

COMPOUND SPECIFIC D/H ISOTOPES FOR ORGANIC GEOCHEMICAL STUDIES

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GC-MS techniques are useful in identifying the carbon skeletons of components and in correlating oils-oils and oils-source rocks, but these studies based on structure alone are not always useful in distinguishing their natural product precursors. Compound specific isotope analysis provides an extra dimension often allowing one to establish the natural origins of components in complex mixtures. Isotope ratio monitoring-gas chromatography mass spectrometers (irm-GCMS), whereby a gas chromatograph (GC) was linked to an isotope ratio mass spectrometer *via* a combustion interface, allowing the determination of $^{13}\text{C}/^{12}\text{C}$ ratios of individual trace compounds within complex mixtures were developed in the 1990's.

Recent developments of irm-GCMS technology now include the capability of these instruments to successfully measure D/H of individual organic components in complex mixtures. For D/H analysis, the sample is again (i.e., as for $^{13}\text{C}/^{12}\text{C}$ analysis) entrained in a helium carrier gas, separated by GC and individual components separately analysed by the isotope ratio mass spectrometer. As the components elute from the GC column, the hydrogen bound in the organic components is quantitatively converted into H₂, graphite and CO by pyrolysis at high temperatures, where a ceramic tube (Al₂O₃, no packing, > 1200 °C) or a quartz tube (packed with chromium 1000 °C) is used as the reactor. However, there are several difficulties associated with D/H isotope analysis. For example, H₃⁺ produced as a by-product of ion-molecule collisions; and (ii) Helium (m/z 4) may have an influence on the measured masses (m/z 3). Efforts have been made to overcome these problems and will be discussed.

Stable hydrogen isotopes show larger variations in their natural abundances than those of carbon in the environment and in biochemical processes. Isotope geochemistry of hydrogen is also particularly interesting because hydrogen is present in terrestrial environments and even below the subsurface in geological formations in different forms e.g. H₂O, H₂ and CH₄. Thus, hydrogen is envisaged to play a major role, directly or indirectly in a wide variety of naturally occurring geological processes. At present we are determining D/H of individual hydrocarbons in crude oils and sediments to relate to dD of water in paleoenvironments in which primary producers lived providing information on depositional environments of source rocks, and paleoclimatic conditions in particular relating to the global water cycle. Preliminary dD results of hydrocarbons on some Australian crude oils classify them into different groups based on age and source.
