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Petroleum hydrocarbon fingerprinting of crude oils from umutu/bomu oil fields in Niger Delta, Nigeria

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ABSTRACT

Whole oil Gas Chromatographic analyses of seven different crude oil samples from two oil fields south west Niger Delta, Nigeria which had not been previously characterized geochemically was carried out to determine the source signature of these fingerprints. Normal alkanes and Isoprenoids distribution shows n-C_8 to n-C_{40}. Low molecular weight hydrocarbons (<n-C_8) were not observed, probably because of evaporative loss during sample processing. Various hydrocarbon ratios were used as supporting tool to deduce the geochemical characteristics such as organic matter source, thermal maturity, depositional environment, and extent of biodegradation. Samples U7L and KD 01 have Ph/n-C_{18} values greater than one (>1.0) indicating that the samples were biodegraded, while samples U2L, U45,U4L, KD 02 and KD 03 have Ph/n-C_{18} less than 0ne (< 1.0) suggesting that the samples were non-biodegraded. Distribution of n-alkanes (pr/ph, and isoprenoide/n-alkanes ratios) reflects that the oil samples originated mainly from terrestrial organic sources deposited in an oxic paleoenvironment.

Keywords: Gas chromatography; oxic paleoenvironment; biodegraded, fingerprinting; Niger Delta.

INTRODUCTION

Petroleum hydrocarbons consist of a very large number of compounds found in crude oil, natural gas, coal, and peat. They consist of three major groups of compounds, the alkanes (paraffins), alkenes (olefins), and aromatics. Researchers have increased the need for sophisticated techniques in analyses for excellent hydrocarbon profiling and characterization. Different varieties of instrumental and non-instrumental techniques are currently used in the analysis of crude oils, which include Hydrocarbon fingerprinting or gas chromatography (GC), gas

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chromatography – mass spectrometry (GC-MS), high performance chromatography (HPLC), thin layer chromatography (TLC), ultra violet (UV) spectroscopy [13]. Gas chromatographic technique has been used successfully in the determination of hundreds of hydrocarbons and other organic compounds. It is an ideal tool in analyzing gas and liquid samples, thus allowing the researcher to identify both the type of molecular species present, their concentrations, and also obtain information from hydrocarbon samples (free product) by determining the composition of the hydrocarbons present[6][10].

Crude oil varies widely in appearance and viscosity from field to field, characterization and source identification of oils from various fields is necessary. One of such ways of doing this is by analyzing the hydrocarbon fractions, Petroleum hydrocarbons fingerprinting (Gas chromatography fingerprinting) analysis for quantitative and qualitative oil characterization which is often used for evaluating the range of hydrocarbons in crude oil or rock extract [6].

GC fingerprints requires analyzing entire oil for C_2 - to - C_{45} hydrocarbon range in a gas chromatograph while certain hydrocarbon ratios were employed in evaluating such things as maturity, source, biodegradation and evaporative fractionation [6].

Province Geology.

The Niger Delta is one of the world's largest Tertiary delta systems and an extremely prolific hydrocarbon province. It is situated on the West African continental margin at the apex of the Gulf of Guinea [4]. It occupies an area of about 75,000 km^2 with clastic sequence which reaches a maximum thickness of 9,000 to 12,000m of sediment and a total sediment volume of 500,000km^3 [1].

Stratigraphically, the thick sedimentary sequence is made up of three principal lithostratigraphic units namely, the Benin, Agbada and Akata formations [11]. The Benin formation is the alluvial or upper coastal plain depositional environment of the Niger Delta complex. It consists of mainly fluviatile gravels and sands. It has a thickness in excess of 1820m.

The Agbada formation underlies the Benin formation and is made up primarily of alternating sandstones and shales which are of fluvio-marine origin. The Akata formation is the lowest unit of the Niger Delta complex. It was deposited in a typical marine environment.

The hydrocarbon habitat of the Niger Delta is mostly within the sandstones reservoir of the Agbada formation where they are usually trapped in the over anticlines associated with growth faults [12].

MATERIALS AND METHODS

Sample collection and analyses.

Seven crude oil samples were collected at stratigraphic depths ranging from 10500 to 11200 ft in two onshore producing fields of Umutu and Bomu, south west Niger delta (Fig. 1) using glass vials with Teflon caps which were pre-rinsed with trioxonitrate (v) acid, distilled water and properly dried. The crude oil samples were then placed in placed in a box containing ice packs, stored at a temperature of about 4°C prior to laboratory analysis.

MAP OF STUDY AREA

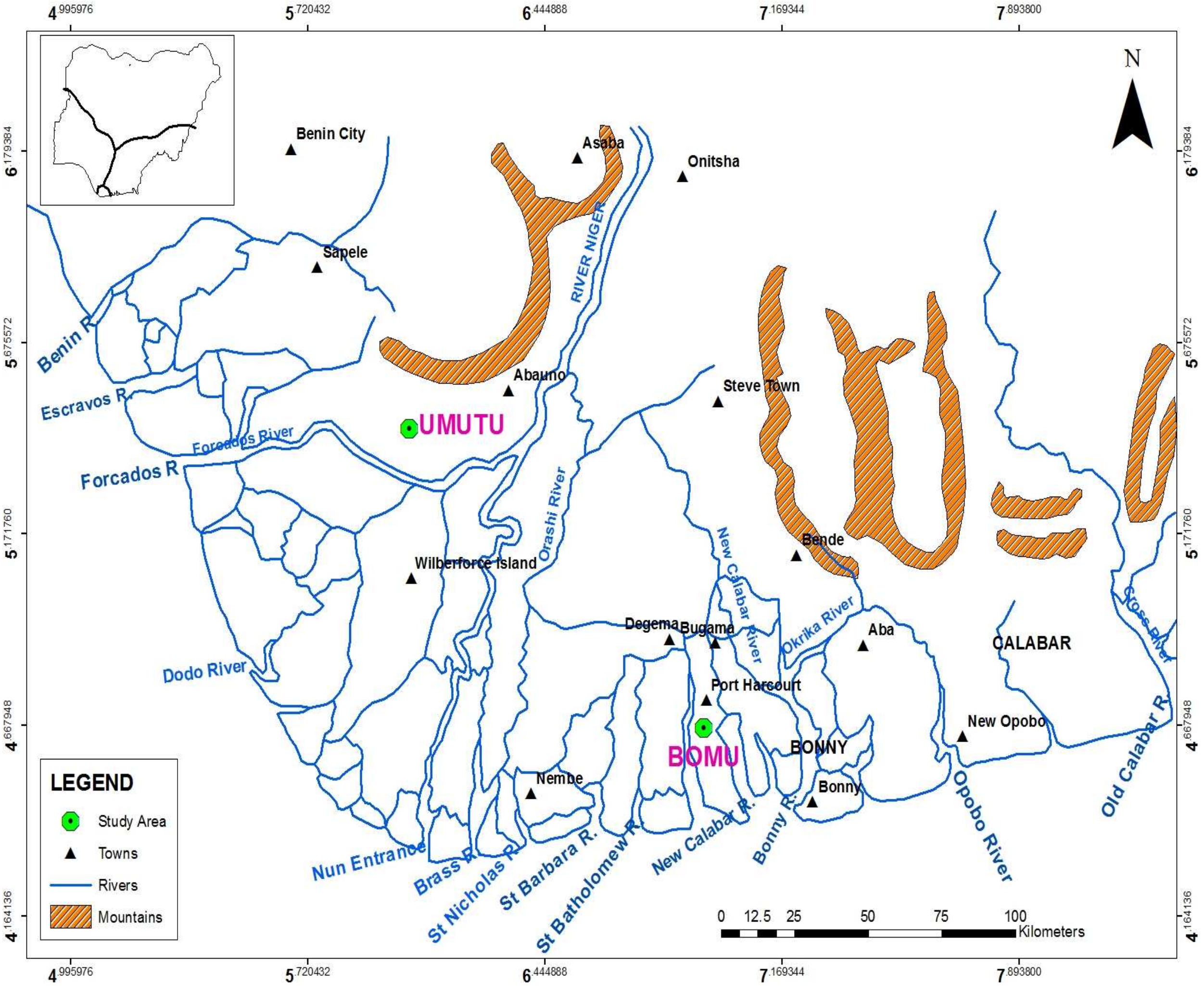

Fig. 1: Map of Niger Delta showing the Study Location

Whole - Oil Gas chromatography Analysis.

The Crude oil samples were subjected to whole oil- Gas chromatographic analysis. This was achieved by using Shimadzu 14B series Gas Chromatograph, equipped with Flame Ionization Detector, 30m × 0.25 mm film thickness 0.25 μm fused silica capillary columns, coated with methyl silicone. The sample (1 μL) was injected in splitless mode by means of syringe through a rubber septum into the column. Detector (FID) and injector temperatures were kept at 250 and 280°C, respectively. The oven temperature was programmed from 60 to 280°C at 4°C /min with an initial hold time of 1 min and final hold time of 15 mins. Helium at a linear velocity of 2 mL/min was used as carrier gas. The data were collected from retention time: 0-71 minutes [10].

RESULTS AND DISCUSSION

The gas chromatograms of crude oil samples showed close similarity as shown in fig 2 to 9.

They all showed high concentrations of the low molecular weight hydrocarbons. The distribution pattern of some the chromatogram is monomodial except that of sample U4L which is a bimodial distribution of n-alkanes indicating an input of mixed marine and terrestrial organic matter [7]. Low molecular weight hydrocarbons (<*n*-C8) were not observed, probably because of evaporative loss during sample processing. The chromatograms of samples KD01, KD02 and KD03 shows a slight prominence of higher molecular weight n-alkanes (C_{28} to C_{34}) which were depleted in the chromatograms of U2T, U7T, U45T and U4L, This may be due to the level maturity of the crude oil samples [14].

Normal Alkanes and Isoprenoids Distribution.

n-Alkanes from *n*-C8 to *n*-C37 are seen in the chromatograms of all oil samples. In crude oil correlation, the ratios of isoprenoids to *n*-paraffin are often used for oil- source correlation, maturation and biodegradation studies [3]. Various ratios of isoprenoids to *n*-alkanes were computed such as the Pr/Phy, Pr/n-C_{17}, Ph/n-C_{18}, nC_{25}/nC_{18}, (Pr + C_{17})/ (Ph +C_{18}) (Table 1). The crude oil samples have high Pr/Phratio which ranges from 8.78 to 32.27. Pr/Ph ratios were used to assess the depositional environment of the crude oils. The high Pr/Ph ratios suggest oils derived from source rock with a significant terrestrial contribution, deposited in an oxic paleoenvironment [3][5][6][8]. Several authors have used a plot of Pr/*n*-C_{17} versus Ph/*n*-C_{18} to classify oils and rock extracts into different groups as shown in Fig.10, Source, maturation, migration and biodegradation are the major factors responsible for differences in crude oil composition. Values less than 1.0 are indicative of non-biodegraded oils. Both Pr/*n*-C_{17} and Ph/*n*-C_{18} decrease with maturation due to increasing prevalence of the *n*-paraffin. The values of Pr/Ph, Pr/*n*-C_{17} and Ph/*n*-C_{18} for analyzed crude oils are given in Table 1. Samples U7L and KD01 have Ph/*n*-C_{18} values greater than one(>1.0) indicating that these samples are biodegraded, while samples U2L, U45,U4L, KD02 and KD03 have Ph/*n*-C_{18} less than 0ne (< 1.0) suggesting that these samples are non-biodegraded [6].

Fig 10 also shows that the crude oils under investigation are from mixed organic matter source.

3.3 Carbon preference index (CPI)

Carbon Preference Index was the first maturity indicator applied to crude oils [9][10]. Some researchers observed immature rocks often had high CPI values (>1.5), whereas those of mature oils were almost always below 1.0. Listed in Table 1 are the calculated values of CPI of the crude oils samples. Some of the values are close to1.0, which shows that some of the crude oils are mature while samples KD02 is immature.

Table 1. Normal alkanes/isoprenoid ratios.

Sample	Pr/Phy	Pr/n-C_{17}	Ph/n-C_{18}	nC_{25}/nC_{18}	CPI	(Pr+C_{17})/(Ph +C_{18})
UMT 2T	23.72	2.86	0.19	0.04	0.77	5.14
UMT 7L	8.78	5.57	1.32	0.26	0.87	5.90
UMT 45	32.27	5.79	0.97	0.23	1.07	18.63
UMT 4L	23.72	2.86	0.19	0.04	0.77	5.14
KD 01	8.78	5.57	1.32	0.26	0.87	5.90
KD 02	32.26	5.79	0.97	0.23	1.23	18.63
KD 03	23.72	2.86	0.19	0.04	0.77	5.14

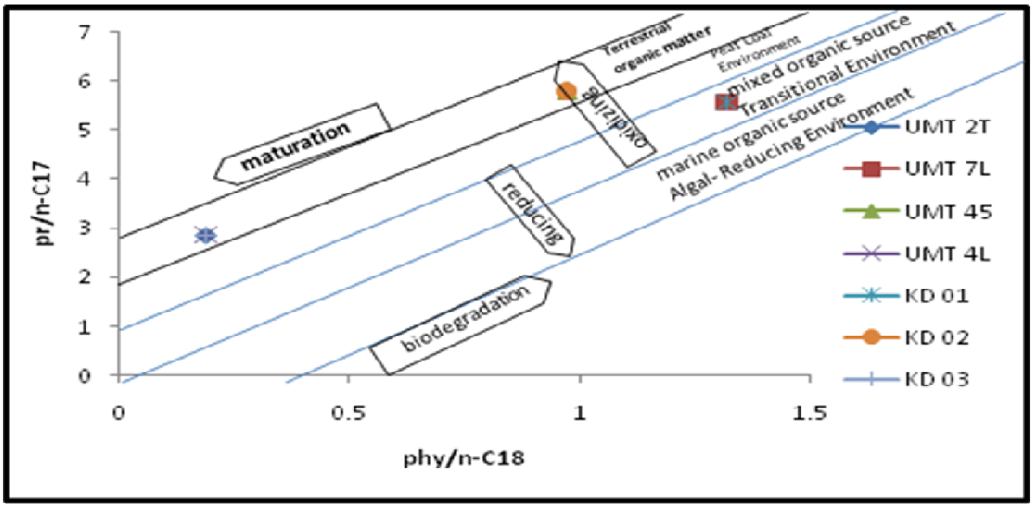

Fig 2. Cross plot of Pr/ nC_{17} versus Phy/nC_{18}

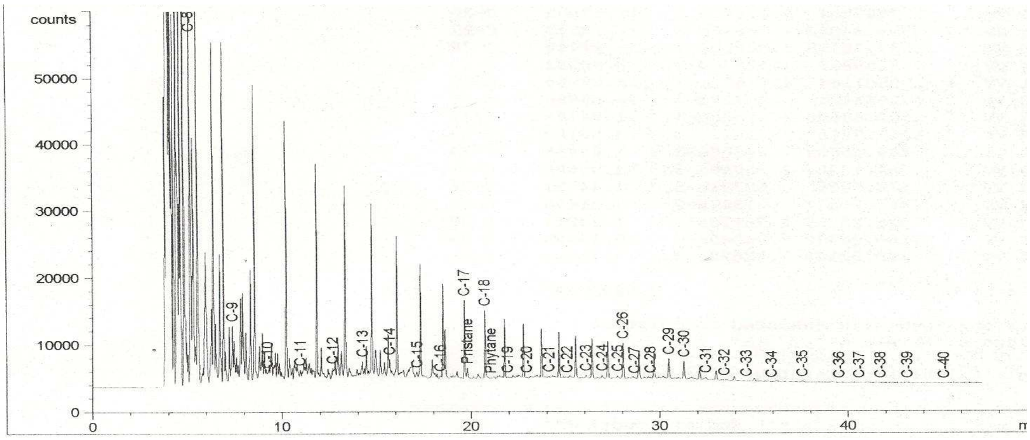

Fig 3. Representative whole oil Gas Chromatogrphic fingerprint of oil sample U2T

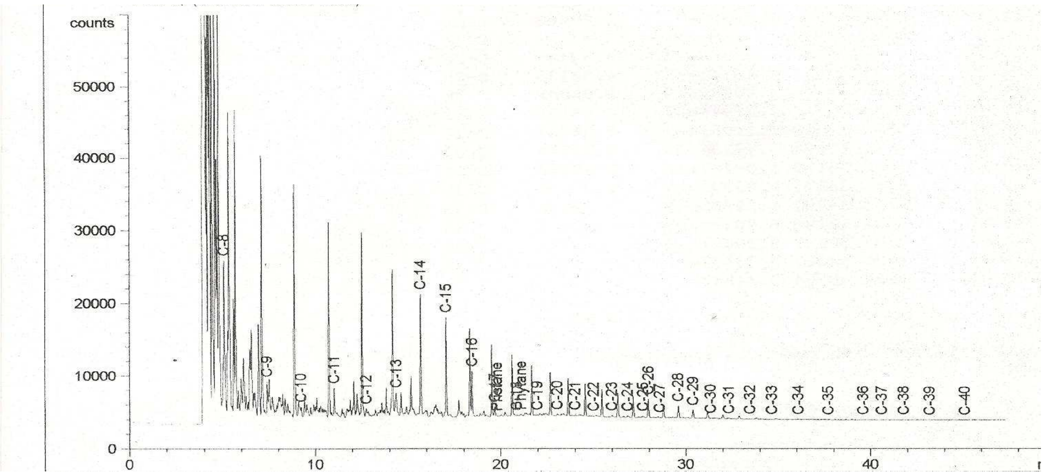

Fig 4. Representative whole oil Gas Chromatogrphic fingerprint of oil sample U7L

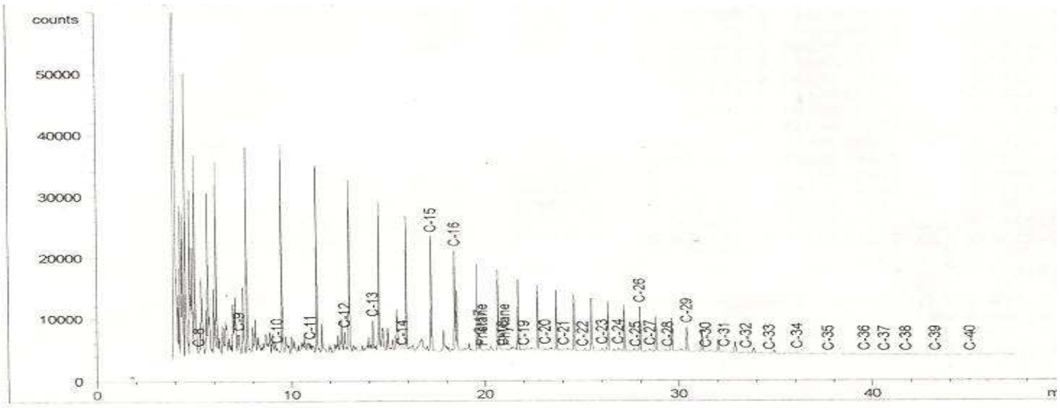

Fig 5. Representative whole oil Gas Chromatogrphic fingerprint of oil sample U45

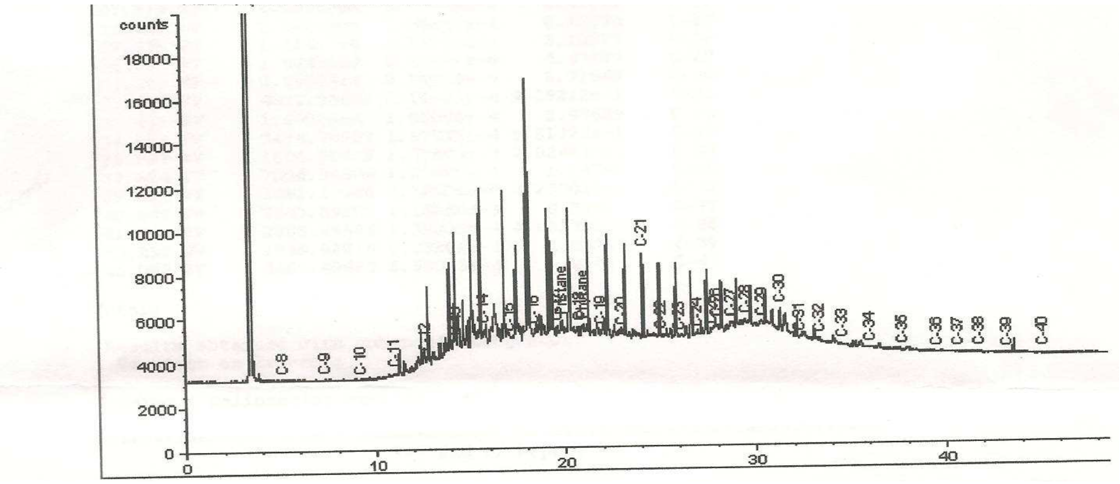

Fig 6. Representative whole oil Gas Chromatographic fingerprint of oil sample U4L

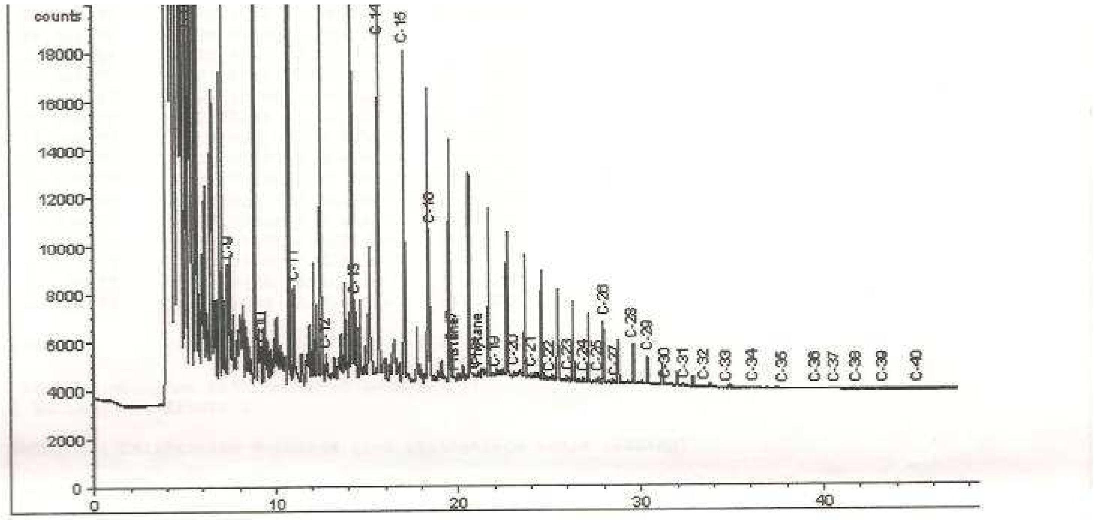

Fig 7. Representative whole oil Gas Chromatogrphic fingerprint of oil sample KD01

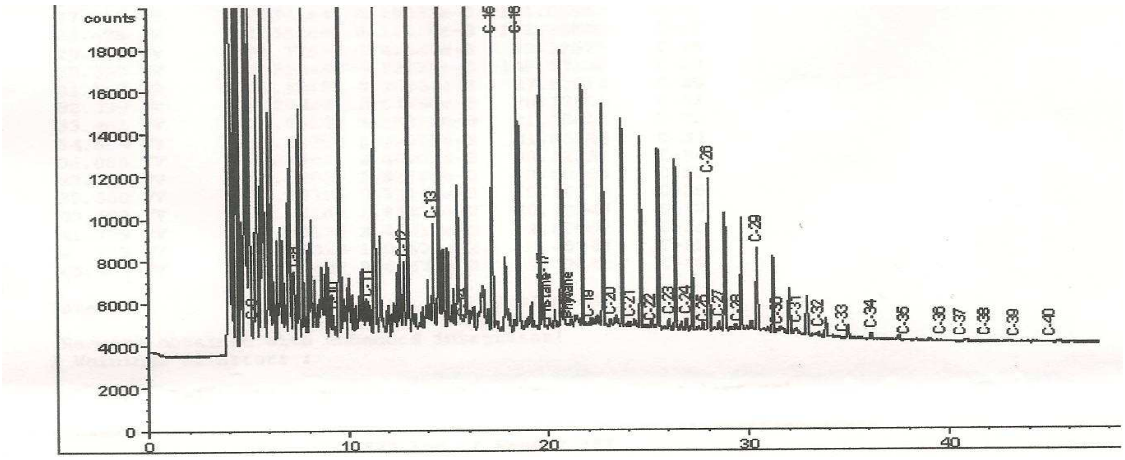

Fig 8. Representative whole oil Gas Chromatogrphic fingerprint of oil sample KD02

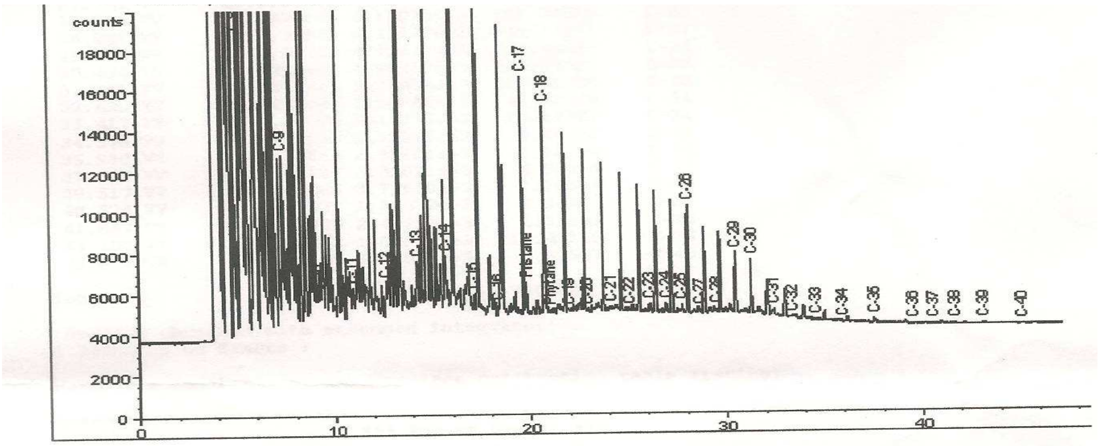

Fig 9. Representative whole oil Gas Chromatogrphic fingerprint of oil sample KD03

CONCLUSION

Petroleum Hydrocarbon fingerprinting of crude oils from the two fields under study has provided an insight into source signature of the hydrocarbon materials under investigation. The molecular hydrocarbon composition of these crude oils revealed that the oils were formed in source rocks containing mixed kerogen (marine and terrestrial) deposited in an oxic paleoenvironment. The distribution of n-alkanes/ isoprenoids and the high Pr/Ph ratios suggest that the oils were derived from source rock with a significant terrestrial contribution, deposited in an oxic paleoenvironment The calculated CPI helped in determining the maturity level of the crude oils but lacked any maturity trend.

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REFERENCES

[1] Adedosu, T. A., and Sonibare, O.O., *Journal of Applied Sciences* **2005.**5: p.906-909.
[2] Connan J. Biological markers in crude oils. In Petroleum Geology in China. 4th ed **1980**: Pennwell Oklahoma.. P. 48–70.
[3] Didyk, B.M., *et al., Nature.* **1978**.272: p. 216–222.
[4] Doust, H..Geological society, Landon. special publication **1990**. P.365.
[5] Ekweozor, C. M., *et al., Chem Geol*. **1979**. 27: p. 11-28.
[6] Hunt, J.M. Petroleum Geochemistry and Geology. **1996.** Freeman and company. *New York, USA* p. 231 – 238.
[7] Manilla, P.N. and Onyema, O.M. *Journal Chemical Society of Nigeria*.**2008.** 33: p. 225-234
[8] Mello, M.R., Maxwell, J.R.,. *AAPG Mem*., **1990**. 50: 77–97.
[9] Muhammad, I. J.*et al., Chin.J.Geochem*. **2010**. 29:p. 82–93
[10] Peters, K.E., C.C. Walters, and J.M. Moldowan, The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments. **1999**, Cambridge: Cambridge University Press.
[11] Short, K.C., and Stauble, A.J. *AAPG*. **1967.** 51: p. 761–779.
[12] Sonibare, O. *et al., Journal of Petroleum Science and Engineering*. **2008**.61: p. 99 -107.
[13] Wang, Z., and Fingas, N. F. *Marine Pollution Bulletin*. **2003.** 47: p. 423-452.
[14] Waples, D.W. and Machihara, T. *AAPG*. **1991**. 9: p 91.