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An Alternative Ionization Technique for LC-MS/MS Analysis of Perfluoroalkyl Substances (PFAS) in Environmental Samples

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NEMC 2020

Perfluoroalkylated Substances (PFAS)

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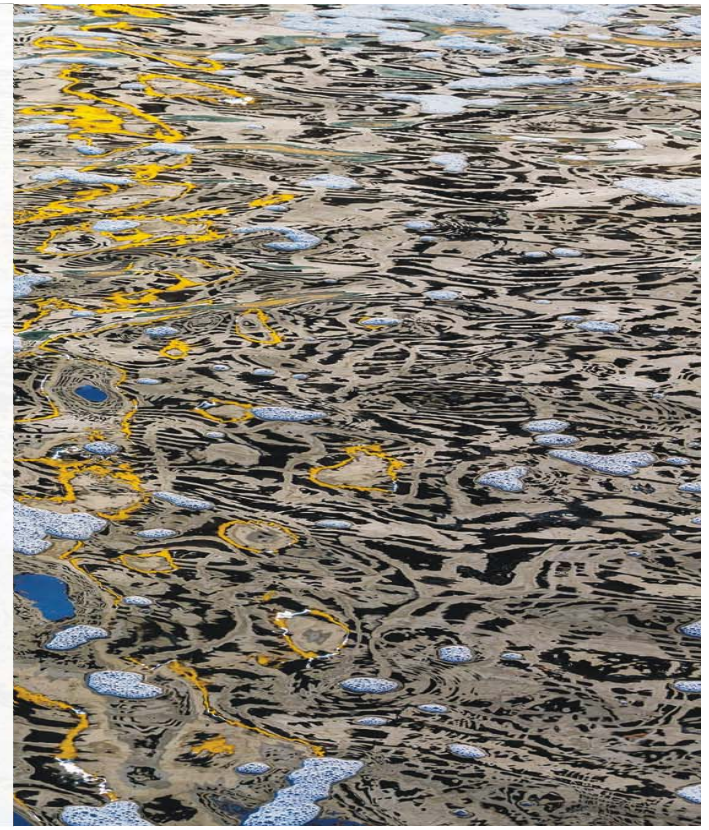
- PFAS = PFC = AFFF
- First **created** in the **1930s**
- **Widespread applications**
  - Non stick **coatings**, **surfactants**, food **packaging**, firefighting **foams**
  - **Polymerization aid** for polytetrafluoroethylene (PTFE) and other fluoropolymers – how PFOS and PFOA became famous
- **Stable** and **persistent** in the environment (POP)
  - Bio-accumulative
- **Identified** in environmental samples **worldwide**
  - Found in arctic **polar bears**
  - Most humans have a range of **PFAS in** their **blood**
- PFOA/PFOS have implied **health effects**



Wide variety of chemical properties

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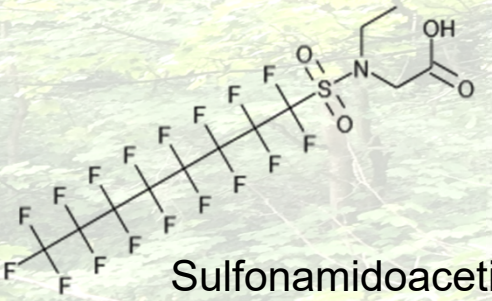
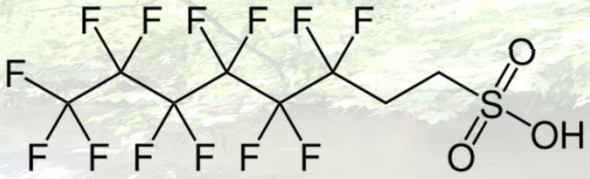
Perfluoro Carboxylic Acid
(PFOA)

Perfluoro Sulfonic Acid
(PFOS)

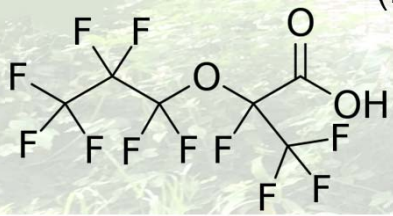


Sulfonamidoacetic
acid
(N-EtFOSAA)

Perfluoro Telomer Acid
(FHEA or 6:2 FTA)

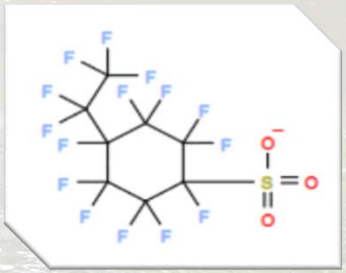


Perfluoro Telomer Sulfonate
(6:2 FTS)



Emerging PFAS
(GenX)

Cyclic
(PFecHS)



Alternative ionization modes

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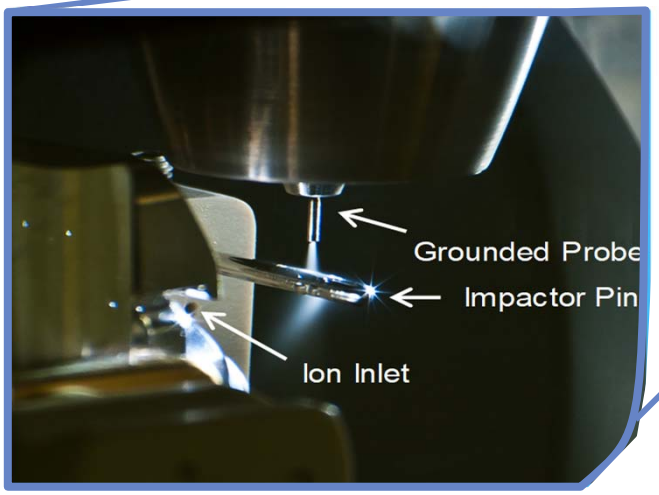
From ESI



To UniSpray

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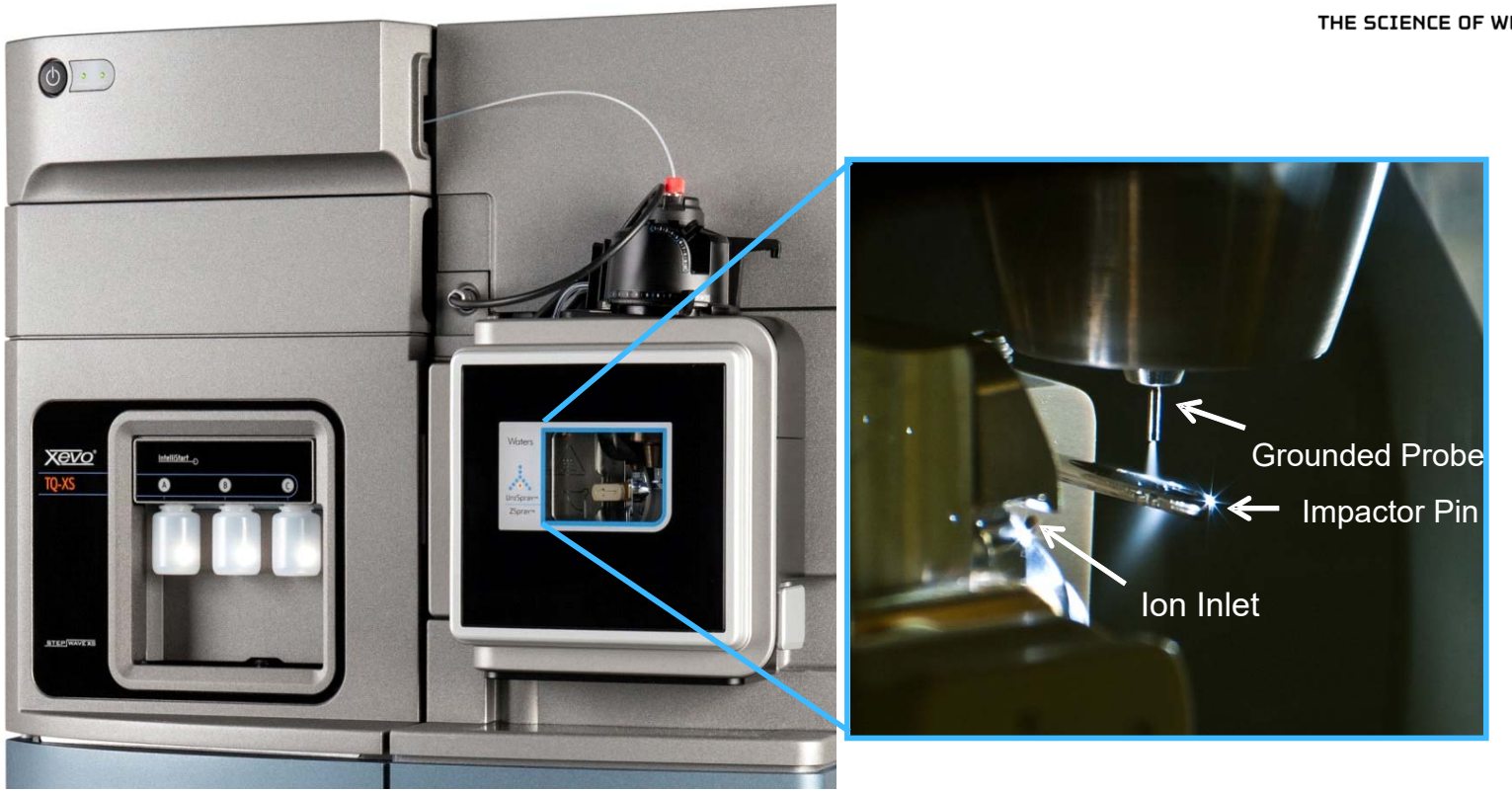
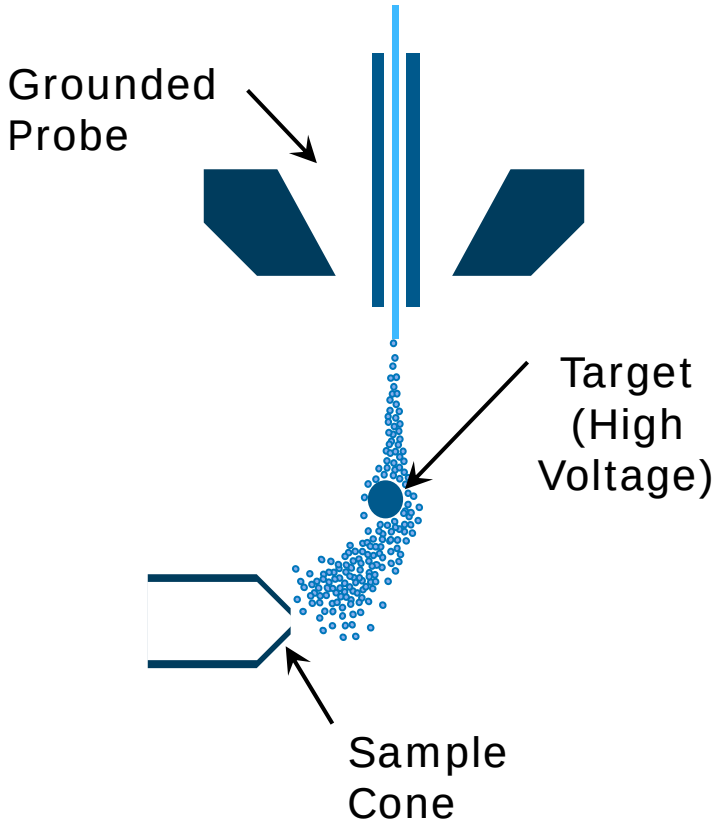
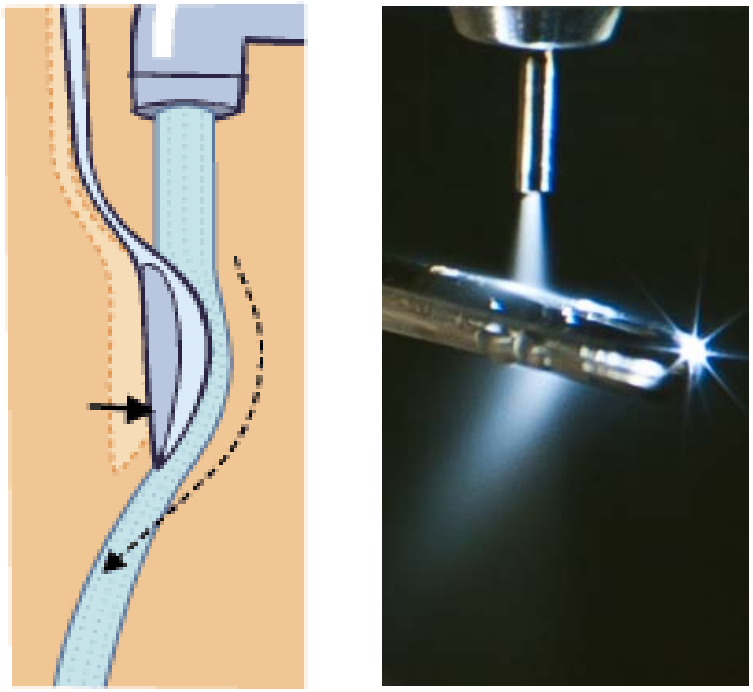


How Does UniSpray Work?





Coanda Effect

Initial UniSpray Performance Data

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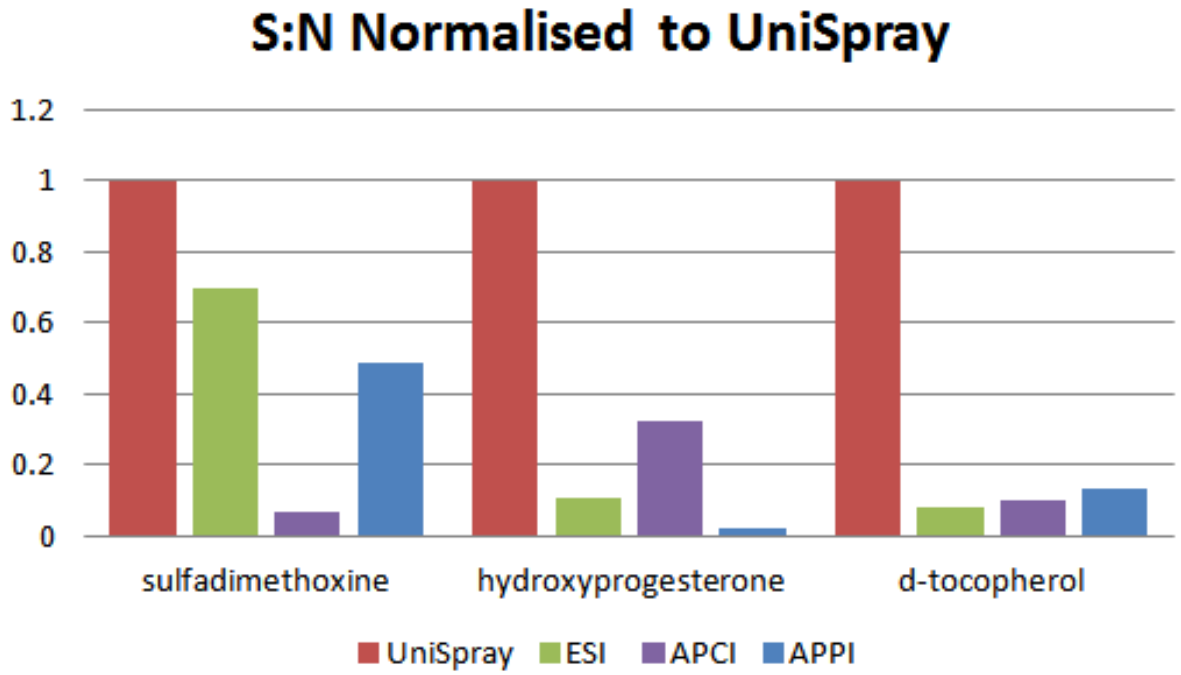

Method Used for ESI vs USI Comparison

Source Parameters

- Instrument: Xevo TQ-S micro
- Ion Mode: ESI-
  - Capillary Voltage: 0.5 kV
  - Desolvation Temperature: 350° C
  - Desolvation Flow: 900 L/hr
  - Cone Flow: 50 L/hr
- Ion Mode: USI-
  - Capillary Voltage: 1.0 kV
  - Desolvation Temperature: 400° C
  - Desolvation Flow: 900 L/hr
  - Cone Flow: 100 L/hr

MS Method

- Developed using QuanOptimize
  - Automated optimization of MRMs, CV, CE

LC Method

- Instrument: Acquity I Class with PFAS Kit
- Column: Acquity BEH C18 2.1mm x 100 mm, 1.7 µm
- Mobile Phase A: 95:5 H2O:MeOH + 2 mM ammonium acetate
- Mobile Phase B: MeOH + 2 mM ammonium acetate
- Injection Volume: 30 uL
- Gradient:

Time (min)	Flow (mL/min)	%A	%B
0	0.3	100	0
1	0.3	80	20
6	0.3	55	45
13	0.3	20	80
14	0.4	5	95
17	0.4	5	95
18	0.3	100	0
22	0.3	100	0


PFAS
Contamination

LC modifications for PFAS analysis

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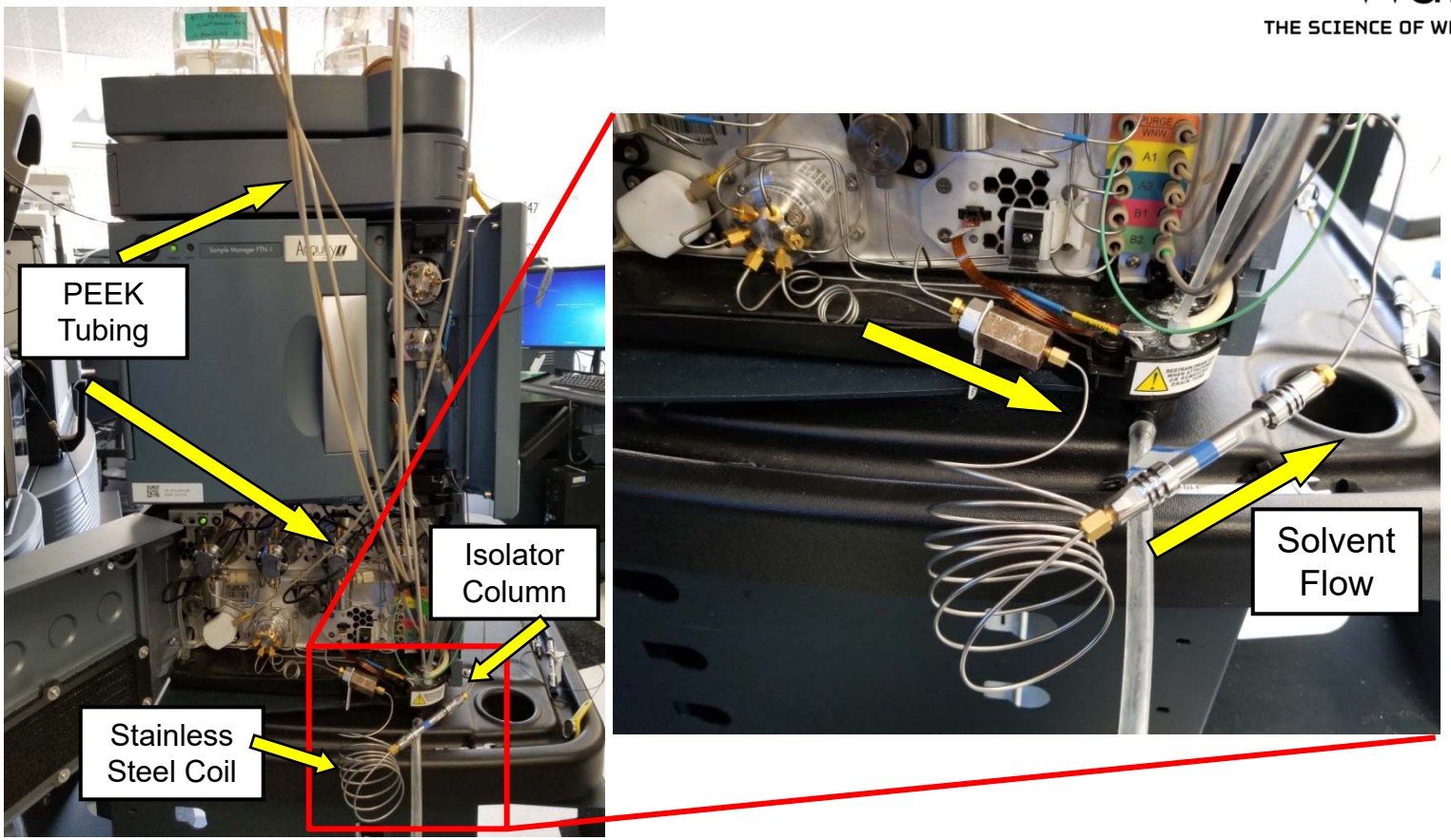

PFAS Compared ESI vs USI

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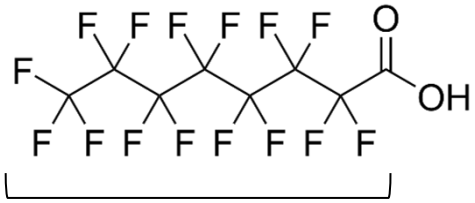
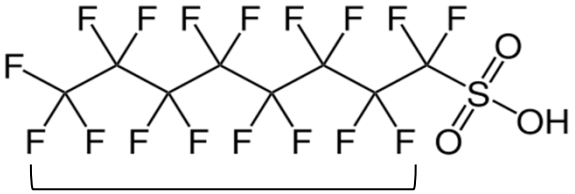
Carboxylates	Sulfonates
 C4 – C14	 C4 – C10
Emerging	**Precursors**
GenX ADONA 11Cl-PF3OUdS 9Cl-PF3ONS PFEESA PFMBA NFDHA	4:2/6:2/8:2 FTS FOSA NMeFOSAA/NEtFOSAA

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How Does UniSpray Work for PFAS?

Increase in Response and Signal:Noise

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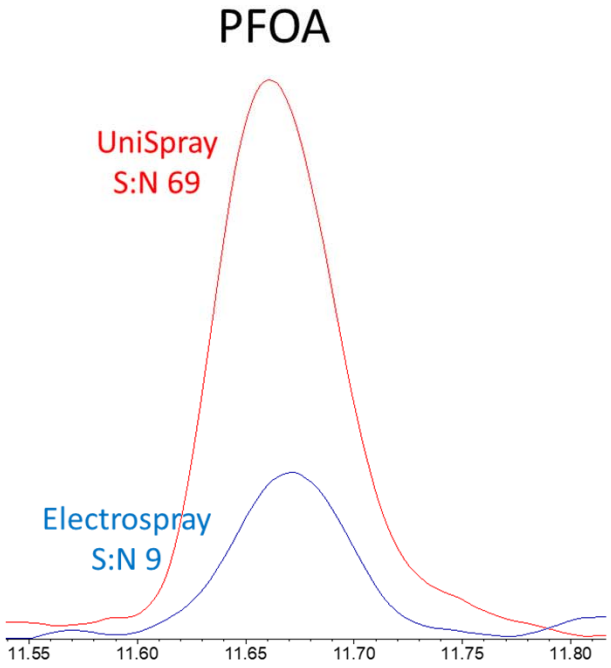

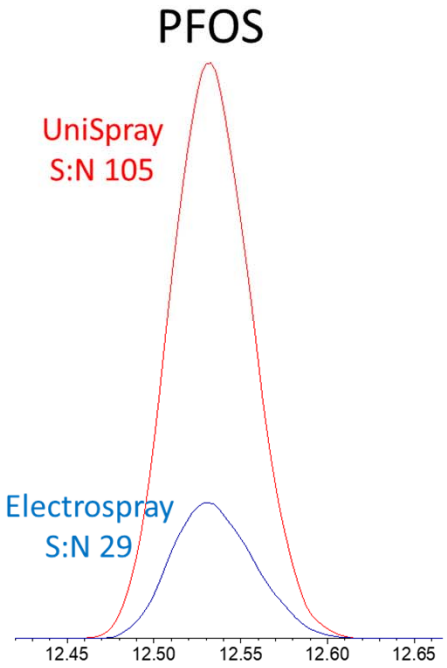

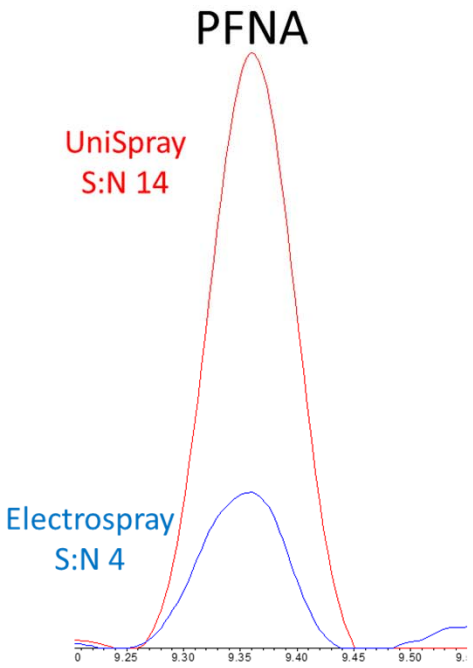

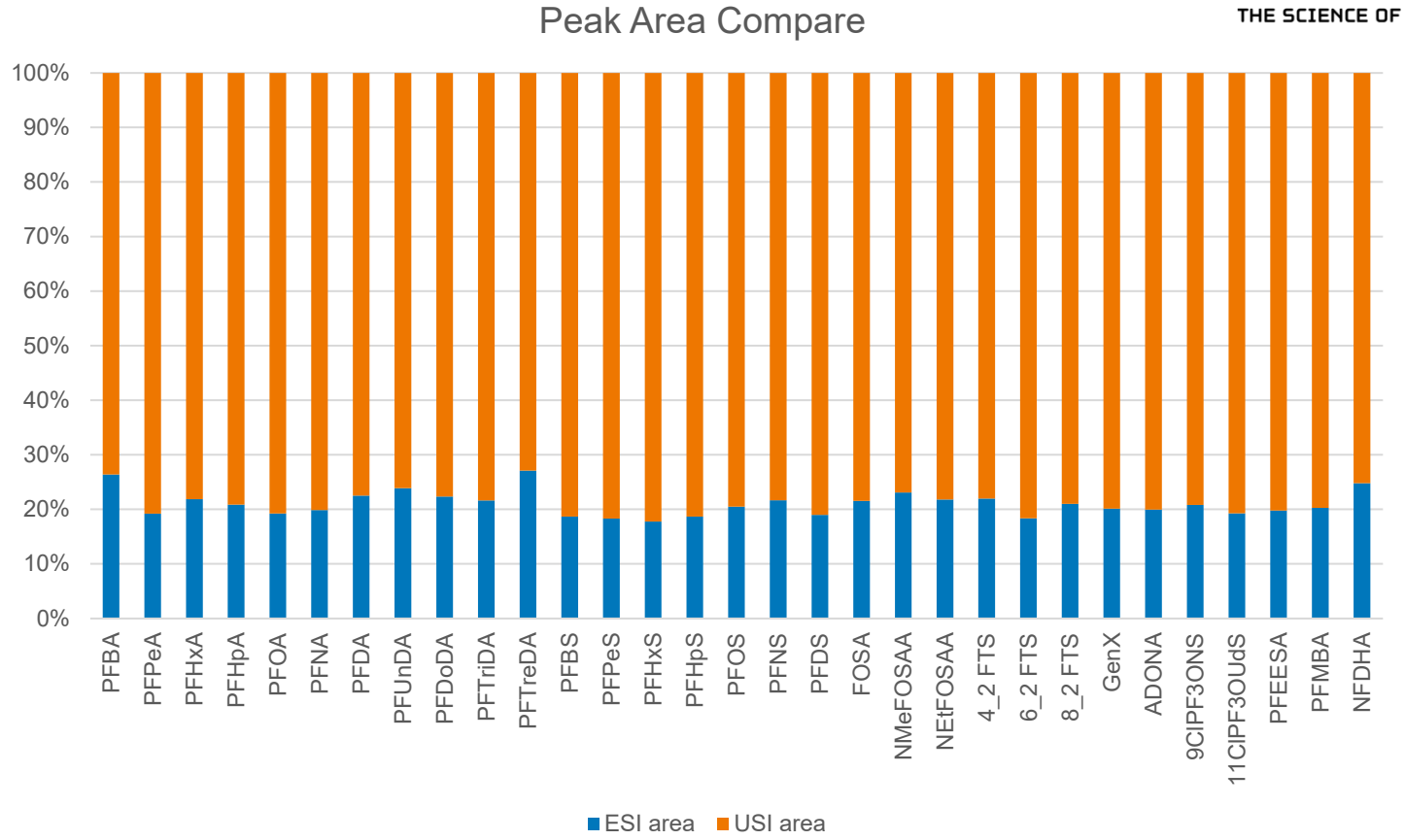

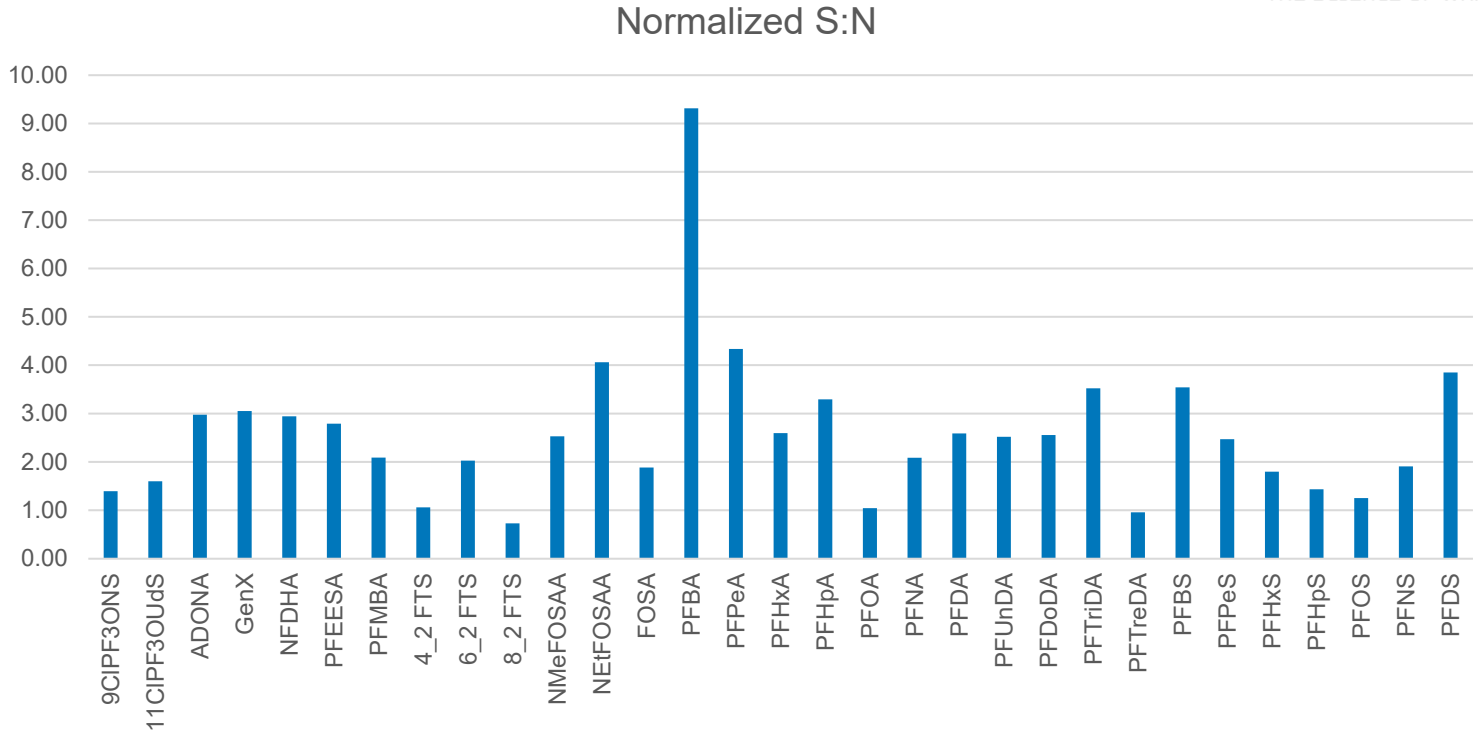

S:N of USI / S:N of ESI

GenX

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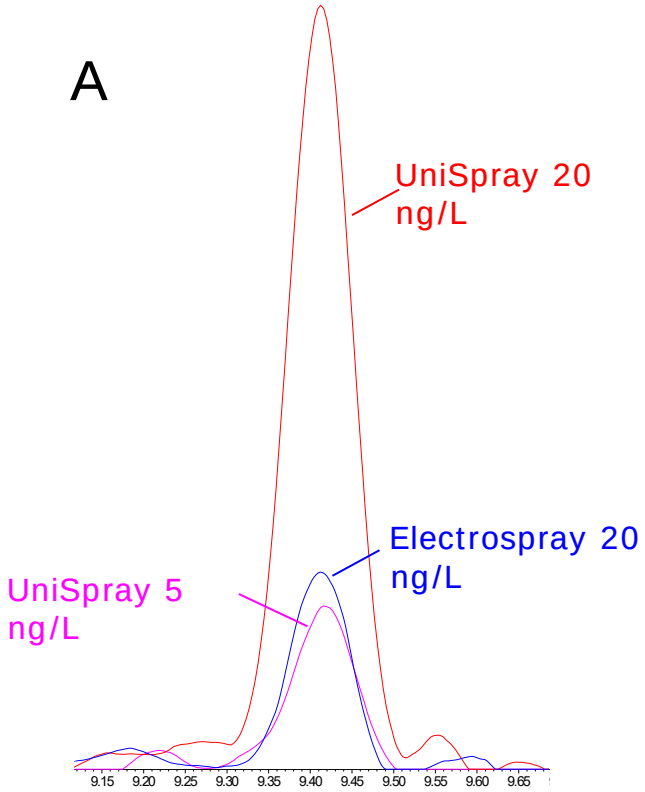
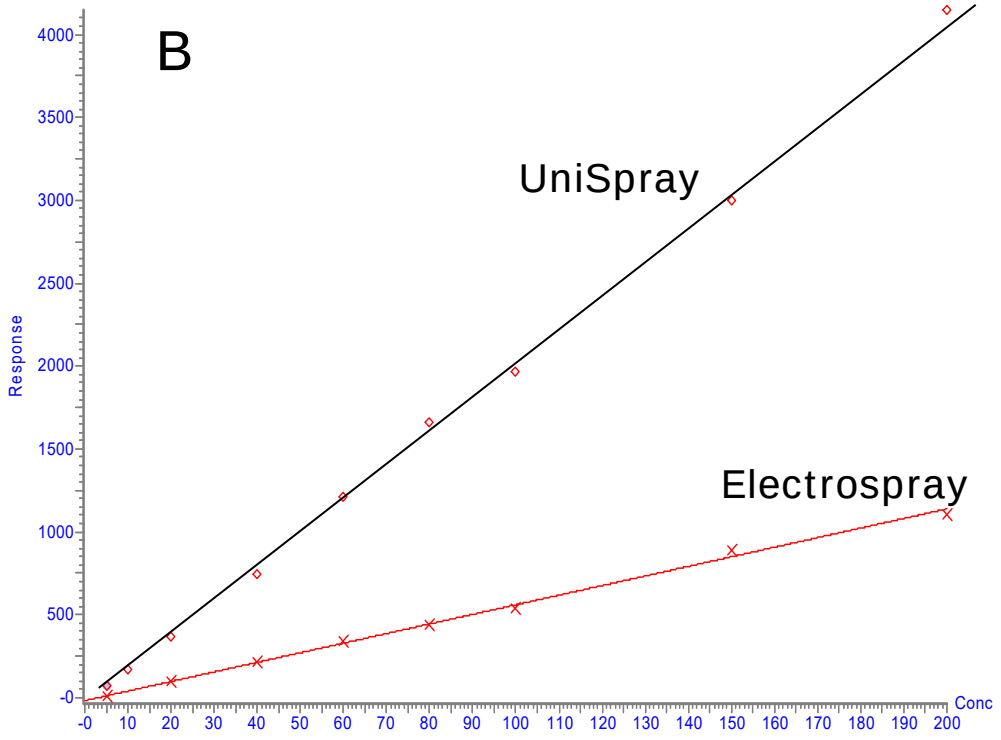
A



B



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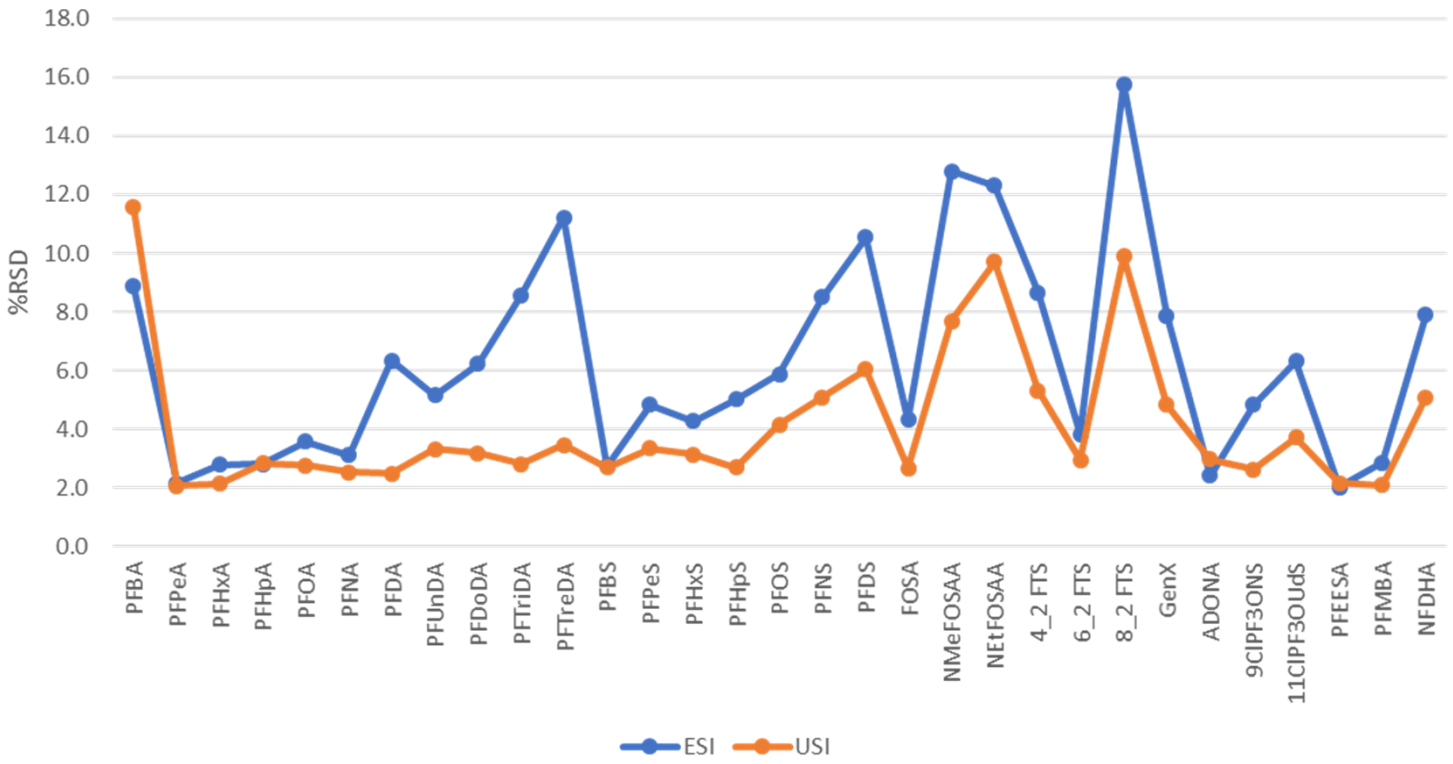
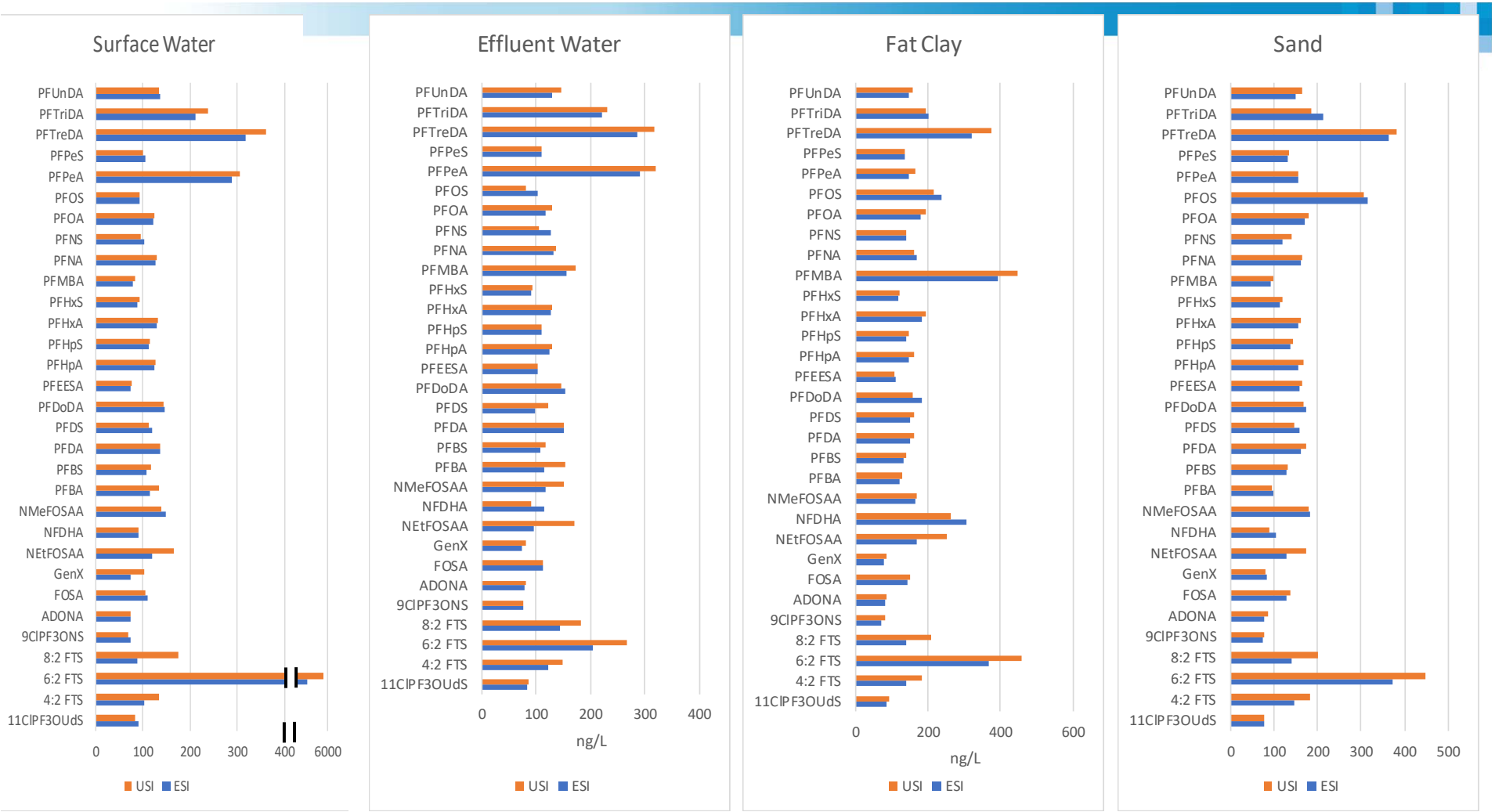
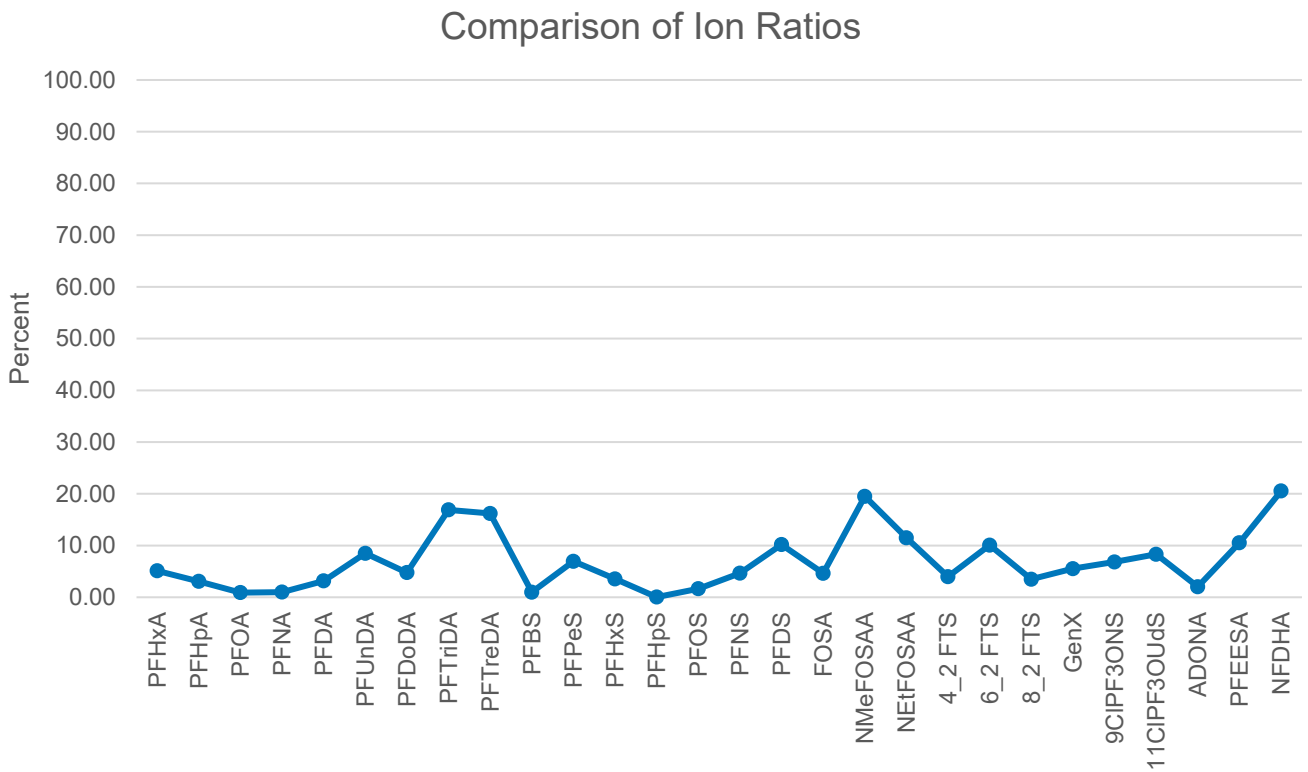
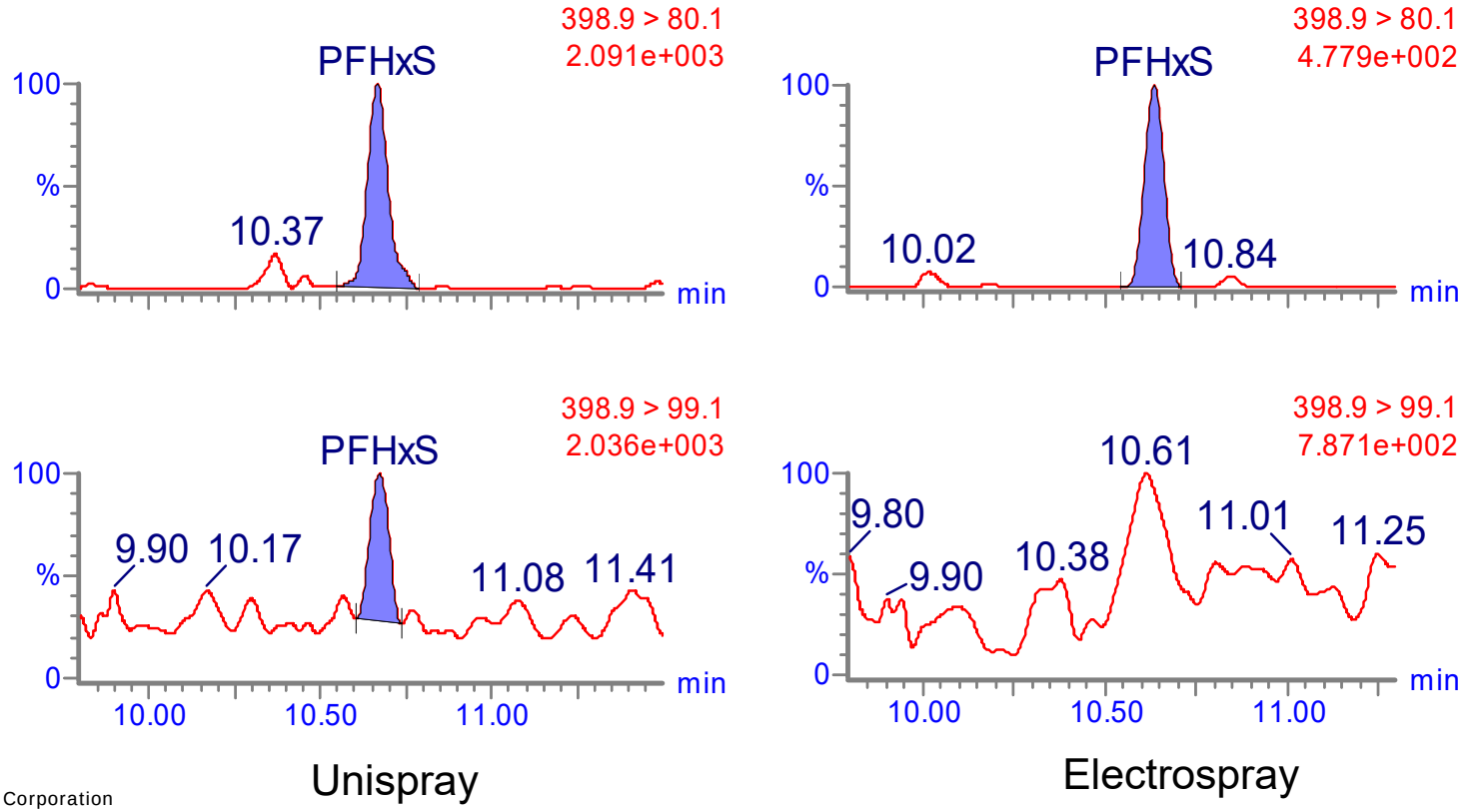




What about Ion Ratios?



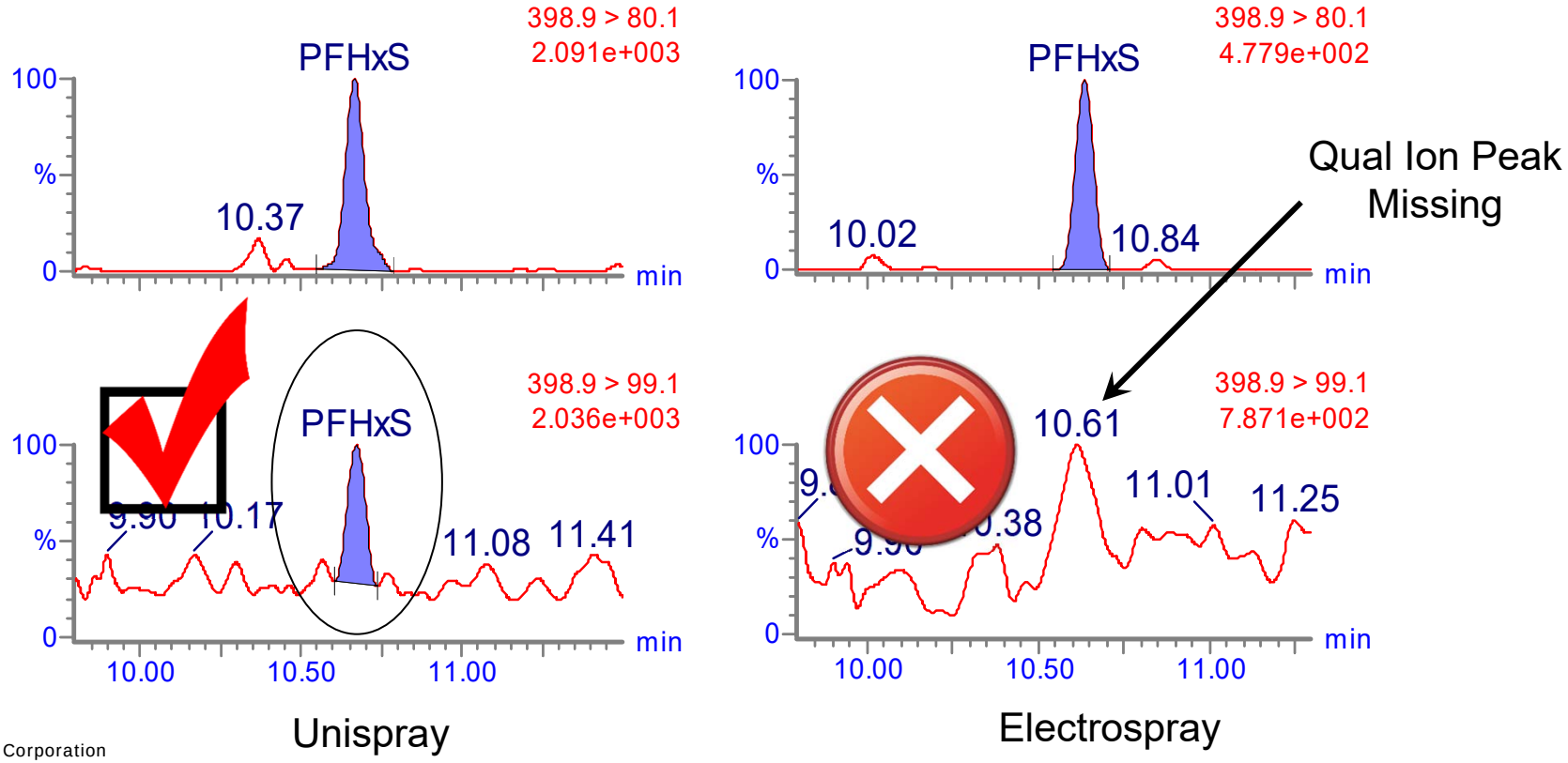
Low End Calibration Curve (5 ng/L)



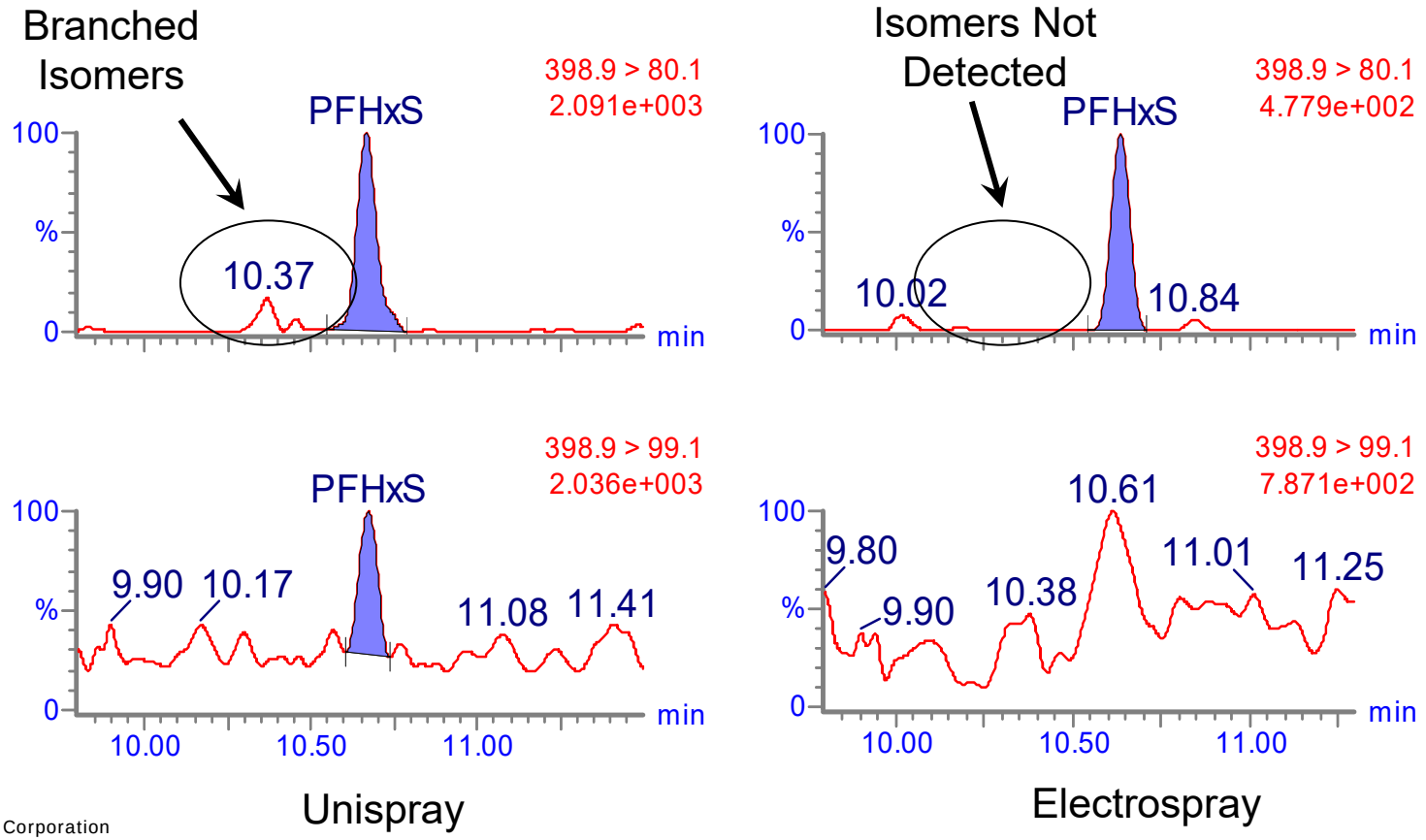
Unispray

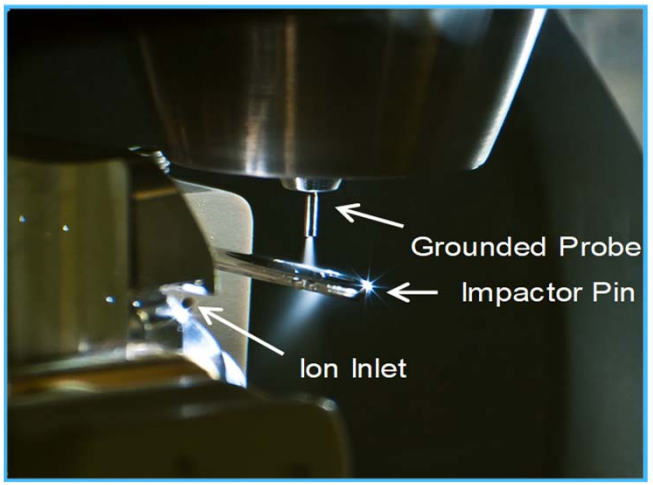
Electrospray

Low End Calibration Curve (5 ng/L)

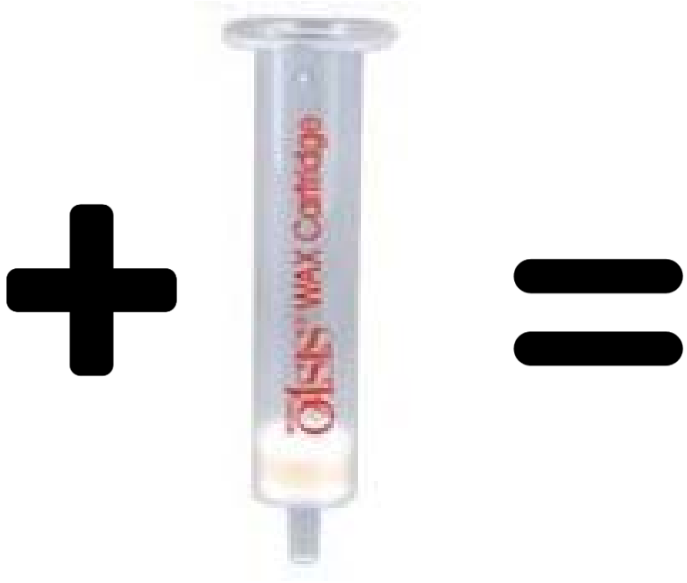


Low End Calibration Curve (5 ng/L)





2-5x increase in response



250x sample enrichment

How low could you go?

Complete PFAS Solutions

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2020 Proficiency Testing Scheme Schedule

ERA
www.eraqc.com

Acknowledgements

- Stuart Oehrle
- Doug Stevens
- Ken Rosnack
- Jenifer Lewis