Characteristic Investigation for Source and Degradation of Crude Oil Using Steranes and Terpanes biological Markers

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1. Introduction

Those saturated aliphatics and low numbered PAHs in moderately degraded or fresh oil samples can be used as source tracing and weathering studies. However, in highly degraded samples, these compounds are completely disappeared frequently. Therefore, it is impossible to get valuable information through normal, branched alkanes to PAHs. In this case of samples, biological markers, containing original source information persistently, can be the unique material for geological studies. Terpanes and steranes, representative biomarkers, are highly resistant to degradation and nearly unaffected long-term weathering[1]. Therefore, they can provide valuable information for the source identification, the status of weathered degree and the fate of spilled oil in environment. Terpanes and steranes in sediments are converted from corresponding biogenic precursors, and exist as many stereoisomers with different $\alpha/\beta$ and/or R/S configurations that have different thermodynamic stability. In common stage of a sedimentary burial, the thermodynamically unstable isomers are gradually replaced by the geological stable isomers reaching a known equilibrium point and providing a measure of the maturity of organic matter[2]. These processes are combinations of a series of bacteriological actions and low temperature reactions generally referred to as diagenesis, catagenesis, and metagenesis.
2. Experiment

Initially extracted oil residues in field collected samples with dichloromethane and obtained their GC–FID chromatogram for the purpose of screen. Field samples for further specific geochemical study were selected based on their GC–FID chromatogram exhibiting a considerable amount of compositional heterogeneity and various stages of alteration. Considering soil types and weathered patterns on GC–FID chromatograms, The extracts of selected sample was fractionated into three classes of aliphatics, aromatics and asphaltenes. Aliphatic and aromatic groups were used to obtain geochemical data. Geochemical data was obtained by using a HP–6890 gas chromatograph equipped with a 30m DB–5 MS capillary column (0.25 mm I.D. × 0.25 μm film thickness) and interfaced to a HP–5973 quadrupole mass spectrometer (both from Agilent Technology) operating in an electron ionization (EI) mode. Helium was used as carrier gas with a flow rate of 1.0 mL/min, 1 μL aliquots were injected in a splitless mode, temperatures of injector, ion source and detector were 320℃, 300℃ and 250℃, respectively. The GC oven temperature program was at initial 1 min hold at 40℃, increase to 150℃ (6℃/min) and to 300℃ (10℃/min) then hold for 25 min, leading to total analysis time of 59 min.

3. Results and Discussion

In order to define the degree of weathering progress and long-term biodegradation, compared the extracted ion chromatogram m/z=191 for terpanes and m/z=217 for steranes of the oil residues in the surface sediments to the referenced crude oil. Those biomarker parameters based on m/z=191 and m/z=217 were used for evaluating the weathered degree of spilled oil. Those GC/MS ion chromatograms of m/z=217 are shown in Fig. 1. Peak assignments labeled in the Fig. 1. are summarized in Tables 1. Structural identifications are based on mass data in the selected ion monitoring mode, pattern recognition of mass spectra, comparison of GC retention time with reference standards, and literature data[3].

Terpanes are distributed in a wide range of retention time from 31 to 53 min. Which composed of 17α, 21β–hpane series (C$_{31}$–C$_{35}$) occur as 22S and 22R epimers in range of retention time 41–53 min with two main hopanes C$_{29}$–17α(H),21β(H)–30–norhopane and C$_{30}$–17α(H),21β(H)–30–hopane, C$_{23}$–C$_{29}$ terpanes and 5 series of hopane epimers. Hopanes with 17α, 21β configuration in the range of 27–35 carbon atoms are characteristic of petroleum. Steranes based on mass fragmentograms of m/z=217 are distributed in a range of RT from 34 to 41 min, and they are composed of diasteranes and C$_{30}$ steranes, the dominance of C$_{27}$, C$_{28}$, and C$_{29}$ ααα and αββ regular steranes with their 20S and 20R epimers.