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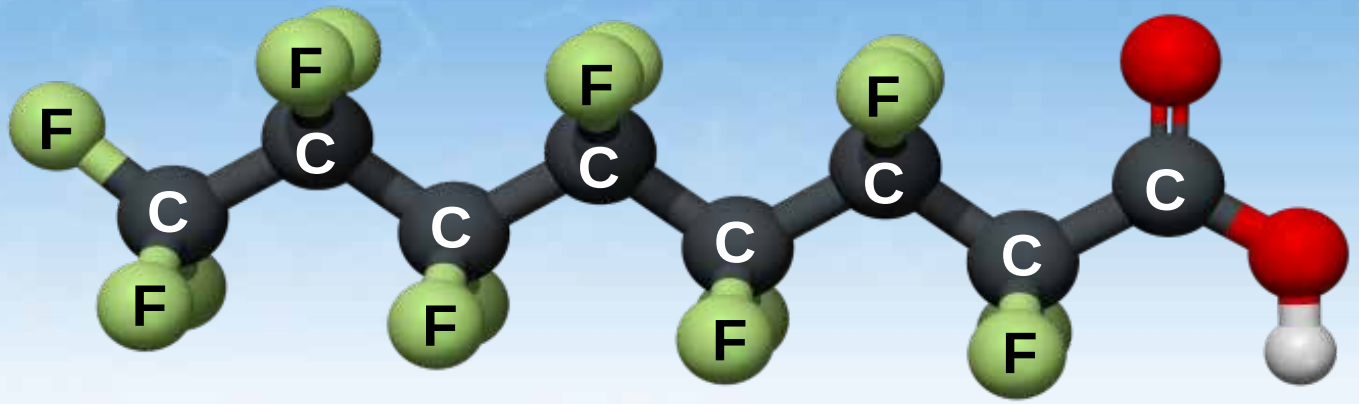
EPA, ASTM, ISO and Modified Methods, Oh My! Navigating Analytical Options for PFAS

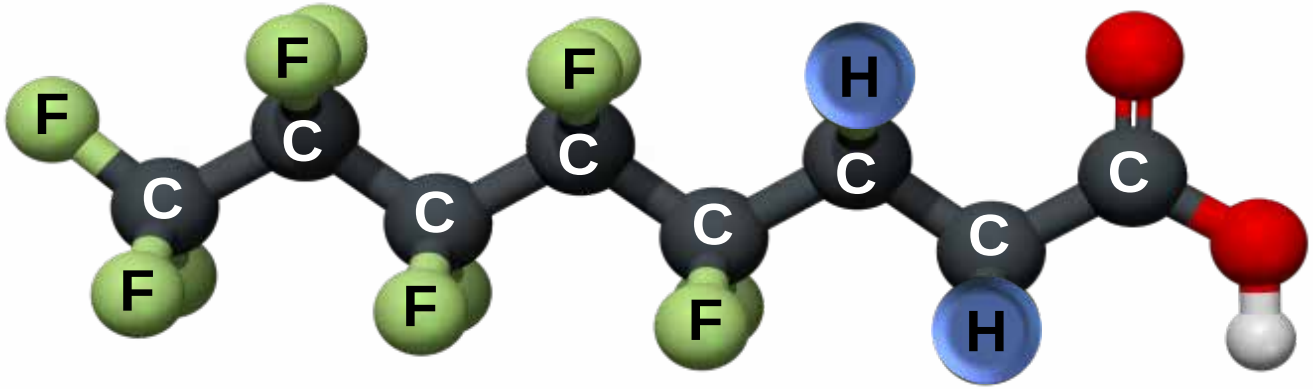
Taryn McKnight – Product Manager

Per and Poly?

Perfluorinated = Completely Fluorinated



Polyfluorinated = Incompletely Fluorinated



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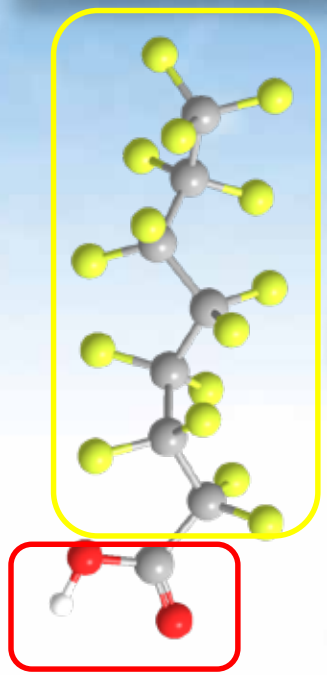
Surfactant Properties

Fluorocarbon "Tail" = Hydrophobic, Oleophobic



Functional Group "Head" = Hydrophilic

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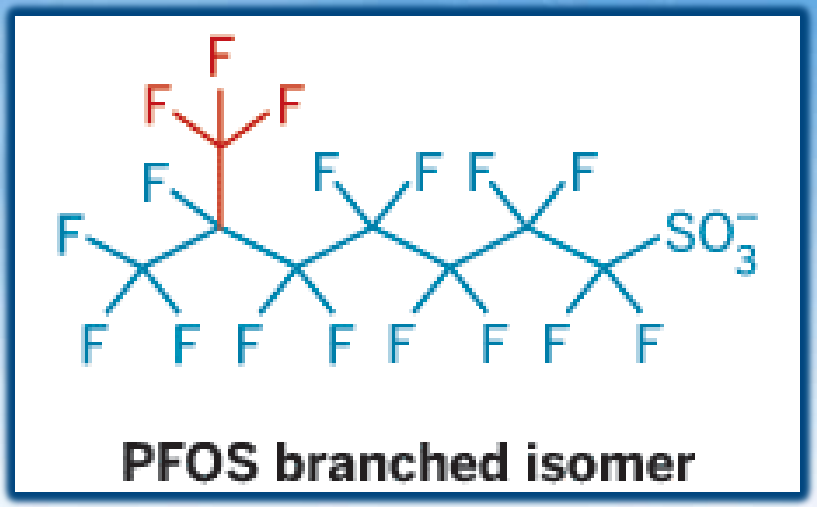
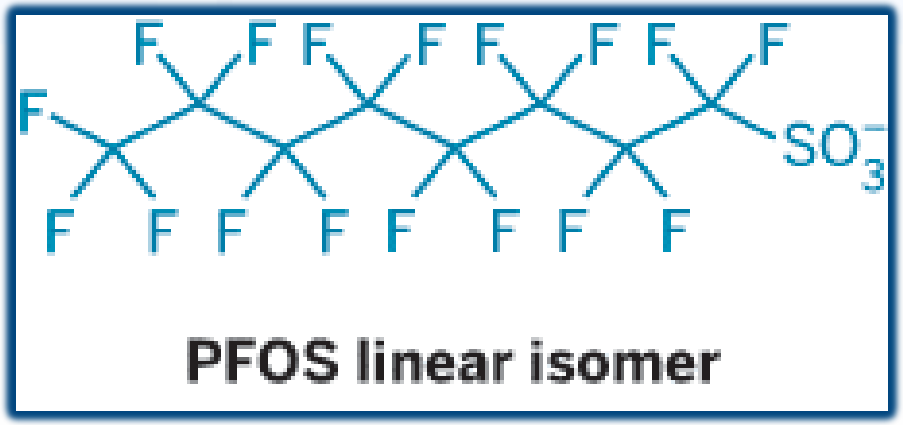
Branched & Linear Isomers



PFOS branched isomer



PFOS linear isomer

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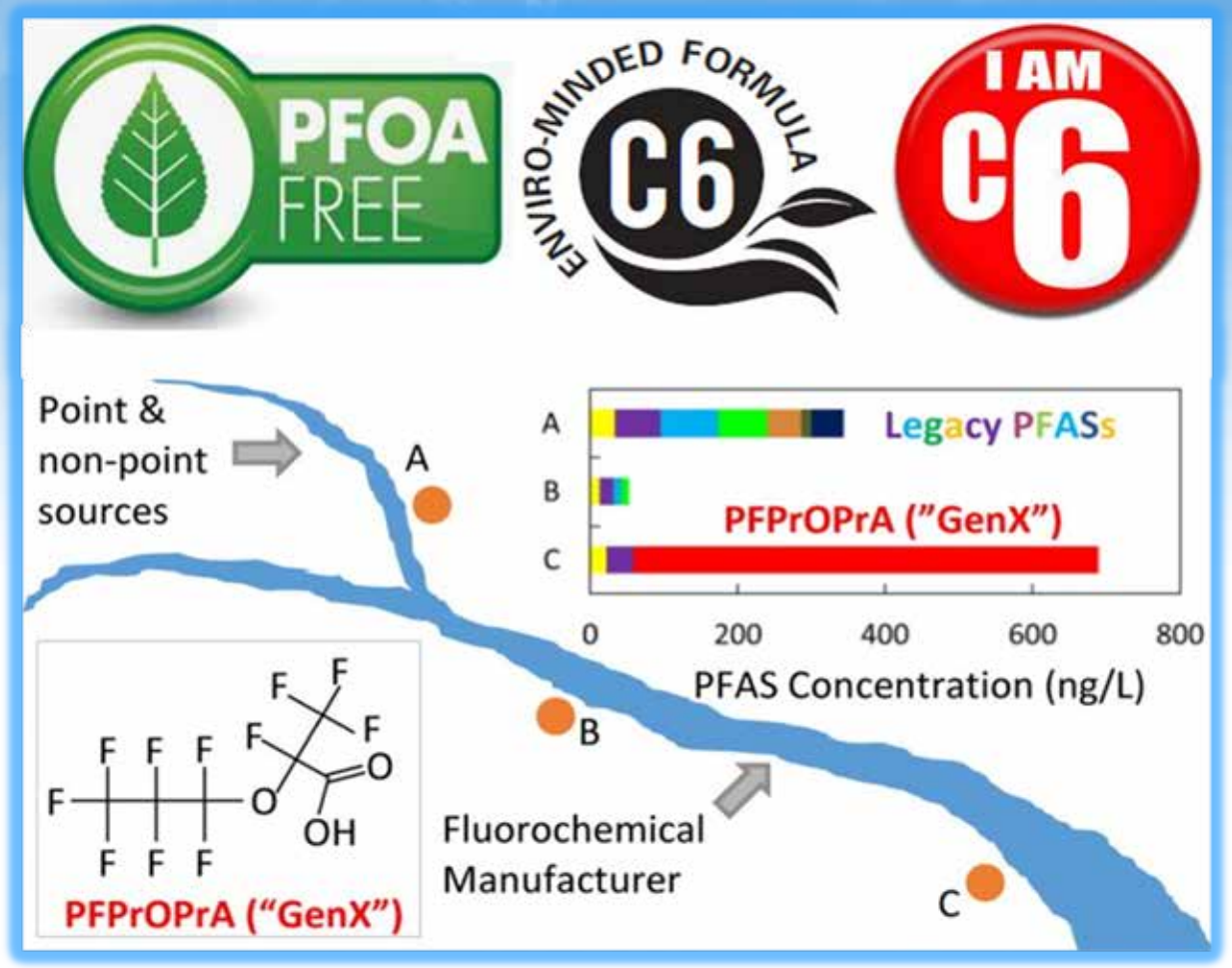
Replacement Chemicals



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Analyte Description
Perfluorobutanoic acid (PFBA)
Perfluoropentanoic acid (PFPeA)
Perfluorohexanoic acid (PFHxA)
Perfluoroheptanoic acid (PFHpA)
Perfluorooctanoic acid (PFOA)
Perfluorononanoic acid (PFNA)
Perfluorodecanoic acid (PFDA)
Perfluoroundecanoic acid (PFUnA)
Perfluorododecanoic acid (PFDoA)
Perfluorotridecanoic Acid (PFTriA)
Perfluorotetradecanoic acid (PFTeA)
Perfluorobutanesulfonic acid (PFBS)
Perfluorohexanesulfonic acid (PFHxS)
Perfluoroheptanesulfonic Acid (PFHpS)
Perfluorooctanesulfonic acid (PFOS)
Perfluorodecanesulfonic acid (PFDS)
Perfluorooctane Sulfonamide (FOSA)
N-methyl perfluorooctane sulfonamidoacetic acid (NMeFOSAA)
N-ethyl perfluorooctane sulfonamidoacetic acid (NEtFOSAA)
Perfluoro-1-pentanesulfonate (PFPeS)
Perfluoro-1-nonanesulfonate (PFNS)
6:2FTS
8:2FTS
4:2FTS
DONA
HFPO-DA (GenX)
F-53B Major
F-53B Minor

NPW & Solids

EPA Draft
Target Analyte List

Replacement
Chemicals

Why are PFAS an Analytical Challenge?

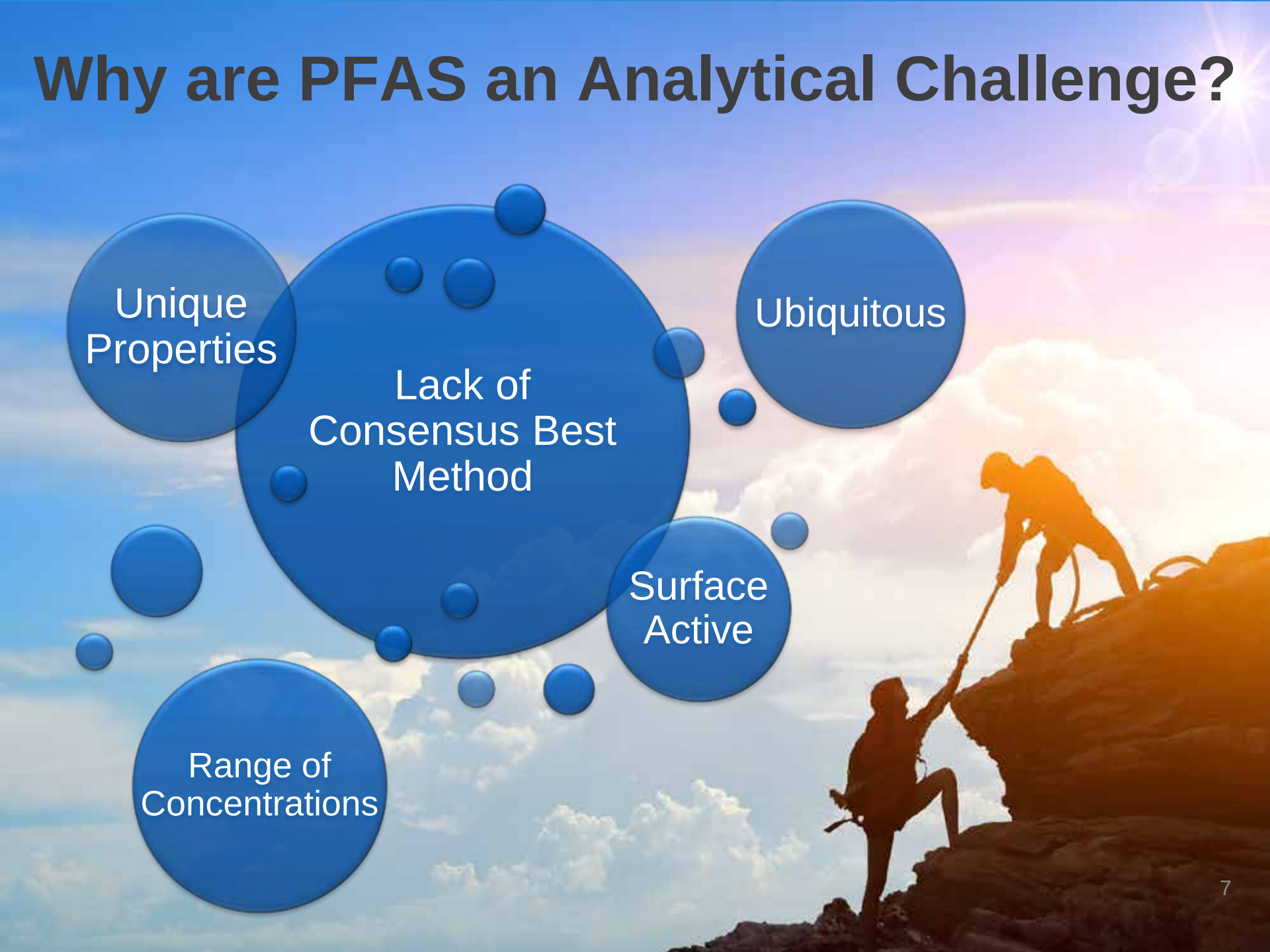
Unique Properties

Lack of Consensus Best Method

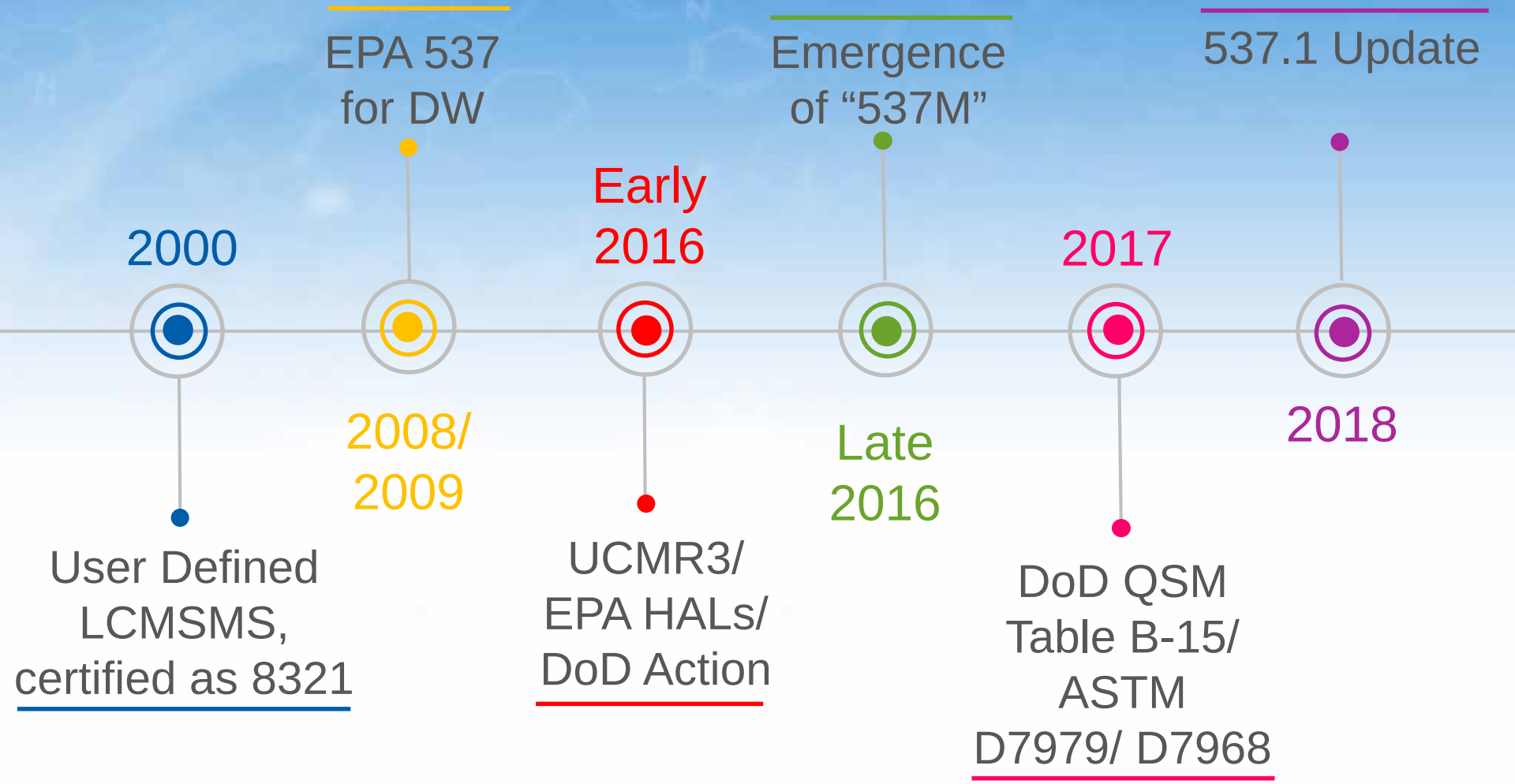
Ubiquitous

Surface Active

Range of Concentrations



Methods Timeline – Past to Present



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EPA Method 537.1
"A Drinking Water Method Only"

Features	Method 537.1
Matrices	Drinking Water
Analyte List	14 + 4 replacement chemicals
Sample size	250 mls
Extraction	SPE SDVB
Analysis	LCMSMS
Branched/Linear	Yes, for available standards
Quantitation	Internal standard
Reporting Limits	(2 ppt - 40 ppt)

Groundwater, Soil, Tissue?

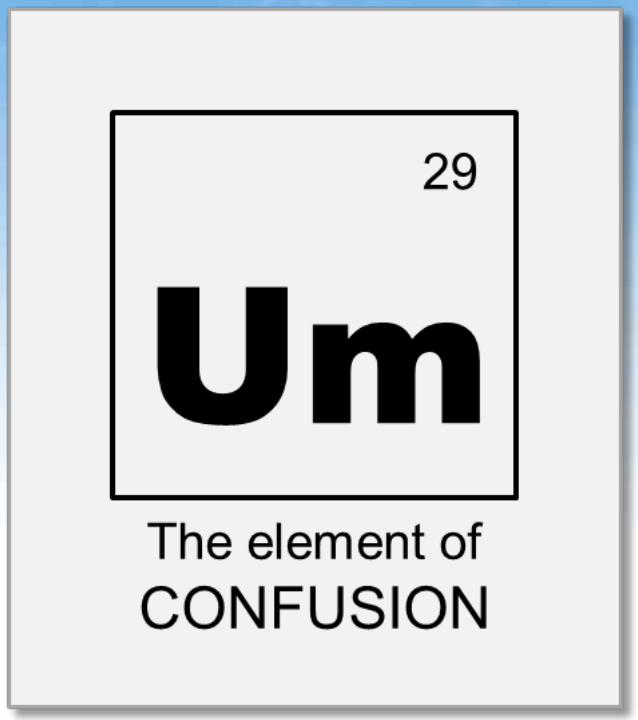
What method do we use for non-potable water & solid matrices?

537 “Modified”

ISO 25101

ASTM D7979

ASTM D7968



DoD QSM B-15

EPA Draft 8327

EPA 1600 series

EPA 537.1 (rev 1.1)

EPA 533

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

Available vs. Future

7979
- Non-potable Aqueous
- No SPE, Direct Inject, External Standard

8327
- SW-846 Draft Method for Non-potable Aqueous
- No SPE, Direct Inject, External Standard
- *Public Comment Period Closed Aug 23, 2019*

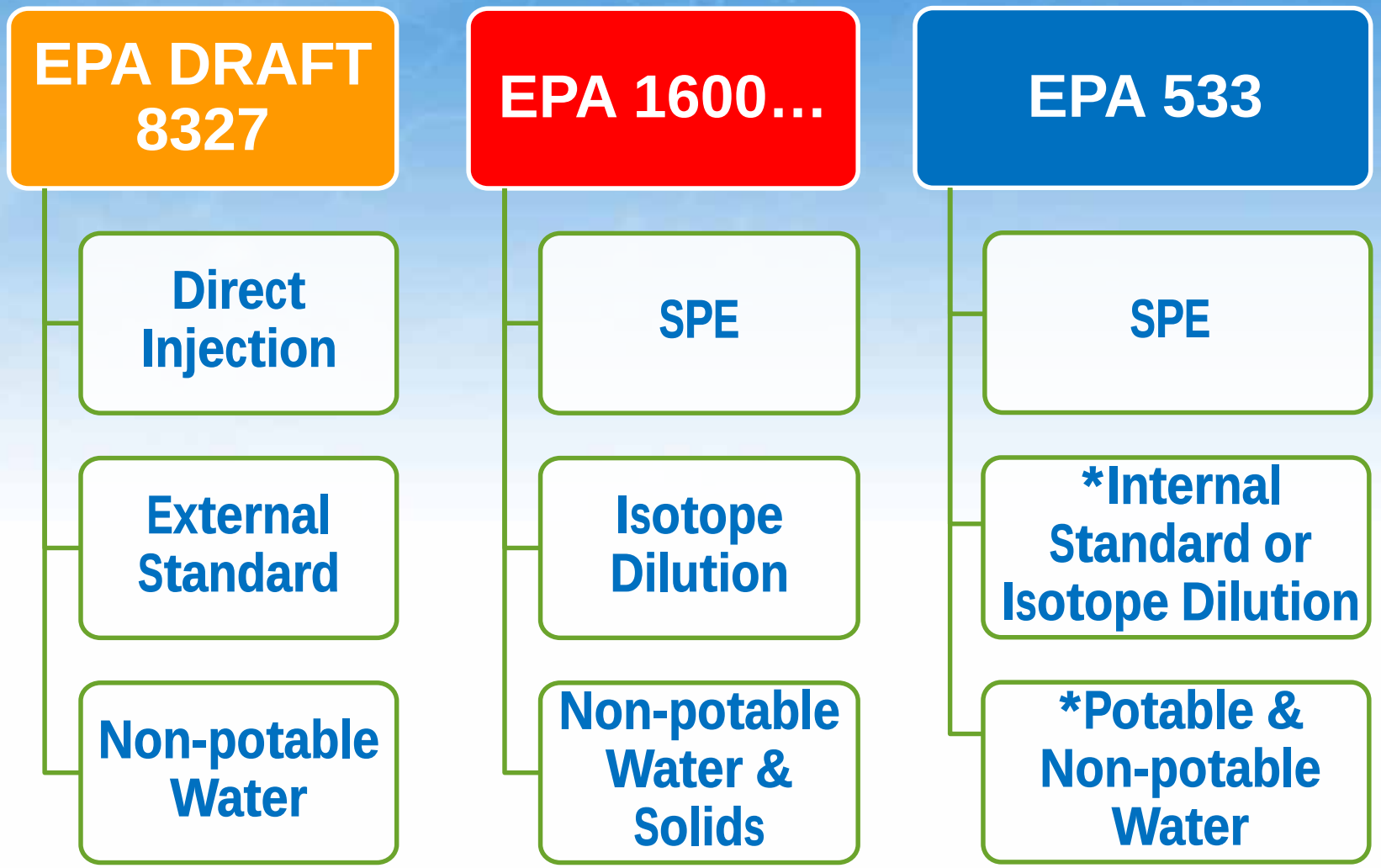
537M
- User Defined Method, All Matrices
- SPE, Isotope Dilution, Comparable to DoD QSM Table B-15

1600s
- EPA Draft Method, All Matrices other than DW
- SPE, Isotope Dilution, Comparable to DoD QSM Table B-15
- *Unknown, perhaps late 2020*

537.1
- EPA Published Method, Drinking Water Only
- SPE, Internal Standard

533
- EPA Draft Method, Drinking Water, possibly non-potable
- SPE, Isotope Dilution and/or Internal Standard, TBD
- *Reviewing 3rd Party Validation NOW*

Future EPA Methods



*Potentially, method is still under development

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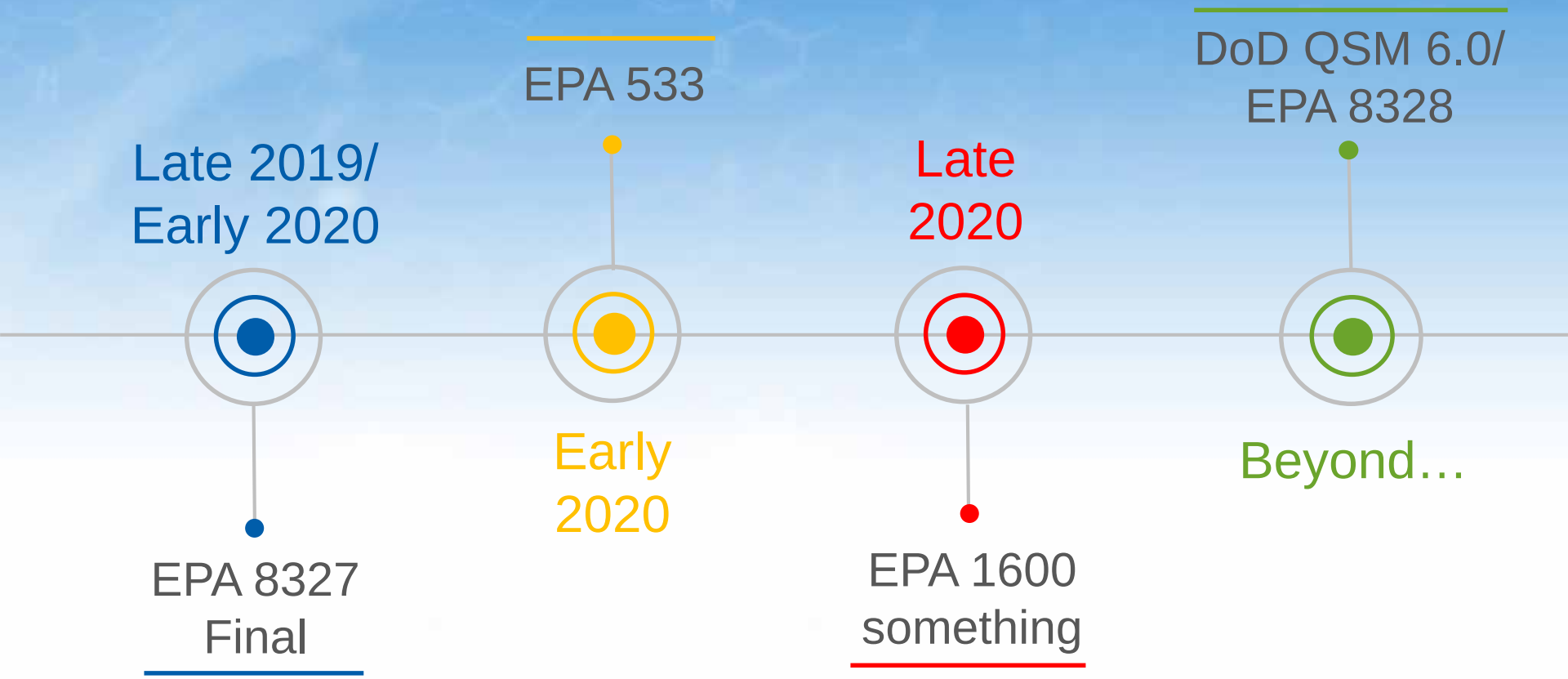
Methods Timeline – Possible Future



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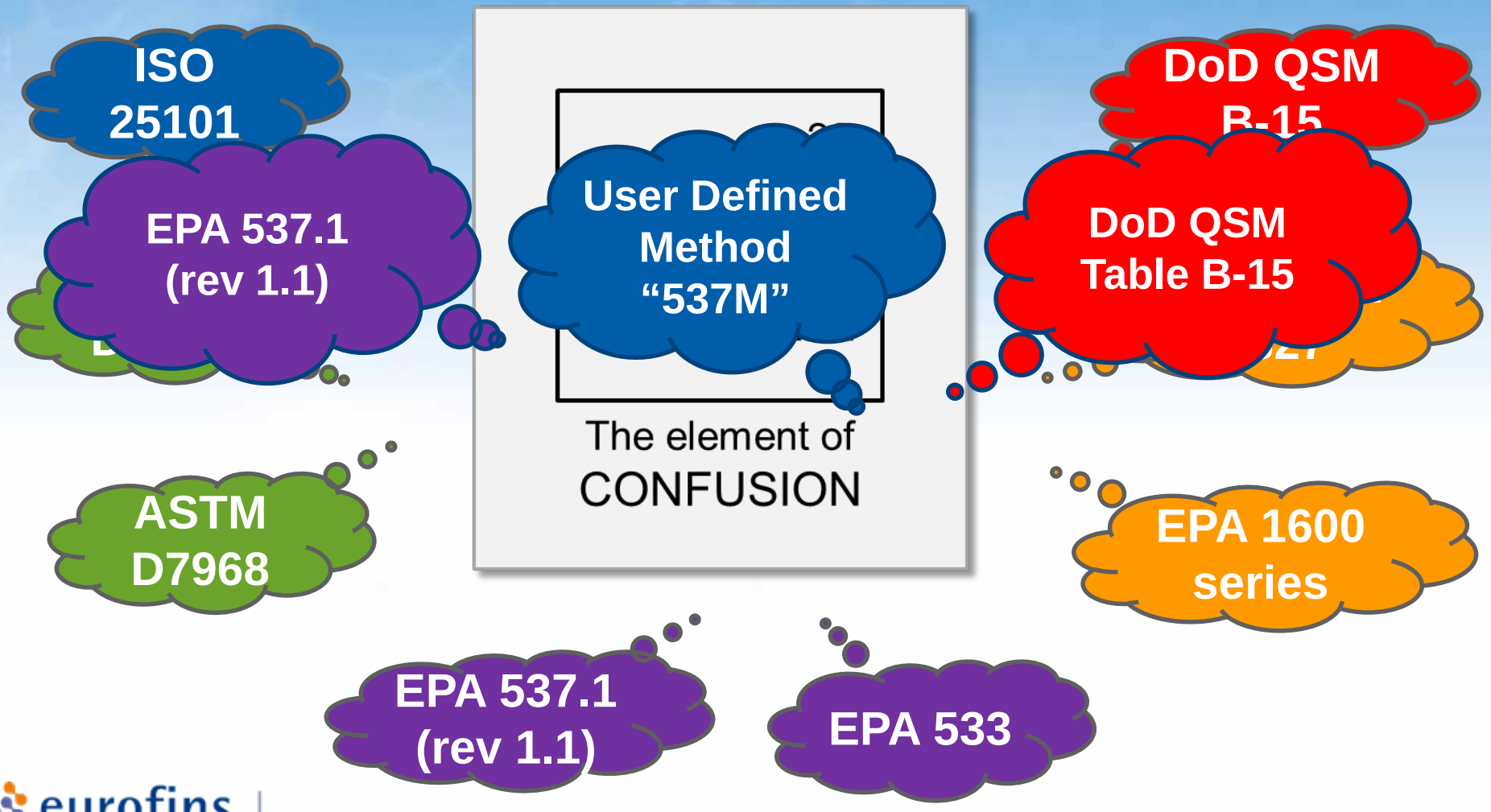
537 "Modified"

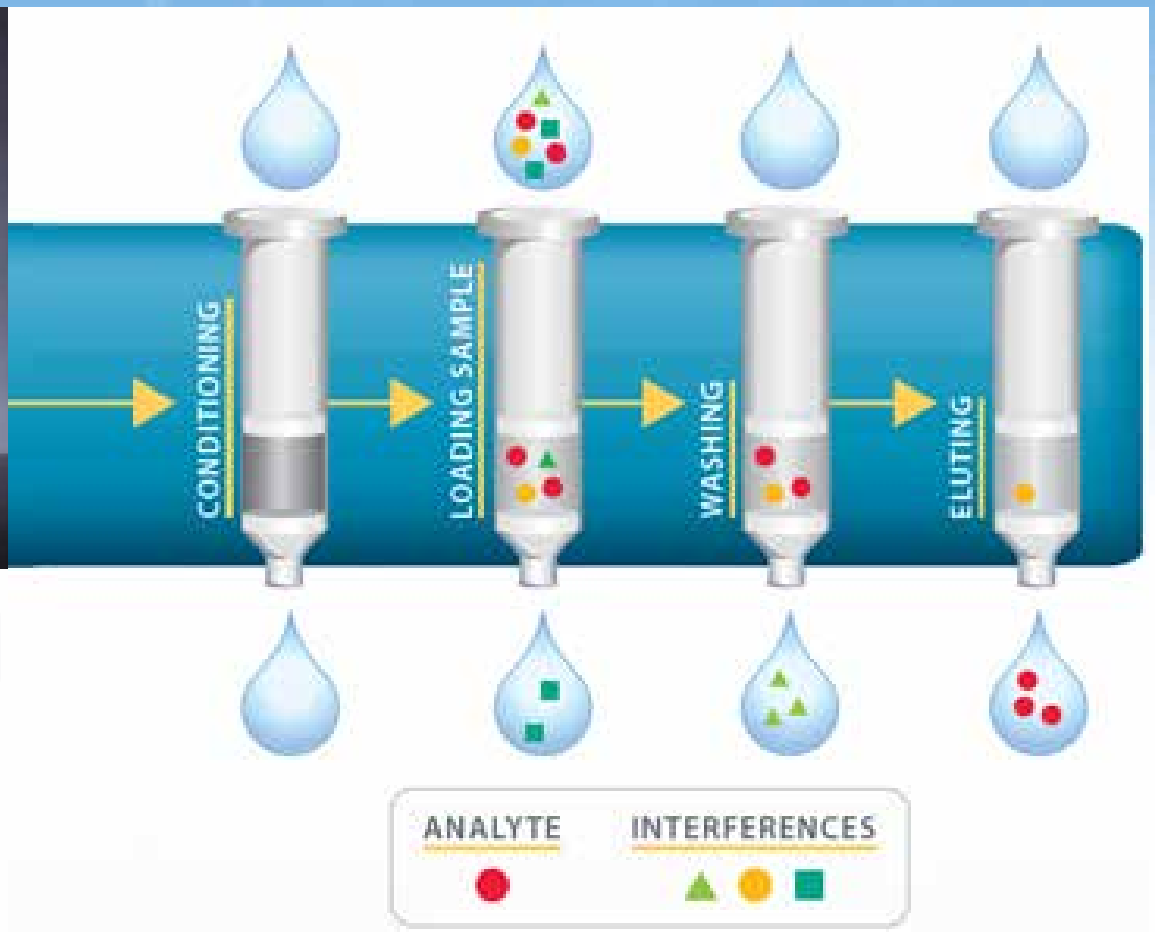


PFAS Method Comparison Table for Aqueous Matrix

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

[1] – Compliant with DoD QSM 5.1 Table B-15

Solid Phase Extraction (SPE)



SEPARATION CHEMISTRY

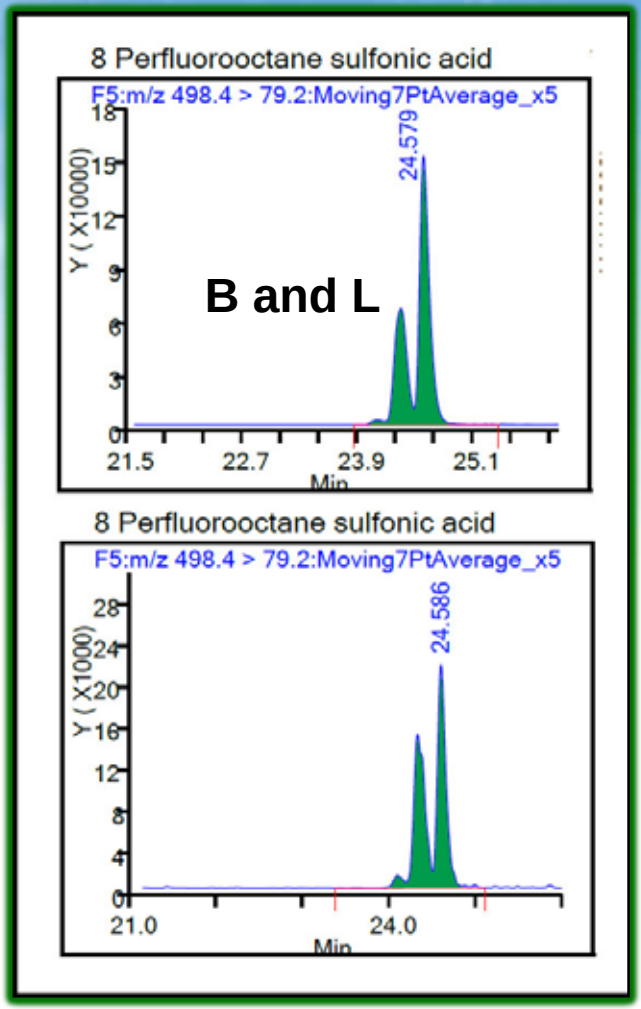
Branched and Linear Isomers

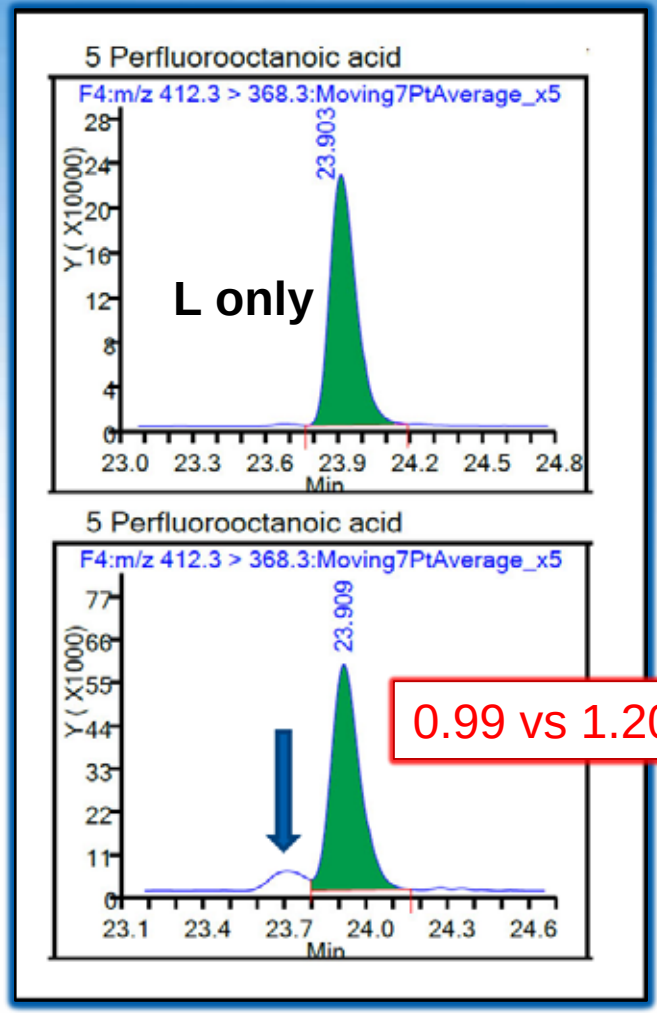
PFOS

PFOA

Standard

Sample





0.99 vs 1.20 ng/ml

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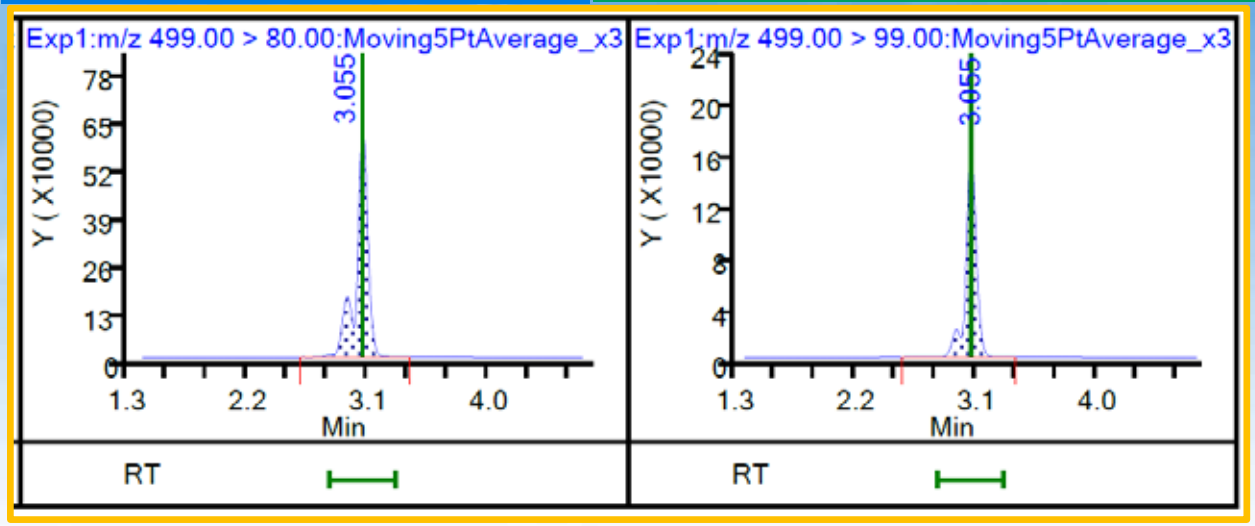
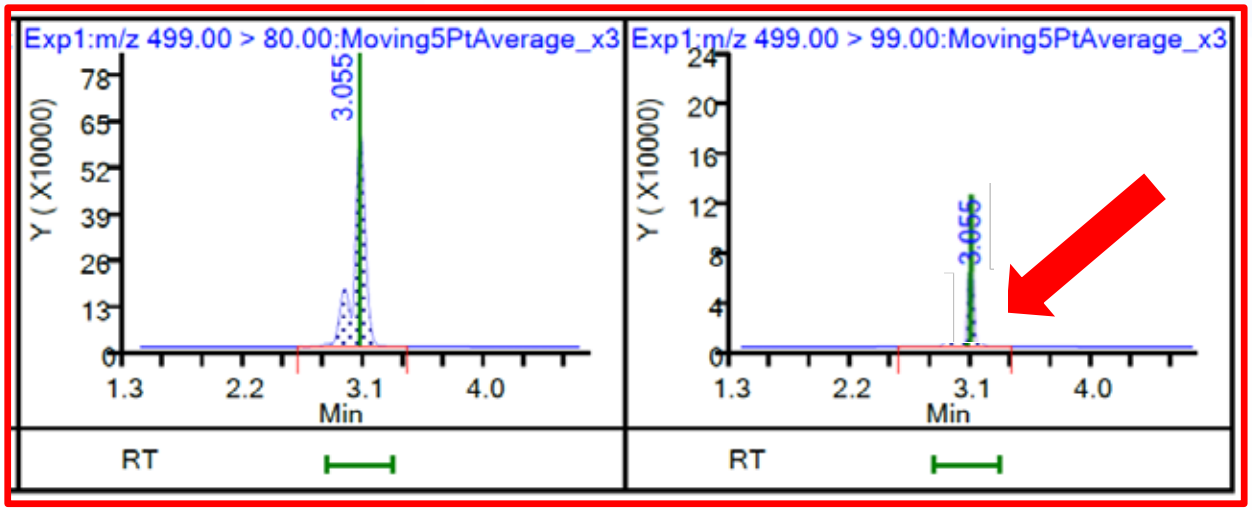
Secondary Ion Transition - PFOS

Primary Ion Transition | Secondary Ion Transition

Standard

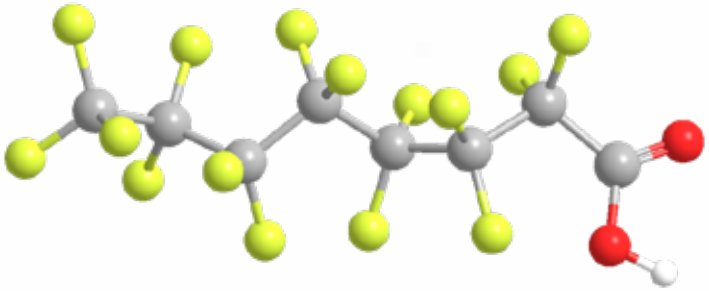


Sample

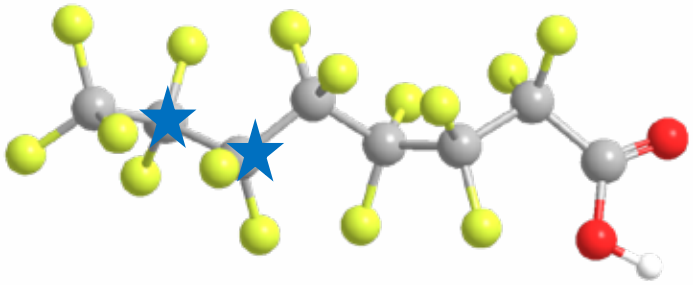


Isotope Dilution – Labeled Analogues

The Parr Family = Native PFOS



The Incredible Family = Labeled PFOS



★ = ^{13}C

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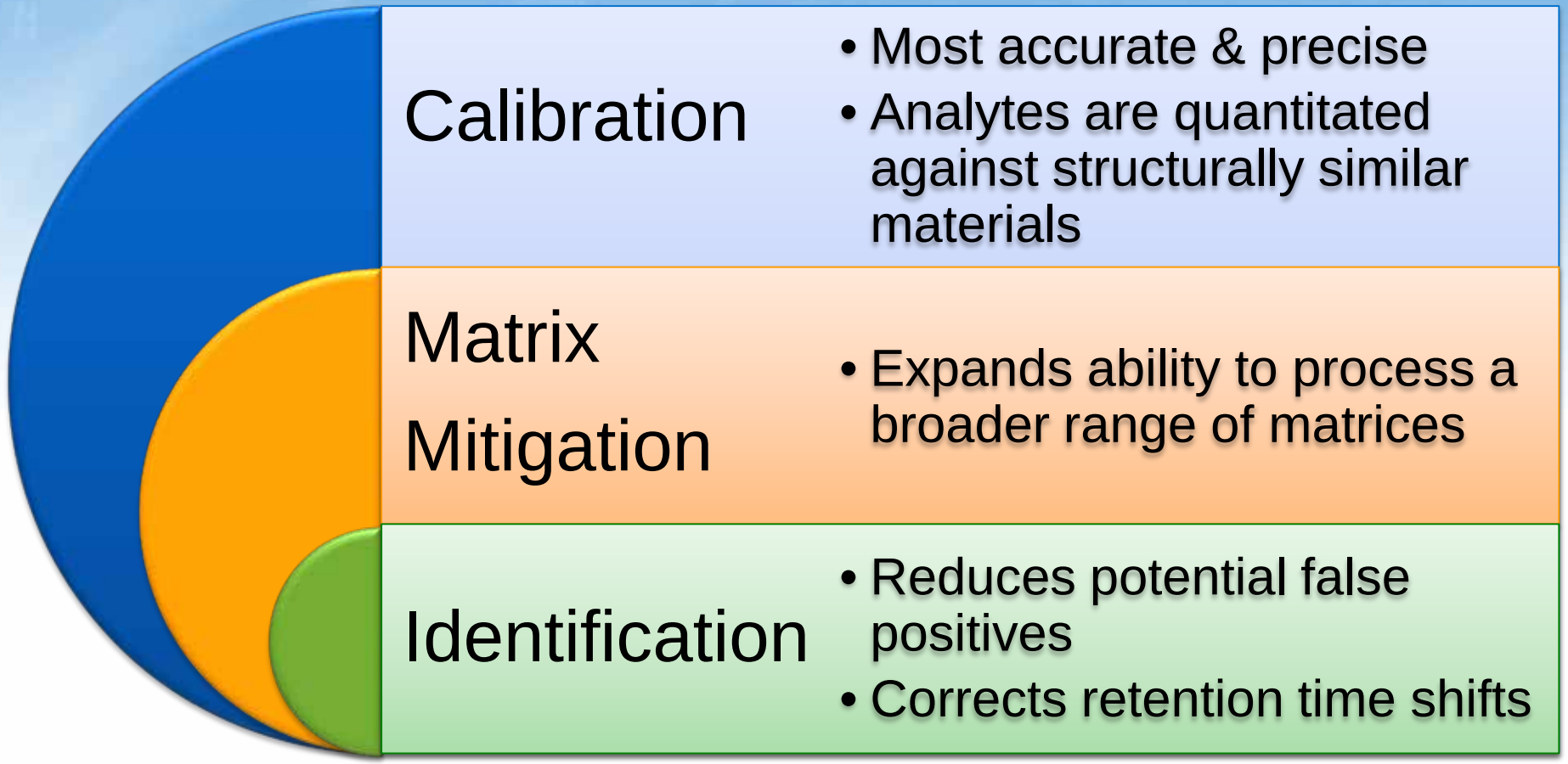
Benefits of Isotope Dilution

"What affects the native analyte, equally affects the isotope"



Isotope Dilution vs Internal Standard

	PFOA	Spike amount	Isotope Dilution Result	% recovery (ID)	Recovery Corrected Result	Internal Standard Result	% recovery (IS)
A	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)
B	Field Sample		**40** ★		**80** ★	**40** ★	
	Matrix Spike	40	20	50%		20	50%
	Spike Duplicate	40	20	50%		20	50%

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What Have the States Done?

Analytical Requirements
State specific criteria

MN

WI

Method Criteria
State specific criteria

NELAC & DoD QSM
Recommended certs

MI

PA

Method Criteria
537-Isotope
Dilution Hybrid

CA

DoD QSM
Requires compliance with QSM Table B-15

NJ

Method Criteria
537-Isotope
Dilution Hybrid

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Challenges Ahead
2019