

SUITABILITY OF GAS CHROMATOGRAPHY FLAME IONIZATION DETECTOR (GC-FID) FOR FINGERPRINTING RESERVOIR FLUIDS IN MATURE AND MARGINAL FIELDS OF NIGER DELTA

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Abstract

Identification and allocation of reservoir fluids are major challenges faced by Petroleum engineers especially when being related to cost, management and time. As highlighted in this work, there are various Geo-chemical techniques used in identifying crude oil samples. Some of these techniques include; Gas Chromatography, High Temperature Gas Chromatography, 2-Dimensional Gas Chromatography, Gas Chromatography Flame Ionization Detector and Gas Chromatography Mass Spectrometry. And each of these techniques has different areas of application depending on the reservoir fluids characteristic. Of these techniques mentioned, the suitability of Gas Chromatography Flame Ionization Detector for fingerprinting reservoir fluids in the Niger delta is discussed. This work therefore analyzed and compared two crude samples from two oil fields of Niger Delta, using analytical techniques for source identification purposes. Normal alkanes and isoprenoids distribution showed nC_7 to nC_{37} carbon atoms. Low molecular weight hydrocarbons less than nC_7 were not observed probably due to evaporative losses during sample processing. Visual comparison of the chromatograms also showed that samples were similar. The hydrocarbon ratios were able to deduce the source, maturity, depositional environment and extent of biodegradation. Normal paraffin and Isoprenoid peak height profiles, when subjected to measurement error, provided quantitative evaluations of the relative likelihood that the samples were from source rocks containing mixed organic compounds deposited in an Oxic Paleoenvironment.

1.0 Introduction

Geochemical fingerprinting is a rapidly expanding discipline in the earth and environmental sciences and is anchored in the recognition that geological processes leave behind chemical and isotopic patterns in the rock record. Each source crude oil therefore has a unique fingerprint that can potentially be determined by varieties of instrumental and non-instrumental techniques. Many of these patterns informally referred to as geochemical fingerprints differ only in fine detail from each other. For this reason, the approach of fingerprinting requires analytical data of high precision and accuracy. It is therefore not surprising that the advancement of geochemical fingerprinting occurred alongside progress in analysis techniques. For real time applications of geochemical fingerprinting, in which large sample throughput, reasonable cost and fast turnaround are key requirements, combined geochemical techniques are employed.

Some of the applications of fingerprinting technology to the oil and industry include;

- a. To develop an understanding of source rock and crude oil relationships
- b. To identify the sources of oil spills especially at the surface
- c. Allocation of commingled fluids during production
- d. Reservoir characterization
- e. Study of environmental pollution

2.0 Objective

This paper seeks to attain the following objectives:

- i. Review different geochemical techniques used in identifying crude oil samples
- ii. Review field data of crude samples in Niger delta using GC-FID technique
- iii. Determine the suitability of GC-FID technique for identifying crude samples in the Niger Delta
- iv. Determine potential problems and proffer solutions on how they can be managed or utilized

Geochemical fingerprinting approach is based on the well-established proposition that crude oil spills (weathered or unweathered), or separate reservoirs tend to differ from one another in composition due to the chemical record of all the processes that have affected it before, during and after reaching the trap. When there is sufficient (even small) difference in the composition of the fluids, periodic geochemical monitoring can be done to determine their sources or production from each zone. To trace the source of any environmental sample, one must be able to specify the differences between source sample and spill sample that can be expected to arise from weathering (Blumer et al 1972). Any significant differences not attributable to weathering, establish that the samples are different.

3.0 Geochemical Techniques Used In Identifying Crude Oil Samples

Crude oil is a naturally occurring mixture consisting predominantly of hydrocarbons [alkanes (paraffins), alkenes (olefins), and aromatics] with other elements such as Sulphur, Nitrogen and Oxygen appearing in the form of organic compounds which in some cases form complexes with metals. The mixture of crude oil is highly complex and the complexity increases with boiling range. The instrumental techniques of chromatography, ultraviolet and infra-red spectroscopy together with mass spectrometry facilitate knowledge of the detailed hydrocarbon type, composition, concentrations and molecular species of crude oil.

3.1 Gas Chromatography (GC):

GC has the advantages of high column efficiency, high sensitivity, fast analysis, speed and ease to be combined with other analytical methods (mass spectrometry). Thus it is widely used to analyze crude oil and its products. However, because of thermal instabilities of capillary column and the stationary phase, the maximal column temperature of conventional GC is about 325⁰C, and the analysis limited to hydrocarbons with carbon number less than 35. This fact limits the application of GC on the analysis of alkanes with high carbon numbers (C40+) which are

important for some areas including organic chemistry. The GC separation then is based on molecular weights and boiling points.

3.2 High Temperature Gas Chromatography (HTGC):

HTGC is a complement for the limitations of 1D-GC, developed to supplement the low temperatures of GC, which can then be used for components of high molecular weight in crude oil. It has excellent mechanical properties at high temperature, but it also has a very strong catalytic and absorptive effect. The most frequently used detection method for HTGC is Ionization flame detector (FID). Other detection methods have also been used; mass spectrometry (MS), Atomic Emission Detection (AED) and inductively coupled plasma mass spectrometry (ICP-MS).

3.3 2 - Dimensional Gas Chromatography (2D-GC):

Since Liu and Philips depicted comprehensive 2-dimensional gas chromatography in 1990s (Liu & Philips, 1991; Vendevre et al, 2007), the technology of 2D-GC has developed rapidly and has been applied in the areas such as biological, environmental, food, forensics, petroleum, pharmaceuticals and fragrances. 2D-GC employs two capillary columns of different selectivity coupled by a modulator. The advantages of 2D-GC include;

- i. Structured Chromatograms: in a 2D-GC, the chromatograms of the compound are well ordered, allowing a better interpretation than disordered ones. The pattern of peak placement is itself informative and may make it possible in many mixtures to identify most or all of the components with good reliability (Adahchour et al 2008).
- ii. Better separation: 2D-GC separates components along primary dimensions and also along secondary dimension. Sometimes, compounds co-eluted with conventional 1D-GC technology can be separated by 2D-GC along the secondary dimension.
- iii. Larger capacity: 2D-GC peaks are distributed in the whole plane rather than in one line. This therefore makes its capacity larger than that of conventional 1D-GC.
- iv. Higher sensitivity: compared with 1D-GC, the sensitivity of 2D-GC is increased by 1.5-50 folds. The trace amount of analytes can be detected with 2D-GC.

All these characteristics make 2D-GC a particular useful technique for analyzing complex mixture, for example Petroleum. The ordered distribution of the effluent has been used for quick screening of oil, recognizing the difference between individual oils.

3.4 Gas Chromatography Flame Ionization Detector (GC-FID)

Flame ionization detector (FID) is a scientific instrument that measures the concentration of organic species in a gas stream. It is frequently used as a detector in gas chromatography. The first Flame ionization detector was developed in 1957 by scientists working for CSIRO in Melbourne, Australia. It is the most sensitive gas chromatographic detector for the hydrocarbons such as butane or hexane. The FID is the most widely and successfully used gas chromatography detector for volatile hydrocarbons and many carbon containing compounds.

3.5 Gas Chromatography Mass Spectrometry (GC-MS)

Mass spectrometry is an invaluable identification technique. It is characterized by high repeatability of quantitative results, already the difference of one unit in atomic mass unit is recorded by the mass detector (Onyeabor J.O 2014). Although the retention time of peaks in the GC column serves as a means of qualitative analysis, confirmation of individual peaks can be made by using Mass spectrometry. This is partly because retention time is a function of carrier gas, column temperature, column pressure drop, stationary phase, void volume between injection port and detector. Thus to confirm the identities of the above compounds, GC-MS is most appropriate.

4.0 Methodology

The overall methodology to identifying a source is to compare the properties of the oil in question to properties of known sources until a positive identification beyond reasonable doubt is found or until the oils are demonstrated to be from other sources. Depending on the oil samples involved, the analytical requirements may range from only a GC analysis to an extensive assortment of tests.

In the case of GC analysis, the normal paraffin and isoprenoids are analyzed and compared in approximate range from C₇-C₃₅ depending on the GC capabilities. The difficulty in comparing oils depends largely on their degree of similarity in the range of comparison, as such certain hydrocarbon ratios are employed in analyzing the oil compositions.

Two crude samples were collected and analyzed from fields OML 124 and OML 126 been operated by Addax petroleum Exploration Nigeria, of the Niger delta field. OML124 contain sample labeled IZOMBE while the sample from OML 126 was labeled OKWORI. The API gravity and the specific gravity of the samples are:

Table 1- API and Specific gravity of oil samples

Sample	API gravity	Specific Gravity
IZOMBE	29.3	0.880
OKWORI	37.6	0.837

Gas chromatographic (GC) technique was used for the analysis of the oil samples received. This was done using Hewlett Packard 6890 GC equipped with a 50mm × 0.25mm × 0.5µm film thickness of PONA (cross linked Methyl Siloxane capillary column). A flame ionization detector detected and separated the components. The carrier gas was helium flowing at a rate of 40ml/s and the oven was programmed from 35°C to 320°C at 3.00°C/min. the initial and final temperatures were held for 5min and 20min respectively. The peak areas were electronically integrated and identification was based on retention times and comparison with authentic standards. The peak integration was achieved using the HP Chemstation software.

5.0 Whole oil fingerprinting results

The samples were analyzed for whole oil fingerprinting using GC-FID. The GC chromatograms represent the total hydrocarbon make up of the oil samples

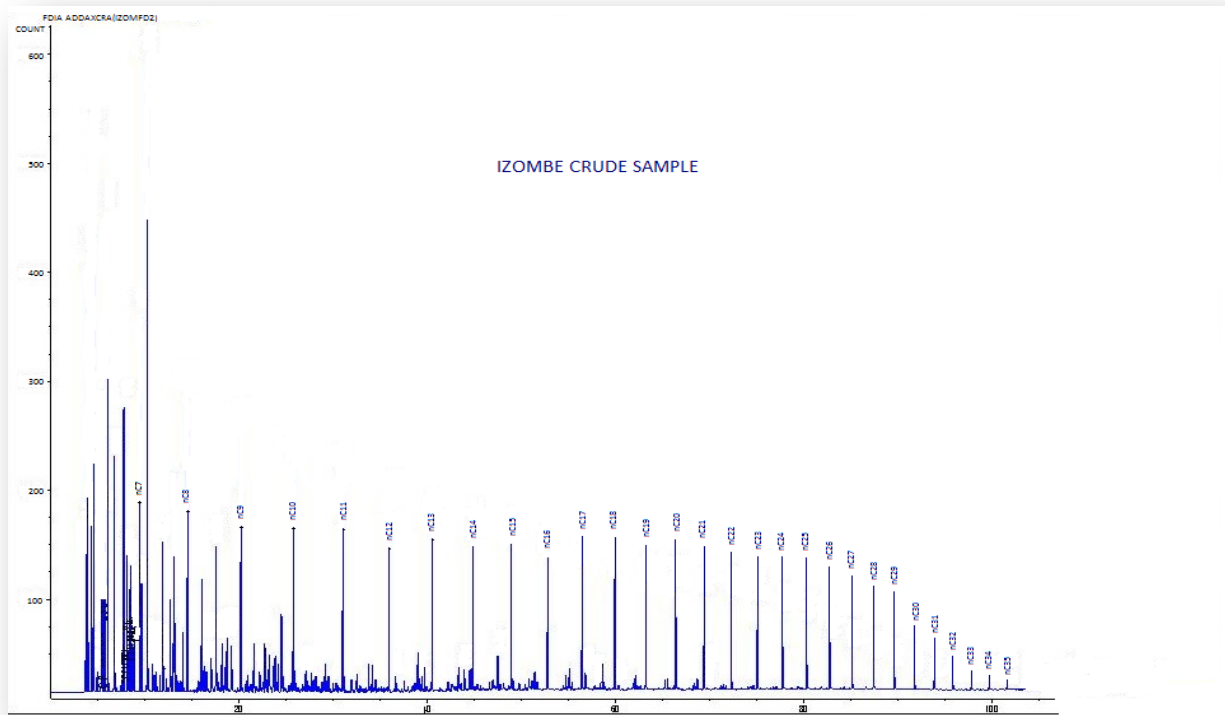


Figure 1- Gas Chromatogram for Izombe crude sample

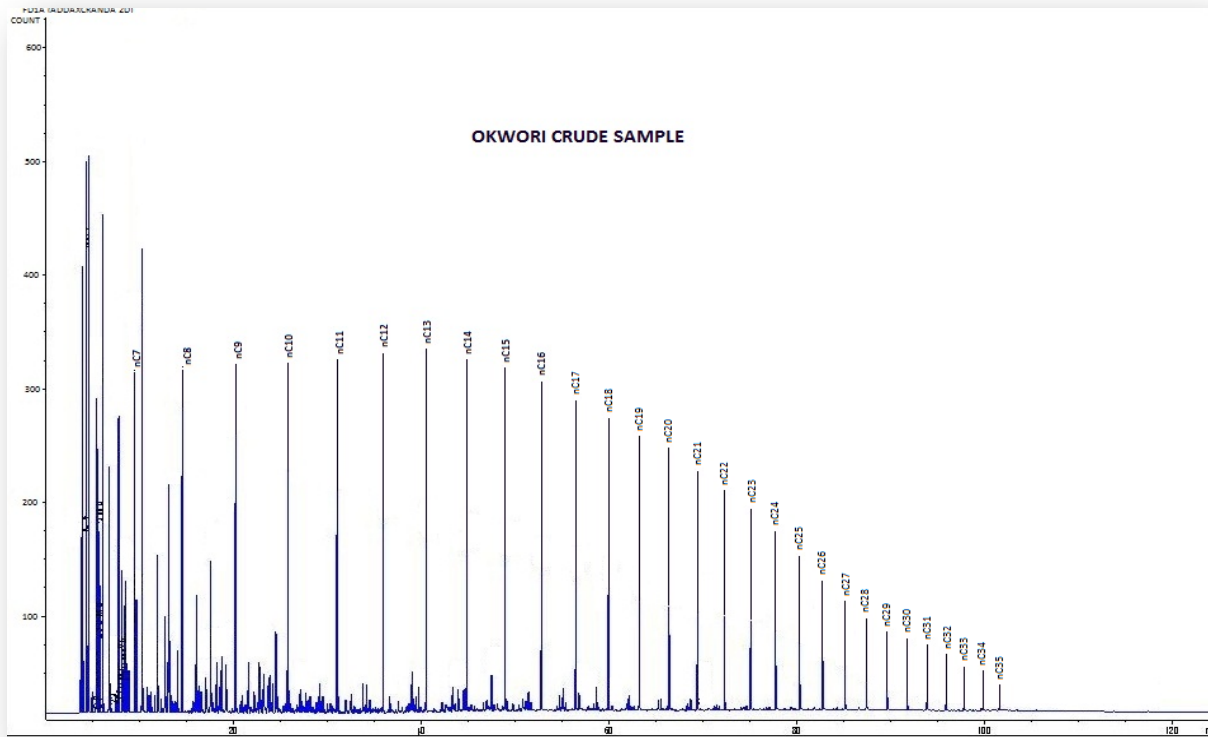


Figure 2- Gas Chromatogram for Okwori crude sample

Analysis shows that both Izombe and OKWORI crude samples contained detectable hydrocarbons with chain length of 35 carbon atoms.

6.0 Radar plots

The radial plots of the straight chained hydrocarbon composition (SCHC) versus Abundance of the crude samples from OML 124 and OML126 fields showed the following distribution:

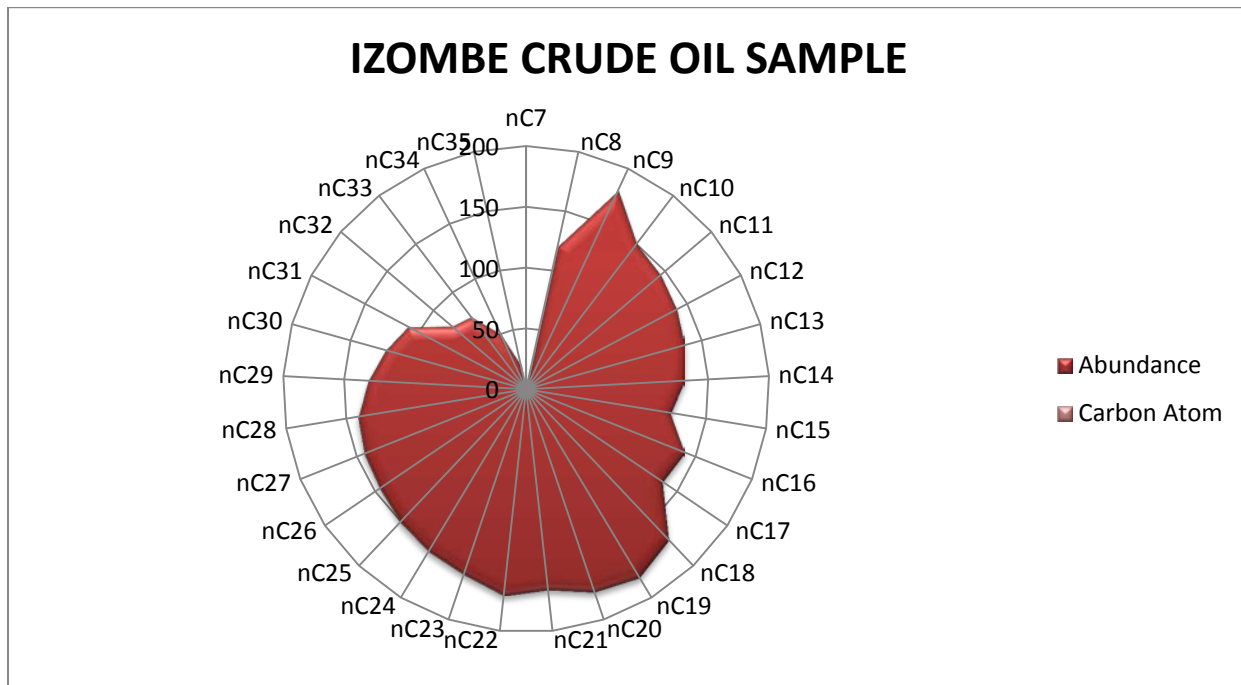


Figure 3- Radial plot for Izombe crude sample

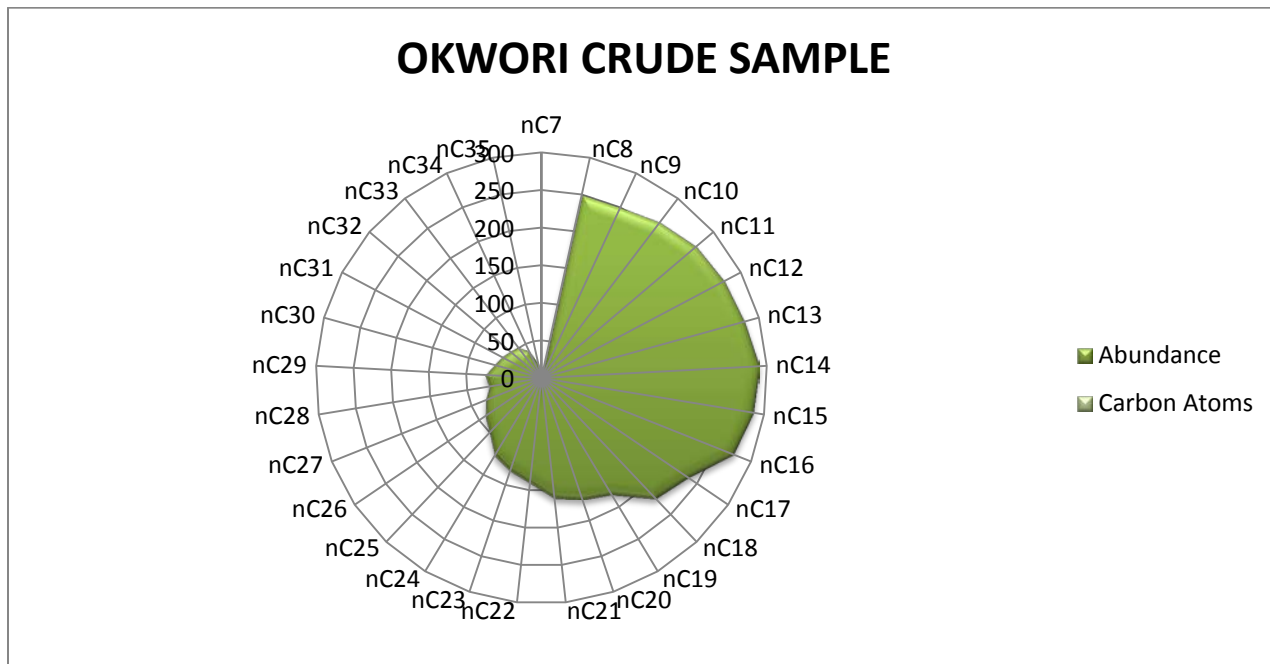


Figure 4- Radial plot for OKWORI Crude Sample

7.0 Carbon Abundance

The plot of carbon atoms versus abundance showed that Izombe crude sample from OML 124 had a relatively high abundance of heavy ends (C16-C35) than the light end (C7-C15) carbon atoms. Whereas OKWORI crude sample from OML 126 has relatively high abundance of light ends (C7-C15) carbon atoms than the heavy ends (C16-C35).

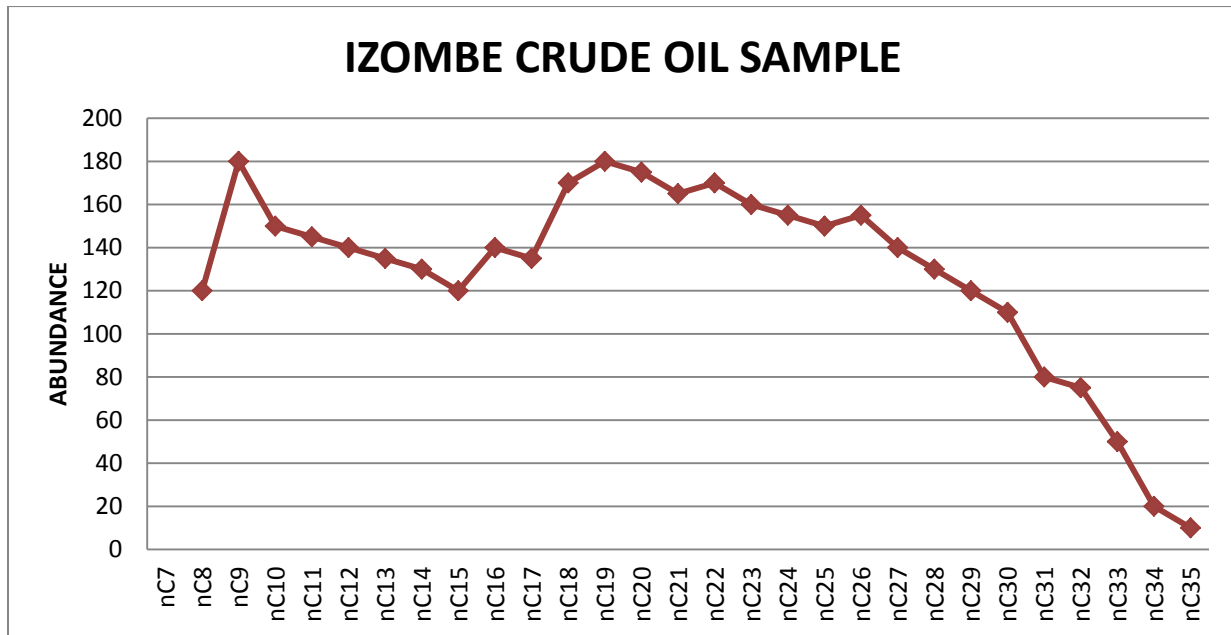


Figure 5-Plot of Carbon atom versus Abundance for Izombe

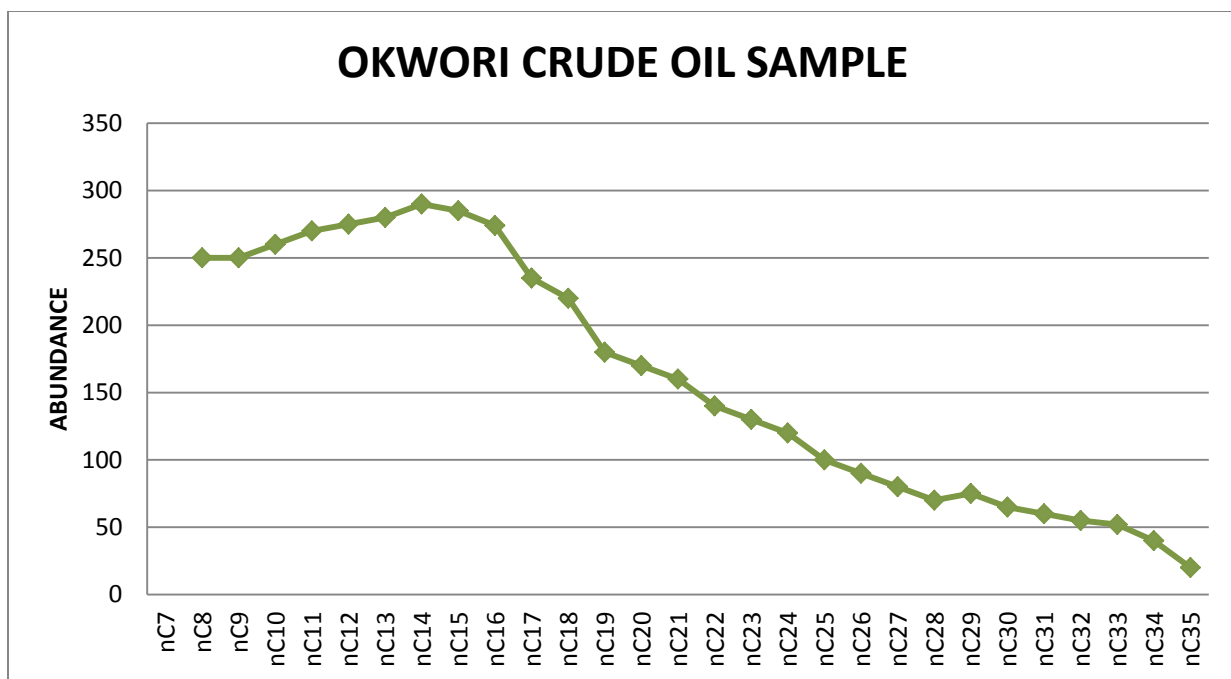


Figure 6 - Plot of Carbon Atom versus Abundance for OKWORI

8.0 Pristane / Phytane Ratio

The cross plots of P_r/nC_{17} versus P_h/nC_{18} and the P_r/P_h ratios for Izombe and OKWORI are shown below. The plots confirm the observed profile of the chromatograms.

Crude samples	P_r	nC_{17}	P_n	nC_{18}	P_r/nC_{17}	P_h/nC_{18}	P_r/P_h
IZOMBE	198	166	80	176	1.2	0.5	2.5
OKWORI	157	226	57	195	0.7	0.3	2.8

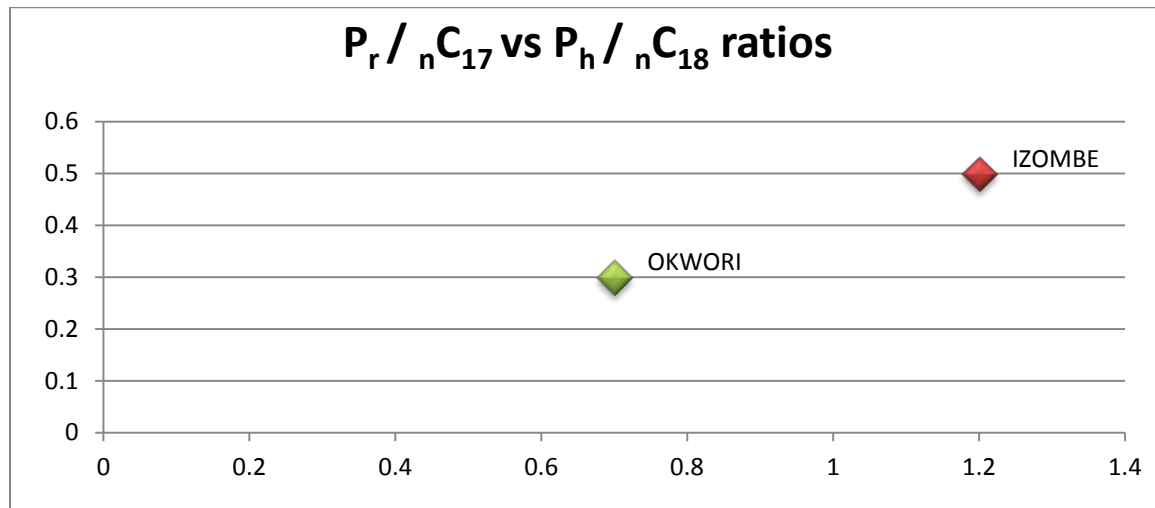


Figure 7-Plot of P_r/nC_{17} versus P_h/nC_{18} for Izombe and Okwori

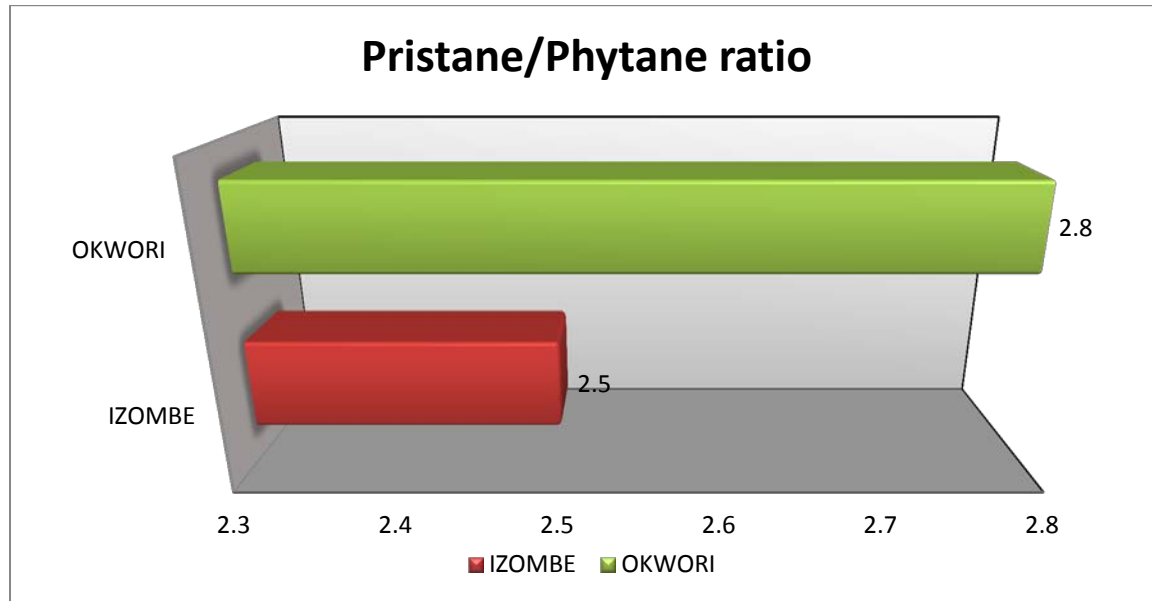


Figure 8-Clustered bars showing Pr/Ph ratios for Izombe and Okwori

Considering the samples, the Pr/Ph ratios range from 2.5 (Izombe) to 2.8 (OKWORI). The average Pr/Ph ratio is 2.7. The P_r/nC_{17} ratio ranged from 0.7 for OKWORI to 1.2 for Izombe and averaging 1.0, whereas the P_h/nC_{18} ratio ranged from 0.3 for OKWORI to 0.5 for Izombe with the average being 0.4.

9.0 Analysis

The methods and result discussed thus far shows that in order for 2 crude samples to be considered to be from a common source, they should appear common by a number of measures as illustrated by the normal paraffin and Isoprenoid profiles of GC-FID and radial plot analyses. If any of these measures indicates a low probability of commonality, then they might be considered to be from different sources.

The distribution pattern of the chromatogram for OKWORI is mono-modal while that of IZOMBE shows a bimodal distribution of n-alkanes indicating an input of mixed marine and terrestrial organic matter. Low molecular weight hydrocarbons were not observed, probably because of evaporative loss during sample processing.

Normal alkanes from n-C7 to n-C35 are seen in the chromatograms of the two oil samples, and these are confirmed by their respective radial plots. In crude oil correlation, the ratio of isoprenoids to n-paraffins is often used for oil source correlation, maturation and biodegradation studies. The crude samples have low Pr/Ph ratios which range from 2.5 to 2.8. The Pr/Ph ratios were used to access depositional environment of the crude oil. The low Pr/Ph ratios suggest that the oil samples were derived from source rock with a significant marine contribution. Values less than 1.0 are indicative of non-biodegraded oils. Both Pr/nC_{17} and Ph/nC_{18} decrease with maturation due to increasing prevalence of the n-paraffin.

10.0 Conclusion

Although the GC-FID used in this work runs on a low cost, low maintenance requirement, relatively resistant to misuse and can measure concentrations at very high and low levels, yet it is limited to the basic hydrocarbon information and degree of weathering, cannot detect inorganic substances and oxidizes all compounds that pass through it.

Gas Chromatography Flame Ionization detector (GC-FID) is majorly used when there is need to fingerprint crude oil with light hydrocarbon compounds devoid of other substances like Sulphides, Nitrides and oxygenated compounds. From this analysis, it is thus safe to conclude that GC-FID is suitable for use in the analysis of crude from Niger Delta fields.

References

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Nomenclature

- AED = Atomic Emission Detection
FID = Ionization Flame Detector
GC = Gas Chromatography
GC-FID = Gas Chromatography Flame Ionization Detector
HTGC = High Temperature Gas Chromatography
ICP-MS = Inductively Coupled Plasma Mass Spectrometry
Mm = Millimetre
MS = Mass Spectrometry
OML = Oil Mining Lease
 P_r/P_h = Pristane / Phytane Ratio
1D-GC = 1 - Dimensional Gas Chromatography
2D-GC = 2 - Dimensional Gas Chromatography



$^{\circ}\text{C}$ = Degree Celsius
 μm = Micrometre