CHARACTERIZATION OF HIGHER PLANT TERPENOIDS BY GC × GC-TOFMS

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Diterpenoids and triterpenoids are widely distributed in plant natural products. They are utilized in chemotaxonomy (Otto and Wilde, 2001), reconstruction of paleoenvironment and paleovegetation and characterization of petroleum systems (Peters et al., 2005). In general the conifer and angiosperm higher plant biomarkers have diterpenoid and triterpenoid signatures. Here we study the higher plant terpenoids from the saturate fractions of few Cenozoic oils and sediments, Assam Basin, India. Comprehensive GCxGC TOFMS is a powerful technique for the separation and identification of biomarkers which could be utilized for paleobotanical studies and characterizing petroleum compositions (Eiserbeck et al., 2012).

The oils and sediments contain triterpenoids such as des-A-triterpanes, oleananes, bicadinanes, hopanes and C₃₀ triterpenoids. Paleocene-Eocene oils and sediments contain C₁₈-C₂₀ diterpanes which are absent from Oligocene-Miocene oils and sediments. In traditional 1D GC-MS rosane and ent-beyerane, both tricyclic and tetracyclic C₂₀ diterpanes respectively, co-elute (Figure 1a). Comprehensive GC×GC-TOFMS system separates both the compounds in the first dimension based on their retention time in x-axis and in the second dimension based on their polarity in y-axis (Figure 1b). Here we see that drimanes, C₁₈, C₁₉ and C₂₀ diterpanes are classed into separate groups based on their elution and polarity. Ent-beyerane occurs within a line of the chromatographic plane in the second dimension, which classes other tetracyclic diterpanes like phyllocladane and kaurane. Relatively higher polarity is attributed to the C₂₀ tetracyclic diterpanes due to their later chromatographic elution in the second dimension. n-Alkanes which are usually abundant in sediments and oils elutes much earlier in the second dimension than the terpenoids. Triterpenoids such as the alkylated hopanes and mortanes, rearranged oleananes, oleananes, bicadinanes and olefins are also separated in both the dimensions. In oils, the C₃₀ triterpanes coelute with hopanes and other oleanoid triterpanes, which are resolved in GC×GC system. The higher sensitivity enables us to detect unsaturated triterpanes from oils. Olefins such as olean-12-ene, olean-18-ene neo-hop-13(18)-ene and other oleanoid triterpanes are present in low abundance in oils, which are separated from the co-eluting triterpanes. Most of them are detected in oils from Paleocene-Eocene reservoirs and absent from Oligocene reservoir oils. This could be due to effects of primary migration or migration contamination from immature source rocks therefore different migration and maturation histories from Oligocene-Miocene oils. ββ Hopanes which are difficult to detect from the oils using traditional GC-MS systems could be identified in GCxGC systems.

In this study, comprehensive GC×GC-TOFMS has been successfully applied in the separation of different diterpanes and triterpanes and also group compound classes based on elution and polarity. It is useful to identify compounds with increased sensitivity and separation especially dealing with compounds with co-elution and low abundance which are difficult to detect in traditional GC-MS systems.
**Figure 1** m/z 123 selected ion chromatogram of Eocene crude oil in: a. GC-MS and b. Comprehensive GC×GC TOFMS.

**References**

