Simple Modification of Liquid Chromatographic (LC) System to Reduce Perfluorinated Alkyl Acids (PFAAs) Background for EPA Method 537

Lily Sanchez, Lee Yoo - Advanced Water Quality Assurance Laboratory, Orange County Water District, Fountain Valley CA 92708

Summary

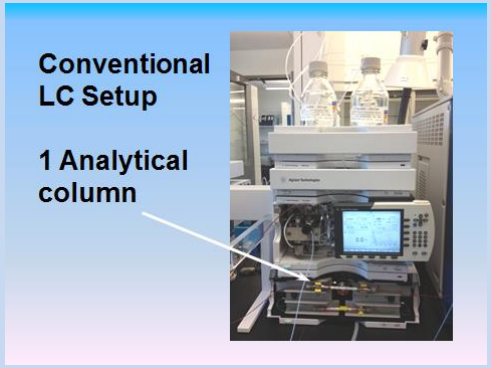
PFAAs background is found every where in the laboratory supllies and equipment such as LC solvent lines, polytetrafluoroethylene (PTFE) product, glassware, vials, aluminum foil, etc… PFAAs background causes peak tailing problems , effect the % recovery for QC at MRL level, and place great impact in the results of the following compounds - PFOA, PFNA and PFHpA .
To overcome this problem the Orange County Water District (OCWD) Lab has modified the LC set up to separate the PFAAs background from the target compounds This simple modification proves to be highly effective for meeting the QC requirements of the Unregulated Contaminant Monitoring Rule 3 (UCMR3) EPA Method 537.

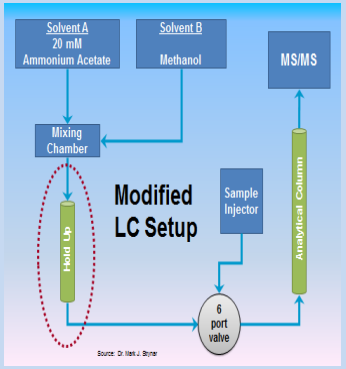
Method Introduction

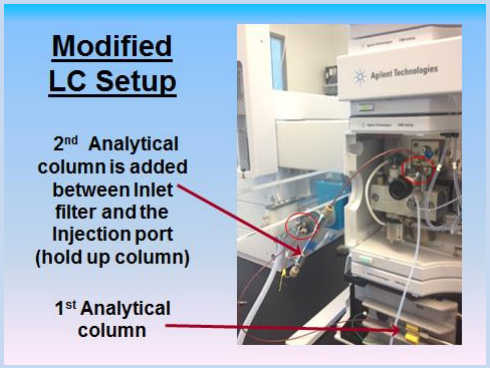
Perfluorinated Alkyl Acids (PFAAs) found in environment and groundwater prompted Federal Program UCMR3 EPA Method 537 (EPA 537 is one of seven EPA methods for UCMR3) It's solid phase extraction (SPE) combines with liquid chromatography/tandem mass spectrometry (LC/MS/MS) method for determine six selected (out of 14) PFAA in drinking water.

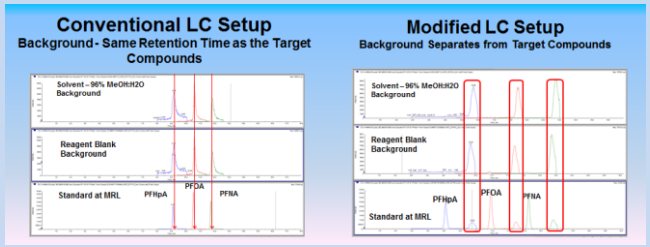
1. PFBS – Perfluorobutanesulfonic acid
2. PFHxS – Perfluorohexanesulfonic acid
3. PFOS – Perfluorooctanesulfonic acid
4. PFHpA – Perfluoroheptanoic acid
5. PFOA – Perfluorooctanoic acid
6. PFNA – Perfluorononanoic acid

The Method Reporting Limit (MRL) is ranged from 0.01 – 0.09 ppb for UCMR3 samples. Analyses were carried out using the ABSCIEX QTRAP 5500 and/or 6500 – Negative Electrode Spray Ionization (ESI)
A 250mL water sample is extracted and concentrated to dryness then adjusted to 1mL final volume with 96:4% (vol/vol) methanol:water. The mobile phase consists of 20mM Ammonium Acetate and Methanol. 5-ul extract is injected onto a C18 analytical column (150 x 2.1mm x 5um) heated to 35^{0}C. Another C18 analytical column (50 x 2.1mm x 5um) is used as a delay column.

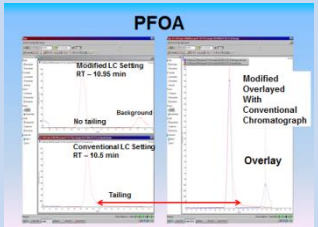




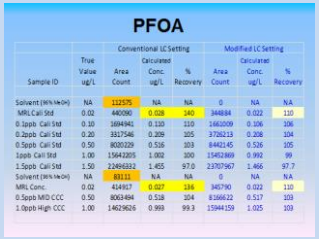


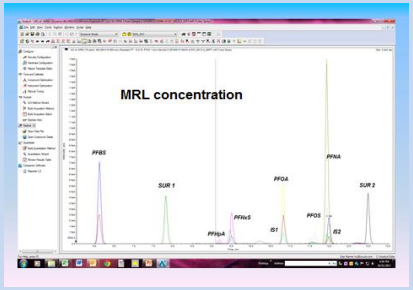


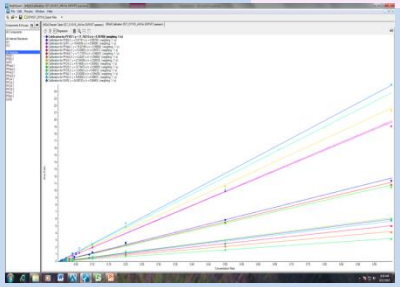
Peak shape



Comparison of Area Count







QA/QC

SAMPLE COLLECTION, PRESERVATION AND HANDLING

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

*The sampler must wash their hands before sampling.

*The samplers wear nitrile gloves while filling and sealing the sample bottles.

*Upon receiving the samples in the lab
check for free chlorine
stored at or below 6 °C
protected from light until analysis

QA/QC

Sample preparation, extraction

QC requires for each batch of samples (1-10)

1. Method Blanks (Reagent Blank – RB)
2. Lab Fortified Blank (LFB)
   LOW LFB – at MRL concentration
   LFB - Mid or high level concentration of calibration curves
3. Sample duplicates, matrix spike & spike dup
4. Internal Standard
5. Surrogate Standard

6. Field Reagent Blank (FRB) – analyze ONLY if the sample has hit target

Method Development Challenges

–If the stock standard concentrations between 2 vendor do not match, need a 3rd vendor to confirm the standard concentration
–Make working standards fresh every month to avoid compound breakdown problem (PFNA, PFHpA & PFOA)
–Each sample takes minimum 45 minutes to 1.5 hour to concentrate the sample to dryness
–Peek tubing between injection port and analytical column needed to be changed regularly

Advantages

- Separation of Background from Target Compounds
- Sharper peak and no peak tailing
- Eliminate False Positive for Result Concentration at MRL Level
- Accurate % Recovery for QC at MRL Level

Disadvantages

- Additional cost of 2nd analytical column
- Additional Pressure to the LC system ~1,000 psi
  - Conventional LC Setting Pressure ~ 3500 psi
  - Modified LC Setting Pressure ~ 4500 psi

Conclusion

Through simple LC modification, we separate the background from PFOA, PFNA and PFHpA during the analysis; improve the QC %recovery and meet all the criteria required by UCMR3 EPA method 537.

Acknowledgments

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All OCWD Organic Support Staff

Questions? Contact

Lily Sanchez
(lsanchez@ocwd.com)
714-378-3344