Cape Fear Public Utility Authority

Project update for the period covering October 1 – 31st, 2017

Summary:

The focus of this month's efforts has been on method validation and figures of merit as outlined in the previous month's report; we are on target with our timeline. A mixture of perfluoroctanoic acid and perflouro-2-propoxypropanoicacid were used as initial surrogates since these compounds represent the linear saturated and ether homologues respectively. Baseline separation of both compounds has been achieved using ultrahigh performance liquid chromatography/mass spectrometry. The ion trap mass spectrometer is operated in multiple reaction monitoring mode where a precursor mass is isolated and subsequently fragmented and scanned by the mass spectrometer. The ion trap mass spectrometer is considered a tandem-in-space instrument and provides a full scan spectrum of the products ions generated. This gives multiple qualifier ions that aids in confirmation of the analyte of interest in addition to retention time. This can be observed in the product scan of perflouro-2-propoxypropanoic acid (figure 2a) and perfluorooctanoic acid (figure 2b). Typical calibration curves are presented for perflouro-2-propoxypropanoic acid (figure 3a) and perfluorooctanoic acid (figure 3b). Generating calibration curves of both compounds over several days gave average slopes and standard deviations of 223±28 and 4033±656 for perflouro-2-propoxypropanoic acid and perfluorooctanoic acid respectively illustrating the precision of the measurement. The average goodness of fit (R^2) for perflouro-2-propoxypropanoic acid and perfluorooctanoic acid was 0.998 and 0.999 respectively. Spike recoveries have been assessed for perfluorooctanoic acid using Cape Fear River water as the matrix. Briefly, a known concentration of (86 ppb) was

added to unfiltered upper Cape Fear River (Horseshoe Bend) and processed for LC/MS analysis. A corresponding unspiked sample was processed as well for background concentration and subtracted from the spiked sample. Recoveries for perfluorooctanoic acid were 80 % and 108 % (n=2). This range is within the requirements for EPA Method 537 of 70-130%. The limit of detection for perflouro-2-propoxypropanoic acid is 1 pg mass on column and 27 pg mass on column for perfluorooctanoic acid.

We are in discussion with Zerenex Molecular based in the United Kingdom for custom synthesis of perfluoro-2-methoxyacetic acid (PFMOAA) for quantification and structural conformation of this compound. Several of the standards outlined in the September presentation have been ordered for structural conformation and quantification as well. Lastly, the biosolids have been all been extracted and cleaned up over anion exchange column awaiting analysis by LC/MS.

The goals of the coming month are the following:

1. Complete the percent recoveries of PFAS in river water.
2. Incorporate the isotopically labeled internal standards in the analysis.
3. Obtain a new preparative solid phase extraction phase that selectively retains the fluorinated compounds. The mechanism of retention is different than the traditional anion exchange phase commonly used. If this new phase works than it will allow us to only investigate and characterize fluorine containing organic compounds. See this link for an example: http://fluorous.com/fspe.php
4. Complete analyses of biosolid samples.

Figure 1: Extracted ion chromatograms of perflouro-2-propoxypropanoic acid (a) and perflourooctanoic acid (b) analyzed by ultra high performance liquid chromatography/mass spectrometry. The ion trap mass spectrometer was operated in multiple reaction monitoring mode.

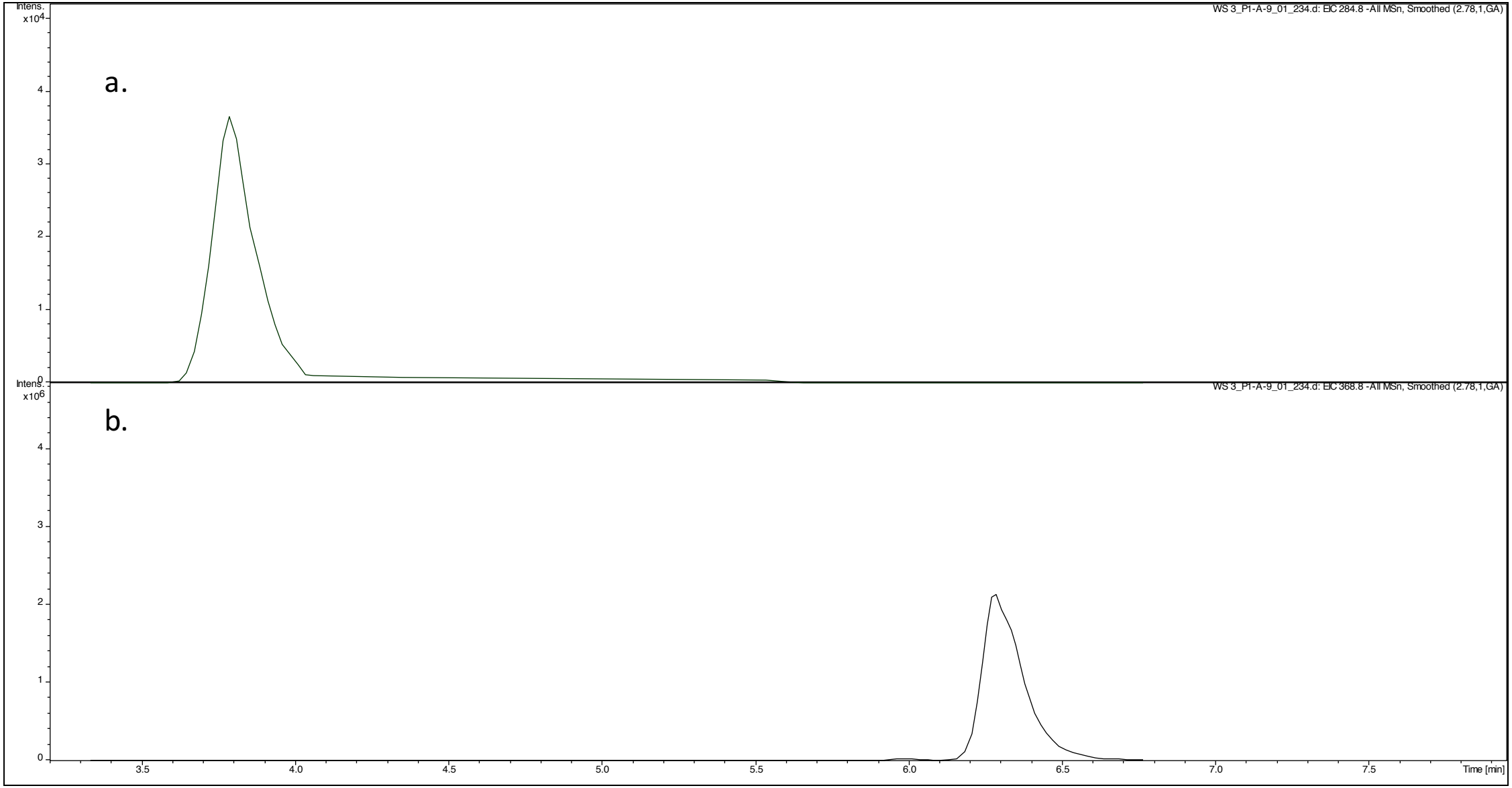


Figure 2: Product scans of perflouro-2-propoxypropanoic acid (a) and perflourooctanoic acid (b) analyzed by ultra high performance liquid chromatography/mass spectrometry. The ion trap mass spectrometer was operated in multiple reaction monitoring mode.

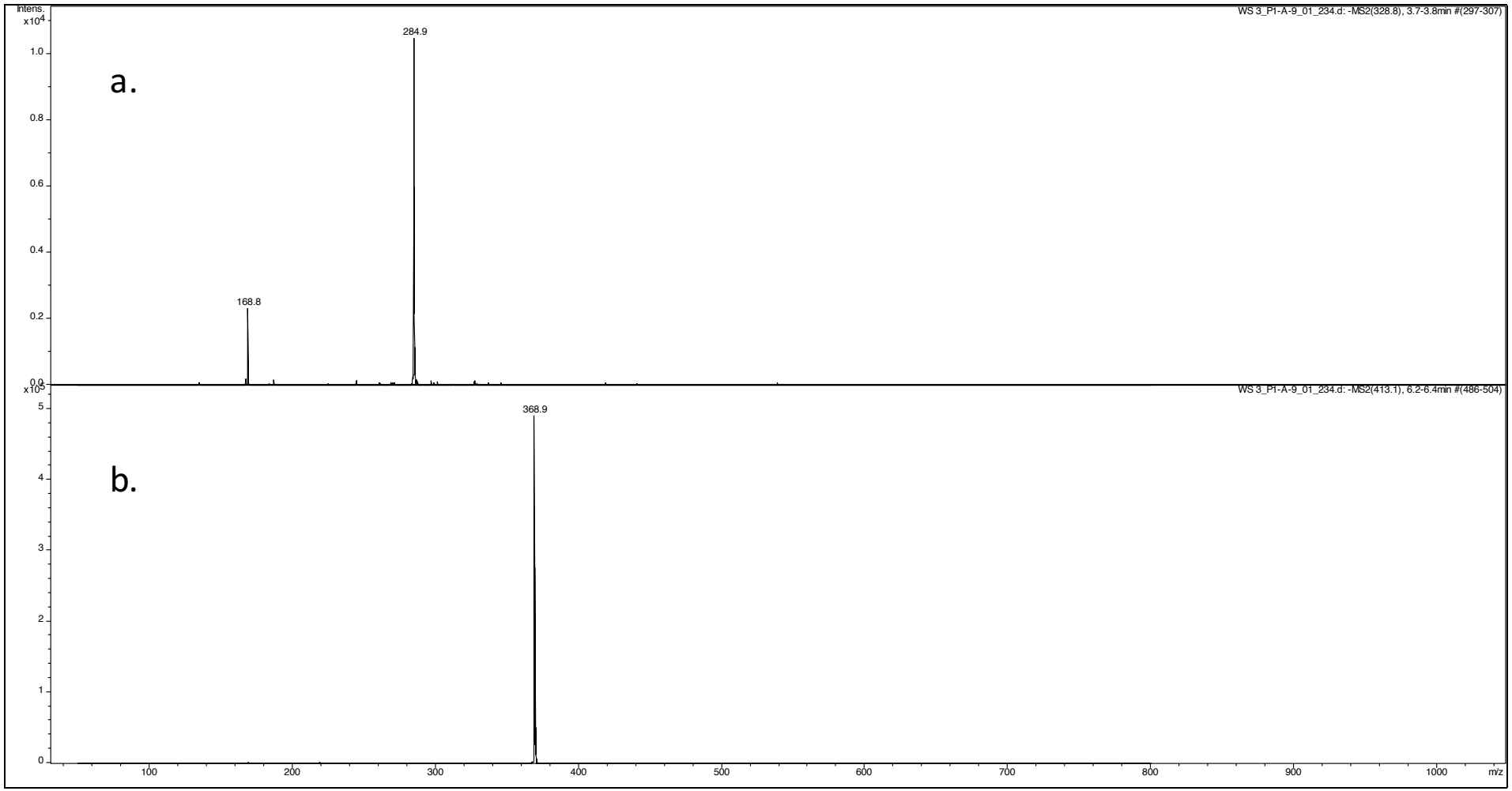
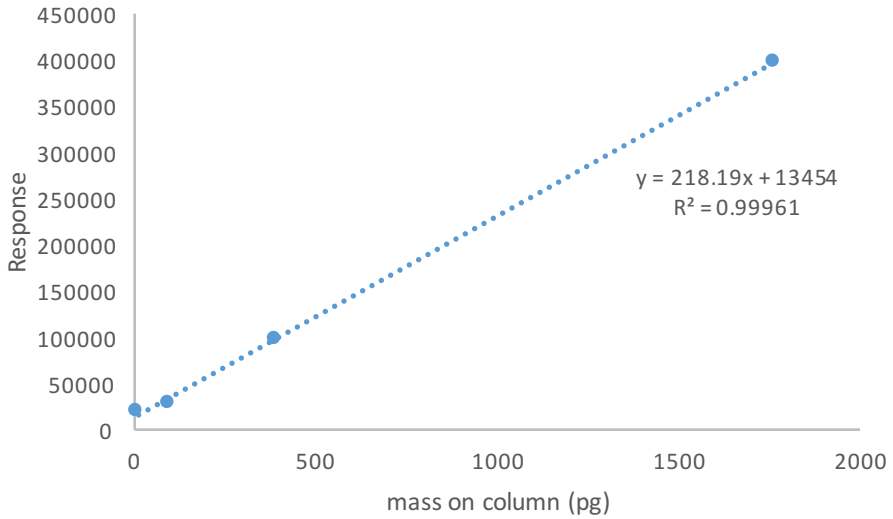


Figure 3: Typical calibration curves of perflouro-2-propoxypropanoic acid (a) and perflouorooctanoic acid (b) analyzed by ultra high performance liquid chromatography/mass spectrometry. The average slope and standard deviation of replicate calibration curves (n=3) for perflouro-2-propoxypropanoic acid is 223±28 while the perflouroocanoic acid is 4033±656.

a.



b.