



Comparison of ASTM D7979 PFAS compounds by the ASTM method versus Solid Phase Extraction

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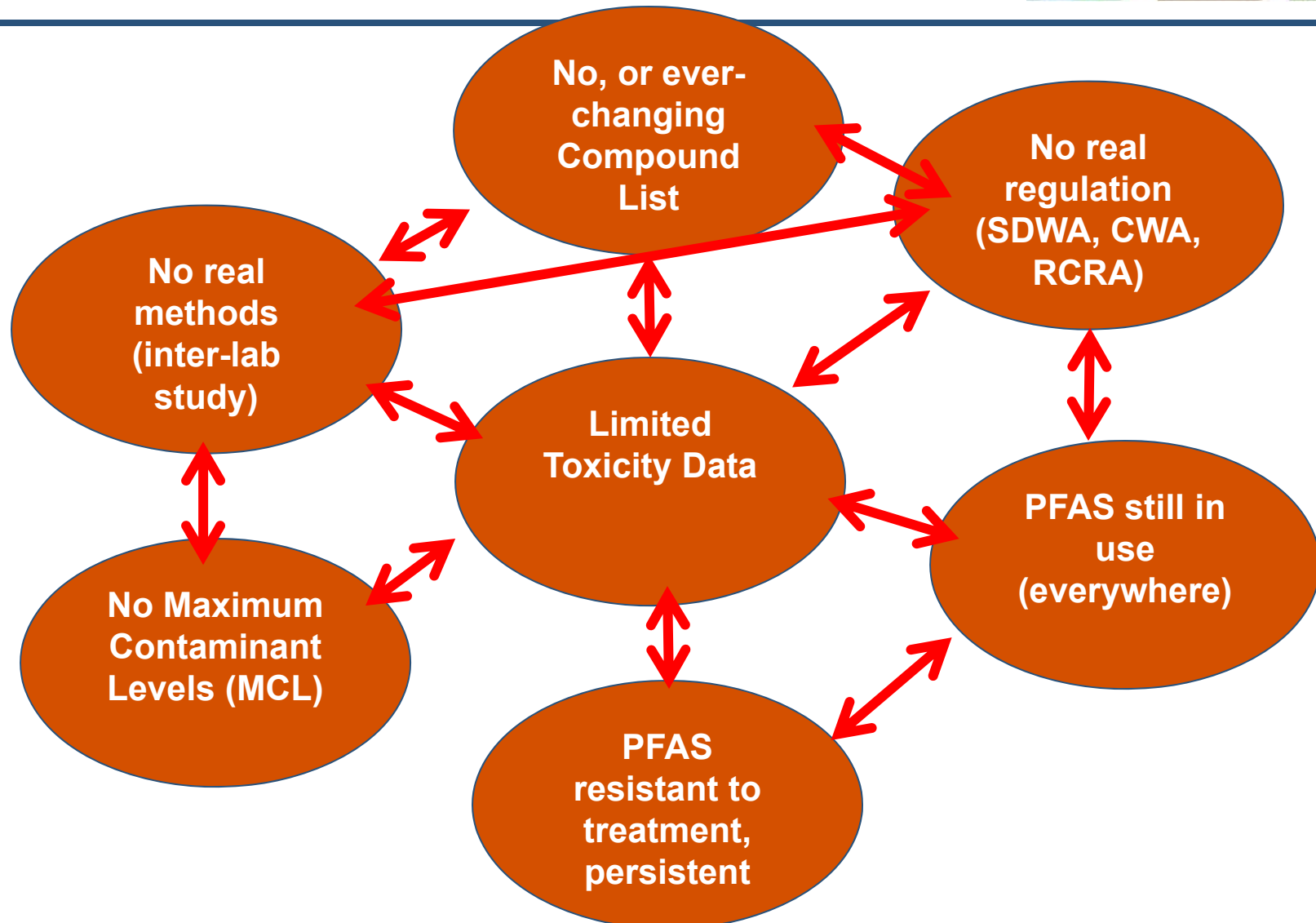


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Southampton, PA

There are few/no EPA “regulations” for PFAS



How many PFCs should we look for?



- **2 (PFOA & PFOS)?**
- **6 UCMR3 compounds?**
- **12 or all 14 EPA 537 compounds?**
- **21 compounds (NYDEC, etc.)?**
- **24 or more compounds (DOD, NHDES, MIDEQ, EPA, ASTM, etc.)?**
- **Emerging PFCs (GenX, ADONA, etc.)?**

Which method should we use?



- **EPA 537?**
- **EPA 537M?**
- **In-House?**
- **ASTM D7979 or D7968**
- **ISO?**

Method	EPA 537	D7979	ISO CD 21675	D7968
Validation	Single lab (ORD/UCMR3)	Two Lab (Region V and ASTM)	Multiple Lab	Single lab (Region V and ASTM)
Extraction	SPE 250 ml → 1 ml	Dilute 5 ml with 5 ml MeOH, Filter, direct inject	SPE 1000 ml 500 ml 250 ml 100 ml 50 ml	Extract 2 g with 10 ml (1+1) MeOH
Holding time	Extract in 14 analyze in 28 days 5g/L Trisma ≤ 6°C	28 days ≤ 6°C	4 weeks 5±3 °C	28 days ≤ 6°C

Comparison of matrices tested



Method	EPA 537	D7979	ISO 21675	D7968
Matrix	Drinking Water	Water and sludge (<0.2% Solids)	Water (<0.2 % solids)	Soil
Matrices	Cincinnati tap, ground, surface, UCMR samples	Reagent water, Chicago river water, POTW effluent, POTW influent, 2 POTW with overflow	Drinking water, river water, seawater, wastewater	Ottawa sand, Frederick sand, Annapolis clay, Vicksburg clay, Vicksburg silt

Comparison of method quantitation



Method	EPA 537	D7979	ISO	D7968
Analytes	14 + 3 surrogates and 3 internal standards	21 + 9 surrogates	30 + (31 IS)	21 + 9 surrogates
Quantitation Range	5 – 15 ng/L (at 1/250)	5 – 8000 ng/L	> 0.002 ng/L	25 – 20,000 ng/Kg
Quantitation	IS	ES, (ID, or IS allowed)	ID or ES*	ES, (ID, or IS allowed)

* For analytes with no isotope, and for extraction/method optimization



Comparison of Method calibration criteria

Method	EPA 537	D7979	ISO	D7968
Calibration	≥ 5 points	5 – 9 points	≥ 5 points	5 – 9 points
Force through origin	yes	no	no	no
Fit	RSE ≤ 30%	RSE ≤ 30%	ISO 8466-1	RSE ≤ 30%
Asymmetry	0.8 – 1.5	Not required	Not required	Not required
	Require chromatographic separation of branched and linear isomers			
Confirmation ion	Not required	Yes, if available	Yes, if available	Yes, if available

Comparison of Method batch QC criteria



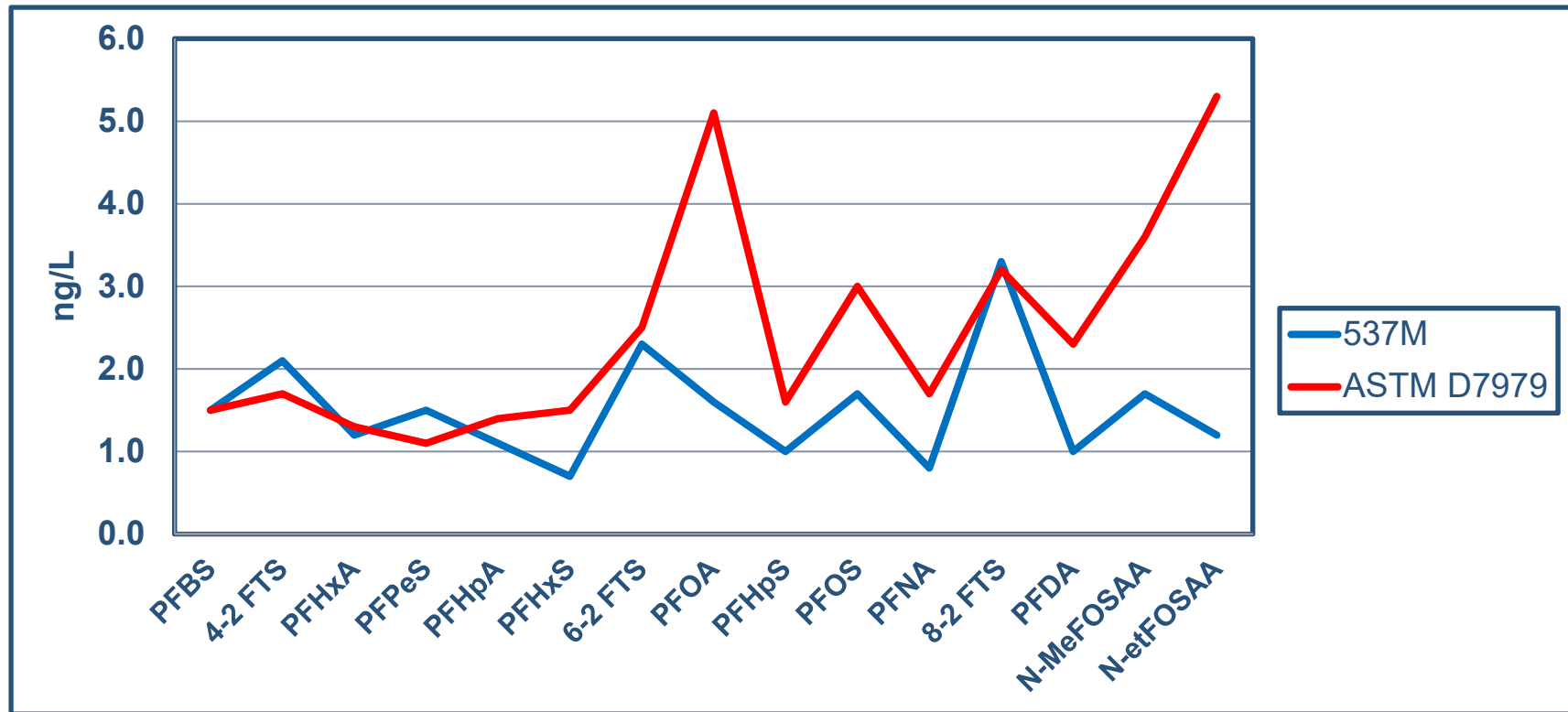
Method	EPA 537	D7979	ISO	D7968
Batch size	≤ 20 samples	≤ 30 samples	≤ 20 samples	≤ 30 samples
Blank	≤ 1/3 MRL	≤ 1/2 “RLCS”	≤ 1/10 ML	≤ 1/2 “RLCS”
MRL	50 – 150 %	35 – 150%	No information	35 – 150%
IS	< 50% Area Drift	Not required (70-130%)	70 – 125%	Not required (70-130%)
Surrogate recovery	70 – 130 %	70 – 130 %	70- 125% (IS)	70 – 130 %

Comparison of sample specific batch QC criteria



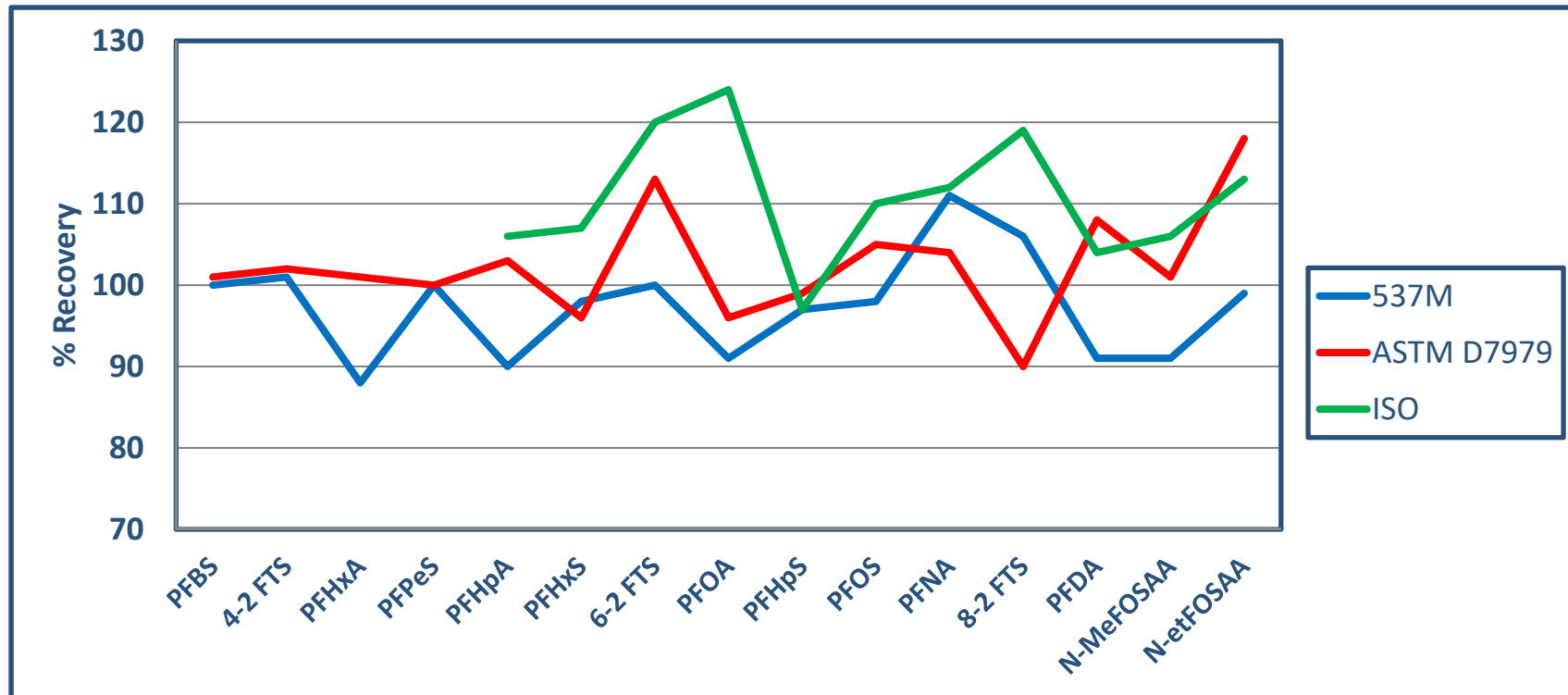
Method	EPA 537	D7979	ISO	D7968
MS/MSD recovery	70 – 130 %	70 – 130 %	70 – 125%	70 – 130 %
RPD	≤ 30 %	≤ 30 %	No criteria, see ILT data	≤ 30 %

Comparison of MRL between ASTM and EPA 537M*



*Modification of target list only

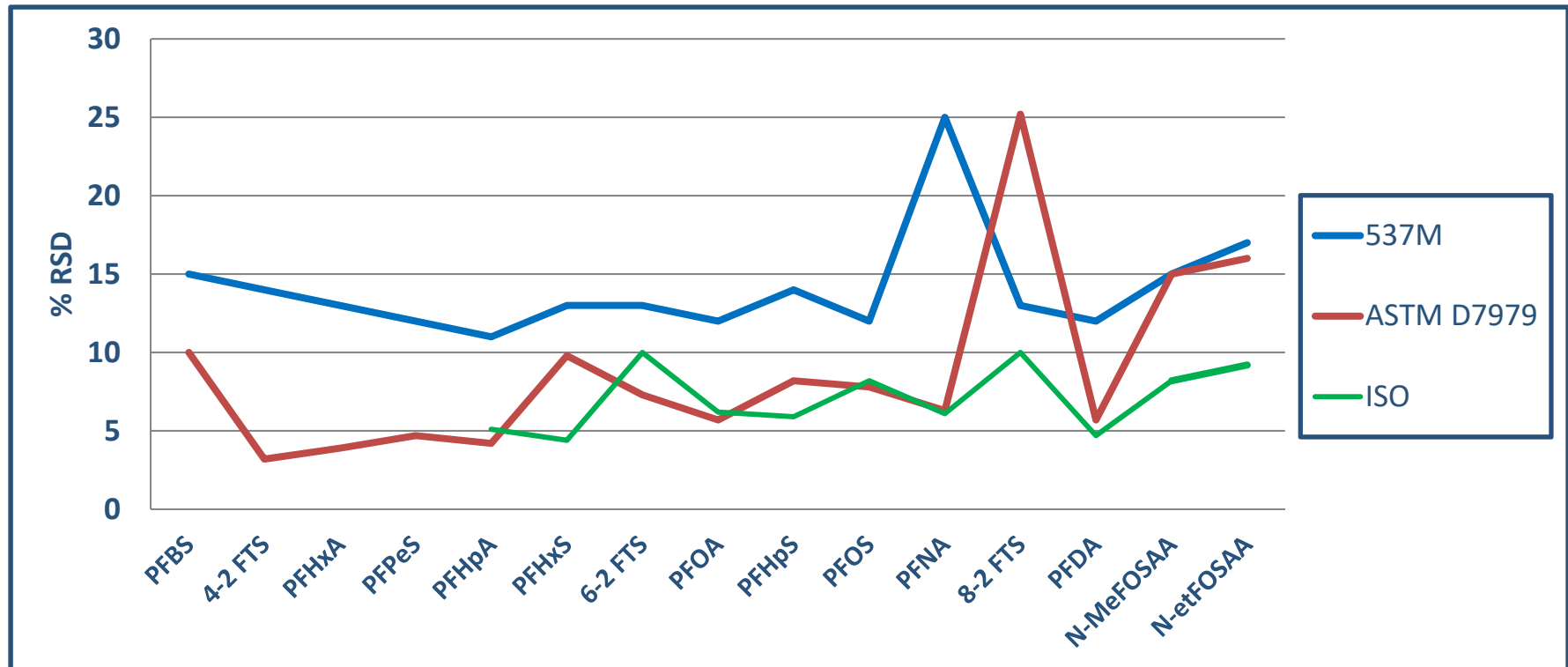
Comparison of %Recovery between ASTM EPA 537M*, and ISO 21675**



*Modification of target list only

** ILT data 10 – 20 labs in river water

Comparison of %RSD between ASTM EPA 537M*, and ISO 21675**



*Modification of target list only

** ILT data 10 – 20 labs in river water

Problems encountered when running PFAS



- **No PFAS listed as CWA “Toxic Pollutant”**
 - **No NPDES**
- **PFAS not listed as CERCLA hazardous substance**
 - **No federal cleanup or reporting**
- **Limited toxicity data**
 - **No SDWA MCL**



In absence of PFAS “regulation”:



- **There is no established list of analytes**
 - Which ones to run?
- **No “approved” methods by program**
 - What method?
- **Multitude of “modified” EPA 537**
 - Cannot modify SDWA methods

EPA Method 537 is a drinking water method

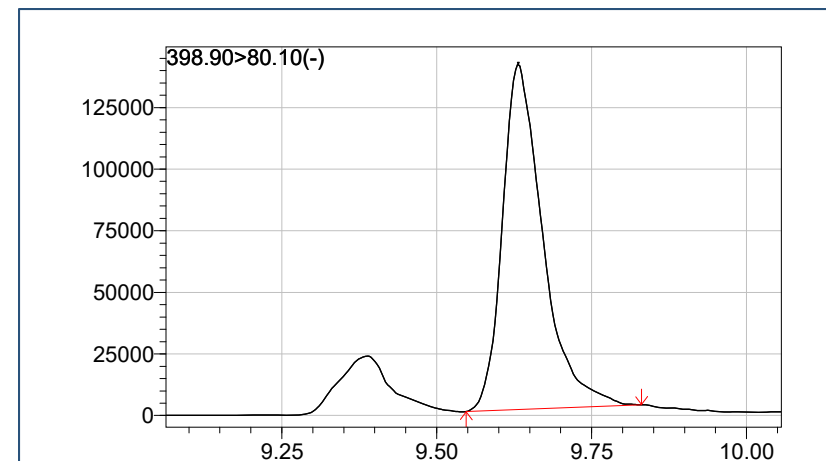


- **EPA needs an “approved” method to establish an MCL**
 - **EPA 537 a UCMR method for Drinking Water**
- **EPA 537 is not:**
 - **For non-potable water**
 - **A soil/solid waste method**

What does “modified” EPA Method 537 mean?



- **EPA 537 Modified (how?)**
 - **Additional analytes only?**
 - **No SPE or in-line SPE (loss?)**
 - **Different SPE media (WAX)**
 - **Isotope Dilution**
 - **Faster runs (be careful)**



Be sure to do this, when modifying a method

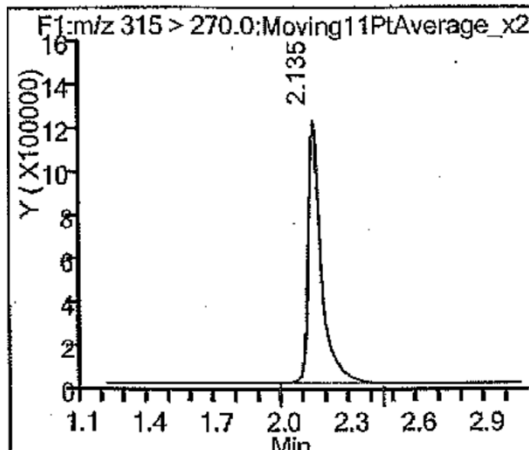


- **Good Chromatography required.**
- **Short run-times may not work on real matrices.**
- **Ion Ratios between primary and confirmatory required- removes false positives.**
- **In the next 2 slides the isotope peak shape should look similar to the analyte.**

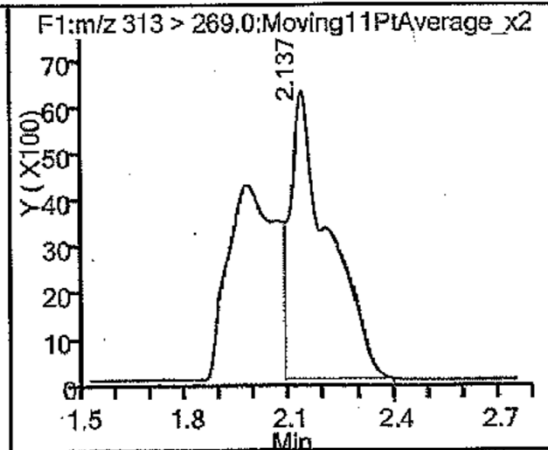
Real matrix data from a short run-time = "bad peaks"



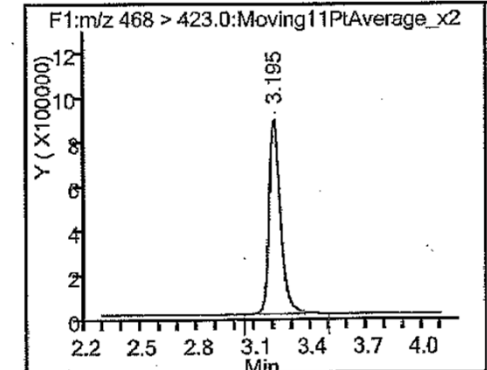
D 6 13C2 PFHxA



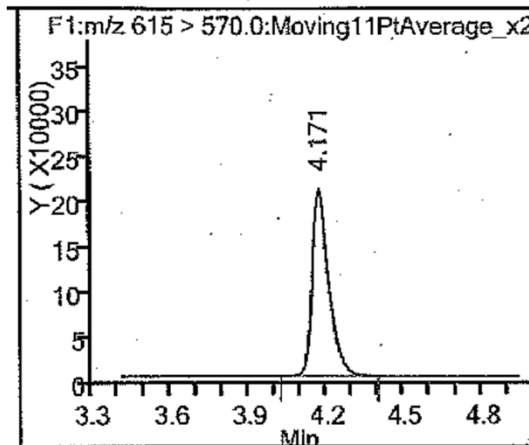
7 Perfluorohexanoic acid



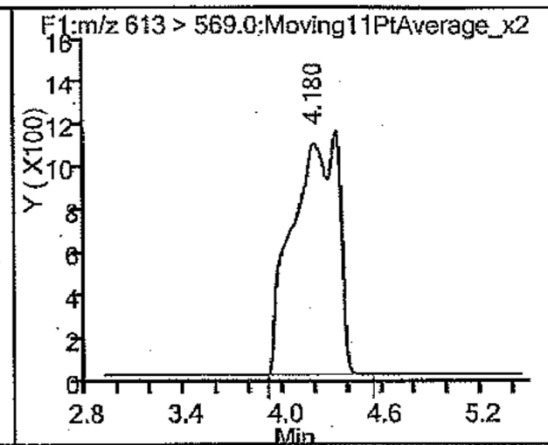
D 19 13C5 PFNA



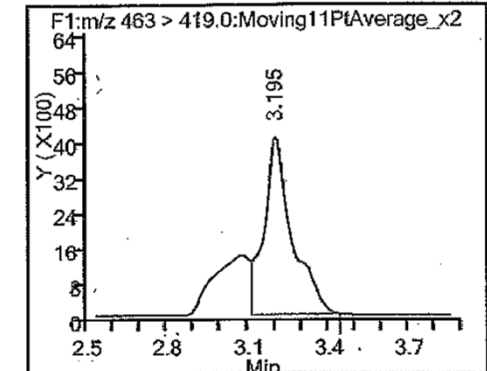
D 30 13C2 PFDoA



29 Perfluorododecanoic acid

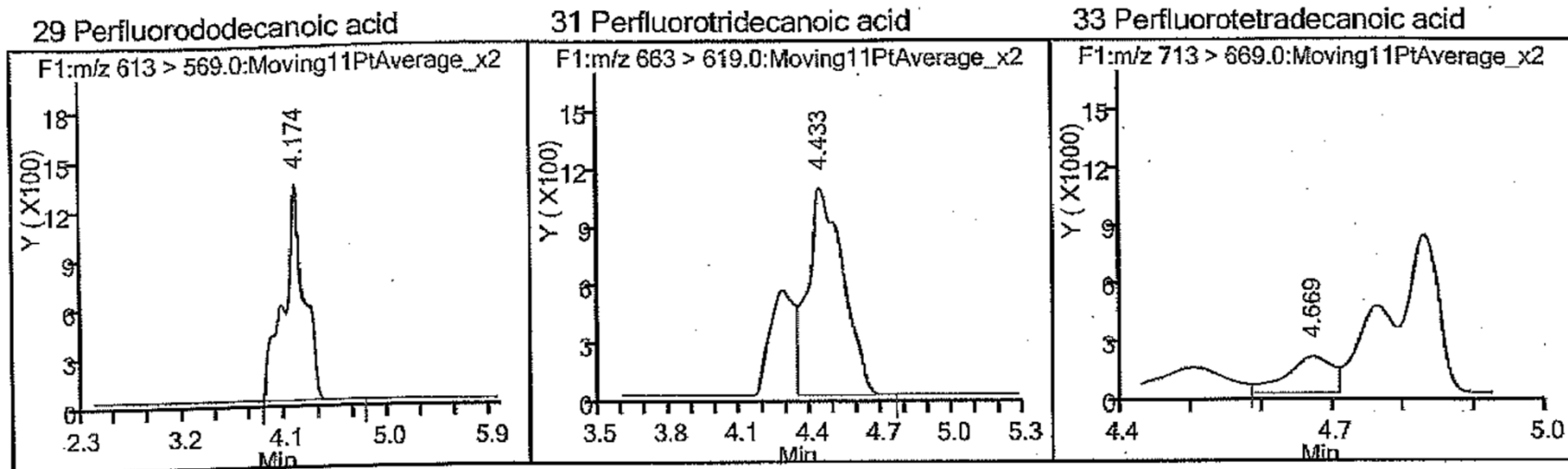


20 Perfluorononanoic acid



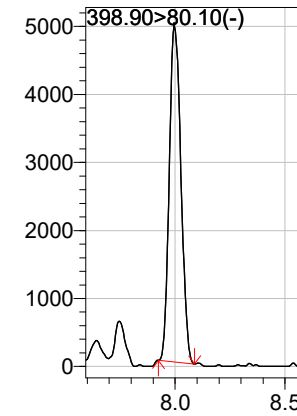
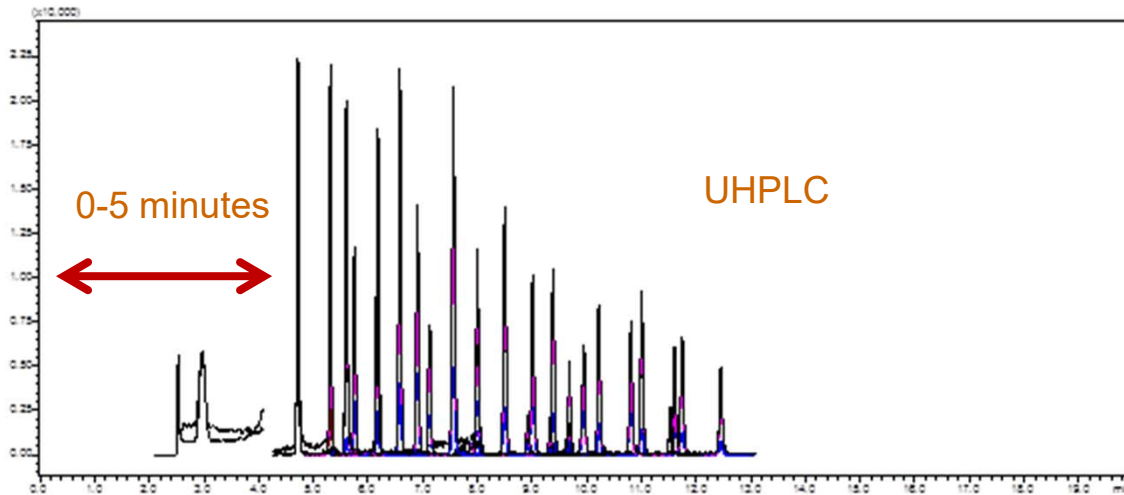
Note: All RT = < 5 minutes

Real matrix data from a short run-time – “bad peaks”

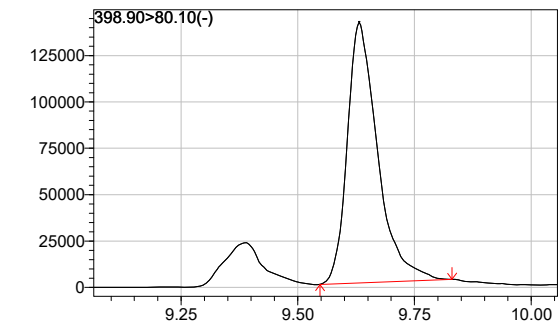
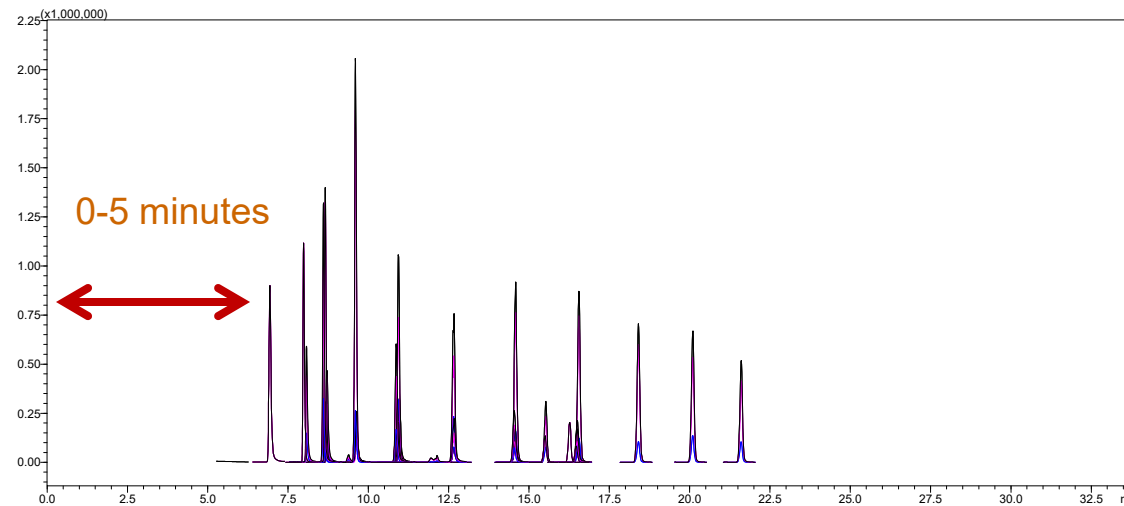


Note: All RT = < 5 minutes

Chromatography must split isomers, separate peaks -

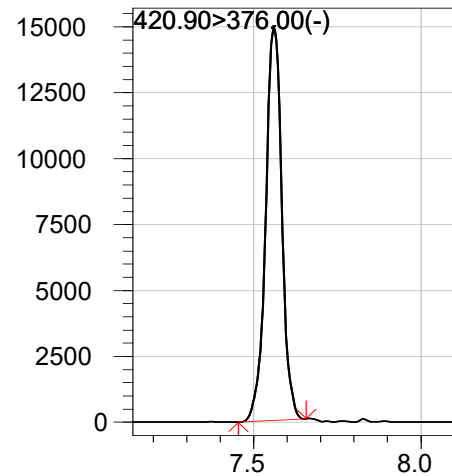
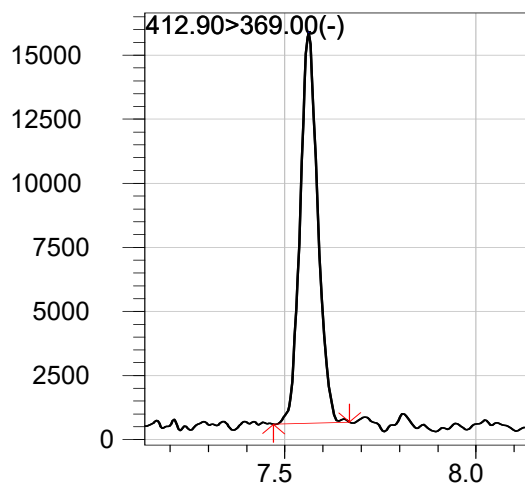


ASTM D7979

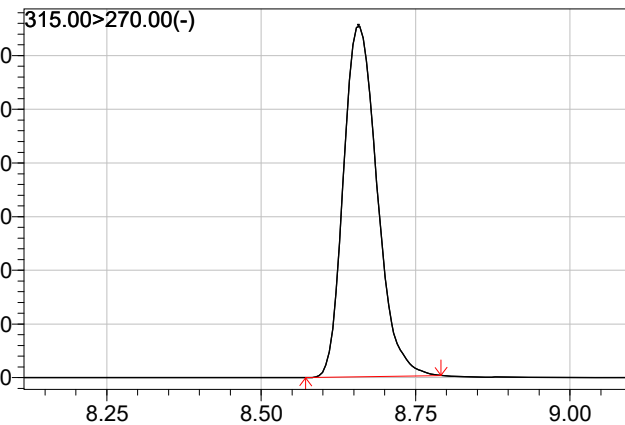
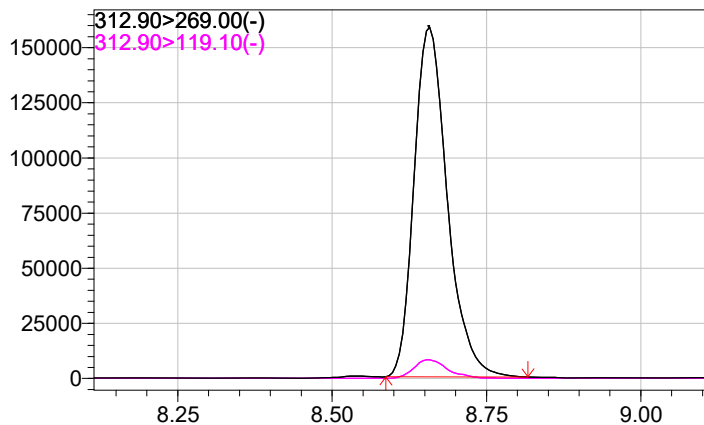


EPA 537

Chromatography must split isomers, separate peaks -



ASTM D7979,
analyte and SS



EPA 537, analyte
and SS

Potential existing PFAS methods



- **EPA regulatory methods require an inter-lab study**
 - **ASTM D7979 (water) to SW846 (8327)**
 - **ASTM D7968 (soil) to SW846?**
 - **EPA 537 updated (Drinking water)**
 - **Use ISO methods in US?**
 - **(no or limited associated QA/QC)**

LC/MS/MS is targeted analysis



- **LC/MS/MS methods only “see” what you are looking for**
 - **Targeted list**
 - **How many more are not measured?**
- **Use High Resolution method for discovery of unknowns**
 - **Single mass – still need a standard**

Summary



- **Three “methods” were compared:**
 - “direct injection” external standard calibration
 - SPE with injection internal standard calibration
 - SPE with (lab added) isotope dilution calibration

- **All methods have very similar QA/QC acceptance criteria**

- **All methods have similar MRL (no data for ISO)**

- **All methods have similar accuracy/precision**

Any Questions?



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Thank You!