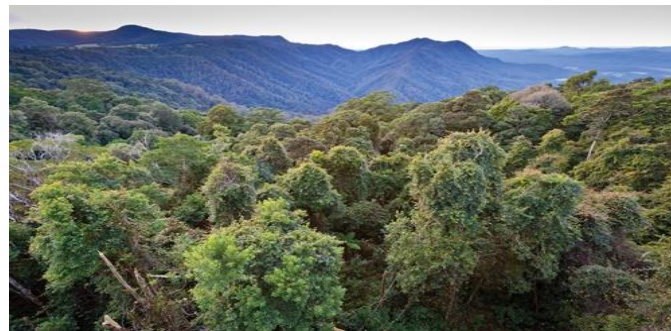




PFAS: Advanced Laboratory Analytical Discussion

We acknowledge the Traditional Owners of the country on which we meet today, and recognise their continuing connection to land, waters and culture. We pay our respects to their Elders past, present and emerging.



PFAS: ADVANCED LABORATORY ANALYTICAL DISCUSSION



Taryn McKnight,
PFAS Practice Leader
Eurofins Environment
Testing America

Complex & Pertinent Matrices

**Landfill Leachate
Biosolids
Ambient and Source Air**

Complex Matrices: Landfill Leachate

1

- Wide range of concentrations, matrix mitigation critical

2

- Short chain dominant: PFBA/PFBS/5:3 FTCA

3

- Can represent <1% of mass flow
- Can be minor source to aqueous environment



Polyfluoroalkyl compounds in landfill leachates Jan Buschab, et al

National Estimate of Per- and Polyfluoroalkyl Substance (PFAS) Release to U.S. Municipal Landfill Leachate Lang JR, et al

Complex Matrices: Wastewater, Biosolids

1

- WWTP conventional treatment not effective for PFAS

2

- Land applied Biosolids are a potential source of PFAS in the environment

3

- Biphasic samples require special processing



Polyfluoroalkyl compounds in landfill leachates Jan Buschab, et al
National Estimate of Per- and Polyfluoroalkyl Substance (PFAS) Release to U.S. Municipal Landfill Leachate Lang JR, et al

Complex Matrices: Source Air Emissions



- Hazardous Waste Incinerators



- Sewage Sludge Incinerators



- Thermal Oxidizers



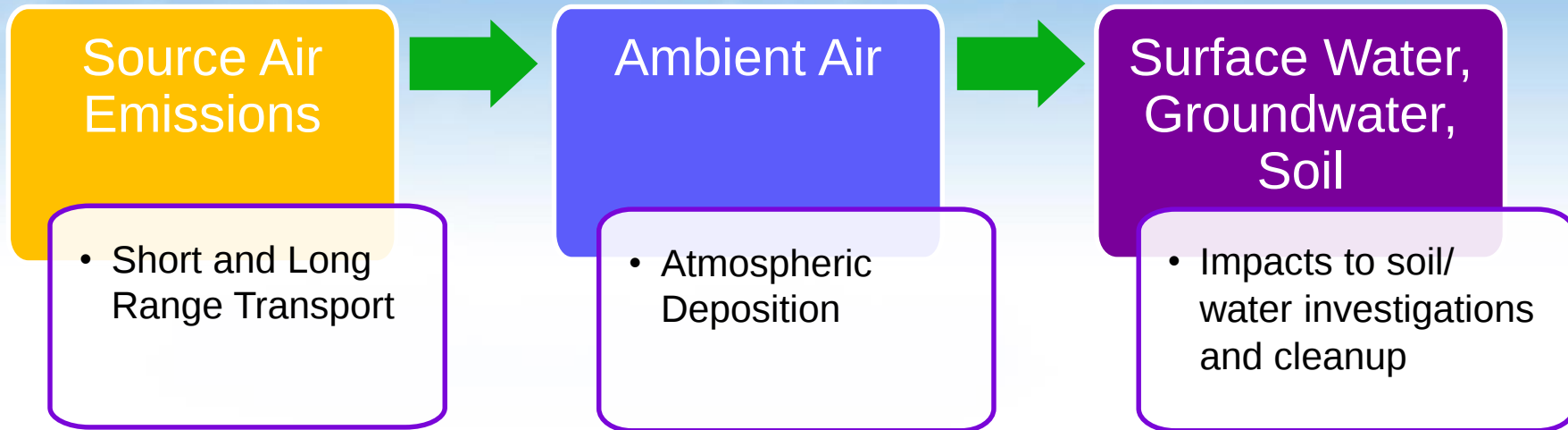
- Thermal Desorbers “Dirt Burners”



- Chemical Plants and Process Vents



Why is this a problem?



2020 National Defense Authorization Act



IN

DoD prohibited from using PFAS AFFF after October 2024

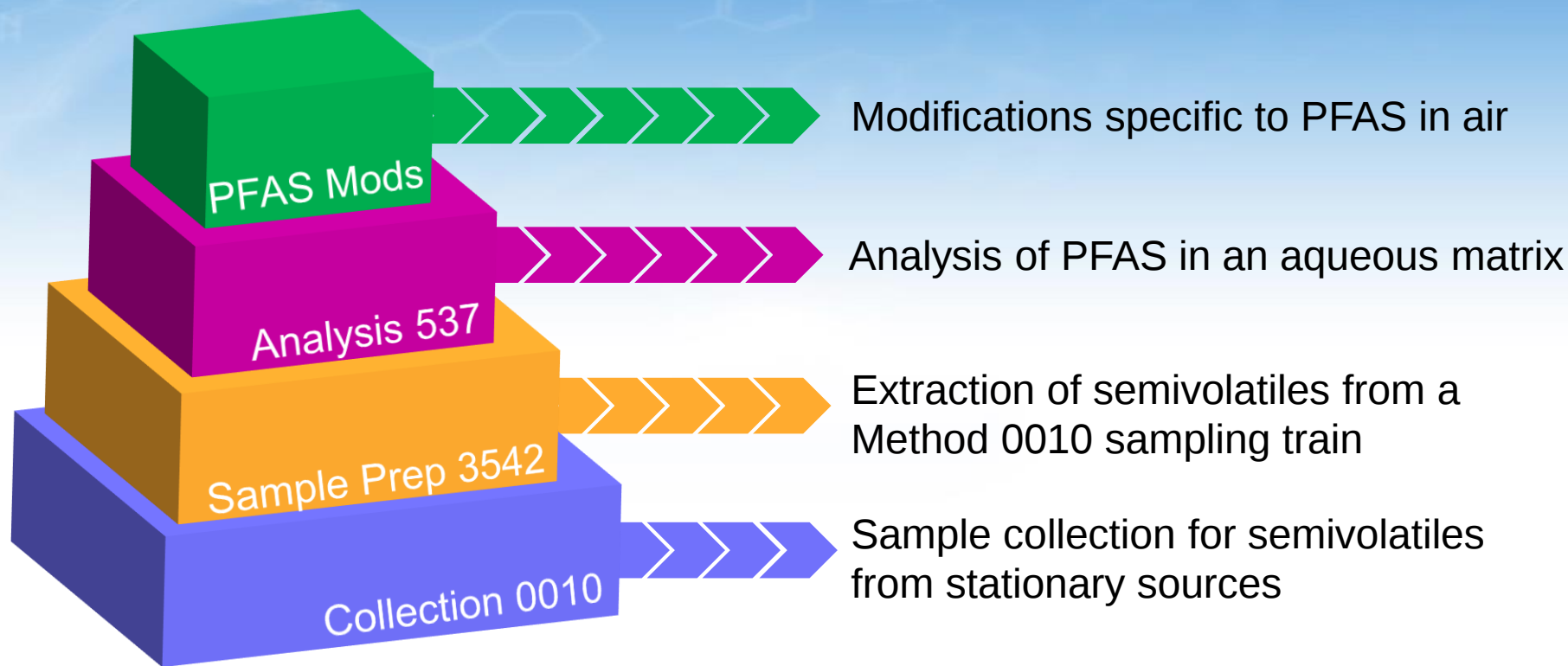
DoD is required to “work expeditiously” to test, monitor, remove, and remediate PFAS in DW, SW or GW upon request of state Governor

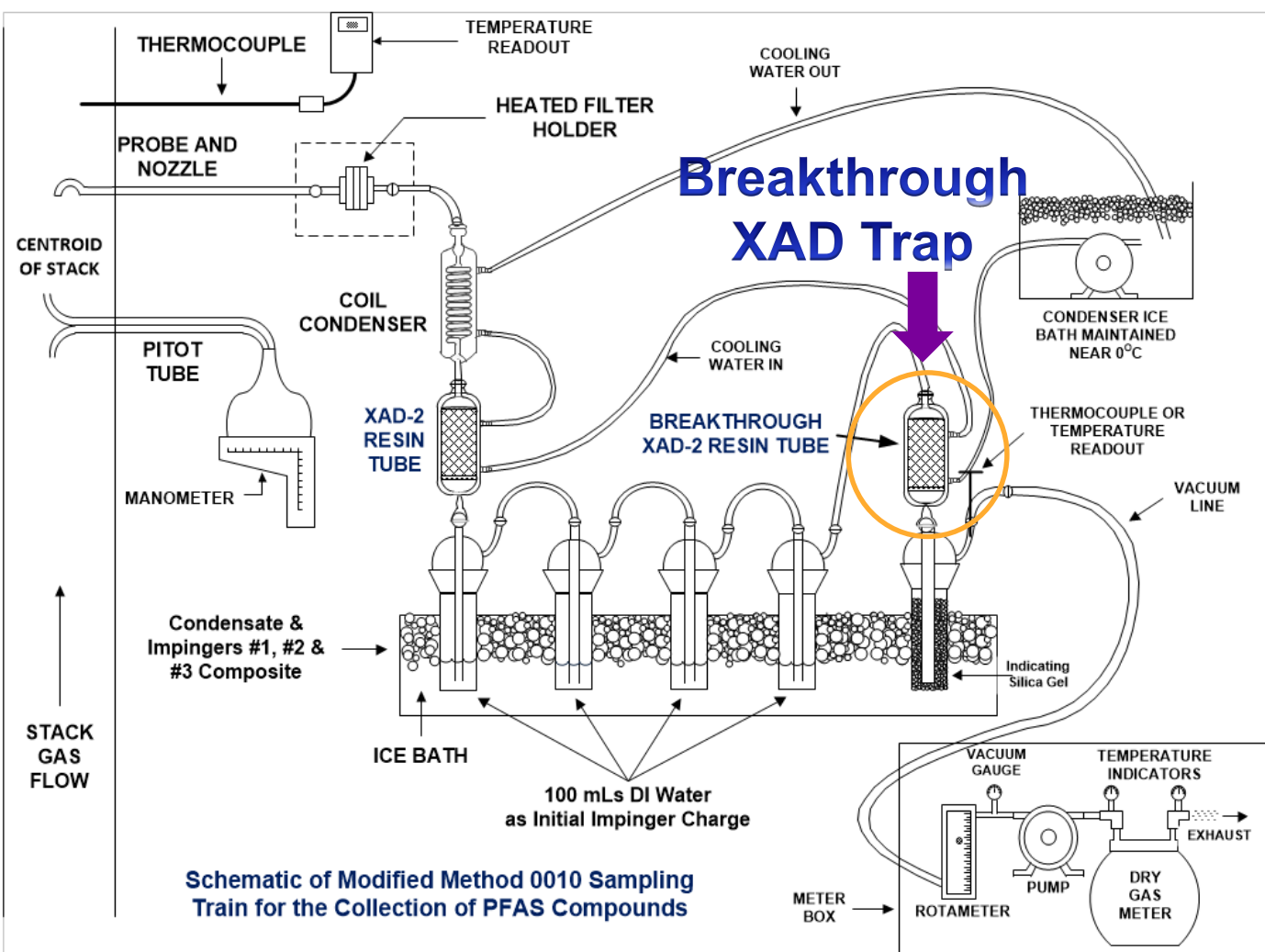
All incineration must be conducted in accordance with the Clean Air Act and at a permitted facility

Requires EPA to take final action on 2015 proposal to amend the SNUR for long-chain PFAS under TSCA

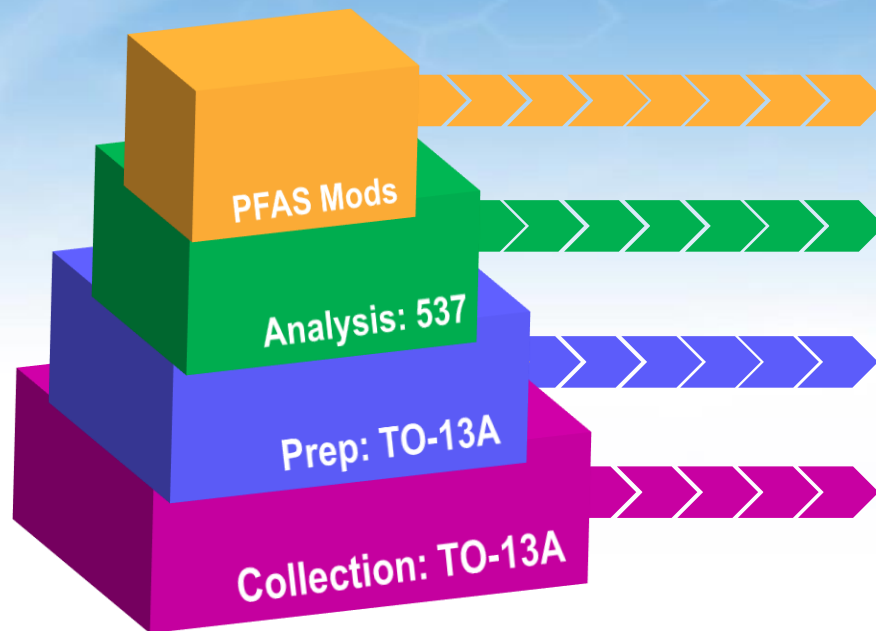
DoD required to seek agreements with municipalities or DW utilities located near military installations to share monitoring data...

EPA Standard Methods – Building Blocks





PFAS in Ambient Air



EPA Standard Methods Building Blocks

LC/MS/MS Isotope Dilution
Extended range of analytes
(36 PFAS) at ~ 2 pg/m³

Successful development of
modified preparation procedures

High-vol collection
with PUF/XAD

EMERGING TECHNOLOGIES

**Total Organofluorine
Non-target Analysis**

TOP Assay

PFAA Precursors



85°C

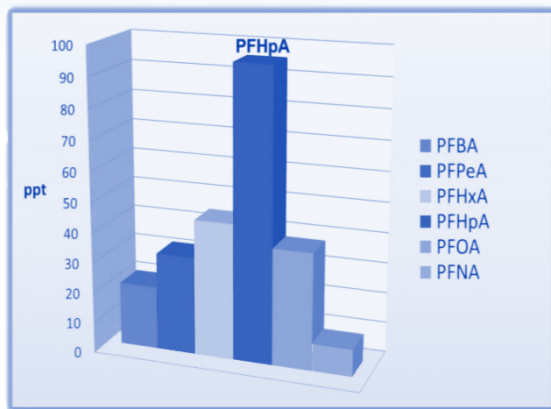
OH•

OH•

OH•



PFOA + other
PFCAs

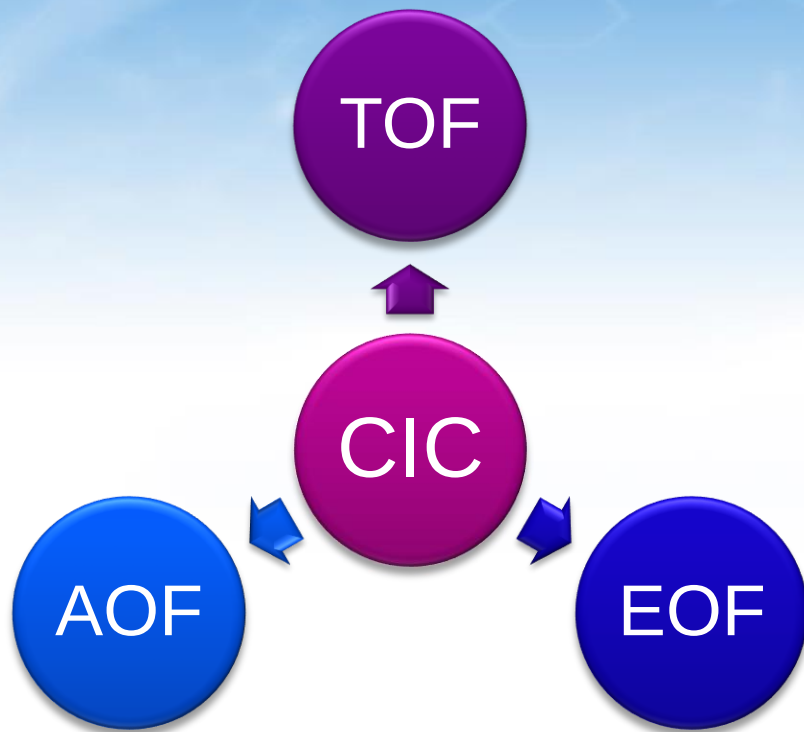


TOP Conversion of 8:2 FTS



- Worked with Houtz to offer TOP Assay in 2016
- Mapped conversion of multiple individual precursors
- Applied to wide range of matrices
- Challenges with use and data interpretation

Total Organofluorine Analysis



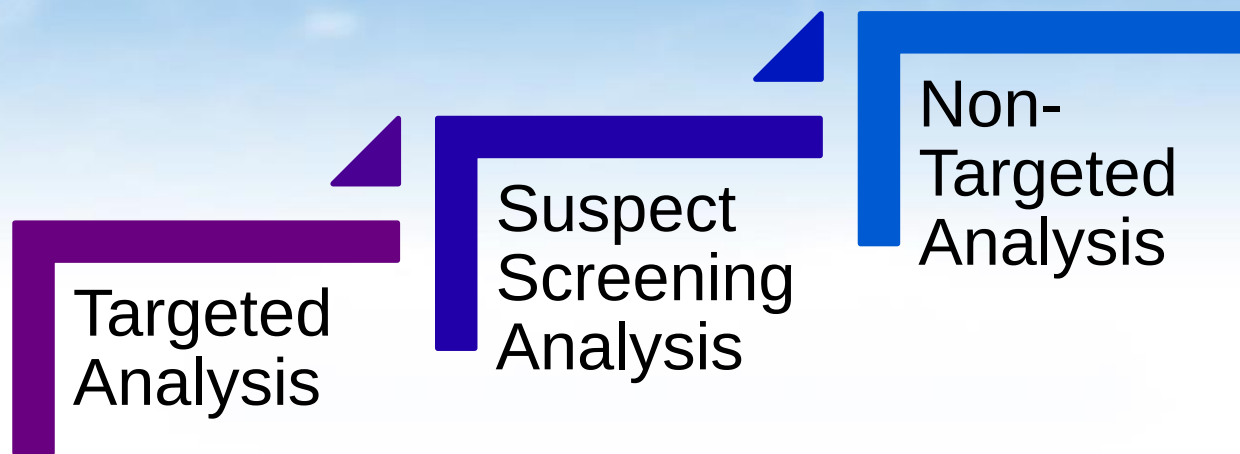
CASE STUDY

Total Organic Fluorine (TOF)	410 mg F/kg
Extractable Organic Fluorine (EOF)	390 mg F/kg
LC-MS/MS ΣPFAS (n=28)	120 mg/kg



CIC: Combustion Ion Chromatography

Non-Target Analysis



Quadrupole
Time of Flight (QToF)

METHODS UPDATE

**Short Chain Compounds
Methods In-progress
Defensible Analytical Techniques**

EPA Method 533

“A Method for Short Chain PFAS”



533	537.1
Drinking Water	Drinking Water
Branched/Linear Isomers -YES	Branched/Linear Isomers -YES
14 of the same and 11 unique compounds	14 of the same and 4 unique compounds
SPE WAX	SPE SDVB
Hold Time: 28/28 days	Hold Time: 14/28 days
LCMSMS with confirmation ion	LCMSMS - no confirmation ion
Isotope Dilution	Internal standard
Recovery Correction - YES	Recovery Correction – NO
RLs: Not defined	RLs: 2ppt - 40ppt

Tissue, Soil, Groundwater, Air?



What methods do we follow for non-potable water, solids and air?

DW

537.1

18 Analytes
Internal Standard

DW

533

25 Analytes
Isotope Dilution

**NPW &
Solids**

User-defined

24-40 Analytes
Isotope Dilution

**Current
Methods**

**Future
Methods**

**NPW &
Solids**

Draft 8327

24 Analytes
External Standard

**NPW &
Solids**

1600 series

40 Analytes
Isotope Dilution

Air

Source Air = OTM45
Ambient Air = ??
Analytes??

**“PFAS by LCMSMS Compliant
with Table B-15 QSM 5.1 or
latest version”**



Key Elements in Reducing Variability

Preparation

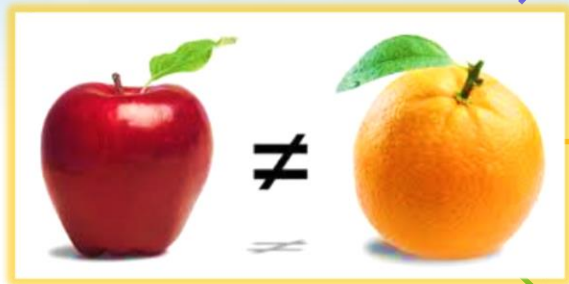
- Cleanups
- Rigorous Extraction
- Use of IDAs prior to prep

Quantitation

- Isotope Dilution
- Branched and Linear
- Secondary Ion Transitions

Experience

- Years of LCMSMS experience
- Redundancy and control measures applied
- Complex matrix approach



537.1 vs DRAFT 8327 vs 537M

PFAS Method Comparison Table for Aqueous Matrix

	Features	Method 537.1	EPA DRAFT 8327	User Defined "537 Modified" ¹
	Matrices	Drinking Water	Non-potable aqueous	All aqueous matrices
	Sample size	250 mL	Any allowed (5mL used)	250 mL
1	Analysis	LCMSMS	LCMSMS	LCMSMS
2	Aqueous Extraction	SPE SDVB	DAI	SPE Waters WAX
3	Branched/Linear Isomers	Yes, for available standards	Yes, for available standards	Yes, for available standards
4	Confirmation Ion	No	Yes	Yes
5	Quantitation	Internal standard	External standard	Isotope dilution
	Reporting Limits	(2 ppt - 40 ppt)	(10ppt - 8000ppt)	(2ppt - 20ppt)
	Recovery Correction	No	No	Yes

¹ – Compliant with DoD QSM Table B-15

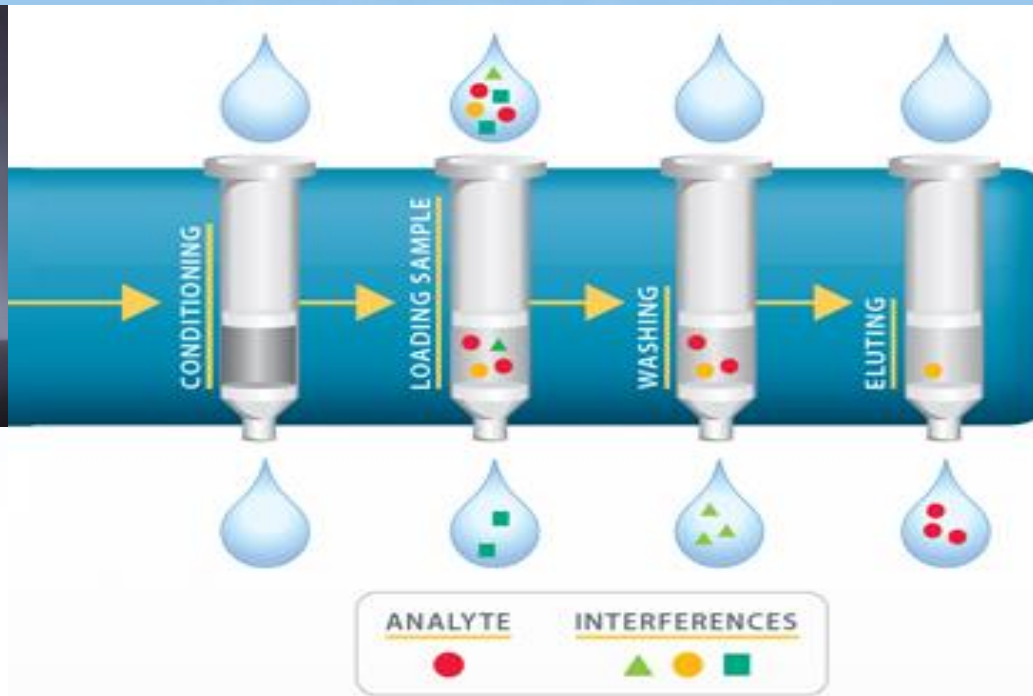

$$\frac{2}{1,000,000,000,000}$$

LC/MS/MS – Liquid Chromatography

Solid Phase Extraction (SPE)



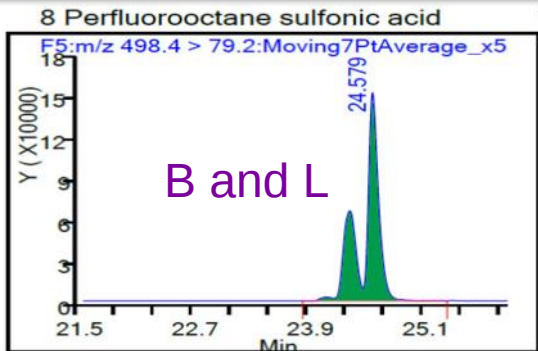
SEPARATION CHEMISTRY



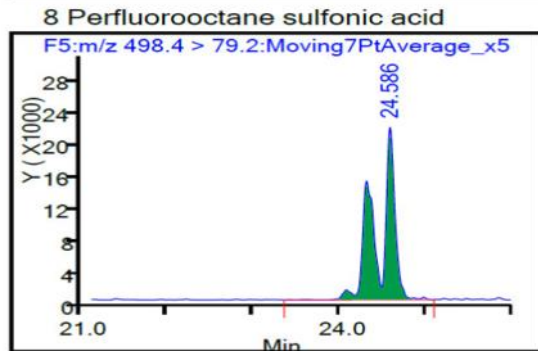
Branched and Linear Isomers

STANDARD

PFOS

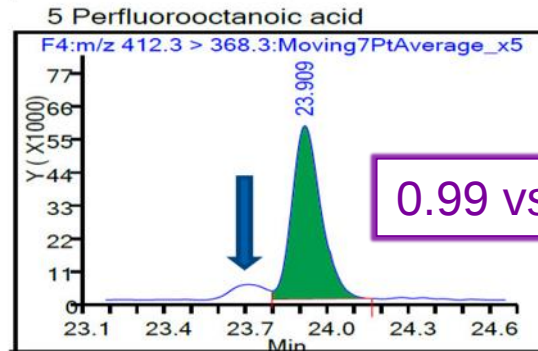
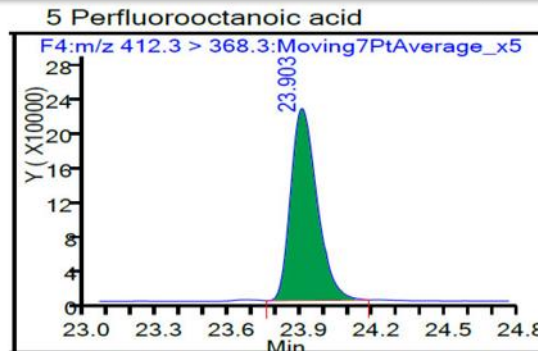


B and L



SAMPLE

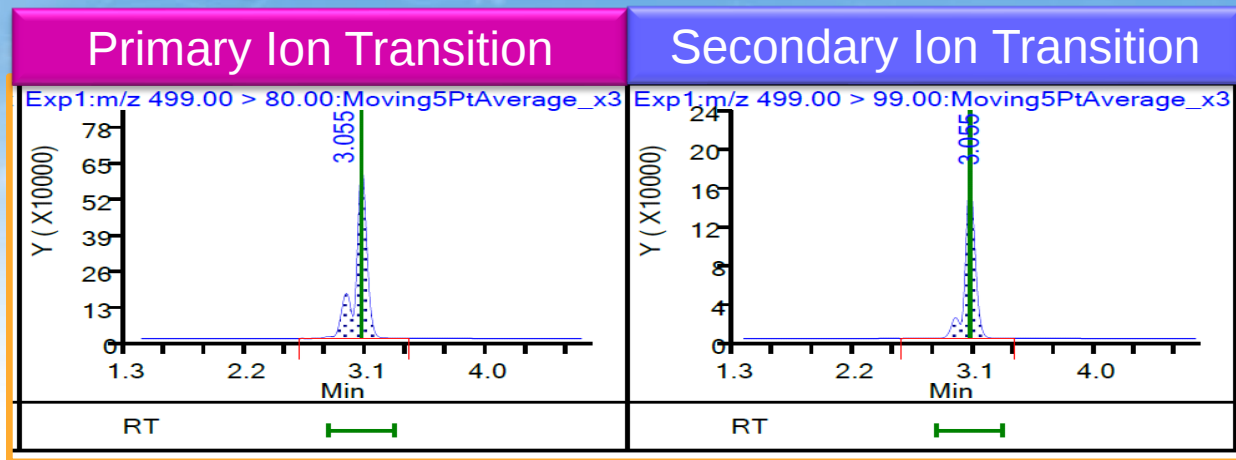
PFOA



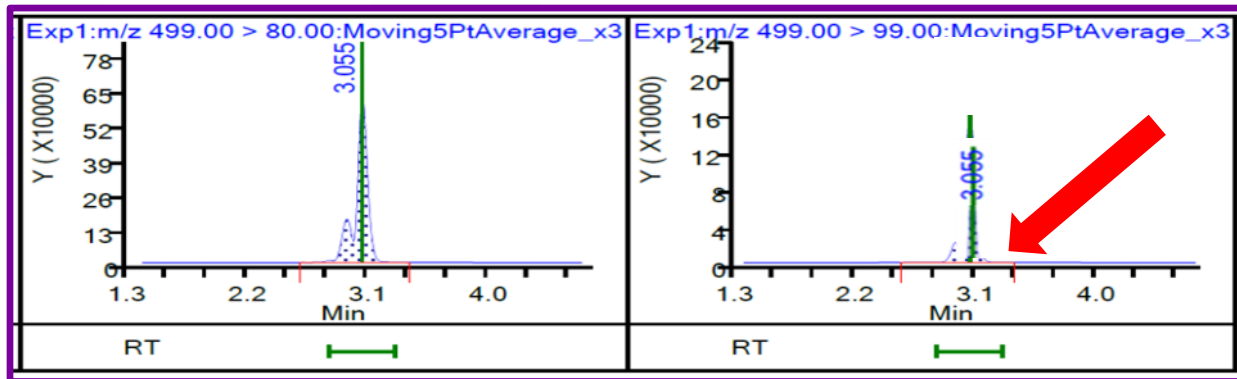
0.99 vs 1.20 ng/ml

Secondary Ion Transition - PFOS

STANDARD



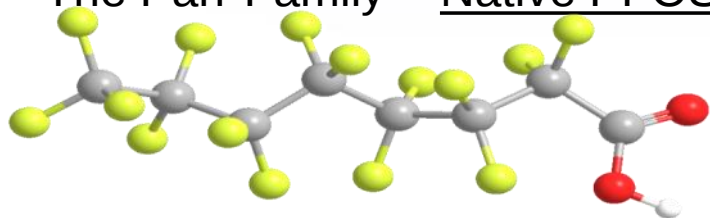
SAMPLE



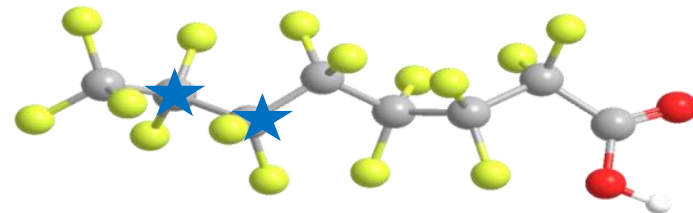
Isotope Dilution – Labeled Analogues



The Parr Family = Native PFOS



The Incredible Family = Labeled PFOS



★ = ^{13}C 27

Benefits of Isotope Dilution

What affects the native analyte will equally affect the isotope

Calibration

Most accurate and precise method

Target analytes are quantitated against structurally similar materials, the isotopes themselves

Matrix Mitigation

Expands ability to process a broader range of matrices

Compound Identification

Reduces the potential for false positives

Reduces the potential for error; corrects for retention time shifts

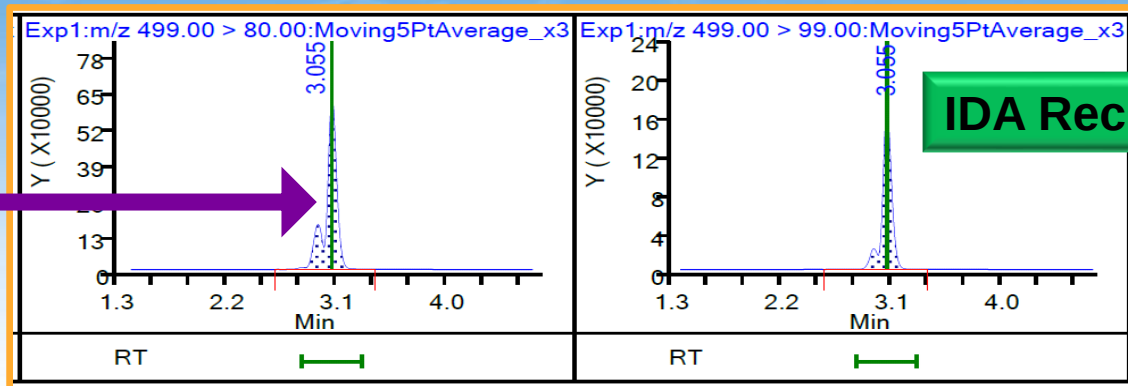
Isotope Dilution vs Internal Standard

PFOA	Spike amount	Isotope Dilution Result	% recovery (ID)	Recovery Corrected Result	Internal Standard Result	% recovery (IS)
Field Sample		10		11	9	
Matrix Spike	34	40	88%		40	91%
Spike Duplicate	34	42	94%		42	97%

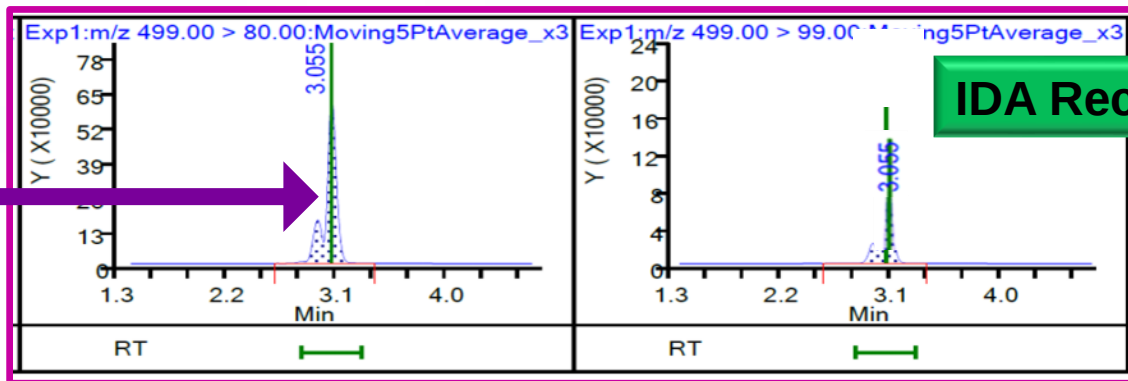
MeFOSAA	Spike amount	Isotope Dilution Result	% recovery (ID)	Recovery Corrected Result	Internal Standard Result	% recovery (IS)
Field Sample		40		80	40	
Matrix Spike	40	20	50%		20	50%
Spike Duplicate	40	20	50%		20	50%

IDA response must be $> 10:1$ S/N

Native = 100 ppt



Native = 100 ppt



How Eurofins Can Assist



Expertise

- >10 Years of PFAS **Experience**
- Unparalleled **Performance** in NMI Proficiency Testing since 2015

Capacity

- **Major** LC-MS/MS plus GC & LC-QToF-MS **Capacity**
- Industry leading capacity for **Fast TAT**

Innovation

- Extensive Analyte **Lists** and **Matrices** including air, biota & serum
- **Gold Standard** Analytical Techniques including “PFAS Fingerprinting”

Ease of Use

- Consistent and **Defensible** Data – **Results** you can **Trust**
- **Nationwide** Coverage
- **Global** Leaders

THE
INDUSTRY
LEADER



eurofins

Environment Testing





Contact:

Dr Bob Symons– Regional Technical Manager
Eurofins Environment Testing Australia & New Zealand
BobSymons@eurofins.com

Test inquiries to: EnviroSales@Eurofins.com

[Click here to register for future EnviroTalks](#)

What's next?

SARS-CoV-2 in Wastewater

Unknown Unknowns (QToF)

Mobile Asbestos Testing

Microplastics

Air Toxics