Enabling detection of perfluoroalkylphosphonic acids (PFPAs) using MALDI-TIMS-TOF mass spectrometry

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Per- and polyfluoroalkyl substances (PFAS) are anthropogenic chemicals characterized by high carbon-fluorine bond strengths and polar head group. The long-term stability and resistance of PFAS to biological and environmental degradation renders these compounds as emerging contaminants of concern associated with adverse health effects. Thus, the development of robust analytical methods for the characterization of PFAS in a variety of matrices is necessary. Conventional analysis is often conducted by chromatographic-mass spectrometry workflows; however, numerous challenges are presented (*i.e.,* complex sample preparation/pretreatment, extensive analysis time, disposition to contamination, excessive solvent consumption) that can be overcome by employment of alternative chromatography-free techniques. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) is a "soft" ionization technique that enables rapid *in-situ* analysis with high mass resolution and sensitivity providing a critical tool for the identification, localization, and quantification of PFAS in biological and environmental samples. Previous work in our group has shown detection of perfluoroalkyl sulfonic acids and perfluoroalkyl carboxylic acids using MALDI-TOF MS with trapped ion mobility spectrometry (TIMS). In this work, we aim to enable the detection of perfluoroalkylphosphonic acids (PFPAs). Different MALDI matrix compositions and instrument laser conditions were optimized for PFPAs of varying perfluorinated carbon chain length in water samples, including 2-(perfluorohexyl)ethylphosphonic acid and (perfluorooctyl)ethylphosphonic acid. Our preliminary results demonstrated successful detection of the deprotonated ions of these PFAS with a 2:1 9-aminoacridine:N-napthylethylenediamine dihydrochloride (9-AA:NEDC) binary mixture as a novel matrix for MALDI analysis. Future studies will aim to achieve quantification at environmentally relevant concentrations for PFPAs using high throughput MALDI-TIMS-TOF.