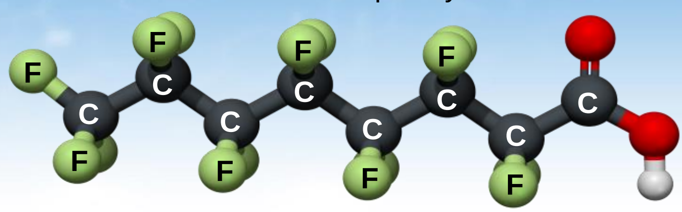
PFAS: Producing Defensible Data

Taryn McKnight,
PFAS Practice Leader
Eurofins Environment Testing America

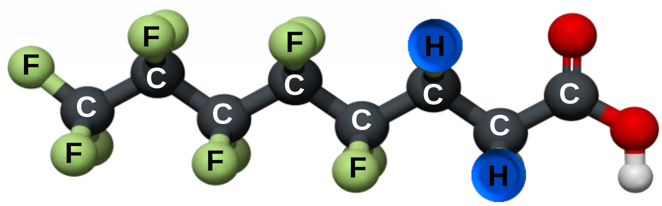
1

Per and Poly?

Perfluorinated = Completely Fluorinated



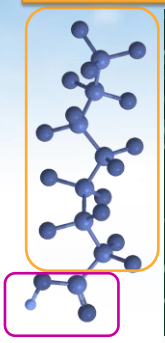
Polyfluorinated = Incompletely Fluorinated



eurofins | Environment Testing America

Surfactant Properties

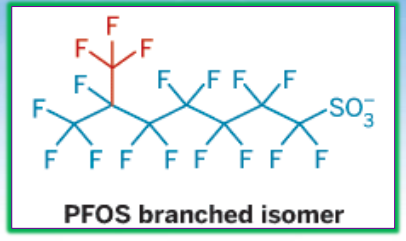
Fluorocarbon “Tail” = Hydrophobic and Oleophobic



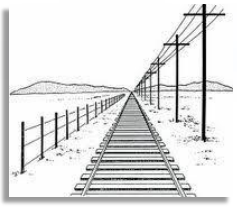
Functional Group “Head” = Hydrophilic

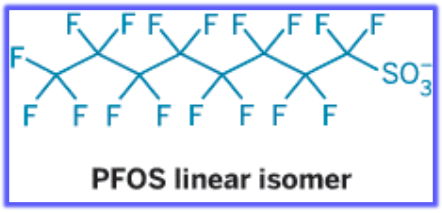
eurofins | Environment Testing America

Branched & Linear Isomers



PFOS branched isomer





PFOS linear isomer

eurofins | Environment Testing America

Replacement Chemicals

	Legacy Manufacturers		
Original Chemical	PFOA	PFOS	PFOS
Replacement Chemical	HFPO-DA "GenX"	DONA	F-53B

eurofins | Environment Testing America

5

Why are PFAS an Analytical Challenge?

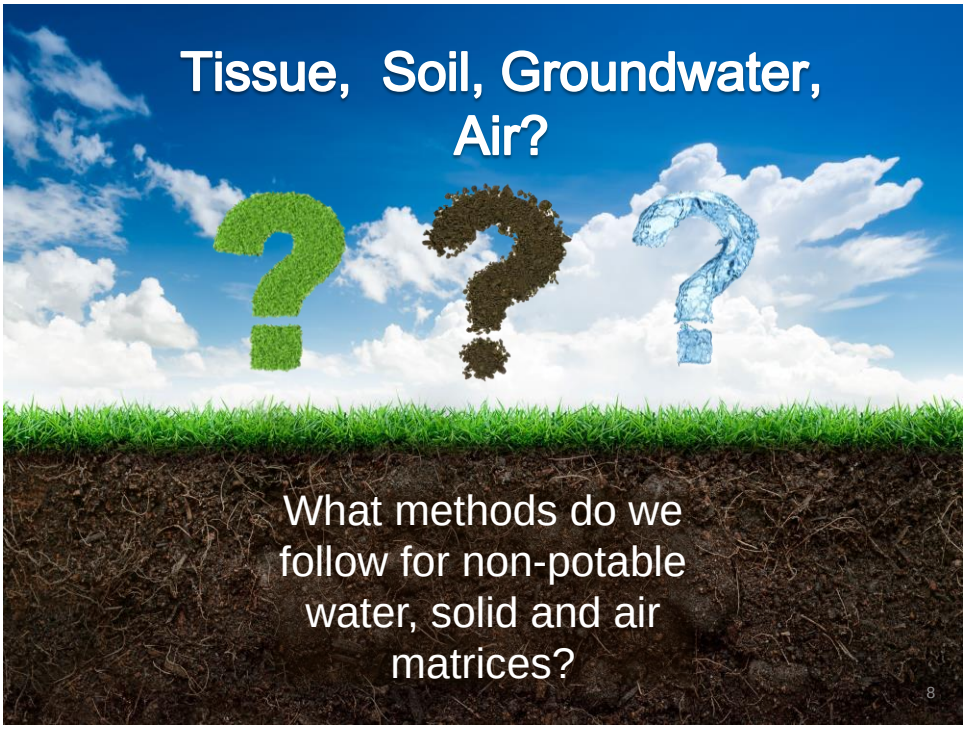
6

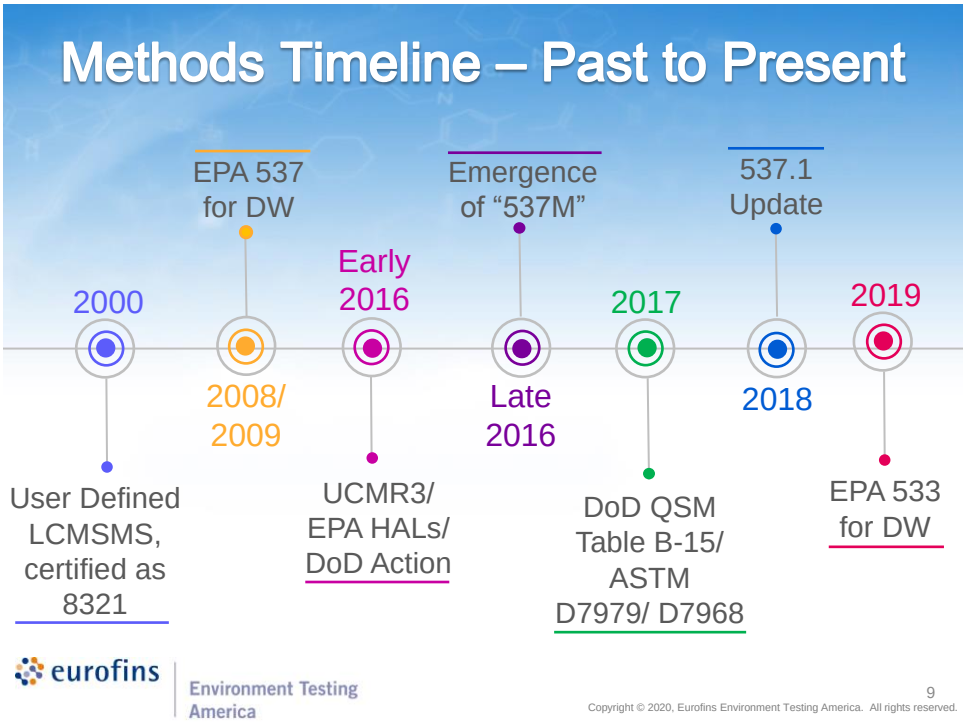
EPA Method 533
"A Method for Short Chain PFAS"

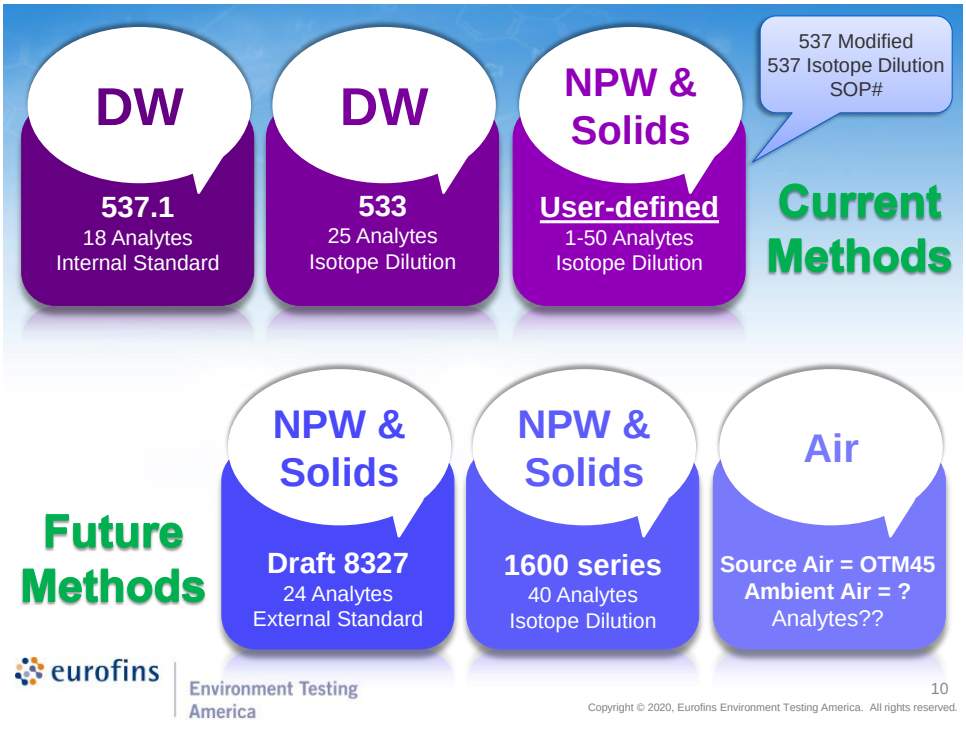
533	537.1
Drinking Water	Drinking Water
Branched/Linear Isomers -YES	Branched/Linear Isomers - YES
14 of the same and 11 unique compounds	14 of the same and 4 unique compounds
SPE WAX	SPE SDVB
Hold Time: 28/28 days	Hold Time: 14/28 days
LCMSMS with confirmation ion	LCMSMS - no confirmation ion
Isotope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

eurofins | Environment Testing America

7




Methods Timeline – Past to Present
2000
User Defined LCMSMS, certified as 8321
2008/ 2009
EPA 537 for DW
Early 2016
UCMR3/ EPA HALs/ DoD Action
Late 2016
Emergence of "537M"
2017
DoD QSM Table B-15/ ASTM D7979/ D7968
2018
537.1 Update
2019
EPA 533 for DW
eurofins
Environment Testing America
9
Copyright © 2020, Eurofins Environment Testing America. All rights reserved.


DW
537.1
18 Analytes
Internal Standard
DW
533
25 Analytes
Isotope Dilution
NPW & Solids
User-defined
1-50 Analytes
Isotope Dilution
537 Modified
537 Isotope Dilution
SOP#
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??
eurofins
Environment Testing America
10
Copyright © 2020, Eurofins Environment Testing America. All rights reserved.

Methods by Matrix

EPA 537.1 & EPA 533

- Finished Drinking Water

User-Defined Method

- Groundwater
- Wastewater
- Surface water
- Stormwater
- Soil
- Sediment
- Biosolids
- Leachate
- Sludge
- Tissue
- Air
- AFFF
- Products
- Serum

eurofins | Environment Testing America

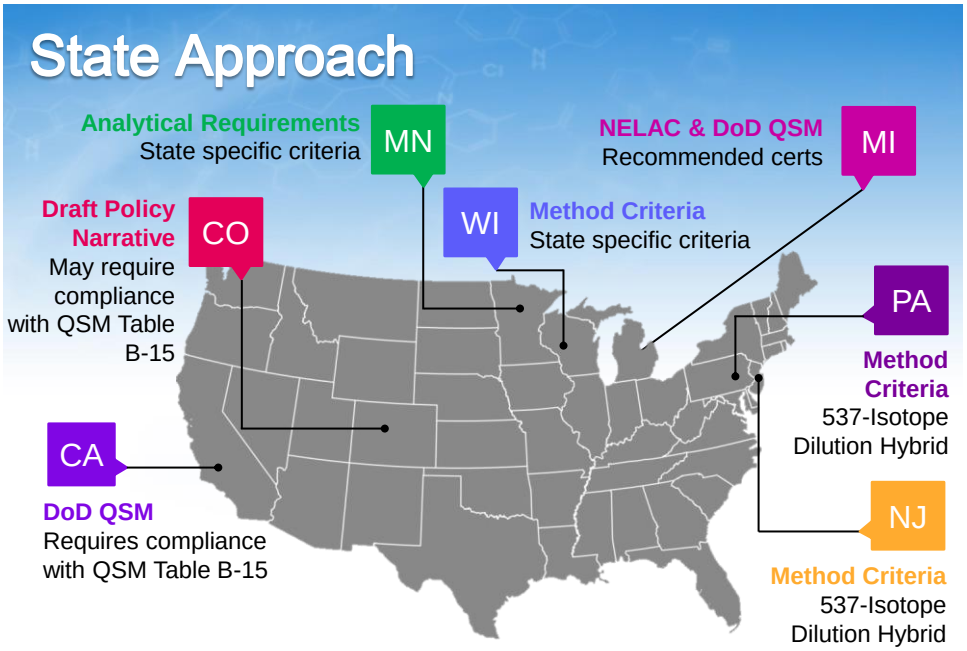
11

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

www.denix.osd.mil/edqw/documents/manuals/qsm-version-5-3-final/

12

State Approach



eurofins | Environment Testing America

13

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

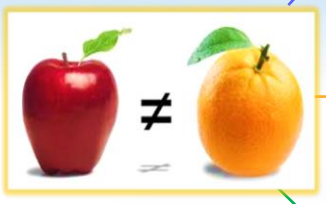
EPA Draft Target Analyte List

Replacement Chemicals

14

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

eurofins | Environment Testing America

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

eurofins | Environment Testing America

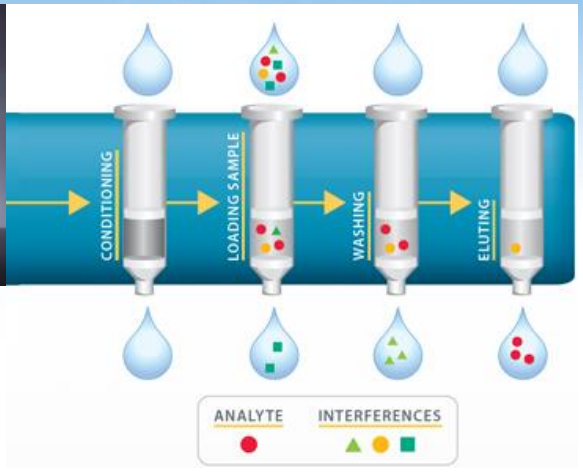
$$\frac{2}{1{,}000{,}000{,}000{,}000}$$

LC/MS/MS – Liquid Chromatography

17

Solid Phase Extraction (SPE)

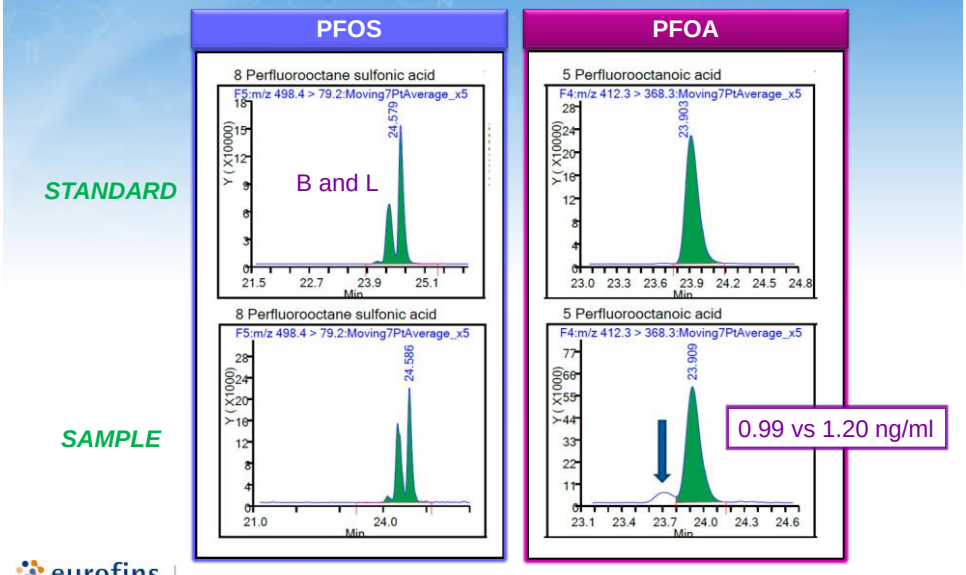
SEPARATION CHEMISTRY



eurofins | Environment Testing America

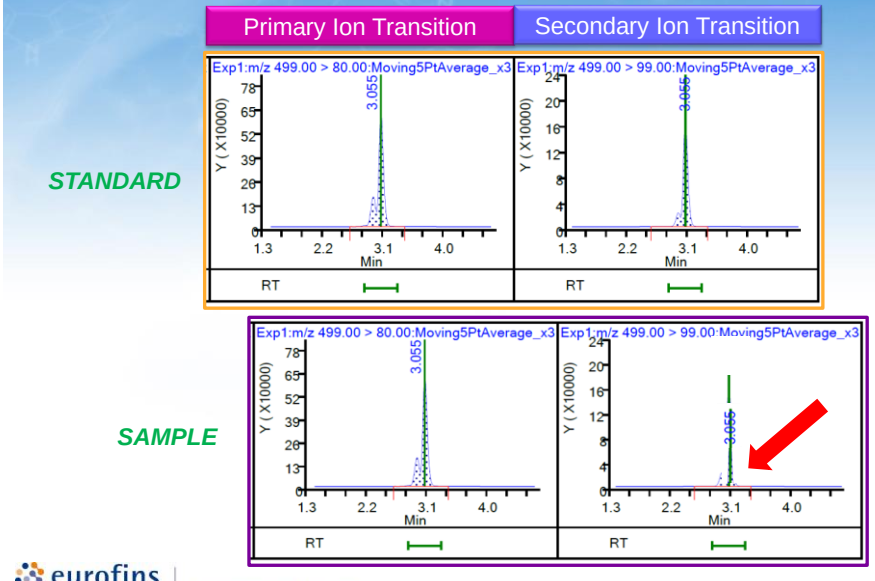
18

Branched and Linear Isomers



eurofins | Environment Testing America

Secondary Ion Transition - PFOS



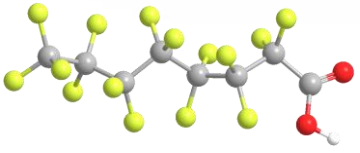
eurofins | Environment Testing America

Isotope Dilution – Labeled Analogues

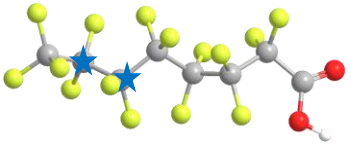
+  =

The Parr Family = Native PFOS

The Incredible Family = Labeled PFOS



+ ★ =



★= ^{13}C

eurofins | Environment Testing America

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

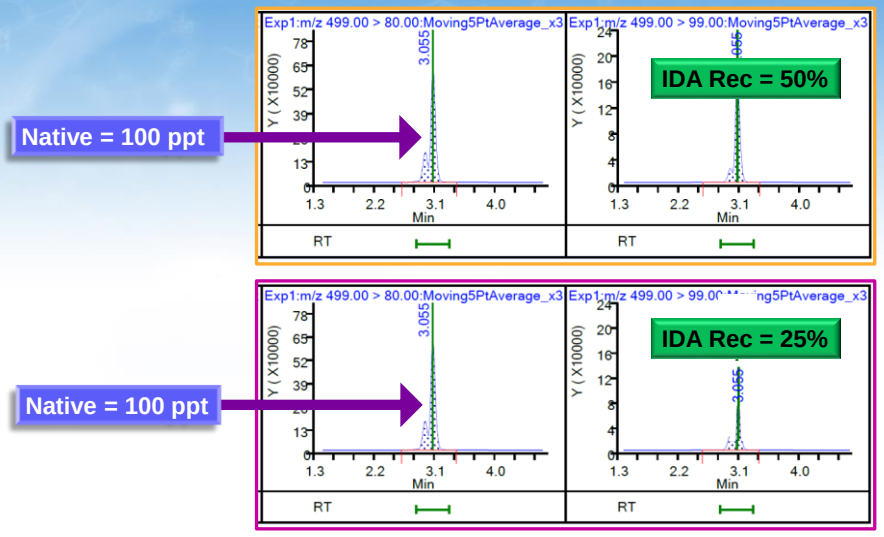
Compound Identification

Reduces the potential for false positives

Reduces the potential for error; corrects for retention time shifts

eurofins | Environment Testing America

EIS response must be > 10:1 S/N



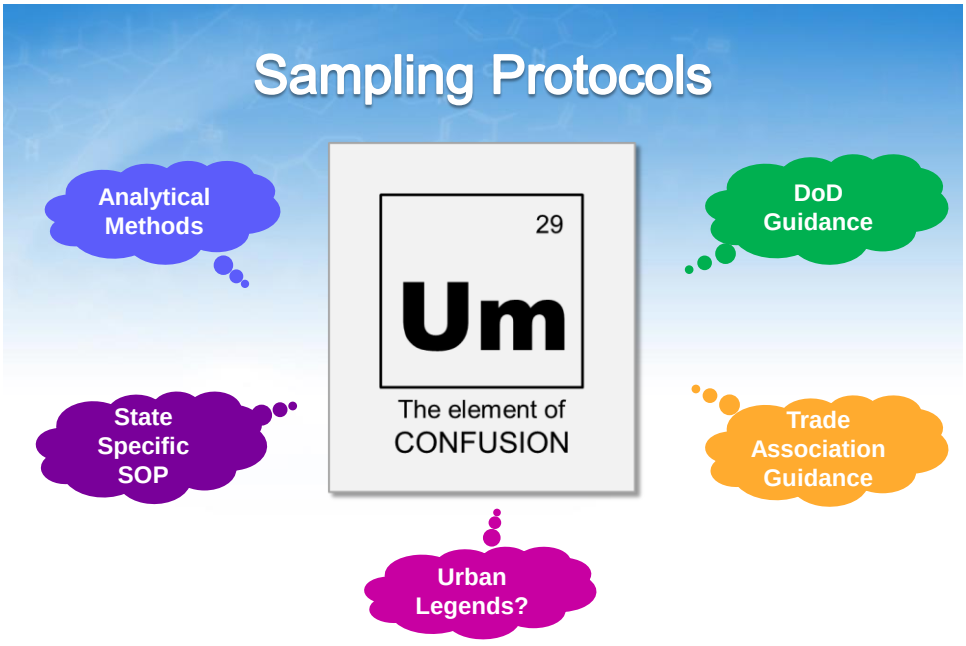
eurofins | Environment Testing America

Isotope Dilution vs Internal Standard

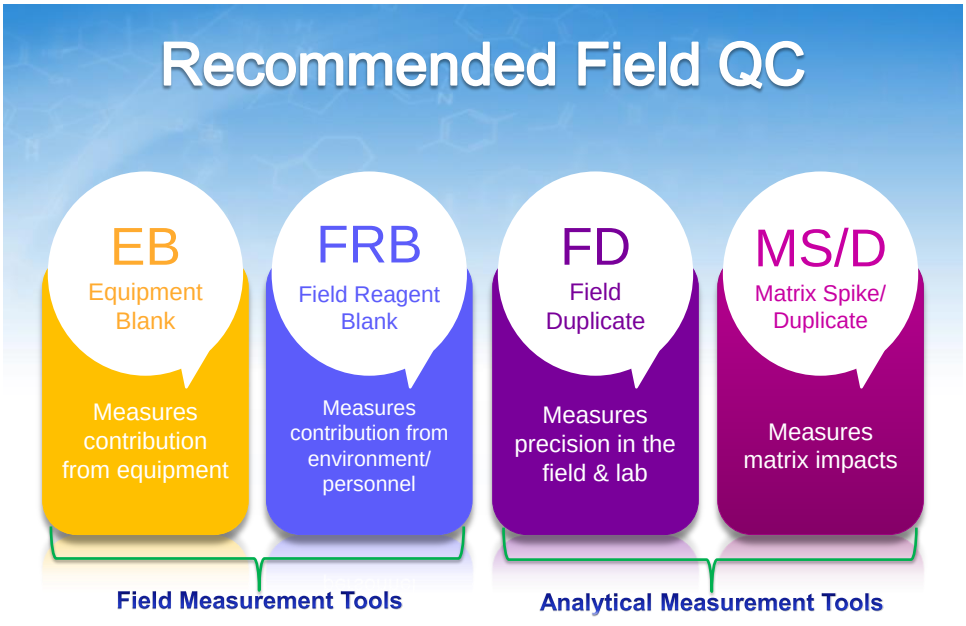
PFOA	Spike amount	Isotope Dilution Result	% recovery (ID)	Recovery Corrected Result	Internal Standard Result	% recovery (IS)
Field Sample		10		11	9	
Matrix Spike	34	40	88%		40	91%
Spike Duplicate	34	42	94%		42	97%

MeFOSAA	Spike amount	Isotope Dilution Result	% recovery (ID)	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%

eurofins | Environment Testing America



eurofins | Environment Testing America



eurofins | Environment Testing America

Managing Artifacts

Field Crew:

personal care, clothing, food, visitors, notebooks, tarps

Sampling Equipment:

verified to be PFAS free?

Sample Collection:

wash hands, wear gloves, don't filter, include field QC

eurofins | Environment Testing America

Bottle Types by Collection Method

537.1
533
ISO25101
D7979

Poly-propylene

Modified MM5
Modified TO-13A

Glass

HDPE

DoD QSM 537 Modified 533

"Extraction type (whole bottle vs. sub-sampling) play a more significant role than material type (PP or HDPE)"

Robel et al., 2018

eurofins | Environment Testing America

Holding Times

537.1 & QSM	533	EPA Draft 8327	User-defined 537M
Extract: 14 days Analyze: 28 days	Extract: 28 days Analyze: 28 days	Extract: 28 days Analyze: 28 days	Extract: 14 days Analyze: 40 days*

*Lab SOP Specific

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Monitoring/ER19-1205

eurofins | Environment Testing America

29

Bottle Kit – Supplies List

eurofins | Environment Testing America

30

Packaging/Shipping

SHIPPING CONTAINER
Double Bag/Segregate

PRESERVATION
Real Ice

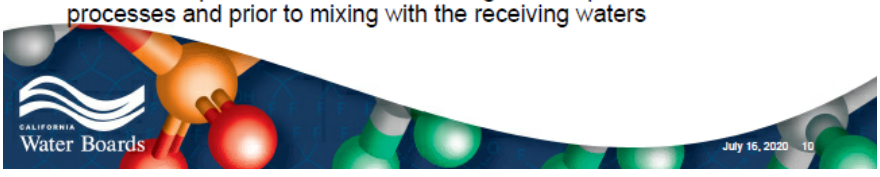
PACKAGING
Sealable Bags

31

CA Water Board – POTW PFAS Orders

Treatment System Sampling

- Samples shall be representative and taken before the monitored flow joins or is diluted by any other waste stream, body of water, or substance
- 24 hr sample using a composite sampler is preferred – however, there are challenges and limitations to prevent cross contamination so collecting a grab sample maybe better suited for the facility. An updated sampling guide will be available soon on the Water Board's PFAS website.
- Influent samples shall be taken from locations prior to primary settling
- Effluent samples shall be taken following the completion of all treatment processes and prior to mixing with the receiving waters



eurofins | Environment Testing America

32

Taryn McKnight
PFAS Practice Leader
916.347.6815
taryn.mcknight@eurofinset.com

eurofins | Environment Testing America

THANK YOU FOR ATTENDING