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GAS CHROMATOGRAPHY-MASS SPECTROMETRY ANALYSIS OF CHROMATOGRAPHIC FRACTIONS OF NIGERIAN BITUMEN

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ABSTRACT

This research was carried out to separate bitumen sample obtained from Agbabu in Ondo state into two fractions by elution glass column chromatography using alumina and mixed silica-alumina as the stationary phase. The aliphatic and aromatic fractions with raw bitumen sample dissolved in n-hexane were analyzed using Gas Chromatography-Mass Spectrometry. The results show that the nature of the stationary phase has an impact on the colors of the fractions obtained. The aliphatic fraction eluted with alumina stationary phase contains 25 compounds with a total composition of 86.5% and the most significant compound was Cyclotrisiloxane, hexamethyl- with a composition of 13.9%. The aromatic fraction eluted with alumina stationary contains 24 compounds with a total composition of 99.1% and the most significant compound was 1,3-Bis(trimethysily)benzene with a composition of 13.4%. The aliphatic fraction eluted with mixed silica-alumina stationary phase contains 21 compounds with a total composition of 98.3% and the most significant compound was (Z)-9-Octadecenoic acid with a composition of 26.1%. The aromatic fraction eluted with mixed silica-alumina stationary phase contains 16 compounds with a total composition of 99.2% and the most significant compound was benzo[h]quinoline,2,4-dimethyl- with a composition of 10%.The bitumen sample dissolved in n-hexane contains 45 compounds with a total composition of 98.4% and the most significant compound was (Z)-9-Octadecenoic acid with a composition of 27.5%.

KEYWORDS: Bitumen, Alumina, Stationary Phase, Aromatic Fraction, Aliphatic Fraction, Gas Chromatography-Mass Spectrometry.

INTRODUCTION

Naturally occurring deposit of bitumen are formed from the remains of ancients' microscopic algae and the once-living things. These organisms died and their remains were deposited in the mud on the bottom of the ocean or lake where they lived under the heat and pressure of burial deep in the earth, the remains were transformed into materials such as bitumen, kerogen or petroleum[1]. As bitumen is also found in meteorites and archean rocks, it is possible that some bitumen are primordial material formed during accretion of the earth and reworked by bacteria that consume hydrocarbons [2].

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In Nigeria, natural bitumen has been found in Ondo, Lagos, Ogun, Edo, and Enugu States with a combined proven reserve of about 14.86 billion barrels. Geologically, the main bitumen belt in Nigeria occurs on the eastern margin of a coastal sedimentary basin known as the Benin Basin, which extends through Togo and Benin Republic to Western Nigeria. The crystalline basement rocks form the foundation of the whole area [3]. Ondo State is the most noted area of bitumen activities in the belt and has offices of Nigerian Bitumen Development Project located at Akure and Ore. Generally some distinct bitumen-impregnated hydrocarbon types of occurrence have been identified within the Nigerian bitumen belt from topsoil downwards and location to location as: Outcrop, rich sands, lean sands, shales and heavy crudes [4,5].The average bitumen content of Nigerian tarsand is about 20% by weight. Very rich natural bitumen deposits are found in Ondo State around the region of Idiobilayo, Foriku, Agbabu, Okitipupa, and Aiyibi. Generally tarsands are composed of bitumen, water and some mineral accessories. Tarsands with 5 – 10% by weight bitumen content are designated as good or medium grade [6,7].

MATERIALS AND METHOD

Bitumen was collected from Agbabu village in Ondo state. It was extracted from its well by inserting a long and thick rod into the well in order to extract part of the bitumen that accumulates in the well. The reagents and chemicals used were of analytical grade and were used without any further purification.

SAMPLE PREPARATION

The sample was collected from Agbabu village in Ondo state. The sample collected was a viscous and blackish sample which was kept properly under a cool condition and was kept from been contaminated by various particles or contaminant by keeping it in a dry clean cupboard.

COLUMN CHROMATOGRAPHIC FRACTIONATION OF BITUMEN

The method adopted was reported by [8]. The samples were fractionated on a glass column chromatography using alumina (active) as the stationary phase and two different solvent; n-hexane and dichloromethane, as the mobile phase. The column was prepared by plugging the lower part of the column with small amount of quart wool or glass wool, this step was followed by addition of activated alumina to the column to required volume and plugging the upper part of the column with glass wool and the column was rinsed with 10ml n-hexane for 3 times. Finally, the 0.5g of the bitumen sample to be fractionated was placed on top of the column. The column was then eluted with two different solvent to give two different fractions: 10 mL of n-hexane, 10 mL of dichloromethane, and another 10 mL of dichloromethane, and the fractions were collected in three separate clean, pre-weighed glass vials, the first fraction contains aliphatic (straight and branch chain) hydrocarbons, the second fraction contains mixture of aliphatic(straight and branch chain) hydrocarbons and aromatic (ring-containing) hydrocarbons, and the third fraction contains aromatic (ring-containing) hydrocarbons.

The first and the third fractions were labeled sample A and sample B [9].The above procedure was carried out again using the mixture of activated alumina and silica as the stationary phase in the column and the two fractions obtained; aliphatic (straight and branch chain) hydrocarbons and aromatic (ring-containing) hydrocarbons in two separates glass vials and was labeled sample C and sample D [10].

0.2g of the raw bitumen sample was also weighed and dissolved with 2 mL n-hexane in a glass vial and was labeled sample E. Sample A, B, C, D and E were then analyzed using GC-MS.

PROCEDURE FOR GC-MS ANALYSIS

Method of [11] was used for the analysis. After fractionation, the aliphatic, aromatic fractions and raw bitumen were analyzed using GC MS. Just before the analysis, the aliphatic (sample A and C) and aromatic fractions (sample B and D) were dissolved in hexane and dichloromethane respectively, in order of 1000 µL, in separate vials. From each vial, 1 µL of solution was injected into the column by the GC-MS machine.

The GC is coupled to a mass spectrophotometer (detector) which has the function of recording the mass spectrum of the chemical compounds as they come out of the GC and after fragmentation process by a stream of electron in the mass spec, helium gas was used as the carrier gas. Peaks in the chromatograms produced by these analyses were identified by a combination of references to their mass spectra and the pherobase mass spectra database and by comparing retention times and abundance with those of known standards in the Library [12].

DATA ANALYSIS

The GC-MS results or data was interpreted both qualitatively and quantitatively. Qualitative interpretation involves all series of tasks of studying, identifying, naming and classification of chemical compounds of the analyzed mixtures. Chemical compounds can be identified on the basis of their mass spectrum, which is basically aunique fingerprint for each molecule. This fingerprint can then be utilized to identify unknown compounds [13].

RESULTS AND DISCUSSION

ELUTION COLUMN CHROMATOGRAPHY

Table 3.1 below shows the colors of the two fractions i.e aliphatics and aromatics obtained from the elution column chromatography of bitumen samples separated using alumina and mixed alumina and silica as the stationary phase. The table shows that the color of the fractions deepens on proceeding from the aliphatic to the aromatic which is from yellow to brown while the raw bitumen dissolves in n-hexane gives a dark brown color. The result also shows that the nature of the stationary phase also has an impact on the colors of the fractions obtained. For example, the colour obtained in fraction B using alumina is brown and dark brown using mixed silica-alumina stationary phase. Thus, from this result, fractions obtained from elution column chromatography of bitumen sample can be differentiated using colors [14].

Table 3.1.Comparison of the colors of fraction of elution column chromatography of bitumen sample separated using alumina and mixed silica-alumina stationary phase

Stationary Phase	Fraction A (Aliphatic)	Fraction B (Aromatic)
Alumina	Yellow	Brown
Silica-Alumina	Yellow	Deep Brown

GAS CHROMATOGRAPHY-MASS SPECTROMETRY

The relative percentages and identities of the constituents of the aliphatic fractions obtained from the bitumen sample separated using alumina stationary phase are shown in Table 3.2 below. The table contains 25 compounds of 86.5% composition identified from their mass spectra. The predominant compound in the fraction of the oil was Cyclotrisiloxane, hexamethyl- with a composition of 13.9 %.

Table 3.3 presents the relative percentages and identities of the constituents of the aromatic fractions obtained from the bitumen sample separated using alumina stationary phase, the table contains 24 compounds of 99.1%

composition identified from their mass spectra, the predominant compound in the fraction of the oil was 1,3-Bis (trimethylsilyl) benzene with a composition of 13.4 %.

Table 3.2.Chemical composition (%) of constituents of the alyphatic fraction of the bitumen sample separated using Alumina stationary phase

S/No	Compounds	% Composition
1.	3-methylhexane	5.8
2.	2-Pentyn-1-ol	1.1
3.	Cyclopentane,1,3-dimethy-	1.1
4.	2-cyclohexenol	0.4
5.	Cycloheptane	0.6
6.	2,6,7-trimethyldecane	0.9
7.	2,6,7-trimethyldecane	0.8
8.	Toluene	0.4
9.	Bifenox	0.2
10.	Methanol(6,8,9-trimethyl-4-1[1-propenyl]-3-oxabicyclo[3.3.31] non-6-en-1-yl	0.2
11.	Phenylhydrazine, 4-nitro-N2-(chloro)(2-thienyl)methylene-	0.3
12.	Dodecanoic acid	0.9
13.	Phosphorochloridothioic acid	0.2
14	Hexanoic acid	0.3
15.	(Z)-3- Hexen-1-ol	0.8
16.	Dodecahydropyrido[1,2-b]isoquinolin-6-one	1.4
17.	Cyclotrisiloxane,hexamethyl-1H-indole,5-methyl-2-phenyl-	1.2
18.	1-Propene,3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-	1.4
19.	Silicic acid,diethylbis (trimethylsilyl)ester	2.9
20.	2-Ethylacridine	5.8
21.	2,4,6-Cycloheptatrien-1-one,3,5-bis-trimethylsilyl-	7.4
22.	Trimethyl[4-(2-methyl-4-oxo-2-pentyl) phenoxy]silane	22.7
23.	Vanadium,(.eta.7-cycloheptatrienylium)(.eta.5-2,4-cyclopentadien-1-yl)-	11.4
24.	5-Methyl-2-phenylindolizine	5.5
25.	Cyclotrisiloxane, hexamethyl-	13.9
	Total	86.5%

Table 3.3.Chemical composition (%) of constituents of the aromatic fraction of the bitumen sample separated using Alumina stationary phase

S/No	Compounds	% Composition
1.	3-methylhexane	2.0
2.	3-Hexanal	0.3
3.	Undecane,3-methylene-	0.6
4.	1,3-Dimethylcyclopentane	0.3
5.	Trans-1,2-Dimethylcyclopentane	0.5
6.	Heptane	0.9
7.	Methylcyclohexane	1.3
8.	Toluene	0.3

9.	3-buten-2-one,4-5(5,5-dimethyl-1-oxaspieo[2.5]oct-4-yl	0.3
10.	Piperazine-1-carboxamide oxime,4-(3-fluorobenzyl)-	0.3
11.	2-Buten-1-one, 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-	0.2
12.	Dodecanoic acid	1.9
13.	Tetradecanoic acid	1.1
14	2-Ethylacridine	0.5
15.	Hexadecanoic acid	10.4
16.	N-Methyl-1-adamantaneacetamide	0.8
17.	2-Ethylacridine	0.9
18.	1-Nonadecene	26.5
19.	Octadecanoic acid	13.0
20.	Vanadium,(.eta.7-cycloheptatrienylium)(.eta.5-2,4-cyclopentadien-1-yl)-	3.6
21.	Vanadium,(.eta.7-cycloheptatrienylium)(.eta.5-2,4-cyclopentadien-1-yl)-	10.3
22.	Cyclotrisiloxane,hexamethyl-	4.7
23.	Cyclotrisiloxane,hexamethyl-	5.0
24.	1,3-Bis(trimethylsilyl)benzene	13.4
	Total	99.1%

The relative percentages and identities of the constituents of the aliphatic fractions obtained from the bitumen sample separated using mixed silica-alumina stationary phase is shown in Table 3.4 , the table contains 21 compounds of 98.3% composition identified from their mass spectra. The predominant compound in the fraction of the oil was (Z)-9-Octadecenoic acid with a composition of 26.1 %.

Table 3.4.Chemical composition (%) of constituents of the alyphatic fraction of the bitumen sample separated using mixed silica-alumina stationary phase

S/No	Compounds	% Composition
1.	3-methylhexane	5.5
2.	Cis-1,3-Dimethylcyclopentane	1.3
3.	Heptylcholoacetate	1.0
4.	Decylbromoacetate	0.4
5.	Cis-1,3-Dimethylcyclopentane	0.5
6.	Hexan-3-one	0.6
7.	Toluene	0.3
8.	Dodecanoic acid	1.6
9.	Brallobarbital	0.2
10.	Tetradecanoic acid	1.0
11.	1-0ctadecene	0.3
12.	Methadone N-oxide	0.6
13.	n-hexadecanoic acid	9.8
14	5-Methyl-2-phenylindolizine	0.9
15.	(Z)-9-Octadecenoic acid	22.6
16.	Octadecanoic acid	11.8
17.	Silane,1,4-phenylenebis[methyl	3.4
18.	Vanadium, (.eta.7-cycloheptatrienylium)(.eta.5-2,4-cyclopentadien-1-yl)-	10.4

19.	Vanadium, (.eta.7-cycloheptatrienylium)(.eta.5-2,4-cyclopentadien-1-yl)-	5.2
20.	Cyclotrisiloxane, hexamethyl-	5.0
21.	Tetrasiloxane, decamethyl-	13.3
	Total	98.3%

Table 3.5 presents the relative percentages and identities of the constituents of the aromatic fractions obtained from the bitumen sample separated using alumina stationary phase, the table contains 16 compounds of 99.2% composition identified from their mass spectra. The predominant compound in the fraction of the oil was benzo[h]quinoline,2,4-dimethyl- with a composition of 10 %.

Table 3.5.Chemical composition (%) of constituents of the aromatic fraction of the bitumen sample separated using mixed silica-alumina stationary phase

S/No	**Compounds**	**% Composition**
1.	Propanoic acid,2-methyl-,2-ethyl hexyl ester	0.1
2.	Dodecanoic acid	2.1
3.	Tetrasecanoic acid	1.3
4.	Thiocarbamic acid,N,N-dimethyl,S-1,3-diphenyl-2-butenyl ester	0.6
5.	n-hexadecanoic acid	9.7
6.	Vanadium,(.eta.7-cycloheptatrienylium)(.eta.5-2,4-cyclopentadien-1-yl)-	0.5
7.	Dodecanoic acid,2,3-dihydroxypropyl ester	1.3
8.	(Z)-(-Octadecenoic acid	25.1
9.	Octadecanoic acid	15.0
10.	2,3-2H-4-Methyl-imidazole-2-one	3.1
11.	Cyclotrisiloxane,hexamethyl-	1.1
12.	Benzo[h]quinoline,2,4-dimethyl-	10.0
13.	Silicic acid,diethylbis(trimethylsilys) ester	4.9
14	Indolizine,2-(4-methylphenyl)-	5.4
15.	Silane,1,4-phenylenebis[trimethyl]	14.0
16.	Cyclotrisiloxane,hexamethyl	5.0
	Total	99.2%

Table 3.6.Chemical composition (%) of constituents of the bitumen sample dissolved in n-hexane

S/No	Compounds	% Composition
1.	Cycloheptane	0.2
2.	Cycloheptane	0.4
3.	1-Silacyclo-2,4-hexadiene	0.1
4.	9-Methylbicyclo[3.3.1]nonane	0.2
5.	Ketone,1,5-dimethylbicyclo[2.1.0]pent-5-yl methyl	0.1
6.	Bicyclo[4.1.0]heptan-3-one,4,7,7-trimethyl-,[1R-(1.alpha.,4.beta.,6.alpha.)]-	0.2
7.	Trans-2,3-Epoxydecane	0.2
8.	Cyclotetradecane	0.5
9.	(E)-2)-Hexenal	0.7
10.	(E)-9)-Eicosene	0.6
11.	1-Tridecene	0.6
12.	(E,E)-2,4-Decadienal	0.5
13.	(E,E)-2,4-Decadienal	0.3

14.	(E,E)-2,4-Decadienal	0.6
15.	(E,E)-2,4-Decadienal	0.7
16.	2-Octenal, (E)-	1.7
17.	4-Chloro-2,4-dimethylhexane	1.3
18.	1,1-Bicyclopentyl	0.3
19.	2-Cyclohexen-1-ol	0.4
20.	3-Cyclohexen-1-carboxaldehyde,3-methyl-	0.3
21.	E-2-Tetradecen-1-ol	0.5
22.	Dodecanoic acid	1.2
23.	Dodecanoic acid	2.2
24.	Dodecan-2-ol	0.2
25.	2-Dodecen-1-ol	1.2
26.	(Z)-9-Tetradecenoic acid	0.6
27.	Oxirane,heptadecyl-	0.7
28.	Tetradecanoic acid	2.3
29.	(Z)-9- Tetradecenal	0.4
30.	Methyl 6,8-dodecadienyl ether	0.5
31.	2-Octadecyl-propane-1,3-diol	0.5
32.	Z-6-Pentadecen-1-ol acetate	1.2
33.	Propiophenone,2-(trimethylsiloxy)-	0.7
34.	n-hexadecanoic acid	10.6
35.	Silane, trimethyl[5-methyl-2-91-methylethyl)phenoxy]-	1.4
36.	1,3-Bis(trimethylsilyl)benzene	0.9
37.	2-Ethylacridine	0.8
38.	(Z)-9-Octadecenoic acid	27.5
39.	Octadecanoic acid	14.4
40.	Vanadium,(.eta.7-cycloheptatrienylium)(.eta.5-2,4-cyclopentadien-1-yl)-	1.2
41.	Cyclotrisiloxane, hexamethyl-	4.1
42.	Cyclobarbital	3.2
43.	Vanadium,(.eta.7-cycloheptatrienylium)(.eta.5-2,4-cyclopentadien-1-yl)-	1.5
44.	Tetrasiloxane, decamethyl-	3.4
45.	Cyclotrisiloxane, hexamethyl-	7.3
	Total	98.4%

The relative percentages and identities of the constituents of the bitumen sample dissolved in n-hexane is shown in Table 3.6, the table contains 45 compounds of 98.4% composition identified from their mass spectra. The predominant compound in the fraction of the oil was (Z)-9-Octadecenoic acid with a composition of 27.5 %.

The results shows clearly that the nature of the stationary phase may affect the percentage composition of aliphatic and aromatic compounds in the oil since the since the result presented in table 3.2 and 3.4, table 3.3 and 3.5 are different. Also the presence of octadecanoic acid in the oil indicates oxidizing depositional environment for the source.

CONCLUSIONS

Going by the distribution of major compounds in bitumen sample, there is need based on the importance of these compounds and its toxic effect, to analyze bitumen, it can be categorically said to be important in chemical industries all over the world especially in various fields in the petroleum industry, and also it is toxic to aquatic lives due to the oxygen containing compounds which contribute to oil acids.We can then conclude according to the GC-MS analysis of chromatographic fraction of Nigerian bitumen that aliphatic and aromatic fractions in bitumen must be determined for industrial processes.

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