Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.38039

Enabling stable isotope fingerprinting of PFAS using Orbitrap IRMS: A tool for source attribution of fluorinated organic compounds

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Per- and polyfluoroalkyl substances (PFAS) are a critical threat to ecosystem and human health. PFAS exhibit a known and growing list of toxic effects, making their mitigation a priority for limiting negative environmental consequences. Engineered solutions for deconstructing PFAS are in development and may become a powerful tool for environmental remediation. However, the prevalence of various PFAS compounds in a wide range of industrial sites, agricultural systems, and consumer products can make it challenging to link an environmental contaminant to a specific source – an important connection for guiding and improving the efficiency of remediation efforts. Stable isotope fingerprinting has demonstrated utility for linking samples to their source in contaminant studies, chemical forensics, and food authentication amongst other efforts. Isotope ratio mass spectrometry (IRMS) is the workhorse for stable isotope fingerprinting and has been the dominant analytical platform for previous contaminant studies. However, IRMS analysis requires complete analyte conversion to simple gases (which can be challenging given the chemical recalcitrance of PFAS), necessitates relatively large sample sizes (which is incompatible for compounds like PFAS that are toxic at trace concentrations), and cannot resolve distinct, intra-molecular stable isotope signatures (that could provide an additional forensic signature). To circumvent these challenges, we sought to evaluate whether Orbitrap IRMS could enable stable isotope fingerprinting of PFAS. We used perfluorooctanoic acid (PFOA) as a model PFAS compound for initial testing and developed an Orbitrap method for measuring $\delta^{13}C$ of both the full molecule and a decarboxylated fragment of PFOA. Of the 23 commercial samples we examined, 91% of pairwise comparisons confirmed distinct isotope values, suggesting sufficient variation exists to serve as a fingerprinting tool. Further, intramolecular stable isotope distribution within PFOA showed correlation with structural isomers of the compounds which may provide an additional signature indicative of synthetic method. While the true capabilities of Orbitrap analysis for molecular-level stable isotope analysis are still coming into focus, Orbitrap has transformative potential for unlocking stable isotope signatures in PFAS to help combat these emerging contaminants.