SHORT COMMUNICATION

INFRARED AND ULTRAVIOLET SPECTROPHOTOMETRIC ANALYSIS OF CHROMATOGRAPHIC FRACTIONS OF CRUDE OILS AND PETROLEUM PRODUCTS

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ABSTRACT. Samples of light, medium and heavy Nigerian crude oils and petroleum products including diesel oil, engine oil (SAE 40) and gasoline (PMS) have been separated into four fractions of saturates, monoaromatics, diaromatics and polyaromatics by elution liquid chromatography. The fractions obtained were analysed using IR and UV-visible spectrophotometry. The infrared data confirmed the presence of methyl and methylene groups in the saturate fractions of the crude oils and petroleum products. The C=C stretching vibrations and C–H out of plane bending vibration of aromatics were also found in the mono-, di- and polyaromatics fractions. The characteristic UV spectra of alkyl benzenes and naphthalenes were observed in the monoaromatic and diaromatic fractions, respectively. The spectra of the polyaromatic fractions indicate the presence of anthracenes and phenanthrenes.

KEY WORDS: Crude oils, Petroleum products, Diesel oil, Engine oil, Gasoline

INTRODUCTION

Crude oil or petroleum is a complex mixture of hydrocarbons representing several classes of compounds, the most important of these being alkanes, naphthenes and aromatics [1]. These classes are not sharply divided as the aromatic compounds often contain alkane substituents and many of the ring structures are mixed aromatics and naphthenes. They also have heterocyclic compounds of oxygen, sulfur, nitrogen, phosphorus and trace amounts of metals especially vanadium, nickel and iron. These constituents may significantly affect the refining processes as well as the analysis procedures [2].

The ever-increasing chemical utilization of crude oils and petroleum products calls for a better knowledge of the composition, structure and properties of their fractions [3]. Several analytical techniques for characterization of crude oils and petroleum products have been developed. The need for petroleum characterization has been responsible for the development of several procedures in analytical chemistry. Improved analytical methods are useful in processing and refining for efficient utilization of valuable resources and lowering the cost of operation. In environmental protection, improved analytical methods are also required to measure the impact of oil pollution incidents and to identify the sources and kinds of contaminants for immediate attention [4]. The application of elution chromatography to the fractionation of undiluted virgin crude oils has been investigated by Karr *et al*. [5]. Some other workers have reported hydrocarbon class separation schemes for petroleum using liquid chromatography and capillary column gas chromatography [6, 7].

Jewel and co-workers [8] have reported a separation scheme that separates heavy-end petroleum distillate into acid, base, neutral, saturate and aromatic fractions while Hirsh *et al.* [9] have developed a chromatographic separation procedure using gradient elution through a single dual-packed adsorption column that separates high-boiling petroleum distillates, into four

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concentrates, i.e. saturates, monoaromatics, diaromatics and polyaromatics. The fractions were characterized using infrared and ultraviolet spectrophotometery [3, 10-13].

In an earlier report, we have presented the results of the characterization of crude oils and petroleum products by fractional distillation and elution liquid chromatography and the analysis of the fractions by gas chromatography [14].

The objective of the present study is to adapt the existing methods for the characterization of crude oils and petroleum product fractions using elution liquid chromatography and then to analyse the fractions using ultraviolet and infrared spectroscopic techniques. The ultraviolet and infrared analyses were used for final assessment of the separation achieved by elution chromatography. The crude oil samples analysed include Gulf crude oil (heavy base crude), Bonny terminal (light and medium crude oil) obtained from the NNPC Portharcourt, Nigeria. The petroleum products analysed include diesel oil (the commercial product obtained in the market), gasoline (PMS) and engine oil (SAE 40) and were obtained from NNPC Warri Refinery and Shell Company.

EXPERIMENTAL

Chemicals. All the chemical used in this study were of analytical reagent grade and were used without further purification. A 50 mL standard laboratory burette used to carry out the elution liquid chromatography was cleaned with a mixture of chromic acid and sulfhuric acid. This was followed by rinsing it with distilled water and acetone and it was allowed to dry in air. The column was carefully packed with silica-gel and was prewetted with 25 mL of n-hexane [14-16a].
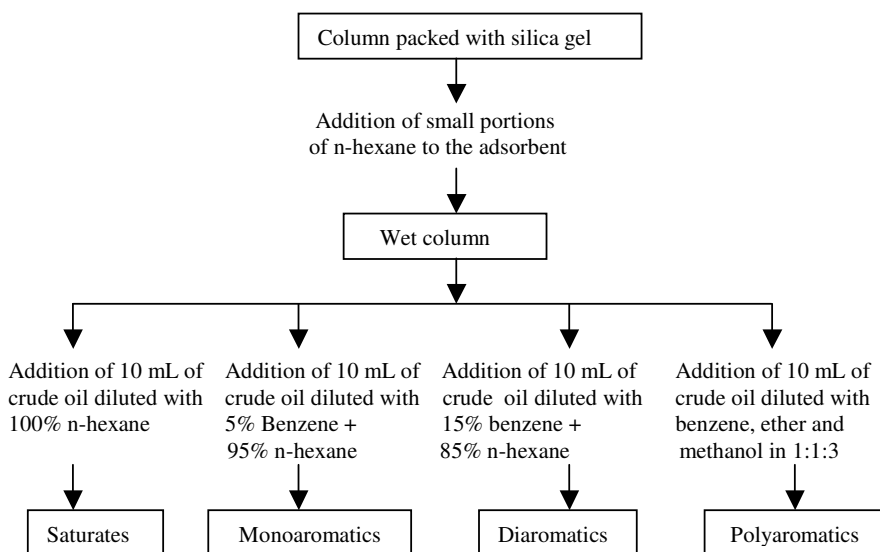

Figure 1. Flow chart of the separation scheme [17, 18].

Elution liquid chromatography. Elution liquid chromatography for the fractionation of crude oils and petroleum products into saturates, monoaromatics, diaromatics and polyaromatics was carried out in the column. The procedure involved introducing 10 mL of the oil simple or petroleum product dissolved in 13 mL of n-hexane to the top of the column. The column was

then eluted at an approximate flow rate of 2-3 mL/min with 100 % n-hexane for saturates, 5 % benzene/95 % n-hexane for monoaromatics, 15 % benzene/85 % n-hexane for diaromatics and 60 % methanol/20 % diethyl ether/20 % benzene for polyaromatics. The concentrates of the four fractions were collected by consecutive elution. The separation scheme used for the elution liquid chromatography is given in Figure 1 [17, 18] and it is a modification of other schemes reported in the literature [2, 18, 19]. The solvent was removed from the individual eluted fractions by atmospheric distillation [15, 16a, 20]. These fractions were then analysed using infrared and ultraviolet visible spectrophotometry.

Physical measurements. Infrared spectra of the fractions were obtained from thin films between KBr windows at a sample thickness of 0.1 mm on a Mattson FTIR spectrophonometer. The ultraviolet visible spectra of the fractions were recorded on a Unicam Helios UV/VIS spectrophotometer. An aliquot of a standard solution of the sample in n-heptane was placed in a 1 cm sample cell. The reference cell was filled with n-heptane. The sample was then scanned from 500 nm in the visible region to 200 nm in the UV region.

RESULTS AND DISCUSSION

Elution column chromatography. The colours of the four fractions (saturates, monoaromatics, diaromatics, and polyaromatics) obtained from elution column chromatography of various crude oils and petroleum products are presented in Table 1. The table clearly shows that the colour of each fraction deepens on proceeding from light to heavy crude oils. Thus the colour of fraction 1 is golden yellow, yellow and dark yellow for the light (Bonny light), medium (Bonny medium) and heavy (Gulf) crude, respectively. Generally, for each crude oil, the colours of the fractions deepen on proceeding from saturates to polyaromatics. For example, for light crude, the colour is golden yellow, yellowish brown and dark brown for fractions I, II and both III and IV, respectively. Similar trends were also observed for the saturates, monoaromatic and diaromatic and polyaromatic fractions of the petroleum products studied. For example, for gasoline (PMS), the observed colours are pale yellow, yellow and deep yellow for fractions I, II and both III and IV, respectively. Thus colour can be used to characterize the fractions obtained during elution column chromatography of crude oils and petroleum products. The only exceptions are fractions III and IV which have about the same colours for all the crude oils and petroleum products. The present results agree with our earlier report [14].

Table 1. Colours of fractions of elution column chromatography of crude oils and petroleum products.

Sample	Fraction I Saturates	Fraction II Monoaromatics	Fraction III Diaromatics	Fraction IV Polyaromatics
Bonny (Light crude)	Golden yellow	Yellowish brown	Dark brown	Dark brown
Bonny (Medium crude)	Yellow	Deep brown	Deep brown	Black tar
Gulf (Heavy crude)	Dark yellow	Dark brown	Dark brown	Black tar
Gasoline (PMS)	Pale yellow	Yellow	Deep yellow	Deep yellow
Diesel oil	Deep yellow	Pale yellow	Pale yellow	Golden yellow
Engine oil (SAE 40)	Deep yellow	Yellow	Golden yellow	Golden yellow

Infrared spectra analysis. The infrared frequencies of the saturate fractions, aromatic fractions and the petroleum products of the saturates, monoaromatic, diaromatic and polyaromatic fractions are presented in Table 2. The IR spectra of the saturate fraction showed the C-H aliphatic absorption bands between 2800-2940 cm^{-1}. In alkanes, C-H absorption always occurs below 3000 cm^{-1} except in strained ring compounds [16b]. The spectra also showed the

characteristic absorptions of methylene (-CH$_2$) group at around 1450 cm^{-1} and the methyl (-CH$_3$) group at around 1375 cm^{-1}. The C-C stretch is not interpretatively useful because it has many peaks [16b]. The spectra also showed the usual aliphatic absorption bands at 2920, 1450 and 1375 cm^{-1}. In addition to these bands a weak =C-H stretching peak of aromatic hydrocarbons were found just above 3000 cm^{-1} region [3, 16b]. The peaks appeared as shoulder on the strongest aliphatic C-H stretching vibration for mono-, di- and polyaromatics of all the samples except for the polyaromatic fraction of engine oil. Also there were sharp absorptions of moderate intensity at 1600-1635 cm^{-1}, which is due to the C=C stretching vibrations of aromatics and several strong C-H out of plane bending vibration at wavenumbers less than 900 cm^{-1}, which is due to H attached to sp^2 hybridized carbon. Also, long chain methylene groups gave rise to a peak at 720 cm^{-1} region [16b]. The spectra also showed a broad absorption band 3400-3450 cm^{-1} which is due to the stretching vibration of O-H groups and there were many weak combination and overtone absorptions that appeared between 2000 and 1667cm^{-1}. These results agree with literature reports [3, 7, 13].

Table 2. The IR frequencies of the saturate fractions, the aromatic fractions and the petroleum products of the saturates, monoaromatic, diaromatic and polyaromatic fractions of the crude oils.

Samples	Characteristic frequencies (cm^{-1})
Saturates fraction	
Bonny light	3430, 3188, 1609, 871, 885, 723
Bonny medium	2731, 1635, 870, 724
Gulf oil	3398, 2730, 1635, 1304, 884, 723
Gasoline	2940,1465, 1380, 983,730
Diesel	2729, 1634, 1304, 871, 723
Engine oil	3422, 2675, 1808, 1636, 1304, 884, 723
Monoaromatic fraction	
Bonny light	3402, 1952, 1808, 1604, 1481, 884, 723
Bonny medium	3428, 1952, 1808, 1466, 812, 724, 674
Gulf oil	3414, 1952, 1808, 1487, 884, 723, 674
Gasoline	2944, 1465, 1387, 979, 730
Diesel	3446, 1952, 1607, 1304, 973, 723
Engine oil	3092, 1808, 2029, 1634, 952, 723, 674
Diaromatic fraction	
Bonny light	3401, 1953, 1808, 1605, 1304, 872, 723
Bonny medium	1954, 1805, 1605, 1304, 882, 724
Gulf oil	3406, 3038, 1959, 1808, 1605, 983, 723,
Diesel	674
Engine oil	3444, 3199, 1953, 1808, 1605, 954, 723
	3412, 2729, 1952, 1808, 1605, 954, 723
Polyaromatic fraction	
Bonny light	3084, 2633, 1953, 1605, 871,721
Bonny medium	2569, 1955, 1606, 934, 722
Gulf oil	3455, 3256, 2042, 1954, 1606, 934, 722
Gasoline	2940, 2377, 1472, 1381, 962, 730
Diesel	2040, 1954, 1605, 732, 674,
Engine oil	2605, 2041, 2529, 2171

Ultraviolet spectra analysis. The ultraviolet absorptions wavelengths of the monoaromatic, diaromatic and polyaromatic fractions of the crude oils and petroleum products are presented in Table 3. The usual procedure, when one is confronted with the ultraviolet spectrum of an unknown substance, is to compare the spectrum, in its general shape and in the intensity and position of its peaks, with the spectra of reasonable model compounds. The model compounds

are chosen to possess as nearly as possible the same chromophore as that suspected for the unknown [21].

Table 3. UV spectral data of mono-, di- and polyaromatic hydrocarbon fractions of crude oils and petroleum products.

Samples	UV spectral data			
Monoaromatic fraction	λ (nm)	A	λ(nm)	A
Bonny light	233	2.274	257	1.020
Bonny medium	234	2.327	257	1.238
Gulf	233	2.319	257	1.195
Gasoline	230	0.839		
Diesel	235	2.463	255	1.714
Engine oil	234	2.322	263	1.006
Model compounds: toluene 254 nm, o-xylene 263 nm, aniline 230 nm, phenylacetylene 235 nm				
Diaromatic fraction				
Bonny light	233	2.261	256	1.073
Bonny medium	233	2.310	256	1.152
Gulf	232	2.159	257	0.927
Gasoline	230	0.614		
Diesel	238	2.630	252	2.640
Engine oil	240	2.707	262	1.906
Model compounds: naphthalene 255 nm, benzophenone 252 nm				
Polyaromatic fraction				
Bonny light			252	2.924
Bonny medium	240	2.835	255	2.801
Gulf			256	2.956
Gasoline	225	0.438		
Diesel	247	2.794	251	2.800
Engine oil	231	1.647	263	0.551
Model compounds: anthracene 253 nm, phenanthrene 251 nm				

The assignment of precise structure to the compound type is affected by the tendency of alkyl substitution or any other substituent (auxochrome) on the aromatic nucleus, in the sense that there is a small interaction between the σ-bonded electrons of the alkyl group and the π-bond system to cause a bathchronic shift. Moreover, each additional auxochrome adds 2 to 5 nm to the wavelength of major absorption bands [22]. All the monoaromatic hydrocarbon fractions showed the characteristic spectra of the alkybenzenes (either monosubstituted or disubstituted) while diaromatic hydrocarbon fractions show the characteristic spectra of naphthalenes and substituted naphthalenes [23], with polyaromatic contamination in the spectra of both compound types.

The absorption bands of the substituted polycyclic aromatic hydrocarbons can be estimated from the spectra of the unsubstituted polyaromatic compounds. These polyaromatic compounds include pyrenes (245 nm), anthracenes (255 nm), phenanthrenes (255 nm), triphenylenes (265 nm), benzanthracenes (270 nm), benzphenenanthrenes (270 nm), chrysenes (274 nm), 1,2-benzanthracenes (295 nm), 3,4-benzphenanthrenes (295 nm), benzpyrenes (385 nm), perylenes (435 nm), etc. [24]. Their spectra are usually complicated, and for that reason are useful as fingerprints. This is particularly so in that the relatively non-polar substituents, such as alkyl and acetoxyl groups, have only a small effect on the shape and position of the absorption peaks of the parent hydrocarbon [24]. The polyaromatic fractions of the crude oils show absorption bands at 253 nm and 251 nm, thus suggesting anthracene and phenanthrene as the major polyaromatic compound types in the fraction [25]. The absence of the major absorption in the 295-435 nm

region indicates that there is no significant amount of 1,2-benzanthracenes, 3,4-benzphenanthrenes, benzpyrenes and perylenes in the polyaromatic hydrocarbon fractions analysed. The absorbances at each of the characteristic wavelengths are also given in Table 3. Thus, the results of the ultraviolet analysis agree with those reported earlier [3, 23].

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