

# Determination of Mass Balance for Fluorine Using Three Analytical Techniques (LC-MS-MS, F NMR, and Fluorine-ISE) as a Practical Tool for Testing Ultrasonic Treatment for Degradation of Per- and Polyfluorinated Alkyl Substances

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**Background/Objectives.** Per- and polyfluoroalkyl substances (PFAS) are a large and complex class of anthropogenic compounds. PFAS have recently caused a strong public and regulatory response due to their ubiquitous presence in the environment, their persistence, and potential toxicity to humans. The sonolytic process, as driven by the propagating acoustic wave in liquids at frequencies ranging from 200 kHz to 1000 kHz, has been proven to be an effective method for the degradation of PFAS. The sonolytic degradation of PFAS is believed to be caused primarily by high-temperature pyrolysis. However, a complete mass-balance for fluorine has not been reported in the literature and some studies have reported a very low yield of end products and incomplete mineralization. The overall objective of this project is to perform a mass balance for fluorine using three independent analytical techniques: a triple quadrupole liquid chromatography mass spectrometer (LC-MS), fluoride- ion selective electrode (F-ISE), and  $^{19}\text{F}$  - nuclear magnetic resonance ( $^{19}\text{F}$ -NMR). This fluorine mass balance approach will determine the efficacy of the sonolytic process in achieving complete mineralization of PFAS in high-concentration waste.

**Approach/Activities.** In this project, the sonochemical degradation of PFAS in synthetic high concentration waste using an intermediate scale (10 L) multi-frequency ultrasonic reactor was evaluated. The performance of the intermediate reactor was assessed for treating synthetic high concentration PFAS waste with carboxylic and sulfonic perfluoroalkyl surfactants ranging in chain length from four to eight carbons at three different initial concentrations: 6, 55, 183  $\mu\text{M}$ . The impact of co-occurring PFAS on the degradation of individual PFAS was also observed. The triple quadrupole LC-MS (Agilent 6470 Triple Quadrupole LC/MS System) was employed for identification and quantification of 25 PFAS (EPA 533) in synthetic high concentration PFAS waste. A fluoride-ion selective electrode (F-ISE) was used for quantification of the formation of fluoride ions.  $^{19}\text{F}$ -NMR spectroscopy, a non-targeted analysis that can quantify different PFAS chemicals in the sample, was employed to measure the reduction of total PFAS in sample before and after treatment.

**Results/Lessons Learned.** It was found that for the sonolytic treatment of synthetic high-concentration PFAS waste, long-chain PFAS decrease in concentration faster than short-chain PFAS. PFBA presented the slowest removal rate of the PFAAs detected. *LC-MS analysis showed no-significant increase in the concentration of short-chain PFAS, indicating the complete mineralization of PFAS achieved in the sonolytic treatment.* Similarly, F-ISE technique showed an increase in the formation of fluoride, a benign product for PFAS mineralization. The  $^{19}\text{F}$  -NMR showed a reduction in  $\text{CF}_3$  and  $\text{CF}_2$  in terms of both peak height and peak area. Only the  $\text{CF}_3$  peaks in the NMR data were used to quantify the PFAS degradation. While NMR results differ slightly from the degradation determined from triple quadrupole LC-MS analysis and F-ISE measurement, the relative percent difference (RPD) of the degradation between the three different methods for initial PFAS concentration of 55  $\mu\text{M}$  ranged from 7.8% to 19.2%. The  $^{19}\text{F}$  NMR can be a powerful tool to test the viability of treatments for destroying PFAS in high-

concentration PFAS waste. NMR can simultaneously detect both the organic fluorine, namely the CF<sub>3</sub> peak typical to all PFAS materials, and the desired inorganic product, F<sup>-</sup>.