CHARACTERIZATION OF NIGERIAN CRUDE OIL ALIPHATICS BY GAS CHROMATOGRAPHIC ANALYSIS

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ABSTRACT. Detailed analysis was carried out on the Nigerian crude oil aliphatics using SiO_2:Al_2O3 (2:1) liquid chromatographic techniques followed by computerized gas chromatographic analysis of the n-hexane soluble fractions. The various oil parameters used as the basis for characterization are discussed, and the most promising fingerprint indices are recommended.

INTRODUCTION

The ever-increasing discharges and spills of crude, residual and distillate oils in coastal waters has been the realization of the need of modern analytical techniques for differentiation and characterization of crude oils. Various methods have been used for characterization of petroleum and petroleum products, amongst them are trace metal analysis [1-5]; mass spectrometry [6-8]; infrared spectroscopy [9-13] and nuclear magnetic resonance spectroscopy [14-16]. However, gas chromatographic analysis appears to be a simple technique which utilizes both the qualitative and quantitative aspects of gas chromatograms for characterization of petroleum oils. Samples are usually compared by using only the "heart fraction" of the gas chromatograms eliminating the volatile and heavy-end components from consideration. Sazonova *et al.* [17] used multidimensional gas chromatography for determining the fractional composition of crude oils and natural gas condensates and for defining the detailed light hydrocarbon (C_1-C_9) content. Tameesh and Hanna [18] determined pristane, phytane, carbon preference index and normal hydrocarbons to C_{36} by direct injection of the crude oil. The application of high-resolution gas chromatography for geochemical studies of petroleum-source rock correlation was reported by Riva [19]. Other workers [20-23] have also used gas chromatography to characterize petroleum and petroleum products.

Little attention has been given on the analysis of Nigerian crude oils using gas chromatographic technique. In the present study, however, analysis of Nigerian crude oil aliphatics using a combination of adsorption liquid chromatographic fractionation and gas chromatographic analysis is reported.

EXPERIMENTAL

Materials. Crude oil samples were obtained from Shell Petroleum Development Company of Nigeria Limited (Bonny Light crude from Rivers State; Forcados Crude from Delta State and Ughelli Petroleum crude, U.P.C. from Edo State); Mobil Oil Producing (Eket crude from Akwa

Ibom State); Chevron Nigeria Limited (Escravos crude from Delta State) and Texaco Nigeria Limited (Oloibri crude from Rivers State). They were collected in sealed glass containers (1 dm^3 capacity) and stored in a refrigerator at 4°C prior to laboratory analysis.

Reagents. Alumina gel (80-200 mesh, Davidson Chemical Company); silica gel (70-230 mesh, ASTM); dichloromethane (purified, Baker and Adamson); n-hexane (purified, Aldrich Chemical Company) and analytical grade benzene were used. Dicholromethane was purified by washing with 5% sodium carbonate solution followed by water, and dried over anhydrous calcium chloride. It was then distilled with the fraction boiling between 40-41° being collected.

Hexane was purified by washing with concentrated sulphuric acid, then with distilled water and dried over anhydrous calcium chloride. It was then distilled with the fraction boiling at 69 ± 0.5° being collected.

Analytical methods. The analytical scheme (Figure 1) employed for the fractionation of the crude oils was as described by Selucky *et al.*[24]. The scheme was reported to provide a good hydrocarbon class fractionation. The complex mixture was separated into fractions more amenable for gas chromatographic analysis.

Deasphaltization of the crude oils. Crude oils (2 g) were dissolved in 5 cm^3 of dichloromethane and the solution was transferred to 200 cm^3 Erlenmeyer flask. Hexane (100 cm^3) was added slowly with magnetic stirrer and stirring was continued for 1 h. The solution was kept in the refrigerator for 2 h. The cold solution was filtered, leaving the precipitate (asphaltene) on the filter paper. The asphaltene was thoroughly washed with hexane and the solvent was removed in a rotary evaporator.

Silica-alumina gel chromatography of deasphalted oil. Twenty five grams of fully activated (16 h at 400°) 80-200 mesh alumina gel was packed into the bottom of 0.65 cm i.d. x 70 cm long capillary column, and 50 g of activated (16 h at 265°) 70-230 mesh ASTM silica gel was packed on top. The packed column was pre-wetted with n-hexane and 1 g of the oil was introduced onto the column by means of a capillary rubber tubing. The rubber tubing was rinsed several times with n-hexane. The column was eluted with 200 cm^3 of n-hexane for saturates followed by aromatics and heterocompounds using benzene/n-hexane (1:1) and methanol respectively as eluants. The solvent was stripped from n-hexane fraction in a rotary evaporator.

Column chromatography on silver nitrate impregnated silica of the hexane elute from silica-alumina gel. A glass column (as above) was wrapped in aluminium foil and packed with silica impregnated with 10% silver nitrate. For the preparation of packing, 450 g of silica gel were placed in a 2 dm^3 round bottom flask wrapped in aluminium foil. Isopropanol (750 cm^3) containing 50 g of silver nitrate was added and the flask was shaken overnight. The solvent was removed in a rotary evaporator and the impregnated silica was dried in a vacuum oven at 150° with exclusion of light and air.

The sample was applied as concentrated hexane solution onto a column. The column was eluted with 100 cm^3 of n-hexane for saturates, followed by removal of retained materials using benzene as eluant. The solvent was removed from the n-hexane fractions in a rotary evaporator and transferred to clean glass vials.
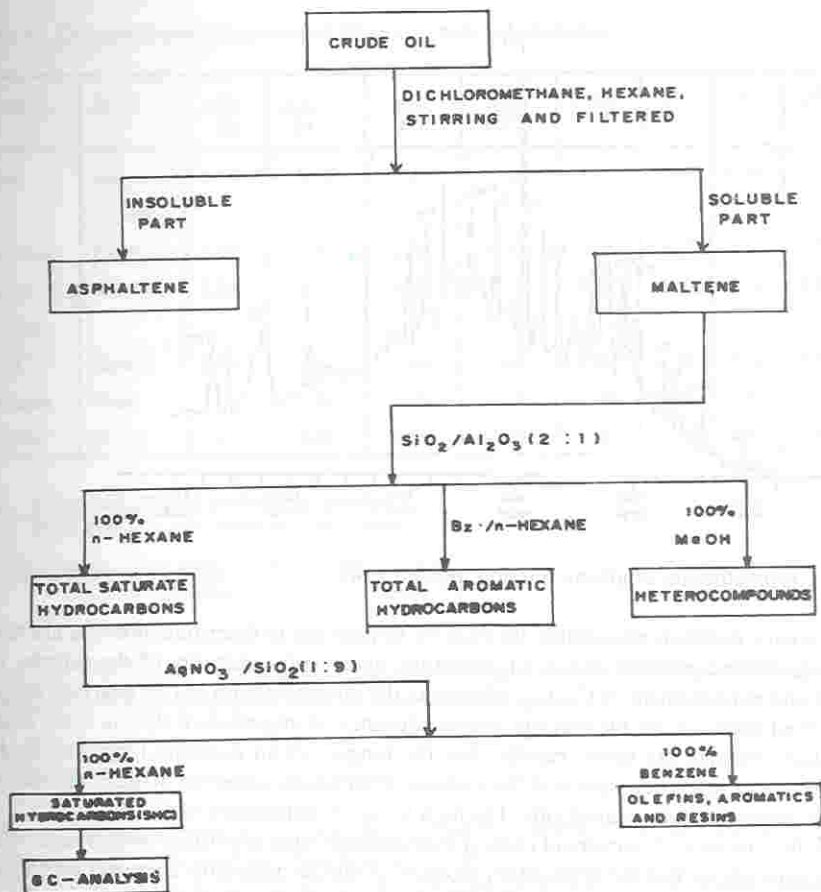
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                        ┌─────────────────┐
                        │   CRUDE  OIL    │
                        └────────┬────────┘
                                 │  DICHLOROMETHANE, HEXANE,
                                 │  STIRRING  AND  FILTERED
                    ┌────────────┴────────────────┐
              INSOLUBLE                        SOLUBLE
                PART                             PART
        ┌─────────────────┐              ┌─────────────────┐
        │   ASPHALTENE    │              │    MALTENE      │
        └─────────────────┘              └────────┬────────┘
                                                  │  SiO₂/Al₂O₃ (2 : 1)
              ┌───────────────────────────────────┼───────────────────────┐
         100%                              Bz·/n-HEXANE              100%
       n-HEXANE                                                    MeOH
  ┌─────────────────┐          ┌─────────────────┐        ┌─────────────────┐
  │ TOTAL SATURATE  │          │ TOTAL AROMATIC  │        │ HETEROCOMPOUNDS │
  │  HYDROCARBONS   │          │  HYDROCARBONS   │        └─────────────────┘
  └────────┬────────┘          └─────────────────┘
           │  AgNO₃/SiO₂(1:9)
  ┌────────┴───────────────────────────────────────┐
 100%                                         100%
n-HEXANE                                     BENZENE
┌─────────────────┐                  ┌─────────────────┐
│   SATURATED     │                  │ OLEFINS, AROMATICS│
│HYDROCARBONS(SHC)│                  │   AND RESINS    │
└────────┬────────┘                  └─────────────────┘
┌─────────────────┐
│  GC-ANALYSIS    │
└─────────────────┘
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Figure 1.   Flow chart of the fractionation scheme of crude oil.

RESULTS AND DISCUSSION

The scheme for the fractionation of the crude oil is shown in Figure 1. The n-hexane soluble fraction in Nigerian crude oil samples were chromatographed. The chromatogram of the n-hexane soluble fractions for one of the Nigerian crude oil samples (U.P.C.) analyzed is shown in Figure 2. The peaks on each chromatogram were identified by using the peak of $n-C_{13}$ internal standard as a reference peak. The n-alkane distribution permit us to distinguish between

Gas chromatographic analysis. A computerized PU 4400 series gas chromatograph instrument equipped with a flame ionization detector was used for analysis. A 1.50 m x 2.0 mm o.d. glass was used, packed with 10% OV-101 on 60/80 Chromosorb W. The operating conditions were as follows: carrier gas: He, 4.0 mL/min; detector: H_2, 35 mL/min; air: 300 mL/min; injector temperature: 200°; detector temperature: 300°; column temperature 50° with 2-min hold, and programmed with an increase of 6°/min to 280°; attenuation: 5; injection mode: split-less; injection volume: 2 µL.
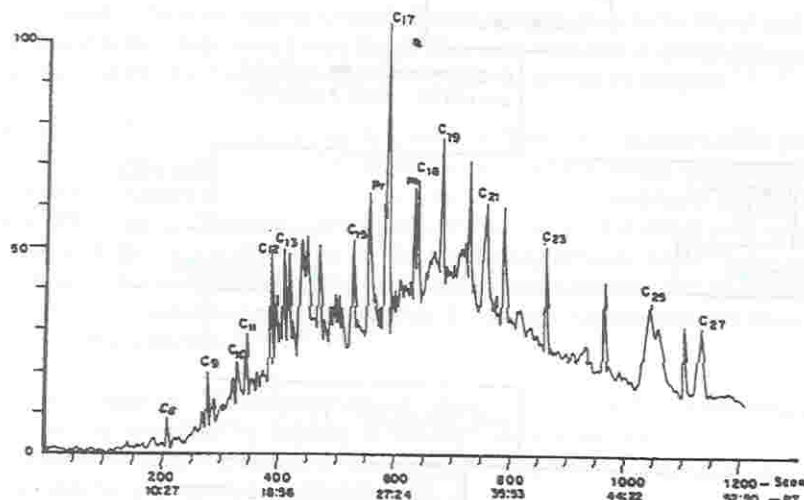
Figure 2.   Chromatogram of alkane fraction in U.P.C. oil.

the type of source materials responsible for each oil sample and to determine possible alteration
from biodegradation, possible effects of migration, and relative maturity of the sample. The
dominance and enhancement of C_{15}-C_{20} alkanes in the chromatogram of oils analyzed suggest
marine-derived materials for the oils and greatest distance of migration of the oil, since shorter
chain n-alkane migrate far more rapidly than the longer chain n-alkane [25]. The marked
increase in the odd-even dominance of the n-alkane distributions observed in the chromatogram
of the oils is suggestive of matured oils. The high level of abundance of C_{15}, C_{17} and C_{19} n-
alkanes and the presence of isoprenoid class of hydrocarbons such as pristane and phytane in the
crude oil, again indicate that the degradation products of marine organisms are major constituents
of the organic material in the crude oils [26-29].

    The gas chromatographic profiles of all the samples are identical, so it may be assumed that
these oils are from the same source materials, formed under different geological conditions. The
isoprenoid and n-paraffinic composition of crude oils are expected to vary from one source bed
to another since the composition of each crude oil is dependent on the source material, and
history of its formation with respect to time, pressure and temperature, and thus suggest a basis
for comparison. By use of the compositional parameters (Table 1), comparison may be made
between crude oil samples from different locations. The following ratios of the adjacent peak
heights on the gas chromatogram, i.e. pristane-phytane (Pr/Ph); n-heptadecane-pristane (n-C_{17}/Pr);
n-octadecane-phytane (n-C_{18}/Ph); n-heptadecane-n-octadecane (n$_1$C /n$_1$C) and carbon-
preference-index (CPI) which are extensively used in organic geochemical investigation [29] were
calculated. In addition to the above ratios, the following, i.e. r_o, r_e and σ (parameters defined in
Table 1) and summation ratios of peak heights of pristane and phytane to the total peak heights
of n-paraffins $\Sigma(Pr + Ph)/\Sigma$ (n-Paraffins) were also determined to evaluate their applicability
in fingerprinting the oil types. These ratios, calculated directly from peak heights above the
baseline are as given for each crude oil in Table 1. The values for the odd-even predominance (or
CPI) of n-alkane in the oils analyzed cluster within a narrow limit near a value of 1.0, indicating
that the crude oils analyzed contain n-paraffins which are almost equally distributed between

Table 1. Compositional parameters of Nigerian crude oil aliphatics.

Sample	State	$\dfrac{Pr}{Ph}$	$\dfrac{n\text{-}C_{17}}{Pr}$	$\dfrac{n\text{-}C_{18}}{Ph}$	$\dfrac{n\text{-}C_{17}}{n\text{-}C_{18}}$	CPI*	$r_o^{\#}$	$r_c^{\#}$	$\sigma^{\#\#}$	S**
Eket	Akwa Ibom	1.14	1.54	1.27	1.38	1.04	0.51	0.49	1.59	0.11
Escravos	Delta	1.24	1.02	1.38	0.92	0.94	0.48	0.52	1.21	0.10
Bonny Light	Rivers	0.28	2.23	0.80	0.78	0.94	0.46	0.54	0.68	0.14
U.P.C.	Bendel	0.93	1.67	1.04	1.49	1.09	0.52	0.48	1.31	0.13
Forcados	Delta	1.38	1.00	1.26	1.96	0.96	0.48	0.52	0.75	0.12
Oloibiri	Rivers	1.41	0.93	1.24	1.06	0.95	0.48	0.52	0.87	0.14

$$*CPI = \frac{\Sigma Peak\ heights\ of\ odd\ numbered\ carbon\ atoms}{\Sigma Peak\ heights\ of\ even\ numbered\ carbon\ atoms}$$

$$r_o = \frac{\Sigma Peak\ heights\ of\ odd\ numbered\ carbon\ atoms}{\Sigma n\text{-}Paraffins} = \frac{CPI}{CPI + 1}$$

$r_c = 1 - r_o$; $^{\#\#}\sigma = R_o/R_c$, where R_o = Range of peak heights for odd numbered carbon atoms, and R_c = Range of th peak heights for even numbered carbon atoms.

$$S** = \frac{\Sigma(Pr + Ph)}{\Sigma n\text{-}Paraffins}$$

molecules containing even and odd numbers of carbon atoms. Thus, this ratio alone cannot be used to distinguish oil samples from different locations.

The Pr/Ph ranged from 0.28 for the Bonny light oil to 1.41 for the Oloibiri oil, the C_{17}/Pr ranged from 0.93 for the Oloibiri oil to 2.24 for the Bonny Light oil, the C_{18}/Ph ranged from 0.80 for the Bonny light oil to 1.40 for the Escravos oil, the C_{17}/C_{18} ranged from 0.78 for the Bonny light oil to 1.50 for the U.P.C. oil, the σ ranged from 0.68 for the Bonny light oil to 1.59 for the Eket oil, while r_o and r_c cluster within a narrow limit near 0.50 and $\Sigma(Pr + Ph)/\Sigma(n\text{-Paraffins})$ clusters near a value of 0.10. The variation in the value of the ratios Pr/Ph, C_{17}/Pr, C_{18}/Ph, C_{17}/C_{18} and σ of oil samples have thus satisfied the first criterion of any identification technique of allowing a quick and accurate differentiation between samples and thus suggest a basis for the applicability of the ratios (measurable from gas chromatogram) for fingerprinting the oil type.

CONCLUSION

The study was carried out to appraise the applicability of gas chromagraphic technique to identification and differentiation of crude oils from different locations despite the similar salient features of their chromatogram. The ratios Pr/Ph, C_{17}/Pr, C_{18}/Ph, C_{17}/C_{18} and σ varied considerably from one sample to another, and are therefore recommended for use in fingerprinting the oil type. For most of the crude oil aliphatics studied, Pr/Ph, C_{17}/Pr, C_{17}/C_{18} and CPI are greater than one, an evidence in support of strong predominance of odd-numbered carbon atoms over the even-numbered carbons atom which is indicative of petroleum-free plants [31].

This method is particularly suited to the identification and differentiation of crude oils,

distillate fuel oils and other petroleum fractions which contain significant concentration of n-alkane fraction of moderately low boiling point.. It is much less suitable for the identification and differentiation of heavy residual oils because they contain mainly the high boiling constituents.

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