THE SIGNIFICANCE OF GC-MS/MS IN OIL-SOURCE ROCK CORRELATION

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Application of gas chromatography-mass spectrometry (GC-MS) and more recently gas chromatography-mass spectrometry/mass spectrometry (GC-MS/MS) represents the unique method for investigations of crude oils and their correlation with source rocks. GC-MS and GC-MS/MS of crude oils and extracts of source rocks, oil shales and coals provide identification and quantification of numerous individual compounds. Among them, biological markers (biomarkers) are of the greatest importance. Biomarker molecules are used for evaluating the source organisms, the reconstruction of depositional environment and the maturity assessment. Biomarkers also can provide information of source rock mineralogy (lithology) and age. Steroids and terpenoids are the most useful biomarkers for correlation purposes. Most of them can be routinely identified by GC-MS, however for identification of the most specific compounds GC-MS/MS is required.

The distribution of C_{27}-C_{29} regular steranes (*m/z* 217) is widely used for assessment of the source of organic matter (OM). However, this approach has limitations, because certain marine algae produce sterols with 27 to 29 carbon atoms. C_{30} steranes (4-desmethyl-24-*n*-propylcholestanes) are much more useful as source indicators, since they are highly specific for marine OM input [1]. However, identification of these biomarkers usually requires application of GC-MS/MS (transition 414 → 217). Apart from steranes, diasteranes, geoisomers having, 13β(H)17α(H), or 13α(H)17β(H) configuration are usually present in the crude oils. High diasterane/sterane ratio is typical of petroleum derived from clay-rich source rocks. Diasteranes are usually abundant in acidic, suboxic to oxic depositional environments. Finally, high diasterane/sterane ratio can result also from high thermal maturity or heavy biodegradation. In the routine GC-MS several diasterane isomers co-elute with sterane isomers which makes accurate quantification of these biomarkers impossible. GC-MS/MS (M^+ → 217) separating the compounds according to number of C-atoms allows precise identification and quantification all of sterane and diasterane isomers.

Gammacerane is pentacyclic triterpenoid which is specific for a stratified water column in marine and non-marine depositional environments, commonly resulting from hypersalinity

at depth [2]. Care must be taken to accurately quantify gammacerane using the GC-MS (m/z 191). Because of its high degree of symmetry, two identical m/z 191 fragments are generated in the mass spectrometer from gammacerane. Thus, a sizable peak on the m/z 191 mass chromatogram represents a low concentration of gammacerane compared with other terpanes. Therefore, GC-MS/MS, 412 → 191 transition is recommended for precise identification of gammacerane.

C_{30} tetracyclic polyprenoids (TPP) are most prominently observed in samples derived from low salinity, i.e. fresh to brackish lacustrine environments, and are generally present in low levels in samples derived from saline, i.e., marine and saline lacustrine, environments [3]. The ratio of C_{30} tetracyclic polyprenoids to sum of C_{26} 27-norcholestanes (which are low in lacustrine and prominent in marine samples) is used to distinguish lacustrine and marine settings. However for identification of both, C_{30} tetracyclic polyprenoids and C_{26} 27-norcholestanes, GC-MS/MS (414 → 259 and 358 → 217, respectively) is required.

Application of GC-MS/MS (454 → 191 and 468 → 191) allowed the identification of series of C_{33} and C_{34} isohopanes (31-methylbishomohopanes, 31-methyltrishomohopanes and 32-methyltrishomohopanes). The ratio of isohopanes to hopanes is useful for distinguishing marine, lacustrine and oils from coaly sources [4].

Series of "early eluting hopanes" (M^+ → 191), as well as C(14a)-homo-26-nor-17α(H)-hopanes (HHs, C-ring with 7 carbons instead of the usual 6; M^+ → 369) have been identified by GC-MS/MS. The C_{30} HH/C_{30} 17α(H)21β(H)-hopane ratio has proved applicable to a wide range of maturation, whereas the ratio of C_{30} "early eluting hopane" to C_{30} 17α(H)21β(H)-hopane is useful to distinguish moderately mature and highly mature OM [5].

In difference to numerous source and maturity related geochemical parameters, parameters related to age of OM are scarce. The most useful age parameters, 24-nordiacholestane ratio (NDR) and 24-norcholestane ratio (NCR) [6] are based on distribution and abundance of C_{26} steranes. Identification and quantification of these biomarkers requires GC-MS/MS (358 → 217).

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