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Techniques and Methods of Organic Geochemistry as Applied to Petroleum Exploration

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ABSTRACT

The organic geochemistry, with the passage of time has evolved as a useful approach to exploration for oil and gas. The paper describes the general principle of organic geochemistry, as applied to oil and gas exploration and prospect evaluation. The concept and the techniques are presented in considerable detail. The basic techniques / methods used to identify and evaluate the potential source rocks with respect to the organic richness, quality of organic matter and various stages of thermal maturation are also highlighted. The most common techniques used are organic carbon, pyrolysis, hydrocarbon extraction, gas chromatography, vitrinite reflectance and mass spectrometry for the source rock analysis, crude oil analysis and oil-source rock correlation studies.

INTRODUCTION

The purpose of this paper is to provide an introduction to the concepts, methods and applications of petroleum geochemistry. Organic geochemistry is the only effective mean of directly addressing the problems associated with the nature, type and quality of hydrocarbons, which are expected to be discovered. The techniques are based on the concept that oil and gas is generated in organic rich source rocks that have been exposed to sufficient combination of temperature and time to cause hydrocarbon generation, which are then expelled to migrate along carrier beds and other conduits to traps. Methods used include geochemical characterization of crude oils, source rock evaluation and correlation of oil to source rocks. These geochemical methods provide information on the amount and type of hydrocarbons that actually may be available for entrapment.

The first requirement of any geochemical exploration programme is the establishment of source rocks which are organic rich fine-grained rocks capable of generating oil and gas. The prediction of hydrocarbon trap capacity without effective source rocks is of little value. Therefore, the organic geochemical techniques can be used to obtain a reasonably clear picture of chemical processes involved in petroleum formation.

The application of geochemistry as an exploration tool in oil and gas exploration is comparatively new and is being successfully utilized to address the problems associated with the amount and nature of reservoir fluids. The sophisticated instrumental techniques have been developed to get coherent picture of petroleum generation. Source rock evaluation is an integral part of an exploration programme that may be used to assess the prospect of any sedimentary basin.

In essence, the application of organic geochemical techniques can yield important information regarding the factors responsible for controlling the generation of hydrocarbons in a sedimentary basin and the mechanism of migration and ultimate accumulation in reservoirs.

PARAMETERS FOR SOURCE ROCK EVALUATION

There are four basic parameters used in the source rock evaluation studies. These are:

1) Organic Richness
2) Organic Matter Quality
3) Thermal Maturity
4) Genetic correlation of oils and source rocks.

The sophisticated instrumental geochemical techniques have been developed to assess these parameters.

1. Organic Richness of Source Rocks

Organic richness is the basic parameter, which is used to assess the generating potential of source rocks. There are number of factors which contribute to the richness of source rocks. These include environment of deposition, type of kerogen, and post depositional conditions such as weathering, which may seriously affect the quantity and quality of source rocks. The most common techniques used for organic richness determinations are:

1.1. Total Organic Carbon (TOC)

The total organic carbon content of a rock is a direct measure of its organic richness. Sufficient quantity of organic matter must be present in a sedimentary rock before it is qualified as a potential source rock for subsequent hydrocarbon generation. In general, higher the concentration of marine organic matter, the better the source potential. Shales containing less than 0.5% TOC and carbonate with less than 0.2% TOC are generally not considered as a source rock and no further analysis is performed on these samples. TOC is easy to measure. The dried rock samples are crushed and treated with hydrochloric acid to remove carbonates. After acid treatment, the sample is subjected to oxidation, so that non-carbonate carbon is converted to CO_2 or CO. This is usually done in a Leco furnace, which measures evolved CO_2 by IR

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Cell. The schematics showing various steps for the determination of TOC is shown as figure 1.

1.2. Pyrolysis

Pyroly-sis is the process whereby a sample of rock is heated under controlled temperature condition for a certain time interval. Organic compounds are released in two stages. In the 1st stage free hydrocarbons present in the rock (S1) are released and in the 2nd stage, volatile hydrocarbons formed by thermal cracking are released (S2).

The analysis is carried out by an instrument designed to heat the sample in a programmed manner. Flame ionization detector and thermal conductivity detector are used to measure the evolved hydrocarbons (S1) and (S2) and non-hydrocarbons like CO2 and water. The most widely used equipment is Rock-Eval. It is used to estimate three geochemical parameters.

1. The S1 peak, which represents the amount of free hydrocarbons at 300°C.
2. The S2 represents the hydrocarbons generated by thermal cracking of kerogen at temperature range of 400 – 800°C.
3. The S3 peak represents the amount of CO_2 produced from kerogen. It is collected at a temperature range 70 – 250°C.

It is the best screening technique to identify possible source and reservoir intervals, which can be used for detail analysis.

A typical pyrogram is shown in figure 2.

1.3. C+15 Extractable Bitumen and Hydrocarbons

The bitumen extracted from the sediment is often referred as extractable organic matter (EOM). It usually represents 5 to 10% of the total organic matter in fine-grained sedimentary rocks. Though there exist many other factors, but the detail compositional analysis of EOM in conjunction with kerogen yields the necessary information to make at least semi-quantitative predictions about the amount of petroleum which have been or will be generated by a given amount of source rock. For the extraction of EOM, the rock sample is grinded to a fine powder and continuously extracted in a soxhlet extractor for 15 hours. Following removal of the solvent, the residual bitumen is fractionated into saturated, aromatic hydrocarbons. Data values are expressed as concentration in parts per million (ppm). The concentration of extractable organic matter is used in evaluating oil potential. Generally, the samples containing value of EOM less than 300 ppm are not processed further.

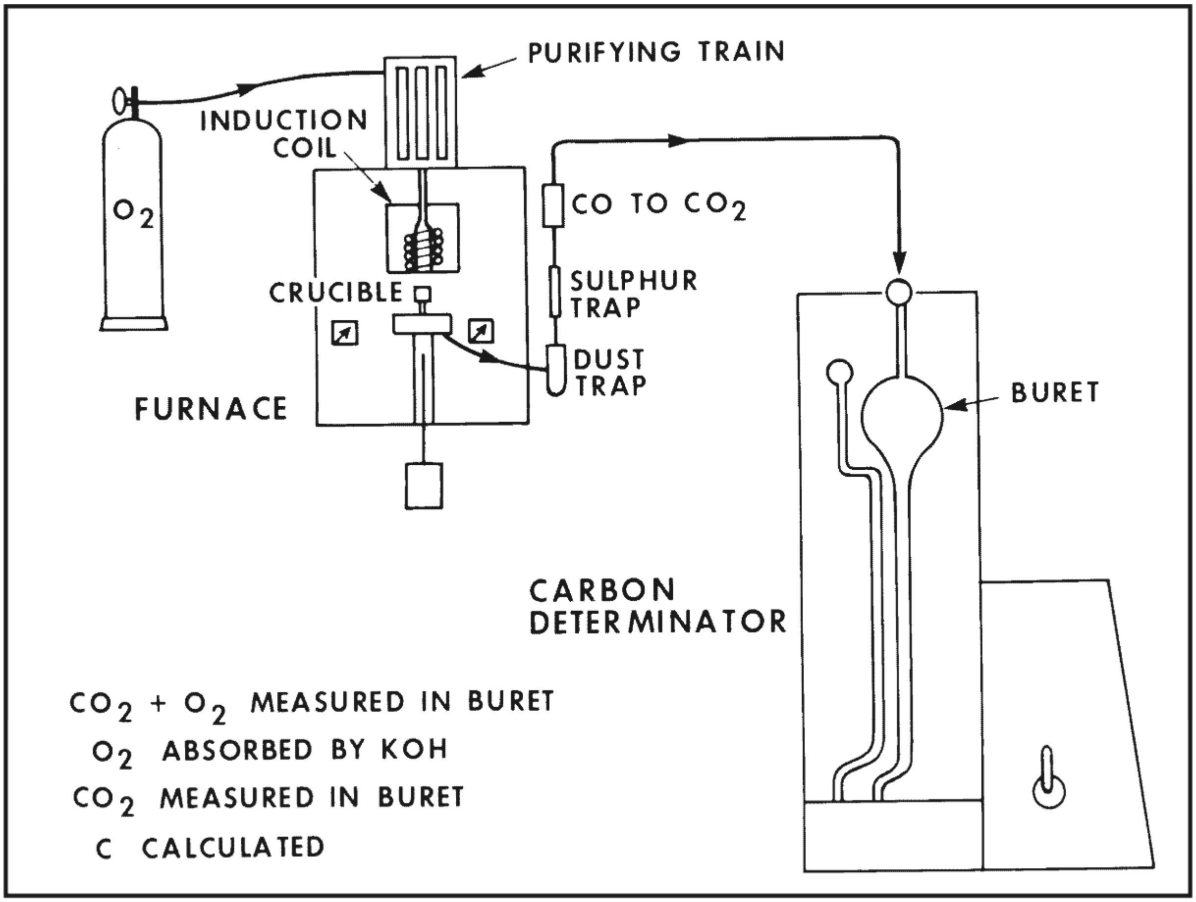

Figure 1- LECO carbon analyzer for TOC estimation.

2. Organic Matter Quality

The quality of the organic matter determines the chemical composition of the hydrocarbons. The type of organic matter and hence its capacity to generate oil can be determined by means of transmitted / reflected light microscopy or by elemental analysis of kerogen. Visual methods, however, have no direct bearing on kerogen convertibility or yield and this must be compared to chemical data. Objective chemical techniques and subjective optical methods are complementary and both are used for defining the quality of organic matter.

2.1. Optical Microscopic Method

On the basis of microscopic examination, the organic matter is classified as:

(i) Alginite (amorphous)
(ii) Exinite (herbaceous)
(iii) Vitrinite (woody)
(iv) Intertinite (coaly)

The composition of organic matter influences the kinetic, thermal maturation and the type of hydrocarbon generated from the organic matter.

2.2. Elemental Analysis

Elemental analysis of carbon, hydrogen, and oxygen indicates the oil and gas generating potential of the organic matter in the sediments. The elemental composition is function of both kerogen type and thermal maturity. The elemental analysis is used to define three main types of kerogen as shown in figure 3. The said figure known as Van Krevelen diagram, provides a useful approach to classification of kerogen. Type-I has the highest hydrogen and lipid content and therefore a high genetic potential for hydrocarbons. Type-II also has high content of hydrogen and lipids, mostly derived from marine plankton deposited in a reducing environment. Type-III contained less hydrogen and more oxygen than the other types and it is derived mainly from terrestrial plants.

2.3. Pyrolysis

Pyrolysis technique is used to evaluate the quality of organic matter using two indices, the hydrogen index (S2/Organic Carbon) and the oxygen index (S3/Organic Carbon). The two indices can be plotted and three main types of kerogen i.e. type-I, II and III are readily recognized.

2.4. Extractable Organic Matter (EOM)

Soluble organic matter (bitumen) which is obtained by the extraction of grinded rock sample is a measure of source quality. The quality of source rock is demonstrated by evaluating the amount of extractable organic matter and the amount of total hydrocarbons (saturated and aromatic). Generally rocks having hydrocarbon less than 50 ppm are characterized as non-source whereas having hydrocarbons 500-1000 ppm as good quality source rocks.

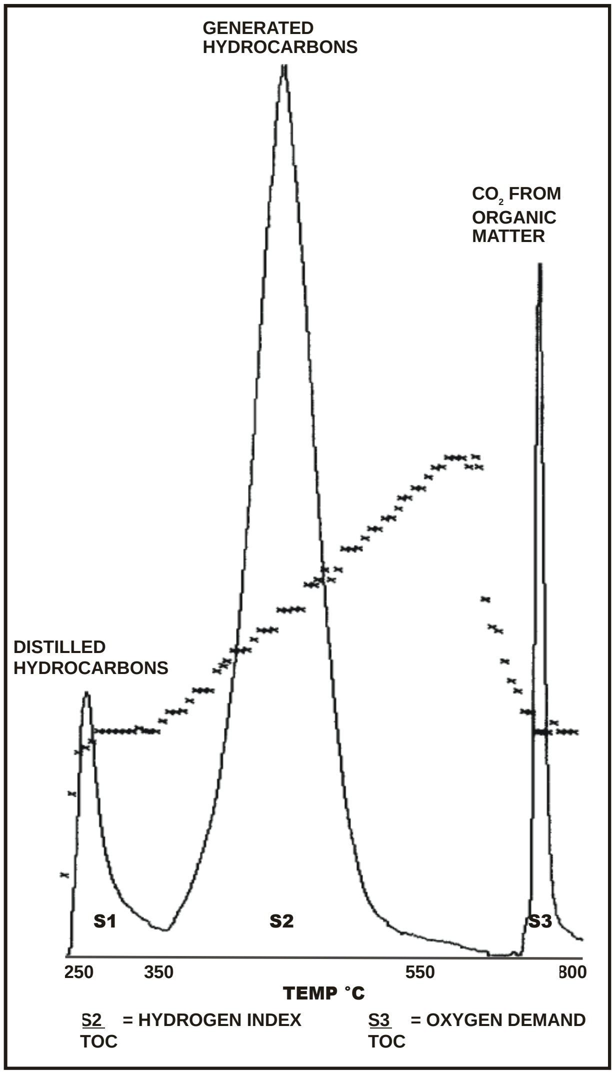

Figure 2- Typical pyrogram from Rock Eval showing S1, S2 and S3.

3. Thermal Maturity

The thermal alteration of organic matter with increasing temperature by burial is maturation. The maturation stages of organic matter in fine-grained sedimentary rocks is summarized in figure 4 and discussed as follows:

3.1. Stages of Organic Matter Maturation

The maturation of organic matter is classified into three stages:

3.1.1. Diagenesis
3.1.2. Catagenesis
3.1.3. Metagenesis

3.1.1. Diagenesis: It is a low temperature transformation of organic matter. Chemical and microbial transformation

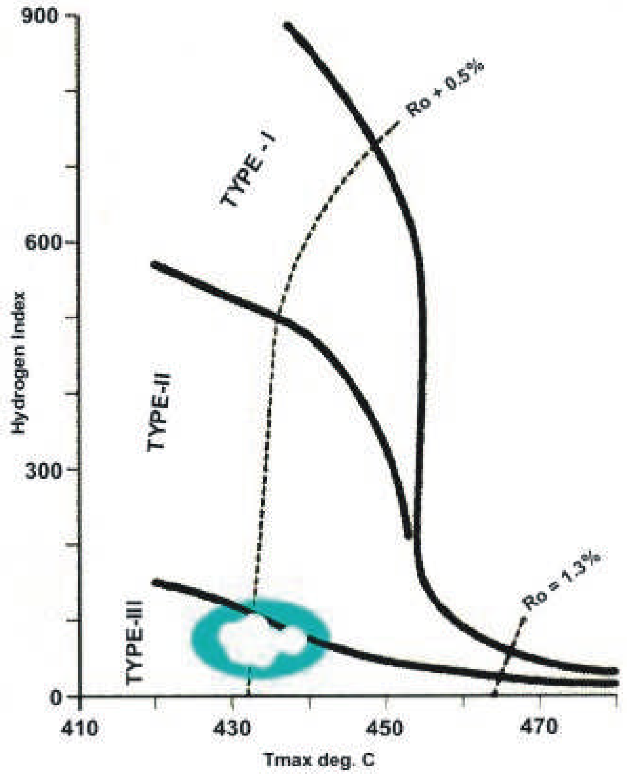

Figure 3- Van Krevelen diagram showing three main types of kerogen (Hunt, 1979).

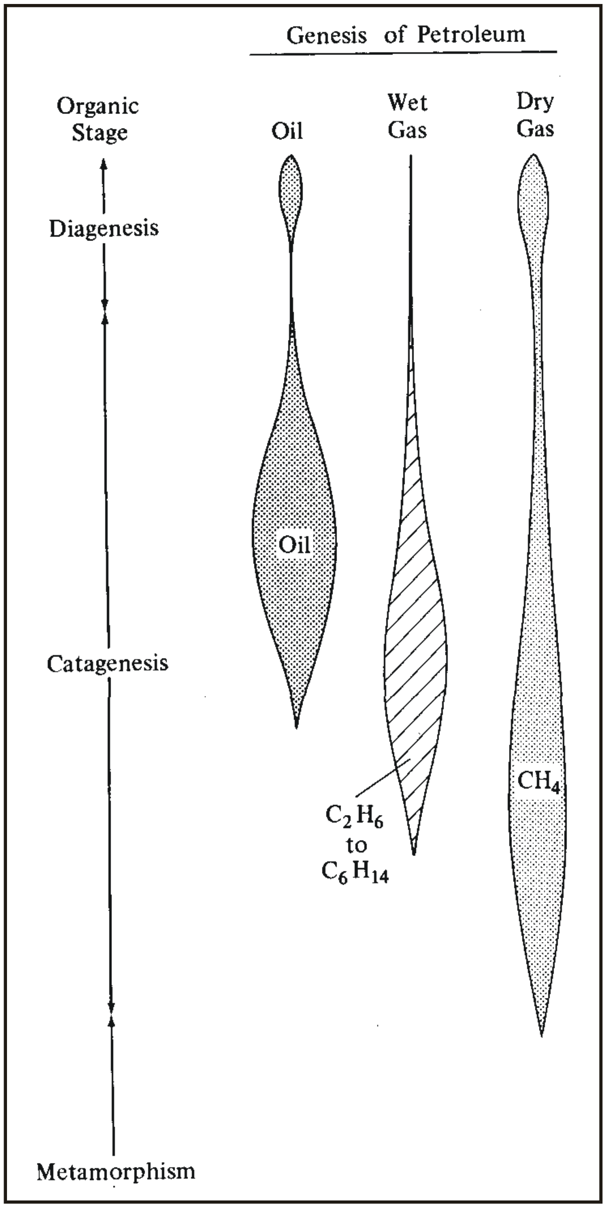

Figure 4- Maturation stages of organic matter in sedimentary rocks (Hunt, 1979).

destroys some of the organic matter and alters the chemical composition of the remainder. The organic matter formed as a result of diagenetic reactions consists of many types of molecules. The sizes of these molecules vary from very small to large. Diagenesis is generally defined as covering temperature range from the surface to about 50ºC.

With the depth of burial, porosity, permeability decreases and temperature increases. As temperature rises, thermal reactions become increasingly important.

3.1.2. Catagenesis: After the diagenetic transformation, all kerogens are thermally immature and undergo various thermal transformation stages to generate oil and gas. Alginite with its high hydrogen content is the most oil prone. It yields more hydrocarbons per unit of organic matter than any other type. Exinite also yields liquid hydrocarbons, generally with high alkane content. Vitrinite is mostly gas prone while intertinite with its low hydrogen content has virtually no hydrocarbon potential.

Catagenesis occurs at a temperature between 50°C and 150°C. With increasing temperature kerogen loses oxygen and hydrogen and as a result of thermal decomposition, smaller molecule of bitumen is generated.

With increasing temperature, the generation of bitumen increases at the expense of kerogen. The composition of bitumen depends upon the original source material and the degree of thermal maturation. Initially, the bitumen concentration increases rapidly with increasing temperature, however, the reaction rate decreases as the cleavage sites in the kerogen become scarce. Catagenesis is the main stage of oil formation. The quantity and quality of oil or gas generated depends on the kerogen type. Type-I kerogen generates normal crude oils and type-II kerogen produces waxy crude oil. Type-III is gas prone while type-IV produces essentially no oil or gas.

The following exemplify the catagenesis:

1. Shifting of the heavy end bias of C+15 hydrocarbons to a light end bias.
2. Normal paraffin increases at the expense of branched and cyclic paraffins.
3. The odd carbon preference disappears.
4. Certain ratios such as n C_{18}/phytane increase.

3.1.3. Metagenesis: At this stage, the oil generation has stopped and the maturation of oil generated during catagenesis stage proceeds, oil is thermally transformed and become progressively lighter. At the metagenesis stage, only methane, hydrogen sulphide and non-reactive kerogen residue remain. Metagenesis generally occurs at a temperature above 150ºC and results in the complete destruction of liquid hydrocarbons, forming gas which is also generated from kerogen.

These stages of thermal metamorphism are also established by optical examination of kerogen using vitrinite reflectance measurements, recording the percentage of incident light, which is reflected by the individual particles. Vitrinite reflectance increases regularly with increased thermal alteration. Therefore, the thermal maturity of the sediments can be determined.

The main phase of petroleum generation occurs between 0.60% Ro to 1.2% Ro, with little variation depending upon the type of material. At reflectance value below 0.6%, the likelihood of substantial oil generation within a formation is small. At Ro value above 1.2% metagenesis stage of metamorphism is reached and any oil generated will start to undergo thermal cracking resulting in gas rather than oil. At Ro values above 2.0 %, only gas remains.

4. Techniques for the Evaluation of Thermal Maturation

4.1. Pyrolysis

The pyrolysis techniques allow a rapid characterization of kerogen type and the thermal maturity stage. The four parameters are measured.

S1	Measure the hydrocarbon present in the rock
S2	Measure the hydrocarbon generating potential of kerogen
S3	Measure the amount of carbon dioxide
Tmax	is the temperature for the thermal cracking of kerogen.

The level of thermal maturation is indicated by the value of Tmax. The value of Tmax below 435°C indicates immaturity, the value of 435-470°C indicate main phase of oil generation while value greater than 470°C reflects over mature zone.

4.2. Elemental Analysis

The maturation of kerogen with increase in temperature can be assessed from the elemental analysis of carbon, hydrogen and oxygen. In thermal maturation, oxygen is removed from kerogen as CO_2 and H_2O hydrogen as hydrocarbon and water and carbon as hydrocarbons and CO_2. Oil generating kerogen have H/C ratio usually above 1 and a hydrogen content of 6% or more. H/C ratios of gas generating kerogen are usually below 0.8

4.3. Vitrinite Reflectance

Vitrinite reflectance technique is also one of various techniques used for determining the maturation of rocks. The maturation of rocks is indicated by mean of reflectivity (Ro). The samples having VR value below 0.5% are considered as immature. Maximum oil generation occurs around 0.8 – 1.0% Ro and the end of oil generation is around 1.3%. The higher values observed for gas generation range from 1.3 – 3.0% Ro (Figure 5).

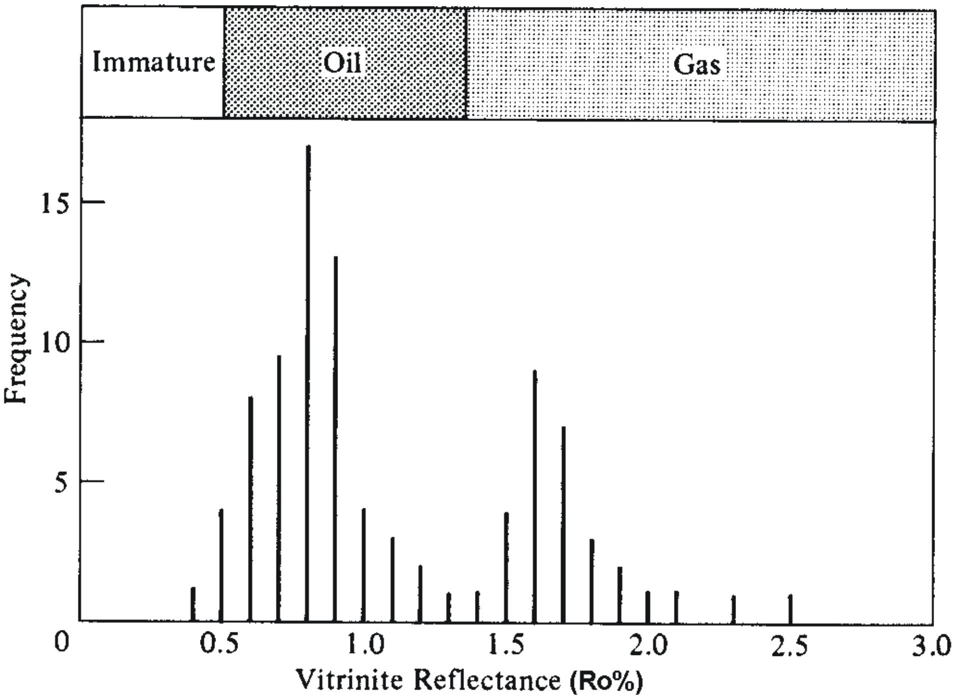

Figure 5- Histogram (Hunt, 1979).

4.4. Gas Chromatography

The gas chromatographic technique is also very useful for determining the maturation of sedimentary rocks. Normally two changes occur during catagenesis; a gradual disappearance of the odd – even predominance and a shift toward the lower molecular weight range because of the synthesis of smaller molecules and cracking of larger molecules. The change in the n-paraffin distribution through diagenesis and catagenesis is shown in figure 6. It can be seen as soon as the source rock attain sufficient maturity the concentration of n-alkene between C_{13} – C_{18} will be at peak and will show a steady decrease in high molecular weight hydrocarbons.

5. Oil – Source Rock Correlation

Oil source rock correlation studies are carried out in any basin in which reservoired oil has been found. The basic objectives of correlation is (a) to establish the geochemical character of the oil (b) to determine the number of genetically related crude oil families within that area (c) to carryout genetic correlation of potential and effective source rocks (d) to define the control governing the generation, migration and accumulation of oil within reservoir facies. In the first instance, source rock quality of different stratigraphic units is defined and then, based upon the available criteria the oil to source rock relationship is established. There are number of correlation parameters, which are used for characterizing crude oils and matching crude oil source facies data. The techniques used include the following:

5.1. API Gravity

API gravity is a measure of density. Most normal oils have API gravity from 25 to 45. Gravity less than 10 API indicate that oil is denser than water.

5.2. Sulphur Content

Most oils are low sulphur oils, containing less than 0.5%. High sulphur oils are less common and are normally sourced from non-destic organic rich source rocks.

5.3. Variation of Carbon Isotopes in Kerogen and Petroleum

Kinetic isotope – fractionation processes may provide information on the generation, maturation and genetic correlation of oil source rocks. Study of the variation carbon isotopes in natural gases, crude oils revealed the possibility of differentiating and classification of source rocks and crude oils.

The most commonly used isotope ratio is C_{13}/C_{12}. The deuterium/hydrogen (D/H) ratio is occasionally used for oil but it is commonly used for gases.

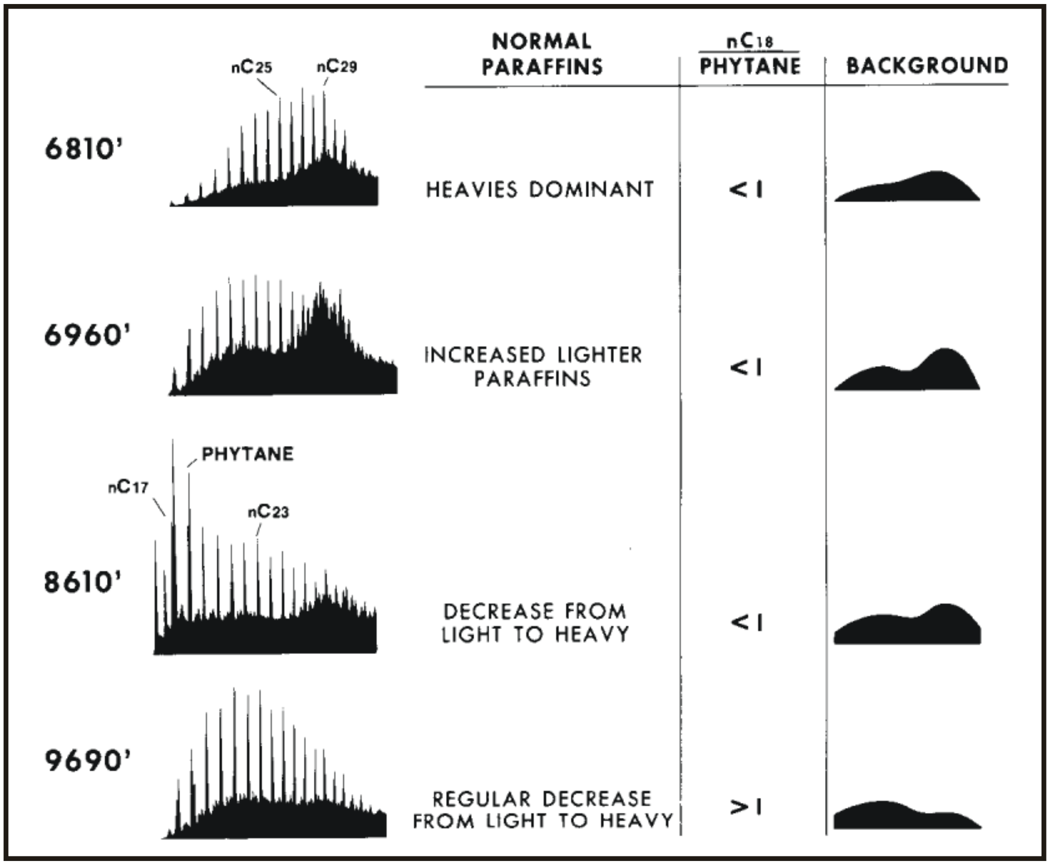

Figure 6- Changes in the n-paraffin distribution with depth through diagenesis and catagenesis.

On the average, oils are about 2% more negative than the kerogen, from which they were extracted. Oils and Kerogen derived from highly reducing evaporites are often isotopically heavy.

5.4. Compound Classes

The oils/ bitumens are determined by column chromatography. The proportion of each compound class (saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltenes) can give indications about both source and maturity.

Low content of hydrocarbons in an extract indicates immaturity. Large proportions of hydrocarbons in an extract indicate either maturity, contamination by drilling fluid additives or presence of migrated oil.

5.5. n – alkane Distributions

The n-alkane distribution of saturated hydrocarbon fraction is carried out by gas chromatography. A typical gas chromatogram is shown in figure 7. By analyzing and estimating the distribution of various compounds, number of ratios and concentrations of hydrocarbons are used for correlation including the following:

5.5.1. Carbon Preference Index (CPI): Carbon Preference Index (CPI) is a useful parameter for correlation between samples of similar maturity.

5.5.2. Isoprenoid Distribution: Isoprenoid ratios, particularly pristane/ phytane ratios (pr/ph) are useful correlation parameter. Very high ratios are associated with terrestrially influenced sediments including coals. Pr/ph ratios substantially below 1.0 are taken as indicators of highly reducing depositional environments.

5.5.3. Isoprenoid/n-alkane ratios: Isoprenoid and n-alkane data provides valuable information on bio-degradation maturity and diagenetic conditions. With increasing maturity n-alkanes are generated faster than isoprenoids, resulting in a decrease in isoprenoid/n-alkane ratios. Biodegradation, in contrast, removes n-alkanes faster, increasing isoprenoid/alkane ratios.

5.5.4. Polycyclic – hydrocarbon biomarkers: The estimation of biomarker distribution in saturated and aromatic fraction is determined by GC/MS analysis. These include diterpanes, triterpanes and steranes. The mass chromatograms are shown in figure 8. Diterpanes are useful correlation parameters when resinite is an important source contributor.

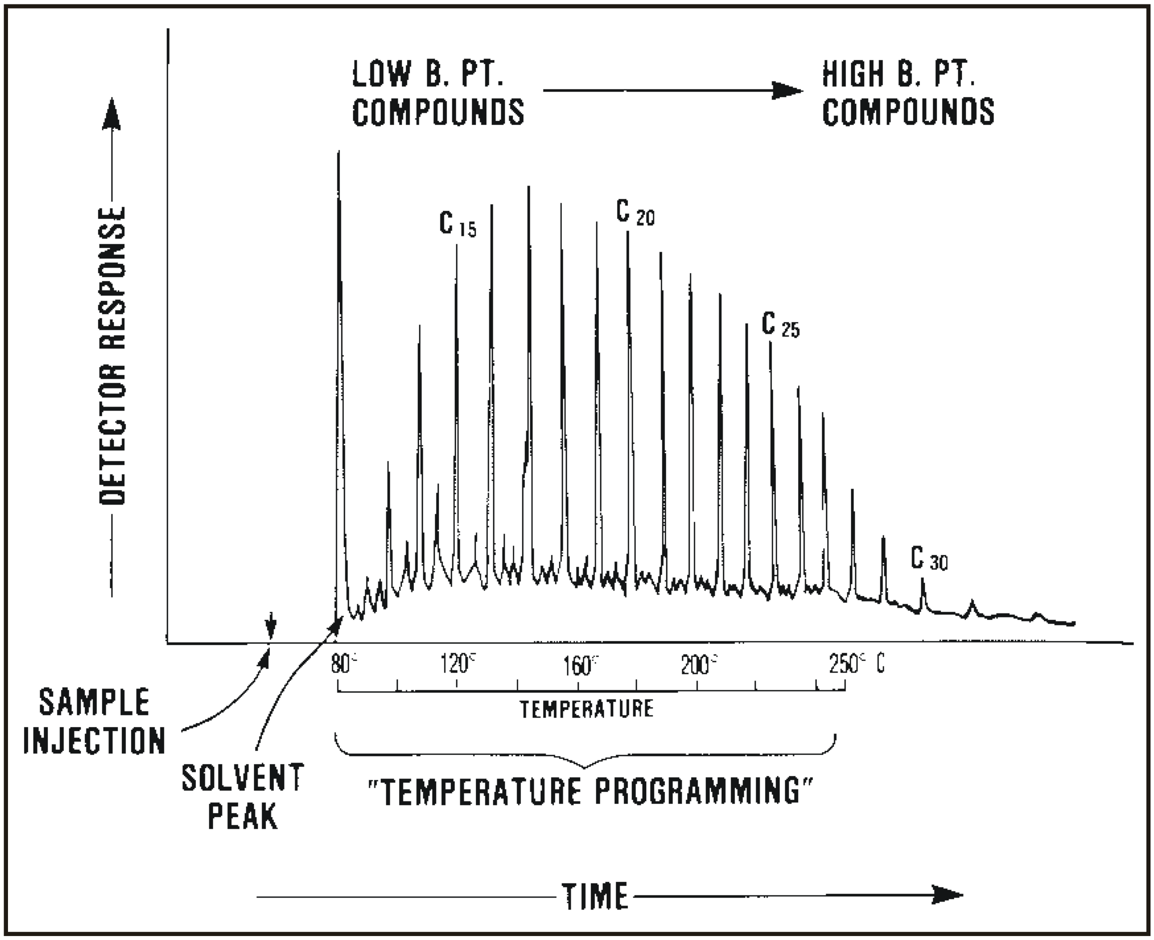

Figure 7- Typical gas chromatogram showing n-alkane distribution.

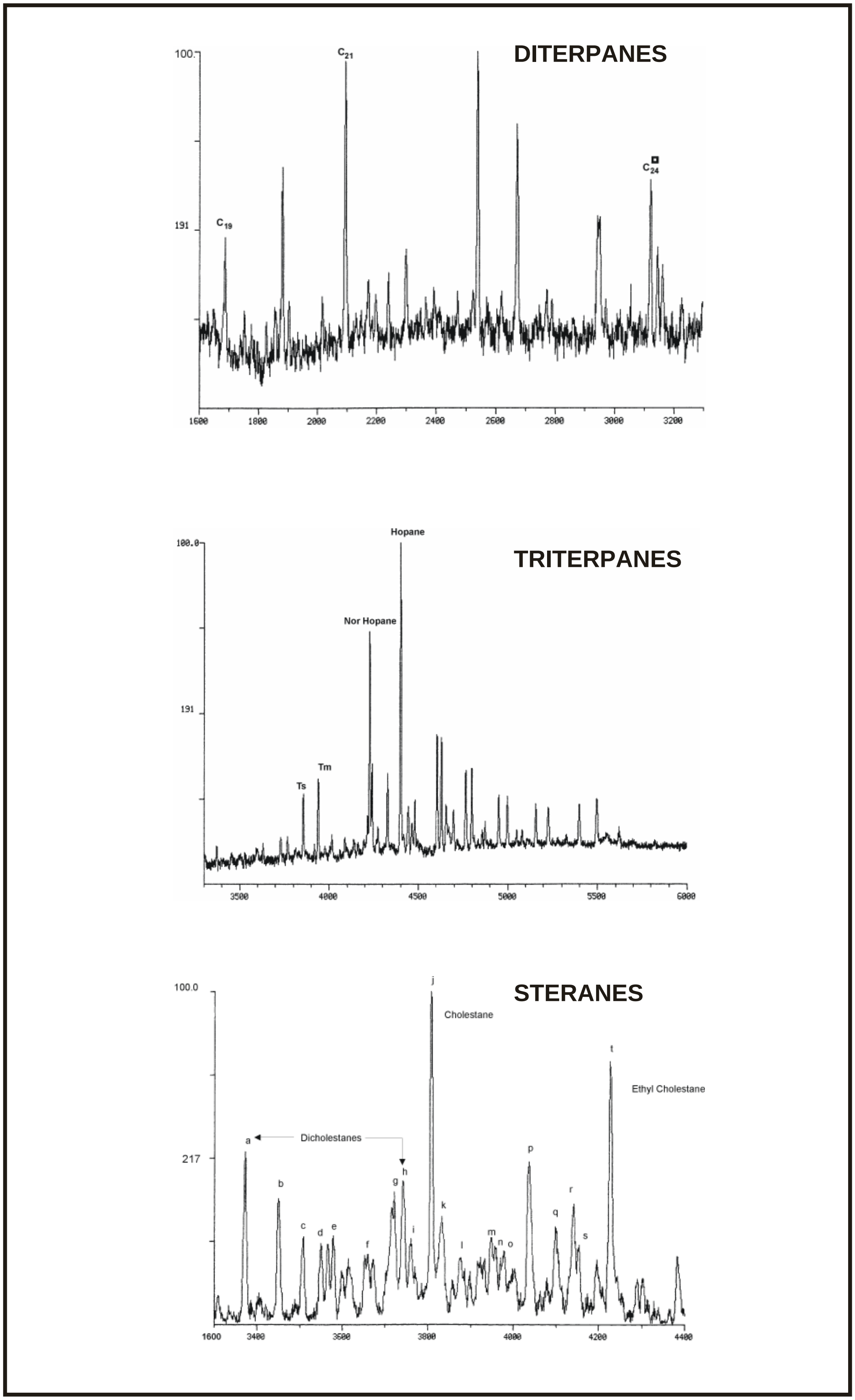

Figure 8- Typical mass chromatogram showing distribution of diterpanes, triterpanes and steranes.

Triterpanes have proven very valuable as correlation parameters because they are sensitive to diagenetic conditions, biodegradation and in some cases, to the type of organism from which the organic matter is derived. The ratio of C_{29} to C_{30} regular hopane appears to be related to depositional environment.

Steranes are also valuable correlation parameters because of the direct dependence of C_{27}, C_{28}, and C_{29} regular steranes concentration on their precursor C_{27} and C_{29} sterols. C_{27} sterols dominate in marine organisms whereas C_{29} sterols are more common in terrestrial plants.

CONCLUSION

Organic Geochemistry has become a widely accepted tool in oil and gas exploration .The objective is to identify and establish areas of mature, oil and gas-generating source rocks and define the migration pathways, which may lead to accumulation of oil and gas. The organic geochemical techniques are based on the premise that oil and gas is generated in organic rich source rocks, which when subjected to elevated temperature and time, convert the organic matter to oil and after generation, hydrocarbons are expelled to migrate along carried beds to traps.

The knowledge derived from the application of these techniques can be gainfully utilized to establish the petroleum system for hydrocarbon charge prediction to determine whether an un-drilled trap has an access to hydrocarbon migration from mature source rocks. Therefore to understand the oil and gas generation, various techniques and method outlined will be used for potential prospect appraisal.

REFERENCES

Andrew, S. and K.F.A. Mackenzie, 1984, Aapplication of biological markers in petroleum geochemistr, Adv. in Petrol. Geoche; *In:* J. Brooks and Dietrich Welter (eds.); Academic Press, London, Orlando and New York, v.1, p.115-214.

Barker, C., 1974, Pyrolysis techniques for source rock evaluation, AAPG bull. no.58, p.2349-2361.

Barnard, P.C., A.G. Collins and B.S. Cooper, 1981b, Organic maturation studies and fossil fuel exploration; *In:* J. Brooks (ed); Academic Press, London, Orlando and New York; p.337-342.

Barwise, A.J.G. and E.V. Whitchead, 1980, Advances in organic geochemistry 1979; *In:* A.G. Douglas and J.R. Maxwell (eds.); Pergamon Press, Oxford, p.181-192.

Bjorøy, M., P.W. Brooks, and K. Hall, 1983, Advances in organic geochemistry 1981; *In:* Bjorøy, M. et al., (eds.); John Wiley, Chichester, p.87-93.

Douglas W. Waples, 1984, Thermal models for oil generation; *In:* Jim Brooks and Dietrich Welter (eds.); Advances in petroleum geochemistry, Academic Press, London, v.1, p.7-67.

Durand, B., 1983, Advances in organic geochemistry 1981; *In:* Bjorøy, M. et al. (eds.); John Wiley, Chichester, p.117-128.

Hunt, J.M., 1979, Petroleum geochemistry and geology; *In:* James Gilluly (ed.); W.H. Freeman and Company, San Francisco.

Mackenizie A.S., U. Disko and J. Rullkotter, 1983, Determination of hydrocarbon distributions in oils and sediment extracts by gas chromatography – high-resolution mass spectrometry. Org. Geochem. 5, p57-63.

___ and J.R. Maxwell, 1981, Organic maturation studies and fossil fuel exploration; *In:* J. Brooks (ed.); Academic Press, London, Orlando and New York, p.239-254.

Seifert, W. K. and J.M. Moldowan, 1978, Application of steranes, terpanes and mono-aromatics to the maturations, migrations and source of crude oils; Geochim. Cosmochim. Acta 42, p.77-95.

___ and J.M. Moldowan, 1979a, The effect of biodegradation on steranes and terpanes in crude oils; Geochem. Cosmochim. Acta 43, p.111-126.

___ and J.M. Moldowan, 1979b, Applications of biological marker chemistry to petroleum exploration; Tenth World Petroleum Congress, 1979, Special Paper 8, p.425-440.

___ and J.M. Moldowan, 1980, Advances in organic geochemistry 1979; *In:* A.G. Douglas and J.R. Maxwell (eds.); Pergamon Press, Oxford, p.229-237.