

CHARACTERIZATION OF INSOLUBLE ORGANIC MATTER OF THE LOKPANTA OIL SHALES ANAMBRA BASIN, BY QUANTITATIVE INFRARED SPECTROSCOPY.

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ABSTRACT

Conventional infrared (IR) spectroscopy was used to get quantitative information on the structure of the isolated kerogen of the Lokpanta oil shales in the Anambra basin. The kerogen was extracted from six shale samples collected from different geographical locations in the basin. Only about 1 to 14% of the kerogen present in the fine-grained sedimentary rock extract was recovered from the sedimentary organic residue. Quantitative IR spectroscopy indicates that the kerogen structure consists of about 19% of aliphatic groups (bands around 2920- 2900, 1450- 1420 cm^{-1}); 53% of C=C, C=O, COO groups (bands around 1610 -1600 cm^{-1}) and 28% of aromatic groups (bands around 900 -560 cm^{-1}). These percentages indicate that these kerogens are relatively richer in oxygen bearing functional groups than aliphatic and aromatic groups. This suggest not only that the kerogens are of intermediate maturity but also that they likely correspond to type 11 series, are marine - derived, anoxic, capable of generating oil and gas and originated from the same parent materials. Variation in the intensity of IR bands shows that kerogens from Lokpanta -Lekwesi area are more mature relative to those from Ndeaboh - Awgu.

KEY WORDS: Infrared spectroscopy, kerogen, characterization, oil- shales, source -rock, insoluble organic matter, correlation, Lokpanta, Anambra basin.

INTRODUCTION

Sedimentary rocks contain two general types of organic matter- the soluble and the insoluble. Soluble-organic matter (SOM) is isolated by treating the pulverized rock sample with organic solvents. The insoluble type is disseminated in sedimentary rocks and is insoluble in non- oxidizing acids, bases and organic solvents (Welte, 1969). Insoluble organic matter (also called dispersed sediment or kerogen) is the progenitor of most oil and gas and is of different aqueous and terrestrial origins, contrasting chemical structures and different hydrocarbon potentials (Dow, 1977; Tissot and Welte, 1978). The characterization of source rocks requires the investigation of both the extractable soluble organic matter and the insoluble organic matter; using different experimental techniques including infrared (IR) spectroscopy (Rullkotter *et al*; 1990).

IR spectroscopy is an important and extensively used analytical tool for determining the structure of organic materials. Quantitative or semi-quantitative IR spectroscopy allows the rapid characterization of gross chemical structural features of complex organic-derived materials such as kerogen or coal. The use of quantitative IR spectroscopy, particularly combined with other physical methods to follow the maturation of kerogen, has been reported (Rouxhet *et al*; 1980, Victorovic *et al*; 1981). However, there is a paucity in the literature regarding the structural evaluation of Nigerian coals and kerogen, particularly as elucidated by modern IR techniques. In this paper, this technique has been applied and has proved very useful in the comparative analysis of structurally related samples to

characterize the insoluble organic matter of the Lokpanta oil shales. The results obtained compare favourably well with data obtained on the basin's source rocks employing other techniques (Agagu *et al*; 1982; Ekweozor *et al*, 1983; Ekweozor *et al*, 1990; Unomah *et al*, 1991).

MATERIALS AND METHODS

Sample Collection and Preparation

The samples examined in this study were spot-sampled along stream channels and adjoining areas from Lokpanta-Lekwesi, Ndeaboh-Lokpanta, Ndeaboh-Awgu, Isiogbo and Mburubu locations in the Anambra basin (Figure 1). The dry, fine grained and dark grey shales were wrapped in aluminium foil and placed in labelled sample bags.

Preparation of Kerogen Concentrates

To obtain the insoluble organic matter (kerogen) from the shales the powdered shale samples were extracted with dichloromethane (DCM) in a Soxhlet apparatus.

Exactly 25.0g of the solvent-extracted shale samples was weighed and treated with 20.0ml of 2M HCl. This removed the carbonates present in the extracted sample. A two-fold digestion was carried out on the sample using concentrated aqueous HCl/HF (30:70) at 50°C. The whole digestion was stirred for 24 hours with a magnetic stirrer hot-plate and the supernatants were pipetted out.

After several careful washings with distilled water the samples were oven-dried at relatively low

Table 1: Cultural, Morphological and Biochemical Characteristics of Bacterial Isolates

Colonial Characteristics	Staining Reaction and Arrangement	Catalase	Coagulase	V - P	M - R	Oxidase	Nitrate Reduction	Indole production	Motility	Citrate Utilization	H ₂ S Production	Urease	Maltose	Fructose	Lactose	Glucose	Organisms	
1. Greenish colonies, convex and irregular surface with entire edge.	Gram negative slender rods in singles and pairs	+	-	+	+	+	-	+	+	-	A	A	A	AG			<i>Pseudomonas sp.</i>	
2. Creamy colonies with wavy projecting margin.	Positive rods in chains, with central non-projecting spores.	+	ND	ND	ND	ND	+	ND	+	+	ND	+	A	-	-	-	<i>Bacillus sp.</i>	
3. Yellow dome - shaped colonies	Gram positive cocci in tetrads and clusters.	ND	ND	-	+	+	-	+	ND	+	-	ND	ND	ND	ND	ND	<i>Micrococcus sp.</i>	
4. Golden yellow pigments with even edges.	Gram positive cocci in clusters.	+	+	-	+	+	-	ND	+	+	ND	A	A	-	-	-	<i>Staphylococcus aureus</i>	
5. Creamy colonies with even edges.	Gram positive rods in singles and chains.	ND	ND	-	+	-	+	-	ND	+	-	ND	ND	ND	ND	ND	<i>Enterobacter</i>	
6. Creamy colonies that are firm and compact and difficult to pick.	Gram positive filamentous rod shaped organisms bearing spores	ND	ND	ND	ND	ND	ND	ND	-	-	ND	ND	+	ND	A	-	A	<i>Streptomyces sp.</i>

Key:
 + = Positive
 - = Negative
 ND = Not determined
 V-P = Voges Proskauer Test
 M-R = Methyl Red
 A = Acid
 G = Gas
 Acid and Gas Production

Table 1: Results of kerogen isolation

Sample Number	Location	Wt. of solid extract used (gm)	Wt. of isolated kerogen concentrate (gm)	Percent by wt. of kerogen (%K)
13	Lokpanta-Lekwesi	22	3.00	13.64
37	Ndeaboh-Lokpanta	25	1.62	6.48
75	Ndeaboh-Lokpanta	25	1.91	7.64
92	Ndeaboh-Awgu	24	2.13	8.88
130	Isiogbo	25	0.39	1.56
140	Mburubu	27	1.17	4.33

Table 2: Quantitative analysis and band assignments for the IR spectrum of Lokpanta-Lekwesi (Sample 13) kerogen concentrate

Percent by wt. of kerogen (%k)	Area under the curve (A)	Percent Transmittance (% T)	"a"	Band centre (cm ⁻¹)	Assignment
13.64	28	25	7.62	3560	OH/NH stretching
	52	45	8.47	1600	C-C of aromatic ring, C=O, COO ⁻ groups
	5	52	0.70	1380	CH ₃ and OCH ₃ deformation
	3	64	0.34	1100	C-O of alcohols, linear and cyclic ethers
					Aromatic C-H bend
	10	70	1.05	600	Substituted aromatic vibrations.
	12	68	1.29	470	

Table 3: Quantitative analysis and band assignments for the IR spectrum of Ndeaboh-Lokpanta (Sample 37) kerogen concentrate

Percent by wt. of kerogen (%k)	Area under the curve (A)	Percent Transmittance (% T)	"a"	Band centre (cm ⁻¹)	Assignment
6.48	72	23	48.31	3500	OH/NH stretching.
	14	28	7.72	2900	aliphatic CH, CH ₂ , CH ₃ stretching modes.
	247	58	65.72	1600	C-C of aromatic rings
	64	58	17.03	1440 1380	C=O, COO ⁻ , carboxylate groups. aliphatic CH ₂ , CH ₃ , OCH ₃ deformations.
	116	93	19.25	560	Aromatic C-H band subst. aromatic vibs.

processes which affected the organic matter during or after its sedimentation and diagenesis (Benaliouhaj *et al*, 1990).

From the well-known relationship, Total organic carbon (TOC) = SOM + KEROGEN, it follows that the TOC of the shales depends on the kerogen concentration. An increase in kerogen concentration implies an increase in TOC values. Ekweozor and Unomah (1990) in a preliminary study of oil shales in the Benue Trough reported that TOC values of the Lokpanta oil-shales range from 2.0 to 7.4wt % (of dry rock). It follows therefore, that shales from the Lokpanta-Lekwesi, Ndeaboh-Lokpanta and Neaboh-Awgu areas, with about 13.6, 7.6, 8.9wt % kerogen concentrates

respectively, are better suspects for high TOC values and high maturity level capable of generating oil or gas.

Qualitative Functional Group Analysis and Band Assignments

Qualitative analysis is based on the presence or absence of absorption bands at frequencies characteristic of the groups to be identified. Typical spectra of the shallow kerogens of the Lokpanta oil shales obtained were compared with the spectrum of the KBr pellet. Reference works (Robin and Rouxhet, 1978; Rouxhet *et al*, 1980; Painter *et al*, 1981; Mielczarski *et al*, 1986) have helped to attribute the absorption bands

Table 4: Quantitative analysis and band assignments for the IR spectrum of Ndeaboh-Lokpanta (Sample 75) kerogen concentrate

Percent by wt. of kerogen (%k)	Area under the curve (A)	Percent Transmittance (% T)	"a"	Band centre (cm ⁻¹)	Assignment
7.64	148	55	35.22	3460	OH/NH stretching.
	47	60	10.25	2920	aliphatic CH, CH ₂ , CH ₃ stretching modes.
	181	82	28.90	1610	C-C of aromatic rings, C=O, COO ⁻ , carboxylate groups.
	49	81	7.92	1440	aliphatic CH ₂ , CH ₃ bend.
	21	68	4.0	580	aromatic C-H band subst. aromatic vibrations.

Table 5: Quantitative analysis and band assignments for the IR spectrum of Ndeaboh-Awgu (Sample 92) kerogen concentrate

Percent by wt. of kerogen (%k)	Area under the curve (A)	Percent Transmittance (% T)	"a"	Band centre (cm ⁻¹)	Assignment
8.88	149	34	49.35	3460	OH/NH stretching.
	10	42	2.68	2920	aliphatic CH, CH ₂ , CH ₃ stretching modes.
	100	71	15.86	1610	C-C aromatic rings, C=O, COO ⁻ , carboxylate groups.
	36	76	5.33	1420	aliphatic CH ₂ , CH ₃ bend.
	355	77	51.92	1080	C-O stretching of alcohols, linear and cyclic ethers.
	665	80	93.61	740, 600	aromatic C-H band subst. aromatic vibs.

Table 6: Quantitative analysis and band assignments for the IR spectrum of Isiogbo (Sample 130) kerogen concentrate

Percent by wt. of kerogen (%k)	Area under the curve (A)	Percent Transmittance (% T)	"a"	Band centre (cm ⁻¹)	Assignment
1.56	56	24	149.57	3480	OH/NH stretching.
	5	28	11.45	2900	aliphatic CH, CH ₂ , CH ₃ stretching modes.
	107	55	124.71	1600	C-C of aromatic rings, C=O, COO ⁻ , carboxylate groups.
	34	58	37.58	1420	aliphatic CH ₂ , CH ₃ deformation.
	5	63	5.09	1150	C-O stretching of phenols, aromatic ethers.
	4	60	3.27	1110	OH deformation.
	12	60	12.82	1050	C-O str. Of alcohols, linear and cyclic ethers.
	51	85	38.46	600	aromatic C-H band subst. aromatic vibrations.

in each spectrum to different functional groups and chemical bonds as shown in Tables 2-7.

The band around 3460cm⁻¹ is assigned to hydrogen bonded O-H stretching with a possible N-H contribution. This band is attributed not only to water, but also hydroxyl groups substituted in the alkali halide lattice. This is due to the ubiquity of water in KBr preparations, irrespective of the method of preparation or drying to completely remove water bands. This band though weak, always reappears on cooling (Painter *et al.*, 1981). In addition to water absorbed by the KBr disc, water is bound to the multicomponent kerogen system itself in a complex manner (Senesi and Sipos, 1985).

The bands around 3500cm⁻¹ (-OH group) and 1560cm⁻¹ (carboxyl group in salt form -COO⁻) on the KBr spectrum are approximately 0.02 and 0.05 transmittance unit respectively. The absorption band at 1560cm⁻¹ of the KBr seems to be masked by the absorption band at 1600cm⁻¹ of the sample. The absorption band around 2920cm⁻¹ is assigned to CH, CH₂ and CH₃ modes and is a measure of total aliphatic C-H concentration.

The aliphatic C-H stretching modes (2920-2900cm⁻¹) give rise to the well-known frequencies at 1440 and 1380 cm⁻¹ attributed to aliphatic CH₂ and CH₃ bending modes. Moreover, since it is difficult to distinguish

between the vibrational frequencies of aliphatic chains and alicyclic or hydro-aromatic systems in complex structures such as kerogen, the term aliphatic group is used to include all these types.

Absorption bands near 1600cm⁻¹ occur in a wide range of single -and condensed -ring aromatic compounds and they are known to arise from ring vibrations (Painter *et al.*, 1981). This band is present in the spectra of all the kerogens isolated from the Lokpanta oil shales. The band is assigned to the C-C skeletal stretching vibrations of aromatic and polyaromatic ring systems, that is, intensity enhanced by the presence of substituents, predominantly phenol. Another possibility is that the absorption band arises from a strongly conjugated C=O, -COO⁻, carboxylate groups and quinonic functions. Conjugation shifts the C=O frequency to lower ranges (range of 40- 17cm⁻¹). It is generally accepted that the absorption between 1350 and 1000cm⁻¹ (though the assignment is complicated) possibly contains bands corresponding to C=C aromatic, C-C, C-O and OH of phenols and alcohols, and C-O ether vibrations (Painter *et al.*, 1981, Benaliouh and Trichet, 1990). It is on the basis of this, that the bands around 1155, 1150, 1110, 1080 and 1050cm⁻¹ are assigned.

Quantitative IR Spectra

Quantitative IR spectroscopy is one technique which allows the rapid characterization of gross chemical structural features of complex organic-derived materials such as kerogen. Tables 2 to 7 present the relative abundance of the functional groups of the kerogens in the form of calculated numerical values 'a'. To characterize the kerogen samples quantitatively, particular attention has been paid to the following bands in the spectra:

2920 – 2900 cm^{-1} (aliphatic stretching); 1610 – 1600 cm^{-1} C=C, C=O, COO⁻ groups); 1450 – 1420 cm^{-1} (aliphatic CH₂ and CH₃ bending) and 900 – 560 cm^{-1} (aromatic) (Benaliouhaj and Trichet, 1990).

Kerogen concentrate from Lokpanta-Lekwesi area apart from containing greater number of oxygen-containing compounds (C=O, -COO⁻) with a calculated numerical value of 8.47 (about 73.59%) also contains more aromatic groups (a=2.34), than aliphatic groups (a=0.70). The high content of C=C, C=O, and COO⁻ groups, and high aromatic group is suggestive of the type, maturity and depositional environment of the organic matter deposited in this area (Tissot *et al.* 1974; Massoud and Kingdon, 1989). Kerogens isolated from shales of the Ndeaboh-Lokpanta area are richer in aliphatic groups and oxygen containing functional groups than aromatic groups. They have calculated numerical values of 24.75 (22.56%); 65.72 (59.90%) and 19.25 (17.54%) for sample 37 and 18.17 (35.58%); 28.90 (56.59%) and 4.00 (7.83%) for sample 75 respectively.

Kerogens from Ndeaboh-Agwu location contain greater number of aromatic groups than both aliphatic and oxygen containing compounds (Table 5). This

suggests that kerogen in this area might have undergone some form of thermal alteration. Kerogens from Isiogbo and Mburubu areas of the basin show a remarkable content of oxygen-bearing functional groups as well as aliphatic groups than the aromatic groups (Table 6 and 7). This might be due to the pattern of oxidation reduction of the organic matter during or after its sedimentation and diagenesis. Table 8 is the summary of the relative percentage of aliphatic groups (2900 + 1440 cm^{-1}); C=C, C=O, COO⁻ groups (1610-1600 cm^{-1}) and aromatic groups (900-560 cm^{-1}) when the sum of the areas of the referred bands is considered equal to 100 (Benaliouhaj and Trichet, 1990).

Generally, the insoluble organic matter of the Lokpanta oil shale facies is richer in oxygen-containing functional groups (53%) than aromatic groups (28%) and aliphatic groups (19%). The variation in the composition of functional groups could be related to the maturity level of the organic matter of the shale kerogens. Verheyen *et al.* (1983) showed that:

- (i) increase in aromatic structures (3050, 900-750 cm^{-1}).
- (ii) decrease in aliphatic structures (2920, 1455 cm^{-1}), and
- (iii) decrease in oxygenated structures (3430, 1710, 1800-930 cm^{-1});

are the general trends observed for kerogen and coaly substances with increasing maturity level. Therefore, the high content of oxygenated structures (53%) and low content of aliphatic structures (19%) in the Lokpanta oil shale facies suggest that kerogens of the Lokpanta shales are of intermediate maturity or might have undergone some form of thermal alteration. Moreover, the absence of a band near 3030 cm^{-1} and the presence

Table 7: Quantitative analysis and band assignments for the IR spectrum of Mburubu (Sample 140) kerogen concentrate

Percent by wt. of kerogen (%k)	Area under the curve (A)	Percent Transmittance (% T)	"a"	Band centre (cm ⁻¹)	Assignment
4.33	88	30	67.74	3460	OH/NH stretching.
	15	37	9.36	2900	aliphatic CH, CH ₂ , CH ₃ stretching modes.
	256	65	90.96	1600	C-C of aromatic rings, C=O, COO ⁻ , carboxylate groups.
	26	61	9.84	1430	aliphatic CH ₂ , CH ₃ bend.
	5	66	1.75	1155	C-O stretching of phenols, aromatic ethers.
	550	77	16.50	600	aromatic C-H bend subst. aromatic vibs.

Table 8: Summary of relative percentages of the major functional groups present in the Lokpanta oil-shale kerogens.

Sample Number	Aliphatic groups (2900 + 1440) a'	C=C, C=O – COO' (1610-1600) a'	Aromatic groups (900-560) a'	Total	Rel % of		
					Aliphatic	C=C, C=O, COO' groups	Aromatic groups
13	0.70	8.47	2.34	11.51	6.08	73.59	20.33
37	24.75	65.72	19.25	109.72	22.56	59.90	17.54
75	18.17	28.90	4.00	51.07	35.58	56.59	7.83
92	8.01	15.86	93.61	117.48	6.82	13.50	79.68
130	49.03	124.71	38.46	212.20	23.11	58.77	18.12
140	19.20	90.96	16.50	126.66	15.16	71.81	13.03
TOTAL	119.86	334.62	174.16	628.64			
Rel. %	19	53	28	100			

Table 9: Degree of oxidation/maturation of organic matter of the Lokpanta oil shales

Sample Number	Location	Area of the 1610 – 1600cm ⁻¹ band	Area of the 2920 – 2900cm ⁻¹ band	lox
13	Lokpanta-Lekwesi	52	0	52.0
37	Ndeaboh-Lokpanta	247	14	17.6
92	Ndeaboh-Awgu	100	10	10.0
130	Isiogbo	107	5	21.4
140	Mburubu	256	15	17.1

of absorption between 900-560cm⁻¹ indicate that aromatic rings in the structure of these kerogens in particular are highly substituted (Verheyen and Johns, 1981).

Nature and Origin of the Organic Matter

Previous workers (Robin and Rouxhet, 1978; Verheyen and Johns, 1981; Benaliolhaj and Trichet, 1990) have shown that the chemical structure of kerogen can be related to that of humic materials and reflects the nature of organic source material and environment of deposition. A closer examination of the spectra revealed that the absorption spectra by the different kerogens present strong similarities. Robin and Rouxhet (1978) showed that such similarities are due to the fact that they originate from the same type of parent material. They further noted that the change in relative intensities are according to the parent material and the degree of evolution. It follows therefore that this similarity observed between the spectra of the Lokpanta oil shale kerogens is in accordance with a similar biological origin for the organic matter associated with all the kerogen.

Moreso, it is noted that kerogens that contain more oxygenated functional groups not absorbing at 1710cm⁻¹ but contain less ester groups corresponds to a

type II or III kerogen. The absorption around 1630cm⁻¹ is much higher for kerogens of series III than for those of series I and II. However, since Lokpanta oil shale kerogens contain more of the oxygenated structures not absorbing at 1710cm⁻¹ (about 53%) coupled with the fact that they also contain an appreciable and corresponding amounts of aliphatic groups (19%) as well as aromatic groups (28%) it is evident that they correspond to type II kerogens. This is in agreement with data obtained by Ekweozor and Gormly (1983) and Ekweozor and Unomah (1990) who had also worked on the Lokpanta oil shales using a number of other convergent results. This type is mainly formed from marine organic matter (planktons) in a reducing environment and is capable of generating oil and gas (Tissot *et al*, 1974; Durand and Monin, 1980).

Variation in the Intensity of IR Absorption Band and Thermal History

The observed differences between the intensity of IR absorption bands can be interpreted in terms of oxidation-reduction processes which affected the organic matter during or after its sedimentation and diagenesis. The method

$$I_{ox} = \frac{\text{Area of the } 1710\text{cm}^{-1} \text{ band} + \text{Area of the } 1610\text{cm}^{-1} \text{ band}}{\text{Area of the } 2900\text{cm}^{-1} \text{ band}}$$

used by Benaliolhaj and Trichet (1990) in interpreting the variation of intensity of IR absorption bands of organic matter is followed in the determination of the variation. This ratio is an index capable of illustrating and measuring the degree of oxidation and/or maturation of organic matter. Although the Lokpanta oil shale does not show absorption band at 1710cm^{-1} , the method has proved useful and table 9 shows the results obtained. It is evident from the table that kerogens from the Lokpanta-Lekwesi area display marks of oxidation which are more intense than all others followed by kerogens from the Isiogbo, Ndeaboh-Lokpanta, Mburubu and Ndeaboh-Awgu areas respectively. In other words kerogen from the Lokpanta-Lekwesi area are more mature than those from Isiogbo, Ndeaboh-Lokpanta, Mburubu or Ndeaboh-Awgu; while kerogens from Ndeaboh-Awgu area display the least mark of maturation compared to all others.

CONCLUSION

This paper has shown that quantitative infra-red can be used as a means of characterizing potential source rocks (kerogens) and obtaining information on source material and relative maturities. The work has revealed that shales from the Lokpanta area contain high kerogen concentrates and are likely to be of high TOC values. Oil shales from Isiogbo area are poorer in kerogen content and this could be a consequence of geothermal heating. Qualitative and quantitative analyses of functional groups have shown that the structures of these kerogens consist of about 19% of aliphatic groups (bands around $2920\text{-}2900$; $1450\text{-}1420\text{cm}^{-1}$); 53% of C=C, C=O, COO⁻ groups (bands around $1610\text{-}1600\text{cm}^{-1}$) and 28% of aromatic groups (bands around $900\text{-}560\text{cm}^{-1}$). Also the aromatic rings in the structure of these kerogens are highly substituted.

Kerogens of the Lokpanta oil shales are observed to be of intermediate maturity, originated from the same parent materials and possibly correspond to type II series from marine-derived organic matter in a reducing environment. Moreso, kerogens from Lokpanta-Lekwesi area are more mature while kerogens from Ndeaboh-Awgu area display the least marks of maturation compared to all others.

REFERENCES

- Agagu, O. K. and Ekwezor, C. M., 1982. Source rock Characteristics of Senonian Shales in the Anambra Syncline, Southern Nigeria. *Jour. Min. Geol.* 19: 52-61.
- Benaliolhaj, S. and Trichet, J., 1990. Comparative Study by Infrared spectroscopy of the organic matter of phosphate-rich (Oulad Abdoun basin) and black shale (Timahdit basin) series (Morocco). In *Advances in Organic Geochemistry 1989* (Edited by Durand B. and Behar F.) *Org. Geochem.* 16: 649-660.
- Dow, W. G., 1977. Kerogen Studies and Geological Interpretations. *J. Geochem. Explor.* 7: 79-99.
- Durand, B. and Monin, J. C., 1980. Elemental analysis of kerogen. In *Kerogen, Insoluble Organic Matter from Sedimentary Rocks*. (Edited by Durand, B.) Editions Technip, Paris. pp. 1-338
- Ekwezor, C. M. and Gormly, J. R., 1983. Petroleum Geochemistry of Late Cretaceous and Early Tertiary shales penetrated by the Akukwa - 2 well in the Anambra Basin, Southern Nigeria. *Jour. Petrol. Geol.* 6: 207-216.
- Ekwezor, C. M. and Unomah, G. I., 1990. First discovery of oil shale in the Benue Trough, Nigeria. *Fuel* 69, 502-508.
- Massoud, M. S. and Kinghorn, R. R. F., 1989. A new classification for the Organic components of kerogen. *Jour. Petrol. Geol.* 8: 85-100.
- Mielczarski, J. A.; Denca, A. and Strojek, J. W., 1986. Application of Attenuated Total Reflection Infrared spectroscopy to the characterization of coal. *Appl. Spectrosc.* 40: 998-1005.
- Painter, P. C., Snyder, R. W., Starsinic, M., Coleman, M. M., Kuehn, D. W. and Davis, A., 1981. Concerning the Application of FT-IR to the study of coal: A Critical Assessment of Band Assignments and the Application of Spectral Analysis Programs. *Appl. Spectrosc.*, 35: 475-485.
- Petters, S. W., 1978. Stratigraphic evolution of the Benue Trough and its implications for the upper cretaceous paleogeography of West Africa. *Jour. of Geol.*, 86: 311 - 322.
- Robin, P. L. and Rouxhet, P. G., 1978. Characterization of kerogens and study of their evolutions by infrared spectroscopy: Carbonyl and Carboxyl groups. *Geochim. Cosmochim. Acta.* 42. 1341-1349.
- Rouxhet, P. G., Robin, P. L. and Nicaise, G., 1980. Characterization of kerogens and of their evolution by infrared spectroscopy. In *kerogen, Insoluble Organic Matter in Sedimentary Rocks*. (Edited by Durand, B.) pp. 163-190. Editions Technip, Paris.
- Rullkotter, J. and Michaelis, W., 1990. The structure of kerogen and related materials. A review of recent progress and future trends. In *Advances in Organic Geochemistry 1989* (Edited by Durand, B. and Behar, F.) *Org. Geochem.* Pergamon Press, Oxford. 16: 829-852.
- Senesi, N. and Sipos, S., 1985. Molecular weight distribution, analytical and spectroscopic characterization of humic fractions sequentially isolated by organic solvents from a brown coal humic acid. *Org. Geochem.* 8, 157-162.

- Tissot, G.; Durand, B., Espitalie, J. and Combaz, A., 1974. Influence of nature and diagenesis of organic matter in the formation of petroleum. *Am. Assoc. Petrol Geol. Bull.*, 58: 499-506.
- Tissot, B. P. and Welte, D. H., 1978. *Petroleum Formation and Occurrence*, Springer-Verlag, Berlin pp. 81-91.
- Unomah, G. I. and Ekweozor, C. M., 1991. Petroleum Source-rock Assessment of the Campanian Nkporo Shale, Lower Benue Trough, Nigeria. *Nig. Min. Geo. Soc. Abstracts*, 27th Annual Conference.
- Van Krevelen, D. W., 1984. Organic Geochemistry – old and new. *Org. Geochem.* 6: 1-10.
- Vassalo, A. M.; Fredericks, P. M. and Wilson, M. A., 1983. FTIR Studies of Deuterium Incorporation into coal, Associated Mineral Matter and Hydrogenation Residues. *Org. Geochem.* 5: 75-85.
- Verheyen, T. V. and Johns, R. B., 1981. Structural Investigations of Australian Coals –1. A characterization of Victorian Brown Coal Lithotypes and their kerogen and humic acid fractions by IR spectroscopy. *Geochim. Cosmochim. Acta* 45: 1899-1907.
- Verheyen, T. V.; Johns, R. B. and Esdaile, R. J., 1983. Structural investigations of Australian coals – IV. A characterization of the variation in rank of bituminous coal fractions by elemental analysis and IR spectroscopy. *Geochim. Cosmochim. Acta.* 47: 1579-1587.
- Victorovic, D.; Pfenndt, P. A. and Krsmanovic, V. D., 1981. Structural Investigation of Aleksinac shale kerogen by chemical and spectroscopic Methods; In: *Advances in Organic Geochemistry 1981*. Edited by Bjory et al, pp. 620-627.
- Welte, D. H., 1969. Organic Geochemistry of Carbon. In: K. H. Wedepol (ed), *Handbook of Geochemistry* 2. Springer.