

BIOMARKER CHARACTERIZATION OF EOCENE CRUDE OILS FROM CAMBAY BASIN UTILIZING COMPREHENSIVE GCXGC-TOFMS

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Biomarkers are informative fossil molecules present in the crude oil or/and sediments which aids in understanding of biodiversity, palaeodepositional environment and evolutionary history of Earth in deep time. Moreover, considering the importance of biomarkers in geochemical and environmental research, it is essential to generate a precise and detailed composition investigation of crude oils. However, due to presence of plethora of compounds present in the crude oil, it is difficult to identify and quantify compounds for traditional gas chromatography mass spectrometry because of low chromatographic resolution.

Comprehensive two-dimensional gas chromatography (GCXGC) together with time-of-flight mass spectrometry (TOFMS) is a robust analytical tool having great potential to separate complex mixtures of hydrocarbon especially present in geological and environmental samples. This technique with rapidly expanding applications established the fact that the application of GC×GC-TOFMS could be a windfall in the field of gas chromatography (Eiserbeck et al., 2012, and reference therein).

The aim of this study is to apply the GCXGC-TOFMS technique and to analyze crude oils of Narmada-Tapti block, Cambay Basin by separating chromatographic resolution of GCXGC and processing the full scan mass spectra by TOFMS. This paper offers a case study for the successful utilization of GCXGC-TOFMS for comprehensive geochemical characterization of certain crude oils from Cambay Basin, with strong emphasis to the isomers of triterpenoids and steroid in the saturated and aromatics fractions.

The saturated fractions show aliphatic hydrocarbons which are dominated by *n*-alkanes (C₁₅ to C₃₉) along with branched and cyclic isoprenoids. The major isoprenoids detected in the saturated fractions are pristane (Pr) and phytane (Ph). The distribution of *n*-alkanes and acyclic isoprenoids are considerable for assessing the origin and source of organic matter as they are widespread in the biosphere. In cyclic isoprenoids, the major class of compounds recognized are bicyclic sesquiterpenoids, steranes (regular and rearranged) and triterpenoids with three, four and five rings (Figure 1). The studied samples contain bacteria derived triterpenoids along with their methylated series in considerable amount. An extended series of tricyclic terpanes and steranes have also been identified. The abundance of C₂₉ regular steranes dominate over C₂₇ and C₂₈ steranes indicates higher plant contribution to the organic matter. Angiosperm-derived triterpenoids viz. oleanane and bicadinane have also been detected in the analysis of GCXGC, which is difficult to comprehend in Cambay oils by monodimensional GC because of low abundance and get co-elutions with hopanes and steranes.

The total ion chromatograms of aromatic fraction are dominated with naphthalenes, phenanthrenes and its alkylated homologues, diaromatic tricyclic terpanes, triaromatic steranes, C₃₂, C₃₃ and C₃₄ benzohopanes, C₃₀ diaromatic secobicadinanes and many polyaromatic hydrocarbons (PAHs). Diaromatic secobicadinane identified in crude oils which are derived from polycadinene dammar resins, produced by the diterocarpaceae tree of a tropical angiosperm family (van Aarssen et al., 1990). The occurrence of diaromatic secobicadinanes suggests that the organic matter falls into the early catagenetic zone (Chattopadhyay and Dutta, 2014). Many oleanane and lupane skeletons derived PAH including

2,2,3-trimethyl-1,2,3,4-tetrahydropicene (M+ 324), 7-methyl-1'-ethyl-1,2-cyclopentanochrycene (M+ 310), lenosta(eupha) pentaene (M+ 376), lenosta(eupha) hexaene (M+ 374), 24,25,26-trisnor-lupa-1,3,5(10)-tetraene (M+ 342), des-A-26,27,28-trisnor-oleana-5,7,9,11,13,15,17-heptaene (M+ 274), 24,25,26,27-tetranor-lupa-1,3,5(10),6,11,13-heptaene (M+ 342) and 8,14-seco-oleanane (M+ 356) have been detected. These aromatic triterpenes considered to degradation products of micro-organism (Trendel et al., 1989).

The presence of peculiar biomarkers like eudesmane, oleanane, bicadinane, ionene, cadalene, secobicadinane and oleanane and lupane derived aromatic compounds perceived in the crude oils signifying a substantial contribution of angiosperm to the precursor biomass. High Pr/Ph values indicate that the organic matter was deposited in a sub-oxic environment. Hopanoids, des-A-triterpenoids and C-ring cleaved triterpenoids detected in the fractions indicate that there is a considerable contribution of micro-organism activity to the organic biomass. The presence of rearranged hopanes and steranes and calculated parameters based on certain biomarkers indicates shale as source rock. Various maturity parameters signify that the Cambay-Tarapur block oils have reached the initial catagenetic stage. The proficiency of GCXGC achieves an improved insight on biotic contribution and palaeodepositional environment of the Cambay Basin oils.

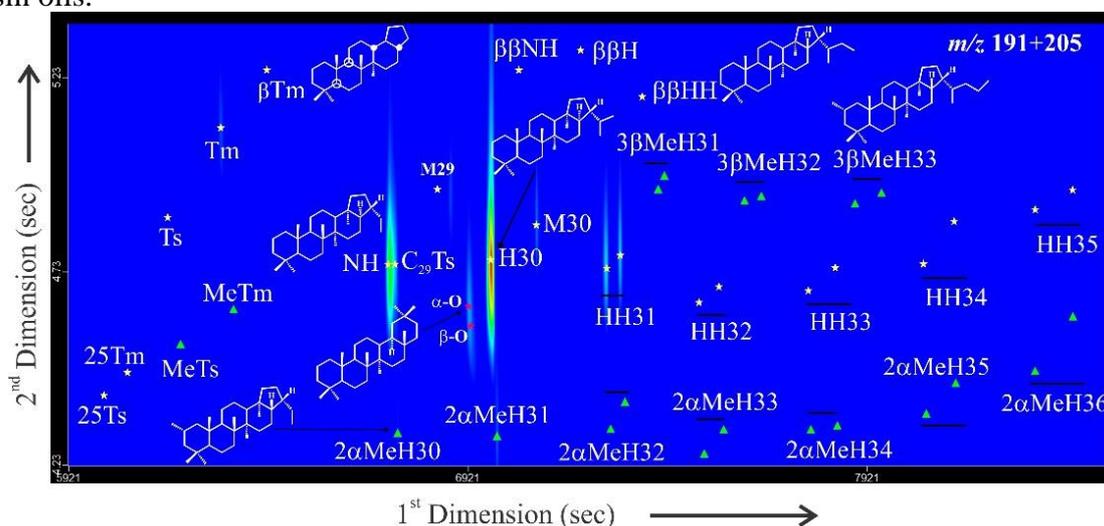


Figure 1: selected ion chromatogram (m/z 191+205) showing distribution of hopanes and methylated hopanes. Key:- H: hopanes; HH: homohopanes, M: moretanenes; O: oleanane; Ts: trisnorhopane; Tm: trisnorhopanes; MeH: methylated hopanes; MeTs: methyl trisnorhopane; MeTm: methyl trisnorhopane.

References

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