ASTM Methods for the Analysis of Perfluorinated Compounds (PFCs) Using a Quick Sample Extraction/Preparation Followed by UPLC/MS/MS Analysis

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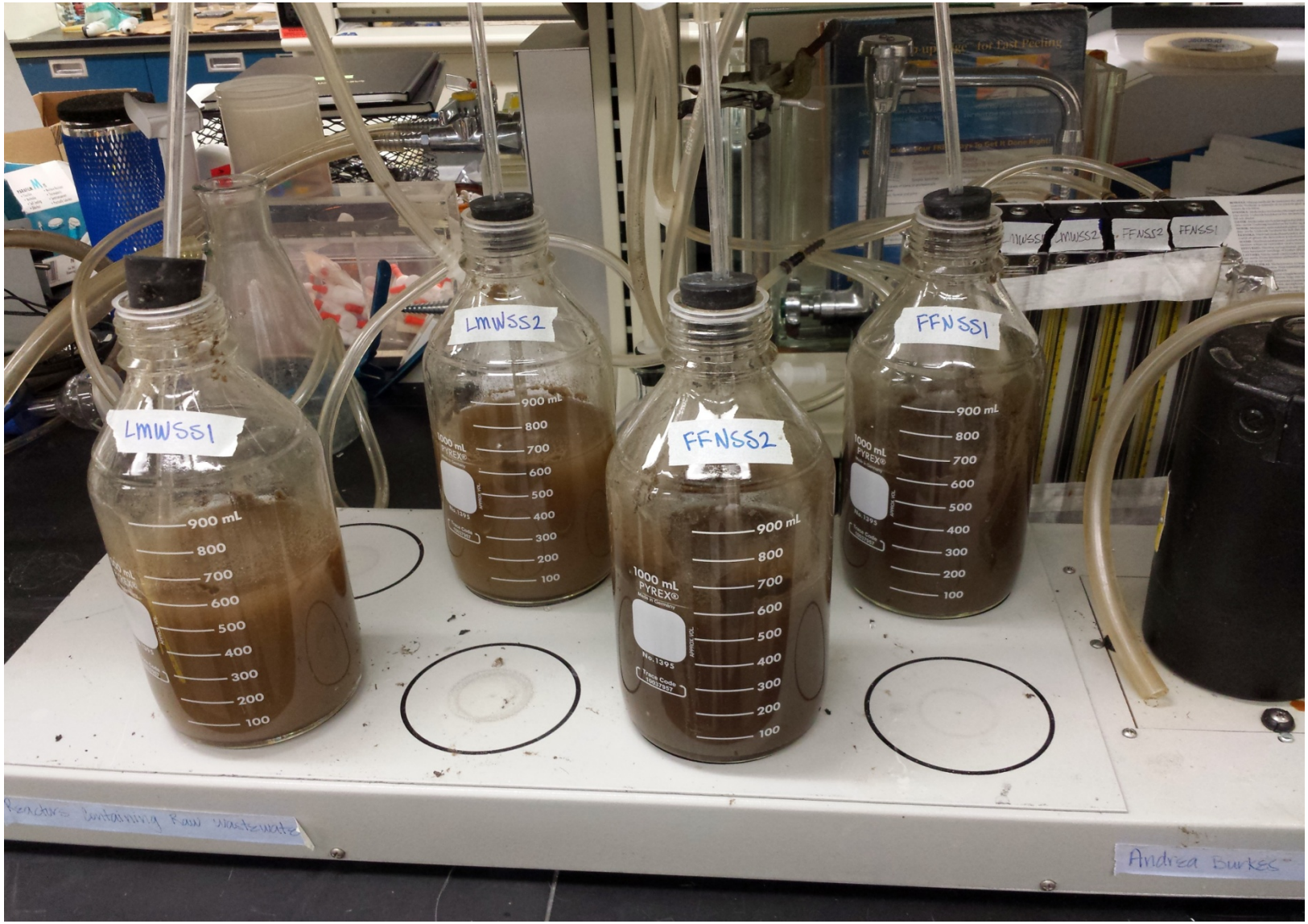
Introduction

- CRL Region 5 Involvement
  - Tailor methods to our customers needs
    - Reporting limits
    - Several matrices
- Previously Published methods on PFCs

ORD/NRMRL Studies Requiring PFC Analysis

- Semi-Continuous Activated Sludge Reactor Study (SCAS)
  - Evaluating Biodegradation of PFCs
- Land Application of Biosolids Study
  - Evaluating Biodegradation/loss of PFCs

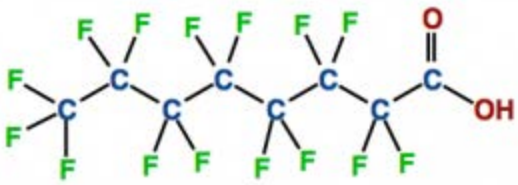
SCAS reactors during aeration and stirring



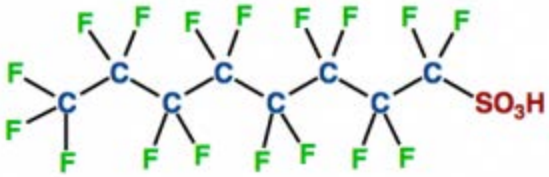
Biosolids Application Day 1 Sampling

ORD Target List

- **Perfluoroalkyl Sulfonates (PFAS) :**
- Perfluorobutyl Sulfonate (PFBS) – $C_4F_9\ SO_3^-$
- Perfluorohexyl Sulfonate (PFHxS) – $C_6F_{13}\ SO_3^-$
- Perfluorooctyl Sulfonate (PFOS) – $C_8F_{17}\ SO_3^-$
- Decafluoro – 4 – (pentafluoroethyl)cyclohexane Sulfonate (PFechS) – $C_8F_{14}\ SO_3^-$
- **Perfluoroalkyl Carboxylates (PFCA)**
- Perfluorobutonoate (PFBA) – $C_4F_7O_2^-$
- Perfluoropentonoate (PFPeA) – $C_5F_9O_2^-$
- Perfluorohexonoate (PFHxA) – $C_6F_{11}O_2^-$
- Perfluoroheptonoate (PFHpA) – $C_7F_{13}O_2^-$
- Perfluorooctonoate (PFOA) – $C_8F_{15}O_2^-$
- Perfluorononanoate (PFNA) – $C_9F_{17}O_2^-$
- Perfluorodecanoate (PFDA) – $C_{10}F_{19}O_2^-$
- Perfluoroundecanoate (PFUnA) – $C_{11}F_{21}O_2^-$
- Perfluorododecanoate (PFDoA) – $C_{12}F_{23}O_2^-$
- Perfluorotridecanoate (PFTriA) – $C_{13}F_{25}O_2^-$
- Perfluorotetradecanoate (PFTreA) – $C_{14}F_{27}O_2^-$



PFOA - perfluorooctanoic acid



PFOS - perfluorooctanesulfonic acid

A few more…….

- 6:2FTCA – FHEA- 2-Perfluorohexyl ethanoic acid
- 8:2FTCA – F0EA- 2-Perfluorooctyl ethanoic acid
- 10:2 FTCA – FDEA- 2-Perfluorodecyl ethanoic acid
- 6:2 FTUCA – FHUEA- 2H-Perfluoro-2-octenoic acid
- 8:2 FTUCA – FOUEA- 2H-perfluoro-2-decenoic acid
- 7:3 Acid – FHpPA- 3-Perfluoroheptyl propanoic acid

Surrogates

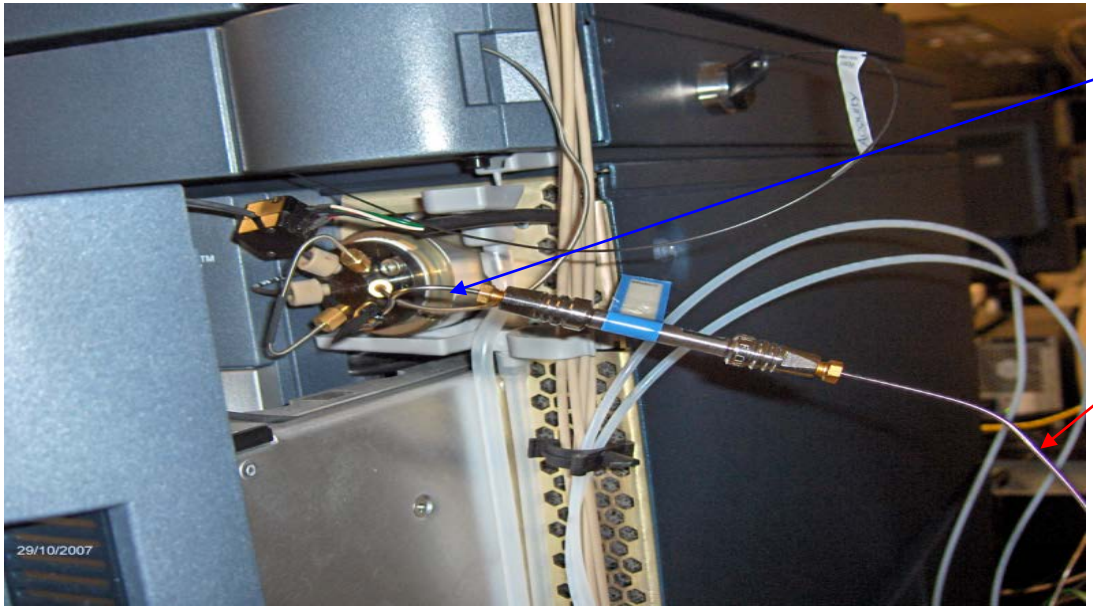
- MPFAS- Isotopically labeled Perfluoroalkylsulfonates
  - MPFHxS- $^{18}O_2$-Perfluorohexylsulfonate
  - MPFOS- $^{13}C_4$-Perfluorooctylsulfonate
- MPFCA- Isotopically labeled Perfluoroalkylcarboxylates
  - MPFBA-$^{13}C_4$-Perfluorobutanoate
  - MPFHxA-$^{13}C_2$-Perfluorohexanoate
  - MPFOA-$^{13}C_4$-Perfluorooctanoate
  - MPFNA-$^{13}C_5$-Perfluorononanoate
  - MPFDA-$^{13}C_2$-Perfluorodecanoate
  - MPFUnA-$^{13}C_2$-Perfluoroundecanoate
  - MPFDoA-$^{13}C_2$-Perfluorododecanoate

Determine Chromatographic Parameters and Detection Levels

- Liquid Chromatography
  - Acquity UPLC® CSH™ Phenyl-Hexyl 1.7 μm, 2.1 x 100 mm column
  - Isolator Column- Acquity UPLC® BEH C18, 1.7 μm, 2.1 x 50 mm column

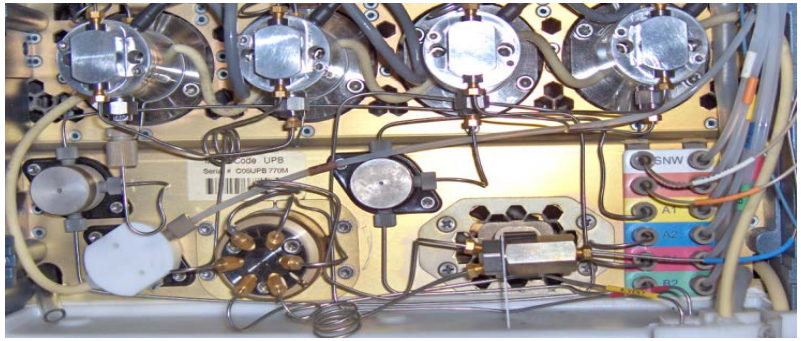
- Detector-MS/MS
  - Waters Xevo® TQ-S

Isolator Column Placement



5uL sample loop

Pump outlet tube



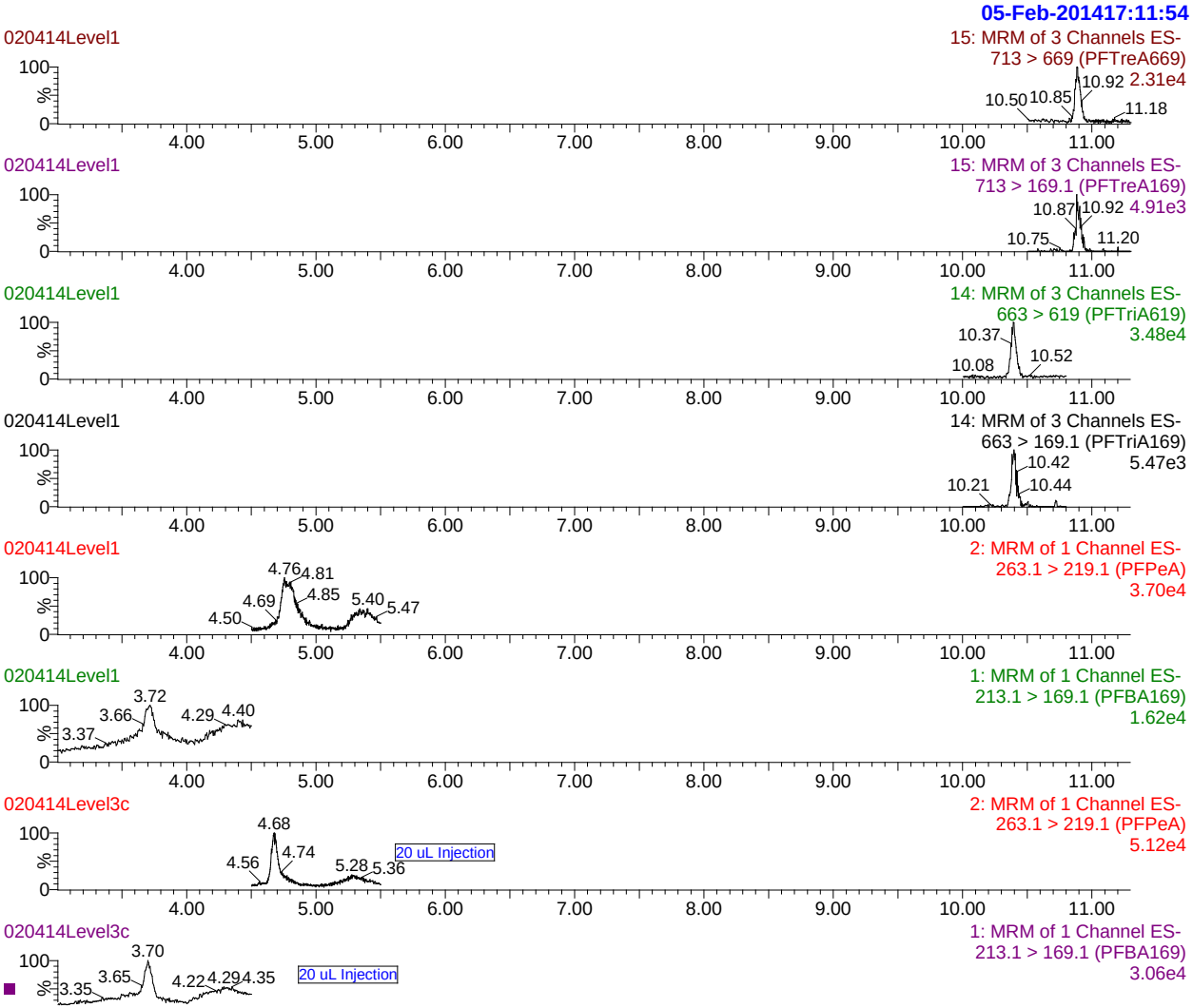
UPLC Gradient

Time (min)	Flow (mL/min)	95% Water: 5% Acetonitrile	Acetonitrile	95% Water: 5% Acetonitrile, 400 mM Ammonium Acetate
0	0.3	95	0	5
1	0.3	75	20	5
6	0.3	50	45	5
13	0.3	15	80	5
14	0.4	0	95	5
17	0.4	0	95	5
18	0.4	95	0	5
21	0.4	95	0	5

Concentration- 5 ppt

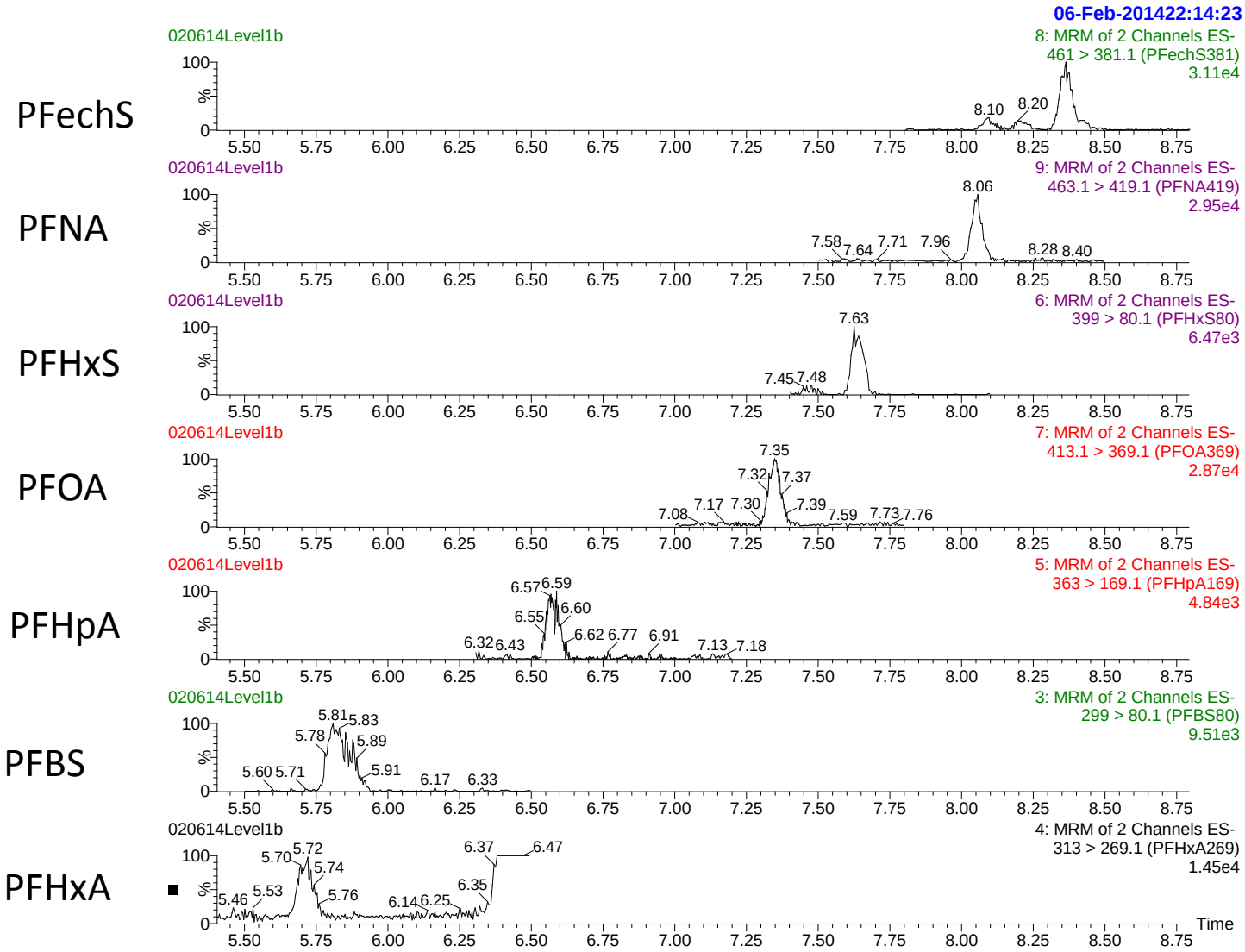
PFTreA

PFTriA



PFBA and PFPeA better w/ smaller Injection volume and raised reporting limits

Concentration- 1 ppt



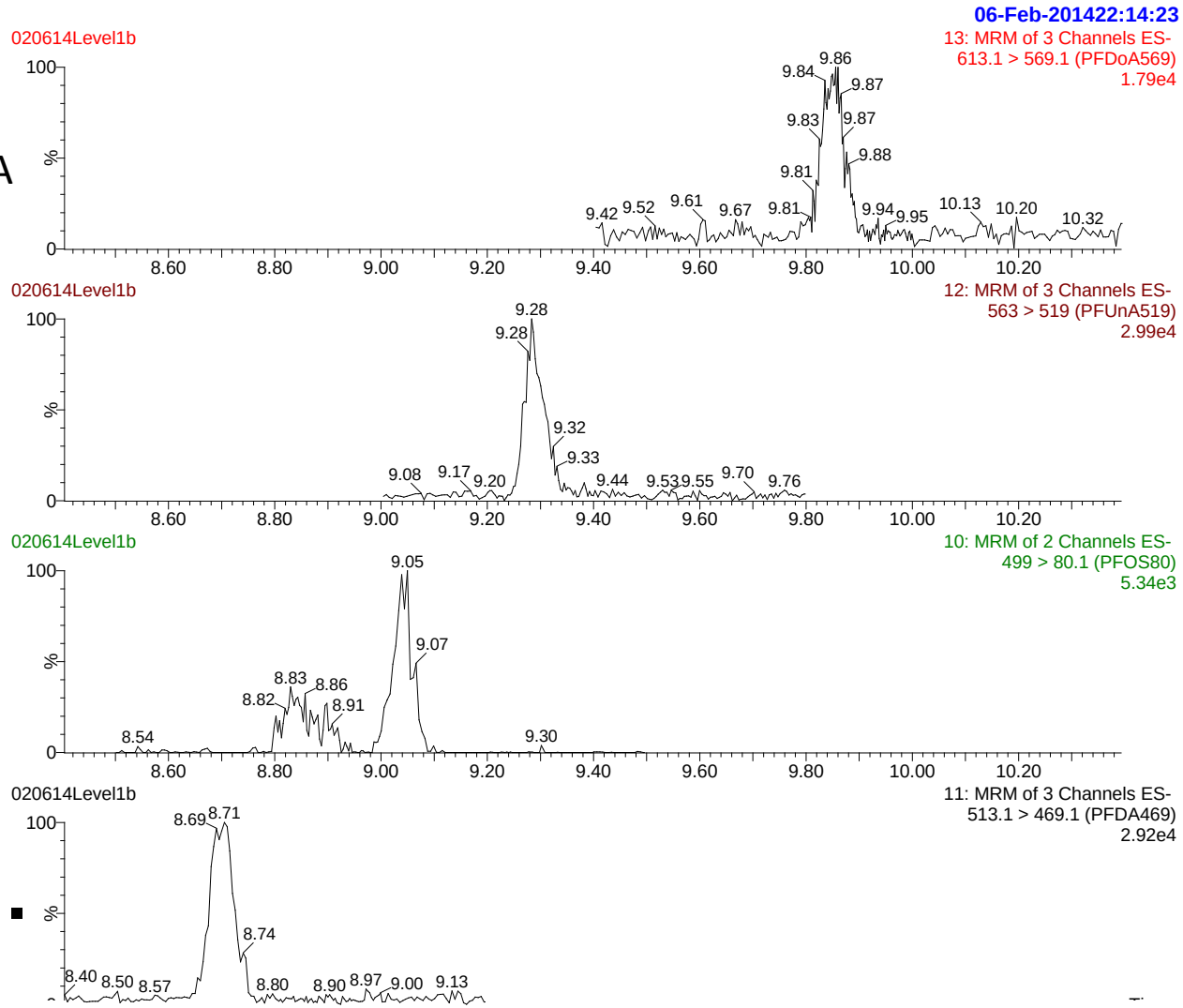
Concentration- 1 ppt

PFDoA

PFUnA

PFOS

PFDA



Calibration (PPT)

Analyte/Surrogate	LV1	LV2	LV3	LV4	LV5	LV6	LV7	LV8	LV9
PFPeA, PFBA	25	50	100	200	300	400	500	750	1000
PFTreA, PFTriA, PFDoA, PFUnA, PFDA, PFOS, PFNA, PFHxA, PFHpA, PFBS, PFechS, PFOA, PFHxS, FOUEA, FHUEA, FHpPA, MPFBS, MPFHxA, MPFUnA, MPFOA, MPFDA, MPFOS, MPFNA, MPFHxS, MPFBA	5	10	20	40	60	80	100	150	200
FHEA, FOEA, FDEA	100	200	400	800	1200	1600	2000	3000	4000

- Default 30 µL Injection Volume

MRM Transitions

- 21 Target Analytes
- 9 Surrogates
- A Primary and Confirmatory Transition for Most Target Analytes
- Primary/Confirmatory Ion Ratio required

Water Sample Preparation

- 5 mL water sample
- Add “Spikes”
  - Wellington MPFAC-MXA- 40 μL of 20 μg/L
    - Labeled PFBA, PFHxA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFHxS and PFOS
- Add 5 mL MeOH
- Shake
- Filter through Polypropylene Filter Unit
  - Pall Acrodisc® 25 mm Syringe Filter, with GxF/0.2μm GHP Membrane
- Add 10 μL acetic acid
- Analyze

Sludge Sample Preparation

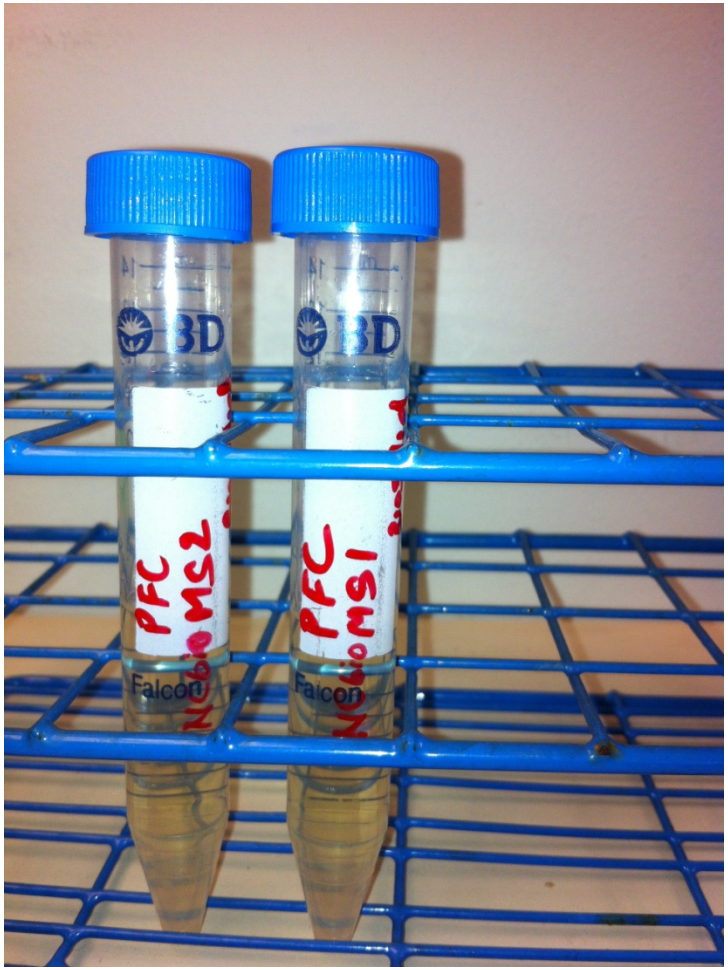
- 5 mL Sludge sample
- Add "Spikes"
  - Wellington MPFAC-MXA
    - Labeled PFBA, PFHxA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFHxS and PFOS
- Add 5 mL MeOH
- Add 20 μL NH_4OH, Shake, check if basic, pH 9-10.
- Mix for 2 minutes
- Decant the liquid and filter through Polypropylene Filter Unit
  - Pall Acrodisc® 25 mm Syringe Filter, with GxF/0.2μm GHP Membrane
- Add 50 μL acetic acid
- Analyze

Soil/Biosolid Sample Preparation

- 2 gram sample
- Add "Spikes"
  - Wellington MPFAC-MXA
    - Labeled PFBA, PFHxA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFHxS and PFOS
- 10 ml of methanol:water (50:50) -shake/vortex for ~ 2 minutes.
- Add 20 μL NH_4OH, shake/vortex for ~ 2 minutes, check if basic, pH 9-10.
- Tumble for 1 hr
- Centrifuge
- Decant the liquid and Filter through Polypropylene Filter Unit
- Add 50 μL acetic acid
- Analyze

Sludge samples

NC Sludge Sample
Before Extraction



NC Sludge Sample
After Extraction

Water Reporting Ranges

Analyte	Reporting Ranges (ng/L)
PFTreA, PFTri, PFDoA, PFUnA, PFDA, PFNA, PFechS, PFOA, PFHxS, PFHpA, PFHxA, FOUEA, FHpPA, FHUEA	10 - 400
PFOS	15 - 400
PFBS	30 - 400
PFPeA, PFBA	50 - 2000
FHEA, FOEA	300 - 8000
FDEA	200- 8000

Soil Reporting Ranges

Analyte	Reporting Ranges (ng/Kg)
PFTreA, PFTriA, PFDoA, PFUnA, PFDA, PFNA, PFechS, PFOA, PFHxS, PFHpA, PFBS, FOUEA, FHpPA, FHUEA	25 – 1000
PFOS, PFHxA	50 - 1000
PFPeA, PFBA	125 – 5000
FHEA	600 – 20,000
FOEA	750 – 20,000
FDEA	500 – 20,000

Matrices Used to Validate ASTM D7979-15

- Reagent Water
- Chicago River Water
- Sewage Treatment Plant I (STP) Effluent
- STP I Influent
- STP II (Effluent with supplemental sewage)
- STP III (Effluent with supplemental sewage)

Matrices Used to Validate ASTM D7968-14

- Ottawa Sand
- Four ASTM Soils
  - Sand
  - Lean Clay
  - Fat Clay
  - Silt

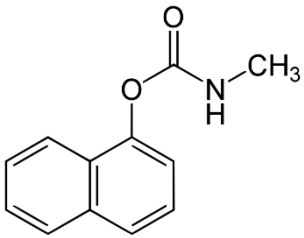
Methods are Performance Based

- Section 4.1- “this test method is intended to be performance based and alternative operating conditions can be used to perform this method provided data quality objectives are attained.”
- Isotope Dilution- is the best for quantitative analysis.
- External Calibration
- Internal Standard

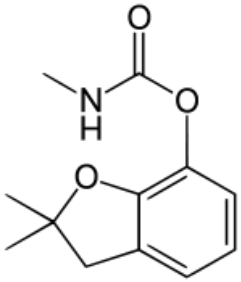
Internal Standard Question

- Do Internal Standards mimic analytes that are not the same?

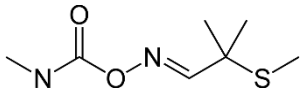
		Analyte and Percent Recovery			
		Carbaryl	Carbofuran (Ring-13C6)	Aldicarb	Methomyl (Acetohydroxamate-13C2, 15N)
Matrix	Reagent	72	83	89	86
	Lake	45	73	91	83
	River	59	69	86	72



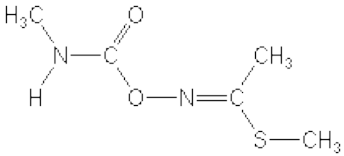
Carbaryl



Carbofuran



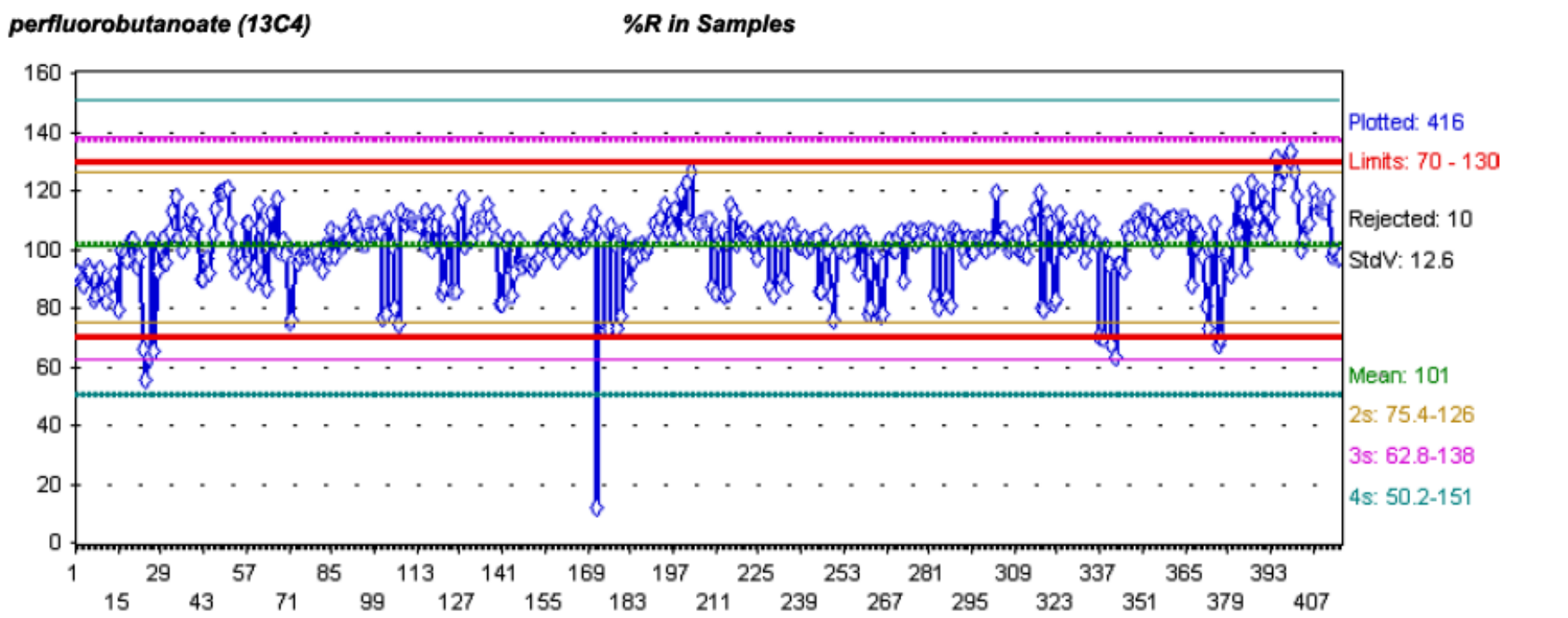
Aldicarb



Methomyl

Recovery Data Over Last 19 Months (Next Couple Slides)

- Example of a Control Chart displaying recovery data for data collected with ASTM D7979-15



ASTM D7979-15 Precision and Accuracy

- Includes all target and surrogate analytes.
- Samples- 101 Blanks, 97 MRLs, 102 BSs, 189 MSs and 416 samples.
- Accuracy
  - Average Recovery: 99.2%
  - Range: 116, 115, 114--------- 91, 87, 84
- Precision (Standard Deviation)
  - Average Precision: 6.08
  - Range: 47.1, 23.8, 23.8---------4.4, 4.2, 3.9

ASTM D7968-14 Precision and Accuracy

- Includes all target and surrogate analytes.
- Samples- 37 Blanks, 31 MRLs, 42 BSs, 26 MSs and 138 samples.
- Accuracy
  - Average Recovery: 90.3%
  - Range: 125, 117, 111--------- 62, 53, 45
- Precision (Standard Deviation)
  - Average Precision: 15.8
  - Range: 181, 48.1, 42.1---------3.9, 3.8, 3.3

Conclusion

- Quick and robust analyses
- Met Customer Needs
- Accuracy range for all compounds
  - Water
  - Soil
- Standard Deviation range for all compounds
  - Water
  - Soil

More Information

- www.astm.org
- http://portal.astm.org
- http://intranet.epa.gov/desktop/astm.html.
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