

MASS SPECTRAL CHARACTERICS OF BRANCHED ALKANES AND THE DETECTION OF THE IRREGULAR ISOPRENOIDS CROCETANE AND PMI IN SEDIMENTS AND OIL

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The mass spectra of branched alkanes show enhanced fragmentations directed by and adjacent to tertiary and quaternary carbon centres. Hydrogen transfer reactions associated with these cleavages may also yield even mass/odd electron ions of high abundance. These diagnostic, even mass ions are conveniently favoured by low energy unimolecular fragmentation processes occurring in the first field free (FFR1) region of sector mass spectrometers and can be conveniently monitored by daughter scans. In highly methylated hydrocarbons, however, the molecular information pertaining to branching locations is dissipated due to the proximity of the alkyl groups.

Isoprenoid hydrocarbons contain a relatively high degree of methylation but their irregular and regular isomers still show quite distinct mass spectra. The tail to tail linked irregular hydrocarbons 2,6,11,15-tetramethylhexadecane (crocetane) and 2,6,10,15,19-pentamethyl-icosane (PMI) have attracted considerable attention in recent environmental and organic geochemistry studies (e.g. Koga et al., 1993, Thiel et al, 1999). These hydrocarbon have been attributed to archaea, with crocetane also a probable biomarker specific for anaerobic oxidation of methane. The anomalously ¹³C-depleted crocetane has recently been detected by compound specific isotope analysis (CSIA) in a range of modern to Tertiary-aged sediment samples (e.g. Thiel et al., 1999) but its detection by GCMS has proved problematic due to co-elution with phytane on most conventional non polar capillary columns. Extreme care is necessary when attempting to distinguish and quantify irregular isoprenoids in the presence of their typically more abundant regular counterparts.

Mass spectrometric protocols have been optimised to discriminate between regular and irregular isoprenoids, and specifically promote the GCMS detection of crocetane and PMI. The presence of crocetane and PMI in a suite of crude oils and sediment samples from anoxic environments was investigated. Multiple (metastable) reaction monitoring (MRM) unambiguously confirmed the presence of crocetane in several Devonian aged oils and several modern and ancient sediments suggesting its occurrence may be more widespread than previously thought. PMI, on the other hand, was only detected in a bitumen sample from the Miocene Monterey Formation and a modern sediment sample from Ellis Fjord, Antarctica suggesting it may occur mostly in rocks younger than 100Myr. Reports of its occurrence in rocks 200Myr and older may be erroneous.

References:

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