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GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS) COMPOSITIONAL ANALYSES OF AROMATIC HYDROCARBONS IN NIGER DELTA CRUDE OILS

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Abstract

The composition of aromatic hydrocarbons used as diagnostic tools in oil correlation studies was investigated in Niger Delta crude oils. Crude oil samples collected from producing wells were fractionated and gas chromatography-mass spectrometry (GC-MS) used to analyze the aromatic fraction. The analysis revealed high abundance of aromatic hydrocarbons which consist of polycyclic aromatic hydrocarbons (PAHs) 92.8% - 93.7% and aromatic steranes 6.3% - 7.2%. PAHs identified include C_1 - C_3 naphthalenes, C_0 - C_2 phenanthrenes, C_0 - C_1 biphenyls, C_0 - C_1 fluorenes and C_0 - C_1 dibenzothiophenes. The considerably high abundance of naphthalenes and low dibenzothiophene/phenanthrene ratio from 0.09 - 0.11 indicated contribution of terrestrial organic matter to source rocks which were deposited in oxic environment. The identified aromatic steranes, monoaromatic steranes (MAS) and triaromatic steranes (TAS), were characterized by the short-chain C_{20} - C_{22} and long-chain C_{26} - C_{29} series. The abundance of TAS over MAS from 2.08 - 2.99 suggest high maturity crude oils for the Niger Delta region. From these results, the characterization of aromatic hydrocarbon compounds in Niger Delta crude oils have provided substantial evidence of their suitability as geochemical markers for crude oil correlation studies.

Key Words: GC-MS; composition; polycyclic aromatic hydrocarbons (PAHs); aromatic sterane; oil correlation.

1. Introduction

The source of crude oil, burial environment and thermal maturity can be inferred from the composition of hydrocarbons in the oil [14,7]. Earlier, focus was placed on the saturate hydrocarbons, such as normal alkanes (*n*-alkanes), isoprenoid alkanes and the biomarkers tri-, tetra-, and pentacyclic triterpane hydrocarbons [2-3,11]. With improvement in analytical methods, crude oil studies are now supplemented with geochemical data from aromatic hydrocarbons [23-24].

Aromatic hydrocarbons in crude oil include naphthalene, fluorene, phenanthrene, dibenzothiophene and their alkylated isomers, as well as anthracene, fluoranthene, benzopyrenes and aromatic steranes [16]. They originate from chemical and geological transformation of natural product molecules, deposited during sedimentary processes, by diagenetic rearrangement or dehydrogenation or by aromatization or fragmentation during catagenesis [21]. Consequently, the occurrence and distribution of certain aromatic geochemical hydrocarbons are diagnostic of the crude oil in which they occur and have proven effective in oil correlation studies [20,17-18]. Ratios of dibenzothiophene/ phenanthrene used in a cross-plot with pristane/ phytane classified crude oils from different source rocks and ages into their paleodepositional environments [8], while the distribution of phenanthrene and its methylated isomers have proven effective in oil-oil correlation by identifying differences in timing of oil generation, maturity and post-generative alteration [1].

In Nigeria's Niger Delta region, studies on crude oil correlation use the distribution of saturate hydrocarbons, such as *n*-alkanes, isoprenoid alkanes and triterpanes [5,10]. Also, the composition of light hydrocarbons, invariance ratio of isoheptanes and ring preference were recently used in crude oil correlation [6,13]. This study investigates the composition and distribution of aromatic hydrocarbons in Niger Delta crude oils, using gas chromatography- mass spectrometry (GC-MS), with a view to providing another geochemical means for crude oil correlation studies.

2. Materials and methods

2.1 Geology of study area and sampling

The Niger Delta is an extremely prolific hydrocarbon province. It is situated in Southern Nigeria on the West African continental margin between longitude 5° - 9° E and latitude 4° - 6° N and at the apex of the Gulf of Guinea [4]. The Niger Delta formed during the mid-Cretaceous and developed properly from Paleocene with the lithostratigraphic sequence divided into three units namely: Akata formation, which consist of thick shales; Agbada formation, which consist of interbedded shales and sandstones and Benin formation, which consist of coastal plain sands [22]. Five crude oil samples were used for this study. The crude oil samples labelled NK-17, NA-23, MU-11, ME-21 and TA-15 were collected from producing wells in Etche L.G.A, Niger Delta region, Nigeria.

2.2 Oil fractionation

50mg of each crude oil sample was weighed into labelled centrifuge tubes and excess pentane added to precipitate the asphaltenes. The samples were allowed to stand for 4 hours and centrifuged at 1,500 rounds per minute (rpm) for thirty minutes to coalesce the precipitated asphaltenes. The pentane soluble fraction was transferred into glass column (30 cm x 1 cm) stuffed with glass wool at the bottom and packed with silica. *n*-hexane was poured into the packed column to elute the saturates, dichloromethane poured to elute the aromatics and dichloromethane/methanol (1:1) mixture poured to elute the resins.

2.3 Gas chromatography-Mass spectrometry analyses

The aromatic fractions were analysed by Hewlett Packard (HP) 6890 gas chromatograph (GC) system fitted to a fused silica capillary column (30 m x 0.25 mm id) and equipped to an HP 5973 mass selective detector (MSD). 1 µl was injected into the GC system with the aid of an automatic liquid sampler (ALS). Oven temperature program was held for 2 min. at 80°C, from 80 – 200°C at 5 °C/min, from 200 – 310°C at 6°C/min. and held at 310 °C for 15 min. The mass spectrometer was operated at electron energy of 70 eV, an ion source temperature of 230°C and interface temperature of 250°C. Polycyclic aromatic hydrocarbons (PAHs) were identified using multiple ion m/z 142, 156 and 170 mass fragments for C_1, C_2, and C_3 naphthalenes; m/z 178, 192, 206, and 220 for C_0, C_1, C_2 and C_3 phenanthrenes; m/z 154, 168 and 182 for C_0, C_1 and C_2 biphenyls; m/z 166, 180 and 194 for C_0, C_1 and C_2 fluorenes; m/z 184, 198 and 212 for C_0, C_1 and C_2 dibenzothiophenes.

3. Results and Discussion

3.1 Gas Chromatography-Mass Spectrometry (GC-MS) analyses

GC-MS analyses of the aromatic fraction of crude oil samples from the Niger Delta, used in this study, identified series of aromatic hydrocarbons. A representative GC-MS total ion chromatogram (TIC) is shown in fig. 1. The TIC chromatogram of aromatic hydrocarbons for the Niger Delta crude oil samples showed well resolved peaks maximizing in the lower carbon number range with decrease in peak height skewed towards higher carbon number range (Fig. 1).

The identified aromatic hydrocarbons are of two groups: the polycyclic aromatic hydrocarbons (PAH) with two or three aromatic rings and the aromatic steranes, which are aromatized products of specific natural product, the steroids. The abundances of the aromatic hydrocarbons were calculated from area integration of each identified peak. The composition of the two groups of aromatic hydrocarbons in the studied Niger Delta crude oils are presented in table 1. The abundance of aromatic hydrocarbons in the studied Niger Delta crude oils were high (table 1). In all the crude oil samples, aromatic hydrocarbon compositions were characterized by high abundance of PAHs compared to aromatic steranes.

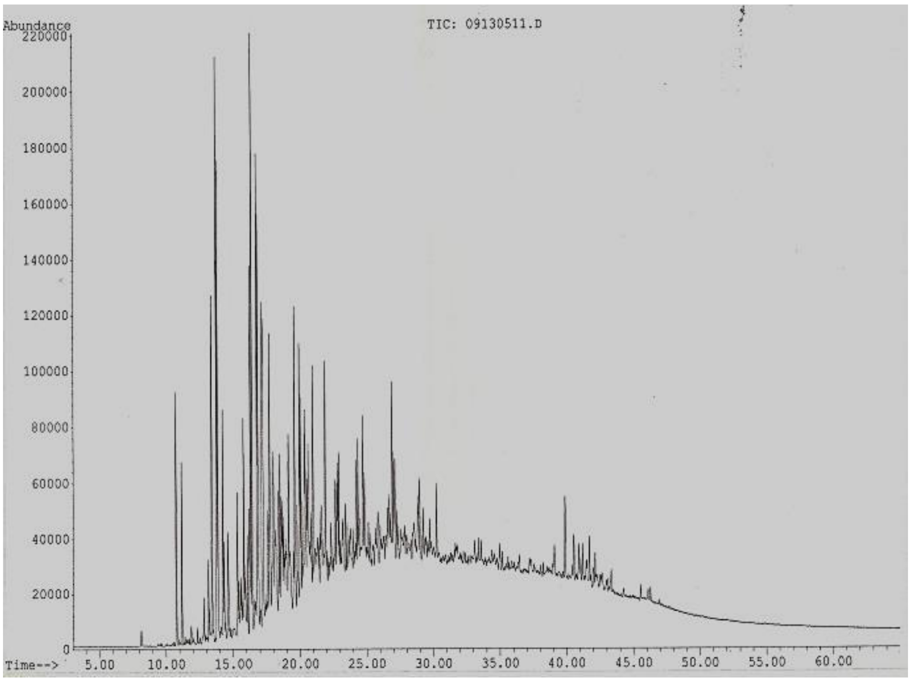

Figure 1 A representative GC-MS total ion chromatogram of aromatic hydrocarbon fraction of crude oil from Niger Delta.

Table 1 Composition of aromatic hydrocarbon groups in Niger Delta crude oils

	Polycyclic aromatic hydrocarbons (PAHs)		Aromatic steranes		
	area	%	area	%	total
NK-17	5,004,983	*93.49*	348,641	*6.51*	5,353,624
NA-23	4,761,254	*93.18*	348,477	*6.82*	5,109,732
MU-11	5,360,881	*93.68*	361,929	*6.32*	5,722,810
ME-21	4,448,312	*92.81*	344,849	*7.19*	4,793,162
TA-15	5,055,617	*93.43*	355,281	*6.57*	5,410,898

PAHs constitute between 92.81% - 93.68% of total identified aromatic hydrocarbons (table 1). These PAH compositions were between 12.90 to 14.81 times more than the aromatic sterane compositions. Crude oils derived from marine planktons are aliphatic or alicyclic in nature, while crude oils derived from land organic matter are aromatic in nature [21]. The considerably high abundance of the aromatic hydrocarbons in all the samples, in particular PAHs, suggest terrestrial organic matter source input for the Niger Delta crude oils.

3.2 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) identified in the studied Niger Delta crude oils by GC-MS analyses include C_1-C_3 naphthalenes, C_0-C_2 phenanthrenes, C_0-C_1 biphenyls, C_0-C_1 fluorenes and C_0-C_1 dibenzothiophenes. Their abundances were calculated quantitatively from the area integration of each identified peak. The naphthalenes were the most abundant PAH. Their abundances were considerably high (fig. 2) and constitute between 64.95 and 71.75% of total PAHs identified. The studied crude oils also contained between 18.49% - 24.82% phenanthrenes, 2.87% - 3.88% biphenyl, 4.49% - 4.69% fluorene and 1.71% - 2.69% dibenzothiophenes (fig. 2). Distribution of the PAH identified in the studied crude oil samples from the Niger delta are shown in fig. 2.

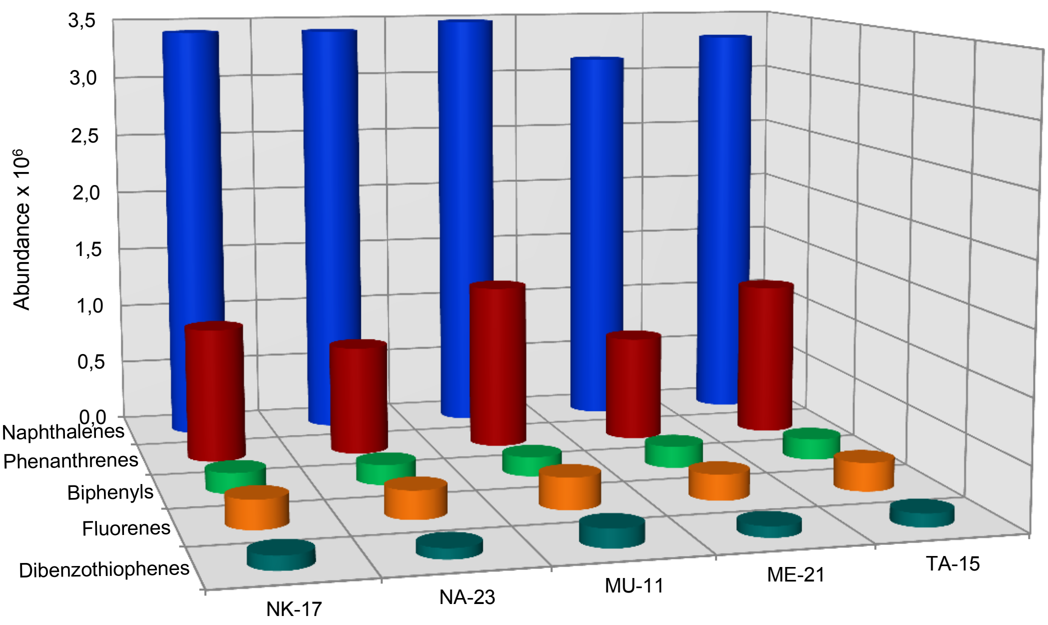

Figure 2 Distribution of polycyclic aromatic hydrocarbons in Niger Delta crude oils

The naphthalenes are reported to originate from the aromatization of the D/E ring of the oleanane biomarkers [12] and their abundance reflect angiosperm higher plant contribution to source rock. Also, the relative distribution of dibenzothiophenes to phenanthrenes has been used to assess the availability of reduced sulphur, from anaerobic organisms, in the depositional environment [8]. Calculated dibenzothiophene / phenanthrene ratios, which range from 0.09 - 0.11 for the studied Niger Delta crude oil samples, were low and reflect limited availability of reduced sulphur in the depositional environment. Consequently, the low sulphur content indicated the studied oils were derived from organic matters deposited in an oxidizing environment. This PAH composition and distribution for the studied oil samples suggest terrestrial organic matter input to source rocks which were deposited in an oxic environment, characteristic of crude oils from Niger Delta [5,19].

3.3 Aromatic Steranes

Aromatization of the tetracyclic steranes, during crude oil formation, gives rise to the mono-, di- and triaromatic steranes. GC-MS analyses of the aromatic fraction of the studied Niger Delta crude oils identified monoaromatic and triaromatic steranes at mass fragments m/z 253 and 231 respectively. Monoaromatic sterane (MAS) homologous identified in the studied Niger Delta crude oil samples range from C_{21} to C_{29} with the C_{23}, C_{24}, C_{25} and C_{26} constituents absent, and for triaromatic sterane (TAS), C_{20} to C_{28} homologous were identified with the C_{22}, C_{23}, C_{24} and C_{25} constituents absent. In all the crude oil samples, it was observed that aromatic sterane compositions were characterized by the short-chain C_{20} - C_{22} and long-chain C_{26} - C_{29} homologous series. The compositions of aromatic steranes in the Niger Delta crude oil samples are presented in table 2. Area integration of each identified aromatic sterane peak was calculated to give the abundance.

Total abundance of C_{27} - C_{29} MAS (80,209 – 107,668) was considerably higher than total abundance of C_{21} - C_{22} MAS (5,116 – 7,630) and constitutes 92.94% to 94.22% of total monoaromatic steranes (table 2). Similarly, total abundance of C_{26} - C_{28} TAS (217, 129 – 234,999), which constitutes 90.48% to 91.25% of total triaromatic steranes was also considerably higher than total abundance of C_{20} – C_{21} TAS (22,525 – 24,178). In general, the long-chain C_{26} - C_{29} aromatic steranes were more in abundance than the short-chain C_{20} - C_{22} homologous; 13.17 - 16.30 times more for MAS and 9.50 - 10.43 times more for TAS. Total abundance of triaromatic sterane (239,983 – 257,623) was higher than the monoaromatic sterane (86,297 – 115,298; table 2). The calculated TAS/MAS ratio for the studied oils showed TAS were 2.08 - 2.99 times more than MAS and constitute between 92.94% to 94.22% of total aromatic steranes identified. The progressive aromatization of the steroids from monoaromatic to triaromatic molecules with increasing thermal maturity leads to the increase in TAS/MAS ratio [9]. This considerably higher content of the TAS suggest that crude oils from Niger Delta were of high maturity.

Table 2 Composition of aromatic steranes in Niger Delta crude oils

	Area				
	NK-17	NA-23	MU-11	ME-21	TA-15
Aromatic Steranes					
MAS	97,586	86,297	104,406	88,524	115,298
TAS	251,055	257,623	257,523	256,325	239,983
TAS/(TAS+MAS)	0.72	0.75	0.71	0.74	0.68
TAS/MAS	2.57	2.99	2.47	2.90	2.08
Monoaromatic steranes (MAS)					
$C_{21}+C_{22}$	6,430	6,088	6,987	5,116	7,630
$C_{27}+C_{28}+C_{29}$	91,156	80,209	97,419	83,408	107,668
$C_{27}+C_{28}+C_{29}/C_{21}+C_{22}+C_{27}+C_{28}+C_{29}$	0.9341	0.9294	0.9331	0.9422	0.9338
$C_{27}+C_{28}+C_{29}/C_{21}+C_{22}$	14.18	13.17	13.94	16.30	14.11
Triaromatic steranes (TAS)					
$C_{20}+C_{21}$	22,969	23,638	22,525	24,178	22,854
$C_{26}+C_{27}+C_{28}$	228,086	233,985	234,999	232,147	217,129
$C_{26}+C_{27}+C_{28}/C_{20}+C_{21}+C_{26}+C_{27}+C_{28}$	0.9085	0.9082	0.9125	0.9057	0.9048
$C_{26}+C_{27}+C_{28}$ $/C_{20}+C_{21}$	9.93	9.90	10.43	9.60	9.50

4. Conclusion

GC-MS analysis of the aromatic fraction of the crude oils from the Niger Delta revealed the high abundance of the aromatic hydrocarbons, polycyclic aromatic hydrocarbons and aromatic steranes. The extremely high abundance of the polycyclic aromatic hydrocarbons, especially the naphthalenes, and the low sulphur content, calculated from dibenzothiophene/ phenanthrene ratio, suggest terrestrial organic matter input to source rocks deposited in an oxic environment. The abundance of the triaromatic steranes, which was more than twice the monoaromatic steranes, indicated that crude oils from the Niger Delta were of high maturity. The aromatic hydrocarbon compounds in Niger Delta crude oils are abundant to permit their use as geochemical markers for crude oil-source rock correlation studies.

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