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The role of analytical chemistry in Niger Delta petroleum exploration: A review

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ABSTRACT

Petroleum and organic matter from which the petroleum is derived are composed of organic compounds with some trace elements. These compounds give an insight into the origin, thermal maturity and paleoenvironmental history of petroleum, which are essential elements in petroleum exploration. The main tool to acquire the geochemical data is analytical techniques. Due to progress in the development of new analytical techniques, many hitherto petroleum exploration problems have been resolved. Analytical chemistry has played a significant role in the development of petroleum resources of Niger Delta. Various analytical techniques that have aided the success of petroleum exploration in the Niger Delta are discussed. The analytical techniques that have helped to understand the petroleum system of the basin are also described. Recent and emerging analytical methodologies including green analytical methods as applicable to petroleum exploration particularly Niger Delta petroleum province are discussed in this paper. Analytical chemistry is an invaluable tool in finding the Niger Delta oils.

1. Introduction

The Niger Delta is one of the major hydrocarbon rich provinces of the world, with estimated reserves of about 40 billion barrels of oil and 187 trillion cubic feet of natural gas. It accounts for nearly two third (2/3) of the overall hydrocarbons reserves of the sub-Saharan Africa. From 1937 to 1993, all oil exploration and production activities in Nigeria particularly in the Niger Delta were more or less restricted to onshore–swamp and offshore areas not greater than 200 m water depth. Today, exploration activities have been carried to the deep water (depth between 200 m and 2500 m), characterized by extreme risk, and high capital investment. Therefore, in order to reduce exploration risks to the minimum, a careful and thorough evaluation of the prospect is highly necessary before plans are made for drilling. To achieve this, a thorough basin evaluation is necessary, typically utilizing integrated geochemical, geological, geophysical/seismic, petrographic, biostratigraphic and sedimentological and sequence stratigraphic data. The geochemical data obtained from previously drilled wells in the basin provide invaluable information for understanding the true status of such basin.

The importance of chemistry in petroleum exploration is based on the fact that organic matter and petroleum derived from them are made up of organic compounds with some trace elements. These compounds can give information on the origin, generation, migration and accumulation of petroleum in a particular basin. Thus, geochemistry helps to locate targets for drilling [1]. In search for petroleum in the Niger Delta, chemistry has been found very useful both at the initial and advanced stages in identifying source rocks and classifying crude oils into families [2–6]. Through classification of crude oils into families, related hydrocarbons may be sought in unexplored areas and different stratigraphic units within the basin. The geochemical properties of the Niger Delta crude oils are fairly documented in the literature [4,5,7–9]. Geochemical studies of the Niger Delta source rocks are also fairly documented in the literature [2,6,10,11]. Geochemical methods of crude oil correlation include biomarker finger prints (steranes and terpanes), hydrocarbon contents, stable isotope ratios, trace elements among other [4,5,7–9]. While geochemical methods for sediments or rock evaluation include gas chromatography, gas chromatography–mass spectrometry, Rock-Eval pyrolysis, elemental analysis, optical microscopic examination, vitrinite reflectance, etc. [2,3,6,10–14]. The main tool to acquire the geochemical data is analytical chemistry. Due to progress in the development of new analytical techniques and interpretative concepts, application of chemistry in petroleum exploration has become more rapid and also capable of solving more specific problems. Common applications include recognition of source rocks and of re-distribution of hydrocarbons, evaluation of maturity and of hydrocarbon potential and oil–oil and oil-source rock correlation [12]. Curiale [13] reported that future correlation success will depend on continuing developments in analytical technology. Analytical chemistry has played a significant role for understanding the petroleum system of the Niger Delta. It is this role that will be considered in the current review. New and improved analytical techniques have helped to unravel some enigmas

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about the true status of petroleum source rock of the Niger Delta [6,14–16].

2. Geochemistry of Niger Delta oils

2.1. Biomarker chemistry

Oils within the Niger Delta Basin occur at different productive horizons at very great depth apart. One of the questions these occurrences pose is whether the oils are of the same origin. Different analytical tools have been deployed to answer the question. Biomarkers can help to answer this question. Biomarkers are geochemical fossils which can convey information about the types of organisms contributing to the organic matter incorporated in sediments. Biomarkers are organic molecules synthesized by plants or animals and incorporated in sediments without or with only minor changes. The carbon skeletons of such molecules are preserved [17]. The interest in geochemistry of Niger Delta oils began in the 1970s with the work of Ekweozor et al. [7], who were interested in triterpanes content of the crude oils. They used two separation techniques; gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) to identify the triterpanes content of a suite of Niger Delta oils. Acyclic isoprenoid hydrocarbons and n-paraffins were also discovered. In 1979, they reported [7] the presence of pentacyclic triterpanes in Niger Delta crude, apart from the presence of previously identified pentacyclanes such as 18αH-oleanane; spirotriterpane; 30-nor-17αH,21βH-hopane; 17αH,21βH-hopane and 22,29,30-trisnor-18αH-hopane-II in crude oils, two new triterpanes; 17βH,21αH-hopane (moretane) and 17βH,21αH-homohopane (homomoretane) were identified for the first time. They were able to use the distribution pattern and fingerprinting of the triterpanes to determine the origin of the oils and discriminated between the eastern Niger Delta oils and western Niger Delta oils. Ekweozor et al. [18] further exploited what GC and GC–MS could avail in terms of petroleum exploration of the Niger Delta, they discovered the ubiquitous presence of a series of novel C_{24}–C_{27} tetracyclic alkanes, which they believed were degraded triterpanes. The degraded triterpanes (C_{24}–C_{27} tetracyclic alkanes) were found to be useful tools for assessing the stages of thermal evolution of petroleum in the reservoir. With the aid of GC–MS oleanane which is known to be an indicator of terrestrially sourced oil was identified in Niger Delta oils [19], which is an indication that Niger Delta oil has significant terrestrial organic matter input. Woodhouse et al. [20] explored the advancement in mass spectrometry by using GC–MS–MS to identify and resolve the mixture of C_{24} tetracyclic and C_{30} pentacyclic terpenoids in crude oil samples from Niger Delta and other basins elsewhere in the world. A mixture of at least nine C_{30} pentacyclic terpanes were found to be present with remarkably uniform distributions in the oil samples. Sonibare et al. [21] used combined analytical tools of GC–MS and isotope ratio mass spectrometry to characterize, based on triterpanes and isotopic composition, crude oil samples from four onshore and offshore fields in the Niger Delta. Their results revealed that the oils were formed from a mixed source (marine and terrestrial kerogen) based on the abundance of pentacyclic triterpanes of hopane and oleanane skeletons and C_{27}–C_{29} steranes in the oils. Various maturity parameters computed for the oils, especially those of aromatic compounds revealed an increasing thermal maturity with increasing reservoir depths (Fig. 1). All the studies in which the various analytical techniques were used to identify the terpenoids also identified n-paraffins and acyclic isoprenoid hydrocarbons especially pristane and phytane, which were used to determine the source of the oils and depositional environments of organic matter from which the oils were derived [7,18–21].

2.2. Advancement of analytical techniques and new compounds in Niger Delta oils

Recently, a number of new compounds were identified in Niger Delta oils because of advancement in analytical techniques, resulting in improved understanding of geochemistry of Niger Delta. Nytoft et al. [22] identified novel C_{15} sesquiterpanes in Niger Delta oils. These compounds were isolated from the oil sample based on their initial identification in gas chromatography and subsequent analysis with proton and ^{13}C nuclear magnetic resonance (NMR). The NMR data helped in elucidation of the structures of these compounds, which were found similar to the ring D and E part of oleanane. They found sesquiterpanes useful as markers of angiosperm input in light oils. Nytoft et al. [23] isolated from a Niger Delta oil the three most abundant rearranged oleanoid triterpanes eluting early in gas chromatography and characterized them using proton and ^{13}C nuclear magnetic resonance spectroscopy. The distribution of these three rearranged oleanoid triterpanes was examined by way of reverse phase high performance liquid chromatography (RP HPLC), gas chromatography–mass spectrometry and GC–MS–MS. Samuel et al. [24] reported novel tricyclic and tetracyclic terpanes particularly non-cheilanthane tricyclic terpanes, consisting of C_{21} and C_{25} compounds and a C_{27} tetracyclic terpane in Niger Delta oils. They used the combined analytical tools of GC–MS, GC–MS–MS and proton and ^{13}C NMR to determine their structural identification, origin and application to petroleum correlation. They used the distribution of these compounds in separation of the oils into at least three distinct source rock organofacies. In all of these recent discoveries of new compounds in Niger Delta oils, the advantage offered by GC–MS–MS was utilized to selectively characterize these novel compounds. In most cases there was absence or very low abundance of these novel compounds in the m/z 191 chromatogram from the GC–MS but the m/z 414 → 123 parent–daughter ion transitions GC–MS–MS afforded the selective monitoring of the compounds from interfering peaks (Fig. 2). Previously, stable isotope measurements are usually carried out on whole oil and bulk saturated and aromatic hydrocarbon fractions of the whole oil. Some authors have attempted to apply this method to classify Niger Delta oils [21,25]. Isotopic measurements performed on bulk hydrocarbon fractions can be significantly influenced by the presence of certain compound classes having specific isotopic compositions within the petroleum fractions [15]. As a result of advancement of analytical capability over time, stable isotopic measurements are now performed on individual abundant and well resolved compounds in crude oils, thus reducing the influence of a few compounds having significant isotopic compositions on other compound classes. This recent analytical technique is called compound specific isotope analysis (CSIA). Samuel [15] used compound specific stable carbon isotope analysis to give better insight into origin of Niger Delta oils. He was able to discriminate a suite of oil samples from Niger Delta, which were initially classified as of mixed organic matter origin into marine and terrigenous

2.3. Aromatic hydrocarbon chemistry of Niger Delta oils

Although, the geochemistry of Niger Delta oils is fairly documented in the literature but up to 2006 all the studies on oil geochemistry of Niger Delta were based on the saturated hydrocarbons content of the crude oils, no study was based on the aromatic hydrocarbons content of the oils. The determination of aromatic hydrocarbons content of oils is not as straightforward as that saturated hydrocarbons especially the n-alkanes. Acyclic isoprenoid hydrocarbons and n-paraffins in whole oils can be determined directly by GC without prior sample preparation step. However, the determination of aromatic hydrocarbons content of crude oil