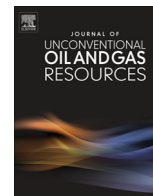




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## Chemical studies of high molecular weight fractions of Nigerian bitumen

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## ABSTRACT

Chemical analysis of high molecular weight fractions of Nigerian bitumen was carried out to ascertain their characteristics which may assist in the development of the natural resource. Bitumen samples were fractionated by silica gel column chromatography into aromatics and nitrogen, sulphur, oxygen (NSO) compounds fractions. The fractions were analyzed for compound types using Fourier Transform Infrared (FT-IR) spectrometer. The elemental analysis of NSO compounds fraction was done using Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) and carbon/nitrogen analyzer. The FT-IR analysis results obtained for NSO compounds fraction showed IR peaks of the following functional groups: C–H (CH<sub>3</sub>), C–H (CH<sub>2</sub>), C=C, C–O, C=O, N–H, C–O–C, C=S, C–N, S=O, suggesting the presence of mixtures of paraffinic, aldehydic, anhydric, naphthenic, and heteroatoms containing compounds, while the results on aromatic fraction follow the same trend except for the absence of C=S C=O and C–N. The results showed higher elemental concentrations in the NSO fraction than the whole Nigerian bitumen and was confirmed by their calculated *T*-test values. The results also indicated that V/Ni ratio for the NSO fraction increased with the age of the producing field. Strong and positive correlations exist between most of the analyzed elements and were confirmed by the expected geochemical relationships between the sample locations as revealed by the result of cross plot analysis. The overall results indicated that refining of the bitumen may experience catalytic poisoning and its exploitation may also cause environmental degradation as well as intrinsic health hazard, considering the cumulative effect of the analyzed chemicals in ecosystems.

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## Introduction

Interest in oil sand as an energy source has increased in recent years in Nigeria as it is a major substitute to the exhausting crude oil. It constitutes a prominent prospect of foreign exchange earner to the country and this has encouraged researchers into effective and intensive studies on the exploration and exploitation of the oil sand bitumen deposits in Nigerian.

Oil sands are naturally occurring mixtures of sand or clay, water and the heavy viscous form of crude oil called bitumen. They are found in large amounts in many countries throughout the world, often in the same geographical areas as petroleum deposits, but are found in large quantities in Nigeria, Canada and Venezuela (Adebisi et al., 2006; Adegoke, 2000). The exploitation and exploration of the Nigerian natural bitumen deposits can best be described to be at the planning stage and it has been estimated to be the sec-

ond largest. It occurs over a 120 km by 6 km belt which stretches from Okitipupa ridge/western edge of Niger delta to as far west of Ijebu-ode in Ogun state (Ekweozor and Nwachukwu, 1989).

Oil sand is ascribed to be an unconventional oils and it is usually identified by their features. A group of unconventional solid, liquid, and gaseous hydrocarbons can be processed into petroleum products, but this heavy, impure oil requires very large energy inputs and high technology to upgrade and pre-process into synthetic crude oil that is then processed by refinery into useful products. Nigeria is blessed with vast untapped deposits of natural bitumen; the exquisiteness about the Nigerian oil sands is that it has shallow overburden and even during hot weather, the bitumen naturally flows out from the ground to the surface in form of an outcrop in many places in the Nigerian oil sand belt.

Several researchers have studied the oil sand deposits of Nigeria. Among these are the works of Ako et al. (1983) which highlighted the relevant aspects of the oil sands as well as exploration strategies; Ekweozor (1991) summarized the physical and chemical characteristics of the oil sand deposits, reserve estimates and textural characteristics of the associated sands respectively. The origin of the Bitumen has also been discussed (Coker,

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1988; Demirba, 2002). Some studies have also been carried out on the Nigerian bitumen deposit such as multi-elemental analysis of the bitumen and oil sands (Adebisi et al., 2006, 2013, 2014) and trace element and physico-chemical characteristics of the sand and water fractions of the Nigerian bitumen were also determined by Adebisi et al. (2005).

The aims of this work are to evaluate the organic compound types and the quantity of trace elements in the higher molecular weight fractions (aromatics & NSO compounds) of Nigerian bitumen and use the determined parameters to evaluate the environmental health implications of the exploitation of the Nigerian bitumen deposit as well as to assist in the development of the fossil fuel. The physical and chemical properties of the oil sand/ bitumen ultimately determine their values, as these properties influence the recovery, processing, conversion, and utilization of this fossil fuel resource. Thus, a comprehensive study of the nature of the chemical composition of the organics and trace elements present in Nigeria bitumen fractions are necessary for the solutions to a number of important theoretical and practical problems in the exploration and exploitation of natural resources. The results of the research work will also provide useful information on the separation and classification of its compound types which will be useful in providing chemical characterization of the Nigerian bitumen.

## Materials and methods

### Sample collection

Samples of oil sand were collected from six different locations namely: Olowo-irele, Ilubirin, Mile 2, Agbabu, Loda and Orisunbare communities in Ondo State, Nigeria (Fig. 1). The samples were collected by scooping the viscous oil sands into air tight containers and conveyed to the laboratory for analysis and each sample was labeled according to the name of the community from which it was collected. Table 1 presents the specific code, location and coordinates of the sampling sites.

**Table 1**

Code, locations and coordinates of the sampling area.

Code	Location	Coordinates	
		Latitude	Longitude
B1	Orisunbare	006° 37' 14' N	004° 49' 52' E
B2	Agbabu	006° 39' 40' N	004° 53' 25' E
B3	Mile 2	006° 36' 54' N	004° 49' 52' E
B4	Loda	006° 39' 10' N	004° 53' 24' E
B5	Ilubirin	006° 38' 15' N	004° 49' 52' E
B6	Olowo-Irele	006° 39' 41' N	004° 53' 25' E

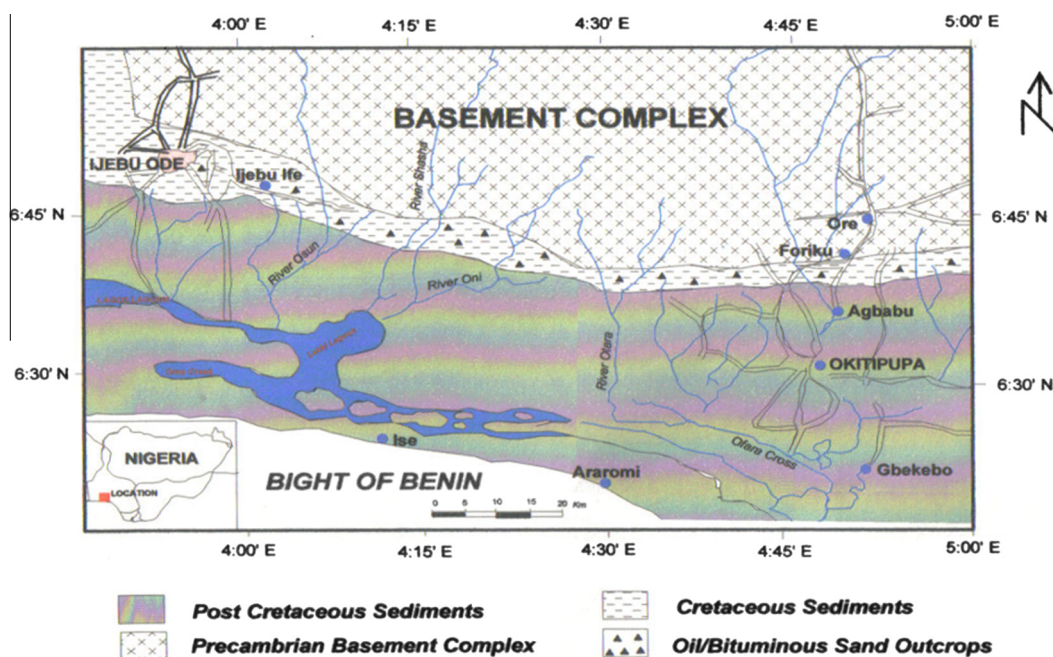
### Extraction of bitumen from oil sands

A measured 20.0 g of each sample was taken, put in a thimble, and dropped inside the Soxhlet extractor connected to a heating mantle and chiller, and 400 mL toluene was used as extracting solvent. To ensure exhaustive extraction, the process lasted for about 8 h, until extracting solvent (toluene) turned colourless (Coker, 1988; Enu, 1985). At completion, the toluene was recovered from the heavy oil by distillation using a rotary evaporator under a controlled temperature and pressure.

### Fractionation of bitumen

The scheme and the names given to the separated fractions obtained from this procedure are presented in Fig. 2.

The stationary phase (silica gel) which has been activated in a muffled furnace at 550 °C for 6 h was employed in column chromatography separation of the bitumen into its fractions, while the chromatographic column (1 m long and 0.04 m internal diameter) used was borosilicate tubing. The fractions were eluted using solvents of increasing polarity at an approximately rate of 0.5 ml/min with 100% n-hexane for saturates, 100% toluene for aromatics and 100% methanol for NSO compounds. The aromatics and NSO compounds collected which constitute the high molecular weight fractions were concentrated using a rotary evaporator at 25 °C and atmospheric pressure.



**Fig. 1.** Geological map of Southwestern Nigeria showing bitumen out-crop belt. Source: Adegoke (2000).

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