



An Infrared Spectroscopic Evaluation of the Petroleum Potentials of Some Oil Shale From Lokpanta in the Lower Benue Trough of Nigeria

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ABSTRACT: The kerogen of thirty randomly sampled outcrops of Lokpanta oil shales in the Lower Benue trough of Nigeria was extracted, isolated and characterized by infra-red (IR) spectroscopy. Quantitative assessment of the kerogen concentrates was made and correlated with the total organic carbon content (TOC) of source rocks. The isolated kerogen concentrates were found to have a mean weight [\pm standard deviation] of $3.86 \pm 0.84\%$ of the dry rock sample. Analysis of the IR spectra was carried out both qualitatively and semi-quantitatively. Extrapolations from structural elucidation revealed that the Lokpanta facies contained few mono-aromatics and cyclohexyl rings. The spectra variously showed good correlations in the 1600cm^{-1} , 1450cm^{-1} and 2900cm^{-1} peak areas. Deduction from results show that although kerogen concentrates varied from 0.76% to 11.06%, over 50% of the sampled outcrops had a percent weight $> 2.5\%$ which is the lower limit proposed for mature, oil - and gas - generating organic matter. © JASEM

The term 'kerogen' was applied for the first time in the description of the shales in Scotland when it was used to refer to the organic mineraloid of indefinite chemical composition (Alphern, 1974; Baker, 1974; Burgess, 1974; Avbovbo and Ayoola, 1981;). In recent years, however, this term (kerogen) has been applied not only to organic matter in oil shales, but also to carbonaceous matter in a wide range of rocks regardless of their oil generating potentials (Dembicki *et al.*, 1983; Tissot and Welte, 1984). Kerogen can therefore be defined as all the disseminated organic matter in non-oxidizing acids, bases and organic solvents; a complex mixture of structural and amorphous phytoclasts of different aquatic and terrestrial origin, with contrasting chemical structures and hydrocarbon potentials [Dow, 1977; Espitalie, *et al.*, 1980; Massound and Kinghorn, 1990]

The organic matter initially deposited with unconsolidated sediments is not kerogen, but a precursor that is converted to kerogen during diagenesis [Hunt, 1977; Staplin, 1979; Horsfield and Douglas, 1980; Agagu and Ekweozor, 1982]. Kerogen characterization and distinction between its various types are essential for source rock evaluation. This is because different types of organic matter have contrasting chemical structures and consequently, different hydrocarbon potentials. Qualitative and semi-quantitative assessment of kerogen concentrates offer one of the geochemical basis for the evaluation of potential source rocks since it has been shown to be successful in following the maturation of kerogen. This paper is

the report of the characterization of the kerogen of Lokpanta oil shales using infra-red spectroscopy.

GEOLOGICAL SETTING AND DEFINITION OF THE LOWER BENUE TROUGH

The Lower Benue trough is one of the three regions of the Benue trough, the other two being the Middle and Upper Benue troughs. Although the exact arial definition of the Benue Trough as a whole has been an issue of controversy, it is clear that it originated from a 'pull-apart' basin associated with the opening of the Atlantic Ocean which ended in the Early Tertiary with the development of the Tertiary Niger Delta (Petters and Ekweozor, 1982; Ekweozor and Unomah, 1990). It was the Santonian deformation that fragmented the Lower Benue Trough into the Abakiliki anticlinorium and the flanking Anambra and Afikpo synclines (Fig. 1). The northern limit of the Lower Benue trough corresponds to the Gboko transform fault that was recognized by Whiteman (1982) while the eastern limit covers the study areas of Lokpanta.

MATERIALS AND METHODS

Field Programme

Thirty [30] outcrop samples of oil shale facies were randomly taken from locations in Acha, Aka-eze, Onoli, Ndeaboh, Mburubu and Isiogbo all in Lokpanta [see Fig. 2 for sample locations] The samples were labeled and brought to the laboratory for analyses.

Laboratory Techniques

Sample Preparation: Routine precautions such as washing of hands (with soap and water) before

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handling outcrop samples were observed. All glass-ware used were cleaned with chromic acid, washed with soap and water, rinsed with distilled water and dried in an oven at 150°C for 3 hours. The surface of the samples were scrapped off so as to remove surface contaminants such as algal growths. Thirty (30) samples were pulverized using medium sized mortar and a Tema disc mill for 15-30 minutes to avoid organic modifications.

Extraction: 50-100g of pulverized rock samples were Soxhlet – extracted for 36 hours using 300ml of dichloromethane. The solvent was distilled off using a hot water bath and under vacuum to an aliquot volume of 2-3ml. The aliquot was then transferred to a weighed clean vial with a micropipette. The remaining solvent was finally removed under nitrogen gas flow and at a temperature of 40°C. For all cases, dilute HCl-activated copper powder was added to the solvent in the round bottom flask during extraction to remove elemental sulphur in the extract. The remaining copper and the sulphide was filtered out after extraction while the rock residue left was stored for subsequent kerogen isolation.

Kerogen Isolation: 40ml HCl was added to 50g of the solvent - extracted rock residue in a teflon beaker, stirred for 30 minutes at 50°C and allowed to settle. This treatment was repeated if effervescence persisted. The supernatant was decanted each time. 40ml of concentrated HCl/HF (30:70% v/v) was added gradually while stirring. This was further stirred magnetically for 12 hours at 50°C. This treatment was repeated twice and the supernatant decanted each time. The residue was thereafter washed several times with distilled water to remove excess acid. Fifty milliliters (50ml) of CdI/KI solution (specific gravity 1.95) was added to the residue, and the aliquot was stirred with a glass rod, ultrasonicated for 30 minutes and finally centrifuged for another 30 minutes using aluminum cups. The floating kerogen was transferred to a filter paper, filtered using vacuum pump, washed with distilled water, dried and stored in a desiccator.

Infra-Red(Ir) Spectroscopy: The IR spectroscopy technique employed for this study is the KBr Pressed Tablet (Disc) technique. In this method, KBr tablets were prepared by grinding the sample (2mg) with a completely dehydrated KBr (200mg) and compressed into transparent tablet. The grinding was done with an agate mortar and pestle (10-15min) and compression was achieved by using

the evacuable die. The prepared disc was thereafter inserted into an IR spectrometer (Philips Scientific Model No: 40 13-15-17494).

RESULTS AND DISCUSSION

Results of the isolated kerogen concentrates of Lokpanta oil shales (Table 1) show an average weight (\pm standard deviation) of $3.86 \pm 0.84\%$ per dry rock sample. Although the percent weight values varied from 0.76 to 11.06%, over 50% of the sampled area showed a percent weight of kerogen greater than 2.50%. Since total organic carbon content (TOC) is a function of the kerogen concentrate and the soluble organic matter (SOM) (or Extractable Organic Matter, EOM), the weighted values of kerogen concentrates may necessarily correspond to the value of the TOC, considering the fact that the value of the EOM is very negligible.

From the foregoing, it means that oil shales from over 50% of the analysed locations may not be immature, and therefore may have reached the stage of catagenesis as corroborated by a previous work carried out by Ekeozor and Unomah (1990). Several past workers such as Agagu (1978), Agagu and Ekweozor (1980), Ekweozor and Strauz (1982), Carrol (1986), and Nwachukwu and Chukwuma (1986) have analysed TOC of shales and subsequently evaluated the type of organic matter in such shales. For instance, Agagu (1978) showed that average TOC was 0.7% for Awgu shale, 1.67% for Ogugu shale and 2.05% for Nkporo shale. Ekweozor and Gormly (1983) showed that TOC for the Paleocene and Cretaceous units penetrated by the Akukwa-2 Well ranged from 0.4 to 3.5%.

Qualitative assessment of the bands in IR spectra shows a good correlation especially in the samples from Onoli/Ndeaboh and Acha. Figs 3 & 4 contain spectral traces of the samples from these areas. Previous experiments with kerogen, using IR spectroscopic analytical method have shown that absorptions around 3500cm^{-1} band is derived from molecular water and N-H groups, while the region $1600-1450\text{cm}^{-1}$ contains the presence of aromatic structures. The few mono-aromatics fused in cyclohexyl rings (as extrapolated from the absorption bands) may be indicative of oil generating organic matter. However, the covariance in the spectral characteristics of the different representative kerogen samples (cf: Table 2) may be as a result of possible contamination of the kerogen by fine-grained minerals.

TABLE 1: % Weight of Kerogen in Dry Rock Sample

Location Code	Weight Of Rock Residue (gm)	Weight Of Kerogen (gm)	% Of Kerogen In Dryrock Sample (% Wt)
1	25.636	0.180	2.26
5	26.617	0.233	1.06
9	25.182	0.277	1.10
13	23.515	1.857	4.88
21	22.016	0.610	1.39
25	25.005	0.765	11.06
30	26.224	0.623	2.05
33	22.696	0.599	2.71
39	23.076	1.831	7.93
52	23.617	1.800	6.01
58	23.648	1.286	0.89
64	24.040	0.414	3.43
80	25.353	1.436	1.62
92	26.729	1.266	3.09
93	24.030	0.699	2.91
122	25.010	1.634	6.53
124	25.008	0.189	0.76
127	26.448	1.479	0.59
132	26.008	1.850	7.40
136	25.632	1.173	4.69
140	23.851	0.190	1.65
158	24.167	8.822	3.40
162	27.381	0.885	3.23
168	25.402	0.305	0.93
177	24.244	1.266	6.30
180	22.609	1.811	8.75
181	24.007	1.370	5.60
182	26.813	0.666	2.17
190	25.048	0.172	2.25
196	22.015	0.514	4.01
Mean Wt. \pm S.D.*	26.45 \pm 4.43	0.93 \pm 0.20	3.86 \pm 0.84

*S.D. = Standard Deviation

TABLE 2: IR Spectral Characteristics Aka - Eze [Code No. 5]

Prominent Peaks	Approximate band [μm]	Approximate band [cm^{-1}]	Intensity	characteristic functional group
A	2.86	3500	broad	N-H stretching
B	6.25	1600	sharp	Cyclic six member ring
C	16.67	600	broad	C-H bending

Onoli [Code No. 52]

Prominent Peaks	Approximate band [μm]	Approximate band [cm^{-1}]	Intensity	characteristic functional group
A	2.86	3500	broad	N-H stretching
B	3.45	2900	sharp	C-H stretching
C	6.25	1600	weak	Cyclic six member ring
D	6.90	1400	medium	Aromatic
E	16.67	600	broad	C-H bending

Ndeaboh [Code No. 89]

Prominent Peaks	Approximate band [μm]	Approximate band [cm^{-1}]	Intensity	Proposed characteristic functional group
A	2.86	3500	broad	N-H stretching
B	3.45	2900	sharp	C-H stretching
C	6.25	1600	weak	Cyclic six member ring
D	6.90	1450	medium	Aromatic
E	16.67	600	broad	Out of plane
F	28.57	350	broad	C - H bend Out of plane C - C bending

Mburubu [Code No. 136]

Prominent Peaks	Approximate band (μm)	Approximate band (cm^{-1})	Intensity	Proposed characteristic functional group
A	2.86	3500	broad	N-H stretching
B	6.25	1600	weak	six - member ring
C	9.09	1100	broad	C-H bending
D	16.67	600	broad	C-H bending
E	23.53	425	broad	C-C bending

Isiogbo (code no. 122)

Prominent Peaks	Approximate band (μm)	Approximate band (cm^{-1})	Intensity	characteristic functional group
A	2.86	3500	variable	N-H stretching
B	6.25	1600	variable	Cyclic six - member ring
C	13.33	750	sharp	Aromatic
D	16.67	600	broad	Out of plane C - H bending

Acha (Code No. 162)

Prominent Peaks	Approximate band (μm)	Approximate band (cm^{-1})	Intensity	characteristic functional group.
A	3.45	2900	Sharp	C-H stretching
B	6.13	1630	Sharp	cyclic six - member ring
C	6.90	1450	Medium	Aromatic
D	16.67	600	Strong, broad	Out of plane C-H bending

Conclusion

The kerogen of outcrops of Lokpanta shales in the Lower Benue Trough of Nigeria was found to have an average weight (\pm standard deviation) of $3.86 \pm 0.84\%$. Although the individual percentage weights vary from 0.76 through 11.06%, over 50% of the study area have weights greater than 2.5% considered to be the lower limit of TOC for oil shales.

Qualitative and semi-quantitative evaluation of the kerogen by infrared spectra showed

absorptions of few aromatics and cyclohexyl rings. The spectra variously showed good correlation in the 1600cm^{-1} , 1450cm^{-1} peak areas, with extrapolations pointing to oil-and gas - generating organic matter.

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