## Issues with the Quantitation and Identification of PFAS; What End Data Users Need to Know

NORTHEAST CONFERENCE THE SCIENCE OF PFAS: Public Health & The Environment

April 6, 2022

David R. Blye, CEAC Principal Chemist



# Waz Up with my PFAS Data?

- Science of PFAS
- Comparability
- Holding Times
- Branched Linear PFAS
- Quant & Qual Ions
- Signal-to-Noise
- Resolution
- Isotope Dilution, EIS, NIS EiEiOooo







# **Current US EPA PFAS Methods**

- US EPA Method 537.0 Drinking Water 2009
- US EPA Method 537.1 Drinking Water 2018 Same as 537.0, but added four PFAS
- US EPA Method 533 Drinking Water December 2019
  - Added 11 PFAS (shorter chains) Finally, isotope dilution quantitation
- US EPA SW-846 Method 8327 Non-DW Aqueous
  - June 2019 (draft) Direct injection, screening only <u>and not usable</u>
    - Environmental Standards draft method comments can be found at <u>https://www.regulations.gov/document?D=EPA-HQ-OLEM-2018-0846-0103</u>
  - September 2021 (Rev 0) (and Method 3512) Addressed many comments, still screening level
- US EPA Method 1633 Non-DW Aqueous, Solids/Biosolids August 2021
  - Posted on the US EPA website, not even a formal draft method, single-laboratory study
  - Environmental Standards drafted method comments on behalf of industrial and advocacy groups.
    - Inconsistencies and major problems (e.g., branched/linear analysis/reporting)
  - DOD currently accrediting laboratories and yet the multi-laboratory is far from complete
  - US EPA anticipates Final Rule for Method 1633 to be 2024
- OTM-45 For PFAS emitted from vents and stacks.
- Ambient Air: No published/validated US EPA methods yet
- Many commercial laboratories are still "making up" analytical methods for PFAS analysis in non-DW matrices.



## **Science of PFAS**

- Academia yes.
- Regulatory bodies slow to move.
- Commercial laboratories have reacted to market demand.

# Lots of Basic Analytical Research is needed!!

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY



# Data Comparability...

- Should data users expect comparability across the commercial environmental laboratory marketplace?
- Yes.....
- Is data comparable from lab to lab?

# NO!!

• Critical to the regulatory process.





# Holding Times... 7-28-90...HIKE

- Confirm receipt temperature is 0 6 °C
  - Analyze (aqueous and leachate) as soon as possible BUT
- In storage of AQUEOUS samples at temperatures ≤ -20°C until preparation...
  - Can store for 90 days
- When temperatures between 0°C and 6°C, aqueous samples may be held for up to 28 days
  - Issues with certain perfluorooctane sulfonamide ethanols and perfluorooctane sulfonamidoacetic acids after 7 days.
- Freezing samples at the lab plastic or glass. FREEZER CAPACITY????
- Transport time to the lab variable
- Thawing samples
- RESEARCH OPPORTUNITY Holding Time Studies.
- What about all the sample data collected to date?

**BUT, THESE ARE FOREVER CHEMICICALS – CORRECT?** 



### **Branched-Linear Isomers**

PFOS anion (C<sub>8</sub>F<sub>17</sub>O<sub>3</sub>S)

- There are 89 possible structural isomers
- There are 11 isomers in most standards
- Technical-grade standard
  - 68.3% linear
  - 30.1% methyl isomers
  - 1.6% dimethyl isomers
- Quantitation-grade standard
  - 78.8% linear
  - 20.4% methyl isomers
  - 0.7% dimethyl isomers





## **Branched/Linear Isomers**

#### PFOS anion ( $C_8F_{17}O_3S$ )

- Technical-grade standard
  - 68.3% linear
  - 30.1% methyl isomers
  - 1.6% dimethyl isomers
- Quantitation-grade standard
  - 78.8% linear
  - 20.4% methyl isomers
  - 0.7% dimethyl isomers
- Dimethyl isomers often not included for quantitation







# **Example of Linear and Branched PFOA**



- Calibration and quantitation with linear only.
- Technical grade standard used for RT window.





# **PFOA in Samples**





# **Quantitative and Confirmation Ions**

- Variability across methods as to if just a Quant lon is good enough.
- Some confirmation ions have weak responses, particularly at low concentrations.
- Ion ratios criteria
- Calibration, verification and instrument sensitivity check standards must all meet ion ratio criteria.
- If concentration > LOQ, confirmation ion response ratio must fall within ± 50% of the ratio observed in the mid-point initial calibration standard.
- What are reasonable Criteria?
- What if a suitable confirmation transition ion does not exist PFPeA?





# Signal-to-Noise (S/N)

- Criteria for both Quantitation and Confirmation ion?
  - BTW, do all labs and methods even use 2 ions? ION RATIO CRITERIA!?
- Quant Ion at least  $\geq$  10:1
  - Noise has < 10% impact on integration</p>
  - Calibration Standards vs. Samples extraction loss and impacts to S/N
- What about secondary Confirmation Ions?
  - At least ≥ 10:1
    - Can they even be  $\geq$  10:1?
  - Should they be least  $\geq 3:1$
- How do we even measure S/N?
- What part of the chromatogram should we use to evaluate S/N?
- RESEARCH OPPORTUNITY Quant and Confirm ions, response and ion ratios.



# Resolution

- Resolution criteria are needed, particularly for branched and linear isomer pairs.
- 50% resolution between monomethyl and linear isomer peaks?
- Variable chromatographic separation is observed in the market.
- Run times are compressed perhaps too much so – because of LC-MS/MS technology and mass specificity.
- PFHpA
- Need more branched and linear quantitative standards.
- Are we even sure that no isomers coelute with the linear compounds?





# **Isotope Dilution, EIS, NIS**

- More isotopically labeled PFAS analogs are needed!!
- Not all PFAS are quantitated by the isotope dilution method
- Extraction Internal Standard (EIS)
- Non-extracted Internal Standard (NIS)
- Variable use of NIS to quantitate EIS vs. monitoring area of the IS
- Dilution
- Fortification
- Reextract a smaller sample aliquot



## What to do?

- Engage smart chemists on your project team.
- Validate PFAS data.
- Basic research still needed.





# Thank You QUESTIONS?



David R. Blye, CEAC Principal Chemist 610.935.5577 dblye@envstd.com

