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TYPING/CORRELATION OF NIGERIAN CRUDE OILS USING SATURATES AND AROMATIC BIOMARKERS

P.N. MANILLA AND P.A. EKING

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ABSTRACT

The Gas Chromatography-Mass Spectrometry (GC-MS) analysis for saturate and aromatic fractions of four Nigerian crude oil samples gave fingerprints indicating a close similarity between the first and second samples, as well as third and fourth samples. The GC-MS fingerprints of the whole oils showed that the samples are of two generic oil families; one with significant terrestrial organic matter input, and another with mixed terrigeneous and marine organic matter. Predominance of C_{29} over C_{27} regular steranes reflects argillaceous (shaly) source rocks. Values obtained for biomarker ratios like βα-mortane/αβ-hopane (0.17, 0.16, 0.16 and 0.15) and αβ 22S/(22S + 22R) (0.58, 0.58, 0.58 and 0.59) showed that the oils were all matured with maturity order of samples 4>3>2>1; and that the phase of oil generation for the onshore and offshore fields may have been reached or surpassed The gammacerane indices (2.22, 2.17, 2.17 and 2.13) and homohopane indices (4.42, 4.64, 3.38 and 3.73) of the crude oils showed some genetic relationships among them, indicating that the onshore and offshore fields can be correlated.

KEY WORDS: Tricyclic terpenes, homohopane index, steranes, oil-oil correlation, biomarkers

INTRODUCTION

Hopanes (pentacyclic triterpees), steranes, and isoprenoids are a range of biomarker compounds, that were resistant to oil weathering processes and were present in ratios which are characteristic of the particular oil. The quantification of these compounds and the subsequent calculation of the various biomarker ratios provided a 'fingerprint' (composition and distribution) of the oil. This then reflected the origin and maturity of the organic matter (Mackenzie et al., 1981; Seifert and Moldowan, 1980). Biomarkers have been found more suitable for geochemical correlation which utilized geochemical information to relate crude oils to each other and to their presumed source rocks. The integration of the geochemical information was found to greatly improve exploration success ratios and to aid drilling site selection (Dow, 1974; Barker, 1975). The basis for geochemical correlation is the recognition of genetic relationships between oil-oil and oil-source rock pairs as reflected by their composition similarities. The ratios of these biomarkers (rather than their absolute concentrations) were stable in the rock extracts and crude oils to allow reliable correlations. Therefore in geochemical correlation studies, the biomarker ratios, together with their distribution, were referred to as "fingerprints" (Tissot and Welte, 1984; Hunt, 1979).

The oleanane index (OI) is given by oleanane/C_{30} hopane indictated the origin of the if it was terrestrial or marine. It has been suggested that the oleanane ratio generally increases from low values in immature rocks to a maximum at the top of the oil-generating window (Ekweozor and Telnaes, 1989). In the Anambra Syncline / Lower Benue Trough, using the oleanane biomarkers as index fossils (Ekweozor and Udo, 1988) showed the biomarkers to be found in rocks which are as old as the late upper Cretaceous, while in the Tertiary Niger Delta, the concentration, composition and distribution of the oleananes in rocks and crude oils are determined mainly by paleodepositional environment and thermal history.

Gas chromatography and gas chromatography – mass spectrometry analysis for pentacyclic terpanes in crude oil samples from three oilfields in the Niger Delta, revealed α, β-hopanes and oleananes as the major pentacyclic triterpanes . Correlation using these triterpane fingerprints showed that the western crude differs significantly from the eastern crudes based on their oleanane content. The relative high concentration of the oleananes in the eastern crude oils reflected a greater input of higher plants to source sediments (Eneogwe, 2003).

This study was carried out on four oil wells (one western offshore; two from Benin and one eastern land) to determine the saturates and aromatic biomakers and their ratios;to know their source, depositional environments and thermal maturity, check the degree of biodegradation of the oils and compare them to the other reported oils from the Niger Delta.( )

STUDY AREA

Four crude oil samples were collected from four different fields in the Niger Delta region of Nigeria in May 2006. The samples were labeled as 1, 2, 3 and 4. Samples 1 is Obiafu/Obrikom crude from Omoku in Rivers State, sample 2 is Aboh crude obtained from deep offshore of Ondo and samples 3 and 4 both came from two different fields in Benin, Edo State

MATERIALS AND METHODS

The solvents (n-pentane, n-hexane, dichloromethane and methanol) used for crude oil fractionation were Fischer optima grade. Silica gel grade 923 (mesh 100 – 200) was used as the stationary phase in the column chromatography. Gas chromatography analysis was performed with a Hewlett Packard Gas chromatograph model 6890 equipped with a flame ionization detector and a split/splitless injector. The GC was fitted to a fused silica capillary column
30m x 0.25µm, a HP 6890 automatic liquid sampler.

PRECIPITATION OF ASPHALTENES

50mg of each oil sample was weighed into labeled centrifuge tubes and excess pentane added to precipitate the asphaltenes. The samples were allowed to stand for four hours and centrifuged at 1,500 rpm for thirty minutes to give the pentane soluble (PS) fraction. The residue in the tubes were transferred to the pre-weighed vials using dichloromethane and evaporated to dryness using liquid nitrogen at 40°C to obtain the asphaltenes (Asp). The weights of the different fractions were determined.

LIQUID CHROMATOGRAPHY

Silica gel was activated at 240°C for four hours and preserved in a desiccator. The activated silica gel was packed

P.N. Manilla, Department of Pure and Industrial Chemistry, University of Port Harcourt, P.M.B. 5323, Choba, Port Harcourt, Rivers State, Nigeria.
P.A. Eking, Department of Pure and Industrial Chemistry, University of Port Harcourt, P.M.B. 5323, Choba, Port Harcourt, Rivers State, Nigeria.

into a glass column (30cm x 1cm) using n-hexane. The pentane soluble (PS) fraction was introduced into the column and eluted with n-hexane to obtain the saturates. Dichloromethane was used to elute the aromatics and dichloromethane/methanol (1:1) mixture was used to elute resins. The solvents were evaporated in a water bath at 40°C and then to dryness with liquid nitrogen at 40°C. The weights of the saturates, aromatics, resins and asphaltenes were determined and the normalized percent reported.

GAS CHROMATOGRAPHY–MASS SPECTROMETRY (GC-MS) BIOMARKERS ANALYSIS

The saturates and aromatic biomarker composition of the oils were determined using a HP 6890 GC-MS, fitted with a split injector, a high resolution column with 0.25mm internal diameter and 0.25μm film thickness. The effluent splitter was connected to Mass Selective Detector (MSD). Helium was used as the carrier gas. Approximately 1.0μl of the fractions (saturates and aromatics) was injected into the GC. For the saturates, the oven was programmed from 75°C held for 2 minutes, then to 200°C at the rate of 5°C per minute, after which another 3°C per minute was applied to 310°C and held for 8 minutes. For the aromatics, the oven was programmed from 80°C held for 1 minute, then to 200°C at the rate of 5°C per minute, after which another 6°C per minute ramp was applied to 325°C and held for 20 minutes. Peaks were identified using standard chromatograms and area integration of each peak was processed by the HP chemstation software (Geochem.2004).

RESULTS AND DISCUSSION

The values of 4.42, 4.64, 3.38 and 3.73 obtained as Homohopane index (HHI) for samples 1, 2, 3, and 4 respectively (Table 1) were low C_{35}–Homohopane indices and indicated that the studied samples were obtained from shaly source rocks (Peters and Moldowan, 1993). This agreed with other parameters like the carbon preference index (CPI) and Odd-Over-Even carbon preference (OEP).

The sterane distribution was characterized by the predominance of C_{29} over C_{28} regular steranes in all the samples (Table 2) and was characteristic of terrestrial organic matter input. The high occurrence of C_{29} over C_{27} in all samples, also indicated shaly source rocks for the samples. The C_{29}/C_{30} hopanes ratio of 0.60, 0.61, 0.61 and 0.63 for samples 1, 2, 3, and 4 respectively confirmed this.

Tricyclics/17α(H)-hopane ratios for the four samples were 3.60, 3.10, 2.50 and 2.90 respectively (Table 2). These values show that the oils are genetically related, with a close relationship existing between samples 1 and 2, as well as 3 and 4 (Peters and Moldowan 1993).

From Table 1, sample 4 is seen to have the highest Pr/Ph ratio (4.07) followed by sample 1 (3.79), then 3 (3.75). These high ratios were attributed to terrestrial organic matter input under oxic condition (Eneogwe and Ekundayo, 2003; Peters and Moldowan, 1993). Sample 2 has the lowest Pr/Ph ratio (2.66). This is consistent with source rocks deposited in a sub-oxic to oxic depositional environment.

Table 1: Acyclic isoprenoid/n-alkane ratios and thermal maturity parameters

PARAMETERS	CRUDE OIL SAMPLES			
	1	2	3	4
Pristane/phytane(Pr / Ph)	3.79	2.66	3.75	4.07
Carbon preference Index (CPI)	1.10	1.60	1.0	1.15
Homohopane Index (HHI)	4.42	4.64	3.38	3.73
βα- Moretanes/αβ-hopanes	0.17	0.16	0.16	0.15
C_{29}-ααα 20S/(22S+20R)Steranes	0.34	0.34	0.47	0.51
C_{32} αβ 22S /(22S+22R)	0.58	0.58	0.58	0.59
*TA / (MA + TA) (%)	69	78	81	95

*TA and TM are Tri- and Mono-aromatic steroids respectively

Ratios were calculated from peak areas of compound The percentages of gammacerane (Table 2) in the four samples (2.22, 2.17, 2.17 and 2.13 respectively) are low, suggesting oxidizing, saline conditions during organic matter deposition in lacustrine environments (Hunt, 1996; Peters and Moldowan, 1993).

The steranes ratio (C_{29} ααα 20S/(20S + 20R) for the four samples were 0.34, 0.34, 0.47 and 0.51 respectively (Table 2) increased with thermal maturation (Peters and Moldowan, 1993); and indicated the order of maturity of the samples was 4 > 3 > 2 & 1. Samples 3 and 4 are considered marginally mature oils since they fall near the sterane equilibrium zone of maturation level, 0.5 – 0.55 (Peters and Moldowan, 1993).

The ratio αβ22S/(22S + 22R) calculated from theC_{31}- or C_{32}- homohopane results rose from 0 to 0.6 during maturation indicated the phase of oil generation for all the samples, have been reached or surpassed. The value of 0.59 for sample 4 also points to the fact that it is the most mature of all the samples

Triaromatic / (Monoaromatic + Triaromatic) steroids ratio {TA / (MA + TA)} was also obtained for the samples. The values were 69%, 78%, 81% and 95% for samples 1, 2, 3 and 4 respectively (Table 2) (Mackenzie et al.1981). This added to the fact that all the crude oil samples under study were matured, and the order of maturity was: 4 > 3 > 2 > 1 as observed from other maturity parameters already reported.

The Diasteranes/Regular Steranes ratios for the four samples give low values – 0.31, 0.30, 0.44 and 0.49 respectively (Table 2). These low ratios suggested the oils were nonbiodegraded, since it showed no selective destruction of steranes relative to diasteranes (Peters and Moldowan, 1993).

Table 2: Other biomarker parameters for characterization/correlation of the crude oil samples

CHARACTERISTIC COMPOUNDS AND RATIOS	CRUDE OIL SAMPLES			
	1	2	3	4
Total C_{27} Steranes (%)	19.85	19.97	20.00	20.68
Total C_{28} Steranes (%)	21.19	21.49	22.01	21.00
Total C_{29} Steranes (%)	44.25	44.03	46.17	45.23
Total C_{30} Steranes (%)	28.27	28.00	19.79	17.44
Oleanane Index	36.4	30.8	10.1	11.0
Oleanane/C_{30} Hopane	0.75	0.74	0.36	0.37
Gammacerane (%)	2.22	2.17	2.17	2.13
C_{30} Sterane Index	0.04	0.04	0.1	0.1

Sterane/Hopanes	0.36	0.36	0.15	0.15
C_{29}/C_{30} Hopanes	0.60	0.61	0.61	0.63
Tricyclics/17(H)-Hopane	3.60	3.10	2.50	2.90
Ts/Tm	0.58	0.59	0.78	0.90
Diasteranes/Regular Steranes	0.31	0.30	0.44	0.49

The GC-MS analysis of the saturate and aromatic fractions (figs 1-8) of the samples gave fingerprints which showed samples 1 and 2 were similar; while samples 3 and 4 looked alike. The four crude oil samples had common biomarker compounds, as displayed by the bars charts. This confirms the whole oil GC chromatograms in the samples (Manilla and Eking, 2006). The tricyclic terpanes m/z 191 peak in the fragmentograms of the four samples (figs 9-12) showed similar pattern for the thermally resistant C_{19} – C_{29} tricyclic terpanes – samples 1 and 2 having a higher oleanane concentration while 3 and 4 showed a lower oleanane concentration (Eneogwe, 2003). Steranes mass fragmentograms peaks at (m/z, 217, 218, and 231) also showed the same trend (figs13-16). The fragmentograms (figs 17-20) for the aromatic biomarkers (m/z 231 and 253), also divided the oils into two groups as observed for the tricyclic terpanes and steranes mass fragmentograms.

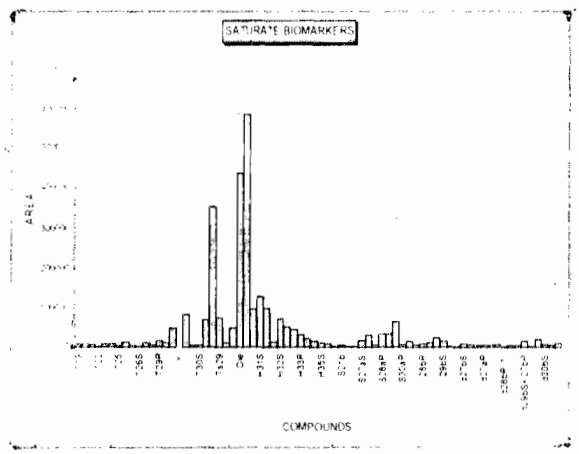

Figure 1 Bar chart representation of sample 1 chromatogram

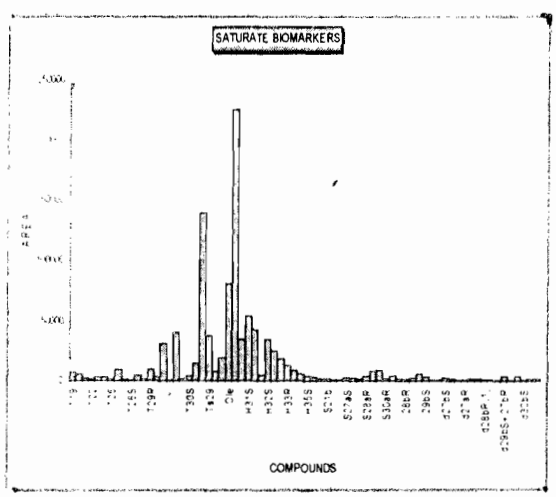

Figure 2 Bar chart representation of sample 3 chromatogram

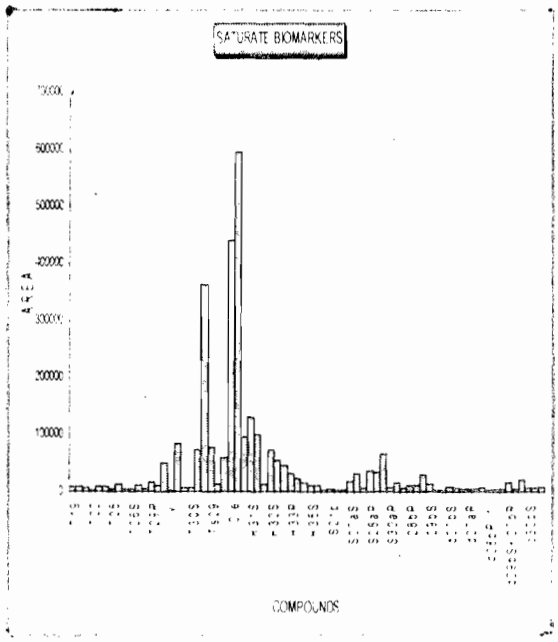

Figure 3 Bar chart representation of sample 2 chromatogram

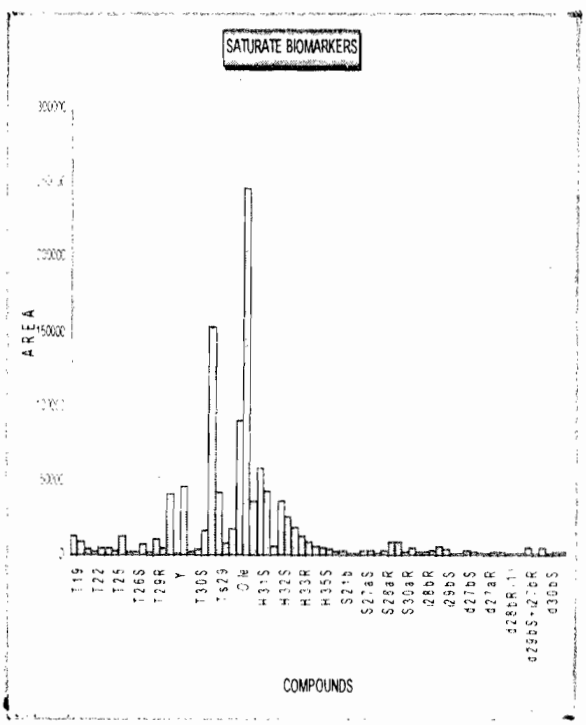

Figure 4 Bar chart representation of sample 4 chromatogram

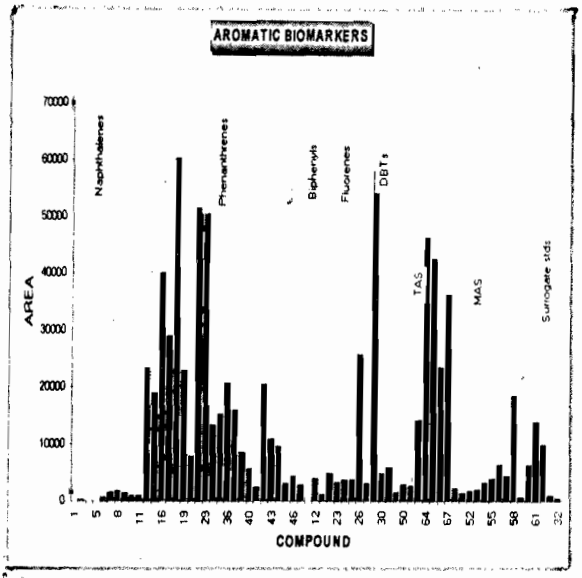

Figure 5: Aromatic biomarkers chromatogram of sample 1

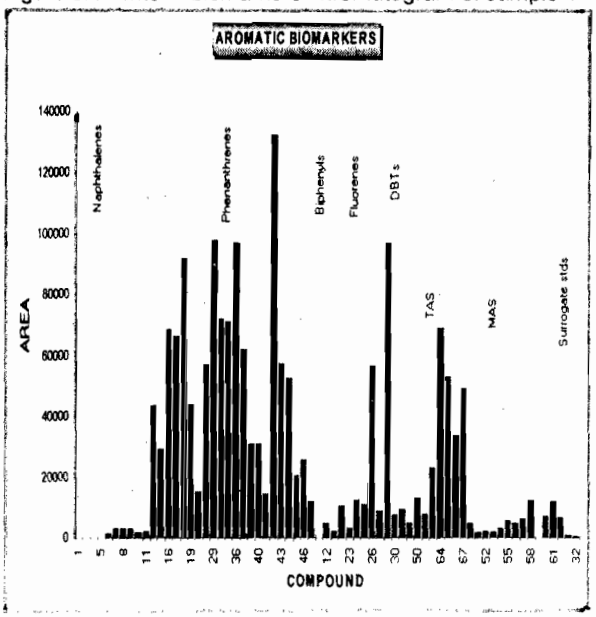

Figure 6: Bar chart representation of the chromatogram (sample 2)

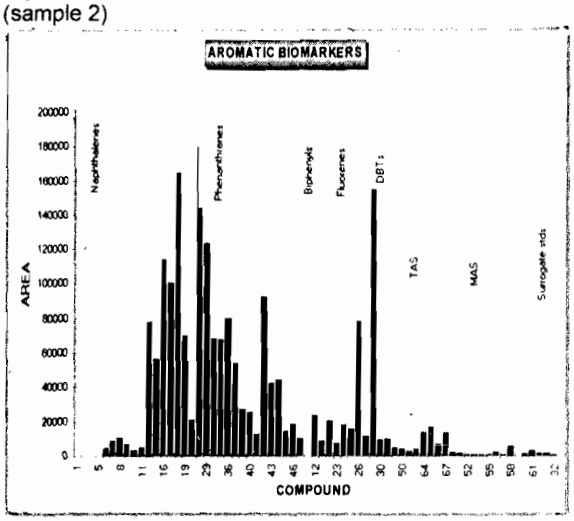

Figure 7: Bar chart representation of the chromatogram (sample 1)

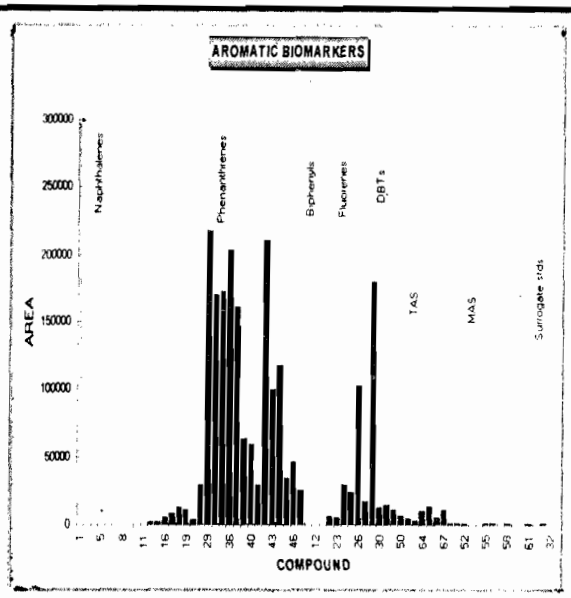

Fig8: Bar chart representation of the chromatogram (sample 4)

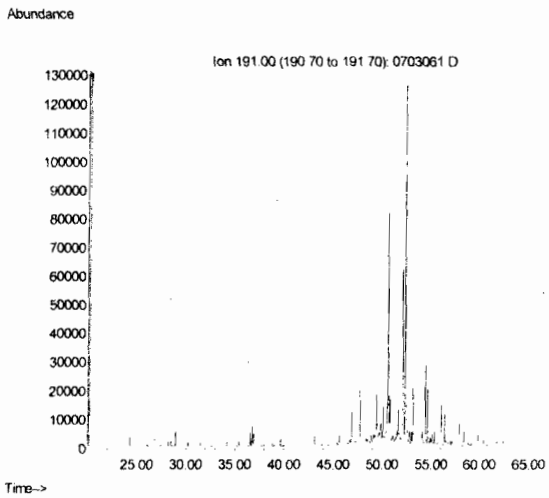

Fig.9: Terpane m/z 191 fragmentogram for sample 1

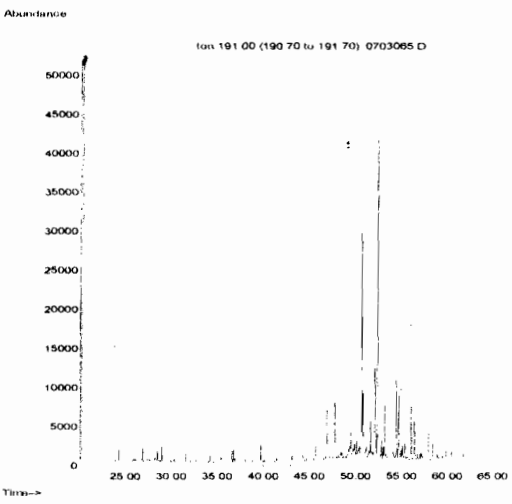

Fig.10: Terpane m/z 191 fragmentogram for sample 3

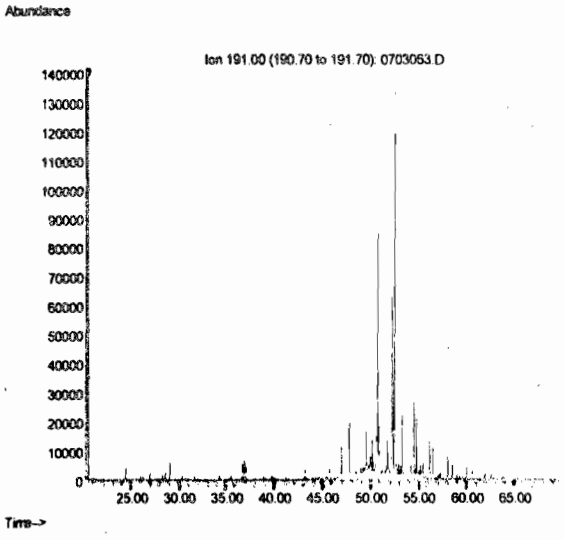

Fig.11: Terpane m/z 191 fragmentogram for sample 2

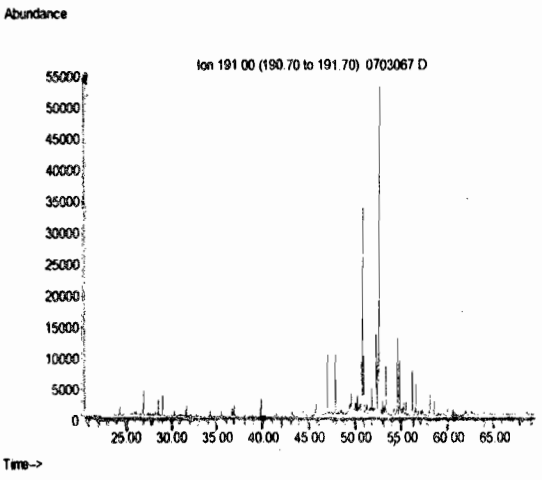

Fig 1.2: Terpane m/z 191 fragmentogram for sample 4

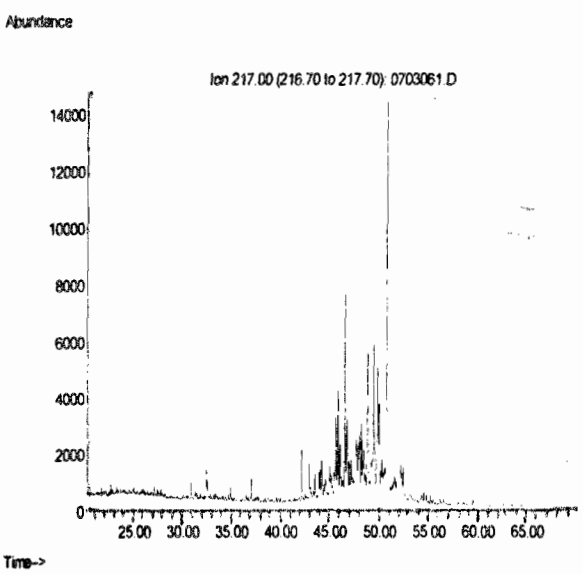

Fig.13: Sterane m/z 217 fragmentogram for sample 1

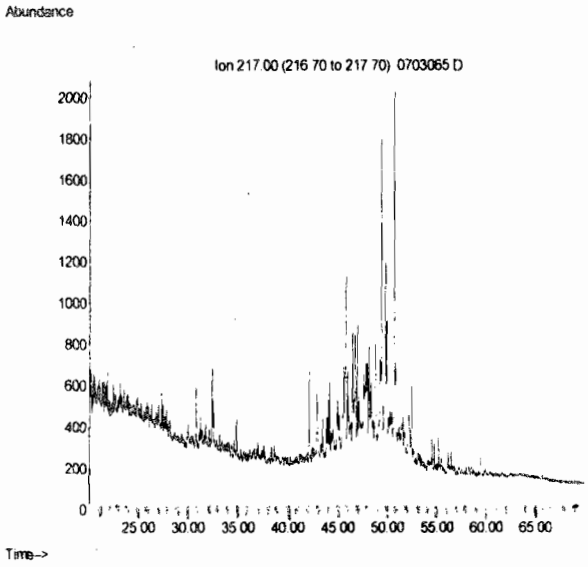

Fig.14: Sterane m/z 217 fragmentogram for sample 3

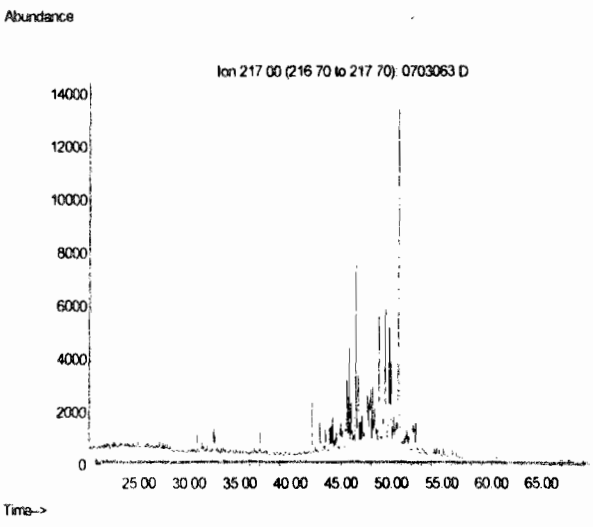

Fig.15: Sterane m/z 217 fragmentogram for sample 2

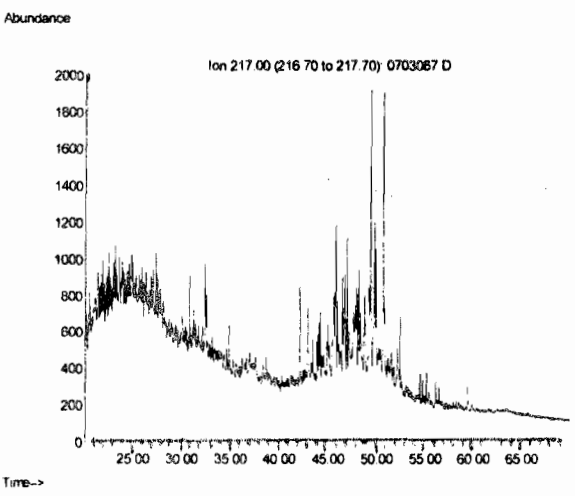

Fig.16: Sterane m/z 217 fragmentogram for sample 4

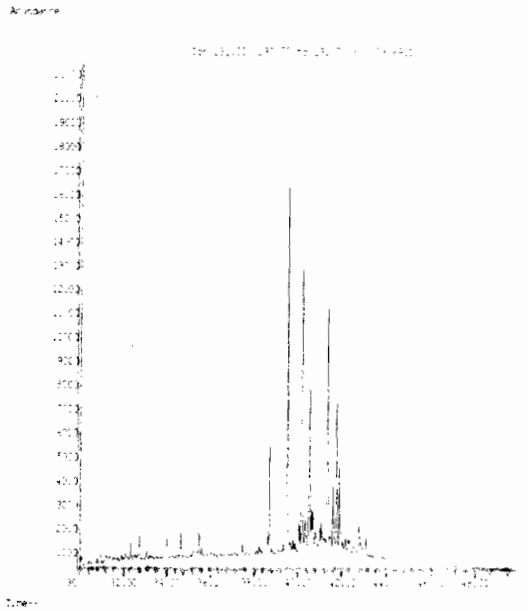

Fig.17: Aromatic biomarkers m/z 231 fragmentogram for sample 3

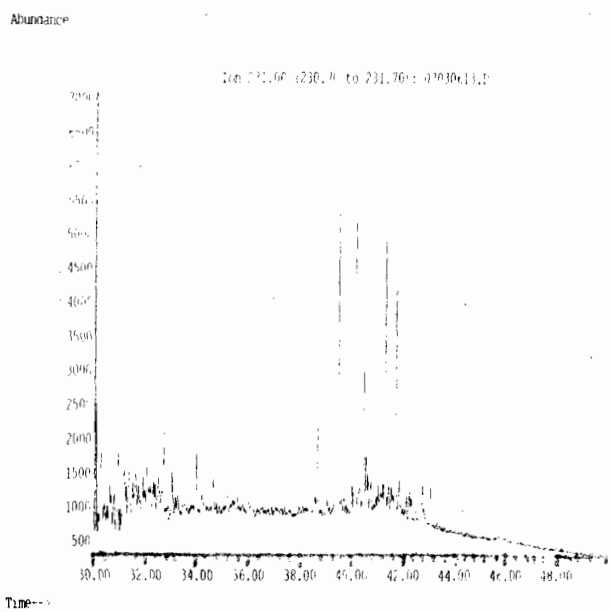

Fig. 18: Aromatic biomarkers m/z 231 fragmentogram for sample 1

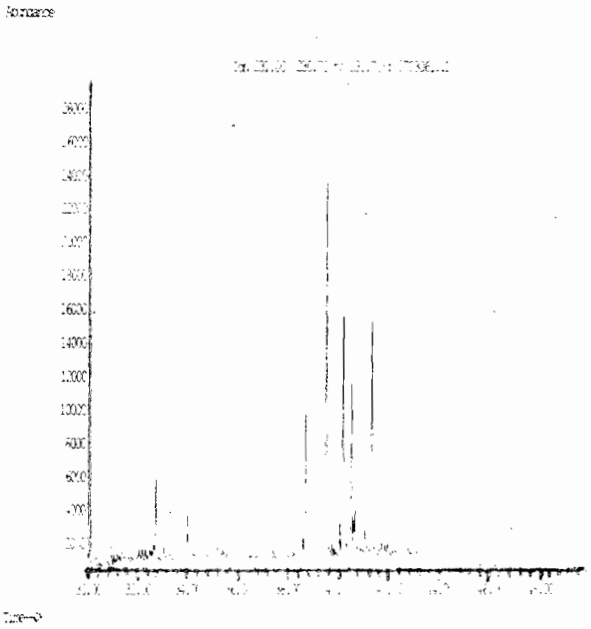

Fig.19: Aromatic biomarkers m/z 231 Fragmentogram for sample2

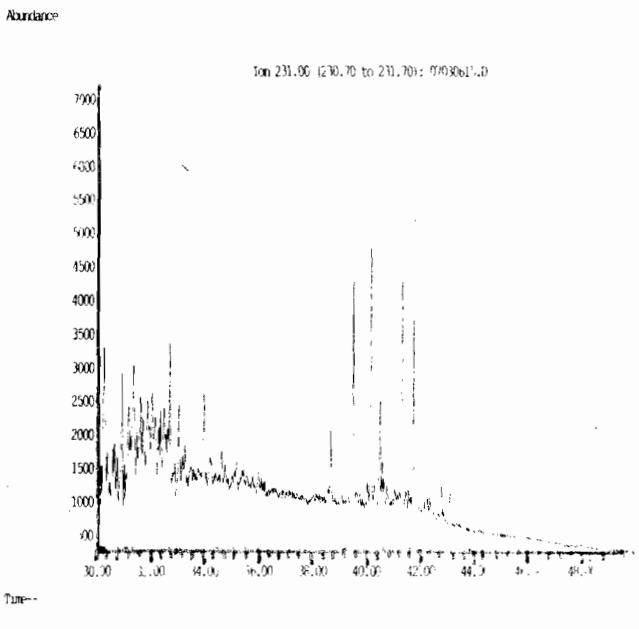

Fig.20: Aromatic biomarkers m/z 231 Fragmentogram for sample 4

CONCLUSION

The GC-MS fingerprints obtained for the saturate and aromatic fractions of the studied crude oil samples, together with various biomarker ratios separated them into two oil families: a predominantly terrestrial petroleum system generated from rocks with abundant terrestrial organic matter input (samples 1 and 2 belong to this group), and a petroleum system with a mixed terrestrial and marine organic matter input (for samples 3 and 4). Oils from these two families were seen to be deposited in an oxidizing environment.

The CPI, HHI, and OEP have shown that the oil samples were all sourced from argillaceous (shaly) source rocks (tertiary source rocks); presumably the shales of Agbada and Akata formation, known to be the primary source rocks of the Niger Delta crude oils (Tuttle et al., 2004).

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