Development of an Organofluoride Method to Quantify Total Per- and Polyfluoroalkylated Substances (PFAS)

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Agenda

- Brief Background

- Study Objective

- Experimental

- Results

  - Comparison of different quantitative methods

  - Investigation of reaction mechanism

- Conclusions

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Background

- More than 4000 per- and polyfluoroalkylated substances (PFAS) have been introduced to the global market

- There are several challenges to quantify the total PFAS in environmental samples

- Only a limited number of analytes can be quantified using current targeted analysis

- There is a need for a holistic approach to provide an estimate of the cumulative PFAS by quantifying the total organic fluorine present in environmental samples

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Other Total PFAS Methods

- Particle Induced Gamma-Ray Emission (PIGE)

  - Surface analysis - measures atomic fluorine

  - Potential advantage - easily applied to complex fluoropolymer matrices

Oxidation Techniques:

- Total Organofluoride- Combustion Ion Chromatography (TOF-CIC)

  - Applied for aqueous matrices and blood samples

- Total Oxidizable Precursor Assay

  - Conservative estimate of the total concentration of PFAA precursors

  - More expensive technique - Sample needs to be analyzed 2 times for PFAAs – before and after oxidation

  Ritter et al. 2017; Houtz and Sedlak 2012; Miyake et al. 2007, Yeung et al. 2008, Wagner 2013

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Objective

- To develop a rapid potentiometric method to measure free fluoride generated by reductive defluorination of PFAS

- To produce rapid indication of the presence of total PFAS in contaminated samples

- To optimize the technique using neat chemicals followed by application on field samples.

- To understand the defluorination mechanism involved in these reactions.
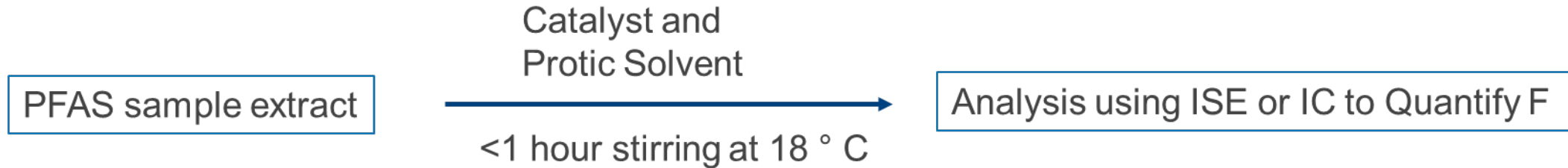
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Hypothesis

Different quantitative methods were tested to quantify the free fluoride formed:

- Ion selective electrode probe(ISE),
- Ion Chromatography,
- Quantitative ^{19}F Nuclear Magnetic Resonance (NMR), and
- Liquid Chromatography Tandem Mass Spectroscopy (LC-MS/MS) - PFAS

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Experimental

| PFAS sample extract | Catalyst and Protic Solvent ──────────> <1 hour stirring at 18 ° C | Analysis using ISE or IC to Quantify F |

- Defluorination Experiments were conducted on PFOA and PFOS
  - Conditions were optimized for the reaction times, catalyst concentration and protic solvents
  - The effect of primary (1°), secondary (2°), and tertiary (3°) protic solvents on the defluorination of PFOA was tested.

- Defluorination confirmation analysis and mechanistic studies were conducted using quantitative ^{19}F NMR and LC-Time of Flight (ToF)/MS

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Experimental – Quality Control

- No Fluoride detected in control experiments

    - Organofluoride control blank (No PFAS)

    - Catalyst Control (No catalyst)

- Fluoride Recovery - 95% recovery

- Quantitation of F^- in low ppb using ISE and IC

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Results - Effect of Protic Solvent on the Defluorination of PFOA

Reaction Time	Protic solvent	% Loss of Fluoride	No. F atoms
30 minutes	1° Protic Solvent	39.9 %	6
30 minutes	2° Protic Solvent	50 %	~8
45 minutes	3° Protic Solvent	39.9 %	6
45 minutes	Alternating Isopropyl alcohol & Methanol	70 %	11

- Addition of 2° protic solvent showed increased defluorination compared to both the 1° and 3° protic solvents
- Alternating addition of both the 1° and 2° protic solvent increased the defluorination to a maximum of 70%.
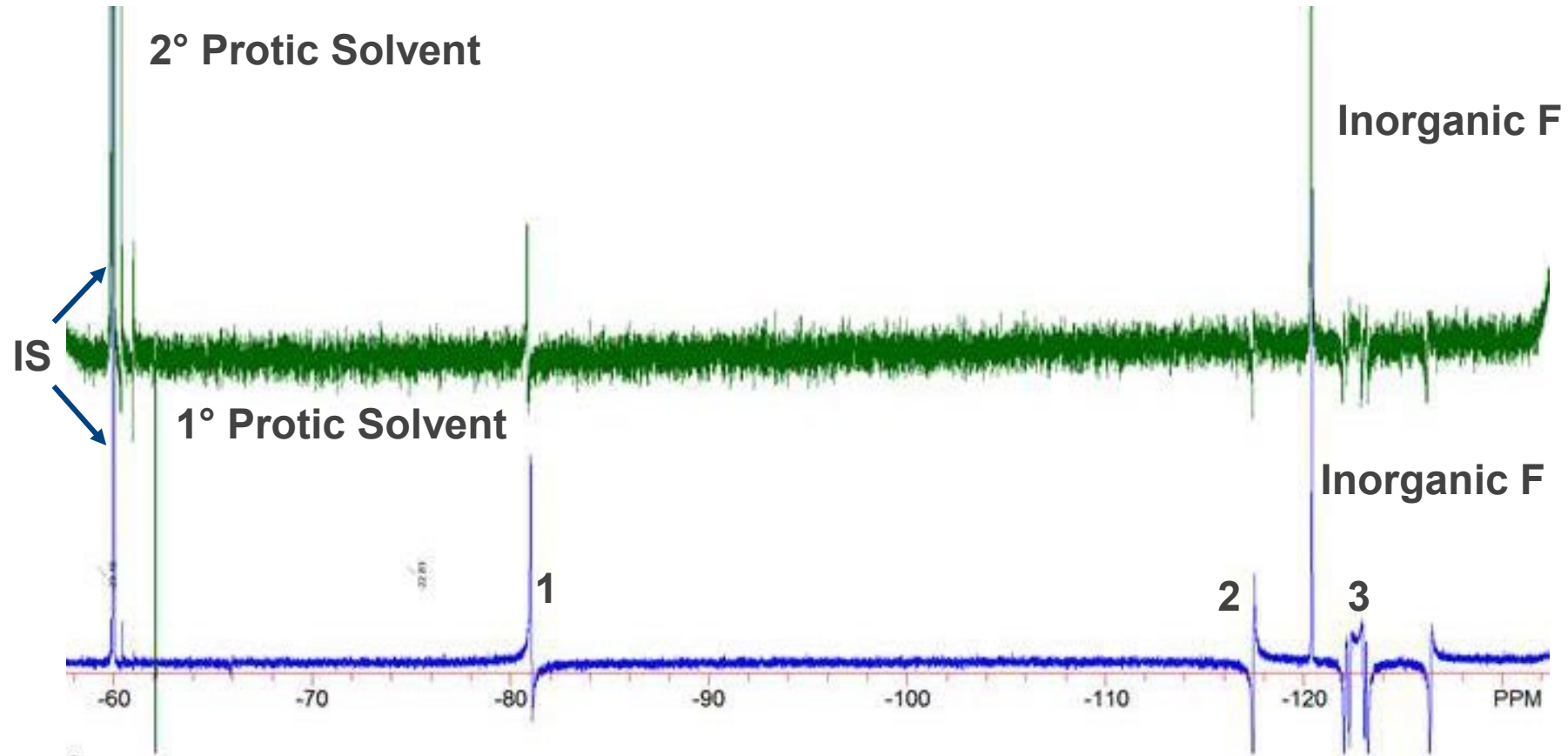
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Comparison of IC and ISE Results

Sample ID	IC Result (µg/mL)	ISE Result (µg/mL)	RPD
Sample 1A 4X	8.08	8.00	1.1%
Sample 1B 4X	8.87	9.00	1.4%
Sample 2A 4X	8.30	7.98	3.9%
Sample 3A 4X	7.79	8.39	7.4%

Calibration Range for F^- :
IC: 20 µg/L – 2500 µg/L
ISE: 250 µg/L - 10000 µg/L

Quantitative ¹⁹F NMR of PFOA

Unreacted PFOA – Peaks 1,2, 3(multiple) - at -80, -118, -121 (4 peaks), and -123 ppm

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LC-ToF/MS Analysis

- Non-targeted analysis confirms that 1° protic solvent and 2° protic solvent follows different mechanism

- Many longer chain fragments were observed in 1° protic solvent including PFHxA with a mass balance of 85% using ^{19}F NMR

- Shorter chain hydrogenated polyfluorinated fragments are formed in 2° protic solvent which explains the loss of these fragments as volatiles and hence poor mass balance

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Fluorine Mass Balance

Analytical Method	Description	2° protic solvent	1° protic solvent	Negative Control (No catalyst)
^{19}F NMR	Unreacted PFOA	5%	58%	90%
	F^- generated	45%	27%	0%
	Total F mass balance	50%	85%	90%
ISE probe	F^- generated	60%	40%	0%
LC-MS/MS	Unreacted PFOA	2%	33.5%	100%

- Formation of shorter chain fragments explains the loss of these fragments as volatiles and hence poor mass balance in reactions with 2° protic solvents
- The results obtained from ISE, quantitative ^{19}F NMR and the targeted analysis confirms the percent defluorination
- Similar percent defluorination was obtained using PFOS

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Conclusions

- Under the optimized conditions, both the PFOA and PFOS showed >70% defluorination which explains the mechanism of defluorination is consistent

- Separation of inorganic fluoride from the environmental samples before the defluorination reaction is under development

- Further studies:
  - The method performance will be tested using shorter chains and other PFAS precursors
  - Method comparison with other existing total PFAS methods
  - Method demonstration using PFAS contaminated field samples

- This novel total organofluoride method can be used as rapid screening tool to measure the free fluoride generated by the quick reductive defluorination of PFAS in the environmental samples.

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Thank You

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For more information visit our website: www.battelle.org/PFAS

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