Analysis of Per- and Polyfluoroalkyl Substances (PFAS) using LC-MS/MS and Manual / Automated Solid Phase Extraction (SPE) Techniques in Ground, Surface, and Reclaimed Water

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NEMC - August 20, 2020

Presentation Outline

- Introduction
- EPA Method 537 – Overview
- Analytical Method, LC-MS/MS Configuration & Setup
- Extraction Procedure, Extraction Setup
- Validation Data for Automated SPE, LFB % Recovery
- Manual SPE vs. Automated SPE
- QA/QC and Challenges
- Conclusion/References
- Acknowledgements

Introduction

Significant increase in the sample load, OCWD Lab has had to overcome two major challenges:

- Continuing validation of any new PFAS compounds and methods, needing to obtain State-ELAP certification prior to testing the public drinking water systems

- Needing to meet a mandated two-week turnaround time to produce data

OCWD Monitoring PFAS Overview

Analyte	Abbreviation
Hexafluoropropylene oxide dimer acid (GenX)	HFPODA
N-ethyl perfluorooctanesulfonamidoacetic acid	EtFOSA
N-methyl perfluorooctanseulfonamidoacetic acid	MeFOSA
Perfluorobutanesulfonic acid***	PFBS
Perfluorodecanioic acid	PFDA
Perfluorododecanoic acid	PFDoA
Perfluoroheptanoic acid***	PFHpA
Perfluorohexanesulfonic acid***	PFHxS
Perfluorohexanoic acid	PFHxA
Perfluorononanoic acid***	PFNA
Perfluorooctanesulfonic acid***	PFOS
Perfluorooctanoic acid***	PFOA
Perfluorotetradecanoic acid	PFTA
Perfluorotridecanoic acid	PFTrDA
Perfluoroundecanoic acid	PFUnA
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11ClPF
9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9CLPF3
4,8-dioxa-3H-perfluorononanoic acid	ADONA

Reporting Limit

	EPA 537 - UCMR3 (2013-2015)	EPA 537 RV1.1	EPA 537.1 (current)
PFBS***	**90 ng/L**	4.0 ng/L	2.0 ng/L
PFHpA***	**10 ng/L**	4.0 ng/L	2.0 ng/L
PFHxS***	**30 ng/L**	4.0 ng/L	2.0 ng/L
PFNA***	**20 ng/L**	4.0 ng/L	2.0 ng/L
PFOS***	**40 ng/L**	4.0 ng/L	2.0 ng/L
PFOA***	**20 ng/L**	4.0 ng/L	2.0 ng/L
PFDA	NA	4.0 ng/L	2.0 ng/L
PFDoA	NA	4.0 ng/L	2.0 ng/L
PFHxA	NA	4.0 ng/L	2.0 ng/L
PFTA	NA	4.0 ng/L	2.0 ng/L
PFTrDA	NA	4.0 ng/L	2.0 ng/L
PFUnA	NA	4.0 ng/L	2.0 ng/L
EtFOSA	NA	4.0 ng/L	2.0 ng/L
MeFOSA	NA	4.0 ng/L	2.0 ng/L
11ClPF	NA	NA	2.0 ng/L
9CLPF3	NA	NA	2.0 ng/L
ADONA	NA	NA	2.0 ng/L
HFPODA	NA	NA	2.0 ng/L

Analytical Method

Parameter	Value
Sample Volume	250 mL
Cartridge	Phenomenex 6-mL/500mg styrenedivinylbenzene (SDVB)
Analytical Column	Gemini C18; 3um, 100 x 2 mm
Delay Column	Luna C18; 5um, 30 x 2 mm
Column Oven Temp.	35 ^{0}C
Injection Volume	5uL
Mobile Phases	A= 20mM Ammonium Acetate in Milli-Q water B= Methanol
Gradient Flow Rate	0.4 mL/Min
Run Time	11 min

LC-MS/MS Setup

ABSciex QTrap 6500+ / Agilent Pump 2600 / LEAP PAL HTC-XT

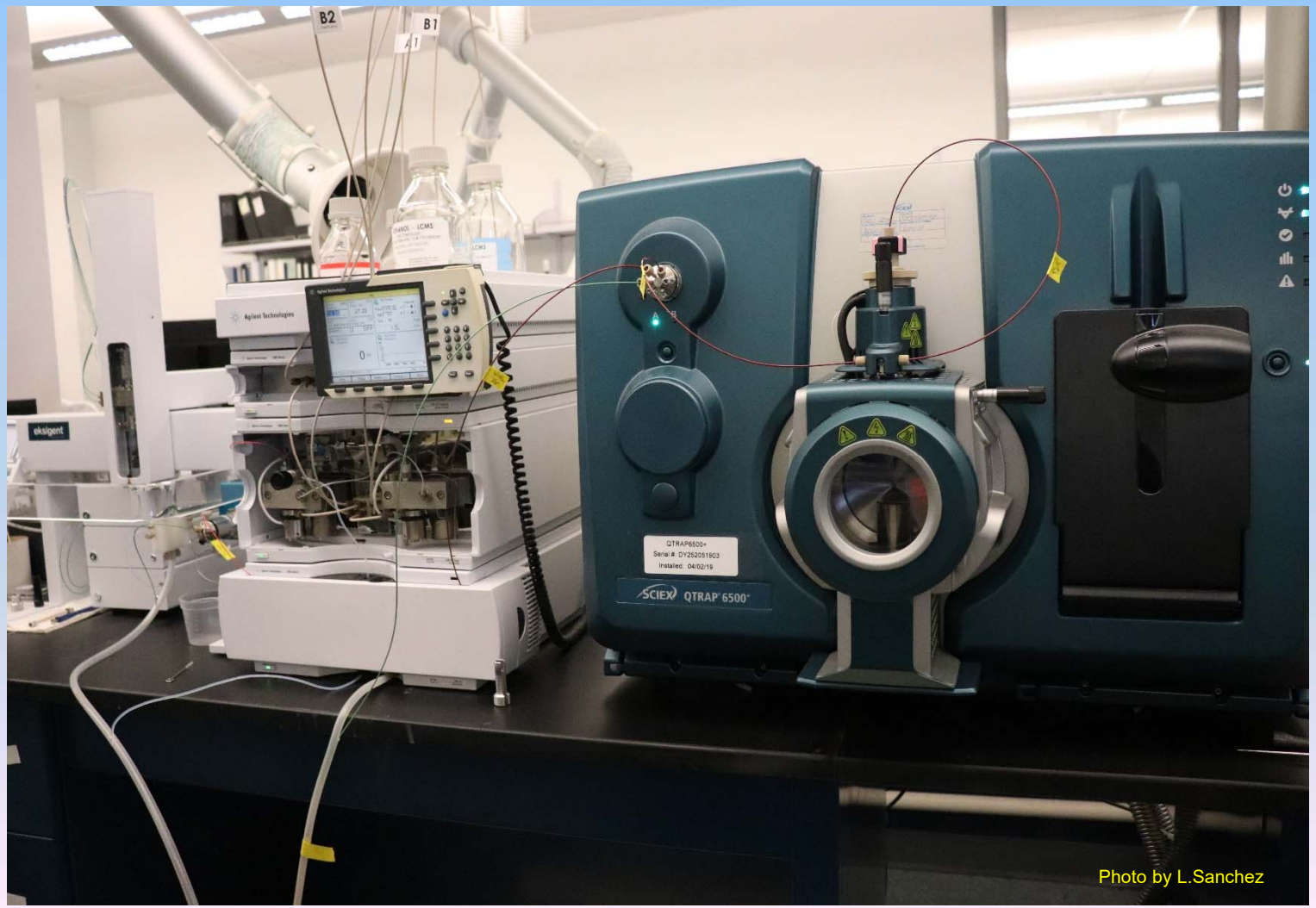
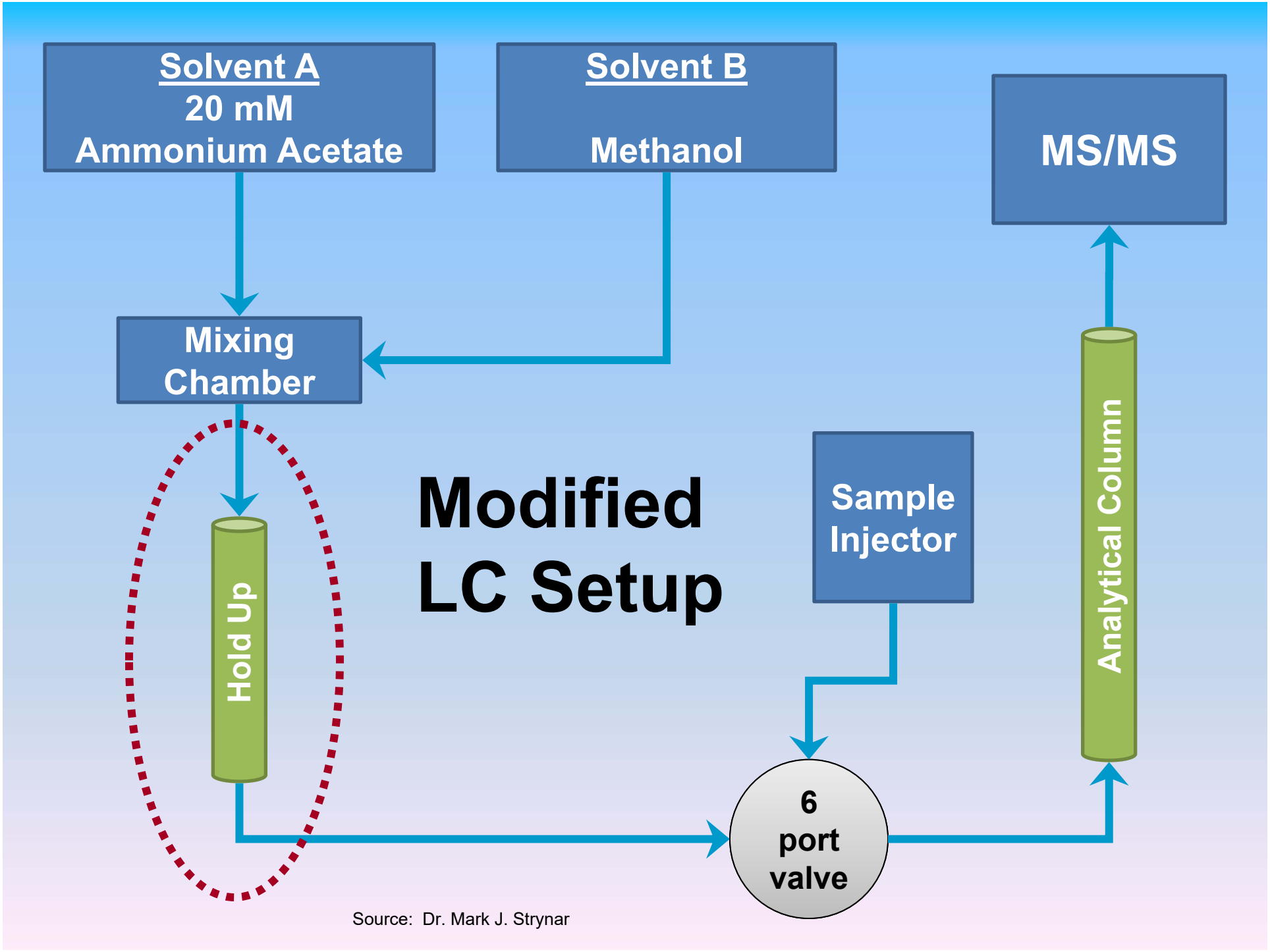


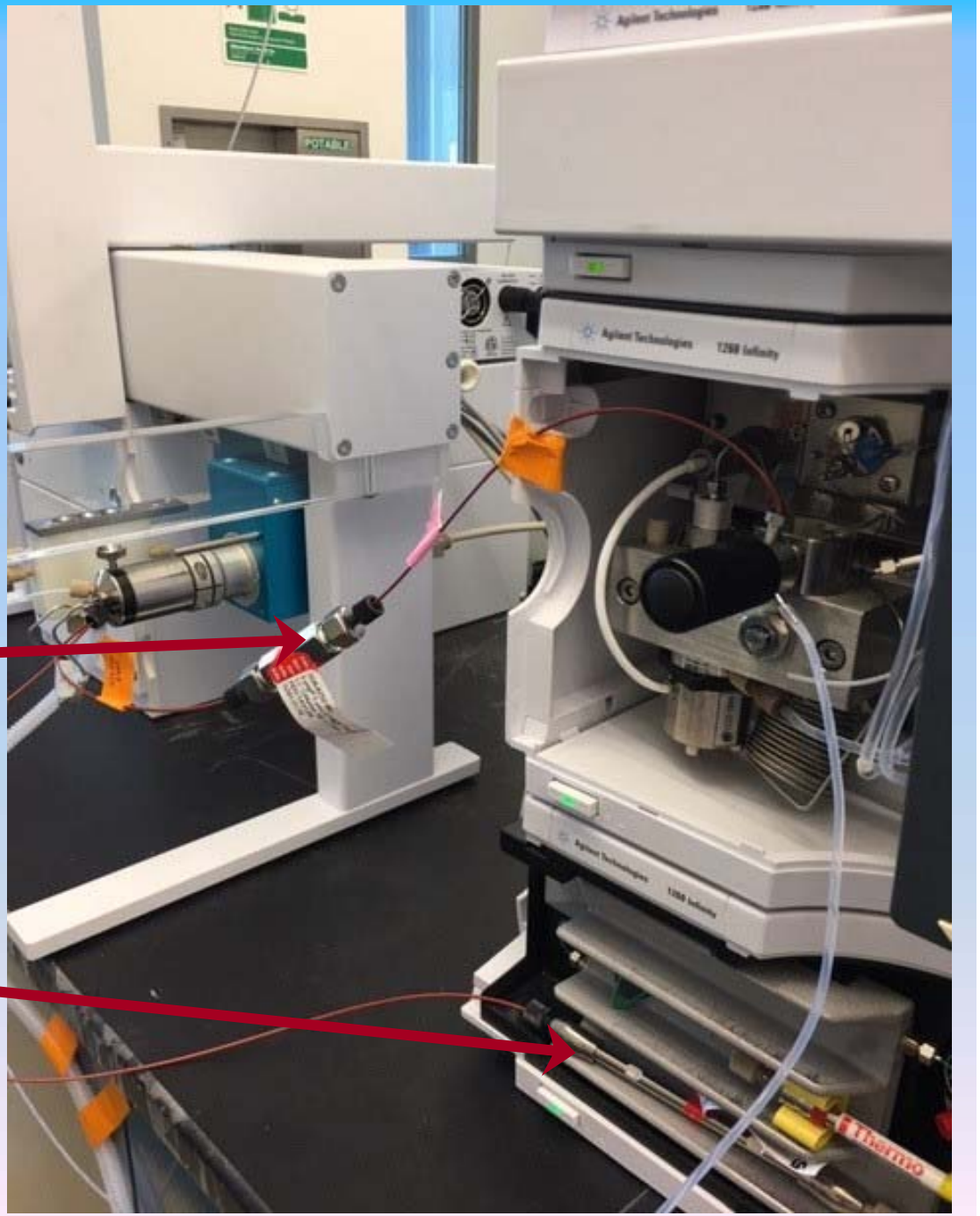
Photo by L.Sanchez


Solvent A
20 mM
Ammonium Acetate
Solvent B
Methanol
MS/MS
Mixing
Chamber
Hold Up
Modified
LC Setup
Sample
Injector
Analytical Column
6
port
valve
Source: Dr. Mark J. Strynar

Modified LC Setup

2nd Delay column is added between Inlet filter and the Injection port

1st Analytical column



Extraction Procedure

Manual SPE

Ground, Surface, Reclaimed Water

Automated SPE-03 by Promochrom (since August 2019)

Ground Water only

Note: "SPE-03" is used where Automated SPE is applicable

SP Extraction Setup

Manual SPE

Photo by P. Alvaro

Promochrom SPE-03

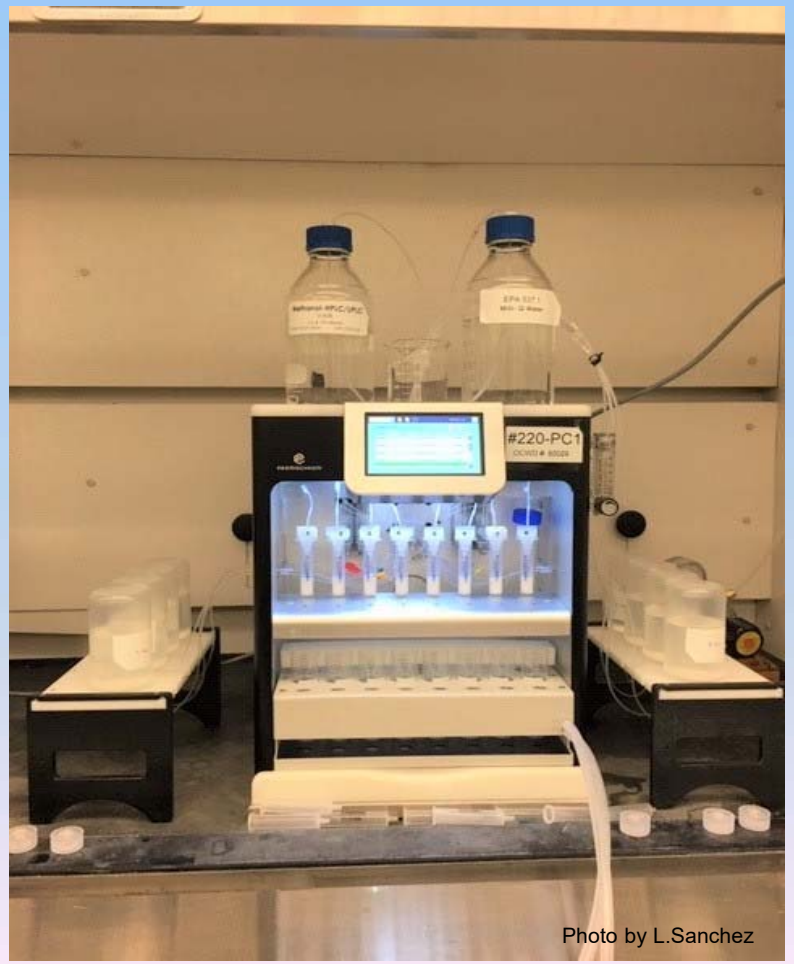


Photo by L.Sanchez

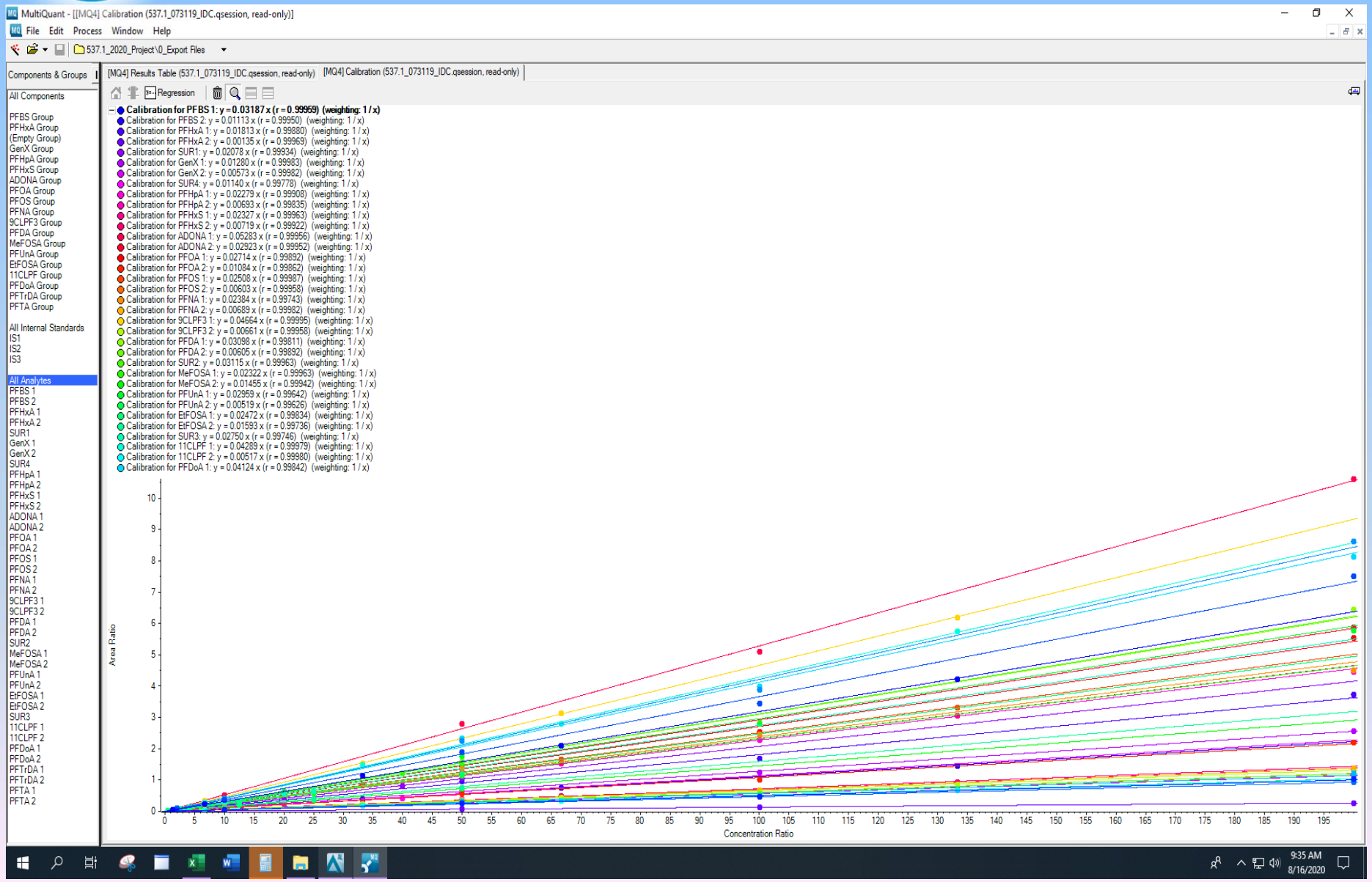
Validation Data for SPE-03

Validating new SPE-03: for all 8 positions
Run blanks – discard the extracts
Run Reagent Blanks to confirm the free PFAS background

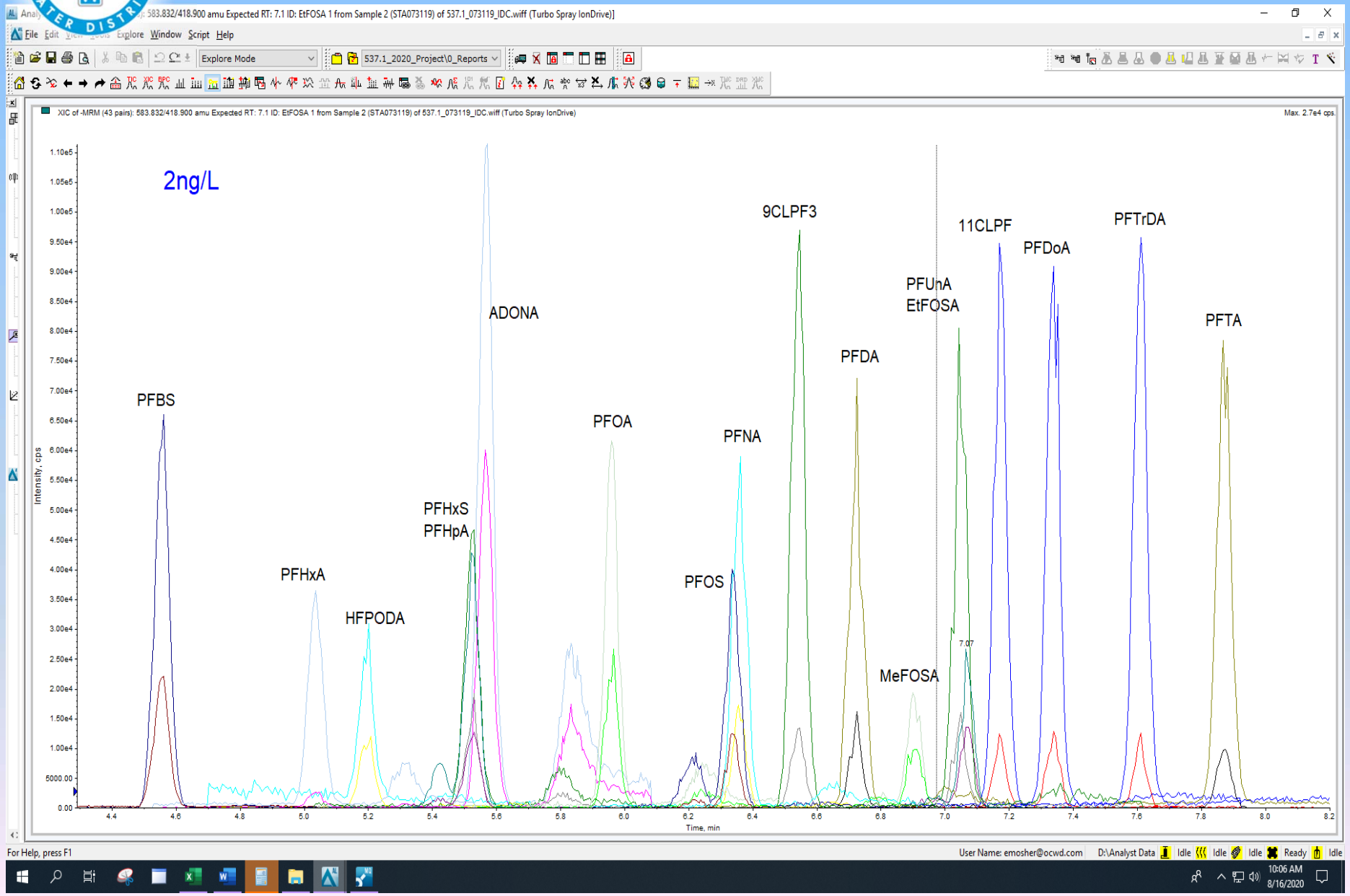
Validating EPA 537.1:

IDC:	Initial Demonstration Capability
MDL:	Method Detection Limit
RB:	Reagent Blanks
PT:	Proficient Test Results

Initial Calibration
Linear Regression through Zero, weighting 1/x



Chromatogram from 2 ng/L Calibration



IDC Study

Analyte	Spiked Conc. (ng/L)	Calibration Range (ng/L)	Rep #1	Rep #2	Rep #3	Rep #4	%RSD
PFBS	50	2-200	42.2	44.0	42.8	38.9	5.2
PFHpA	50	2-200	49.1	55.8	56.4	47.5	8.7
PFHxS	50	2-200	49.9	49.6	48.3	50.4	1.8
PFNA	50	2-200	53.4	53.5	54.8	49.1	4.7
PFOS	50	2-200	49.5	48.1	45.0	47.0	4.0
PFOA	50	2-200	49.2	50.7	56.0	51.7	5.6
PFDA	50	2-200	53.5	45.0	49.5	44.9	8.5
PFDoA	50	2-200	40.2	44.9	44.0	44.0	4.8
PFHxA	50	2-200	45.0	48.5	50.3	42.2	7.8
PFTA	50	2-200	38.7	48.2	44.3	39.9	10.1
PFTrDA	50	2-200	42.5	47.2	47.6	40.6	7.8
PFUnA	50	2-200	44.3	51.7	49.6	46.5	6.8
EtFOSA	50	2-200	51.1	51.3	51.1	50.1	1.3
MeFOSA	50	2-200	52.5	50.0	47.8	51.1	3.9
11ClPF	50	2-200	43.1	42.3	42.2	43.9	1.8
9CLPF3	50	2-200	47.8	49.1	47.0	47.5	1.9
ADONA	50	2-200	49.3	52.2	52.4	47.2	4.9
HFPODA	50	2-200	45.5	49.3	51.0	44.3	6.6

3 Days MDL Study

Analyte	Spiked Conc. (ng/L)	Calibration Range (ng/L)	Day 1			Day 2		Day 3		% RSD	Calculated MDL (ng/L)
			Rep #1	Rep #2	Rep #3	Rep #4	Rep #5	Rep #6	Rep #7		
PFBS	2	2-200	2.06	2.03	1.79	1.88	2.03	2.04	2.11	**5.7**	**0.36**
PFHpA	2	2-200	2.27	2.24	2.03	2.27	2.10	2.30	2.33	**5.0**	**0.35**
PFHxS	2	2-200	2.06	2.02	1.98	2.03	2.11	2.10	2.22	**3.8**	**0.25**
PFNA	2	2-200	2.04	1.89	1.97	2.38	2.16	2.15	2.05	**7.6**	**0.50**
PFOS	2	2-200	2.03	2.02	1.96	2.08	2.07	2.07	2.09	**2.2**	**0.14**
PFOA	2	2-200	2.41	2.14	2.11	2.43	2.32	2.33	1.94	**8.1**	**0.57**
PFDA	2	2-200	1.96	1.78	1.90	2.22	2.04	2.27	2.08	**8.5**	**0.54**
PFDoA	2	2-200	1.64	1.83	1.76	2.40	1.97	1.93	1.84	**12.7**	**0.76**
PFHxA	2	2-200	1.94	2.06	1.89	2.19	1.99	2.10	2.00	**4.8**	**0.30**
PFTA	2	2-200	1.75	1.77	1.77	2.00	1.96	1.94	1.76	**6.0**	**0.35**
PFTrDA	2	2-200	1.90	1.59	1.66	2.14	1.88	1.97	2.16	**11.5**	**0.68**
PFUnA	2	2-200	1.99	1.94	1.85	2.20	1.97	2.07	2.00	**5.5**	**0.34**
EtFOSA	2	2-200	2.05	2.22	2.03	1.98	2.13	2.03	1.98	**4.2**	**0.27**
MeFOSA	2	2-200	1.97	1.81	1.96	2.15	1.98	1.87	2.03	**5.6**	**0.34**
11ClPF	2	2-200	1.74	1.78	1.84	2.06	2.02	1.94	1.96	**6.4**	**0.38**
9CLPF3	2	2-200	1.85	1.98	1.99	1.97	2.00	1.89	1.93	**3.0**	**0.18**
ADONA	2	2-200	2.00	1.93	1.87	2.19	2.08	2.16	1.96	**5.9**	**0.38**
HFPODA	2	2-200	1.96	1.95	1.79	2.04	2.01	2.01	1.81	**5.1**	**0.31**

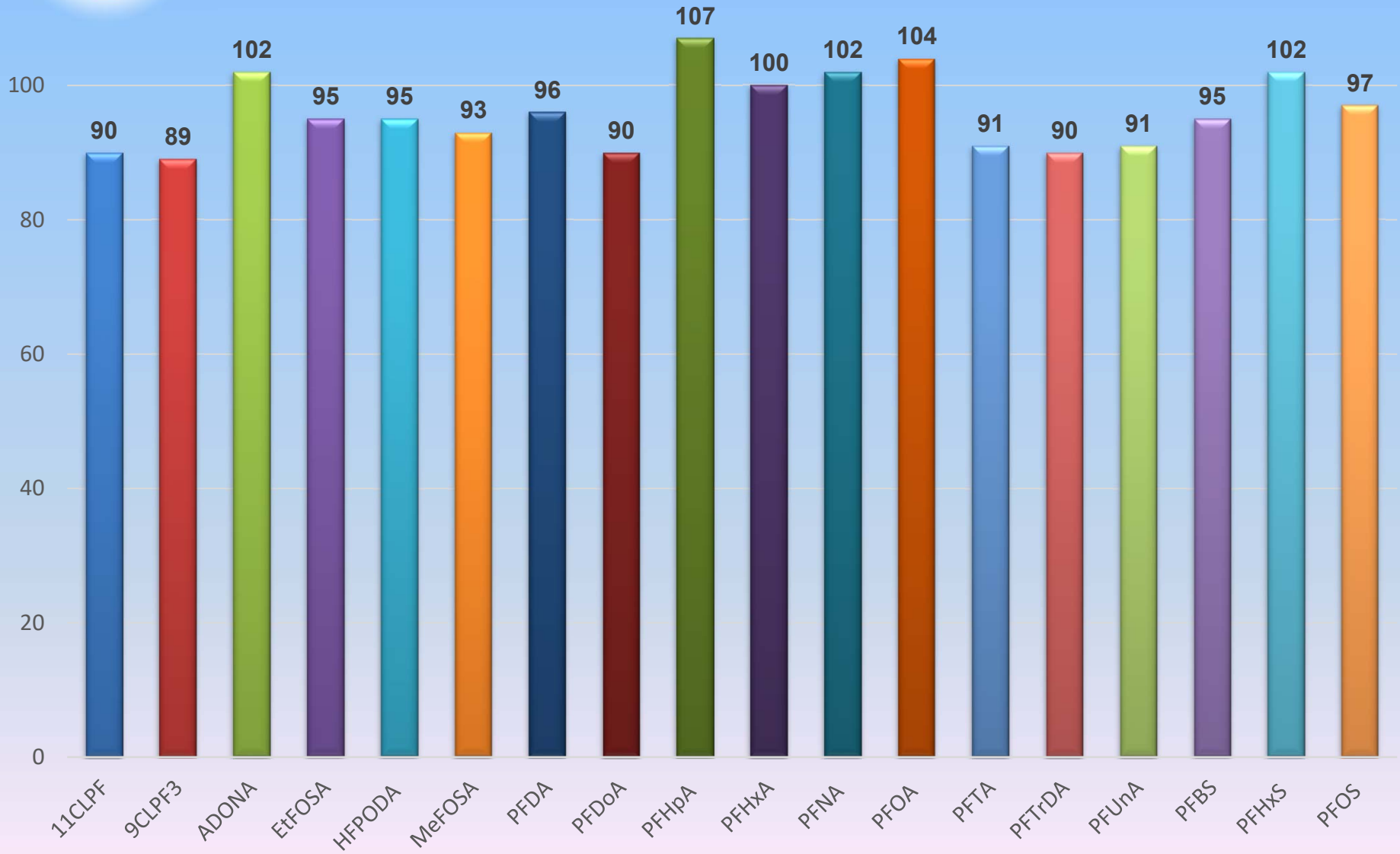
RB from 3 Days MDL Study

Analyte	Spiked Conc. (ng/L)	Calibration Range (ng/L)	Day 1			Day 2		Day 3	
			Rep #1	Rep #2	Rep #3	Rep #4	Rep #5	Rep #6	Rep #7
PFBS	NA	2-200	--	--	--	--	--	--	--
PFHpA	NA	2-200	--	--	--	--	--	--	--
PFHxS	NA	2-200	--	--	--	--	--	--	--
PFNA	NA	2-200	--	--	--	--	--	--	--
PFOS	NA	2-200	--	--	--	--	--	--	--
PFOA	NA	2-200	--	--	--	--	--	--	0.12
PFDA	NA	2-200	--	--	--	--	--	--	--
PFDoA	NA	2-200	0.21	0.26	--	--	0.10	--	--
PFHxA	NA	2-200	--	--	--	--	--	--	--
PFTA	NA	2-200	0.35	0.38	--	--	0.10	0.07	0.07
PFTrDA	NA	2-200	0.35	0.43	--	--	0.11	--	0.07
PFUnA	NA	2-200	--	0.17	--	--	--	--	--
EtFOSA	NA	2-200	--	--	--	--	--	--	--
MeFOSA	NA	2-200	--	--	--	--	--	--	--
11ClPF	NA	2-200	0.23	0.30	--	--	--	--	--
9CLPF3	NA	2-200	--	--	--	--	--	--	--
ADONA	NA	2-200	--	--	--	--	--	--	--
HFPODA	NA	2-200	--	--	--	--	--	--	--

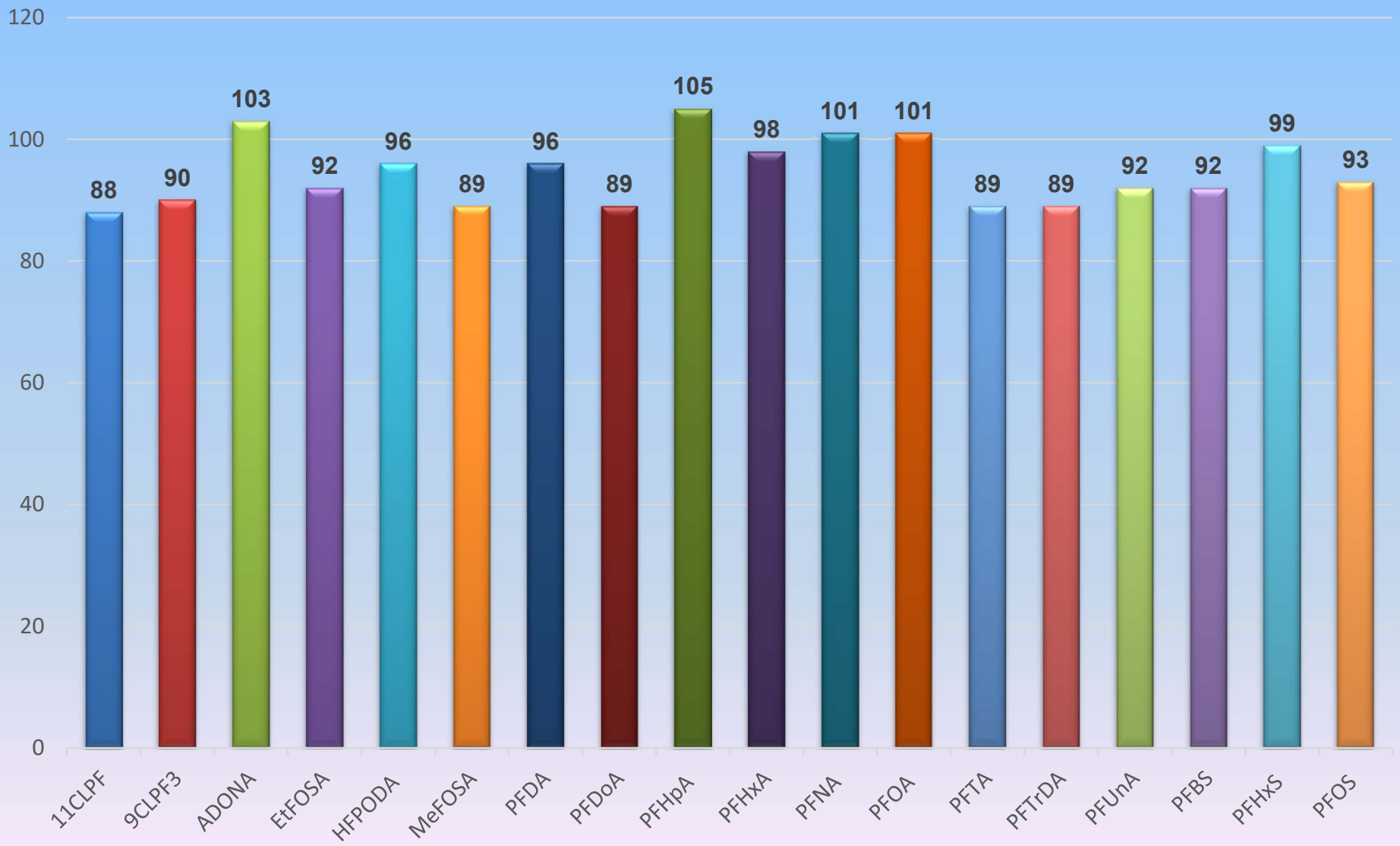
PT Results

Analyte	Result (ng/L)	Assigned Value (ng/L)	% Recovery
PFBS	**255**	**259**	**99**
PFHpA	<2	<50	NA
PFHxS	**323**	**294**	**110**
PFNA	**281**	**252**	**112**
PFOS	<2	<50	NA
PFOA	**456**	**455**	**100**
PFDA	**89.3**	**80**	**112**
PFDoA	**53.1**	**58.7**	**90**
PFHxA	<2	<50	NA
PFTA	<2	<50	NA
PFTrDA	**92.7**	**106**	**87**
PFUnA	<2	<50	NA
EtFOSA	<2	<50	NA
MeFOSA	<2	<50	NA
11ClPF	<2	<50	NA
9CLPF3	<2	<50	NA
ADONA	<2	<50	NA
HFPODA	<2	<50	NA

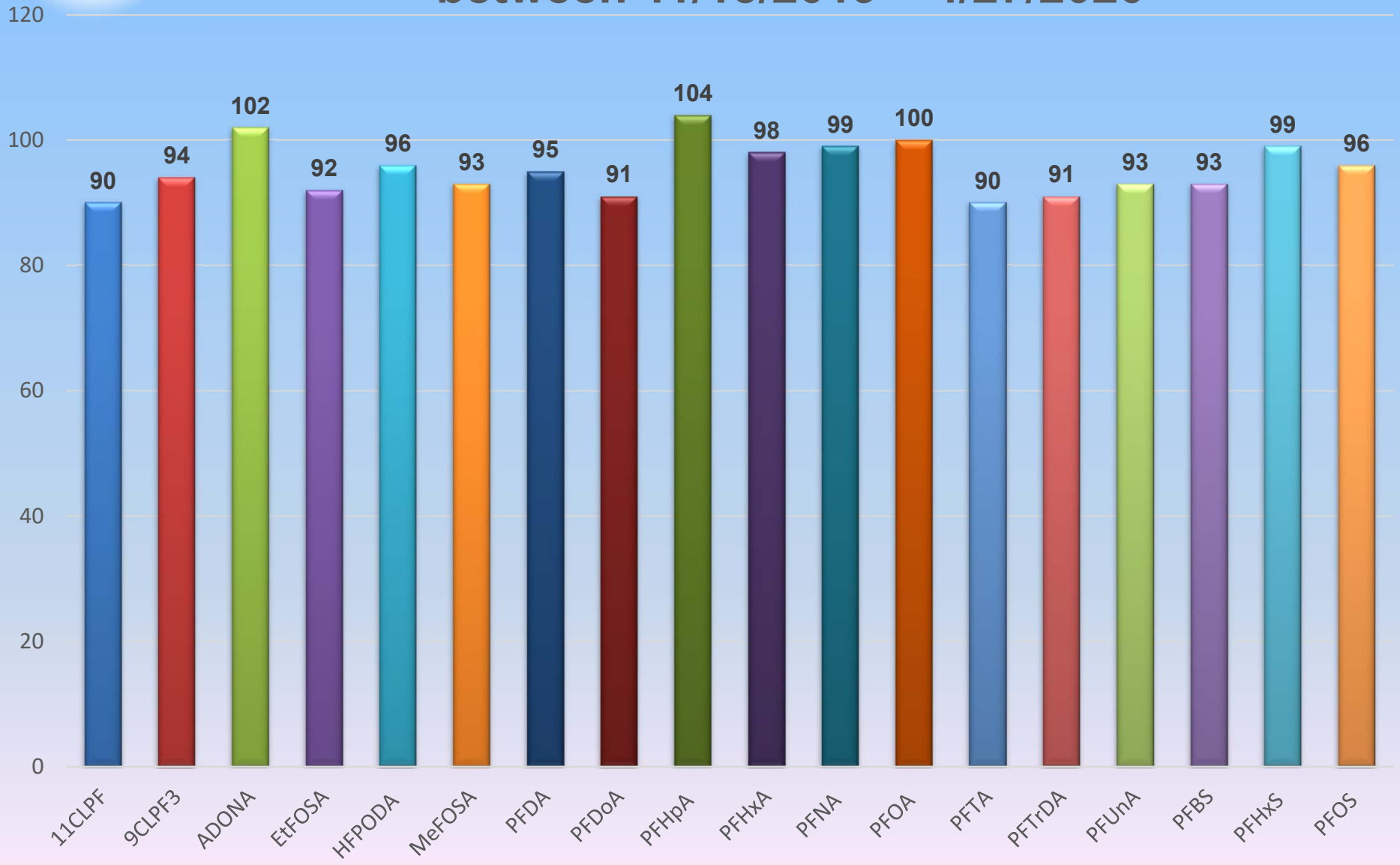
Average % Recovery for 2 ng/L LFB
between 11/15/2019 - 4/27/2020



Average % Recovery for **50 ng/L** LFB
between 11/15/2019 – 4/27/2020



Average % Recovery for **100 ng/L** LFB
between 11/15/2019 – 4/27/2020



Comparison Between Manual SPE and Automated: SPE-03

Manual Extraction (3 systems/one staff)	SPE-03 (3 systems/one staff)
Simultaneous processing 10 samples/one system	Simultaneously processing 8 samples/one system
1 round/day (9-10 hrs. shift)	2 rounds/day (9-10 hrs. shift)
Total samples processed: 30	Total samples processed: 48
Attention is needed during the sample extraction procedure, cannot multi-task	After the system is set up and running, does not need attention and can multi-task

SPE-03

Advantages

- Process 50% more samples in the same allotted time
- Free time to perform additional tasks during sample processing

Disadvantages

- Process cleans ground waters only
- Systems need routine maintenance

Quality Assurance/ Quality Control QA/QC Outlines

PFAS Background Contamination Checking

- Milli-Q Water is stored in the Carboy and tested for PFAS background before use
  - QC waters: Reagent Blanks, Fortified Blanks, and Field Reagent Blank (FRB)
- Milli-Q water from the Carboys are replaced every 3 weeks
- Each new lot of preservative cartridges are tested for PFAS background before use

Sample Preservation and Handling

Preservation reagents are added to each sample bottle prior to the shipment to the field plus Field Reagent Blank (FRB) for each site.

Always wear nitrile gloves when handling PFAS samples.

Upon receiving the samples in the lab:

- check for free chlorine
- check pH
- stored in the refrigerator at 4 ^{o}C

Sample preparation, extraction

- QC requirements for each batch of 1-20 field samples:

  Method Blanks (Reagent Blank – RB)
  Lab Fortified Blank (LFB)
  LOW LFB - at MRL concentration
  LFB - Mid or high-level concentration of calibration curves
  TPFOA - Branch PFOA (2016 EPA Technical Advisory)
  Sample duplicates,
  Matrix spike & spike dup
  Internal Standard (3)
  Surrogate Standard (4)

Challenges

- **Significant increase in sample load and short turn around time to meet the demand**
  - The lab had analyzed close to two thousand samples and QCs between March and December 2019
- **Lower reporting limit means more detections in field samples**
- **Samples are re-extracted to:**
  - confirm first time hit for existing sites
  - new sites with hit targets
  - results do not match with the historical data
- **Surface water and samples with particles**
  - require longer time to process
  - can only extracted by manual SPE procedure
- **Working standards prepared often to avoid compound breakdown problem (PFNA, PFHpA & PFOA)**

Conclusions

There are other options in analyzing PFAS compounds and the Promochrom SPE-03.

- **Efficient**
  - Can process 50% more samples compare to manual extraction procedure
- **Fast and effective**
  - One staff can process 48 samples/day
- **Simple**
  - Easy to maintain and troubleshoot the problems, less down time
  - Easy to use
- **Accurate % Recovery for QC at ALL Levels**

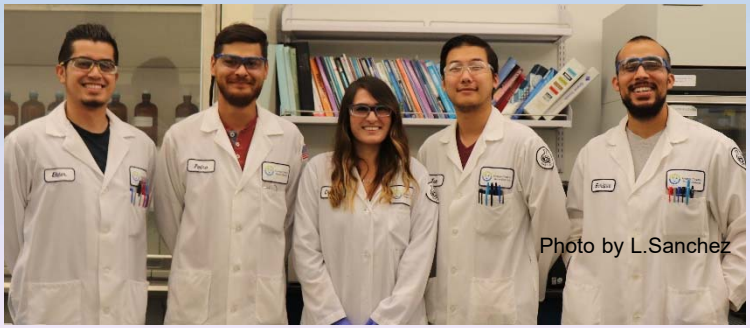
References

- **EPA 537 RV1.1**
- EPA method 537.1
- Technical Advisory – Laboratory Analysis of Drinking Water Samples for Perfluorooctanoic Acid (PFOA) Using EPA Method 537 Rev.1.1
- SCIEX Application Note: Analysis of PFAS in drinking water with EPA Method 537.1 and the SCIEX QTRAP 4500 System.

Acknowledgements

SCIEX/Phenomenex
Promochrom

Many thanks for all the work, dedication, and support that the Orange County Water District Laboratory Organic Staff has given to this project.



Thank you

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