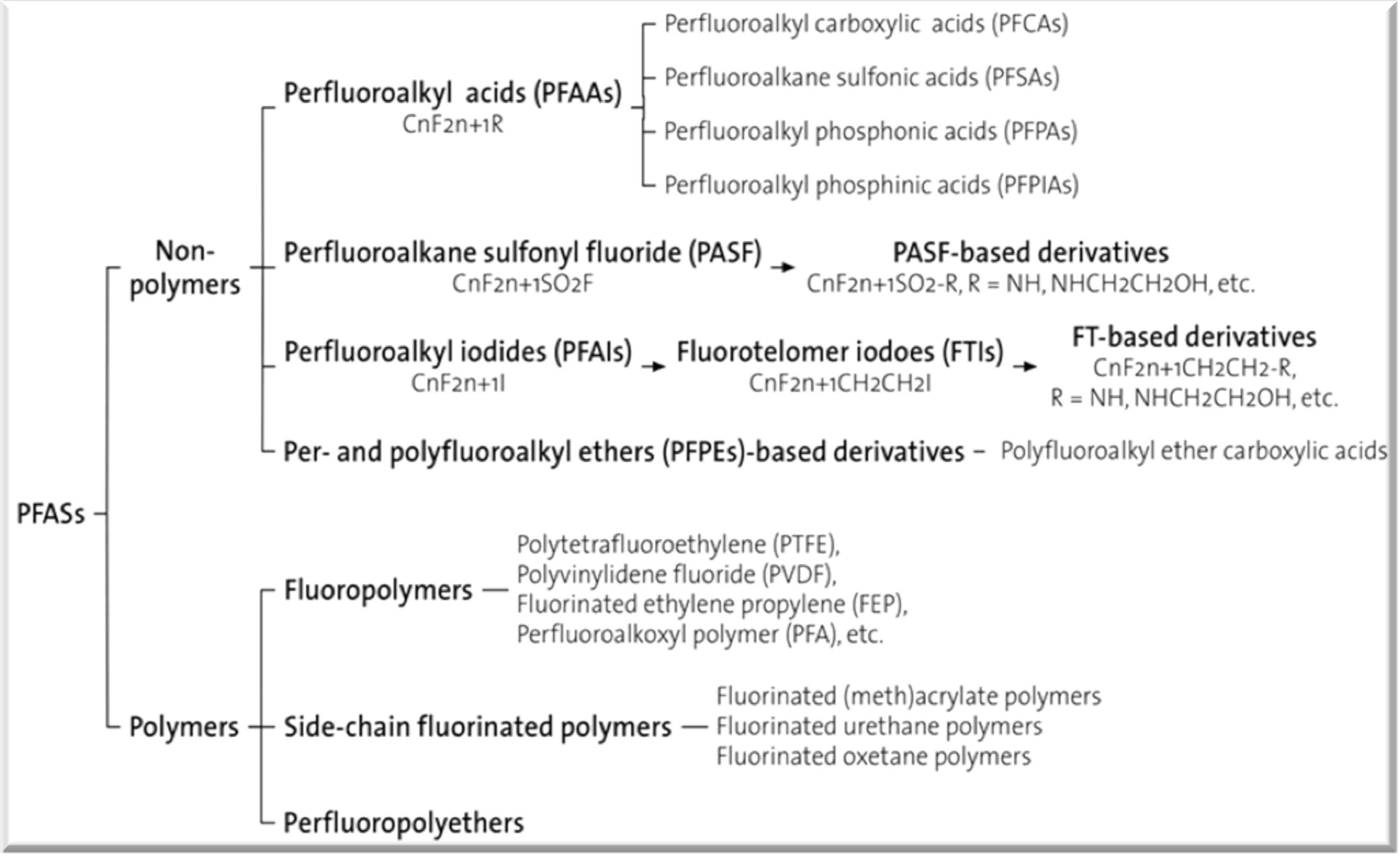
- PFC Workgroup
- Brief PFAS Background
- EPA Method 537- Drinking Water
- CRL PFAS Methods/ASTM D7979 and ASTM D7968
- Holding Time Study
- Contamination
- Sample Collection
- Holding Time/Sample Requirements
- Review of Data generated by other methods/labs
- Conclusion/Ongoing Work

EPA PFAS Workgroup

- Purpose: Develop robust analytical methods and sampling protocols for solids and water other than drinking water.
- Workgroup Co-Leads: OLEM/OSRTI, Region 3, ORD/SSWR
- Program Offices
  - OLEM: OEM, OSRTI, and OCRC
  - OW: OS&T and OGWDW
  - ORD: NRMRL, NERL, NHEERL, and NCEA
  - NEIC, OCIR/RO, OPP/BEAD/ACB
- Regional Offices: 1, 2, 3, 4, 5, 6, 9, and 10

PFAS – Gets Complicated Fast

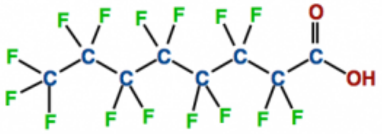
(Not going here in this webinar)



- PFASs
  - Non-polymers
    - Perfluoroalkyl acids (PFAAs) $C_nF_{2n+1}R$
      - Perfluoroalkyl carboxylic acids (PFCAs)
      - Perfluoroalkane sulfonic acids (PFSAs)
      - Perfluoroalkyl phosphonic acids (PFPAs)
      - Perfluoroalkyl phosphinic acids (PFPIAs)
    - Perfluoroalkane sulfonyl fluoride (PASF) $C_nF_{2n+1}SO_2F$ → PASF-based derivatives $C_nF_{2n+1}SO_2\text{-}R$, R = NH, $NHCH_2CH_2OH$, etc.
    - Perfluoroalkyl iodides (PFAIs) $C_nF_{2n+1}I$ → Fluorotelomer iodoes (FTIs) $C_nF_{2n+1}CH_2CH_2I$ → FT-based derivatives $C_nF_{2n+1}CH_2CH_2\text{-}R$, R = NH, $NHCH_2CH_2OH$, etc.
    - Per- and polyfluoroalkyl ethers (PFPEs)-based derivatives – Polyfluoroalkyl ether carboxylic acids
  - Polymers
    - Fluoropolymers — Polytetrafluoroethylene (PTFE), Polyvinylidene fluoride (PVDF), Fluorinated ethylene propylene (FEP), Perfluoroalkoxyl polymer (PFA), etc.
    - Side-chain fluorinated polymers — Fluorinated (meth)acrylate polymers, Fluorinated urethane polymers, Fluorinated oxetane polymers
    - Perfluoropolyethers

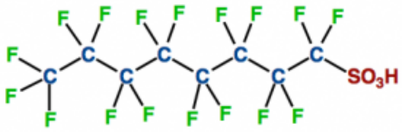
Brief PFAS Background

- PFOA



PFOA - perfluorooctanoic acid

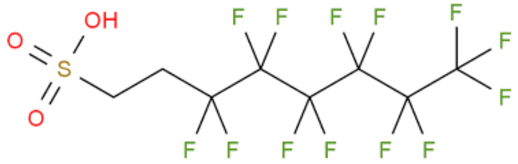
- PFOS



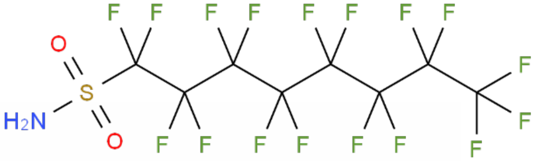
PFOS - perfluorooctanesulfonic acid

PFOA/PFOS Drinking Water Health Advisory- 70 ng/L Combined

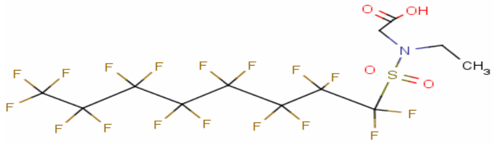
- 6:2 FTS



- PFOSA (FOSA)



- N-EtFOSAA



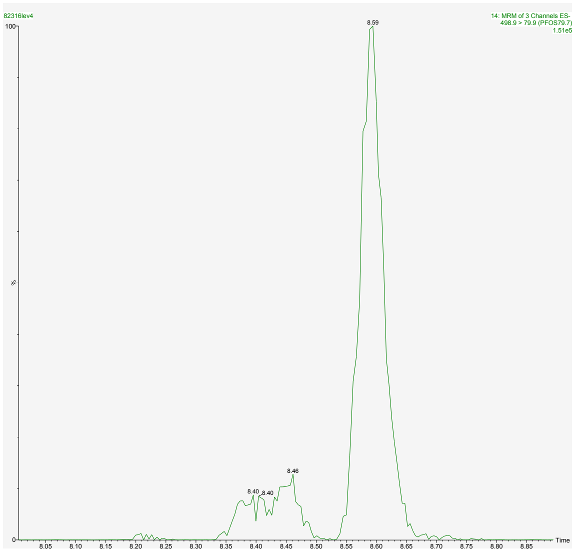
EPA Method 537

- EPA 537 is a Drinking Water Method
  - For Drinking Water Matrices, not for dirty water or soils!
- 14 Analytes
  - PFOS, PFOA, N-EtFOSAA, N-MeFOSAA, PFBS, PFDA, PFDoA, PFHpA, PFHxS, PFHxA, PFNA, PFTreA, PFTriA, PFUnA.
- 3 Surrogates
  - MPFHxA, MPFDA, MN-EtFOSAA
- 3 Internal Standards
  - ^{13}C-PFOA, ^{13}C-PFOS, d_3-N-MeFOSAA

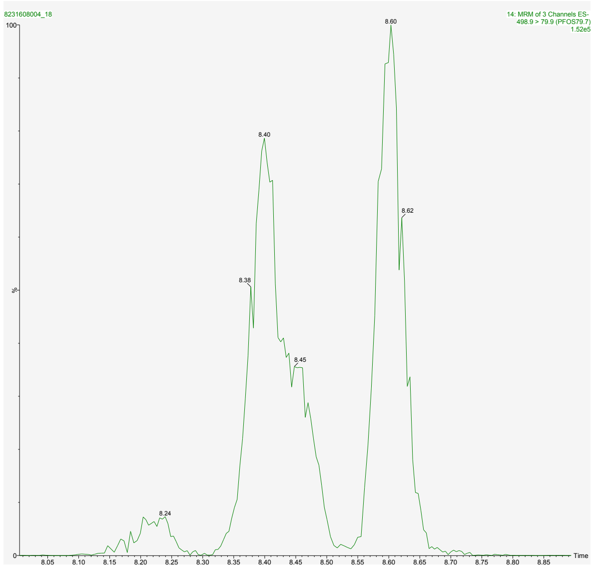
Method 537 Quantitation

- Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)
- One (Single Reaction Monitoring) SRM transition
  - For relatively clean matrix of drinking water, this approach is sufficient
  - For non-drinking water samples, interference is common. Confirmatory transition and ion ratios are useful in establishing analyte concentrations.
  - Example for PFOS:

Calibration Standard



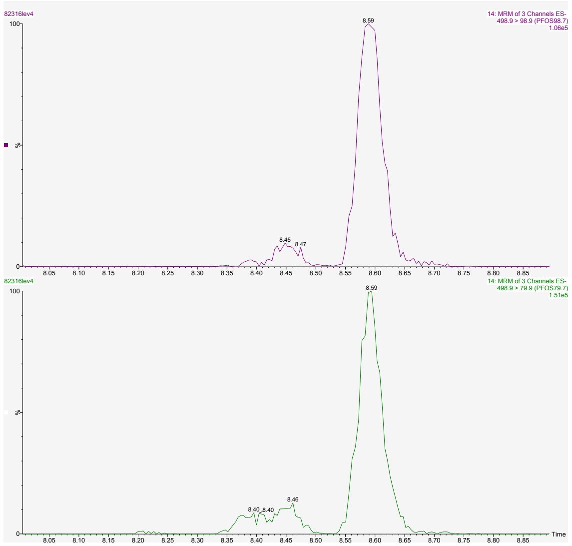
Real Sample



Region 5 CRL PFAS SOP

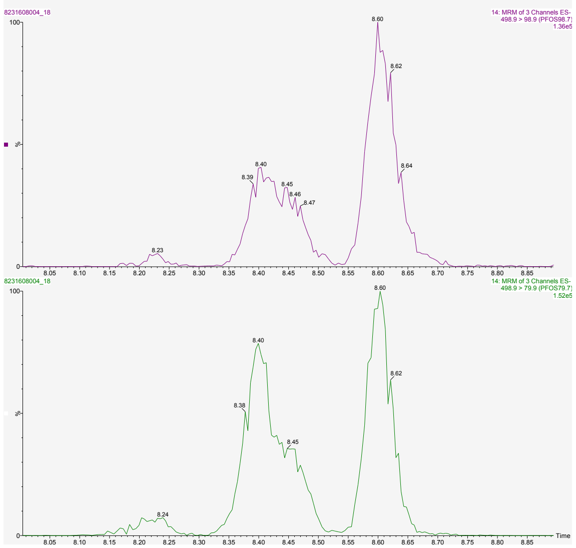
- Two SRM transitions or MRM
  - – Decreases False Positives
  - – More Definitive Identification having Ion Ratio
  - – Example for PFOS, same samples:

Calibration Standard Ion Ratio-1.41



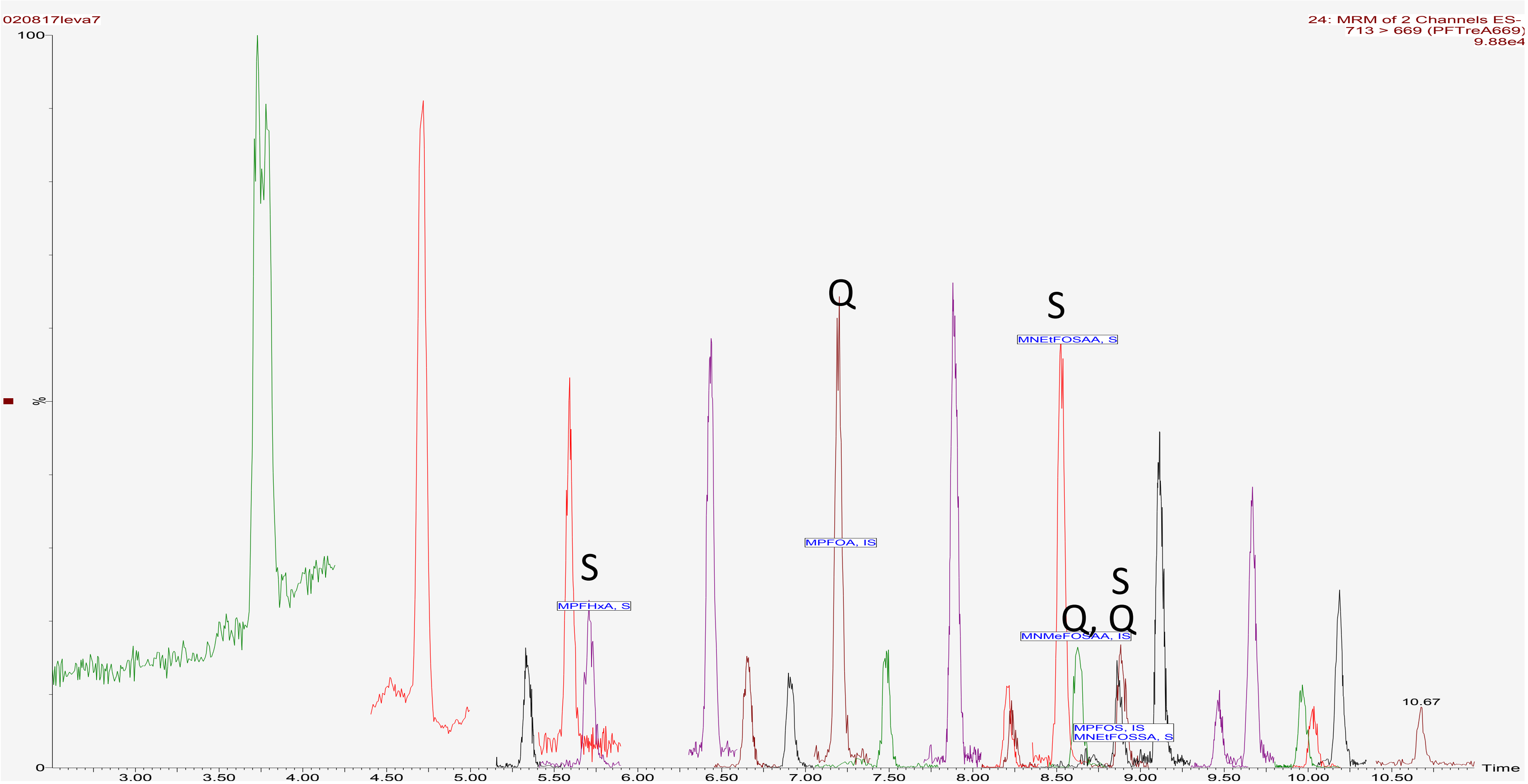
4.3% Ion Ratio Difference **(<u>Within Tolerance</u>)**

Real Sample Ion Ratio-1.35



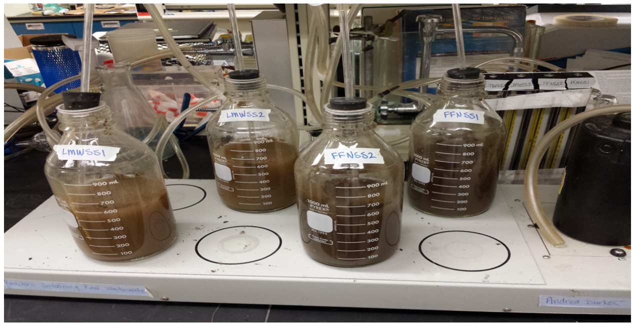
Method 537 Quantitation/Surrogates

- Internal standard quantitation **(Q)**
  - Weak approach for non-drinking water samples, may have a matrix interference that affects the internal standard resulting in bias results for anything quantitated against it.
- Surrogates **(S)**
  - Compare target analyte recovery to the surrogates.



Why not use EPA Method 537 for matrices other than Drinking Water?

- **Method 537 is a drinking water method!**
- Not tested in other matrices
- Require Solid Phase Extraction
  - Won't work for all analytes of interest in one analysis
  - Pre-filter samples with particulates (bias low results)
- Limited number of surrogates to mimic the entire analyte mix
- Only one SRM transition
  - Makes quantitation difficult in dirtier matrices
  - Less confirmatory
- Blow down to dryness
  - Lose volatile PFAS



CRL PFAS Methods

- 24 Analytes of Interest to OSRTI
- External Standard Quantitation
  - Every compound independent of each other
- 2 SRM transitions (If available)
  - PFBA, PFPeA, and PFOSA only one SRM
- Ion Ratios between the 2 SRM transitions required
- 14 Surrogates (19 available now)
- Easy sample preparation, sample manipulations to a minimum.
- Basis - ASTM D7979 and D7968
- Single lab validated on multiple matrices – About 800 Real Samples measured (Not including QC Samples)

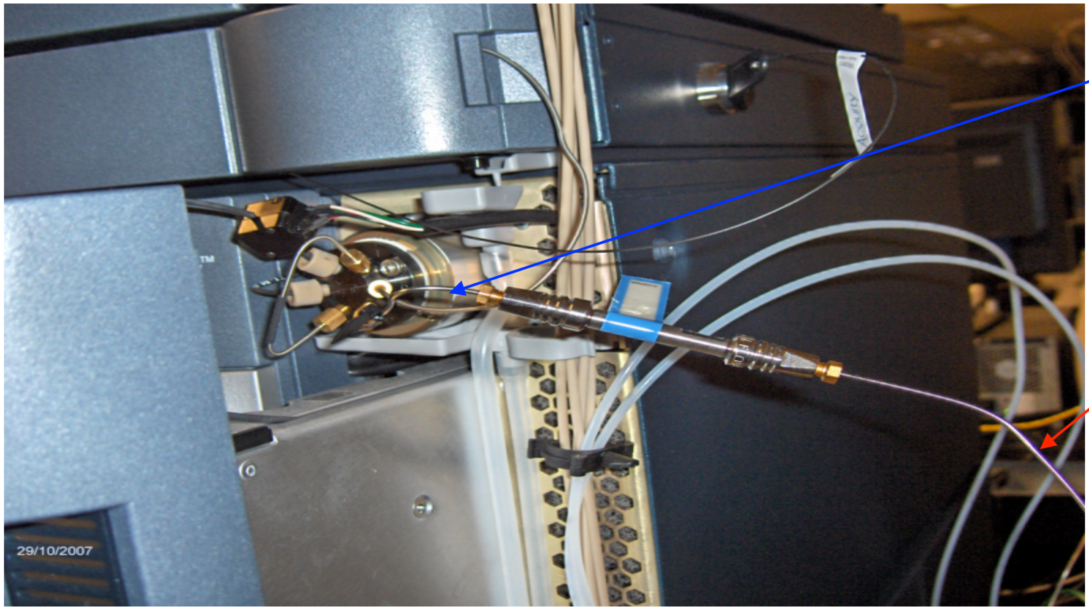
ASTM D7979 and D7968

- Original Methods
  - 21 Target analytes
  - 9 Surrogates (Isotopically labeled)
- Updated Methods (2017 Versions)
  - 31 Target Analytes and 14 Surrogates
    - Ten Additional Target Analytes added to Appendix with all MRM transitions, Tune parameters, recoveries in matrices …
    - Five Additional Surrogates (Isotopes) added to Appendix with all MRM transitions, Tune parameters, recoveries in matrices …

Determine Chromatographic Parameters and Detection Levels

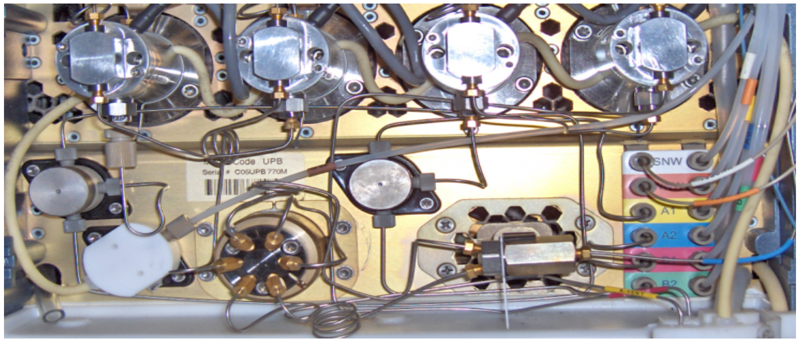
- Liquid Chromatography
  - Acquity UPLC® CSH™ Phenyl-Hexyl 1.7 μm, 2.1 x 100 mm column
  - Isolator Column- Acquity UPLC® BEH C18, 1.7 μm, 2.1 x 50 mm column
- Detector-MS/MS
  - Waters Xevo® TQ-S

Isolator Column Placement



5uL sample loop

Pump outlet
tube



Region 5 CRL PFAS SOP Reporting Limits/Surrogates

Analyte	Reporting Limit (Water) (ng/L)	Reporting Limit (Soil) (ng/Kg)	Surrogate
PFTreA	10	25	New
PFTriA	10	25	
PFDoA	10	25	X
PFUnA	10	25	X
PFDA	10	25	X
PFDS	10	25	
PFOS	10	50	X
PFNA	10	25	X
PFNS	10	25	
PFOA	10	25	X
PFHpS	10	25	
PFHxS	10	25	X
PFHpA	10	25	New
PFHxA	10	50	X
PFBS	10	25	New
PFPeS	10	25	
PFPeA	50	125	New
PFBA	50	125	X
FOSA	10	25	New
4:2 FTS	10	25	X
6:2 FTS	10	25	X
8:2 FTS	10	25	X
NEtFOSAA	10	25	X
NMeFOSAA	10	25	X

Standard Mix Cautions

- Wellington Produces a mix containing twenty-four PFAS and an isotope mix containing nineteen isotopes (Surrogates)
  - Many compounds are not all at the same concentration, have to account for the difference with respect to the counter ion.
  - Some are different isotopes than what are in the ASTM methods.
  - Not a big issue as long as the user is aware of the differences and corrects for them.

Different Isotopes	Analyte	Abbreviation	Transition	SRM	Cone	Collision
1	Perfluoro-n-(1,2,3,4,6-$^{13}C_5$)hexanoic acid	M5PFHxA	Primary	317.9>272.9	10	10
2	Perfluoro-n-($^{13}C_8$)octanoic acid	M8PFOA	Primary	420.9>375.9	15	10
3	Perfluoro-n-($^{13}C_9$)nonanoic acid	M9PFNA	Primary	471.9>426.9	15	10
4	Perfluoro-n-(1,2,3,4,5,6,7-$^{13}C_7$)undecanoic acid	M7PFUnA	Primary	569.9>525	15	12
5	Perfluoro-1-(1,2,3-$^{13}C_3$)hexanesulfonate	M3PFHxS	Primary	401.9>79.8	15	32
6	Perfluoro-n-(1,2,3,4,5,6-$^{13}C_6$)decanoic acid	M6PFDA	Primary	518.9>473.9	15	12
7	Perfluoro-1-($^{13}C_8$)octanesulfonate	M8PFOS	Primary	507>79.8	15	40
Additional Isotopes						
1	Perfluoro-1-(2,3,4-$^{13}C_3$)butanesulfonate	M3PFBS	Primary	301.8>79.8	10	29
2	Perfluoro-n-($^{13}C_5$)pentanoic acid	M5PFPeA	Primary	267.8>222.9	15	9
3	Perfluoro-n-(1,2,3,4-$^{13}C_4$)heptanoic acid	M4PFHpA	Primary	366.9>321.9	10	10
4	Perfluoro-n-(1,2-$^{13}C_2$)tetradecanoic acid	M2PFTreA	Primary	714.9>669.9	20	15
5	Perfluoro-1-($^{13}C_8$)octanesulfonate	M8FOSA	Primary	505.9>77.8	15	30

CRL PFAS SOP Water Sample Preparation (ASTM D7979)

- 5 mL water sample in Polypropylene Tube
- Add “Spikes”
- Add 5 mL MeOH
- Shake- 30 seconds
- Filter through Polypropylene Filter Unit
- Add 10 μL acetic acid
- Analyze

CRL PFAS SOP Sludge Sample Preparation (ASTM D7979)

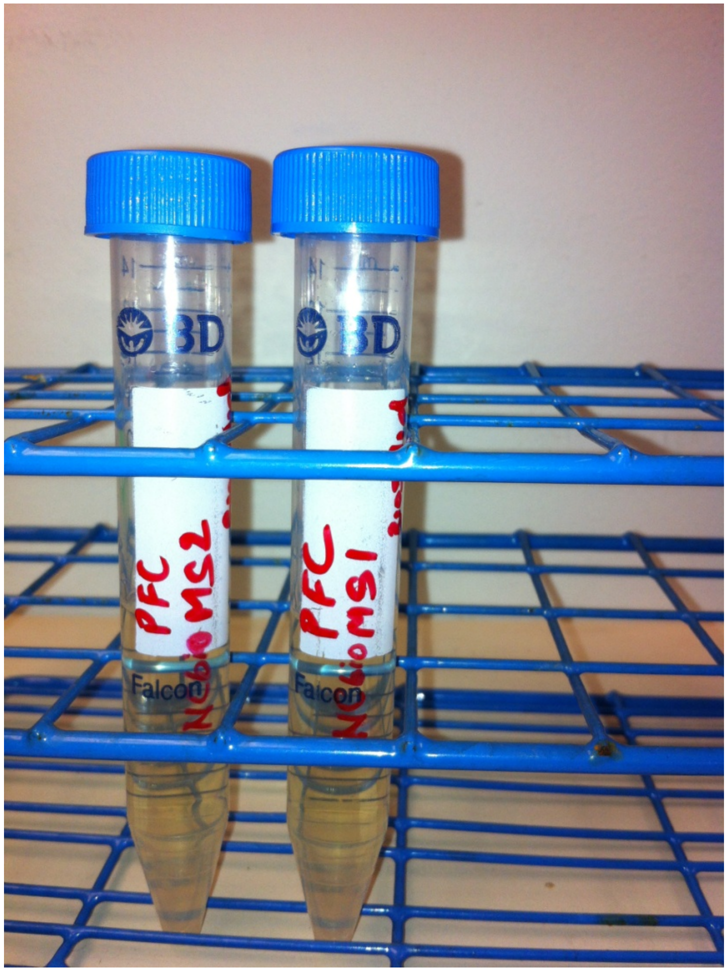
- 5 mL Sludge sample in PP tube
- Add “Spikes”
- Add 5 mL MeOH
- Add 20 μL NH_4OH, Shake, check if basic, pH 9-10.
- Mix for 2 minutes
- Decant the liquid and filter through Polypropylene Filter Unit
- Add 50 μL acetic acid
- Analyze

CRL PFAS SOP Soil/Biosolids Sample Preparation (ASTM D7968)

- 2 gram sample (sub-sample)
- Add “Spikes”
- 10 ml of methanol:water (50:50) -shake/vortex for ~ 2 minutes.
- Add 20 μL NH_4OH, shake/vortex for ~ 2 minutes, check if basic, pH 9-10.
- Tumble for 1 hr
- Centrifuge
- Decant the liquid and Filter through Polypropylene Filter Unit
- Add 50 μL acetic acid
- Analyze

Sludge samples

NC Sludge Sample
Before Extraction



NC Sludge Sample
After Extraction

Matrices Used to do Single Lab Validation using CRL PFAS SOP for Water

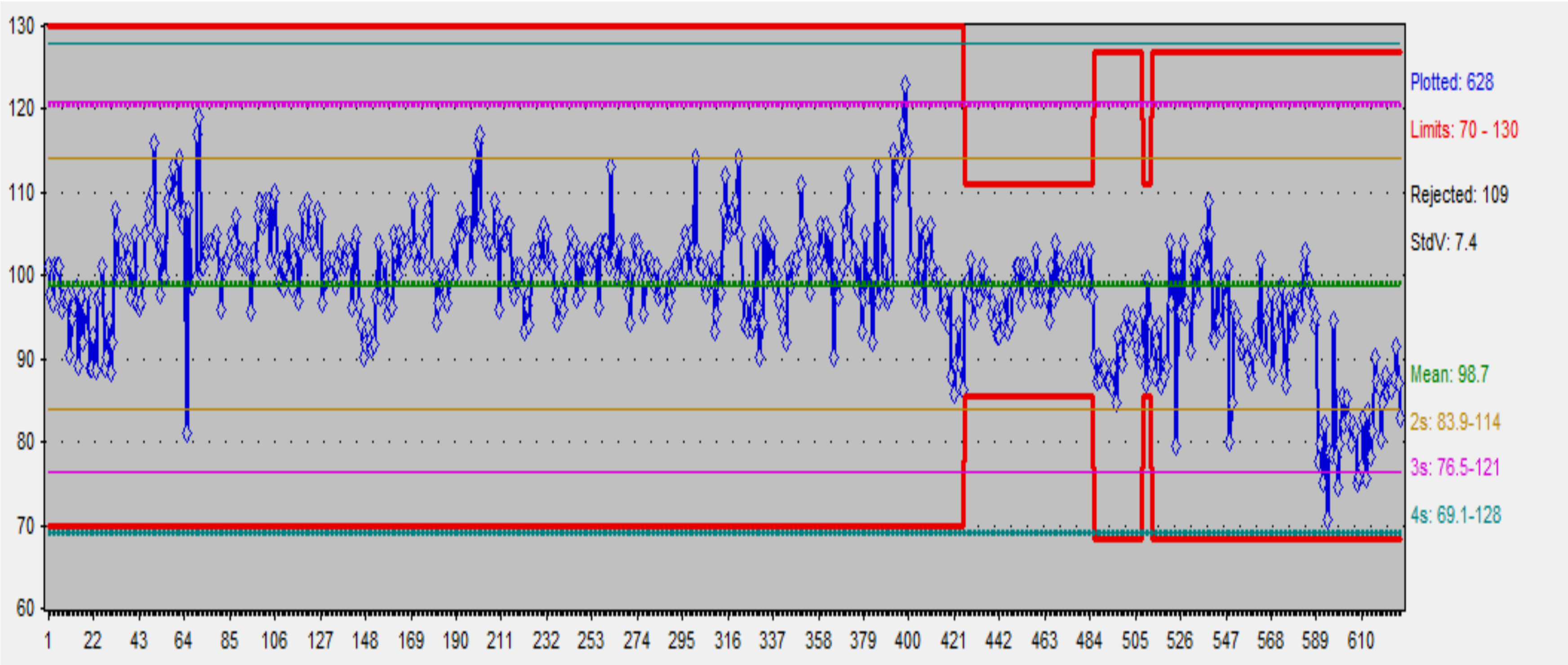
- Reagent Water
- Chicago River Water
- Ground Water: Silurian-Dolomite Aquifer
- Sewage Treatment Plant I (STP) Effluent
- STP I Influent
- STP II (Effluent with supplemental sewage)
- STP III (Effluent with supplemental sewage)

Matrices Used to do Single Lab Validation using CRL PFAS SOP for Soil

- Ottawa Sand
- Four ASTM Soils
  - Sand
  - Lean Clay
  - Fat Clay
  - Silt

MPFOA (Surrogate) Recovery Data in Real Water Samples

- Real Samples (Not Reagent Water)
  - Surface, Ground, Influent, Effluent and Sludge
- Collected by five different Analysts at CRL

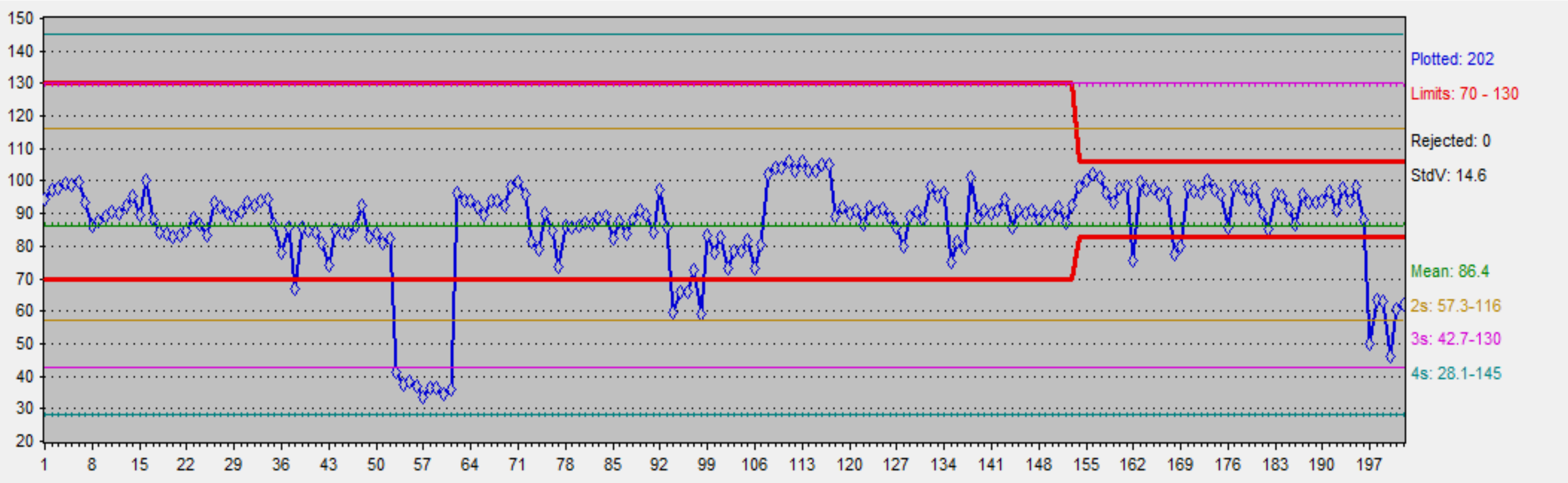


Surrogate Recovery Data in Real Water Samples

Surrogate	Number of Samples	Average Recovery (%)	Standard Deviation
MPFBA	628	95.5	13.9
MPFHxA	628	96.7	7.3
MPFHxS	628	97.9	6.7
MPFOA	628	98.7	7.4
MPFNA	628	99.6	7.4
MPFOS	628	98.7	6.9
MPFDA	628	101	8.5
MPFUnA	628	101	8.8
MPFDoA	628	102	11.5
M4:2 FTS	284	98.2	18.5
M6:2 FTS	280	106	19.5
M8:2 FTS	289	105	17.4
MN-EtFOSAA	284	99	9.2
MN-MeFOSAA	284	94.5	6.74
MPFTreA	82	90.2	15.5
MPFBS	81	95.2	5.4
MPFHpA	81	94.8	5.2
MPFPeA	81	94.2	5.6
MPFOSA	81	96.7	5.1

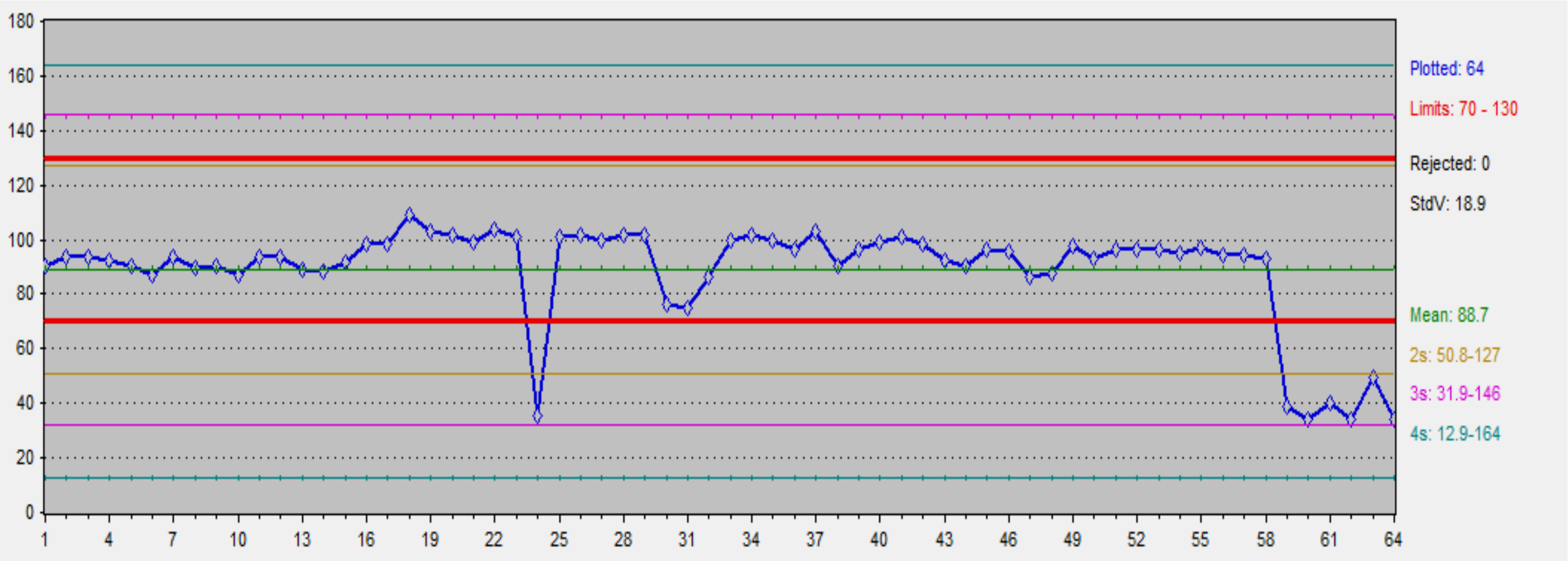
MPFOA (Surrogate) Recovery Data in Real Soil Samples

- Real Soil Data
  - Soils from sites
  - Commercial Soils
  - Biosolids
  - Primary Solids coming into POTW
  - Recoveries in some soils not as good as in others.



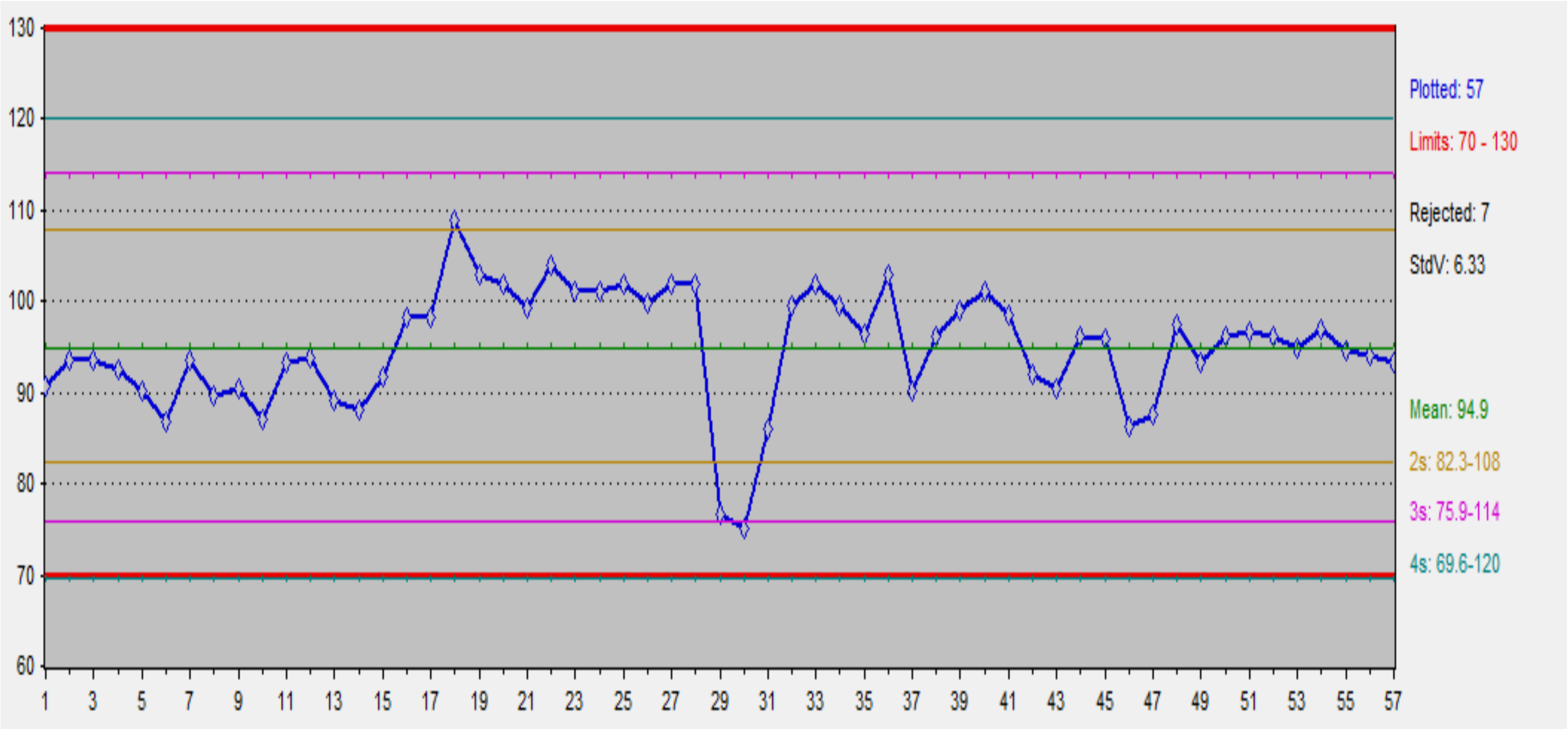
D3-NMeFOSAA
(Surrogate Recovery in Soils)

- Mean: 88.7% Recovery
- Standard Deviation: 18.9



D3-NMeFOSAA (Surrogate Recovery in Soils, removing poor performing matrices)

- Mean: 94.9% Recovery
- Standard Deviation: 6.33



Surrogate Recovery Data in Real Soil Samples (No Poor Performers Removed)

Surrogate	Number of Samples	Average Recovery (%)	Standard Deviation
MPFBA	193	85.3	20
MPFHxA	202	85	17.1
MPFHxS	202	85.3	11.6
MPFOA	202	86.4	14.6
MPFNA	202	86.7	15.9
MPFOS	202	83.5	14.4
MPFDA	202	86.6	17
MPFUnA	202	83.8	21.6
MPFDoA	202	77	27.6
M4:2 FTS	64	130	41.3
M6:2 FTS	62	140	46.9
M8:2 FTS	61	142	51.6
MN-EtFOSAA	64	90.9	26
MN-MeFOSAA	64	88.7	18.9

Surrogate Recovery Data for Milorganite

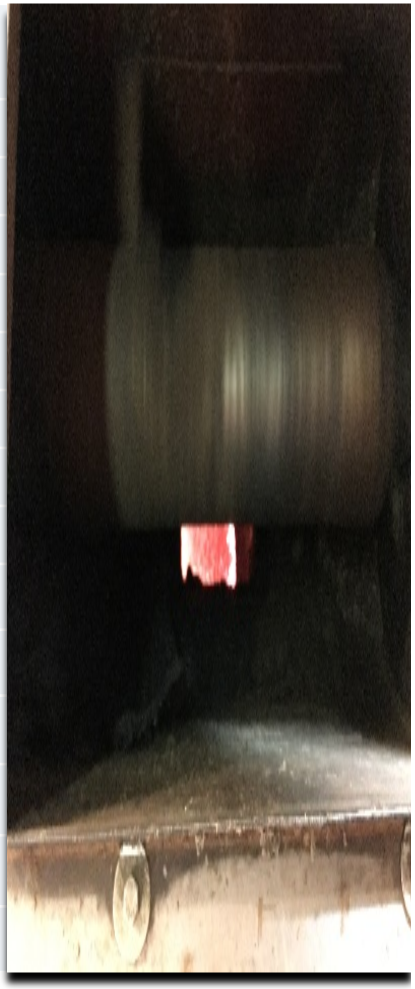
Surrogate	Number of Samples	Average Recovery (%)	Standard Deviation
MPFBA	9	NA	NA
MPFHxA	9	24.9	1.64
MPFHxS	9	53.3	3.08
MPFOA	9	36.7	2.3
MPFNA	9	36.2	2.36
MPFOS	9	52.5	3.7
MPFDA	9	32.7	2.33
MPFUnA	9	28.1	2.07
MPFDoA	9	21.7	1.45

Surrogate Recovery Data for Biosolids

Surrogate	Number of Samples	Average Recovery (%)	Standard Deviation
MPFBA	6	52.6	5.3
MPFHxA	6	69.6	5.6
MPFHxS	6	67.3	4.3
MPFOA	6	68.1	9.9
MPFNA	6	67.9	8.1
MPFOS	6	55.7	4.2
MPFDA	6	64.3	5.5
MPFUnA	6	43.3	3.84
MPFDoA	6	17.9	1.15

Surrogate Recovery Data for Primary Solids Coming into POTW

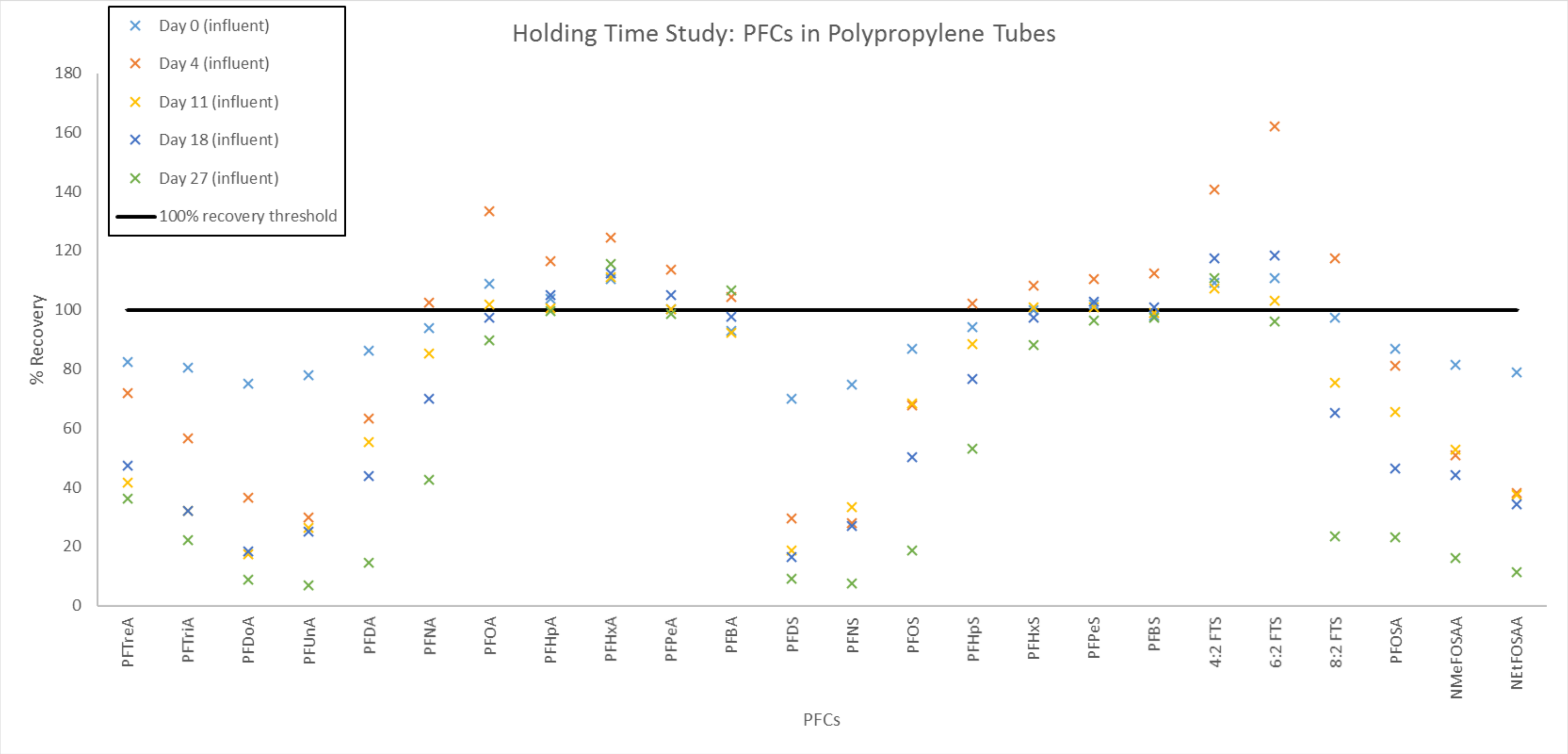
Surrogate	Number of Samples	Average Recovery (%)	Standard Deviation
MPFBA	6	10.6	3.45
MPFHxA	6	48	9.73
MPFHxS	6	59.8	7.62
MPFOA	6	57.5	7.48
MPFNA	6	42.6	7.74
MPFOS	6	46.9	5.52
MPFDA	6	45.7	6.23
MPFUnA	6	25.7	6.75
MPFDoA	6	15.4	5.45
M4:2 FTS	6	194	58.9
M6:2 FTS	6	196	31.3
M8:2 FTS	6	206	25
MN-EtFOSAA	6	18.8	4.61
MN-MeFOSAA	6	38.4	6.15



Holding Time Study in POTW Influent

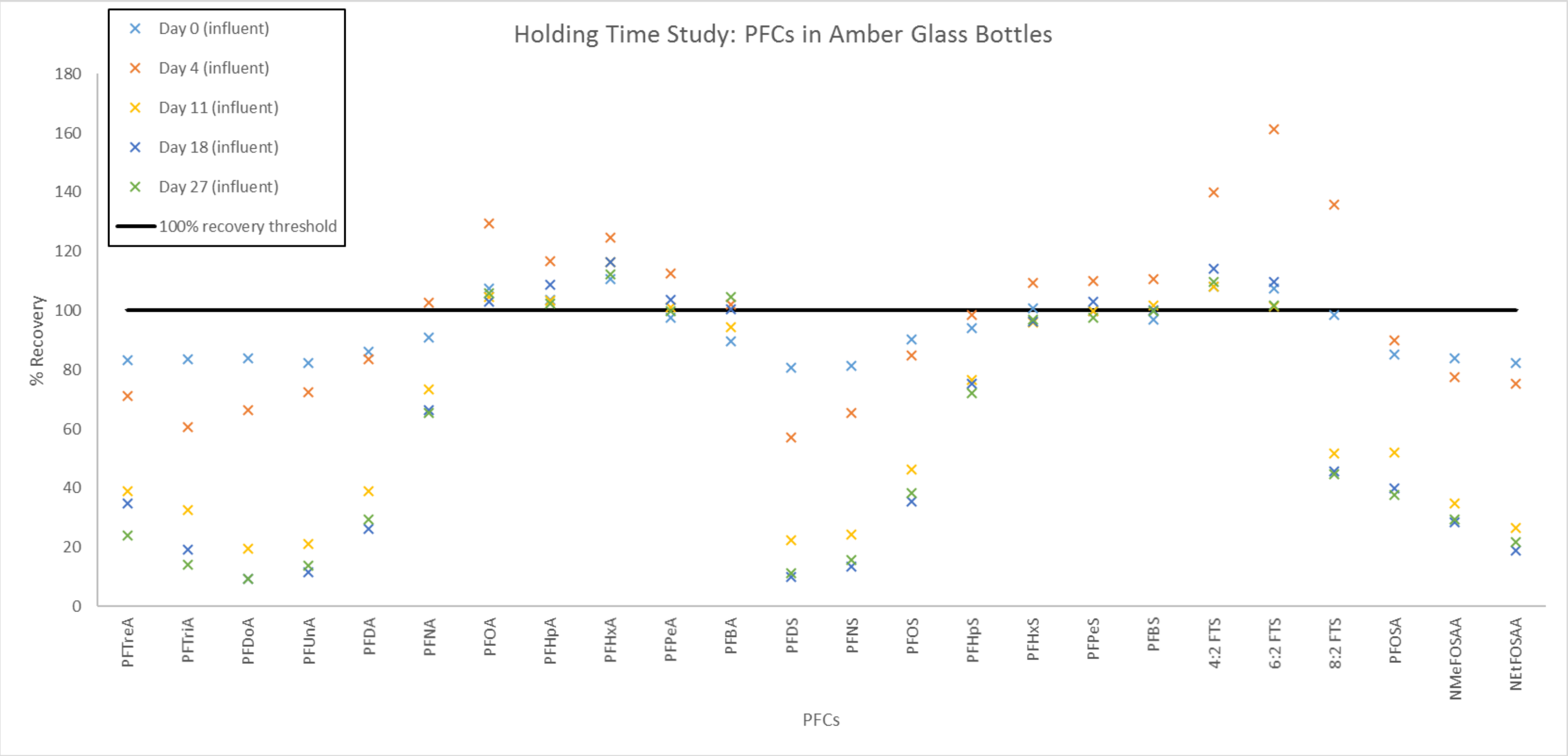
- Compare concentrations sampling the same spiked bottles over 27 days (**<u>Aliquot, not using the entire sample</u>**)
  - Amber Glass
  - Polypropylene
  - HDPE
- Losses over time with each sampling container
- Drastic differences between reagent water and POTW influent recovery results.

Holding Time- Polypropylene tubes (POTW Influent)



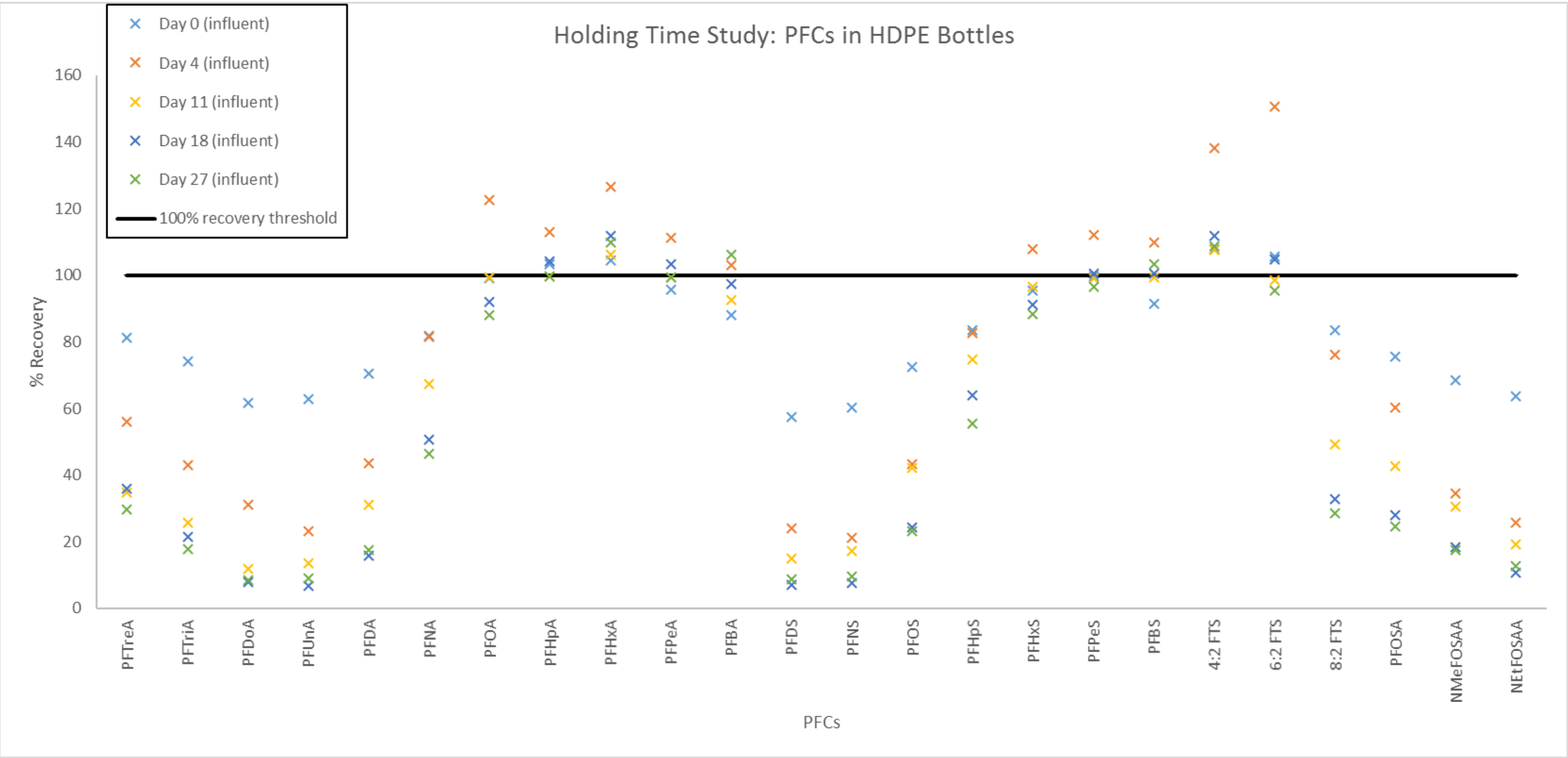
Holding Time- Amber Glass Bottles

(POTW Influent)



Holding Time- HDPE Bottles

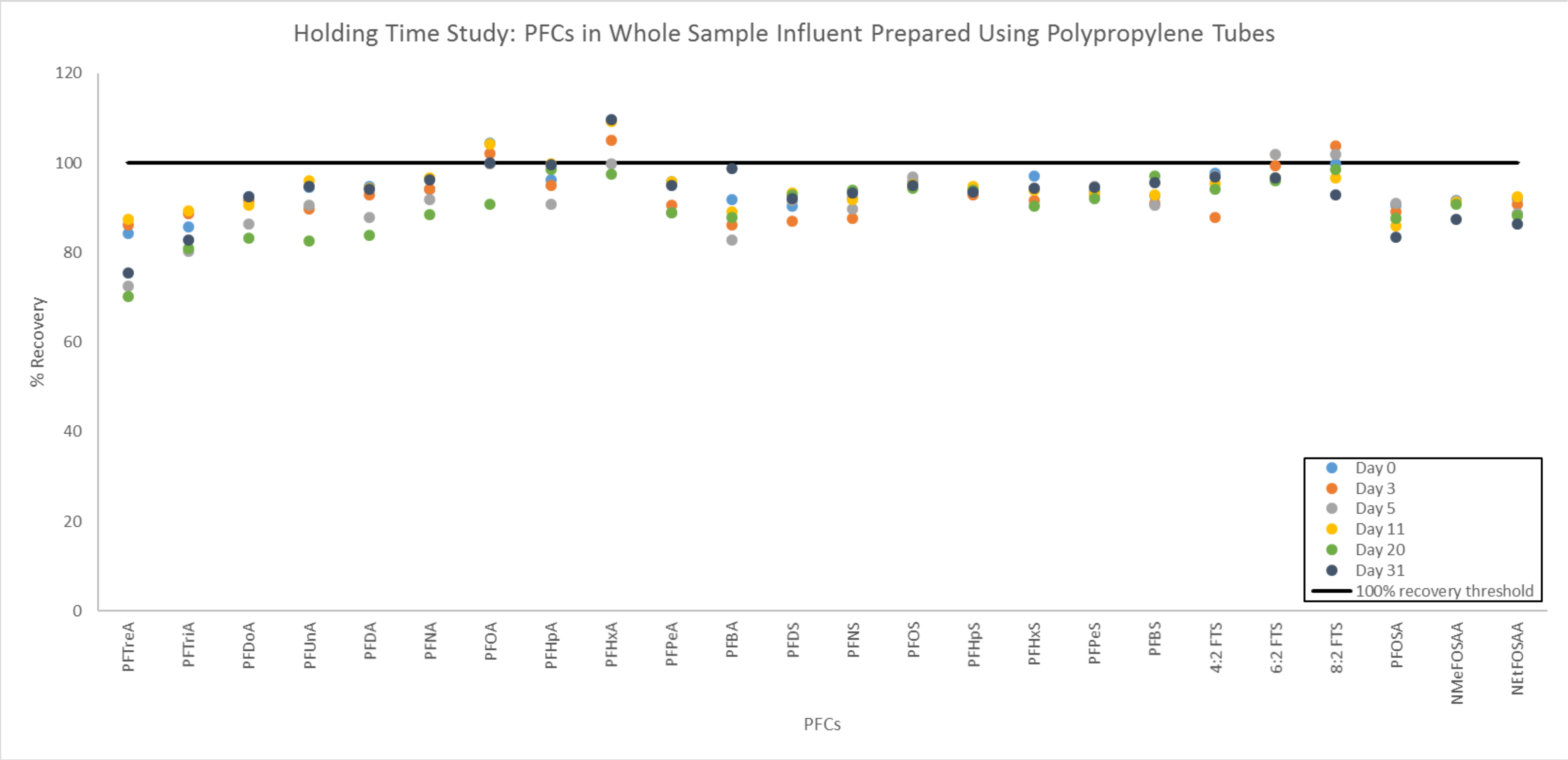
(POTW Influent)



Holding Time Study in POTW Influent using Entire Sample

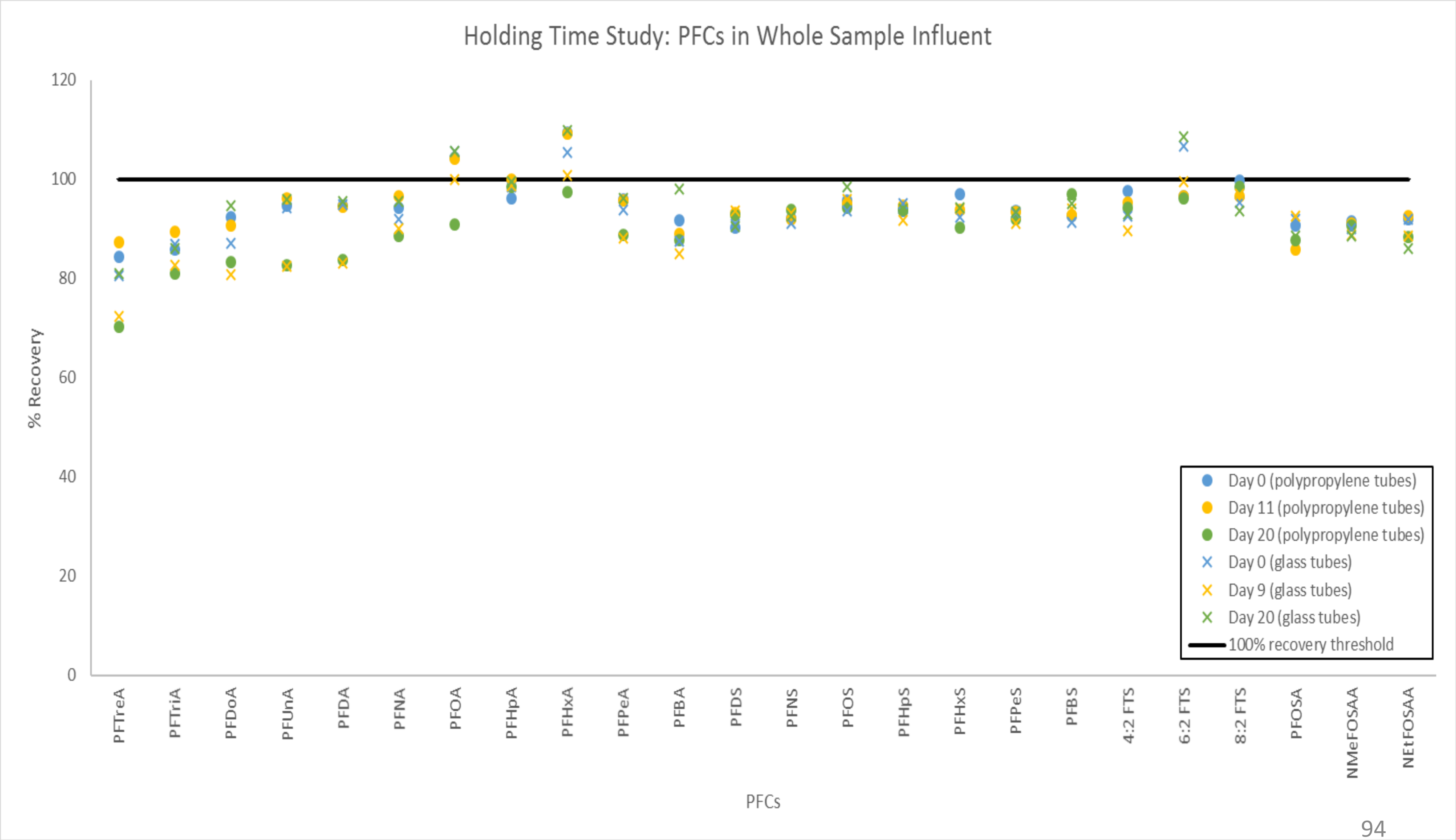
- Spiked into POTW influent and monitored.
- Polypropylene- Eighteen separate spiked samples prepared to use the entire sample. Small sample size – 5 mL.
- Pyrex Glass- Twelve separate spiked samples prepared to use the entire sample. Small sample size – 5 mL.
- Corroborates that the entire sample must be used.

Whole Sample Influent (Polypropylene tubes- 31 days)



Whole Sample Influent

(Compare Glass to Polypropylene)



Contamination

(Be cautious!)

- Teflon® Containing Materials
- Waterproof Field Books
- Plastic Clipboards, binders, or spiral hard cover books
- Post-it Notes
- Chemical (blue) ice packs
- Coated Tyvek®
- Glass Pipettes-PFAS contaminated- PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA

Contamination

(Be cautious!)

- Many types of water resistant, waterproof, or stain-treated clothing, clothing containing Gore-Tex™
- LDPE containers
- Decon 90
- Water from an on-site well
- Aluminum Foil
- Methanol

Sample Collection

- Collect a 5.0 mL sample, grab would be best, in a graduated 15 mL polypropylene BD Falcon tube in the field so that the whole sample is processed in the lab (NO ALIQUOTING).
- In order to have accurate volumes, the weight of the 15 mL polypropylene BD Falcon tube may be taken before and after sampling in order to get an exact volume. The density of water is assumed to be 1.0 g/mL unless the exact density of the water sample is known, then that conversion should be used.

Holding time/Sample Requirements

- 28 Days
- Required to collect a separate sample for each QC Sample (Co-located). Collecting in one container in the field and transferring to other containers may lead to low biased results.
- Have to prepare and use the entire sample.
- Take a couple extra samples in case re-extract required.

If You Review Data Generated by Other Methods

- Previously Published methods on PFCs
  - EPA Method 537, ASTM D7979 or D7968, Journal?
  - Are they really following the methods they cite?
- Using the entire sample?
- Many sample manipulations involved?
- Pre-filter?
- Complicated Sample Preparation?
- Batch QC-Surrogates, duplicates, matrix spikes, reporting limit checks?
- Ongoing Method Performance in Real Matrices?
- Quantitation?
  - SRM or MRM, Ion Ratios?
  - Are they getting poor recoveries of their isotopes and correcting the data using isotope dilution?
  - Isotope dilution- are they diluting samples- diluting out isotope, adding more isotopes after dilution? Not isotope dilution anymore.
  - Equilibration time of the isotopes in the sample?
  - Are the isotopes at a similar concentration as their reporting range?

Conclusion/Ongoing work

- Use Entire Sample
- Quick and robust analyses
- Produce data of known quality
- Multi-lab validating methods
  - Internal EPA (now)
  - External
- Plan is to place in SW-846
- Updated ASTM D7979 (waters/sludges, not drinking water!) and D7968 (soils). www.astm.org

More Information

- Contact: Dennis Wesolowski, US EPA Region 5 Chicago Regional Lab Director
  - 312-353-9084
- Contact: Larry Zintek, Chemist
  - 312-886-2925
  - Zintek.Lawrence@epa.gov

Today's Agenda

- **11:20 Laboratory Perspectives** – *Tim Fitzpatrick, SGS Axys; Charles Neslund, Eurofins*
- **11:35 Facilitated Q & A / Discussion**
  (Please use the chat bubble icon to ask questions.)
- **11:55 Summary & End**

Lab Perspectives:

Best practices in sample preparation and analysis of polyfluorinated environmental contaminants

NEBRA webinar
September 14, 2017

Tim Fitzpatrick, SGS AXYS Analytical Services, Ltd. &
Charles Neslund, Eurofins Lancaster Laboratories Environmental, LLC

eurofins
Lancaster Laboratories
Environmental

SGS AXYS

SGS AXYS FOCUS

- Focus –Ultra Trace Analysis of POPs and CECs (pg or ng levels)
  - POPs (PCB congeners, Dx&F, ultratrace pesticides - all matrices)
  - Emerging Contaminants – PFAS, Flame Retardants, PPCPs, Sterols, Hormones, alkylphenols,etc.
  - HRMS, LC MS/MS, GC/MS, GC-ECD instrumentatior
  - Targeted Metabolomics
- 3 Analytical Areas
  - Environmental (All matrices associated with Bioaccumulation cycle)
  - LifeScience – Bio-monitoring/Eco-Tox and Metabolomics/Human Serum
  - Method Development (i.e. EPA 1668 PCBs, 1614 PBDEs, 1694 PPCPs, 1698 ST/HM, 1699 MRES pesticides – EPA Draft PFAS in Biosolids Method
  - Working in both Research and Applied Areas

SGS AXYS BIOSOLIDS/POTW BACKGROUND

- Participation in EPA National Sewage Sludge Survey (2009) - PPCPs, Sterols and HM
- National Sewage Sludge and wastewater for Environment Canada - Multiple Years PFAS and multiple CECs
- Developed Draft EPA Method for PFAS in Biosolids (2010)
- SETAC 2016 Presentation – *"Behavior of polyfluorinated alkyl substances, including PFOS and PFOA, in Wastewater Systems: Experiences from Multiple Studies in North America"* – 20 Canadian POTWs surveyed influent, effluent and biosolids
- Dioxin 2017 Presentation – *"Validation and Application of a Standards-Enhanced Total Oxidizable Precursor Assay"* (Includes Validation for Biosolids Matrix)
- Method development and Single lab validation in influent, effluent and biosolids for Low Res PCB Congener method in Support of the Clean Water Act (CSRA, EPA Office of Water – 2017)

SGS AXYS

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EUROFINS LANCASTER LABORATORIES ENVIRONMENTAL

- In operation for more than 50 years
- 330,000-square-foot laboratory facility on 27 Acres
- Staff of over 1600 scientists, technicians, and support personnel
- Environmental, Pharmaceutical & Food
- Eurofins US Corporate Office (Finance, HR, IT, Purchasing)
- $200+ million in annual sales
- One of the largest commercial testing labs in the world

ENVIRONMENTAL

- 200K Samples / 1M Tests per year
- 300 Scientists
- $30M+ in annual sales
- Largest single site environmental lab in USA

Facility and Equipment Designed for Ultra-Trace Applications

- 5 instrument laboratories isolated from the wet chemistry laboratories.
- Each lab is equipped with climate controls, separate power sources and limited security access.
- Each facility is custom designed to optimize “analytically clean” workspace, including controlled, filtered lab air distribution and highly scrutinized material use to provide extremely low laboratory blank background levels and minimize detection limits.
- Ongoing proofing of materials and reagents
- Shut-downs instilled if blanks show persistent detections
- Waters Xevo TQS UPLC/MS/MS used for ultra-sensitive applications (picogram level) – State of the art for sensitivity, resolution and ruggedness.

Importance of Control of Background Contribution to Blank Cleanliness

- Instruments used for PFAS analysis retrofitted polyethylene pump seals, PEEK tubing and PEEK mixing chambers to reduce/eliminate potential for PFAS background
- Reagents assayed on a lot to lot basis for acceptable background. Some reagents (methanol) assayed bottle to bottle even within the same lot.
- Single source of water used for and qualified for use in PFAS analysis
- Common laboratory equipment and devices (i.e. pasteur pippettes) not allowed to be used within the lab used for PFAS analysis
- Dedicated lab space for instrumentation and sample handling
- Separate handling procedures for drinking water samples versus AFFF or AFFF impacted sites.

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ANALYTICAL METHODS - BASIC PFAS ANALYSIS – BEST PRACTICE - AQUEOUS AND SOLIDS

Pre- Treatment / Extraction

- Solids:, Acidic and / or Basic Extraction
- Aqueous: pH Adjustment
- Surrogates added (monitoring or IS)

Cleanup and Concentration:

- Weak Anion Exchange (WAX) + (Optional) Carbon
- Reduce Eluent, add recovery standards

LC-MS/MS Analysis

- Neg. ESI monitoring of MRM transitions
- Primary transition for quantification, secondary confirmation

WHAT IS ISOTOPE DILUTION?

- Simply defined as the practice of adding labeled analogs of target analytes to the sample before extraction and prep.
- Proper use of labeled analogs in construction of calibration curve allows for automatic correction for extraction and response deficiencies
- Labeled analogs are identical in chemical property and behavior to the Target Analyte but have a different mass.
- Labeled standards account for many matrix issues, better interference detection for both suppression (false negatives) and enhancement (false positives)
- Ideally a 1:1 ratio for labeled standards to target analytes, but difficult to attain due to lack of commercially available labeled analogs

METHOD COMPARISON TABLE

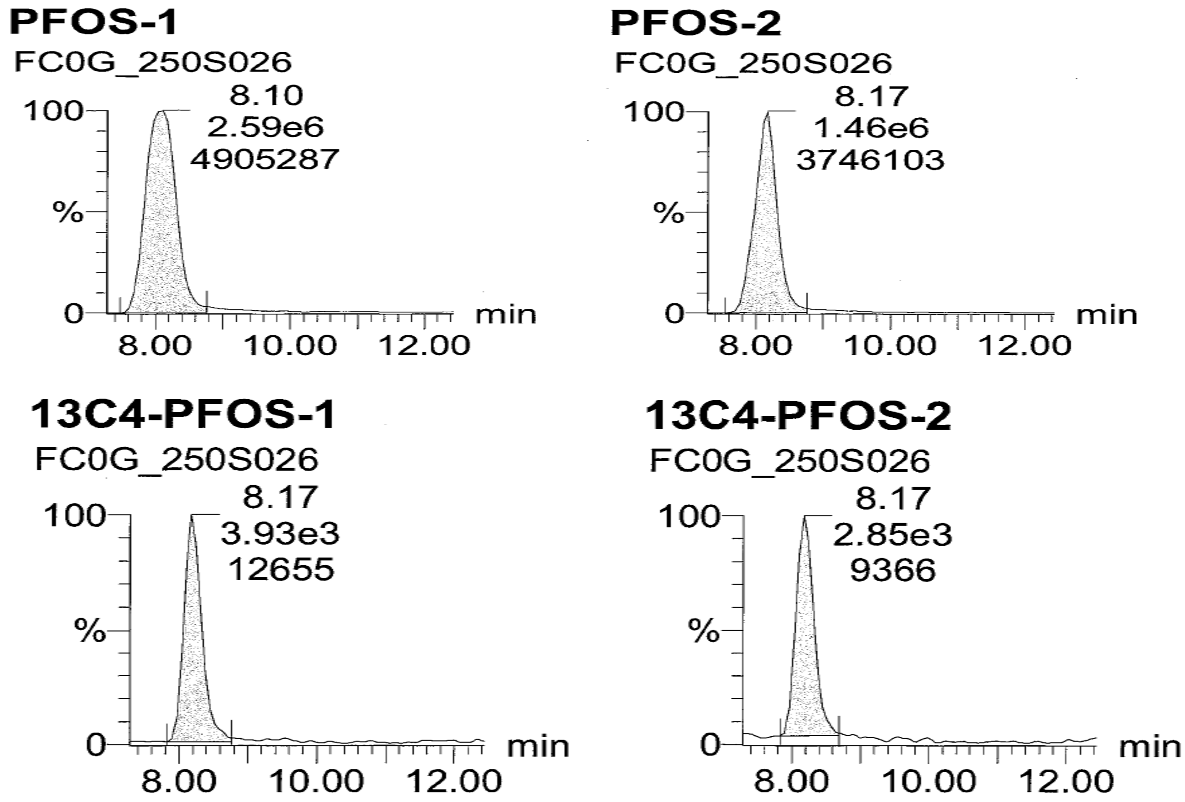
Method	Matrices	Isotopically Labeled Standards	Recovery Correction	Cleanup
AXYS 29 Compound PFAS MLA-110 (537 Mod)	Aqueous,sediment/soil/solid, tissue, serum, urine, biosolids, influent/ effluent	23 labeled surrogate + 8 recovery standards	Isotope dilution/ surrogate correction quantitation	Weak Anion Exchange (WAX) and Carbon based clean-up
ELLE 537 Modified	Aqueous, leachate, soil/ solid, sediment, Biosolids, tissue	23 labeled extraction stds and 4 injection stds	Isotope dilution/ surrogate correction quantitation	WAX and Carbon based clean-up
EPA 537	Drinking Water ONLY	3	None	SDVB
ASTM 7979 ASTM 7968	Aqueous (7979) Soil (7968)	9	None	None – Direct Injection

- Each of these methods are validated and fit for stated purpose
- Matrix extensions require careful thought and method validation
- ISO 17025, DoD and EPA working on improved methods for current needs – 2017 releases expected

PE STUDIES AND INTER-CALIBRATIONS – READILY AVAILABLE TO LABS

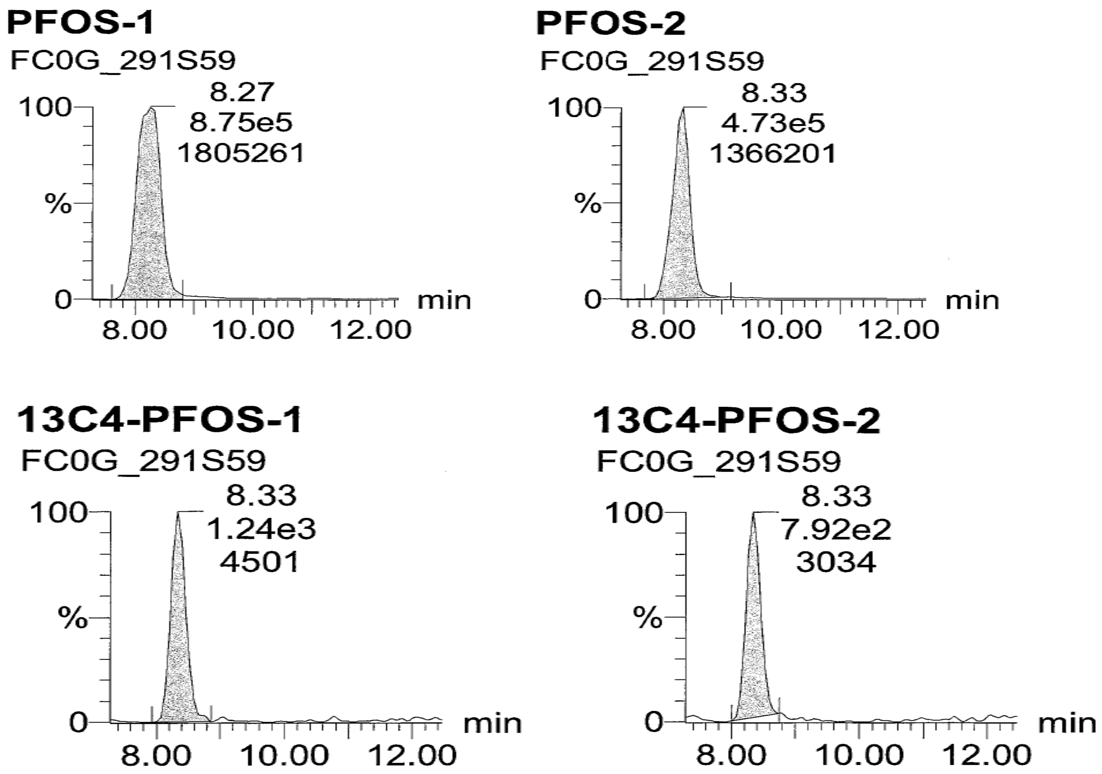
- Available Multi-Matrix Inter-Calibrations
  - Flouros, PerForce, IVM – “World Wide Inter-Calibration Study” – annual since 2005
  - Northern Contaminants – ONMECC - Annual since 2008
  - Norwegian Food Institute – Annual since 2008
  - AU NMI - commenced 2015 (PFOS, PFOA only – spiked surface water and soil)
- Accreditation PE Samples
  - Clean matrix analysis (spiked reagent water, solids)
  - NELAP proficiency program available as of January 2017 (soil and water)
  - Serum accreditation by ISO 17025 – PE samples from AMAP and G-Equis

ISOTOPE DILUTION TO IDENTIFY AND FIX SUPPRESSION AND ENHANCEMENT (SOURCE OF BIAS, LOW LEVEL FALSE POSITIVES)



- INITIAL RUN: PFOS = 24,250 ng/L
- Surrogate Recovery Low (23%) – Is the measured concentration accurate?

ISOTOPE DILUTION TO FIX SUPPRESSION AND ENHANCEMENT (CONT.)



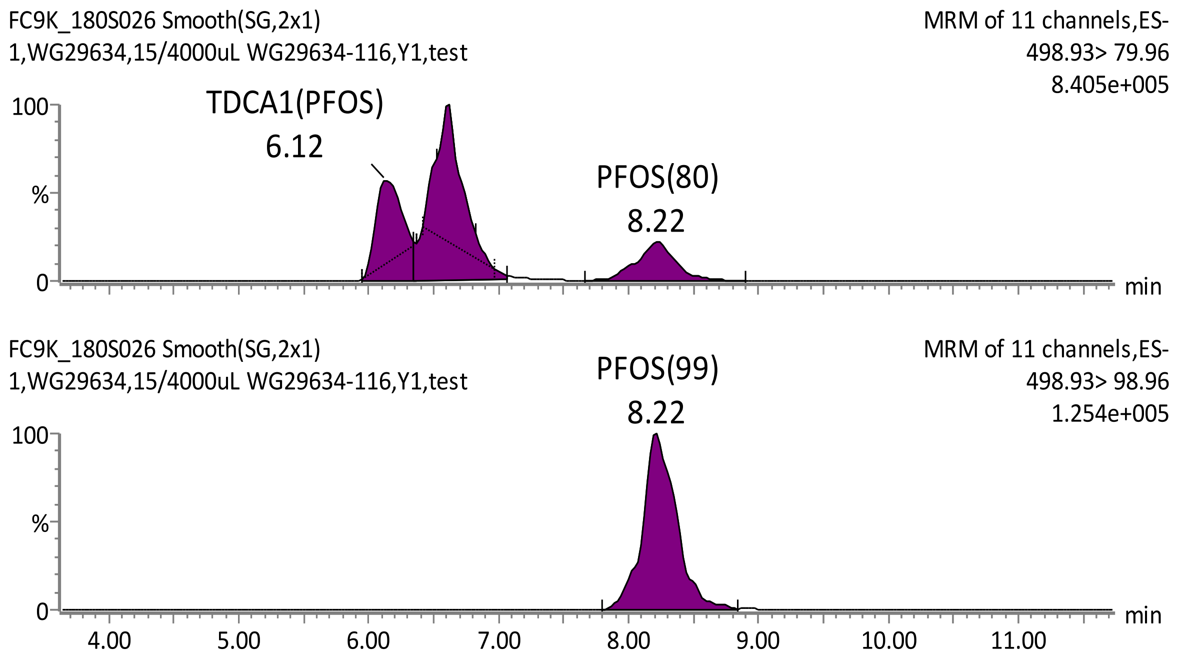
- AFTER 3X DILUTION: PFOS = 32,950 ng/L – Low bias corrected due to isotope dilution
- Surrogate Recovery in-spec (72.3%)

TISSUE LC/MS/MS INTERFERENCES

- False positives of up to 120 ng/g PFOS detected in eggs in previous study
- PFOS and Taurine-conjugated Acid (TDCA) (Bile acids) Same MW, Common Transition

Compound	Parent	Ion 1	Ion 2	Ion 3
Taurochendeoxycholate	498.2	79.8	106.8	123.8
Taurodeoxycholate	498.2	79.8	106.8	123.8
Tauroursodeoxycholate	498.2	79.8	106.8	123.8
PFOS	498.9	79.9	98.9	N/A

TDCA + PFOS – FULL WORKUP



- Recovery of TDCA through WAX cleanup 70-130%: Chromatographic separation/use of 499 -> 99 transition required
- AXYS method separates out TDCA by >2 minutes – Enables use of more sensitive transition for quantitation and 499 -> 99 transition for confirmation
- Use of multiple transitions can mitigate against interferences

TYPES OF CHALLENGING SAMPLES

- Biota – Lipids, other interferences
- POTW Biosolids and Effluents
  - High level of matrix creates suppression and enhancement
  - Default is sample size reduction
- AFFF Groundwater, Products and Tank Rinsates
  - Pre-screen / direct injection protocols in place
    - High Level Samples (PFAS, FTS, related compounds)
  - Potential to create multi-phase liquids (i.e. foam)
    - Decrease sample size, use full sample size
  - Multi-Phase Samples (Solid / Liquid)
    - Multi-phase samples may need phase separation and separate treatment

SUMMARY

- Use of multiple labeled surrogate standards to detect and correct for suppression and enhancement
- Use of recovery standards
- Use of Specialty Instrumentation
- Extract Cleanup Considerations
- Use of confirming MRM transitions to increase detection certainty
- Importance of blank control measures and corrective action implementation
- Benchmarking against matrix-specific PE and Intercals are extremely important

QUESTIONS AND CONTACT INFORMATION

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Summary

- There is no U. S. EPA-approved method for analyzing PFAS in matrices other than drinking water.
- A standardized approach would be helpful.
- Method 537 is for drinking water; "modified" Methods 537 vary and can produce non-comparable results that are good for screening only (not for enforcement or legal defensibility).
- Labs run methods; they will run the method(s) a client requests.
- Existing data are helpful for screening, but more consistency will be needed if regulations are developed.

Summary (cont'd)

- The ASTM Methods D7979 and D7968 are rigorously validated – by U. S. EPA labs.
- Commercial lab isotope dilution methods – Modified Methods 537 – can be reliable, but you have to look hard at the QC data they provide, ask if they have participated in multi-lab validations, etc.
- U. S. EPA is planning to approve solid waste regulation methods for other waters and solids in 2018, but approved Clean Water Act methods for these are years away.
- There are many more complications!
  - Dept. of Defense prefers isotope dilution methods.
  - PFOA & PFOS are being replaced by other PFAS; less known about them.
  - Precursors are increasingly focused on; TOP methods are being developed

Recommendations / Discussion

- **Carefully design your sampling & testing plan.** Know before sampling what the data limitations will be, what they mean, and how they will be used/interpreted.
- **Understand the limitations of analytical methods.**
- **Be a savvy consumer of lab services:** request full QC data for the method(s) (e.g. reporting limits, method blanks, lab control samples, surrogate and isotope recoveries, method reporting limit checks, participation in multi-lab studies, etc.).
- Right now, each state agency and other clients of lab services are going it alone. Should we all urge U. S. EPA to approve – at least for the interim – the ASTM Methods D7979 and D7968? Or is there another way to get on the same page soon?

Thanks for participating today.

Analyzing PFAS in Wastewater, Solids, & Soils

State of the Science **Webinar**

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