Perfluorinated Alkyl Acids (PFAAs):

Practical Answers to Frequently Asked Questions

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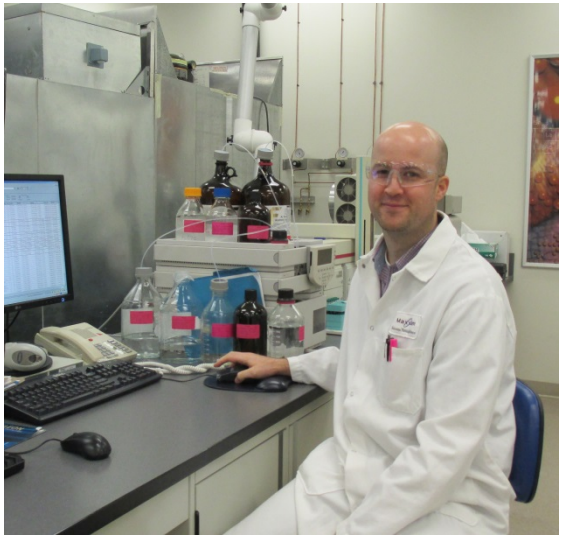
Contributors:



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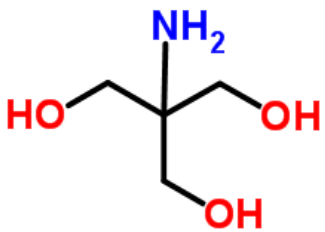
No. 6

What is the purpose of Trizma preservative?

No. 6: What is the purpose of Trizma preservative?



TRIS: tris(hydroxymethyl)aminomethane
TRIZMA: 2-Amino-2-(hydroxymethyl)-1,3-propanediol

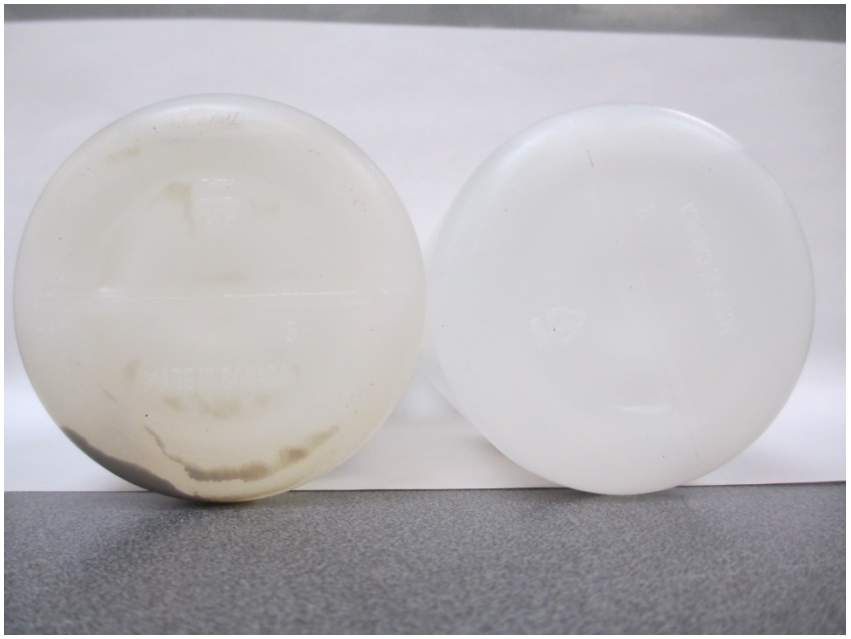
- EPA drinking water regulatory methods typically use sample preservatives to prevent microbial degradation (e.g., $CuSO_4$, DZU, $NaHSO_4$) and to dechlorinate (e.g., ascorbic acid, Trizma buffer, Na_2SO_3) at the time of sampling
- Preservative added: 5g/L
- Used to remove free chlorine and buffer the sample to pH ≈ 7
- Should it only apply to chlorinated water supplies?

Shoemaker, et. al.: "Development of a U.S. EPA Drinking Water Method for the Analysis of Selected Perfluoroalkyl Acids by Solid-Phase Extraction and LC-MS-MS". *J. Chrom. Sci.*, Vol. 47, pp. 3-11 (2009)

No. 5

What is the procedure for handling turbid samples or samples containing sediment?

No. 5: Turbid samples or samples containing sediment?



- Centrifuge, or allow sample to settle, prior to sampling supernatant
- For low levels, where whole bottle is extracted, becomes a non-issue (may introduce a high bias)
- Do NOT filter…

PFC	Filtered (ng/L)	Centrifuged (ng/L)
PFOS	29.3	96.6

No. 4

If PFAAs are such persistent compounds, why is there a 14 day hold time for samples?

No. 4: 14 day hold time for samples?

- *Without an antimicrobial, 14 days is the maximum holding time preferred in current drinking water methods*[1]
- "Default"?
- Then, why have a hold time to begin with?
  - Provides one basis for data comparability

[1] **Shoemaker, et. al.: "Development of a U.S. EPA Drinking Water Method for the Analysis of Selected Perfluoroalkyl Acids by Solid-Phase Extraction and LC-MS-MS". *J. Chrom. Sci.*, Vol. 47, pp. 3-11 (2009)**

No. 3

What are common sources of PFAAs contamination?

No. 3: Common Sources of PFAAs Contamination

- Drive to decrease PFAAs criteria to low ng/L has resulted in the need for higher sensitivity in the analyses
- Increased risk of extraneous contamination from different sources:
  - Sampling equipment (DiGuiseppi et. al., 2015)
    - PFTE tubing – ND (PFOS) to 1400 ng/L (PFBA), depending on source of PFTE
    - Laboratory Proofing
  - Sample containers
    - Glass vs Polypropylene vs Polyethylene
    - Possible negative interference (higher molecular weight PFAAs)
    - Laboratory Proofing
  - Field/Wash water
    - Laboratory supplied vs. “store bought”
    - Low level (10 – 30 ng/L)
    - Laboratory Proofing

No. 2

What are important considerations when calculating PFAAs?

No. 2: Important Considerations…

- Isotope dilution
  - IDMS provides greater accuracy than other calibration methods because it compensates for any matrix effects that may suppress recovery of the parameters being measured.
- Simply put…

  …the recovery of the labeled compound, which is not naturally present in the sample, is an exact representation of the recovery of the native compound which is present in the sample
- Ideal is to have as many isotopically labelled analogues as possible

No. 2: Important Considerations…

- Which MRM transitions are being used to quantify individual compounds
  - Some MRMs are more sensitive than others depending on the isomer being measured. This is important when considering linear vs. branched isomers
  - Transitions to be measured are typically established when the instrument profiles are optimized. However, literature values are used, where known interferences occur
- Calibrations
  - Direct injection vs SPE, i.e., high concentration samples vs low concentration samples
  - Pure linear vs linear/branched mixed standards
  - Which leads to…

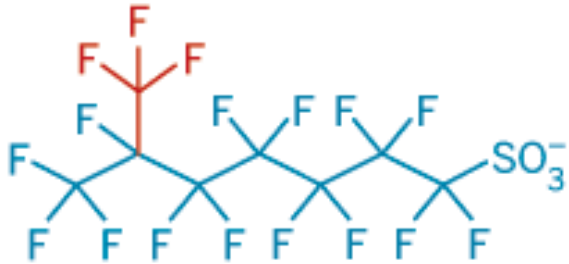
No. 1

Why is it important to distinguish between linear and branched isomers of specific PFAAs?

No. 1: Reporting – Branched vs Linear Isomers

- When interpreting PFOS data, it is important to understand if it is being quantified as the linear or branched chain isomers
- Technical PFOS is a mixture of linear and branched chain PFOS isomers; Linear PFOS is typically pure

PFOS Linear Isomer

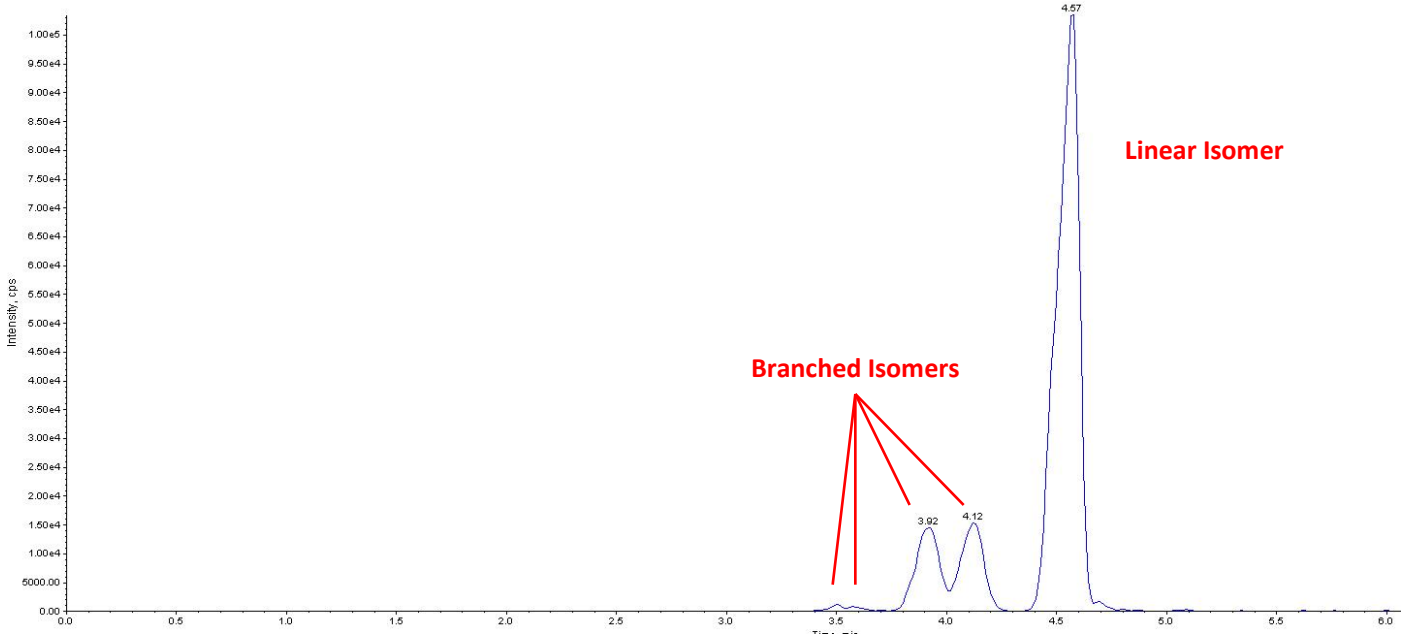


PFOS Branched Isomer (P6MHpS)

Isomer	Wellington[1]	Sigma-Aldrich/ Fluka[2]
Normal (linear)	68.9	82.2
Monomethyl	17.9	9.8
Isopropyl	10.8	10.0
Alpha	1.9	1.2
T-Butyl	0.2	0.4
Dimethyl	0.3	0.5
Total Branched	31.1	21.4

[1] Lot #TPFOS0405: Wellington Laboratories, Guelph, ON, Canada
[2] Batch #312421000: Sigma-Aldrich/Fluka, Buchs, Switzerland

No. 1: Reporting – Branched vs Linear Isomers



- Bias in quantification depending on:
  - the mix of branched PFCs in the technical standard, biases can be seen in individual branched PFCs (further bias)
  - Different instrument response factors based on which isomer and MRM transition are selected
- These are important distinctions because if not considered, quantitative results in real-world samples may be biased by as much as 80%.

No. 1: Reporting – Branched vs Linear Isomers

Three scenarios:

- All LC peaks co-eluted and quantified against a linear PFOS standard
  - Bias as high as 40 - 80%
- All LC peaks co-eluted and quantified against a mixed standard (known amounts of linear and branched)
  - Improved comparability; substantially less bias
- All LC peaks resolved (baseline) and quantified against a technical mixture that has been characterized. Individual calibration curves developed for each branched isomer based on standard values

Decreasing Bias

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Questions?

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