

*Full Length Research Paper*

# Application of geochemical parameters for characterization of oil samples using GC-MS technique

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**Geochemical characterization of eleven (11) oil samples has been carried out; using diagnostic biomarker parameters related to thermal maturity, organic matter source, age and depositional environment. Oleanane was only found in the Nigerian oil, serving as a primary feature in distinguishing it from other oils. All the oil samples appeared to have mixed organic matter input with samples of the same region closely related to each other based on the parameters measured. Biodegradation of some of the samples may have contributed to some of the observed variabilities.**

**Key words:** Biomarker, Oleanane, biodegradation, thermal maturity.

## INTRODUCTION

Biomarkers are specific organic compounds used in assessing the genetic sources of bituminous organic matter derived from biochemical precursors by mainly reductive but also oxidative alteration processes with chemical structures which can be related back to their precursor compounds in contemporary or extinct biota (Simoneit, 2004; Tissot and Welte, 1984; Killips and Killips, 1993). These compounds are present in both oils and source rock extracts, they provide a method to relate the two and can be used to interpret the characteristics of petroleum source rocks when only oils are available (Grimalt et al., 2002). In addition, biomarkers can provide information on the organic source materials, environmental conditions during its deposition, the thermal maturity experienced by a rock or oil, and the degree of biodegradation (El-gayar et al., 2002). Valuable information about lithology, age, degree of biodegradation, thermal maturity of source rock, depositional environment and source of sedimentary organic matter in oils and their source rocks are obtained from them (Peters et al., 2005). Geochemical correlation mainly relies on GC-MS for the analysis of biomarkers and is responsible for the rapid development of organic

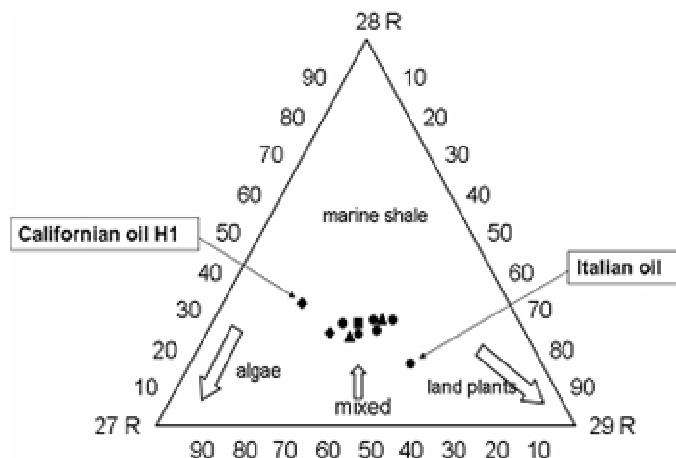
geochemistry and its application in the oil and gas Industry during exploration (Philp et al., 1990; Killips and Killips, 1993); Gas chromatography-mass spectrometry (GC-MS) is a useful technique for analysis of compounds (mostly biomarkers) present in minute quantities (usually ppm) in oils (Peters and Moldowan, 1993). Thus this study aims at describing some of the biomarker compounds present in eleven (11) oil samples from productive oil fields across the world; so that this information will provide useful insight into the oil source-rock properties and contribute to understanding of the oil sources.

## MATERIALS AND METHODS

### Thin layer Chromatography (TLC)

The TLC plates were prepared using aqueous slurry of 0.5 mm thick Keiselgel 60G; the plate was activated for an hour at 100 - 120°C and all contaminants were removed using ethyl acetate. Approximately 15 mg of each sample was taken, and about 0.2 ml dichloromethane (DCM) was added to dissolve the oils before loading them on separate TLC plates at about 2 cm from bottom of the plate. These were run in petroleum ether until the fractions reached the top of the plates, which were then sprayed with Rhodamine 6G dye and finally viewed under UV light at 254 nm; aliphatic and aromatic hydrocarbon fractions were identified and scraped off into different pre-

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**Figure 1.** Ternary diagram showing  $C_{27}$ - $C_{28}$ - $C_{29}$   $\alpha\alpha R$  regular steranes of the oil samples.

**Table 1.** Summary of eleven (11) oil samples obtained from different regions.

Sample	Location	*API gravity	*Sulphur (wt. %)
145	UK	37	0.38
149	UK	19	0.91
150	UK	n a	0.23
160	UK	24	0.44
Mill	UK	39	1.4
169	Italy	22	4.8
Boscan	S/ America.	n a	n a
H1	California	25	n a
H7	California	24	2.1
D13	California	24	2.1
N. oil	Nigeria	n a	0.44

\*This data was provided with the samples and was not measured in this study. API gravity: is a measure of crude oils density at 15.6°C (60°F) and is calculated according to Waples (1985). Sulfur content: was determined by X-Ray Sulfur Meter Model RX-500 S according to ASTM D-42914 procedure, and the results expressed as weight percent. n a = not available

pared elution tubes which were washed with about 40 – 50 ml DCM. The extract for each was reduced in volume using a rotary evaporator and then placed in auto-sample vial. Aliphatic hydrocarbon fractions were taken for GC-MS.

**Gas chromatography –mass spectrophotometry (GC-MS)**

The GC-MS measurements were performed on Hewlett Packard 5972 mass spectrometer operated at ionization energy of 70 eV linked to an HP-5890 gas chromatograph, with a splitless injector (at 280°C), fitted with a flexible silica capillary column of 30 m x 0.25 mm internal

diameter; 0.25 µm film thickness. About 1 µl of each sample was injected by an auto sampler; the oven temperature was programmed from 40 to 300°C at a rate of 4°C/min and held at 300°C for 20 min, using helium as the carrier gas at a flow rate of 1ml/min. The samples were run using full scan, single ion monitoring (SIM) and recorded using HP Chemstation data system.

**RESULTS AND DISCUSSION**

The ternary diagram of  $C_{27}$ - $C_{28}$ - $C_{29}$  steranes is used to distinguish groups of crude oils from different source rocks. Figure 1 shows that almost all of the studied oil samples appeared mixed with both plant and algal input. Italian oil was the only one with a predominance of stigmastane ( $C_{29}$ ) over  $C_{27}$  regular steranes, suggesting terrestrial source rock with more contribution of marine organic sources (Fatma et al., 2003; Peters et al., 2005); and one of the Californian oils appeared to have more cholestanes ( $C_{27}$ ) indicating marine algal input, this could be attributed to effect of biodegradation on the sample (Manzur, et al., 1999).

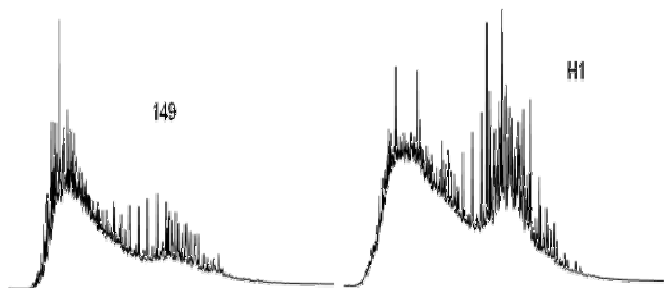
Nigerian oil sample is the only one that shows the presence of oleanane (Table 1). Oleananes are diagenetic products of various 3β-functionalised angiosperm triterpenoids (Murray et al., 1997) whose presence in oils indicate an age range from cretaceous or younger and higher in tertiary sediments which coincide with evolution of angiosperms (Nytoft et al., 2002; Hans et al., 2002; Peters et al., 2005). The Nigerian oil analyzed using GC-MS showed oleanane index value of 46% suggesting a deltaic source rock with strong terrestrial biomass (Waseda and Nishita, 1998).

Pristane/Phytane (Pr/Ph) is an indicator of depositional environment with low specificity due to interference by thermal maturity and source input (Peters et al., 2005). Ten Haven et al. (1987) stressed that high Pr/Ph (>3.0) indicates terrigenous input under oxic conditions and low Pr/Ph (<0.8) indicates anoxic/hypersaline or carbonate environments. Peters et al. (2005) related Pr/Ph ratios with sulphur contents; where low Pr/Ph values are accompanied with high sulfur contents. Table 1 and 2 showed that Italian oil (169) and Californian oil (D13) have Pr/Ph of 0.45 and 0.78; and sulfur contents of 4.8 and 2.1wt.% respectively; which strongly indicate anoxic depositional environment. Also UK oils 145, 150 and 160 have Pr/Ph of 1.25, 1.10 and 1.32 and sulfur of 0.38, 0.23 and 0.44 respectively, which indicate oxic conditions (El-gayar, 2002).

Peters et al. (2005) reported many researchers suggesting  $C_{28}/C_{29}$  sterane ratios as <0.4 for Lower Palaeozoic or older oils, 0.4-0.7 for Upper Palaeozoic-Lower Jurassic oils and >0.7 for Upper Jurassic to Mio-cene oils. Table 2 shows that Italian oil was the oldest possibly from lower Palaeozoic or older; while UK oils 145,149, 150 and 160; and Nigerian oil are believed to be Upper Palaeozoic –Lower Jurassic. Also, Californian oils D13,

**Table 2.** Depositional/age/source and maturity diagnostic biomarker parameters measured from GC-MS analysis.

Sample	Location	C <sub>28</sub> /C <sub>29</sub> sterane	Oleanane (%)	C <sub>29</sub> αββ sterane (%)	C <sub>29</sub> 20S sterane (%)	C <sub>31</sub> 22S (%) hopane	Ts/Ts + Tm	Pristane/Phytane
145	UK	0.41	0	48	48	58	0.60	1.25
149	UK	0.69	0	43	36	59	0.47	0
150	UK	0.67	0	50	51	58	0.66	1.10
160	UK	0.58	0	55	44	56	0.48	1.32
Mill	UK	0.88	0	51	53	59	0.46	0.52
169	Italy	0.39	0	35	45	52	0.12	0.45
Boscan	S/America	0.91	0	38	50	53	0.19	0.88
D13	California	1.48	0	41	47	61	0.37	0.78
H7	California	1.54	0	40	45	55	0.28	0
H1	California	1.53	0	43	49	62	0.31	0
N. Oil	Nigeria	0.69	46	41	37	56	0.46	2.47

**Figure 2.** Total hydrocarbon gas chromatograms indicating the presence of some of the biodegraded oils.

H7 and H1; Boscan and UK Mill are Upper Jurassic-Miocene (Zeev et al., 1998).

The Boscan and Italian oil are the least mature (<0.2) at 0.19 and 0.12 respectively from Ts/(Ts+Tm) as the ratio increases from nearly 0 to 1 with increasing maturity (Waseda and Nishita, 1998). Also, Shi et al. (2005) referred to oils in this range as extremely low in maturity.

The C<sub>31</sub> 22S (%) hopane isomerisation suggested that samples with 50 - 54% have barely entered oil generation, and those with 57 - 62% mean that oil generation is reached or surpassed (Peters et al., 2005); thus all the samples analyzed fall into these categories. The C<sub>29</sub> 20S (%) sterane and C<sub>29</sub> αββ (%) sterane are specific for the immature to mature range but C<sub>29</sub> 20S (%) sterane attains its endpoint value at 55%. None of the samples was below 32% which according to Shi et al. (2005) classified as immature.

Visual Examination of gas chromatograms (Figure 2) showed that some samples are slightly to heavily biodegraded showing the loss of their *n*-alkanes with more prominent unresolved complex mixture (Killops and Killops, 1993). Also, Pristane and Phytane are more resistant to biodegradation than *n*-alkanes; thus absence of the Pr/Ph ratios (Table 2) in UK (149), California (H1 and H7) is an indication of biodegradation (Manzur et al.,

1999). We therefore concluded based on the detailed geochemical characterization of the samples studied (11 samples) in assessing maturity, source, depositional environment, age and or degree of biodegradation using conventional GC-MS techniques, that comprehensive prediction of properties of the source rocks of these oils can be made which are unavailable in this study.

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