

FT-IRMS: unlocking new dimensions and providing unprecedented access to intramolecular isotopic information

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Orbitrap™ based FT-IRMS, both electrospray and gas source, are becoming increasingly accepted in the community as a unique and complimentary approach to classical IRMS techniques for measuring relative abundances of isotopically substituted species. In contrast to classical approaches, no chemical manipulation or gas conversion reactions are required and as a result, no intramolecular information is lost from sample to analysis. Gas source, electron impact ionization coupled to GC sample introduction and Orbitrap MS detection enables high sensitivity, compound specific analyses of non-polar compounds. Peak broadening can be implemented for high precision analyses or direct elution measurements can be utilized for multiple compounds from a single sample. Atmospheric pressure ionization techniques like electrospray ionization offer the specific advantage of performing “soft” ionization, which produces intact molecular ions and provides unique insight into the molecular anatomy of slightly polar to very polar compounds in aqueous solutions. Similar to the GC based approach, peak broadening combined with on-line reference switching enables high precision compound specific measurements from complex mixtures of organics.

Currently, this approach is being applied to inorganic oxyanions and small organic molecules. Utilizing the HRAM capabilities of the Orbitrap™ MS instruments, resolving singly and doubly substituted polyisotopocule molecular ions from adducts and isobars is achieved at resolutions up to 1 million enabling simultaneous quantification. Methods have been developed for nitrate ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$, $\delta^{17}\text{O}$, $\Delta^{17}\text{O}$, $\Delta^{15}\text{N}^{18}\text{O}$, $\Delta^{15}\text{N}^{17}\text{O}$, $\Delta^{18}\text{O}^{18}\text{O}$), sulfate ($\delta^{33}\text{S}$, $\delta^{34}\text{S}$, $\delta^{36}\text{S}$, $\delta^{17}\text{O}$, $\delta^{18}\text{O}$, $\Delta^{17}\text{O}$, $\Delta^{33}\text{S}$, $\Delta^{36}\text{S}$, $\Delta^{34}\text{S}^{17}\text{O}$, $\Delta^{33}\text{S}^{18}\text{O}$, $\Delta^{34}\text{S}^{18}\text{O}$, $\Delta^{17}\text{O}^{18}\text{O}$, $\Delta^{18}\text{O}^{18}\text{O}$) and phosphate ($\delta^{18}\text{O}$, $\delta^{17}\text{O}$, $\Delta^{17}\text{O}$, $\Delta^{17}\text{O}^{18}\text{O}$, $\Delta^{18}\text{O}^{18}\text{O}$), which can achieve sub-‰ precision for ratios of singly substituted isotopocules. Methods have also been developed for small organic molecules such as MSA, caffeine, vanillin, PAHs, hydrocarbons, carboxylic acids and amino acids, where the FT-IRMS approach offers considerable advantages. These new measurement approaches will change the way we solve geochemical, cosmochemical, and biochemical problems moving forward by providing additional isotopic dimensions and access to smaller sample amounts.