Environmental Monitoring and Data Quality Workshop

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Technical Presentation

The Analysis of Polyfluorinated Alkyl Substances (PFAS) including PFOS and PFOA

Karla Buechler – Corporate Technical Director

April 13, 2016

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PFAS - Outline

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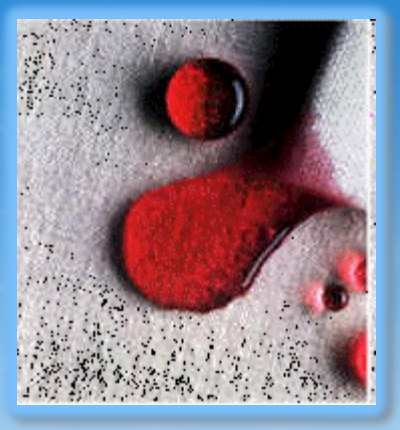


Introduction to PFASs

What are PFASs?

Why all the interest now?

Nomenclature

PFAS – historical timeline

Analytical Best Practices

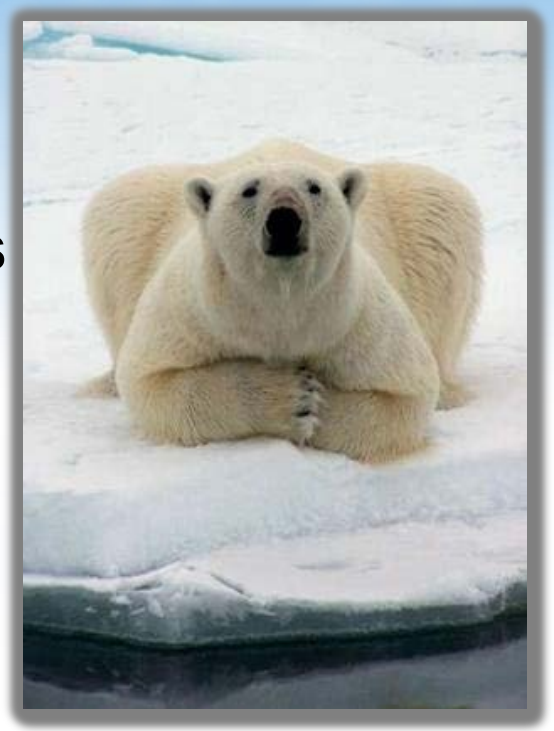
Analytical Methods review

Why so much variability?

How do we reduce variability?

Future Concerns

Questions?



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Briefly - What are PFASs?

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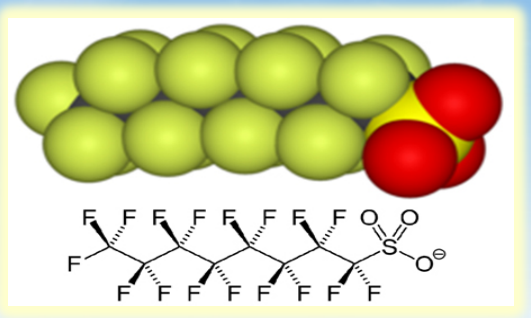
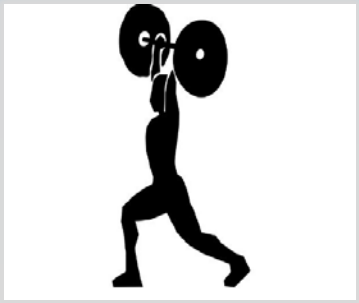
Class of synthetic compounds containing thousands of chemicals formed from **carbon** chains with **fluorine** attached to these chains.



The **C-F** bond is the shortest and the strongest bond in nature.



PFOS and PFOA are fully fluorinated and the most common perfluorinated chemicals (PFCs).

Persistent and resistant to degradation
Found in soil, air and groundwater..

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Why all the interest now?

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1) Detection Capabilities

- 1980's – Parts per Million
- 1990's – Parts per Billion
- 2000's – Parts per Trillion
- Now – Parts per Quadrillion

2) Identified as HPV chemicals

3) Frequency of detected positives

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Nomenclature

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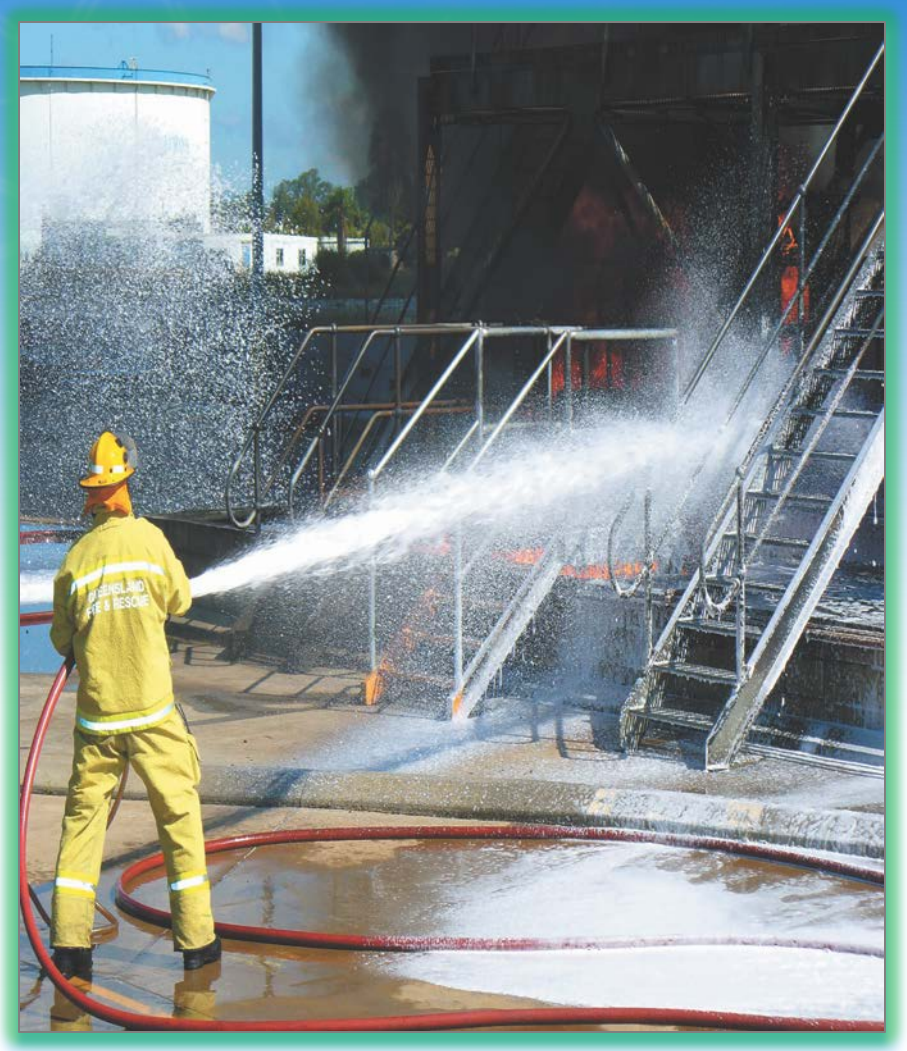
PFAS – Broad term – completely and incompletely fluorinated

PFC – Subset of PFAS completely fluorinated compounds. PFOS and PFOA are PFCs (no hydrogen atoms)

PFAAs – Perfluoroalkyl acids – PFOA and PFOS

AFFF – Aqueous Film Forming Foam (DoD connection)

Fluorochemicals and telomers



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PFAS – Historical Timeline

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When	What Happened
1950s	3M was first to produce PFOS and higher homologues
1966	AFFF was patented as a method for extinguishing liquid hydrocarbon fires and implemented by the DoD in 1969
1990s	**A handful of commercial labs developed propriety methods to meet client needs**
2002	Global manufacturers began to replace LC PFCs with SC PFCs
2005	$235Mil class action lawsuit brought by citizens against DuPont over PFC contamination in the Ohio river
2008, 09	**EPA published Method 537 and Method 537 Version 1.1**
2011	**EPA published Draft Procedure for Analysis of PFCA and PFSA in Sewage Sludge and Biosolids by HPLC/MS/MS**
2012	UCMR3 was signed by the EPA administrator
2014	**ASTM Published Method D7968-14 for PFC in Soil by LC/MS/MS**
2015	**ASTM Published Method D7979-15 for PFC in Water, Sludge, Influent, Effluent and WW by LC/MS/MS**

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PFAS Analytical Methods- Best Practices

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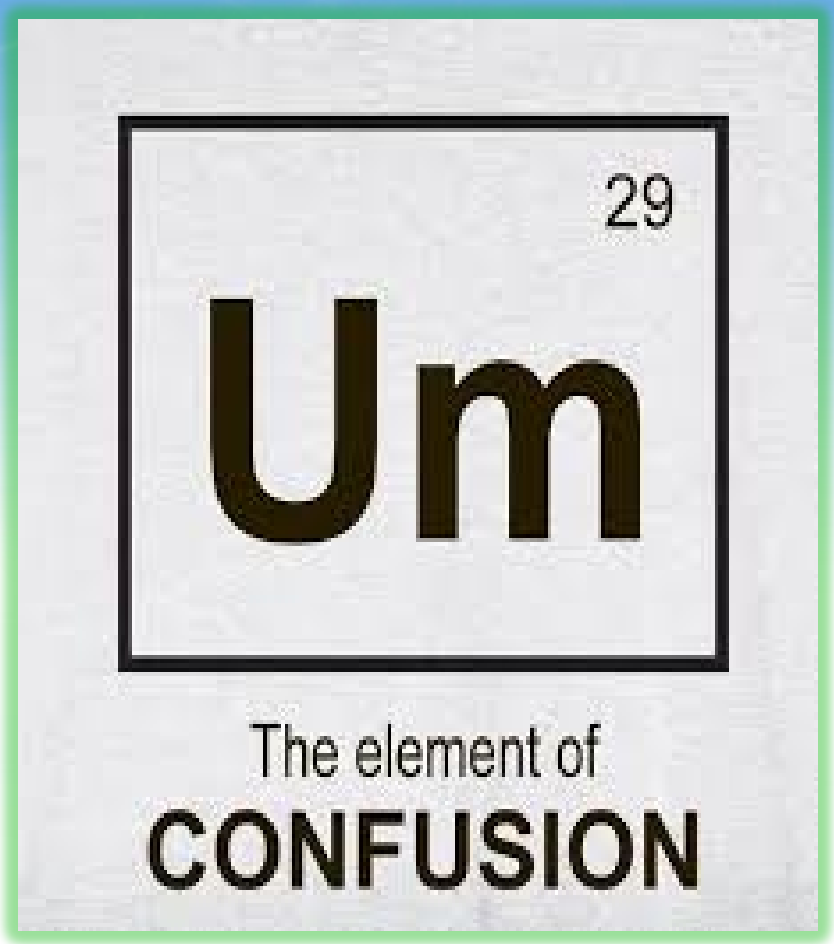
- Manufacturer's methods were adopted by the environmental industry – SW-846 Method 8321
- EPA expanded manufacturer's method for drinking water- Method 537
- EPA expanded Method 537 for biosolids and sewage matrices – Draft EPA Method
- ASTM published D7968-14 for soils
- ASTM published D7979-15 for a wide variety of aqueous matrices



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Aqueous Method Comparisons

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Category	EPA Method 537	ASTM D7979-15	TestAmerica Method 537Mod
Purpose	**Definitive**	Screen	**Definitive**
Matrix	Drinking Water	**Env Water**	**Env Water**
Validated	Single Lab	Single Lab	Single Lab
Sample size	**250 ml**	5 ml	**250 or 500 mls**
Holding times	14/28	28	14/40
Extraction	SPE	RVE liq/liq	SPE
Analytes	14	21	**25**
RL Range	5-15 ppt	10 - 50 ppt	**2 ppt**
Analysis	MRM LCMSMS	MRM LCMSMS	MRM LCMSMS
Quantitation	I.S	E.S	**Isotope Dilution**
B/L isomers	Yes	No	**Yes**
Isotopes	Surrogates	Surrogates	**Matrix Rec Correction**

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Solid Method Comparisons

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Category	Draft EPA Method	ASTM D7968-14	TestAmerica Method 537Mod
Purpose	**Definitive**	Screen	**Definitive**
Matrix	Biosolids	Soil	Soil/Sediment/Tissue
Validated	Single Lab	Single Lab	Single Lab
Sample size	0.5 g	2 g	5 g
Holding times	60/30	28	14/40, 365/40
Extraction	Digest/Sonication	Tumble	Shake/Sonication
Clean ups	**SPE**	None	**SPE**
Analytes	**25**	21	**25**
RL Range	0.25-5.0 ppb	**0.025 - 0.125 ppb**	0.2 - 20 ppb
Analysis	MRM LCMSMS	MRM LCMSMS	MRM LCMSMS
Quantitation	**Isotope Dilution**	ES	**Isotope Dilution**
B/L isomers	**Yes**	No	**Yes**
Isotopes	**Matrix Rec Correction**	Surrogate	**Matrix Rec Correction**

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Why so much method variability?

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- **Inconsistent quantitation of branched and linear isomers**
- Absence of multi-lab validated methods
- Limited certification programs
- Differences in extraction efficiencies – analyte sorbent dependent
- External, internal and isotope dilution quantitation schemes
- **Lack of proven commercially available PT samples**
- Use of isotopically labeled extraction surrogates
- Lack of commercially available standard materials and true second sources
- Target analyte losses during filtration
- Absence of demonstrated cleanup techniques for complex matrices
- **Wide variety of container types and holding times**

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Show Branched and Linear error in PFOS and PFOA

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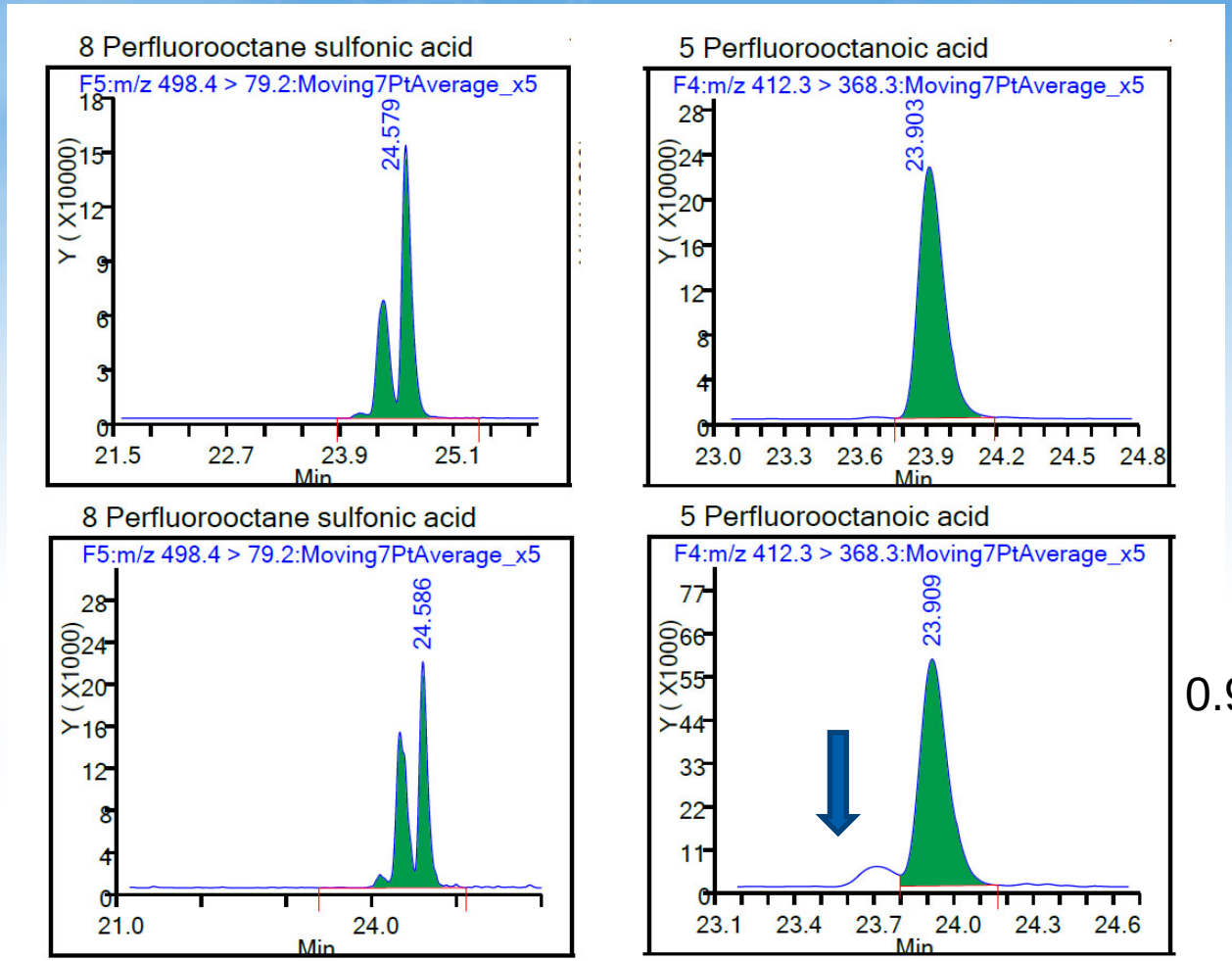
Standard

Sample



0.99 vs 1.20 ng/ml

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PT variability

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- What is the pH?
- Is there headspace in an aqueous container?
- Is the spiking standard stored in methanol?
- What kind of containers and lids are used?
- Does the spiking container have branched and linear isomers?
- Was water PFAS free?
- Were the spiking levels verified by third party?
- Were the acceptance levels verified by third party?

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Sample Collection Guidance More Variability

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"Confusion and clutter are the failure of design, not the attributes of information."

- Samples should be collected in HDPE bottles fitted with unlined (no Teflon) polyethylene screw caps.
- In addition, the sampler should avoid contact with fluoropolymers, aluminum foil, and food wrappers.
- Samples should not be field filtered.
- Samples must be shipped at <10ºC.
- Lack of validated extraction and analytical holding times for a wide variety of PFAS compounds.

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How can we mitigate variability?

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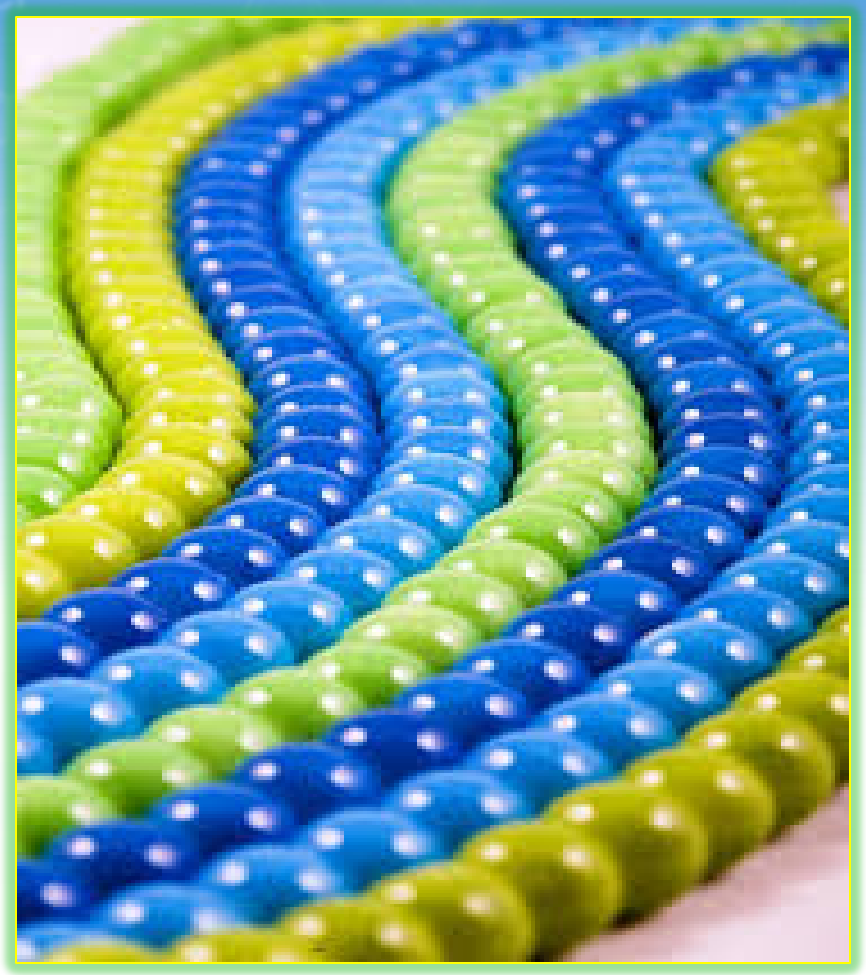
- Apply tandem mass spectrometry technology
- Implement an isotope dilution quantitation scheme
- Compensate for losses with matrix recovery correction
- Share our knowledge
- Invest resources in multi-lab validation



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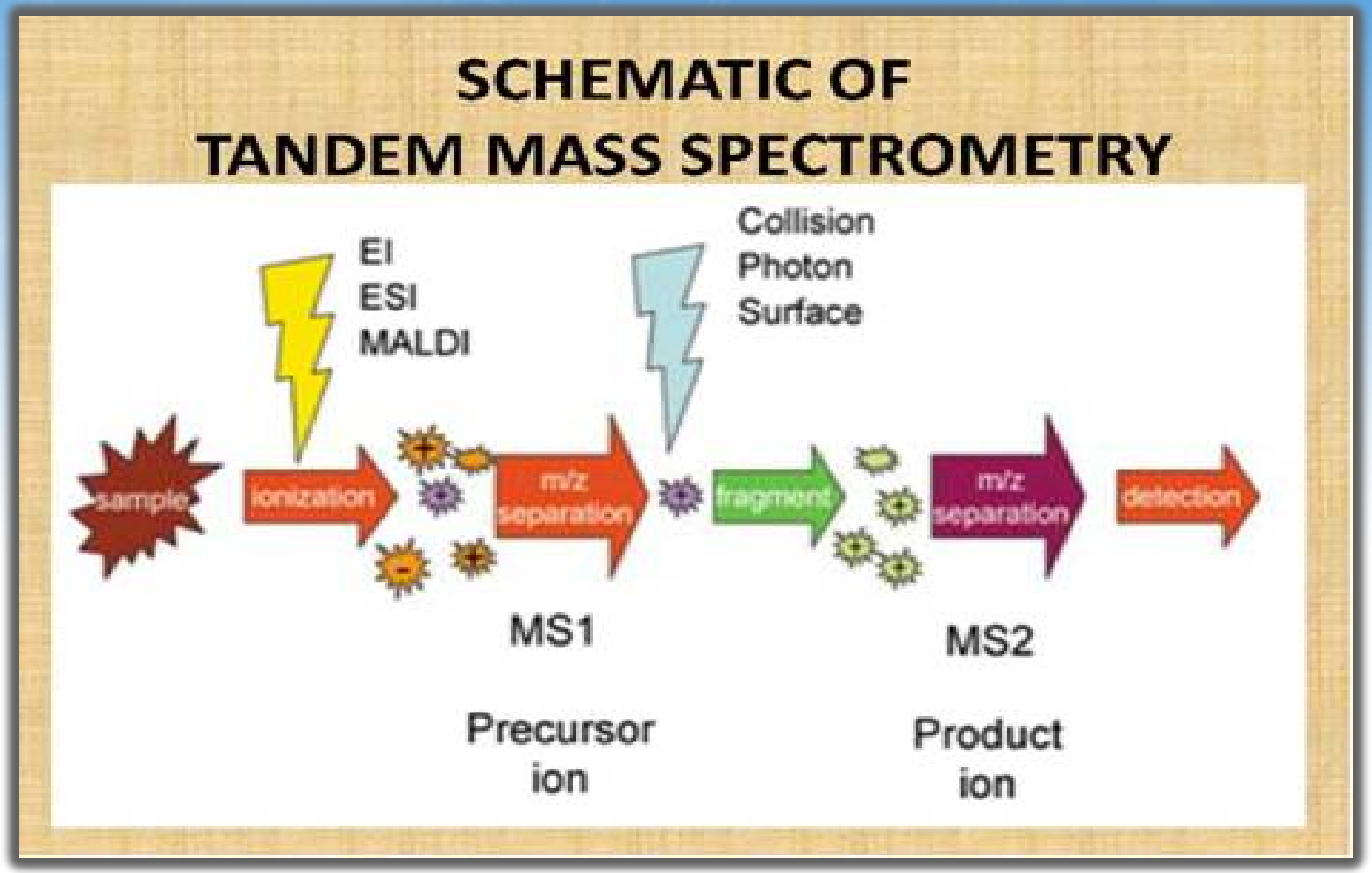
LC/MS/MS – Electrospray Ionization



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Advantages of LC/MS/MS

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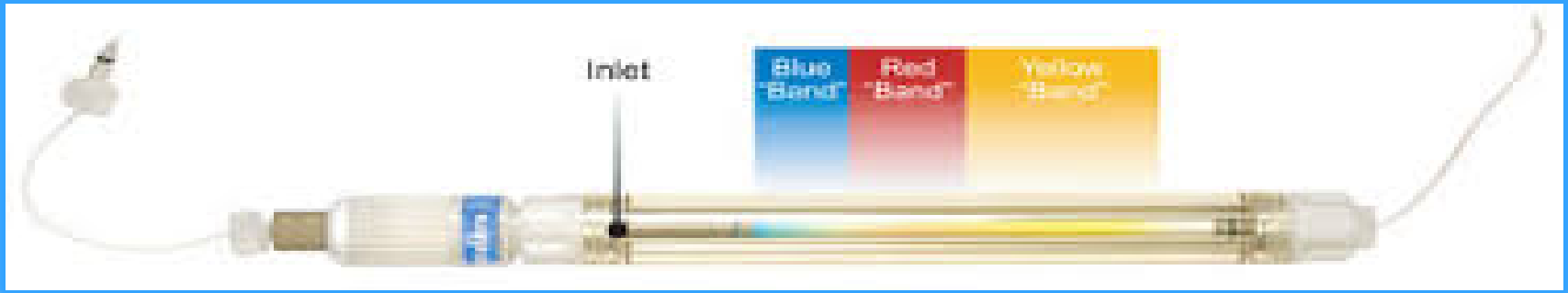

Specificity/Selectivity - A target analyte's MRM response is highly characteristic of its identity. LC/MS/MS analyses are more than **100 times better at filtering interferences** than conventional instrumentation

Sensitivity - Softer ionization than Electron Impact (EI) GCMS – allows for **thermally labile** analytes to be detected

Ruggedness – improved reproducibility for a wide variety of parameters and matrices and improved productivity

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LC/MS/MS Identifications

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Identification based on 3 characteristics:

- **Retention time from ion exchange separation**
- Negative ions formed in electrospray interface
- Molecular ions produced in first stage
- **Transition to characteristic daughter ions, detected in third stage**
- **Ion ratios provide confirmation**

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Advantages of Isotope Dilution Quantitation

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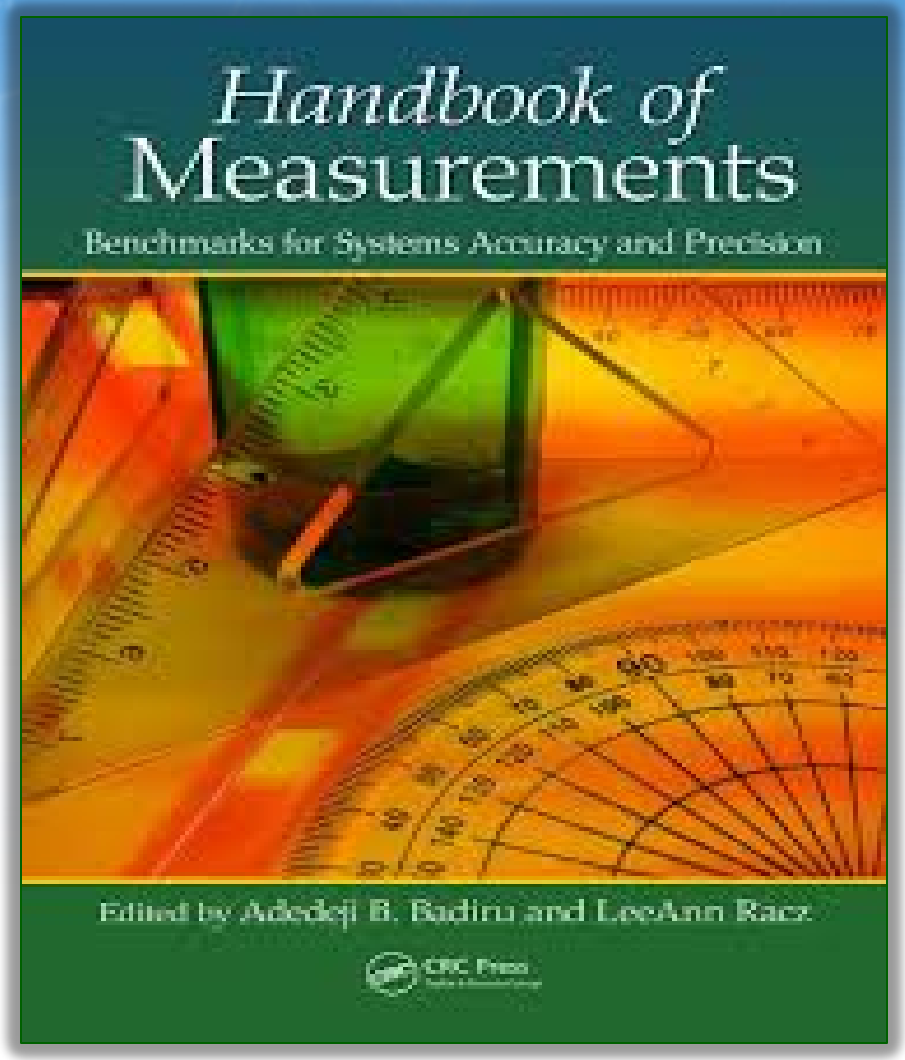
- Most accurate and precise calibration method available
- Partial loss of analyte during preparation is compensated for since chemical interferences are not an issue
- Allows for matrix recovery correction – what affects the native analyte will equally affect the isotope
- Correction for signal drift
- Improved qualitative identification – RT shifts



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Extraction by Method 537 Mod – Aqueous and Solid Matrices

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1. Sample collection and shipment to the lab chilled in HDPE bottles with DW preservative if appropriate.

2. Measure 250/500 mls of sample and spike with isotopically labeled target analytes.

3. Prepare SPE, load sample and elute PFAS off the cartridge with an ammonium hydroxide/methanol solution.

1. Sample collection and shipment to the lab chilled in HDPE bottles.

2. Measure 5 g of sample and spike with isotopically labeled target analytes. Extract with KOH/MeOH. Shake for 3 hours and sonicate for 12 hours

3. Prepare SPE, load sample and elute PFAS off the cartridge with an ammonium hydroxide/methanol solution.

Move on to the Analysis

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Analysis by Method 537 Mod – Aqueous and Solid Matrices

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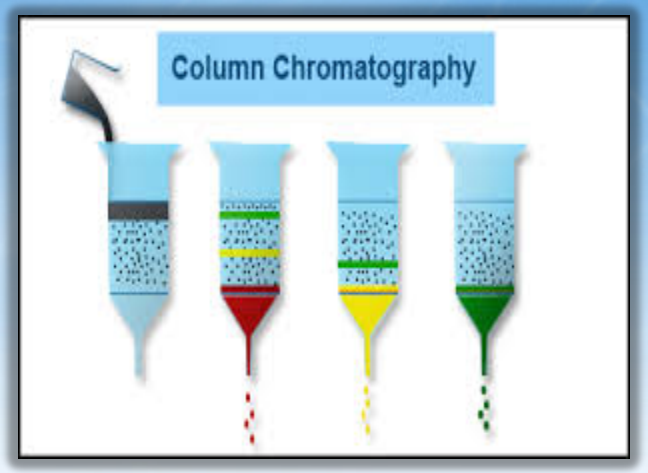

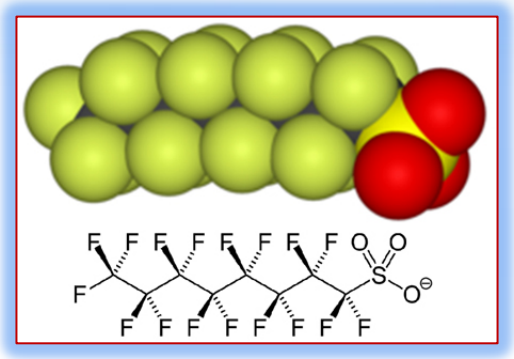

4. Concentrate PFAS extract to dryness. Add methanol to each, soak and vortex to mix well. Then add water to final composition of 80:20 methanol:water

5. Analyze by LCMSMS using a C18 column with a gradient program using 20 mM ammonium acetate/water and methanol. Mass spec is operated in (ESI) negative ion mode.

6. Process and review data. Assess QC elements, narrate anomalies and send report to client.

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Compound Name	Abbr.	CAS #	Method 537	Aqueous (ng/L)		Soil (ug/Kg)	
Perfluoroalkylcarboxylic acids (PFCAs)				RL	MDL	RL	MDL
Perfluoro-n-butanoic acid	PFBA	375-22-4		2.00	0.458	0.200	0.0650
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3		2.00	0.989	0.200	0.1310
Perfluoro-n-hexanoic acid	PFHxA	307-24-4	Y	2.00	0.786	0.200	0.0710
Perfluoro-n-heptanoic acid	PFHpA	375-85-9	Y	2.00	0.802	0.200	0.0880
Perfluoro-n-octanoic acid	PFOA	335-67-1	Y	2.00	0.748	0.200	0.102
Perfluoro-n-nonanoic acid	PFNA	375-95-1	Y	2.00	0.654	0.200	0.0830
Perfluoro-n-decanoic acid	PFDA	335-76-2	Y	2.00	0.440	0.200	0.0570
Perfluoro-n-undecanoic acid	PFUnA	2058-94-8	Y	2.00	0.748	0.200	0.106
Perfluoro-n-dodecanoic acid	PFDoA	307-55-1	Y	2.00	0.584	0.200	0.121
Perfluoro-n-tridecanoic acid	PFTrDA	72629-94-8	Y	2.00	0.551	0.200	0.0920
Perfluoro-n-tetradecanoic acid	PFTeDA	376-06-7	Y	2.00	0.199	0.200	0.0580
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5		2.00	0.123	0.200	0.0520
Perfluoro-n-octandecanoic acid	PFODA	16517-11-6		2.00	0.672	0.200	0.100
Perfluorinated sulfonic acids (PFSAs)							
Perfluoro-1-butanesulfonic acid	PFBS	375-73-5	Y	2.00	0.918	0.200	0.103
Perfluoro-1-hexanesulfonic acid	PFHxS	355-46-4	Y	2.00	0.870	0.200	0.118
Perfluoro-1-heptanesulfonic acid	PFHpS	375-92-8		2.00	0.713	0.200	0.118
Perfluoro-1-octanesulfonic acid	PFOS	1763-23-1	Y	2.00	1.28	0.200	0.126
Perfluoro-1-decanesulfonic acid	PFDS	335-77-3		2.00	1.21	0.200	0.0720
Perfluorinated sulfonamides (FOSA)							
N-ethylperfluoro-1-octanesulfonamide	EtFOSA	4151-50-2		100	13.0	20.0	2.53
N-methylperfluoro-1-octansulfonamide	MeFOSA	31506-32-8		100	22.4	20.0	3.36
Perfluorinated sulfonamidoacetic acids (FOSAA)							
N-ethylperfluoro-1-octanesulfonamidoacetic acid	EtFOSAA	2991-50-6	Y	20.0	5.02	2.00	0.390
N-methylperfluoro-1-octanesulfonamidoacetic acid	MeFOSAA	2355-31-9	Y	20.0	5.64	2.00	1.30
Perfluoroalkylsulfonamidoethanols (PFOSEs)							
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	Et-FOSE (N-Et-FOSE)	1691-99-2		40.0	7.50	4.00	0.750
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	Me-FOSE (N-Me-FOSE)	24448-09-7		40.0	7.30	4.00	0.750
Fluorotelomer sulfonates (FTS)							
1H,1H,2H,2H-perfluorooctane sulfonate (6:2)	6:2 FTS	27619-97-2		20.0	3.82	2.00	0.390
1H,1H,2H,2H-perfluorodecane sulfonate (8:2)	8:2 FTS	39108-34-4		20.0	4.04	2.00	0.680

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Capabilities for Complex Matrices

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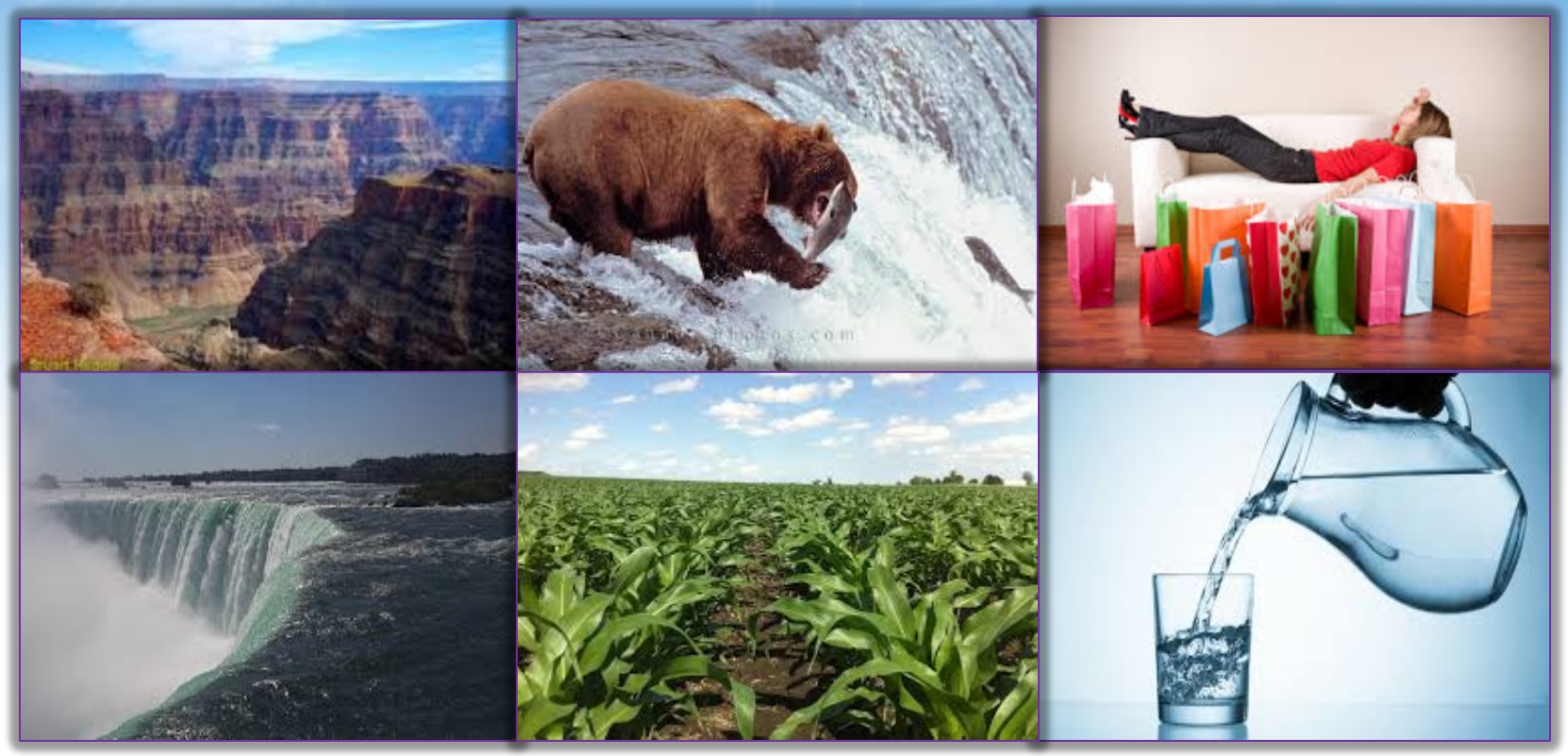

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Did We Solve Our Analytical Problems?

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PROs	CONs
Application of Isotope Dilution	Not multi-lab validated
Long List of Analytes	Hundreds more analytes
Application to complex matrices	Inconsistent application of branched and linear isomers
Ultra trace level detection limits	Requires extensive sample prep
Trizma for Drinking Waters	Trizma for short analyte list only

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Future Concerns

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- The TOP assay and PIGE demonstrate the mass balance is not closed
- Analyte lists are growing for discrete methods, may lead to forensics.
- LC PFASs are being replaced by SC PFASs and little is know about the toxicity
- On-going method confusion must be improved
- On-going data variability must be improved

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Questions ???

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Thank you for attending

The Analysis of Polyfluorinated Alkyl Substances (PFAS) including PFOS and PFOA

Karla Buechler – (916) 374-4378

Karla.Buechler@testamericainc.com

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