Comparison of Three Methods for the Analysis of PFAS

William Lipps, Eurofins Eaton Analytical

Monrovia


South Bend

Full Service Laboratories

Eurofins Lancaster Laboratories Env.
Lancaster, PA

Eurofins Calscience
Garden Grove, CA

Eurofins Spectrum Analytical
Agawam, MA
North Kingstown, RI

Centers of Excellence

Eurofins Air Toxics
Folsom, CA

Eurofins Eaton Analytical
Monrovia, CA
South Bend, IN

Eurofins Frontier Global Sciences
Bothell, WA

Eurofins QC
Southampton, PA

There are a multitude of lists with no defined method that includes all

- 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 (water)?

- EPA 537?
- EPA 537M?
- In-House?
- ASTM D7979
- ISO?

Method	EPA 537	D7979	ISO CD 21675
Validation	Single lab (ORD/UCMR3)	Two Lab (Region V and ASTM) PT samples	Multiple Lab
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
Holding time	Extract in 14 analyze in 28 days 5g/L Trisma ≤ 6°C	28 days ≤ 6°C	4 weeks 5±3 °C

Comparison of matrices tested

Method	EPA 537	D7979	ISO 21675
Matrix	Drinking Water	Water and sludge (<0.2% Solids)	Water (<0.2 % solids)
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

Comparison of method quantitation

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

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

Comparison of Method calibration criteria

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

Comparison of Method batch QC criteria

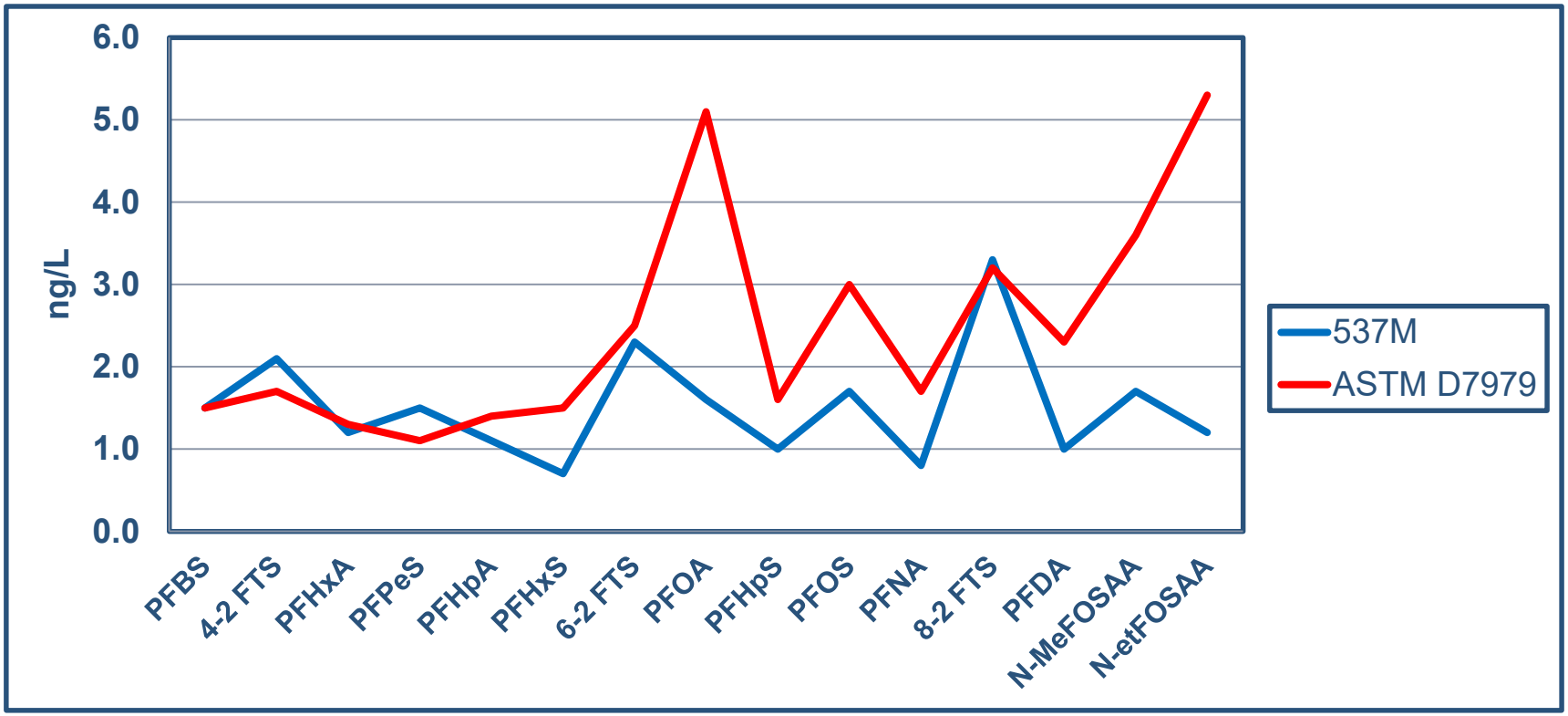
Method	EPA 537	D7979	ISO
Batch size	≤ 20 samples	≤ 30 samples	≤ 20 samples
Blank	≤ 1/3 MRL	≤ ½ "RLCS"	≤ 1/10 ML
MRL	50 – 150 %	35 – 150%	No information
IS	< 50% Area Drift	Not required (70-130%)	70 – 125%
Surrogate recovery	70 – 130 %	70 – 130 %	70- 125% (IS)

RLCS = Reporting Limit Control Standard

Comparison of sample specific batch QC criteria

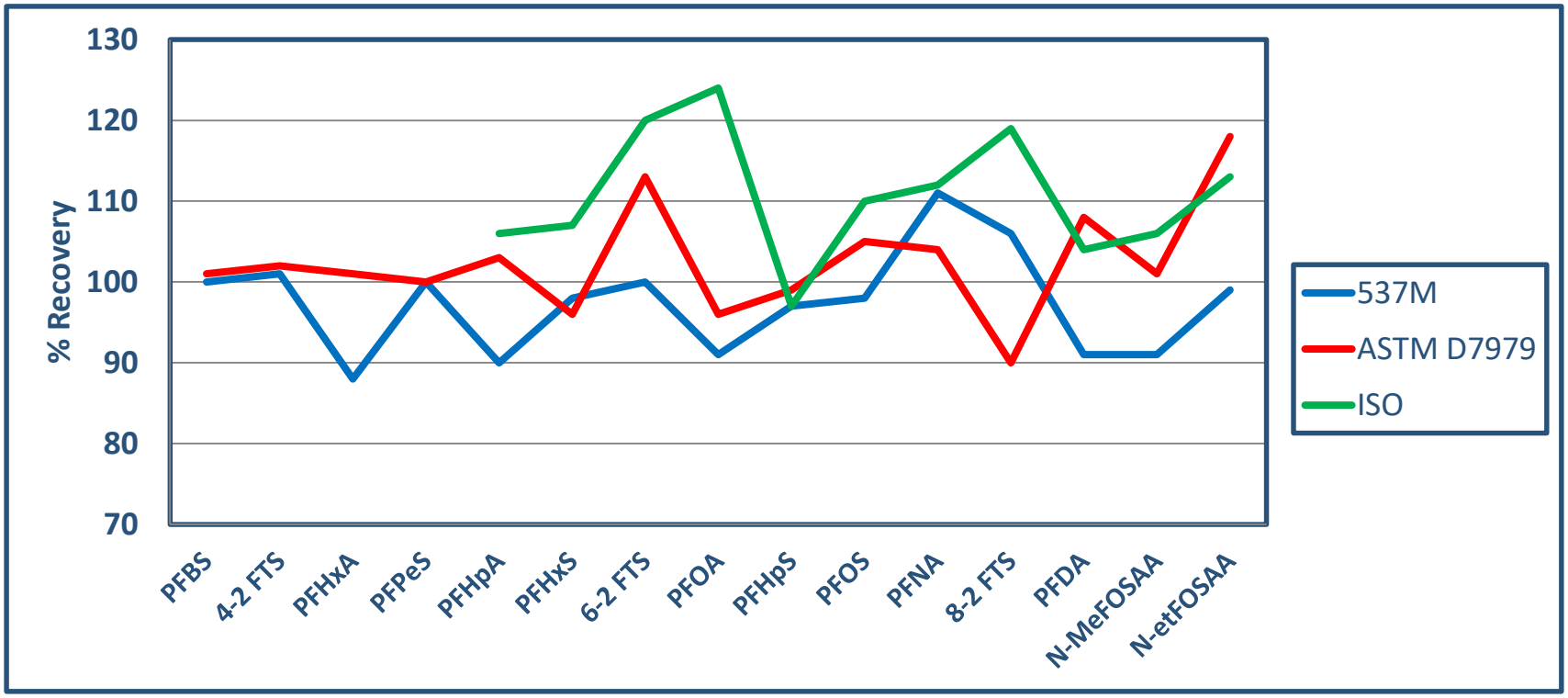
Method	EPA 537	D7979	ISO
MS/MSD recovery	70 – 130 %	70 – 130 %	70 – 125%
RPD	≤ 30 %	≤ 30 %	No criteria, see ILT data

Comparison of MRL between ASTM and EPA 537M*



*Modification of target list only

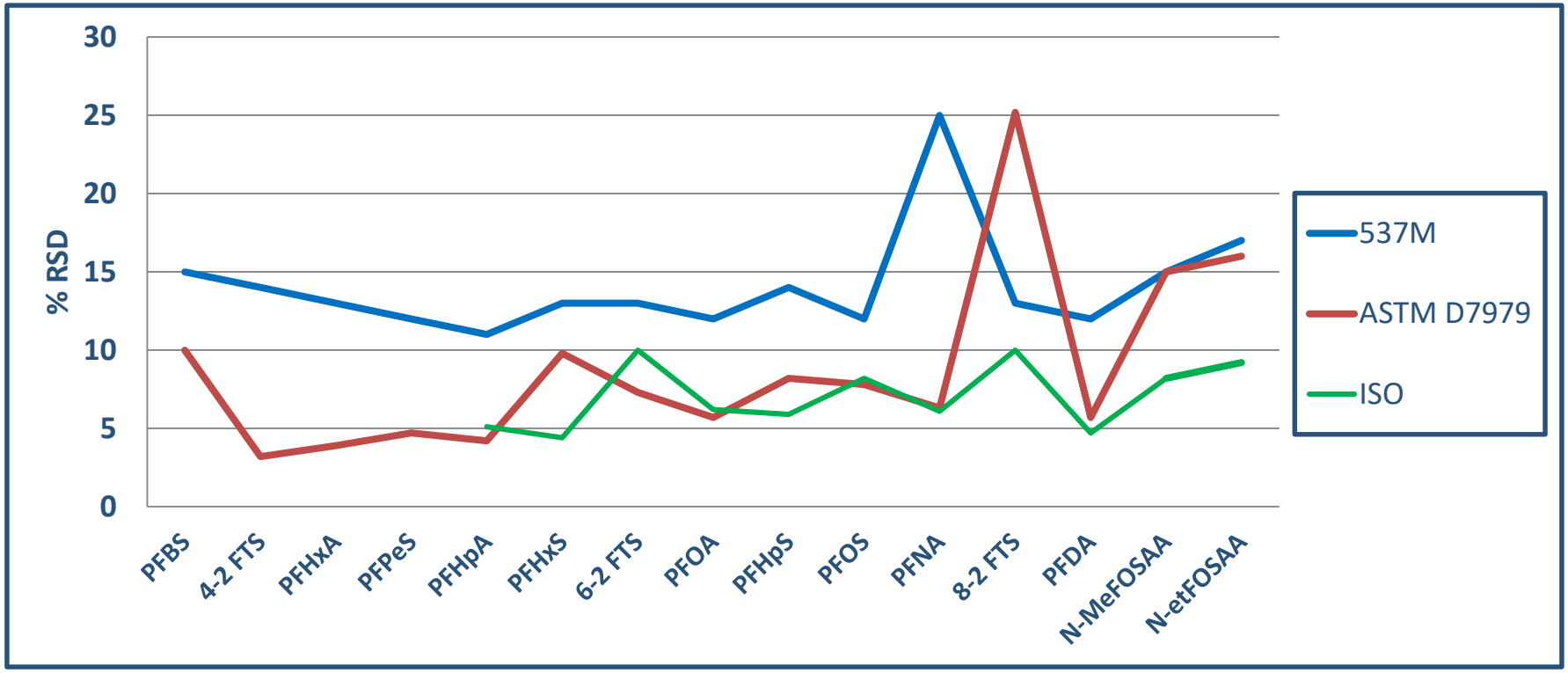
Comparison of %Recovery between ASTM EPA 537M*, and ISO 21675**



*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”:

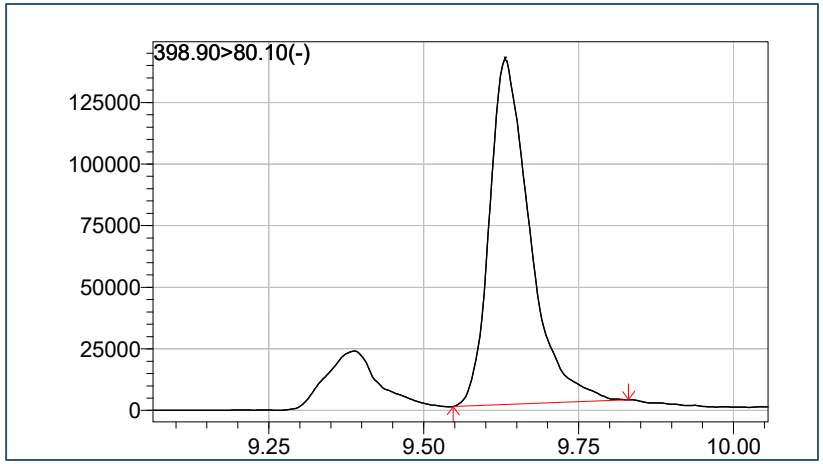
- There is no established list of analytes
  - Which ones to run?
- No “approved” methods by program
  - What method?
- Multitude of “modified” EPA 537
  - Cannot modify SDWA methods

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?

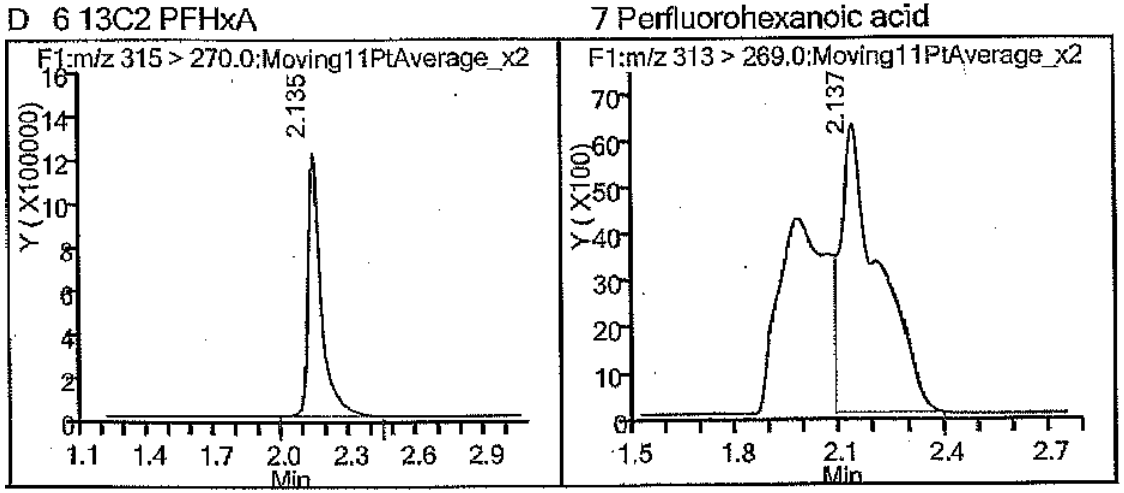
- **EPA 537 Modified (how?)**
  - **Additional analytes only?**
  - **No SPE or in-line SPE (loss?)**
  - **Different SPE media (WAX)**
  - **Isotope Dilution**
  - **Faster runs (be careful)**

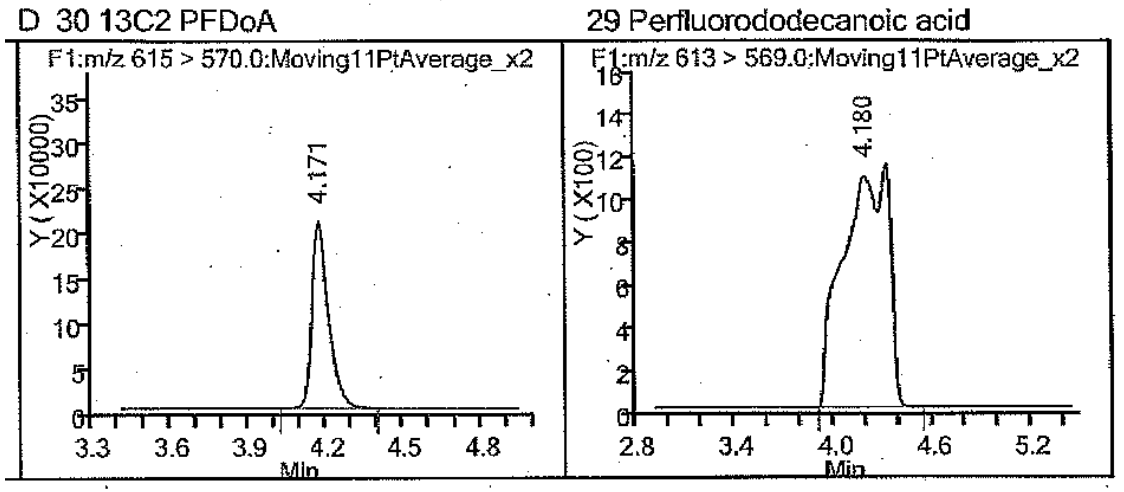


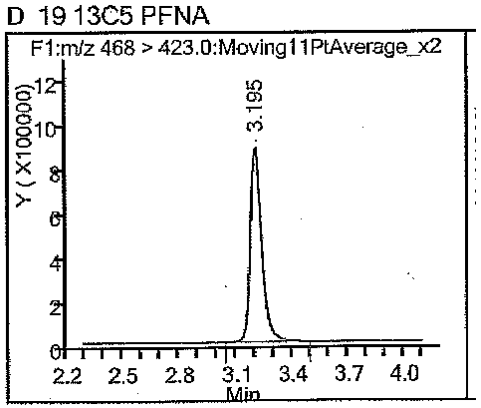
Be sure to do this, when modifying a method

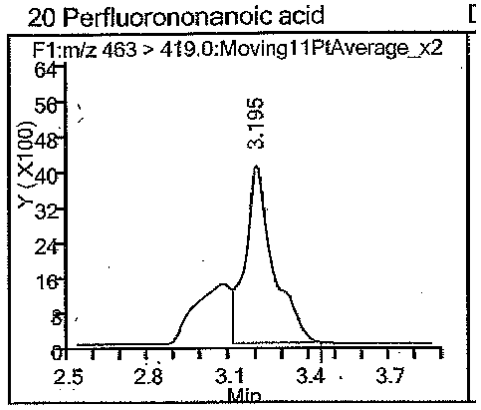
- Good Chromatography required.
- Short run-times may not work on real matrices.
- Ion Ratios between primary and confirmatory required- removes false positives.
- In the next 2 slides the isotope peak shape should look similar to the analyte.

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



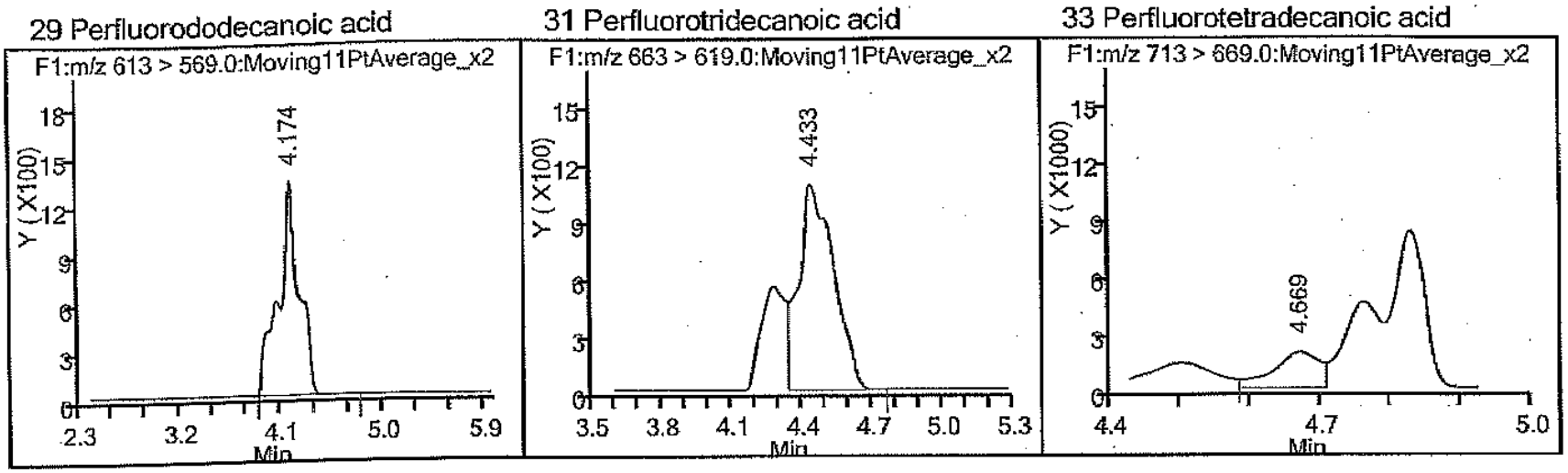






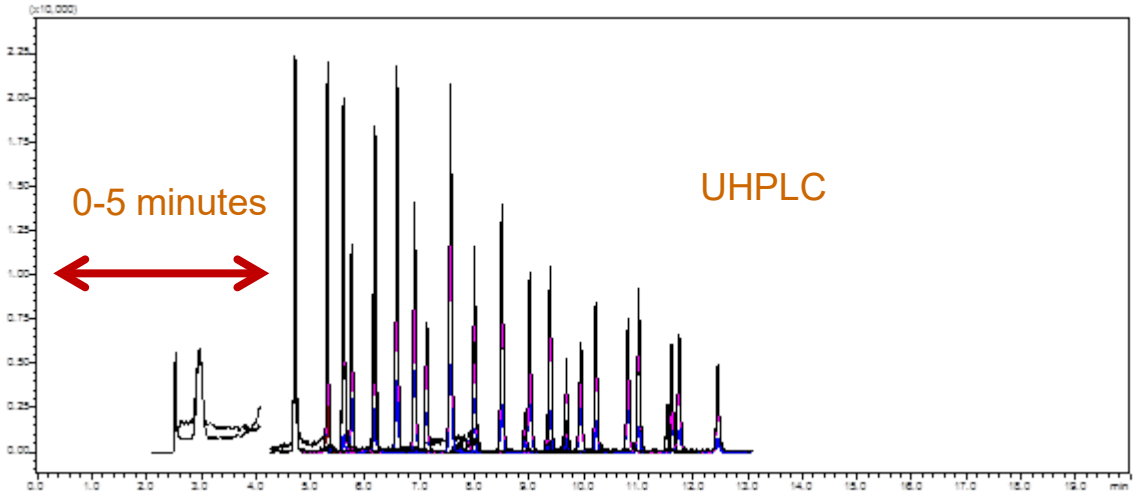
Note: All RT = < 5 minutes

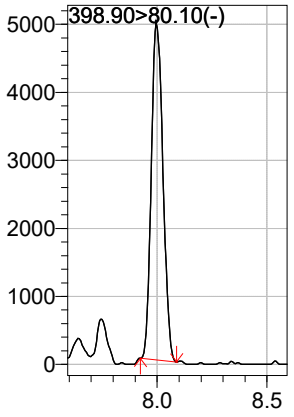
Real matrix data from a short run-time – “bad peaks”



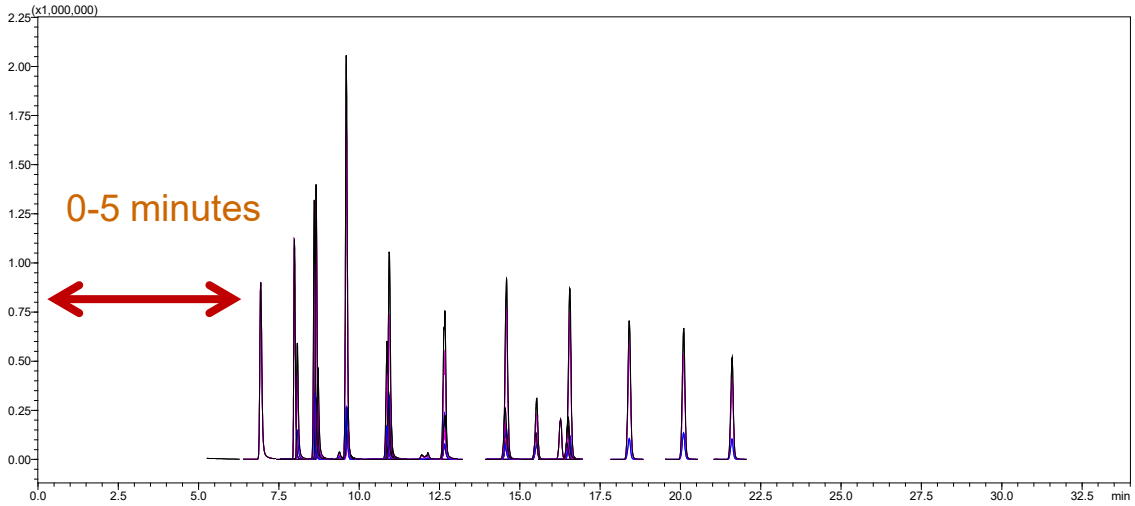
Note: All RT = < 5 minutes

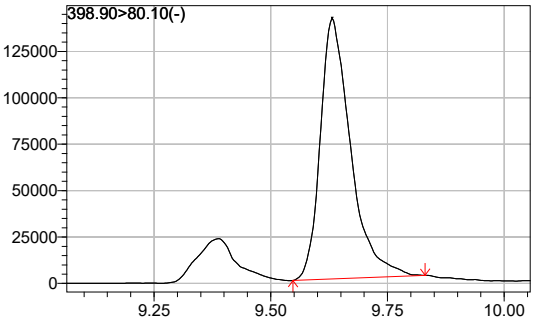
Chromatography must split isomers, separate peaks -





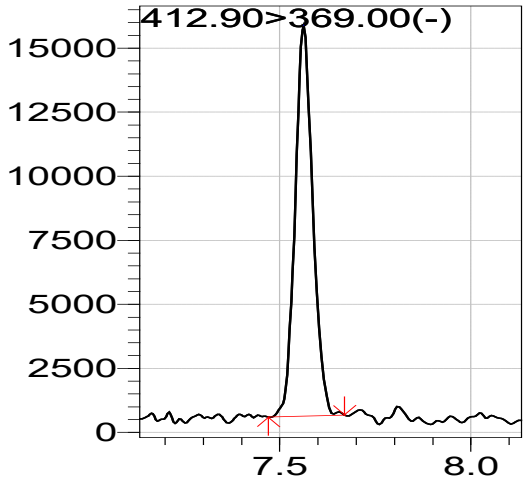
ASTM D7979

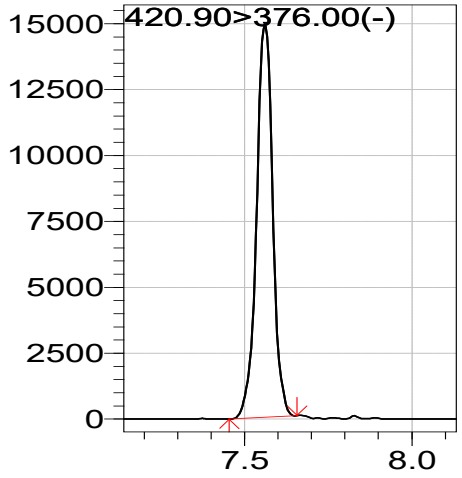




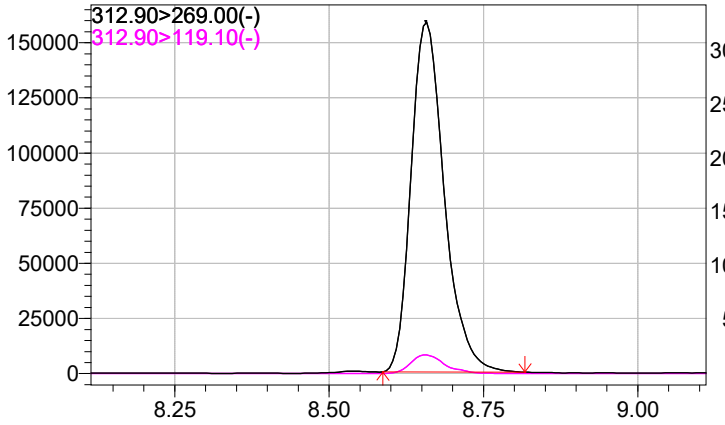
EPA 537

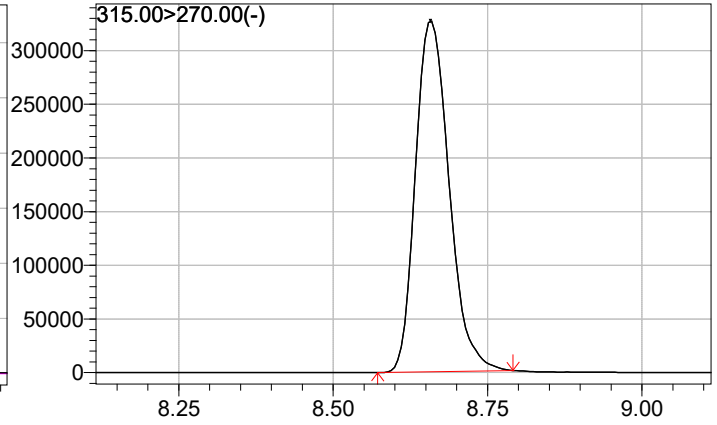
Chromatography must split isomers, separate peaks -





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)**
  - **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?

William Lipps

williamlipps@eurofinsus.com

Eurofins Eaton Analytical, LLC

www.eurofinsus.com

eurofins | Environment Testing

Thank You!