COURSE GUIDE

EMT 512
PETROLEUM AND ENVIRONMENT

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MAIN COURSE

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MODULE 1

UNIT 1 ORIGIN OF CRUDE OIL

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1.0 INTRODUCTION

Petroleum often referred to also as crude oil is from the Latin words *petra* and *oleum*. *Petra* is rock and *oleum* is oil which literally means that petroleum is rock oil. This substance is considered to be the most demanded and consumed substance in the modern day. Its demand is driven by its value and usefulness in the provision of energy for transportation, industrial activities, heating and in the synthesis/production of several useful products such as plastics, detergents and other petrochemicals. It is often referred to as "black gold" because it is brown to black flammable liquid or semi-solid material. Petroleum and natural gas supply more than 50% of the energy demand of the world at large (BP Statistical Review of World Energy 2018). Being such a valuable substance, it is very essential we learn about its origin. This section of the course is therefore dedicated to teach the theories of the origin of petroleum.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- understand the biogenic theory about the origin of crude oil;
- understand the abiogenic theory about the origin of crude oil;
- differentiate between the two theories.

3.1 Origin Theories

Petroleum sold by different sourced countries has not been of the same quality and contents which suggest that composition of the petroleum are not the same for all the sources. The composition of the petroleum will be discussed in Unit 2. This variation in the composition suggests that the various crude oils are from different sources and their composition must be source dependent. There are two theories about the origin/source of carbon fossil fuels including crude oil: the biogenic theory and the abiogenic theory (Kenney *et al.,* 2001, 2002). The two theories have been subject of debate for hundreds of years but the biogenic origin's theory seems to be more accepted.

3.2 Biogenic Origin's Theory

In the biogenic origin's theory, scientists view the production process of crude oil and natural gas as the compression and heating of ancient vegetation buried over geological time scales (millions of years). The theory postulated that fossil fuels are formed from the decay of the remains of prehistoric marine animals and terrestrial plants. These organic matters were mixed with mud and buried under thick sedimentary rock often referred to as source rock.

3.2.1 Raw Materials and Source Rock

Petroleum is postulated under this theory to be the product from the decay of **plants and animals' debris** which were incorporated into sediments at the time of deposition. The details of this decays and the mechanism of formation of petroleum from the source sediment and its accumulation process into the reservoir rock are still not fully understood. These notwithstanding, the constituents of petroleum are very much depended on the nature of the raw material (precursors) from which petroleum is formed which are the local flora and fauna that occur in the source material. It is also dependent of the geochemistry of the source rock. While exactly how crude oils originated is not established, it is generally agreed that crude oils is derived from these marine animal and plant debris being subjected to high temperatures and pressures. It is also suspected that the transformation may have been catalysed by the source rock's constituents. Therefore, petroleum composition varies with locations and age of the field/source rocks beside other variables. It is also very possible for two petroleum wells adjacent to each other to contain petroleum with very different characteristics.

The generally accepted view is that **marine plankton** is the prominent source material for petroleum. However, accumulation of **other organisms**, such as **marine algae**, the remains of **larger marine animals** or even **material from terrestrial sources** are also considered to contribute significantly to the raw materials transformed to produce crude oil. This difference in the raw materials is responsible for the varying composition of crude oil. High-wax crude oils are from source materials containing high quantity of lipids from terrestrial higher plants and of microbial organisms. High-sulphur crude oils are frequently found in carbonate-type source rocks. Thus, the source rocks are equally responsible for variations and alteration of the petroleum's composition.

The source rocks, in the biogenic theory, must possess good permeability (fluid-transmitting capacity). The pores between the grains of the rocks are made of cavities which usually account for the bulk of the storage space (Figure 1.1). The pores for oil raw material storage and formation are from continuously connected openings which provide the property of permeability.

3.2.2 Transformation Process

As earlier stated, biogenic origin's theory postulates that crude oil is formed from the decayed remains of prehistoric marine animals and terrestrial plants over many centuries. These organic matters mixed with mud were buried under thick sedimentary layers of materials under high heat and pressure which caused reactions that made them metamorphose. The first was to produce a waxy material known as **kerogen.** This first process is the **diagenesis** stage. Then it breaks into liquid and gaseous hydrocarbons in a process called **catagenesis**. These reactions are thought to be temperature sensitive reactions that produce recognizable oil. These reactions commence from 50 – 130^{o}C to produce kerogen, and the reactions that continue the breakdown of oil to natural gas (catagenesis) commence at about 180^{o}C. The temperature range of 130^{o}C to 150^{o}C is generally considered the oil window. The reactions that produce oil and natural gas are often modelled as first-order breakdown reactions, where kerogen breaks down to oil and natural gas by a large set of parallel reactions, and oil eventually breaks down to natural gas by another set of reactions. The maturation processes of crude oil biogenic synthesis are therefore of three stages: diagenesis, catagenesis, and **metagenesis**. In diagenesis, there are concurrent and consecutive chemical reactions caused by microscopic aquatic organisms that were incorporated into the buried organic matter from the marine sediment at temperatures up to 50 ^{o}C and ultimately result in the formation of petroleum. The second stage known as catagenesis transforms the kerogen into liquid and gaseous hydrocarbons at a temperatures range of 130 ^{o}C to 200 ^{o}C. Metagenesis alters the organic matter to form petroleum at temperatures above 200 ^{o}C. There are three conditions for crude oil production based on this theory: the present for oil reservoirs to form a rich source rock; a migration conduit; a trap (seal) that forms the reservoir. Summarily, the oil is formed in a source rock, the produced crude oil then migrates through adjacent rock layers until they become trapped underground in rocks called reservoirs, forming an oil field, from which the liquid can be extracted by drilling and pumping (Figure 1.1).

3.2.3 Reservoir Rock

For a rock to serve as a reservoir rock for crude oil it must possess two qualities: **fluid-holding capacity (porosity)** and **fluid-transmitting capacity (permeability)**. The migrating crude oil from the source rock must be able to permeate the reservoir rock and the reservoir rock must be able to hold it from being further transmitted (Figure 1.1). The reservoir rock can possess these properties as a result of varieties of openings in the rocks such as the pores between the grains of which the rocks are made; the cavities inside fossils; the openings formed by solution or fractures; the joints that have been created in various ways among others. These different kinds of openings in the rocks vary from rock to rock types, but these pores are usually the ones that account for the bulk of the storage space. The effective porosity for oil storage results from continuously connected openings. These openings also provide the property of permeability. Thus, a rock must be porous to be permeable, but is no simple quantitative relationship between the two.

Reservoir rocks tend to vary more in permeability than in porosity. Additionally, these two properties are not always identical. The differences arise from the non-representative nature of cores, especially when there are wide variations in the sizes of the openings in the rocks and irregularities in their distribution. Porosity is generally in the range of 5% to 30%; whereas permeability is commonly between 0.005 darcy and several darcys as measured on small samples. It should be noted that pores maybe, at best, only a millimetre or so in width, whereas fossil and solution cavities may sometimes be 30 to 50 times wider. Many joints and fractures are probably only a millimetre across, although they may extend for considerable distances.

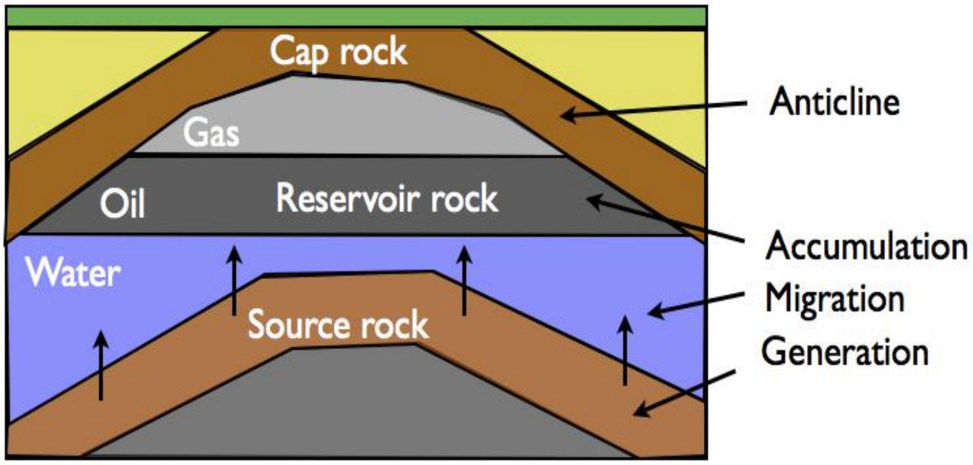


Figure 1.1: Diagram illustrating the formation, migration and accumulation of crude oil (Sourced Online)

3.2.4 Mechanisms of Petroleum Migration

The crude oil production process involves the transformation of the organic matter to crude oil over millions of years in a sedimentary source rock after which the crude oil migrates into an impermeable reservoir rock where the oil is kept for exploration. This migration can be by primary migration mechanism or by secondary migration mechanism. Primary migration involves the movement of hydrocarbons (crude oil and natural gas) from mature, organic-rich source rocks to a point where the oil and gas can collect as droplets or as a continuous phase of liquid hydrocarbon. The secondary migration on the other hand is attributed to various forces of buoyancy and hydrodynamics which cause the movement of the hydrocarbons as a single, continuous fluid phase through water saturated rocks, fractures, faults or conduits leading to accumulation of the oil and gas in traps (reservoirs) from which further migration is prevented. There are a number of complimentary mechanisms of the migration of the crude oil that have been proposed based on geological event and the corresponding migration effects as highlighted in the Table 1.1 below:

Table 1.1: Complimentary mechanisms of the migration of the crude oil

Geological Event	**Migration Effect**
Basin development	Downward fluid flow
Mature basin	Sediments move downward
Hydrocarbon generation	Thermal effects on source sediment
Hydrocarbons dissolve	Pore fluid become saturated
Geothermal gradient changes	Isotherms depressed
Pore fluids cool	Hydrocarbons form separate phase
Hydrocarbons separate	Move to top of carrier fluid (water)

Up-dip migration	Buoyancy effect
Intermittent faulting	Hydrocarbon migration to trap

In some cases the source and the reservoir rocks are in close proximity and migration is considered negligible. It is however not always the case that source beds coincides with reservoir rocks. The common belief is that migration of petroleum before it comes to rest in a trap is through large distances which can be in different direction including vertical migration depend on the prevailing force.

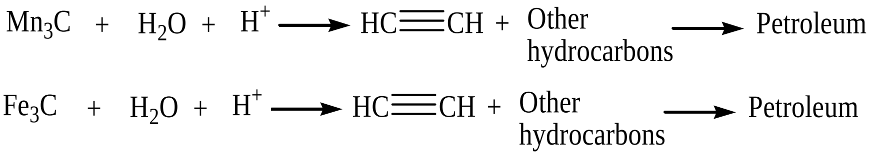
3.3 Abiogenic origin's theory

In contrast to the biogenic origin's theory discussed above, the early postulates about the origin of petroleum were that petroleum started with inorganic substances as source material. In 1866, Berthelot postulated that acetylene (C_2H_2) was the basic raw material for the production of crude oil constituents. The production process of acetylene was from inorganic carbides which were formed by the action of alkali metals on carbonates after which the reaction of the carbides with water will liberate acetylene.

$$CaCO_3 + \text{Alkali metal (Na, K)} \longrightarrow CaC_2 \text{ Calcium carbide}$$

$$CaC_2 + H_2O \longrightarrow HC{\equiv}CH \text{ acetylene} \longrightarrow \text{Petroleum}$$

Another postulate, by Mendelejeff, was that the reaction of dilute acids or hot water with manganese and iron carbides produces a mixture of hydrocarbons of which acetylene is considered to be the basic and prominent material from which petroleum evolved.



$$Mn_3C + H_2O + H^+ \longrightarrow HC{\equiv}CH + \text{Other hydrocarbons} \longrightarrow \text{Petroleum}$$

$$Fe_3C + H_2O + H^+ \longrightarrow HC{\equiv}CH + \text{Other hydrocarbons} \longrightarrow \text{Petroleum}$$

These and many other theories supporting production of petroleum from abiogenic origins are based on the assumption that large amounts of carbon exist naturally in the planet, some of which are in the form of hydrocarbons. These hydrocarbons are less dense than aqueous pore fluids in rock systems; therefore they migrate upward through deep fracture networks. This theory postulates that the biomarkers found in petroleum are as a result of microbial life dwelling the rocks in which petroleum is formed. The roles of the microbial life in the formation, alteration, component determination and/or contamination of the various hydrocarbon deposits are not yet fully explained by the theory.

A significant point at which this theory breaks down is that experimental studies and thermodynamic calculations have shown that at typical pressures of sedimentary rocks in which crude oil are generated (unless it is below 200 km), n-alkanes (common petroleum components) cannot be spontaneously evolve from methane. Moreover, empirical investigations (both chemical and geological) do not support the abiogenic origin concept. Thus, it is more generally accepted, though without conclusive proofs, that petroleum formation is predominantly from the decay of buried organic matters in the earth under pressure.

Despites the merits and demerits of the theories, until conclusive proofs are established that petroleum formation is due a specific geochemistry, alternative theories cannot be dismissed on origin of petroleum.

3.4 Differences between the theories

The differences between the biogenic and abiogenic theories are listed in the table 1.2 below:

Table 1.2: The Differences between Biogenic and Abiogenic Theories

Factor	Biogenic theory	Abiogenic theory
Raw Material	This theory postulated that crude oil is formed from remnants of plant and animal life buried in marine sediments.	Abiogenic theory postulated that crude oil is formed from deep carbon that was deposited in the rocks when the planet was formed.
Events before conversion	• There were large quantities of plant and animal life buried. • Sediments accumulated over the materials slowly create pressure by compressed it and covered it. • At a depth of several hundred meters temperature was developed, • Catagenesis converted the deposit to bitumen and kerogen.	• There are carbon deposits at depths of hundreds of kilometres. • The carbon deposits are a mixture of hydrocarbon molecules that leak upward through the crust. • Much of the material becomes methane
Conversion to petroleum and natural gas	• Catagenesis occurs with increase in the depth of the buried organic matters. • The heat and pressure breaks down kerogen to form	• The methane is converted to heavier hydrocarbons when the material passes through

(methane)	petroleum. • Recent advances in the understanding of chemical processes and organic reactions and significant improvement in knowledge about the effects of heating and pressure during burial and diagenesis of organic sediments support biogenic processes.	temperatures at which extremophile microbes can survive but some of it is consumed.

3.5 Petroleum Occurrence

There are a number of crude oil fields in different countries. An oil field is made up of a number of crude oil wells. Large portion of the crude oil currently explored are from underground reservoirs wells. Surface seepages of crude oil and natural gas occur in many regions and was particular the starting point for the usage of the high boiling material before underground exploration. The occurrence of majority of crude oil reserves recently identified is located in a relatively small number of very large fields. Almost 75% of the global crude oil supply is from about three hundred large oil fields. These fields are primarily concentrated in few countries like Saudi Arabia, Russia, Nigeria, United States, Iran, Norway, Mexico, Venezuela, China, Iraq, Great Britain, the United Arab Emirates, and Kuwait. The Middle East has the largest known reserves. These countries determine the global crude oil supply, price and economics.

4.0 SUMMARY

There are two popular theories about the sources of crude oil: biogenic and abiogenic theories. The biogenic theory postulates that crude oil is from remnants of plant and animal life buried in marine sediments under pressure in source rock over millions of years. The remnants were transformed through three stages: diagenesis, catagenesis, and metagenesis into maturity after which it migrates into a reservoir. Contrary to the postulate of the biogenic origin's theory, the abiogenic theory postulates about the origin of petroleum were that petroleum started with inorganic substances as source material. It postulated that deep carbon, acetylene (C_2H_2), that was deposited in the rocks when the planet was formed was the basic raw material for the production of crude oil constituents. The production process of acetylene was from inorganic carbides which were formed by the action of alkali metals on carbonates after which the reaction of the carbides with water will liberate acetylene. The more commonly accepted theory is the biogenic theory.

5.0 CONCLUSION

This unit discussed the theories about the origin of crude oil which are biogenic and abiogenic theories and concludes that the biogenic theory is more widely accepted. The transformation processes and the qualities of the source and reservoir rocks were also discussed and it was concluded that the composition of crude oil in a specific oil well or field is related to the source raw materials, the source rock and the reservoir rock properties among others.

6.0 TUTOR MARKED ASSIGNMENTS

1. Discuss the transformation process of the plant and animal remnants into crude oil in the biogenic theory of crude oil origin.
2. With relevant equations of reaction, explain the abiogenic theory of crude oil origin.
3. Differentiate between biogenic and abiogenic theories of crude oil origin.

7.0 REFERENCES AND OTHER RESOURCES

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UNIT 2 COMPOSITION OF CRUDE OIL

CONTENTS

1.0 INTRODUCTION

Crude oils are from different sources, generated from different raw materials and source rocks as discussed in Unit 1. They are stored in different reservoir rocks. As a result of these the chemical composition of crude oil varies from crude oil field to field and even from one well to another well in the same field. The composition of crude oil however determines the economic value, in particular the demand for it and the selling price. This unit is therefore developed to explain the various general components of crude oil which is not necessarily a uniform composition.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- identify the different components of crude oil;
- differentiate between the different components, their importance and effects on the cost and processing of crude oil;
- identify crude oil properties and classify crude oil based on different factors.

3.0 MAIN CONTENT

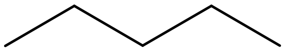
3.1 Hydrocarbons

Crude oil is considered the major source of hydrocarbon in nature because the principal components of crude oils are hydrocarbon compounds. Crude oil contains alkane of all types but not alkenes and alkynes except during processing (like thermal cracking) where alkenes are produced. This section will give descriptions of the various hydrocarbons found in crude oil.

3.1.1 Alkane (Paraffin)

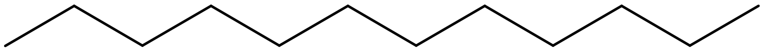
Alkane is a class of straight and branched chain saturated hydrocarbons. It has the general formula C_nH2_{n+2}. Alkane is the major component of crude oil. Its simplest form is when n=1 which is CH_4: methane. This methane is the principal component of natural gas. Other alkanes, ethane (n=2), propane (n=3), and butane (n=4) are also gaseous at atmospheric temperatures and pressure. Crude oil contains straight-chain saturated hydrocarbons (i.e. no branches) are often referred to as normal alkanes (n-alkanes, n-paraffin). Branched alkanes on the other hand are saturated hydrocarbons with an alkyl substituent or a side branch from the main chain. Alkane in crude oil is the basis of the application of its fraction in fuel such as liquefied natural gas (LNG), petroleum motor spirit (PMS) which is gasoline among others.

Examples of some of the straight chain alkanes in crude oil:



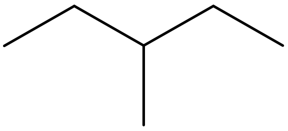
n-pentane

n-hexane

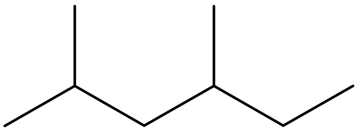


dodecane

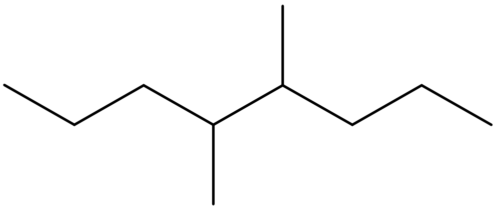
Examples of some of the Branched chain alkanes in crude oil



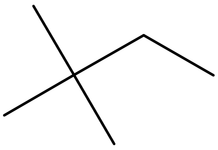
3-methylpentane



2,4-dimethylhexane



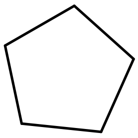
4,5-dimethyloctane



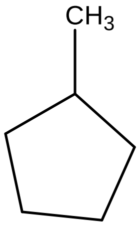
2,2 dimethylbutane

3.1.2 Cycloalkanes (Naphthenes)

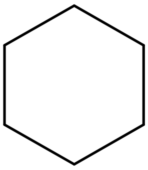
Another class of hydrocarbons that are commonly found in crude oil is the saturated cyclic hydrocarbons normally known as naphthenes. This class is also an important part of the hydrocarbon constituents of crude oils. Their ratio is used to define the type of crude from a well. The type of crude oil can be said to be paraffinic (i.e. containing more of saturated straight and branched chain hydrocarbon) or naphthenenic type (containing more of saturated cyclic hydrocarbon). The lower members of naphthenes are cyclopentane, cyclohexane, and their mono-substituted compounds.



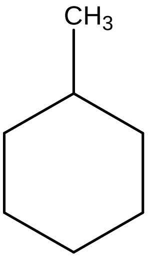
cyclopentane



methylcyclopentane

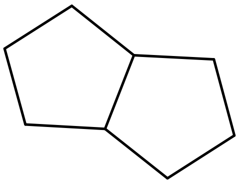


cyclohexane

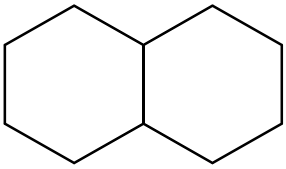


methylcyclohexane

These low members of naphthenes are prominent in the light and the heavy naphtha fractions and are precursors for aromatic hydrocarbons. Methylcyclopentane and cyclohexane can be used to produce benzene while Methylcyclohexane can be dehydrogenated into toluene. Heavier petroleum fractions such as kerosene and gas oil may contain two or more fused cyclohexane rings and other bicyclic hydrocarbons up to C_{19} to C_{22} range.



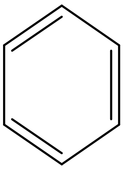
octahydropentalene

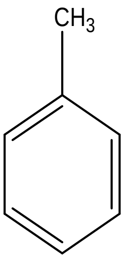


decahydronaphthalene or decalin

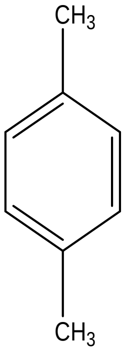
3.1.3 Aromatics

The last class of hydrocarbon present in crude oil is the aromatics. Aromatic compounds such as the simple mononuclear aromatic compounds: benzene (C_6H_6), toluene (C_7H_8) and xylene (C_8H_{10}) are present in crude oils but with varying amounts based on crude oil type. These low members of aromatic compounds are in small amounts in both crude oils and light petroleum fractions.

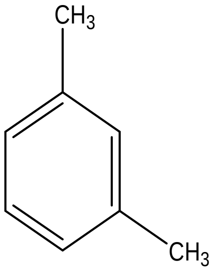

benzene



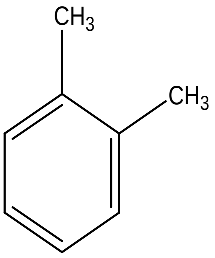
toluene



p-xylene

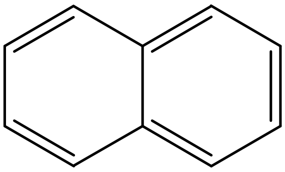


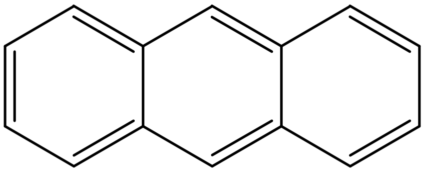
m-xylene

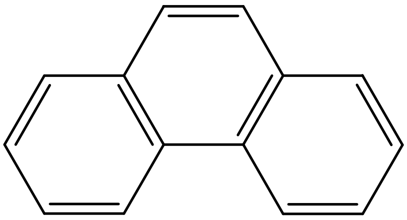


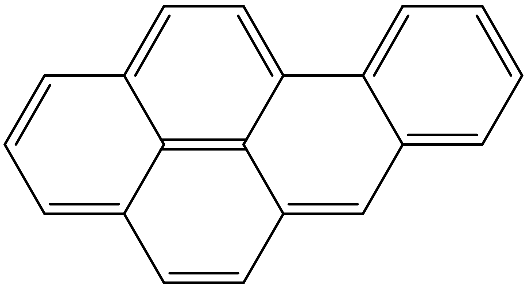
o-xylene

These aromatic components of crude oil - benzene, toluene, and xylenes (BTX) are valuable intermediates for petrochemical productions and are also valuable components of gasoline fraction because they improve its octane rating. Binuclear, Trinuclear and polynuclear aromatic hydrocarbons are also found in crude oil and are present in the heavier fractions of the crude oil distillation process. Some of such are:


naphthalene


anthracene


phenanthrene


benzo-a-pyrene

Other aromatic compounds are the heterocyclic compounds (to be discussed in the next section under non-hydrocarbons). They are found more in the heavy crudes and crude residues. Asphaltenes are terms used for complex mixtures of aromatic and heterocyclic compounds.

3.2 Non-hydrocarbon Compounds

There are four key types of non-hydrocarbon compounds that occur in crude oils and in the refinery streams after distillation. They are the organic sulphur, nitrogen, oxygen and traces of metallic compounds. The presence or absence of these compounds has impact on its economic value and sales. Crude with less sulphur compounds are more valuable in the oil market. This is because impurities poison the catalysts used in the catalytic processes for crude oil conversions. Moreover, production of fuels having high sulphur and nitrogen contents raise environment pollution concern. These compounds also have corrosion promotion tendencies which can negatively affect the pipelines and the refinery facilities.

3.2.1 Sulphur Compounds

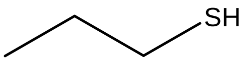
The presence of sulphur in crude oils is not in elemental form but mainly as organosulphur compounds. It may however also be present as hydrogen sulphide (H_2S) which is the only inorganic sulphur compound found in crude oil. The presence of both H_2S and organosulphur compounds is harmful because of their corrosive nature. Organosulphur compounds present in crude oil can either be in form of acidic and non-acidic compounds.

Acidic sulphur compounds are the one that have sulphur-hydrogen bonds (-SH) that can donate proton such as thiols (mercaptans):

alkyl mercaptan

$R-SH$

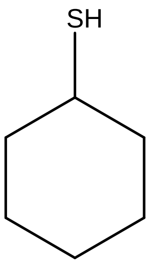
such as



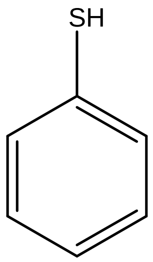
propane-1-thiol

CH_3SH

methyl mercaptan



cyclohexanethiol



benzenethiol

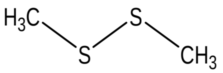
The non-acidic sulphur compounds found in crude fractions are in forms of thiophene, sulphides, and disulfides:

R-S-R

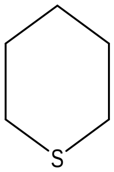
CH_3SCH_3

dimethylsulphide

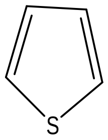
R-S-S-R



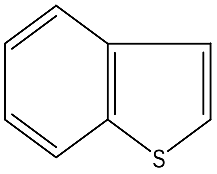
dimethyldisulphide



tetrahydro-2*H*-thiopyran



thiophene



benzo[*b*]thiophene

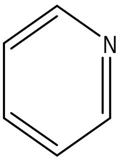
Crude oil can be sour or sweet depending on the sulphur content. Sour crudes contain hydrogen sulphide in high percentage. This classification of crude oil sales based on the sulphur content affect its sales in the global oil market. This is possible because many organic sulphur compounds are heat sensitive thereby generating hydrogen sulphide in the cause of crude processing. Crudes with high-sulphur are less desirable because treating the different refinery streams for acidic hydrogen sulphide increases production costs. Hydrogen sulphide is often removed by either absorption in a suitable absorbent or oxidation of H_2S to recover the sulphur as solid material.

3.2.2 Nitrogen Compounds

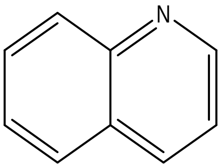
A number of organic nitrogen compounds occur in crude oils. They are mostly found in simple heterocyclic form as pyrrole (C_4H_5N) and pyridine (C_5H_5N). Another significant nitrogen based compound is a complex structure of porphyrin. Generally, the nitrogen content in most crude oils is lower than 0.1 wt%. However, in heavy crudes, the percentage content of the nitrogen based compounds may be up to 0.9 wt %. Nitrogen and sulphur compounds are not desirable in crude because of the poisoning effect of catalysts during crude oil processing. They should be removed during processing using hydrotreatment of petroleum fractions, nitrogen compounds are hydrodenitrogenated to ammonia and the corresponding hydrocarbon. This need for removal impacts significantly on the cost of the petroleum.

Nitrogen compounds present in petroleum may be grouped into basic nitrogen compounds and non-basic nitrogen compounds. The basic compounds are mainly those with pyridine ring, and the non-basic compounds are with pyrrole structure. Examples of the two classes of organic nitrogen compounds are presented below:

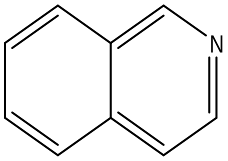
Basic nitrogen compounds



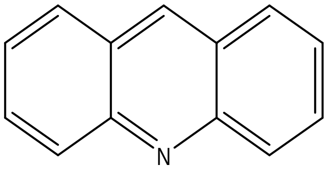
pyridine



quinoline

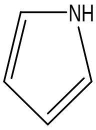


isoquinoline

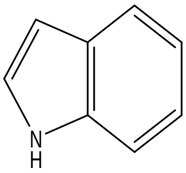


acridine

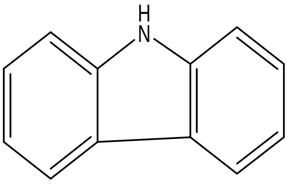
Basic nitrogen compounds



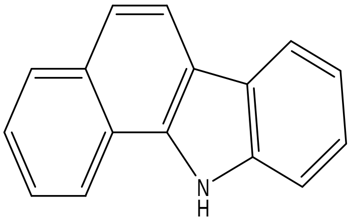
pyrrole



indole



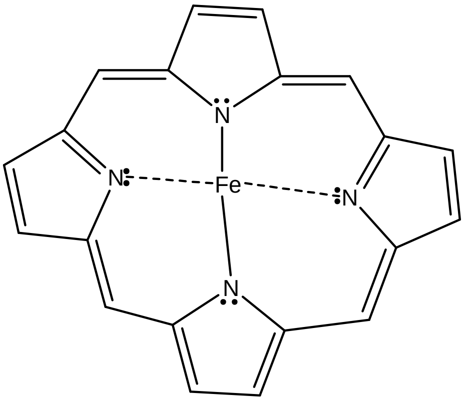
carbazole



benzocarbazole

Porphyrins

Porphyrins are another important nitrogen based compounds. They are complex derivatives of the basic material, porphine. These compounds are used to characterise crude oil and support the biogenic theory of crude oil origin. They are recognized as the degradation products of the chlorophyll and of the hemes (haems) and hematins (haematins), the respiratory pigments of both plants and animals which are in the deposit that form petroleum.



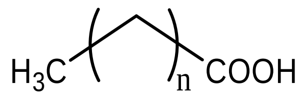
3.2.3 Oxygen Compounds

Another very important component of crude oil is the oxygen based compounds. They are more complex than the sulphur and nitrogen types but do not constitute poison to crude oil processing catalysts. They do not therefore impact negatively on the price of petroleum. Oxygen compounds found in crude oils may be weakly acidic such as carboxylic acids, cresylic acid, phenol, and naphthenic acid or non-acidic like ethers, esters, carbonyls, amides among others.

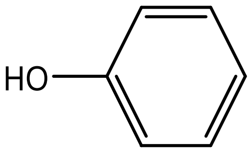
The non-acidic oxygen compounds are often less abundant than acidic compounds in most crude oil well and are often of no commercial value compared to the acidic oxygen compounds.

Below are some examples of the oxygen compounds commonly found in crude oils:

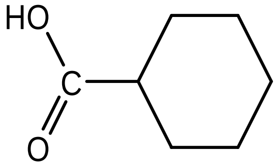
Acidic oxygen compounds



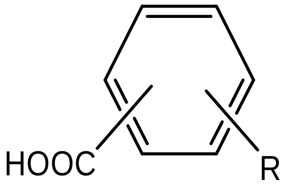
aliphatic carboxylic acids



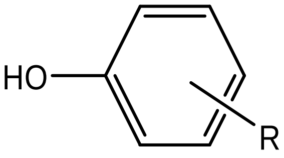
phenol



cyclohexane carboxylic acid

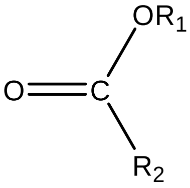


Aromatic acids

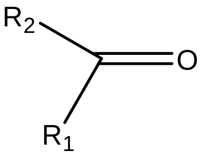


Cresylic acids

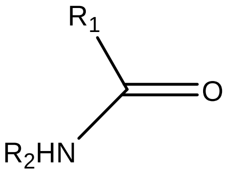
Non-Acidic oxygen compounds



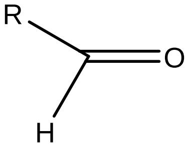
esters



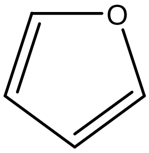
ketones



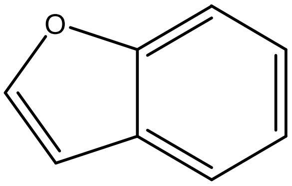
amides



aldehydes



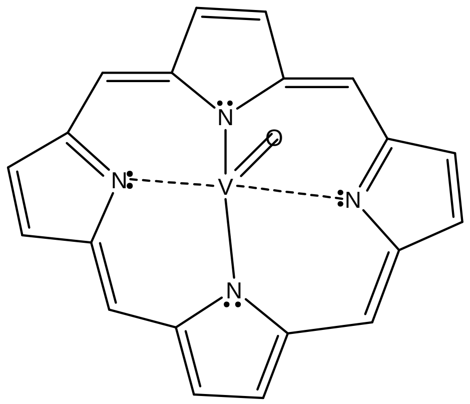
furan

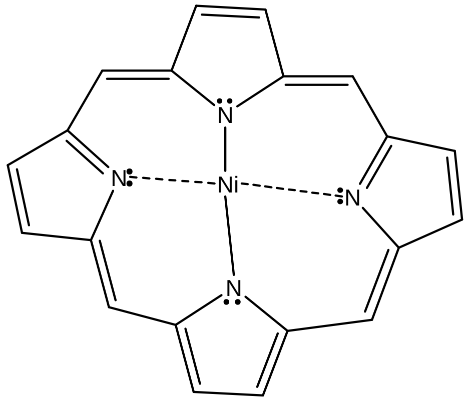


benzofuran

3.3 Metallic Compounds

In the section of nitrogen based compounds, we discussed the porphyrin material in crude oils. These porphyrin rings are mostly completed with a metal. The most important of these metals is vanadium, followed by nickel. Other metals like iron and copper may also be present.





Out of all the metals in the periodic table, only V and Ni have been proven to definitely exist as chelates in significant amounts in a large number of fossil fuel such as crude oils and tar sand bitumen. In general, the organic detritus of sediments from which crude oil is formed varies with the environment since aquatic organisms are different in their chemical makeup. This contributes to the variation in petroleum types: gross differences and structural variations of petroleum constituents. The understanding of the differences is very important in source apportionment of petroleum. Thus, Ni/V ratio is used to investigate variations in the source materials and also variations in the conditions (geophysical) under which the petroleum was formed (Yakubov *et al.*, 2016).

Many other metals occur in crude oils but not in the chelate organic forms. Sodium, calcium, magnesium, aluminium, iron, are present as inorganic salts, such as sodium and magnesium chlorides. Although these metals in crudes are found in trace amounts, their presence is not desirable in petroleum and should be removed. Calcium and magnesium can form salts or soaps with carboxylic acids and act as emulsifiers making crude oil separation from water difficult. Sodium and magnesium chlorides generate hydrochloric acid which will corrode the crude oil processing facilities. Desalting of crude oils to remove sodium and magnesium chlorides is a necessary. Vanadium and nickel can poison many of the catalysts used in crude oil conversion processes. Most of the vanadium and nickel compounds are concentrated in the heavy residues.

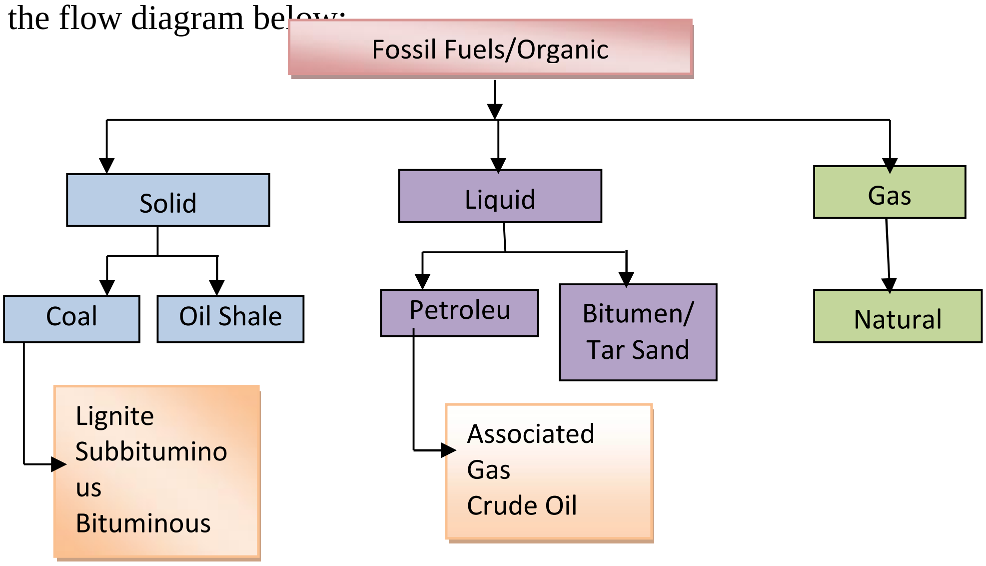
Overall, crude oil is made up of

Carbon - 83.0% to 87.0%
Hydrogen - 10.0% to 14.0%
Nitrogen - 0.1% to 2.0%
Oxygen - 0.05% to 1.5%
Sulphur - 0 .05% to 6.0%
Metals (Ni and V) - <1000 ppm

3.4 Crude oil Classification

The classification of petroleum can be done using many factors. It can be classified as hydrocarbon source based on physical state together with other fossil fuels. It can also be classified based on their chemical composition; based on density or American Petroleum Institute (API) gravity; based on viscosity; based on carbon distribution; correlation index among others.

The classification as hydrocarbon source includes the other fossil fuel as in the flow diagram below:



In summary, petroleum and natural gas are classified as naturally occurring mixtures of hydrocarbons which can be separated into their original hydrocarbon constituents which have not been altered by any applied process. The hydrocarbon constituents, separated from petroleum and natural gas, are the hydrocarbon constituents that existed in the reservoir. Naturally occurring hydrocarbons are major contributors to the composition of petroleum and natural gas.

Another classification of crude oil is based on the hydrocarbon chemical composition of crude oil. Petroleum is therefore classified as:

- Paraffinic: these are crude oils that contain saturated hydrocarbons with straight or branched chains in large quantity but with less quantity of ring structure.
- Naphthenic (Cycloparaffins):Crude oil with high ratio of saturated hydrocarbons containing one or more rings each are classified as naphthenic crude oil. The ring may have one or more paraffin side-chains. This structure is also known as alicyclic hydrocarbons.
- Aromatics: These are crude oil with hydrocarbons containing large quantity of one or more aromatic nuclei such as benzene, naphthalene, and phenanthrene ring systems. The aromatic rings may be substituted with naphthalene rings or paraffin side-chains.

The table 2.1 below gives a summary of chemical composition of the various classes of petroleum based on these three components:

Table 2.1: Chemical composition of the various classes of Petroleum

Crude Oil Classification	Paraffin (%	Naphthene (%)	Aromatic (%)	Wax (%)	Asphalt (%)
Paraffinic	46 – 61	22 – 32	12 – 25	<10	<6
Paraffinic–Naphthenic	42 – 45	38 - 39	16 – 20	<6	<6
Naphthenic	15 – 26	61 – 76	8 – 13	0	<6
Aromatic	<8	57 – 78	20 – 25	<0.5	<20
Paraffinic–Naphthenic-Aromatic	27 – 35	36 - 47	26 - 33	<1	<10

The use of density to classify crude oil is also well accepted. Density (specific gravity) is the principal, and the main specification of crude oil products used as an index of the proportion of gasoline and, particularly, kerosene in crude oil fraction. Crude oils of various types are also rated by specific gravity similar to gasoline and naphtha within certain limits of other properties. The use of density values is converted to American Petroleum Institute (API) gravity using:

$$API = \frac{141.5}{Specific\ gravity\ (at\ 60^{\circ}F)} - 131.5$$

The API gravity expresses the relative masses of crude oils. A low API gravity indicates a heavier crude oil, while a higher API gravity means a lighter crude oil. Specific gravities of crude oils roughly range from 0.82 for lighter crudes to over 1.0 for heavier crudes. This is used to classify crude oil into three categories of paraffin, intermediate, or naphthene base crude oil. Investigation of crude oils from worldwide sources has shown that 85% fell into one of these three classes. Crude oil fractions with API gravity >30.0 is paraffin based (specific gravity < 0.876) while API gravity in the range of 20.1–29.9 is intermediate between paraffin and naphthene and API gravity between <20 is naphthene based (specific gravity > 0.934).

3.5 Crude oil properties

Crude oil properties differs base on origin and the ratio of the different components in the mixture and influence the economic value. For instance, light crude oils yield more light and middle distillates like gasoline which are sold at higher prices making it more valuable. Conversely, crudes containing high quantities of impurities (sulphur and nitrogen compounds) are less desirable because of their adverse effect on catalyst, reaction vessel and pipelines. This implies extra treating cost. Thus the properties of crude oil give the first-hand information about the crude and its value.

The following are some of the important crude oil properties determined by specific tests:

Density, Specific Gravity and API Gravity

The density of crude oil is the express of the mass of unit volume of the crude oil at a specific temperature. The property is determine by a specific gravity bottle and can be reported as API gravity as expressed above.

Salt Content

The salt content of crude oil is expressed in milligrams of sodium chloride per litre of the oil (or in pounds/barrel). It is an indicator of the amount of salt dissolved in water which is present in emulsified form with the crude oil. A high salt content is not desirable in a crude oil because of serious corrosion problems associated with it in the refining process. Salt content that is high is also responsible for plugging heat exchangers and heater pipes. Therefore, if salt content is higher than 10 lb. (NaCl)/1,000barrels of oil, the crude oil must be desalted.

Sulphur Content

As expressed in section 2.4.1, sulphur compounds can be present in crudes. Knowledge of its quantity is important because the amount of sulphur determines the type of treatment required in the refining processes. Determination of sulphur content is carried out by weighing crude oil sample and burning it in air stream to oxidize it to sulphur dioxide and finally to sulphur trioxide. The SO_3 is dissolved in water to give H_2SO_4 and titrated with a standard alkali. Sulphur compounds are easily treated by hydrodesulphurization to produce hydrogen sulphide and the corresponding hydrocarbon.

Pour Point

The lowest temperature at which a crude oil or its product is observed to flow under the test conditions is the pour point of the oil. It is an indicator of the quantity of petroleum wax i.e. long-chain hydrocarbon found in the crude oil. Paraffinic class of crude oil contains higher wax content than other crude types. The pour point of oil is important because the handling and transportation of crude oils and heavy fraction is difficult at temperatures below their pour points. At such temperature, the oil will refuse to flow unless chemical additives (i.e. pour point depressants) are used to improve the flow properties of the fuel. The presence of long-chain n-paraffin of carbon 16–60 atoms will cause a near-ambient temperature precipitation and stop the flow of the oil.

Ash Content

Ash content is used to determine the amount of metallic constituents in a crude oil. Ash are inorganic components that cannot be volatilized at high temperature. The CHNOS components of the crude oil can be oxidized during the ashing process in which there is complete burning the oil to give the stable metallic salts, metal oxides, and silicon oxide. The residual ash could be further analysed for individual elements using atomic absorption spectroscopic techniques.

4.0 SUMMARY

Unit 2 discussed the components of crude oil which are predominantly hydrocarbon. The hydrocarbon components can be either straight or branched chain saturated hydrocarbon (paraffin or alkane) or cyclic hydrocarbon (naphthenes) or aromatics. Crude oils also contain significant quantities of non-hydrocarbon compounds in varying percentage from one crude oil source or well to another. The non-hydrocarbon compounds are sulphur based compound, nitrogen based compound and oxygen based compounds which are not desirable because of their negative effects on the environment and on catalysts used in crude oil refining processes. Beside these, crude oil also contains significant quantity of metals that are source related and also have negative effects on the catalytic refining processes. This unit finally discussed the classification of crude oil into paraffinic, naphthenic and aromatic classes based on percentage composition of these compounds. The survey of crude oil properties was also discussed in the unit.

5.0 CONCLUSION

The components of crude oil are generally the same classes of compounds but their percentage composition vary from well to well or field to field. Ni/V ratio is used to investigate variations in the source materials and also variations in the conditions (geophysical) under which the petroleum was formed. Crude oil is generally classified based on the percentages of paraffin, nathphene and aromatic content. It can also be differentiated in the global oil market into sweet and sour crude based on the sulphur content. To understand crude oil, determination of its properties like API gravity, salt content, sulphur content, ash content, pour point among others is very essential.

6.0 TUTOR MARKED ASSIGNMENTS

1. With the aid of suitable structural illustrations, describe the hydrocarbon contents of crude oil.
2. Using appropriate examples, describe the non-hydrocarbon contents of crude oil.
3. Discuss crude oil classifications.
4. Briefly highlight the different properties of crude oil and their significance.

7.0 REFERENCES AND OTHER RESOURCES

James G. Speight 2006. The Chemistry and Technology of Petroleum by CRC Press 4th Edition Taylor & Francis Group, Boca Raton, USA, ISBN-13: 978-0-8493-9067-8, 955pgs.

Sami Mata and Lewis F. Hatch 2000. Chemistry of Petrochemical Processes 2nd Edition by Gulf Publishing Company, Houston, Texas, 406pgs.

Yakubov, M. R., Milordov, D. V., Yakubova, S. G., Borisov, D. N., Ivanov, V. T., & Sinyashin, K. O. (2016). Concentrations of vanadium and nickel and their ratio in heavy oil asphaltenes. Petroleum Chemistry, 56(1), 16–20. doi:10.1134/s0965544116010072

UNIT 3 COMPOSITION OF REFINED OILS

CONTENTS

1.0 INTRODUCTION

Crude oil is less useful unless subjected to refining processes. The refining of petroleum involves subjecting the crude oil feedstock to a series of physical and chemical processes to obtain varieties of products that are valuable for energy generation, petrochemical products and lots of consumer products such as polymers, detergent, pharmaceuticals, pesticides among others. The first process is the physical process which includes distillation of the constituents of the crude oil feedstock and isolating different fractions. This does not change the chemical composition of the crude oil components. The other is the chemical conversion processes which are either thermal or catalytic conversion processes. It may be cracking or reforming/isomerization process. This section will focus on only the physical refining processes.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- identify the different physical refining processes of crude oil
- identify the different fraction of crude oil and their components
- differentiate between the various fractions of crude oil based on their components.

3.1 Physical Refining Processes

The crude oil refining process start with removal of salt and water from the raw crude oil from the exploration well which is then followed by the distillation processes (atmospheric and vacuum distillation.

3.1.1 Desalting and Dewatering

The very first step in the separation of petroleum into its various constituents is the cleaning of the crude oil by desalting and dewatering it. The aim is to remove water and brine that do always accompany crude oil after exploration from its reservoir into the wellhead. Petroleum upon recovery from the reservoir contains a number of components such as gases, water, and mineral salts/dirt. The pre-treatment operations desalting and dewatering are applied to the crude oil prior to sales/transportation and refining. This quality improvement is require for the shipping/pipeline transportation of the crude to guide against corrosion of the vessels. It is also required for crude oil buyer's specification to guide against causing operating problems such as equipment plugging and corrosion, catalyst deactivation during refinery processing.

Desalting involves water washing operation (Figure 3.1). The process involves the feeding of unrefined crude contains water and dirt using a pump through a heater. The process water is added with another pump and an emulsifier, to aid the mixing and water-washing, before the mixture is charged into an electrostatic desalting unit (gravity settling tank). In the tank, the electric power breaks the emulsion and the water separate from the crude oil. The water washing removes much of the water-soluble minerals and entrained solids and the water settles at the lower part of the tank being denser than the crude oil. The desalted water is collected at the upper part of the tank (Figure 3.1)

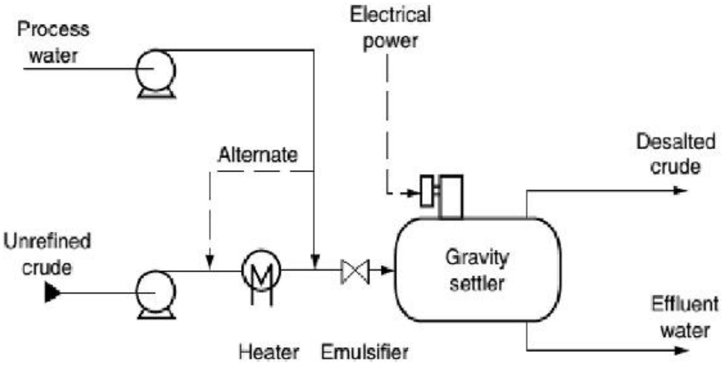


Figure 3.1: Flowsheet of Crude Oil Desalting process (Speight 2006)

3.1.2 Atmospheric Distillation

After desalting and dewatering, the desalted crude oil is charged as feed into the petroleum distillation unit. A fractional distillation tower is used as modern-day refinery (Figure 3.2). This tower brings about efficient fractionation (separation). The feeding process of the petroleum into the distillation tower involves pre-heating by flow-through pipes (i.e. pipe still heater or pipe still furnace) arranged within a large furnace. The heated crude enters into the fractional distillation tower which forms an essential part of the distillation unit. The pipe still furnace performs that heating of the feed to a predetermined temperature at which each fraction in the feed changes into vapour. The vapour is held under atmospheric pressure in the furnace pipe until it is discharges as feed stream into the fractional distillation tower. The feed pass up inside the tower is then fractionated according to the boiling temperatures into gas, gasoline, heavy naphtha, kerosene and gas oils (Figure 3.3). These fractions will be discussed in detail in section 3.4.

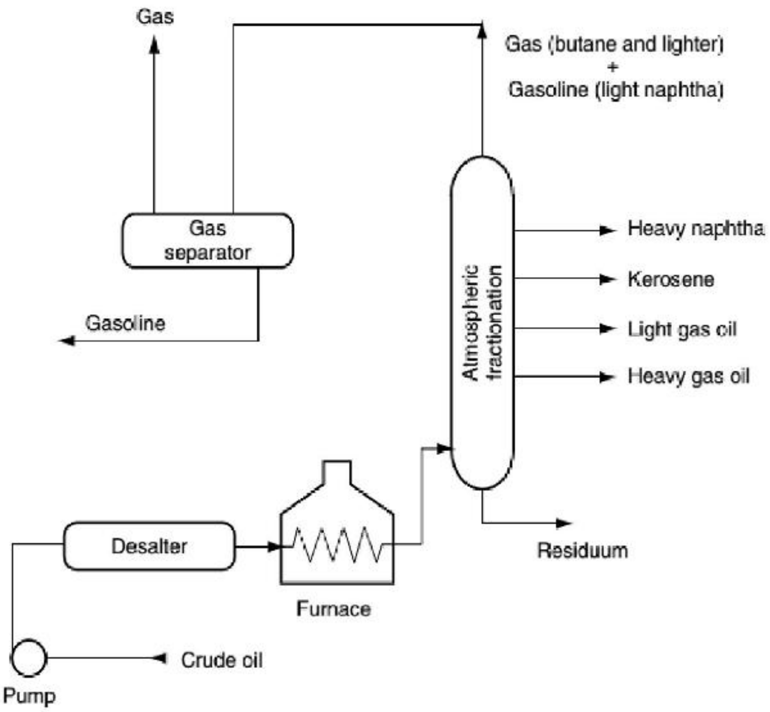


Figure 3.2: Flowsheet of Atmospheric Distillation Process Crude Oil (Speight 2006)

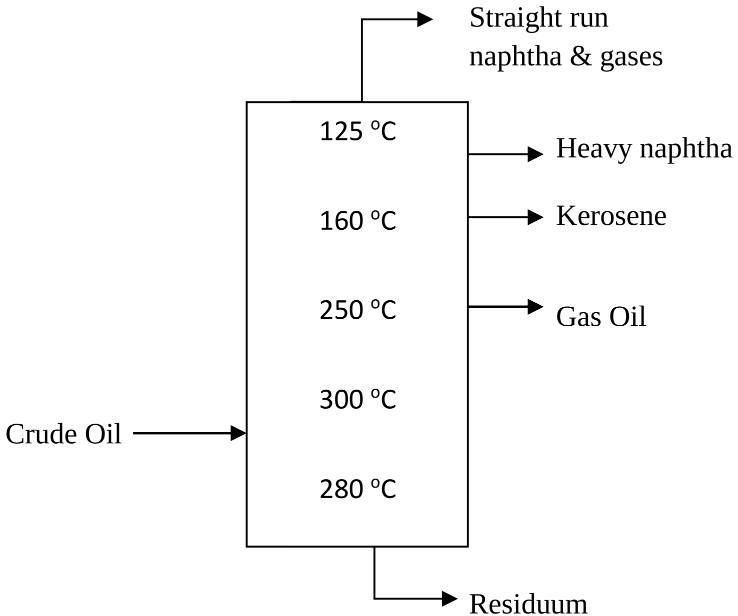


Figure 3.3: The fraction separation temperatures in the distillation column

3.1.3 Vacuum Distillation Process

The lower boiling fraction (Residuum) from the atmospheric distillation is used as the feedstock for the vacuum distillation. Vacuum distillation evolved because of the need to separate the less volatile products, such as lubricating oils, from the petroleum without subjecting the crude oil to high temperature that can lead to cracking conditions. If atmospheric distillation is used, the heaviest boiling fraction obtainable without cracking is limited by the temperature to 350 °C. Vacuum distillation process is therefore a more recent technique and has since been widely used in petroleum refining to address the drawback of cracking at high temperature in atmospheric distillation.

Vacuum distillation (Figure 3.4) operates in a way similar to atmospheric distillation with an additional feature of a vacuum which create a pressure of 50 to 100 mmHg (¼ of the atmospheric pressure 760 mmHg). A vacuum tower is often of larger diameter (14 m) than the atmospheric units so as to minimize pressure fluctuation in the units.

As a result of the operation of vacuum, heavy gas oil is obtainable in the distillation tower at temperatures of about 150 °C and lubricating oil at temperature range of 250 °C to350 °C. In the vacuum tower, the feed and residue temperatures should be kept below the temperature of 350 °C, to avoid cracking. The vacuum residuum is often applied as asphalt.

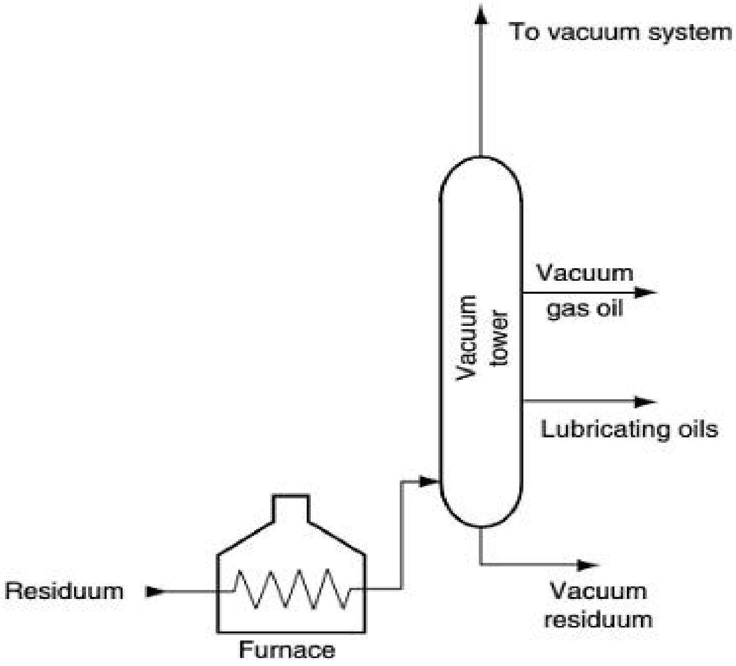


Figure 3.4: Flowsheet of Vacuum Distillation Process Crude Oil (Speight 2006)

3.2 Petroleum Fractions and their components

The petroleum fractions obtained from the distillation towers can be generally classified as gases and naphtha, middle distillates and heavy fraction. This section focuses on the components of these fractions.

3.2.1 Gases and Naphtha

The main hydrocarbon component of petroleum gases is methane. There are however other higher hydrocarbon compound in lesser quantities. Ethane, propane, butane, isobutane are present depending on the nature of the crude oil. There may be presence of other non-desirable gases, such as hydrogen, carbon dioxide, hydrogen sulphide, and carbonyl sulphide which must be removed in the processing.

Naphtha fraction covers the boiling range of gasoline and is made up of mainly saturated constituents with small amounts of aromatics (mono- and di). Unfortunately, most of the raw petroleum naphtha molecules have low octane number and not valuable for direct application in gasoline. The raw naphtha is processed further by reforming, isomerization and combined with other process naphtha and additives to formulate commercial gasoline. The saturated constituents in petroleum gases and naphtha are paraffin from methane (CH_4) to n-decane (n-$C_{10}H_{22}$).

The naphtha fraction is the low boiling paraffin which may be the most abundant compound in a crude oil depending on the source of the crude oil. The paraffin in the naphtha begin at C4 with isobutane as the only isomer. Additionally, the saturated constituents of naphtha fraction include cycloalkanes (naphthenes) with five- or six-carbon rings being the most prominent. Naphthenes such as methyl derivatives of cyclopentane and cyclohexane are more common than the parent unsubstituted structures. Fused ring dicycloalkanes such as cis-decahydronaphthalene (cis-decalin) and trans-decahydronaphthalene (trans-decalin) are also found in naphtha fraction. Finally, petroleum naphtha contains numerous aromatic constituents beginning with benzene and its C1 to C3 alkylated derivatives, benzene derivatives having fused cycloparaffin rings such as tetralin, and naphthalene are all included in this fraction. However, the 1- and 2-methyl naphthalene and higher homologs of fused two-ring aromatics appear in the middle distillate fraction.

3.2.2 Middle Distillates

The middle distillate is the raw material (the feedstock) for kerosene, aviation jet fuel, and diesel fuel production. The mid-distillate fraction of petroleum is rich in saturated species but in contains some quantities of naphthenes and aromatics (either simple single ring compounds: BTX or fused rings with up to three aromatic rings, or fused with heterocyclic compounds). Within the saturated constituents of the middle distillates, the concentration of n-paraffin is regularly from C_{11} to C_{20}. Mono- and di-cycloparaffins with five or six carbons per ring constitute the bulk of the naphthenes in the middle distillate boiling range. The most prominent aromatics in the mid-distillate boiling fractions are the di- and tri-methyl naphthalenes. Other one- and two-ring aromatics are also present but in small quantities.

Kerosene (stove oil) and light gas oil fractions are the most prominent products of the middle distillates of the crude oil physical process and usually represent the last fractions to be separated by distillation at atmospheric pressure. These middle distillates leave the fractions from the heavy gas oil and higher boiling material. In this middle distillate is also the vacuum gas oil which has less saturate constituents compared to the aromatic constituents. The vacuum gas oil is used often as heating oil and as feedstock for diesel fuel. Its most commonly subjected to catalytic cracking to produce naphtha (gasoline feedstock) or extracted to yield lubricating oil. In this vacuum gas oil, the various components' distribution such as saturates (paraffin or iso-paraffin) and naphthenes are dependent on the crude oil source and type. Nevertheless, naphthene constituent is about 60-70% of the saturate constituents unlike the lower boiling fraction that is more of paraffin. The paraffin from C_{20}–C_{44}arestill present in sufficient quantity in the vacuum gas oil.

3.2.3 Heavy Fractions

The heavy fractions often referred to as the low boiling fraction or the vacuum residua for the vacuum distillation are the most complex of petroleum. It contains the majority of the heteroatoms components of the crude oil. The molecular weight of the constituents range up to several thousands. This vacuum residua fraction is so complex that it cannot be characterized individually. Separation of vacuum residua by group type is made difficult by the multi-substitution of aromatic and naphthenic species and the presence of multiple functionalities in single molecules present. This fraction is often the feedstock for thermal cracking or catalytic hydrocracking. It is not often used for direct catalytic reforms and cracking without hydro-treatment because of the presence of heteroatoms that can poison the catalyst and metals like Ni, V that can promote side reactions.

3.3 Chemical Refining Processes

The chemical conversion/refining processes in the petroleum industry are generally used for the following purposes:

1. To upgrade lower-value materials such as heavy residues to more valuable high demand products such as naphtha and LPG. Naphtha is mainly used to supplement the gasoline pool, while LPG is used as a fuel or as a petrochemical feedstock. Thus,

these two products are in higher demand than the others and are produced from the others by chemical conversion processes.

2. To improve the characteristics of a fuel. For example, a lower octane naphtha fraction is reformed to a higher octane reformate product. The reformate is mainly blended with naphtha for gasoline formulation or extracted for obtaining aromatics needed for petrochemicals production.
3. Reduce harmful impurities in petroleum fractions and residues to control pollution and to avoid poisoning certain processing catalysts.

This section will discuss the thermal and catalytic cracking as examples of chemical refining processes.

3.3.1 Chemistry of Thermal Cracking

Thermal cracking is often used to increase gasoline production. The first step in cracking is the initiation process which occurs by thermal decomposition of hydrocarbon molecules to two free radical fragments. This initiation step can occur by a homolytic carbon-carbon bond scission at any position along the hydrocarbon chain. As presented below:

$$RCH_2CH_2CH_2R' \rightarrow RCH_2\dot{C}H_2 + R'\dot{C}H_2$$

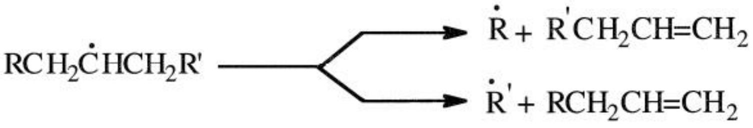
The free radicals then crack at a bond beta (β), yielding an olefin and a new free radical.

$$RCH_2\dot{C}H_2 \rightarrow \dot{R} + CH_2{=}CH_2$$

Further β bond scission of the new free radical $R^{\cdot}$ can continue to produce ethylene until the radical is terminated. Free radicals may also react with a hydrocarbon molecule from the feed by abstracting a hydrogen atom. In this case the attacking radical is terminated, and a new free radical is formed. Abstraction of a hydrogen atom can occur at any position along the chain. However, the rate of hydrogen abstraction is faster from a tertiary position than from a secondary, which is faster than from a primary position.

$$\dot{R} + RCH_2CH_2CH_2R' \rightarrow RCH_2\dot{C}HCH_2R' + RH$$

The secondary free radical can crack on either side of the carbon carrying the unpaired electron according to the beta scission rule, and a terminal olefin is produced.



$$RCH_2\dot{C}HCH_2R' \rightarrow \dot{R} + R'CH_2CH{=}CH_2$$
$$RCH_2\dot{C}HCH_2R' \rightarrow \dot{R}' + RCH_2CH{=}CH_2$$

Hydrogen transfer (chain transfer) may occur when a free radical reacts with other hydrocarbons. There are two major commercial thermal cracking processes, delayed coking and fluid coking.

- **Coking**

Coking is a severe thermal cracking process designed to handle heavy residues with high asphaltene and metal contents. These residues cannot be fed to catalytic cracking units because their impurities deactivate and poison the catalysts. Products from coking processes vary considerably with feed type and process conditions. These products are hydrocarbon gases, cracked naphtha, middle distillates, and coke. The gas and liquid products are characterized by a high percentage of unsaturation. Hydrotreatment is usually required to saturate olefinic compounds and to desulphurize products from coking units. Coking can be carried out in a delay coking unit (Figure 3.5). In the delayed coking unit, the reactor system consists of a short contact-time heater coupled to a large drum in which the preheated feed "soaks" on a batch basis. Coke gradually forms in the drum. A delayed coking unit has at least a pair of drums. A delayed coking unit has at least a pair of drums. When the coke reaches a predetermined level in one drum, flow is diverted to the other so that the process is continuous. Vapours from the top of the drum are directed to the fractionator where they are separated into gases, naphtha, kerosene, and gas oil.

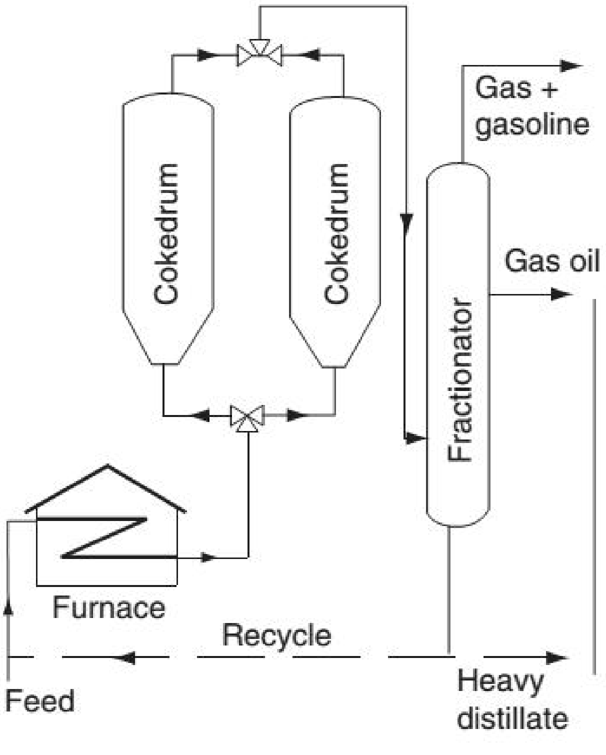
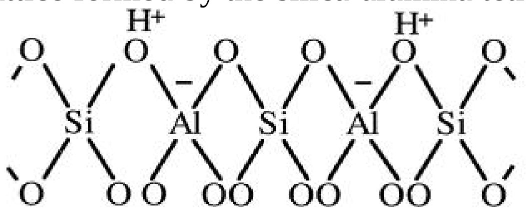


Figure 3.5 - Delayed Coking Unit (Speight 2006)

3.3.2 Chemistry of Catalytic Cracking

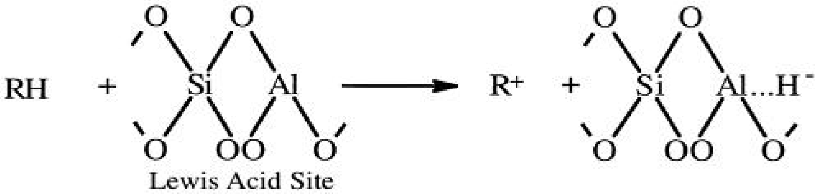
Catalytic cracking is a process used to crack heavy fraction, lower values stocks and produce higher valued, light and middle distillates. The process produces valuable gasoline with higher octane rating than thermal cracking. It also produces light hydrocarbon gases, which are valuable raw materials (i.e. feed-stocks) for petrochemicals' production. Catalytic cracking process's mechanism promotes isomerization reactions which results in branched chain products which is responsible for the better octane number.

The cracking catalysts can be acid-treated clays; synthetic amorphous silica-alumina; zeolites (crystalline alumina-silica). Acid treated clays were initially used in catalytic cracking processes before they have been replaced by synthetic amorphous silica-alumina. Amorphous silica-alumina is more active and stable than the acid treated clays. More recently, zeolite which is crystalline alumina-silica catalyst are incorporated into the amorphous silica-alumina to improve selectivity towards aromatics. Cracking catalysts possess both two sites which are Lewis and Bronsted acid sites. These sites promote the formation of carbonium ion which then promotes the cracking and the formation of branched isomers. The structure of zeolites involves holes in the crystal lattice formed by the silica-alumina tetrahedral shape.

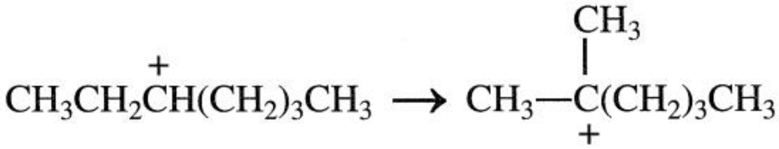


The catalytic cracking reaction is different from thermal cracking in that reactions' mechanism is through formation of carbocation intermediate as against the free radical intermediate in thermal cracking. The carbocations undergo shift in the methyl group to give secondary or tertiary carbocation which is more stable. This makes carbocations undergo process more stable and selective than free radicals. The following reactions illustrate the catalytic cracking process with zeolite:

1. Abstraction of hydride ion from the hydrocarbon feed stock by the Lewis acid site of the zeolite.

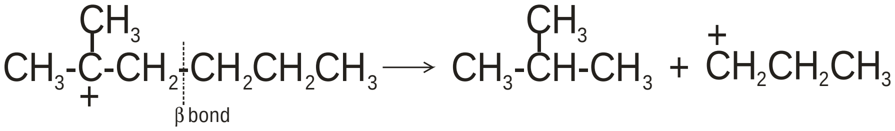


2. 1,2-Methide-Hydride shift to for more stable tertiary hydrocarbon leading to branching



$$CH_3CH_2\overset{+}{C}H(CH_2)_3CH_3 \longrightarrow CH_3-\underset{+}{\overset{\overset{CH_3}{|}}{C}}(CH_2)_3CH_3$$

3. Finally, the cracking reaction involves the carbon-carbon beta bond scission which is the reaction that leads to lower chain product. A bond at a position beta to the positively-charged carbon breaks heterolytically, yielding an olefin and another carbocation which continues the reaction.



$$CH_3-\underset{+}{\overset{\overset{CH_3}{|}}{C}}-CH_2\underset{\beta\text{ bond}}{\vdots}CH_2CH_2CH_3 \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_3 + \overset{+}{C}H_2CH_2CH_3$$

A typical catalytic cracking is carried out in a Fluid Catalytic Cracking (FCC) reactor. The reaction system contains two compartments which are the fluidized bed reactor and the regenerator (Figure 3.6). The catalyst is feed and fluidized in the fluidized bed reactor after which the hydrocarbon feed is loaded. When the catalyst is deactivated by carbon (coke) deposit, it is taken into the regenerator where it is regenerated with hot air which converts the coke to carbon dioxide.

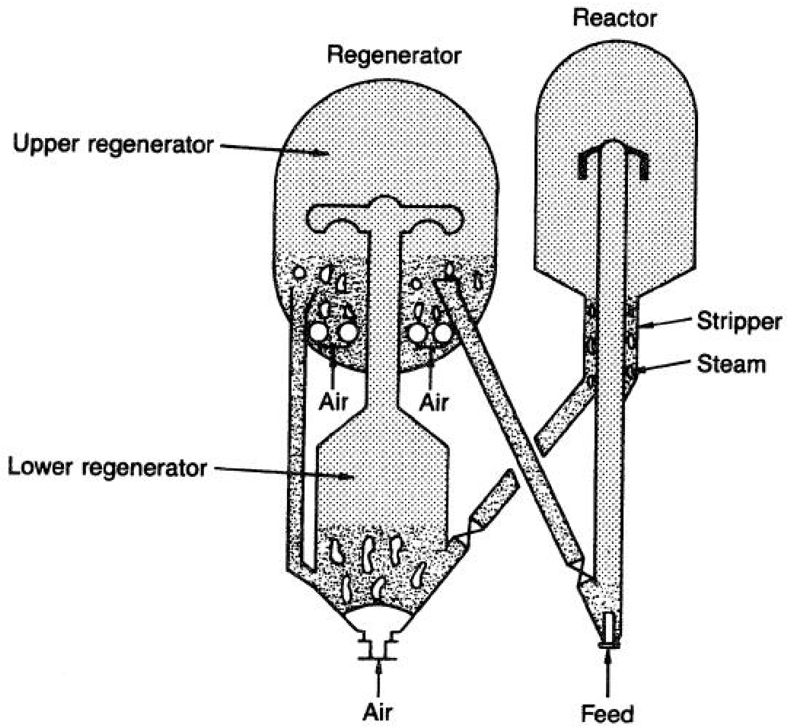


Figure 3.6 - Typical Fluid Catalytic Cracking reactor with regenerator
(Mata and Hatch, 2000)

4.0 SUMMARY

Valuable products are obtainable from crude oil after the refining processes. Crude oil after exploration is subjected to desalting and dewatering because associate water and salts in crude oil are detrimental to its refining. The physical refining processes include atmospheric distillation to obtain fractions like gasses, light naphtha (gasoline), heavy naphtha, kerosene, and gas oil. The residuum from the atmospheric distillation can be further distilled in a vacuum distillation column to obtain vacuum gas oil and lubricating oil. Generally, the petroleum fractions obtained from the distillation towers can be classified as gases and naphtha, middle distillates and heavy fraction.

5.0 CONCLUSION

Though crude oil in itself is considered valuable but its values are manifested in the different products that are derivable from it. The value addition processes to crude oil are the refining processes which include physical processes such as desalting and dewatering; atmospheric and vacuum distillation and chemical processes such as thermal and catalytic cracking among others. The chemistry of thermal cracking is by free radical mechanism while that of catalytic cracking is by carbocation formation leading to branching of the hydrocarbon chain in catalytic cracking. Catalytic cracking is therefore preferred in the production of higher octane rating gasoline compared to thermal cracking.

6.0 TUTOR MARKED ASSIGNMENTS

1. With the aid of suitable flowsheet diagram describe the following processes in crude oil refining:
    a. Desalting and Dewatering
    b. Atmospheric Distillation
    c. Vacuum Distillation
2. Discuss the Chemistry of the following Crude Oil Chemical Refining Processes
    a. Thermal Cracking
    b. Catalytic Cracking

7.0 REFERENCES AND OTHER RESOURCES

Speight, J.G. 2006. The Chemistry and Technology of Petroleum by CRC Press 4th Edition Taylor & Francis Group, Boca Raton, USA, ISBN-13: 978-0-8493-9067-8, 955pgs.

Mata, S. and Hatch, L.F. 2000. Chemistry of Petrochemical Processes 2nd Edition by Gulf Publishing Company, Houston, Texas, 406pgs.

MODULE 2

UNIT 1 OIL POLLUTION IN THE ENVIRONMENT: EXTENT, EFFECTS, SOURCES & FATE

CONTENTS

1.0 INTRODUCTION

Thus far in this course we have consider crude oil, it origin, components, and it refining. There is however generation of waste and environmental pollution issues that have been closely associated with various processes involved in the exploration and refining of crude oil. This section is intended to survey the different global episodes of remarkable oil pollutions and also local oil pollution issue with their resultant effects on the ecosystem, human and socioeconomic activities. The importance of this knowledge is to underscore the need for cleaner technology and sustainable approach to crude oil exploration and refining.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- enumerate the various oil pollution event globally
- identify the reported extent of oil pollution in Nigeria
- highlight the source, fate and effects of oil pollutions

3.0 MAIN CONTENT

3.1 Global Episodes of Oil Pollution

There have been a number of crude oil based pollutions in different countries of the world. Some of these pollutions were as a result of accident from transportation in vessels/ship on the waterways while some are from the exploration of crude oil. One of the notable accidents, which was even considered as one of the most devastating human caused environmental disasters, was the popular Exxon Valdez case of March 24, 1989. An Exxon Shipping Company owned oil vessel/tanker travelling to Long Beach, California, ran into a Bligh Reef in Alaska and spilled 10.8 million gallons of crude oil over some days. The spill caused the death of sea animals with long term effects. The clean-up was with the use of chemical dispersant (surfactant) to break the oil slick and disperse it as oil droplet after which mechanical clean-up was carried oil. Exxon incurred an estimated cost of $2 billion to clean-up the spill and a further $1 billion to settle related civil and criminal charges.

Beside the cases of oil spill as a result of accident, the pollution of environments by crude oil exploration and refining processes. Notable example of this was the Gulf of Mexico event. There was a blowout of the Deepwater Horizon drilling rig in the Gulf of Mexico which resulted in the accidental release of oil into the ocean. This event was classified as the world’s largest discharged recorded history because approximately 4.9 million barrels of light crude oil and 1.7×10^{11} g of natural gases were discharged into the Gulf between April to July 2010 (Kostka *et al.*, 2011, Dubinsky *et al.*, 2013). This caused water, land and air pollution with hydrocarbon with severe ecological and economic effects which will be discussed further in this unit.

Moreover, there were also reports of heavy pollution of the Persian Gulf during the Gulf war. There was a rough estimate of between 0.5 to 8 million barrels of crude oil released directly into Kuwaiti waters in January 1991 because of the Gulf War and 500 million barrels (which is 67 million tonnes) of Kuwait oil was emitted/ignited in the oil field fire in the war (Fowler *et al.*, 1993). This contaminated the

Gulf environment with oil aerosols, soot, toxic combustion products and oil-derived heavy metals with resultant toxic effects on humans, the ecosystem and economic activities.

3.2 Extent of Oil Pollution in Nigeria

The crude oil exploration activities are in the coastline of Nigeria. This Nigerian coastline is reported to be about 853 kilometres in length from the border with the Republic of Benin in the west to the Republic of Cameroon in the east (Nwilo and Badejo, 2005). The region of the coast that is active in crude oil exploration is often referred to as the Niger Delta region. The crude oil exploration activities in the region is the main source of Nigerian budgetary fund and make Nigeria the sixth largest exporter of oil in the world and the largest in Africa. The activities unfortunately are not without significant adverse effect on the environment hosting the activities. It has been reported that between 1976 and 1996, a total of 4647 incidents which resulted in the spilling of approximately 2,369,470 barrels of oil into the Nigerian coastal environment occurred (Nwilo and Badejo, 2005) with very little recovery/remediation. An estimated of 1,820,410.5 barrels (77%) of the spills were not recovered.

Just like the global episode reported above, Nigerian environment has witnessed different oil spillage episodes. The FUNIWA-5 (Texaco) oil-well blow-out was regarded as Nigeria’s worst case of marine oil pollution. This happened when the Texaco (Funwa-5) oil well blew out on January 17, 1980 and released about 400,000 barrels of crude oil into the marine environment (Aghalino and Eyinla, 2009). Another significant oil spillage event is the Mobil/Qua Iboe Oil Spillage of January 12, 1998. One of Mobil’s oil wells witnessed a major oil spillage as a result of leakage from the pipeline linking Mobil’s Idoho’s platform with the onshore terminal in Qua Iboe, Akwa Ibom State. The oil spillage was reported to cover a distance of two hundred kilometres in Bayelsa State and drifted to the Bakassi Peninsula in Cross Rivers State, as well as the shoreline of Lagos State (Aghalino and Eyinla, 2009). More recently the extent of oil pollution of this region has dropped by 27% and clean-up activities in the whole Niger Delta region will cost $50 billion.

3.3 Report on Ogoni Land

The United Nations Environment Programme (UNEP) conducted an independent study of an area southern Nigeria covering about a thousand square kilometres in Rivers State called Ogoniland and the result was published in 2011 (UNEP, 2011). This study was conducted at the request of the Federal Government of Nigeria to reveal the nature and extent of oil contamination of the area that has been the site of oil industry operations for over 50 years. The scope of the conducted Environmental Assessment of Ogoniland include investigating contaminated land, groundwater, surface water, sediment, vegetation, air pollution, public health, industry practices among others. The investigations found out that oil contamination in Ogoniland is widespread with severe negative impacts on the different components of the environment despite the fact that the oil industry is no longer active in Ogoniland. In one of the sites in Eleme local government area (LGA), heavy contamination was still found present after 40 years of the occurrence of the oil spill and after repeated clean-up attempts. This Ogoniland assessment reported lack of resources within key agencies responsible for environmental management as one of the many key factors responsible for the problem. A remote sensing of the area by the study revealed rapid proliferation of artisanal refining, for crude oil distillation in makeshift facilities as a major illegal activity endangering lives and increasing the environmental devastation of the Ogoniland and its environ. This report concluded on the following: soil pollution by petroleum hydrocarbons in land, sediments and swampland was extremely extensive; there is no continuous clay layer, with hydrocarbons in soil as deep as 5 m from the surface found across Ogoniland which implies that the groundwater is exposed to hydrocarbons transported from the surface. The vegetation mangroves are badly affected; roots are coated in a bitumen-like substance up to 1 cm or more thick; fish environment and nurseries for juvenile fish are extensively polluted with negative impacts on the fish life-cycle. Crops planted in the areas directly impacted by oil spills are damaged, and root crops, such as cassava are unusable. Plants in farms generally showed signs of stress and poor yields. There are fires outbreak killing vegetation and creating a crust over the land and making remediation often difficult. These and many more were the unfortunate environmental status of this region till date.

3.4 Sources of Oil Pollution in Niger Delta Nigeria

Incidents of oil spill have been reported to be a common occurrence of up to 6744 times and spilling of over 2.6 million barrels of oil into the Nigerian coastal environment since 1976 till recent years with less than 25% of the spill recovered or remediated (Nwilo and Badejo, 2005). The activities responsible for this environmental degradation from oil spill in the Niger Delta include: ageing of the pipelines without adequate maintenance; criminal activities of the inhabitants of the region such as illegal oil bunkering, pipeline vandalisation, and operation of illegal refinery with crude technology; oil rig blowing by militia's activities; accidental oil rig outs from the flow stations; releases from oil tankers on the high sea , both accidental and deliberate, waste oil disposal into the drains by the road side automobile mechanics among others. Of all these source of discharge into Nigerian environment, the most serious source of oil spill is from criminal, militia activities and the vandalisation of pipelines as a result of civil disaffection with the political process.

3.5 Fate and Mobility of Oil Pollution

The crude oil discharged into the environment is transformed or transported from one point or environmental compartment to another which is referred to as their fate and mobility. The fate and mobility of oil pollution are factors that affect its level of environmental effects. The fate of organic pollutants is governed by the biogeochemistry of the environment and is affected by physicochemical factors such as photolysis, hydrolysis, biodegradation, biotransformation, sorption unto sediments, particle transportation, deposition and resuspension or accumulation, dilution and diffusion, bioconcentration, volatilization into the atmosphere among others. The figure below (Figure 4.1) gives a summary of the biogeochemical cycle of event governing fate of organic pollutants (including oil pollutions). This cycle is affected by a number of factors such as the temperature, presence of emulsifying agents, sunlight intensity, biological reactions among other. The volatilization transports the oil pollutants from the hydrosphere (river, sea water system) or from the land (lithosphere) into the atmosphere as plumes. Bioconcentration transport the pollutants into the biological system (plants and animals). Sorption, deposition and accumulation partitions the pollutants into the sediment phase which serves as sinks for the pollutant and generate lasting effects because they can be resuspended.

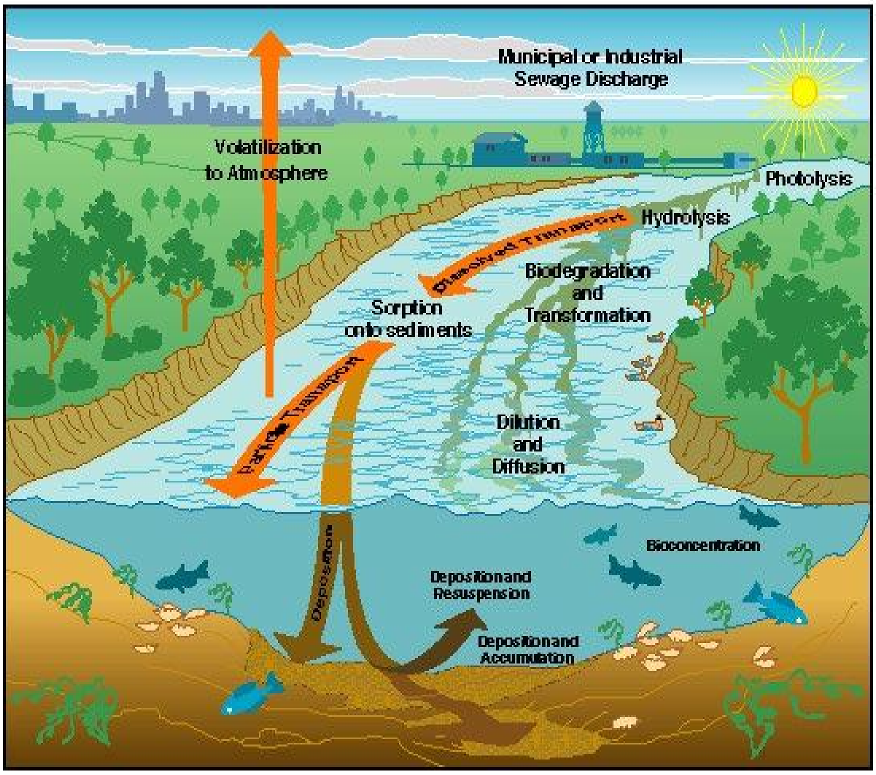


Figure 4.1 Simple Biogeochemical Cycle of the fate and mobility of organic pollutants (sourced online)

3.6 Effects of Oil Pollution

Occurrence of oil spills either in Nigeria or other parts of the world has resulted in devastating effects especially when cleaning up is delayed. Oil spill will lead to oil being washed away, traversing farmland, water systems, evaporated into the atmosphere and reaching the root zone of crops and other plants leading to experience of stress and death. This section is focused on effects of oil pollution on the ecosystem, man and socioeconomic activities.

3.6.1 Effects on the Ecosystem

Oil spill has consequences on land, water, the biological resources and their habitats in general. Oil spill that occurs on land are localized unlike the one on water. It does not spread quickly and its effects also remain localized. The oil often penetrates the soil and contaminates organisms in the soil. Crude oil spill will kill most plants and small trees on contact. Due to this spread limitation and resultant limited area of impact, the effects of oil spill on land are not of great concern as its effects on water systems (Sea and Oceans). Oil spill on land are of different behaviours based on the nature of the soil. If the land is made up of porous soil, oil spill will penetrate the soil and reduce soil water and the availability of water for metabolic activities of the living organisms in and on the soil. If the soil is like clay, silt, or shale which are extremely small, poorly interconnected pores making it relatively impervious, oil spill is only allowed through limited passage and stays more at the surface. Loam soil will retain more water and oil from spill because of its high organic content.

Moreover, the ability of oils to permeate soils and adhere also varies based on the viscosity of the oil. Viscous oils at low ambient temperature, move slowly, form tarry mass when spilled.
Non-viscous products, such as gasoline, move in a manner similar to water and spread faster at any ambient temperature. In agricultural valued loam soil area, crude oil spill does always saturate the top soil 10 to 20 cm and rarely penetrates below 60 cm. The region of the spread is the root region for the agricultural plant. This makes the land not arable. These varying fates of oil when spilled affect the potential of its clean up making it slow and difficult.

Another important effect of oil spills is the toxicity and exposure risk on biological resources. Toxic effects can be classified as acute or chronic, which is the rate of effect of the contaminant on an organism. Acute is toxic effects that occur within a short exposure period relative to the life span of the organism (e.g. within four days of exposure for fish). Acute toxic effects are generally as a result of exposures to high contaminant concentrations. Chronic toxic effects occur during a relatively long period (10% or more of the life span of the organism). They are generally the result of exposures to low contaminant concentrations. Chronic toxic effects are always observable after a significant exposure time. Chronic toxicity is long-term effects and is usually related to changes in growth, metabolism, reproduction, behaviour, ability to survive among others. Likewise, toxic substances' exposure effects may be lethal or sub-lethal. This is often described in terms of the toxicant's concentration that causes death to 50% of a test population of the species within a specified period of exposure time of four days (LC_{50}). Sub-lethal means contaminant is detrimental to the test organism at below the level that directly causes death within the test period. It is described in terms of the concentration of the toxicant that causes an adverse effect or response to 50% of a test population of the species within a specified period of exposure time (EC_{50}). Oil spill effect on biological organism in their habitat can therefore be acute or chronic, lethal or sub-lethal. This may include changes in their reproductive health and feeding behaviour, other behavioural changes, loss of habitat among others.

3.6.2 Effects on Human Health

Some of the components of crude oil are BTEX (benzene, toluene, ethyl benzene and xylenes) and PAHs (polycyclic aromatic hydrocarbons). Benzene is well known to be carcinogenic and volatile. This implies that it can be detected in air samples inhaled by humans and cause cancer. All BTEX are generally volatile organic compounds and are toxic to human health. PAHs are also carcinogenic and can be found in water and soil samples of oil spill area. As a result, people in these host communities where oil pollution is occurring lack access to potable water that is fit for drinking and sanitation. There is exposure risk tendency that can jeopardize their health. In these communities, children were in particular the most affected with risk of illnesses as catarrh, cough, cholera and diarrhoea afflicting them due to exposure to contaminated water.

The Ogoniland UNEP report detected benzene in all air samples at 0.155 to 48.2 $\mu g/m^3$ concentration range which was reported to be higher than concentration measured in other developed regions. 10 per cent of the samples investigated in Ogoniland had higher benzene concentrations than World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA) standard which corresponding to a 1 in 10,000 cancer risk.

3.6.3 Effect on Socioeconomic activities

Oil spills have many deterrents in economic terms beside the damage to natural resource, human and environmental health. These include high cost of cleaning, litigation cost, and government fines among other. These costs are also dependent on a number of factors such as the volume of oil spilled, emergency response during the spill to reduce wide spreading of the spill, the level of impact and what was affected by the spill.

In Nigeria, the major occupations of the people in the communities that host crude oil exploration activities are farming and fishing. The pollution of the environment has made the lands no more arable and has caused fish kill or toxic effects on the fish. The fisheries sector is currently suffering because of the destruction of fish habitat in the mangroves and highly persistent contamination of many of the creeks, making them unsuitable for fishing. This has resulted in occupational loss, unemployment, jobless, reduction in productivity and adverse effects on other economic activities of the people in the host communities. This is regarded as the predisposing factor for militia activities and other illegal and criminal activities being witnessed in the Niger Delta region of Nigeria.

4.0 SUMMARY

The exploration of crude oil and other related activities, accidents leading to oil spill are some of the major global activities responsible for oil pollution and Nigerian environment is not left out. The volume of oil spill in Nigeria is very high as has been attributed to militia activities around the crude oil installations in the country, crude technology employed in illegal refinery, illegal bunkering among others. The fate and the mobility of this oil pollution indicate that the oil is not limited to the pollution point but are converted by the prevailing biogeochemistry and transported to different environmental compartment. This is having adverse effects on the ecosystem, human and the socioeconomic activities in these areas.

5.0 CONCLUSION

This unit has considered the episodes, sources and impacts of oil pollution both on a global scale and in Nigeria. The need to ensure responsible and sustainable exploration and application of crude oil is underscored by the current negative effects that the exploration of crude oil and related activities is having on the host environment. There is the need to introduce government policies that will checkmate the illegal activities largely responsible for oil pollution in Nigeria and also to strength the institutions in the fight against these illegal activities and in the enforcement of environmental regulations.

6.0 TUTOR MARKED ASSIGNMENTS

1. Highlight the various activities that serve as sources of oil pollution in Niger Delta Nigeria.
2. Enumerate the different fate and mobility of crude oil discharge or pollution in the environment.
3. Discuss in details, the effects of oil pollution on the following:
    a. Ecosystem
    b. Human Health
    c. Socioeconomic activities

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UNIT 2 OIL POLLUTION MONITORING AND CONTROL

CONTENTS

1.0 INTRODUCTION

Unit 5 introduced you to the concept of oil pollution, its sources, fate and effects. The empirical evidence of oil pollution and its extent is not in physical observation but in scientific monitoring. There are a number of parameters that can be measured in sites that have been polluted with oil spillage. This unit is dedicated to teaching the knowledge of parameters that can be used to monitor and measure oil pollution. The unit however will not only address the pollution as a problem but will also teach the control of oil pollution as a preventive and corrective solution measure to oil pollution.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- identify the significance of each parameter used in monitoring oil pollution;
- explain the different methods of analysis for parameters used in monitoring oil pollution;
- explain the different preventive and corrective measures that can be used to control oil pollution

3.0 MAIN CONTENT

3.1 Monitored Parameters

The monitoring of oil pollution can be undertaken by the analyses for gross organic component of the water, sediment and soil of the environment where oil pollution has occurred. This will be discussed in section 8.4. Additionally the individual organic compounds can be quantified. The discussions on the individual organic compounds will be done in section 8.5. The methods presented in these two section (8.4 and 8.5) are from the Standard Methods for the Examination of Water and Wastewater (APHA 2005)

3.2 Gross/Aggregate Organic Constituents

In this category of oil pollution monitoring, pollution issues considered and monitored include oxygen-demanding substances and organically bound elements. Parameters like total organic carbon (TOC) and chemical oxygen demand (COD) are used to assess the total amount of organics present in the water, soil and sediment. Alternatively, biochemical oxygen demand is used to evaluate the gross fractions of the organic matter (biodegradable organics present).Oil and grease is useful in the evaluation of material extractable from the polluted sample using nonpolar solvents. Others include dissolved organic halide (DOX) as a measure of organically bound halogens; total petroleum hydrocarbon as a gross measure of crude oil pollution and ultraviolet absorbing organic constituents for measure of UV active compounds in the polluted samples. The relevance of these parameters to oil pollution and their method of analysis will be discussed.

3.2.1 Biochemical Oxygen Demand

Determination of BOD is an empirical test used to evaluate the relative oxygen requirements of wastewaters (including the wash water used in desalting of crude oil), effluents, and polluted waters. BOD measures the molecular oxygen used in the biochemical degradation of organic material with a specified incubation period. The oxygen is used by the micro-organism in the processes of metabolising the organic pollutant thereby measuring the gross amount of the organic pollutant.

Apparatus used for the analysis are incubation bottles, air incubator or water bath. The reagents used are phosphate buffer solution (pH 7.2), Magnesium sulphate solution (22.5 g/L $MgSO_4 \cdot 7H_2O$), Calcium chloride solution (27.5 g/L $CaCl_2$), Ferric chloride solution (0.25 g/L $FeCl_3 \cdot 6H_2O$), acid and alkali solutions (1M) for neutralization of caustic or acidic water samples, freshly prepared Sodium sulphite solution

(1.575 g/L Na_2SO_3). Nitrification inhibitor (if needed) - 2-chloro-6-(trichloromethyl) pyridine, freshly prepared Glucose-glutamic acid solution (150 mg glucose and 150 mg glutamic acid dilute to 1 L in distilled water) and Ammonium chloride solution (1.15 g/L NH_4Cl,adjust pH to 7.2 with NaOH solution). Dilution water used for the BOD analysis is made from either of demineralized, distilled, tap, or natural water.

Procedure

The procedure for BOD determination is seeding and dilution procedures. The first step is to prepare dilutions of the sample with the dilution water either in graduated cylinders or volumetric glassware, and then transfer to BOD bottles or prepare directly in BOD bottles. This is followed by seeding with microbes if it is necessary (i.e. if the microbes are sufficient to degrade the organic matter). The diluted samples are then filled into airtight bottles of the specified size until it overflowing. This is followed by incubating it at the specified temperature for 5 days. Dissolved oxygen (DO) of the sample is measured at day 1 before incubation and at day 5 after incubation. The BOD is computed from the difference between initial and final DO. In case the required oxygen demand may be more that the DO, the sample is diluted with aerated water to ensure accurate result. It is also seeded to enhance microbial activity.

3.2.2 Chemical Oxygen Demand

Chemical oxygen demand (COD) is the amount of a specified oxidant (particularly potassium dichromate) that reacts with the sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. COD is used as a measurement of gross pollutants in wastewater and natural waters. It is related to other gross measurements like biochemical oxygen demand (BOD), total organic carbon (TOC), and total oxygen demand (TOD). As earlier stated, BOD is a measure of oxygen consumed by microorganisms under specific conditions while TOC is a measure of organic carbon in a sample; TOD is a measure of the amount of oxygen consumed by all elements in a sample when complete (total) oxidation is achieved. Thus, it is possible to correlate the values of these parameters for a given sample.

COD determination is based on the principle that most types of organic matter can be oxidized by boiling it in a mixture of potassium dichromate and sulphuric acids. Thus, a polluted sample (with crude oil spill or other industrial effluent) is refluxed (for 2-h) in strongly acid solution with a known excess of potassium dichromate ($K_2Cr_2O_7$). The excess unreacted dichromate is titrated with ferrous ammonium sulphate to determine the amount of dichromate consumed as a measure of the oxidisable matter which is calculated in terms of oxygen equivalent. A blank analysis is carried out and this analysis is carried in replicate to yield reliable data.

The apparatus needed for the analysis are a refluxing system and apparatus needed for titration. The reagents are 0.04167 M standard potassium dichromate solution (12.259 g/L of dried $K_2Cr_2O_7$); sulphuric acid reagent (add 0.55 g Ag_2SO_4 to 100g conc. $H_2SO_4$and let it stand for 1 to 2 d to dissolve); Ferroin indicator solution (dissolve 1.485 g 1,10-phenanthroline monohydrate and 695mg $FeSO_4 \cdot 7H_2O$ in distilled water and dilute to 100 mL); freshly prepared standard ferrous ammonium sulphate (FAS) titrant, about 0.25 M (dissolve 98 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water, add 20 mL conc. H_2SO_4, cool, and dilute to 1 L and standardize this solution against standard $K_2Cr_2O_7$ solution to determine the exact concentration); Mercuric sulphate, $HgSO_4$, crystals or powder.

Procedure

Homogenize the sample if necessary and pipet 50.00 mL into a 500-mL refluxing flask. Add 1 g $HgSO_4$, some glass beads, and very slowly add 5.0 mL sulphuric acid reagent, with mixing to dissolve $HgSO_4$. Cool while mixing to avoid possible loss of volatile materials. Add 25.00 mL 0.04167 M $K_2Cr_2O_7$ solution and mix. Attach flask to condenser and turn on cooling water. Add remaining sulphuric acid reagent (70 mL) through open end of condenser. Continue swirling and mixing while adding sulphuric acid reagent. Cover open end of condenser with a small beaker to prevent foreign material from entering refluxing mixture and reflux for 2 h. Cool and wash down condenser with distilled water. Disconnect reflux condenser and dilute mixture to about twice its volume with distilled water. Cool to room temperature and titrate excess $K_2Cr_2O_7$ with FAS, using 0.10 to 0.15 mL (2 to 3 drops) ferroin indicator. Take as the end point of the titration the first sharp colour change from blue-green to reddish brown that persists for 1 min or longer.

3.2.3 Total Organic Carbon

Total organic carbon (TOC) is another gross measurement of organic pollution which can be determined in water samples or solid samples such as soil and sediment. It is a more convenient and direct expression of total organic content than either BOD or COD earlier discussed. It however does not provide the same kind of information as BOD and COD. TOC, unlike BOD or COD, is independent of the oxidation state of the organic matter. It measures only carbon and does not measure other organically bound elements, such as nitrogen and hydrogen, and inorganics that can contribute to the oxygen demand measured by BOD and COD. Thus, TOC measurement does not replace BOD or COD testing. TOC measurement is vital to the operation of water treatment and wastewater treatment plants. It is used in assessment of drinking water (TOCs range <100 µg/L – 25,000 µg/L maximum).Wastewater may contain very high levels of organic compounds (TOC >100 mg/L). It can therefore be an important parameter in oil pollution assessment. TOC determination principle is based on catalytic heating reaction of the total organic carbon in a sample in a chamber packed with an oxidative catalyst such as cobalt oxide, platinum group metals, or barium chromate. The organic carbon is oxidized to CO_2 and H_2O. The CO_2 from oxidation of organic and inorganic carbon is quantified. The CO_2 quantification can be done instrumentally in a TOC analyser by transporting it in the carrier-gas streams and is measured by means of a non-dispersive infrared analyser. It may also be titrated coulometrically.

The apparatus needed for the analysis include: Total organic carbon analyser (using combustion techniques); Sample injection and sample preparation accessories; Sample blender or homogenizer; Magnetic stirrer and TFE-coated stirring bars; Filtering apparatus and 0.45-µm-pore filters (rinse filters before use and monitor filter blanks). The reagents needed are: Reagent water for preparation of blanks and standard solutions; phosphoric acid or sulphuric acid; Organic carbon standard stock solution (prepared by dissolving 2.1254 g anhydrous primary-standard-grade potassium biphthalate, $C_8H_5KO_4$, in carbon-free water and dilute to 1000 mL; 1.00 mL = 1.00 mg carbon and preserve by acidifying with phosphoric or sulphuric acid to pH ≤ 2, and store at 4°C); inorganic standard stock solution (prepared by dissolving 4.4122 g anhydrous sodium carbonate, Na_2CO_3, in water, add 3.497 g anhydrous sodium bicarbonate, $NaHCO_3$, and dilute to 1000 mL; 1.00 mL = 1.00 mg carbon, keep tightly stoppered and do not acidify); Carrier gas: Purified oxygen or air, CO_2-free and containing less than 1 ppm hydrocarbon (as methane); Purging gas: Any gas free of CO_2 and hydrocarbons.

Procedure

Homogenize samples containing gross solids or insoluble matter. Calibrate, optimize combustion temperature of the TOC instrument and monitor temperature to insure instrument stability. Withdraw a portion of prepared sample or standards using a syringe fitted. Select appropriate sample volume and inject samples or standards into analyzer according to ROC instrument's instructional manual and record response. Carry out replicate analysis until consecutive measurements are obtained that are reproducible to within ±10% relative standard deviation (RSD). Prepare standard curve of organic and inorganic carbon series by diluting stock solutions to cover the expected range in samples within the linear range of the instrument. Plot carbon concentration in mg/L against corrected peak height or area and use the curve for the determination of the unknown TOC in the samples.

3.2.4 Oil and Grease

Determination of oil and grease in different sample matrix (water and soil) of crude oil polluted area is another key parameter. In this investigation, rather than measure an absolute quantity of a specific substance a groups of substances with similar physical characteristics are determined quantitatively on the basis of their common solubility in an organic extracting solvent. Oil and grease is any material recovered as a substance soluble in organic solvent. This test includes other non-volatile materials like biological lipids extracted by the solvent from the sample. Solvents used include petroleum ether or n-hexane.

The conduct of this test is important because some constituents measured by the oil and grease analysis do influence wastewater treatment systems’ operation and effectiveness. Excessive amounts of these components may interfere with aerobic and anaerobic biological processes and decreased the efficiency of the wastewater treatment. The discharged of oil and grease into the environment may cause surface films and shoreline deposits leading to environmental degradation. Investigating the quantity of oil and grease in and environment especially crude oil exploration ones is helpful in proper management, design and operation of wastewater treatment systems and also may call attention to certain treatment difficulties. If specially modified industrial products are absence, oil and grease is often composed primarily of fatty matter from animal and vegetable sources and from hydrocarbons of petroleum origin.

The apparatus needed for oil and grease analysis are separating funnel; distilling flask; glass liquid funnel; Filter paper; Centrifuge with centrifuge tubes; thermostated water bath; vacuum pump; Ice bath; Desiccator.

Procedure

If the sample is solid, it can be subjected to ultrasonic bath solvent extraction or extraction in Soxhlet extractor (see unit 9 for details). If the sample is liquid, use a funnel to transfer known volume of the sample to a separating funnel. Carefully rinse sample bottle with 30 mL extracting solvent (either 100% n-hexane, or solvent mixture) and add solvent washings to separating funnel. Shake vigorously for 2 min. Let layers separate. Drain aqueous layer and small amount of organic layer into original sample container. Drain solvent layer through a funnel containing a filter paper and 10 g Na_2SO_4, both of which have been solvent-rinsed, into a clean, pre-weighed distilling flask. Extract two or more times with 30 mL solvent each time, but first rinse sample container with each solvent portion. Distil solvent from flask in a water bath at 85°C for either solvent system. When visible solvent condensation stops, remove flask from water bath. Cover water bath and dry flasks on top of cover, with water bath still at 85°C, for 15 min. Cool in desiccator for at least 30 min and weigh. Determine the oil and grease by difference from the initial weight.

3.2.5 Total Petroleum Hydrocarbons

Total petroleum hydrocarbons (TPHs) are mixture of short and long chain aliphatic hydrocarbons (C10 – C36 compounds) and aromatic hydrocarbons. They are derived from crude oil and suitable monitoring parameter of oil pollution. TPHs are monitored in soil, sediment and water of oil spills areas. Information about THPs is need to adequately plan for remediation and clean-up of oil spills. There are a number of methods for the determination of TPH. There are a number of spectroscopic and non-spectroscopic methods of analysis of TPHs developed over the years. Some of these are infrared (IR) spectroscopy, Raman spectroscopy, and fluorescence spectroscopy and the non-spectroscopic methods are general gravimetry, immunoassay (IMA), gas chromatography (GC) with flame ionization detection (GC-FID) or mass spectrometry (GC-MS) detector. For GC-FID or GC-MS analysis, the steps involved include the quantitative extraction of the TPH from the environmental media of interest using various extraction methods (as discussed in Unit 7). The extract is then cleaned up and concentrated before the use of GC-FID for the TPH-determination. The details of the GC-FID operations will also be discussed in Unit 8. Another method is the use of FTIR spectroscopic method. The method is quick, simple, and inexpensive with common detection limits of approximately 10 mg/kg in soil.

Procedure

This method uses the spectra of the stretching and bending vibration of hydrocarbon derivatives mainly from the combinations of C-H stretching modes of saturated CH_2 and terminal $-CH_3$ or aromatic C-H functional groups being the common constituent of hydrocarbons. These IR wavenumbers occur within the range of 3000 to 2900 cm^{-1} or at the specific wavenumber of 2930 cm^{-1}. Samples are first extracted with suitable solvent (containing no C-H bonds e.g. CCl_4) and extraction technique and the eluate is cleaned up before being subjected to IR spectrometry. The absorbance of the eluate is then measured at within the range of 3000 to 2900 cm^{-1} or at the specific wavenumber of 2930 cm^{-1} and compared against the calibration curve developed for the instrument. The instrument calibration standard usually is a petroleum hydrocarbon of known TPH concentration.

3.2.6 Ultraviolet Absorbing Organic Constituents

As discussed in previous unit (Unit 2), crude oil contains various aromatic compounds which are ultraviolet (UV) radiation absorb substances. Therefore, UV absorption is a useful surrogate measure of oil pollution in water system or any other environmental media where oil pollution is being monitored. More often than none, there are strong correlations between UV absorption and organic carbon content of oil polluted area. UV absorption may also be used to monitor industrial wastewater effluents; to evaluate organic removal by coagulation; to evaluate carbon adsorption; for monitoring other water treatment processes among others. Specific absorption, the ratio of UV absorption to organic carbon concentration is also very useful in the characterization of natural organic matter in pollution studies. As we shall discuss further under detection of certain individual organic contaminants, UV absorption is useful in quantification of individual organic pollutants after separation with HPLC provided the pollutant is UV active. The UV-absorbing organic constituents describe here is however intended to be used to provide an indication of the aggregate concentration of oil pollution.

The apparatus and reagents needed are: Spectrophotometer, wavelength 200 to 400 nm with quartz cuvette; Organic-free water and filter; 0.1 M HCl (optional) and 0.1 M NaOH (optional) for pH adjustment, Phosphate buffer (optional) by dissolving 4.08 g dried anhydrous KH_2PO_4 and 2.84 g dried anhydrous Na_2HPO_4 in 800 mL organic-free water. Verify that pH is 7.0 and dilute to 1 L with organic-free water. Store the buffer in brown glass bottle at 4°C. Prepare fresh weekly to avoid microbial growth.

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Procedure

Take a 50-mL sample filter by passing it through an organic water pre-cleaned filter. Do a sample pH adjustment with HCl or NaOH or buffered as appropriate but avoid precipitate formation during pH adjustment. Report sample pH value used with recorded absorbance.
Prepare organic-free water blank and the sample in the same manner. To carry out the spectrophotometric measurement equilibrate the instrument set wavelength to 253.7 nm and adjust spectrophotometer to read zero

absorbance with the organic-free water blank. Measure the UV absorbance of sample at 253.7 nm at room temperature in triplicate. Dilute the samples of the absorbance are too high and calculate the UV-absorbing species in the sample using the expression:

$$UV_{\lambda}^{pH} = \left[\frac{\bar{A}}{b}\right] D$$

where UV is the mean UV absorption, cm^{-1} (subscript denotes wavelength used, nm, and superscript denotes pH used if other than 7.0), b= cell path length, cm, $\bar{A}$ = mean absorbance measured, and D = dilution factor (if sample is diluted) resulting from pH adjustment and/or dilution with organic-free water.

3.3 Metals and Radioactive Compounds

The fact that crude oil is associated with rock make is probable that there may be trace level of metals and radioactive compounds in crude oil and its waste discharged into the environment. In Unit 2 also we discussed that some metals are found in crude oil. It is therefore essential that environmental monitoring for crude oil pollution involve determination of metals and radioactive compounds in samples from monitoring area and samples of interest. Metals are often determined by a variety of methods. The choice of method is often dependent on the precision and sensitivity required by the study. Methods that can be used include spectrophotometry, atomic absorption spectrometry (flame or electrothermal (furnace) or hydride and/or cold vapour techniques); flame photometry; inductively coupled plasma (ICP) emission spectrometry; inductively coupled plasma mass spectrometry, and anodic stripping voltammetry. Flame atomic absorption methods are the most generally applied and will be the one discussed in the section.

Procedure

Because of the tendency of interference by organic matter present in the crude oil and to convert some of the metals associated with particulates into free metal digestion of the samples in whatever matrix it is present (water, soil, sediment etc.) is carried out. This must be done before the metal content can be determined by atomic absorption spectrometry or inductively-coupled plasma spectroscopy. Digestion may be carried out with any of the following acid combination depending on the sample matrix and on the aim of the analysis: HNO_3 alone which is adequate if the samples are clean or can be easily oxidized; HNO_3+H_2SO_4 or HNO_3+HCl digestion is if there is large quantity of readily oxidizable organic matter; HNO_3+$HClO_4$ or HNO_3+$HClO_4$+HF digestion if the sample is difficult-to-oxidize organic matter or minerals containing silicates. It will be observed that in all acid combination HNO_3 is constantly involved. This is because all metal nitrate salts are soluble and the aim of digestion is to get the metals into solution. The digested samples can then be read in Flame atomic absorption spectrophotometer of with inductively coupled plasma mass spectrometry. The radioactive metals can be detected with ICP or with counting instruments like the Gas-flow proportional counters or alpha scintillation counter.

3.4 Control of Oil Pollution

As important as monitoring of crude oil pollution is, the control of the pollution is much more important. The control may be preventive or corrective/remediation approach. The preventive measures are often regarded as being better because it is less costly from all angles. This section discusses the preventive and remediation measures towards controlling oil pollutions (Michel and Fingas, 2015).

3.4.1 Preventive Approach

The use of cleaner production technology, the regular routine maintenance of equipment, introduction of best and safe practice and adoption of total quality management procedures, the regular training of worker are some of the key components toward prevention of oil spill. Beside these, there must be strong regulation, environmental protection laws, strong institutions to enforce the laws against crude oil pollution.

The best and safe practices should include structured plans to regularly risk analysis for and to identify potential oil spill point(s); studying previous spills as predictive model for identifying potential ones; acting promptly on danger signal(s); ensuring resources are available to remove possibility of discharge; training workers on Health, Safety and Environment (HSE) Systems; other training to continuous improve oil worker’s skills; testing, regular routine maintenance and ensuring that the regular routine maintenance are carried out; carrying out unannounced drills on emergency response; using of remote sensing to monitor crude oil installation and pipes; use of pipes and tankers that are double layer/hull to prevent spill since the oil must penetrate both layers before being released; investing in research and development aimed and technology development and anticorrosion studies. Government’s institution should also be strengthened to fight the illegal activities that have been implicated to contribute significantly to oil pollution in Nigeria. These among others are preventive measure that will reduce oil pollution.

3.4.2 Remediation

There are a number of remediation methods. The first we will discuss is the chemical agent’s treatment methods. There are numerous chemicals formulated that can be used to interact with oil spill for treatment and to assist in clean-up of oil. This approach should only be used after approval of necessary authorities because of the potential toxic effects of chemicals on aquatic and other wildlife. A typical and common chemical agent is the **surfactants/dispersants**. Surfactants have lipophilic and hydrophilic parts which make them useful chemicals in spill-treating. They promote the formation of small droplets from the oil slicks and the oil droplets are dispersed by these dispersant/surfactants from the top layer slick into the water column by with the aids of wave action and currents. Unfortunately, these dispersants are not perfectly effective in the treatment because the oil is still there but only dispersed and may resurface into slicks. The oil becomes less dispersible with change in weathers, reduction in tidal current force which aids the dispersion, increase in viscosity among others. As a result of this, dispersants have narrow effectiveness window. Moreover, the use of dispersants has been a contentious and controversial one. Typically, use of dispersant in freshwater and in land applications is not acceptable. The use of chemical dispersant is a trade-off. The table 5.1 below summarizes that merits and demerits of using chemical dispersants for the remediation of oil spill.

Another remediation method is the use of **skimmers**. Skimmers are mechanical devices designed for the purpose of removing floating oil only in water systems. They are of varying sizes, applications, capacities and recovery efficiencies. Skimmers are classified according to the area of application such as: inshore or offshore, shallow water, rivers or deep water. They can also be differentiated by the viscosity of the oil they are used on. They can also be classified according to their basic operating principles such as oleophilic surface skimmers; weir skimmers; suction skimmers or vacuum devices; elevating skimmers; and submersion skimmers.

Table 5.1: Merits and demerits of applications of dispersant in oil spill remediation

Merits of Dispersant applications	Demerits of Dispersant applications
Break the oil slick, removes surface oil, allows oxygen penetration and dilutes oil into the water column.	The bioavailability of toxic oil fractions is made temporarily high because of the dispersion
The fact that the oil has been dispersed will increase the surface area and will increase/facilitate the	The dispersion makes the oil spread temporarily to entrained aquatic species (eggs, plankton,

natural biodegradation of the oil.	less mobile animals). This thus increases localized risks to these biotas.
It reduces the exposure of workers recovering the oil at the surface and minimizes impacts on shoreline habitats	It cannot be used under certain weather and water current conditions which promotes formation slicks again.
Dispersants application minimizes impacts on populations with long life-spans (birds, mammals, turtles)	It may increase toxicity, it cannot be used on all oil types and are less efficient on weathered oils.

The efficiency of skimmers is enhanced in high viscosity oils slick (thick oil slick). To achieve this, the oil is collected in booms and the skimmer is then placed where the oil is most concentrated to recover as much oil as possible before and to effectively clean the oil spill. Factors that affect the efficiency of skimmers are: weather conditions at a spill site, wave’s height (>1 m), wave’s currents (>0.5 m/s), water with ice or debris (plant branches, floating wastes, seaweeds etc.) and very viscous oils, tar balls, or oiled debris can clog the intake or entrance of skimmers. Some skimmers are designed to have screens to prevent debris from entering, conveyors to remove debris, and cutters to deal with sea weed.

Another method is the use of **sorbents**. Sorbents are materials that are used to recover oil either by adsorption or by absorption. Sorbents can be either absorbent or adsorbent; they can be natural or synthetic. Natural sorbents can be organic or inorganic. Organic sorbents include: biomass such as agricultural waste (wood products), peat moss, sea weeds, activated charcoal or carbon from biomass among others. Inorganic sorbents may be clays, synthetic materials such as zeolite among others. Sorbents can be applied in different forms such as: in granules, cubes, powder, chunks and can be packaged into pads, rolls, blankets, and pillows, bags, nets, or socks for application. They can be applied to either clean up the final traces of oil spills in water systems or on land after the initial use of the methods described above; used as backup to other means of clean ups; used as a primary means of recovery if the oil spill is of low volume among others.

Another promising remediation method is the use of **micro-organisms** for oil spill clean-up. A number of studies have been carried out to use microbes to degrade oil in crude oil polluted areas. Gammaproteobacteria which including representatives of genera with known oil degraders *Alcanivorax, Marinobacter, Pseudomonas, and Acinetobacter* has been applied successfully for this purpose (Kostka *et al.*, 2011; Dubinsky *et al.*, 2013). The only drawback of this method is the slow rate of degradation.

In-situ burning is another oil spill clean-up technique. It involves controlled burning of the oil at or near the spill site. It is unfortunately a destructive remediation method because the oil cannot be recovered for useful purpose but it is a final solution, it has the potential for removing large oil quantities over an extensive area, it can be operated in less or approximately same time than as other techniques. The technique is most suitable for oil spill on land.

4.0 SUMMARY

The empirical evidences of oil pollution are the collection and analysis of samples from oil polluted area for parameters that are indicators of pollution. This evidences will give credit to the control and remediation efforts of such pollution. This unit discussed the gross measure of organic pollution as monitoring indicator of oil pollution. Relevance and procedure for determination of parameters like BOD, COD, TOC, Oil and Grease among others were discussed in detail. Preventive approaches to oil pollution control like cleaner production technology, the regular routine maintenance, best and safe practice, total quality management procedures, the regular training of worker among others were presented. The use of dispersant, skimmer, microbial degradation, insitu burning among other methods for the remediation was also taught.

5.0 CONCLUSION

Oil pollution monitoring is very essential for evidence based understanding of extent of pollution and policy formulation for preventive and remediation purpose. The application of gross measure of oil pollution provides such evidence based understanding. More importantly, there is the need to continuously enforce prevention of oil pollution and remediation of polluted environment because of the adverse effects of oil pollution.

6.0 TUTOR MARKED ASSIGNMENTS

1. Outline the procedures for the determination of the following:
    a. Biochemical Oxygen Demand
    b. Total Organic Carbon
    c. Oil and Grease
    d. Total Petroleum Hydrocarbon
2. Enumerate the practical steps that can be taken to prevent oil pollution
3. Discuss the following methods for remediation of oil pollution:
    a. Use of Dispersants
    b. Use of Skimmer
    c. Use of Sorbents

d. Microbial degradation
e. In-situ burning

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UNIT 3 SAMPLING PROTOCOL

CONTENTS

1.0 INTRODUCTION

It is always nearly impossible to investigate and analysis the whole population. Thus, it is important to know how to obtain a **representative sample** for analysis. ***A representative sample is one that truly reflects the composition of the material to be analysed within the context of a defined analytical problem***. Without a representative sample, results may be meaningless or even grossly misleading. Wrong selection of sample introduces error that cannot be corrected during the analysis. This section is therefore focused on best and standard practise in the collection of sample for environmental monitoring with particular reference to oil pollution monitoring.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- identify the significance of having a good sampling plan design for the monitoring pollutions;
- explain the different suitable sampling containers and equipment used in monitoring oil pollution;
- explain the different quality assurance steps, sample storage and preservation requirements for oil pollution monitoring.

3.0 MAIN CONTENT

3.1 Pre-Sampling Activities

Before setting out to collect samples, it is very vital that you understand the aims of the analysis and know the appropriate sampling procedure to be adopted for **field sample** collection. In a number of situations, a sampling plan or strategy may need to be devised so as to optimize the value of the analytical information collected. This is necessary particularly if the environmental samples of soil, water or the atmosphere are to be collected for a complex industrial process being monitored. In some situations, legal/regulatory requirements may determine the sampling strategy to be adopted like in the food and drug industries or in dispute cases.

3.1.1 Sampling Plan Design

As previously mention, there must be a strategy/plan for your sampling and such sampling plan must support the goals of an analysis. Factors that must be considered vary with the sampling goals. For instance, in a qualitative analysis the sample’s composition does not need to be identical to that of the substance being analysed. What is important in this case is having enough samples taken to ensure that all components can be detected. In a quantitative analysis, however, the sample’s composition must accurately represent the target population.

In sampling plan design you must ask yourself the following four questions and provide appropriate answers to them to have a correctly designed sampling plan:

1. From where within the target population should samples be collected?
2. What type of samples should be collected?
3. What is the minimum amount of sample needed for each analysis?
4. How many samples should be analysed?

The first question deals with the sampling location within the populations. This can be addressed by the selection of sample using random sampling or selective sampling or systematic sampling or stratified sampling.

Random sampling protocol involves an unbiased estimate/division of the target population’s properties and the collection of samples at random from the target population. This is not a haphazard collection but the use of random table (a statistical table) to select randomly.

The opposite of random sampling is selective or judgmental sampling. In this case available information about the target population is used to help select samples. There are assumptions about the target population included in the sampling plan. Selective sampling is more biased than random sampling and often fewer samples are required.

Systematic sampling falls in between the two extremes of random and selective sampling. In systematic sampling the sampling site/population (e.g. a lake) is divided as in the figure 6.1 below and samples may be collected from either the centre of each unit or at the intersection of grid lines.

Another sampling is the stratified sampling. Here, the target populations are conveniently subdivided into distinct units, or strata and sample collected from each stratum as illustrated in figure 6.2 below.

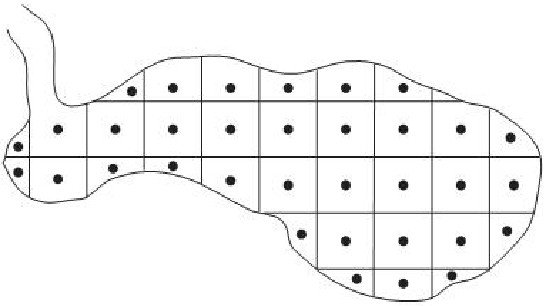

Figure 6.1: Systematic sampling of a lake (Harvey, 2000)

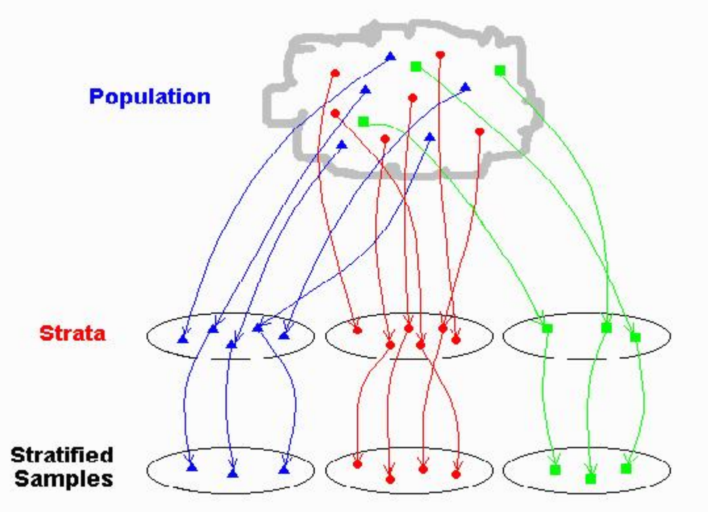

Figure 6.2: Illustration of Stratified sampling

After determining where to collect samples, the second question to answer is what type of sample to collect. There are three (3) common types of samples:

- grab samples,
- composite samples, and
- in-situ sampling.

The most common type of sample is **a grab sample,** in which a portion of the target population is removed at a given time and location in space. A grab sample, therefore, provides a “snapshot” of the target population. A **composite sample** on the other hand consists of a set of grab samples that are combined together to form a single sample. After thoroughly mixing, the composite sample is analysed as representative of the whole population. **In-situ sampling,** uses an analytical sensor placed directly in the target population to collect necessary information about the population. It allows continuous monitoring without removing individual grab samples. For example, the pH of an effluent polluted river moving can be continually monitored by immersing a pH electrode into the flowing river.

The third question is how much sample to be collected based on how much sample is needed for the analysis. To minimize sampling errors sample must be of an appropriate size. If the sample is too small its composition may differ substantially from that of the target population, resulting in a significant sampling error. You may also not have enough for the analysis thus hindering the goal of the analysis by limiting information available. Samples that are too large, however, may require more time and money to collect and analyse, without providing a significant improvement in information obtained from sampling.

The last question is how many samples to collect and in what different matrix (surface water, groundwater, soil, sediment, plant, fish etc.). The essence of this is to provide detailed information about the sampled population with minimal error. This is an important because inappropriate number of samples will introduce maximum sampling error.

3.1.2 Sample Container and Treatment

The table 6.1 below present the appropriate sample containers and treatments for different determinations in environmental pollution monitoring.

Table 6.1: Sample Containers and Treatments for Oil pollution Monitoring

Determinations (Parameters)	**Appropriate Container**	**Sample type**	**Minimum sample size**	**Sample Container's treatment**
BOD	Glass or Plastic	Grab or Composite	1000 mL	Clean bottles with a detergent, rinse thoroughly, and drain before use. Container should be sealed capped type.
COD	Glass or Plastic	Grab or Composite	100 mL	Clean bottles with a detergent, rinse thoroughly, soak in acetone, and drain before use.
TOC	Glass	Grab or Composite	100 mL	Clean bottles with a detergent, rinse thoroughly, soak in bottles with acid, bake at 400°C for at least 1 h and seal with aluminium foil.
Oil & Grease	Glass	Grab or Composite	1000 mL	Clean bottles with a detergent, rinse thoroughly, soak in acetone, and drain before

				use.
Metals (General)	Plastic	Grab or Composite	1000 mL	Clean bottles with a detergent, rinse thoroughly, soak in HNO_3, rinse with deionized water and drain before use.
Each Organic Compound	Glass	Grab or Composite	1000 mL	Clean bottles with a detergent, rinse thoroughly, soak in acetone, and drain before use.
General quality parameters	Glass or Plastic	Grab or Composite	1000 mL	Clean bottles with a detergent, rinse thoroughly and drain before use.

3.2 Sample Collection

The collection of sample for environmental analysis is often carried out with specialized equipment based on the media of the environment of interest. The section is focused on the different sampling equipment for the various environmental media.

3.2.1 Sampling Equipment for Water, Soil and Sediment

Soil: The equipment used for soil sample collection is soil auger (Figure 6.3) especially when the sampling is for profiling at different depth. The soil augers are of different design due to different soil types. The auger is marked 0-15 cm, 15-30 cm. Soil samples collected in each portion of the mark is labelled as top soil (0-15 cm) and bottom soil (15-30 cm). The samples are then analysed and used for the profiling. If profiling is not the aim of the analysis, a hand trowel can be used to collect the top soil sample alone.

Figure 6.3: Image of Various Designs of Soil Auger (Online)

Sediment: Collection of sediment samples are often undertaken with different designs of grab samplers (Figure 6.4). The samplers are used to collect sediment samples is river beds. The variation in the design is due to the depth and the speed of the water current in the water. A Van-veen grab sampler (Figure 6.4a) is often used in deep, fast moving water. It has a rope tied to it that is used to close it after the sediment sample has been collected and to pull it up. The sediment in the collection chamber of the grab sampler is emptied into aluminium foil or suitable containers. The Erkman grab sampler (Figure 6.4b) is often used for shallow, slow moving river and can be deployed by applying pressure (Figure 6.4c) which closes the sampler and collects the sediment in the process. Erkman can also be adapted for use in deep, fast moving water.

Figure 6.4a: Van-veen Grab Sampler

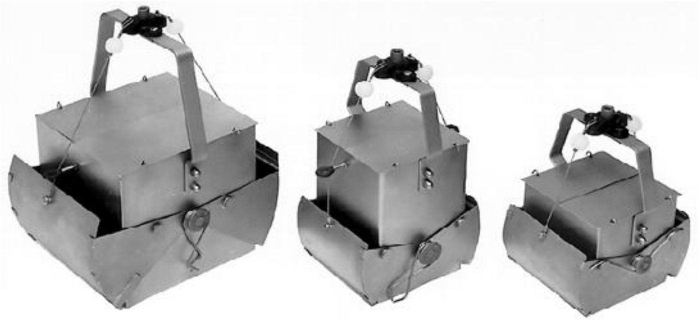

Figure 6.4b: Erkman Grab Sampler (Online)

Figure 6.4c: Erkman Grab Sampler Deployment

Water: Water samples from surface water can be undertaken with simple dipping of sampling container into the water system (below the surface of the water) to collect desired volume of water sample. The collection of groundwater is however not that simple. The figure below is a set-up that can be used locally fabricated for the collection of water samples from groundwater. The set-up contains a power source, a low flow pump and a compressor to create a pressure difference and cause the water to flow, a pipe and a water level meter and a sample collection jar.

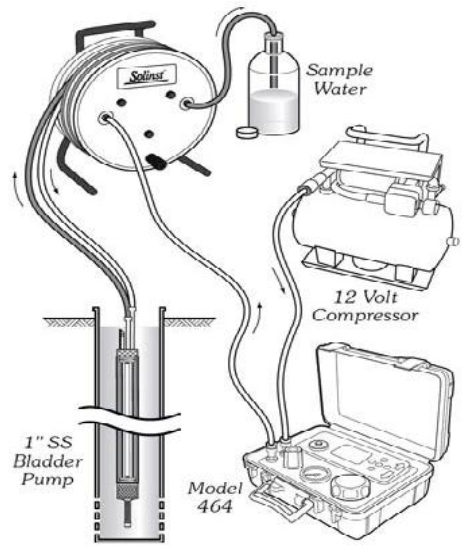

Figure 6.5: Simple set-up for Groundwater Sample Collection (Online)

3.2.2 Sample Collection General Requirements and Quality Assurance

The following general requirements should be observed during sampling to ensure quality of your results:

- Ensure that samples meet the requirements of the purpose of the sampling;
- Handle samples such that they do not deteriorate or become contaminated or become compromised before they are analysed;
- Ensure that all sampling equipment is cleaned and quality-assured before use;
- Ensure that sample containers are cleaned and free of contaminants to avoid false results due to contamination;
- Bake all bottles to be used for organic-analysis sampling at 450°C to ensure removal of organic contaminants;
- Fill sample containers without prerinsing with sample especially if preservative is pre-added to the container. Prerinsing can sometimes cause bias higher results when certain components adhere to the sides of the container.
- Depending on determinations to be performed, fill the container full (most organic compound determinations) or leave space for aeration, mixing, etc. (microbiological and inorganic analyses). If a bottle already contains preservative, take care not to overfill the bottle, as preservative may be lost or diluted.

- When sampling for analysis of volatile organic compounds, leave an air space equivalent to approximately 1% of the container volume to allow for thermal expansion during shipment.
- You may obtain composite samples by collecting over a period of time, depth, or at many different sampling points depending on your sampling purpose and design.
- Carefully consider the technique for collecting a representative sample and define it in the sampling plan.
- Add appropriate preservative when needed and in correct quantity. Use ultrapure preservative to prevent contamination.
- Keep a sampling note with details of sample such as: record of sampling location; identity of sample as written on every sampling bottle; sufficient information about sample identification; date of sampling, hour, exact location (use Global positioning systems - GPS); sample type (e.g., grab or composite); any other data especially those collected at the field such as water temperature, pH, weather conditions, water level, stream flow.
- State details of sample handling in your sampling note. Information such as whether or not the sample has been filtered; preservatives used etc;
- Make sure you properly label sample immediately after collection. Use waterproof ink to record all information.

3.3 Sample Storage and Preservation

The table 6.2 below summaries the storage and preservation requirement for the sample to be used for the chosen analysis:

Table 6.2: Storage and Preservation of Samples

Determinations (Parameters)	Sample preservation/ treatment
BOD	Check pH of all samples before testing and pH to within the acceptable range (6.5 – 7.5). Refrigerate at 4°C and analyse sample as soon as possible (2 days)
COD	Test unstable samples without delay. If delay before analysis is unavoidable, preserve sample by acidification to pH ≤ 2 using conc. H_2SO_4 and refrigerate at 4°C. Blend (homogenize) all samples containing suspended solids before analysis. Make preliminary dilutions for wastes containing a high COD to reduce the error inherent in measuring small sample volumes.
TOC	Store samples in amber glass bottles to protect from sunlight and seal bottle. Refrigerate at 4°C, add H_3PO_4 or H_2SO_4 and analyse immediately

Oil & Grease	Refrigerate at 4°C, add HCl or H_2SO_4 and analyse sample soon
Metals (General)	Add conc. HNO_3 to pH < 2, Refrigerate at 4°C and analyse sample in less than 4 months.
Each Organic Compound	Refrigerate at 4°C, add HCl or H_2SO_4 and analyse sample soon
General quality parameters	Refrigerate at 4°C and analyse sample soon

4.0 SUMMARY

The quality of your analysis results cannot be better than the quality of your samples collected. It is therefore very important that you have an excellent pre-sampling plan or design by correctly answering the questions of: from where within the target population should the samples be collected? What type of samples should be collected? What is the minimum amount of sample needed for each analysis? How many samples should be analysed? You should ensure that you use appropriate sampling equipment and containers, appropriately pre-treat the sampling vessels; collect the sample with adequate quality assurance steps; preserve and handle the sample properly.

5.0 CONCLUSION

Unit 6 of this course has been used to teach the value of sampling protocol for proper monitoring of environmental effects of crude oil activity. Petroleum and its environmental impact can be accurately evaluated with correct sampling protocol. To carry out environmental impact assessment of crude oil activities, the knowledge of the protocol for obtaining accurate representative samples presented in this unit is very instructive.

6.0 TUTOR MARKED ASSIGNMENTS

1. Discuss the relevant questions towards having an excellent sampling design prior to sample collection.
2. Describe with appropriate diagrammatic illustration the sampling equipment for collection of soil and sediment.
3. Highlight the quality assurance and general requirement for sampling.

7.0 REFERENCES AND OTHER RESOURCES

APHA - American Public Health Association (2005). Standard methods for the examination of water and wastewater, 21st Ed. Washington, DC.

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MODULE 3

UNIT 1 EXTRACTION, CLEAN-UP METHODS

CONTENTS

1.0 INTRODUCTION

Sample preparation is an important part of analytical method for determination of any analyte in sample matrix. Sample matrix is made up of the analytes and interferences. It is not appropriate to introduce the sample into the instruments used for analysis. The separation of the analyte into suitable form for injection into the analytical instrument is the objective of sample preparation. For the purpose of monitoring individual pollutants in an oil polluted environmental matrix, the sample preparation methods discussed in this unit are the ones readily available and often applied.

2.0 OBJECTIVES

By the end of this unit, you will be able to:

- explain different extraction methods used for sample preparations

- explain the different clean-up methods used for sample preparations.

3.0 MAIN CONTENT

3.1 Extraction Methods

The determination of organic pollutants in crude oil polluted samples (soil, sediment, water etc.) requires sample preparations. These preparation steps include drying, pulverization of soil samples, and extraction of the analytes with suitable solvents before instrumental analysis. In this section of the course, we will be discussing the extraction methods as a sample preparation process. We will be looking at processes, merits and demerits of liquid-liquid extraction, solid phase extraction, ultrasonic assisted extraction, microwave assisted extraction, accelerated solvent extraction methods.

3.1.1 Liquid-Liquid Extraction Method

The most preliminary and commonly used extraction technique is the liquid–liquid extraction which is often performed in a separating funnel (Figure 7.1). Two immiscible liquids (e.g. the polluted water sample and the organic solvent for the extraction) are placed in the separating funnel and are shaken to ensure interaction and increase the surface area between the phases. The analyte that is more soluble in the organic phase (extracting solvent) is transferred into the organic phase. Afterward, the mixture is stand for a while to separate the liquids into different phases (Figure 7.1), with the denser phase at the bottom and the lighter phase at the top of the separating funnel. Some of the solvent often used for liquid-liquid extraction are solvent that are not miscible with water such as n-hexane, dichloromethane, toluene, diethyl ether, ethyl acetate, petroleum ether among others. This extraction process is a batch process, it is a cold extraction process and it is used for liquid sample.

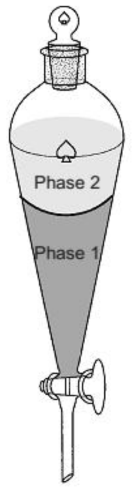

Figure 7.1 Separating Funnel

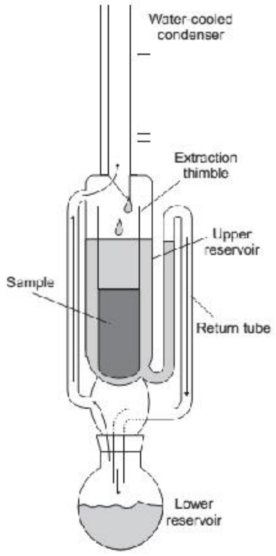

Figure 7.2 Soxhlet Extraction Set-Up

(Figures are from Harvey, 2000)

A similar extraction method that is a continuous extraction method and is a hot extraction process used for solid samples is the Soxhlet extraction process (Figure 7.2). The solvent used for the extraction (similar to the ones used in liquid-liquid extraction) is placed in the round bottom flask or any other solvent reservoir labelled as lower reservoir (Figure 7.2). The solvent is heated to its boiling point and vapourized through the left hand side tube into the condenser where it is cooled and condensed into the thimble containing the sample to be extracted. The thimble is a porous cellulose filter that allows the solvent to interact with the sample. The extract and the solvent are collected in the upper reservoir until the volume of solvent reaches the upper bend of the return tube. The solvent and the extracts are thereby siphoned into the lower reservoir. This process continues until the concentration of the extracts in the sample is reduced and increased in the lower reservoir which is an indication that the extraction has been completed.

3.1.2 Solid Phase Extraction Method

In solid phase extraction (SPE), a solid phase adsorbent is used to extract the analyte from the sample. The extraction process involves Conditioning of the solid phase adsorbent cartridge; Loading of the cartridge with the samples to extract the analytes; Washing and Eluting of the extract from the cartridge with solvent (Figure 7.3). This process is given the acronym CLWE. The cartridges (which can be C18 or HLB - hydrophilic-lipophilic balance etc.) are often conditioned before sample extraction with solvents in increasing order of polarity e.g. 6 mL n-hexane, 2 mL acetone, 10 mL methanol, and 10 mL double-distilled water. It can be used both for the extraction of the target analytes from water sample or for the clean-up of extracted solid samples. The water sample or the sediment extracts must be adjusted to suitable pH for the SPE cartridge type with an acid or base before loading depending on the pH of the sample. The flow rate of the loaded sample should be kept at a relatively slow pace (e.g. 5 mL/min). If the water sample has high level of suspended solid, filter with 0.45-µm filters before loading onto the cartridges. SPE process uses a manifold at adjustable flow rate for extraction. After extraction, the cartridges should be washed with water, vacuum dried or dried under nitrogen gas. The extracts were eluted from the SPE cartridge using suitable solvent for the target analytes. The eluates are often evaporated to dryness or known volume with vacuum-drying or under nitrogen gas. If to dryness it is reconstituted with suitable solvent before taken for instrumental analysis.

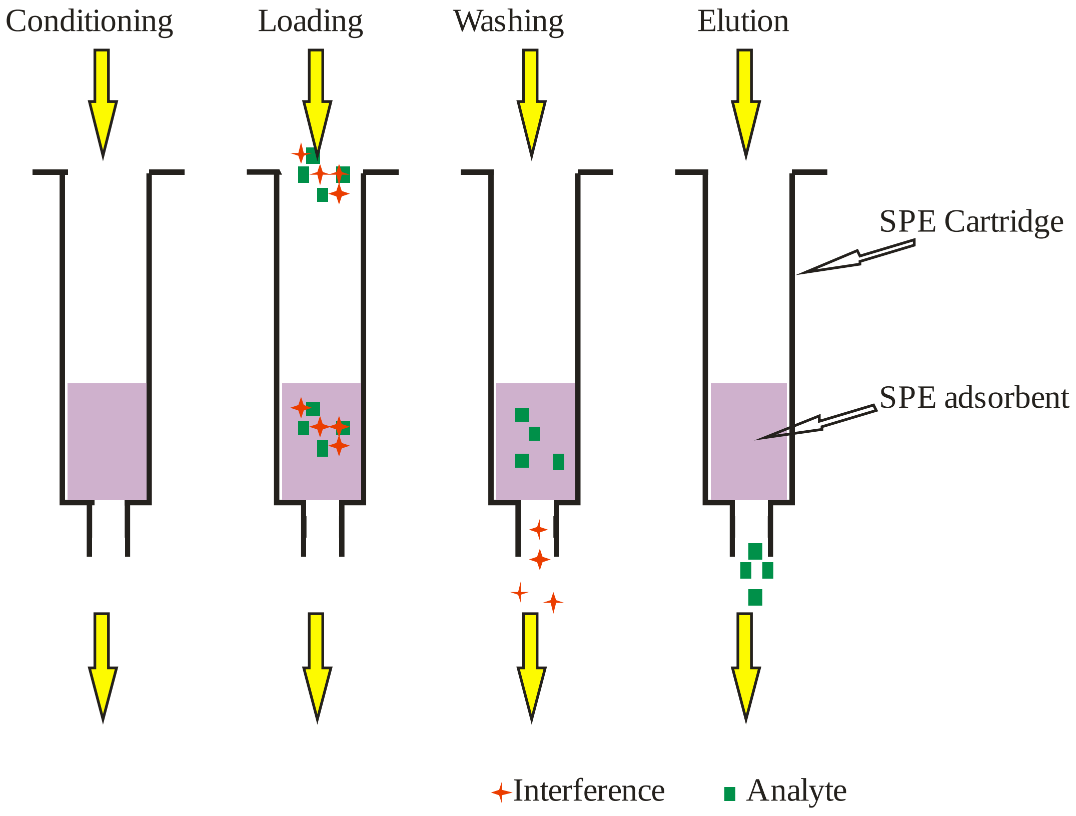

Figure 7.3: A typical solid phase extraction procedure

3.1.3 Ultrasonic Assisted Extraction Method

Ultrasonic assisted extraction is more often used for solid samples (soil, sediment, plant or animal tissues). Specific mass of the sample is extracted successively in an ultrasonic bath with predetermined volume of solvent or mixture of solvents in 3 or more successive extractions. The slurries of the solvent–sample mixtures were thoroughly shaken prior to the extraction and ultrasonicated for 15 – 25 min at room temperature. The acoustic sound of the ultrasonic system aids the effective extraction of the analyte from the sample into the solvent. The sonicated slurries are centrifuged to separate the solvent and the supernatant solvent phases filtered. The different successive extracts is pooled together and evaporated using a rotary evaporator. The extracts can be subjected to SPE clean-up. Ultrasonic assisted extraction is most useful for analytes that are heat sensitive but can be applied for all samples and forms of analytes.

The flow diagram (Figure 7.4) below is a typical example of Ultrasonic assisted and solid phase extraction process (Agunbiade and Moodley, 2014, 2016):

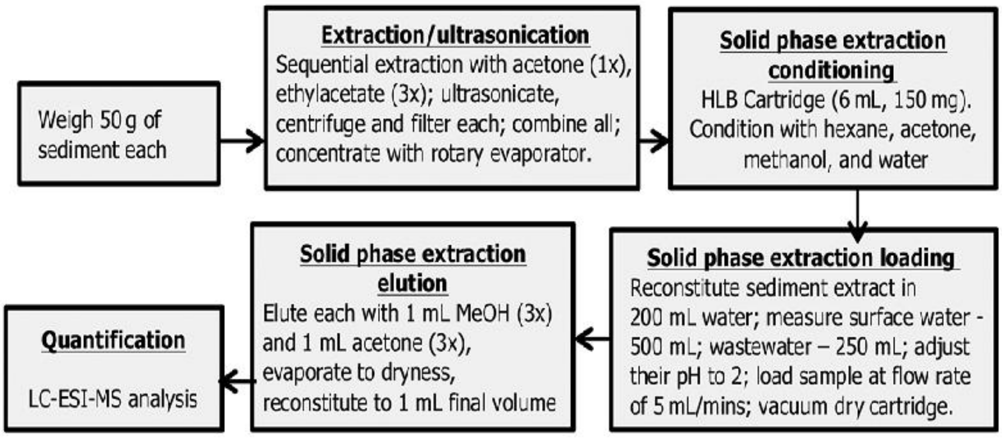

Figure 7.4: Flow Diagram of a typical Ultrasonic assisted and Solid phase extraction process

3.1.4 Microwave Assisted Extraction Method

Microwave assisted extraction of analytes and microwave digestion processes are the same types of sample preparation. The extraction is carried out using microwave radiation as the energy source for heating the sample-solvent mixture. The solvent used can be either microwave-absorbing solvent or non-microwave-absorbing solvent. The sample is placed in a microwave compatible sealed container/vessel (made of Teflon or fused silica: quartz). The vessel must be able to withstand the pressures and elevated temperature. The solvent or mixture of solvents (liquid extraction phase) is added to the sample and a microwave oven is used to heat the mixture. The application of a sealed vessel in microwave assisted extraction creates higher temperature and pressure during the extraction process and reduces extraction time from several hours to few minutes. The materials used to produce the sealed extraction vessel are thermally stable, resistant to chemical attack, transparent to microwave radiation and can withstand heating at elevated pressures. The vessels usually have cap, temperature probe and a pressure relief valve which grant the advantage of control and monitoring of the temperature and/or pressure in the vessels during extraction. Factors that can be used to optimize the extraction include the control of the heating duration, variation in mode of heating from pulsed to continuous heating, variation in the vessel configuration from open to closed, sample agitation/stirring and variation in the rate of cooling after extraction. Disadvantages of microwave extraction include the inability to add reagents during extraction process, limited amounts of sample can be used, there are safety concerns due to the use of high pressures, limited suitability for heat sensitive compounds.

3.1.5 Purge and Trap Extraction Method

Another continuous extraction method that is used for the extraction of a major component of crude oil pollution - volatile organic compounds (VOCs) – is the purge and trap extraction method. It is a liquid–gas extraction technique in which a purge gas is used to quantitatively remove the VOCs from liquid samples (Figure 7.5). The purge gas for the VOCs must be an inert gas (He or N_2) that will not react with the VOCs. The inert gas is passed through the sample, removes the VOCs, carried into a tube and the VOCs are collected on solid adsorbents (Figure 7.5). At the end of the purge extraction, the VOCs can then be removed from the adsorbents for analysis by rapidly heating the tube, flushing with inert gas and injecting directly into the instrument of analysis. Owing to the direct injection the recoveries of the VOC analytes using a purge and trap method is not always reproducible. Thus, the use of internal standards as quality assurance for quantitative work is recommended (To be full discussed in Unit 8).

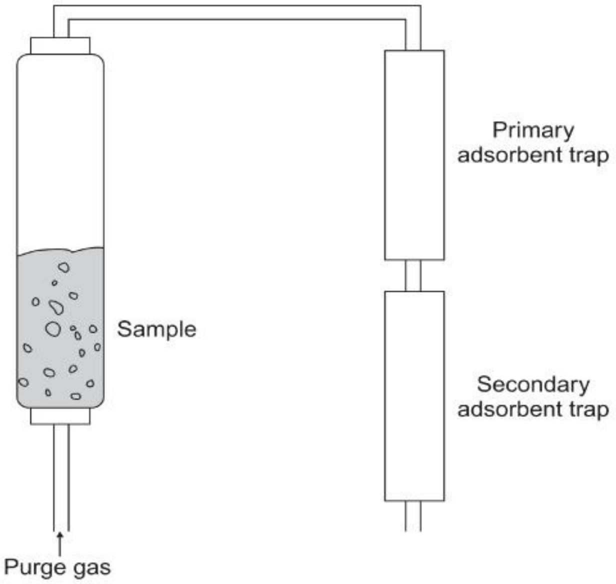

Figure 7.5: A typical Purge and Trap Extraction Set-up

3.1.6 Accelerate Solvent Extraction Method

Accelerated solvent extraction (ASE) which is also known as subcritical fluid extraction uses organic solvents under high pressures and at elevated temperatures (normally 100–140◦C) in an automated system similar to extract analytes from samples. It is similar to the operation of microwave-assisted extraction except that the microwave heating is replaced with a conventional oven. Solid samples to be extracted are placed in the extraction vessel and brought to the desired operating pressure with the use of pump which introduces the solvent or a mixture of solvents into the vessel (Figure 7.6). The vessel is then heated to the desired temperature. At the desired pressure, a pneumatic valve is opened and to allow the extract to be transferred to the liquid trap. If necessary, fresh solvent(s) can be pumped into the extraction vessel to repeat the process until the extraction is completed. ASE has advantages over other methods like conventional Soxhlet extraction techniques because it uses less solvent and is faster; over supercritical fluid extraction (SFE) because carbon dioxide used in SFE does not efficiently extract some polar analytes from complex matrices because of weak solvent strength; ASE uses less solvent than other methods; the higher temperatures used makes it easier for the solvent to overcome intermolecular interactions of the analyte and matrix effects. Its major disadvantage its limited application on thermo-labile analytes; its not selective extraction nature; problem with loss of more volatile analytes when the extract is being transferred to the collection trap; there are no ASE instruments currently available that can be used to interface directly to a chromatographic system as is the case with purge and trap.

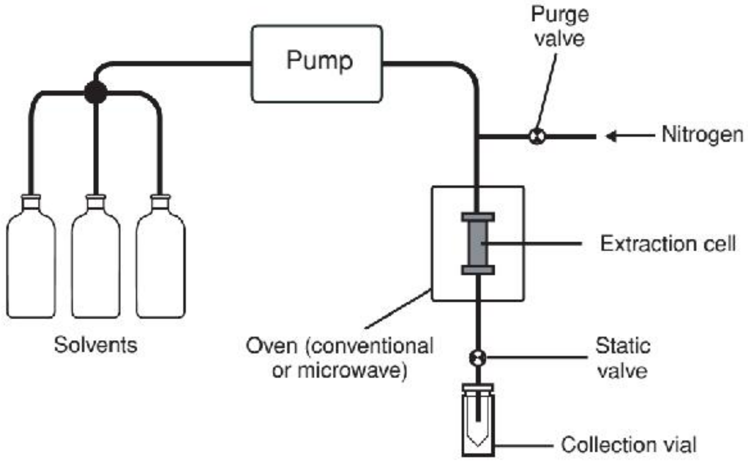

Figure 7.6: Schematic Diagram of Accelerate Solvent Extraction Set-up

3.2 Clean-Up Methods

For samples extracted with solid phase extraction (SPE), there is the advantage that the interference(s) have been removed during the extraction as discussed above (Figure 7.3). Thus, solid phase adsorbent is a modern means of sample clean up. Extracts from Soxhlet extraction, ultrasonic assisted extraction, microwave extraction among others can be subjected to SPE as a clean-up method. Before the use of SPE, column adsorption clean-up methods were used with adsorbents such as silica gel, alumina and florisil depending on the polarity of the interferences. Silica gel has the ability to adsorb polar materials which make it very suitable for clean-up of non-polar analyte like hydrocarbon. If a solution of hydrocarbons and fatty materials in a nonpolar solvent is mixed with silica gel, the fatty acids are removed selectively from solution. Thus, the materials not eliminated by silica gel are considered to be hydrocarbons.

A typical silica gel clean-up procedure will require that you weigh and place 4.0 g silica gel in a chromatographic column; tap the column to settle silica gel; add 2 g anhydrous Na_2SO_4 to the top of the column; pre-elute the column with 6 mL hexane; discard that eluate and pipet 2.0 mL hexane solution with the extract of the sample; elute the column with solvent system of your choice based on the polarity of the analyte you desire to elute.

4.0 SUMMARY

This unit of the course was used to teach the important sample preparation techniques that are state of the art and commonly available for determination of different individual organic pollutants in the environment. The techniques discussed include liquid-liquid and Soxhlet extraction, ultrasonic and microwave assisted extraction, purge and trap extraction, solid phase extraction and accelerated solvent extraction methods. The unit also highlighted the clean-up methods that can be adopted for removal of interferences in extracted samples before injection into instruments for analysis.

5.0 CONCLUSION

The use of appropriate sample preparation methods discussed in this unit is a value addition to the quality of analysis and results obtained in monitoring environmental pollution. Analytical methods that use modern techniques such as ultrasonic and microwave assisted extraction, purge and trap extraction and accelerated solvent extraction are less time consuming, less labour intensive and more effective than the conventional liquid-liquid and Soxhlet extraction. The application of clean-up like SPE and column chromatographic with adsorbents is also very essential towards obtaining reliable data of environment pollution.

6.0 TUTOR MARKED ASSIGNMENTS

1. Describe with suitable illustration the following methods of extraction:
    a. Liquid-liquid extraction
    b. Soxhlet extraction
    c. Solid phase extraction
    d. Purge and trap extraction
    e. Accelerated solvent extraction
2. Describe the various clean-up methods of sample extracts for analysis of organic compounds in environmental samples.

7.0 REFERENCES AND OTHER RESOURCES

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UNIT 2 IDENTIFICATION AND QUANTITATION

CONTENTS

1.0 INTRODUCTION

The indicator of oil pollution is not limited to the aggregate measure of such pollution but include the detection and quantification of the specific compounds with which such environment is polluted. The knowledge of the specific compounds can inform the toxic or exposure risk tendency, the clean-up/remediation approach, policy formulation among others. This unit is designed to teach how to identify and quantify specific pollutants in monitoring oil pollution.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- explain the various methods of identification of specific organic pollutants in environmental samples;
- explain the different methods of quantification of specific organic pollutants in environmental samples;

3.0 MAIN CONTENT

3.1 Individual Organic Compounds

The parameters considered in Unit 5 were the gross measures of organic pollutants used in monitoring the degree of oil pollution or impact of oil spill on an environment. In this section, the identification and quantification of specific compounds that are associated with oil pollution will be discussed. Previous units have addressed the sampling protocol and sample preparation. This section will be dedicated to the instrumentation (analytical tools) and the procedures for detection and to quantitatively measure the individual pollutants in the samples. The components of crude oil earlier discuss will inform the decision to limit the class of compounds to be considered in the section to volatile organic compounds and polynuclear aromatic hydrocarbons.

3.1.1 Volatile Organic Compounds

Volatile organic compounds (VOCs) are one of the major components of crude oil. Compounds in this class include low boiling hydrocarbons (C_1-C_8), organohalides, particularly the trihalomethanes among others. These compounds (especially benzene and trihalomethanes) have been shown to have the potential for teratogenesis or carcinogenesis in human beings. To therefore monitor and minimize the health risks associated with these substances, their sensitive detection, accurate and reproducible quantitation is very important. Suitable instruments for their accurate detection are the hyphenated chromatography methods and their extraction is best done with purge and trap method (Section 7.35). These organic compounds may be detected in ground or surface waters, soil and sediments depending on the part of the environment impacted by oil pollution or part monitored. Samples in groundwater are traceable to percolation from surface discharge or leakage from underground fuel storage vessels or pipelines.

3.1.2 Polynuclear Aromatic Hydrocarbons

Another component of crude oil that is ubiquitous in nature is the polynuclear aromatic hydrocarbons (PAHs). This class of compound are often by-products of petroleum processing or combustion but may also be obtained from pyrolysis of biomass in different anthropogenic activities. These compounds (PAHs) are highly carcinogenic even at part per billion concentration levels. Despite their relative low solubility in water, they are highly hazardous nature and ubiquitous which makes their monitoring in polluted environments, wastewater systems and even potable waters essential. United State Environmental Protection Agency (USEPA) classified 16 PAHs as priority pollutants which are:

Naphthalene; Acenaphthylene; Acenaphthene; Anthracene; Phenanthrene; Fluorene; Fluoranthene; Pyrene; Benzo(a)-anthracene; Chrysene; Benzo(a)-pyrene; Benzo[b]-fluoranthene; Benzo[k]fluoranthene; Benzo(ghi)-perylene; Dibenz[a,h]anthracene; These pollutants cane be identified and quantified with GS or HPLC methods.

3.2 Analytical Tools

The generally used analytical tools for the identification and quantification of specific organic compounds are the hyphenated chromatography methods. These include gas chromatograph-flame ionization detector; gas chromatograph- mass spectrometer detector.

3.2.1 Gas Chromatography Methods

This method is used for volatile and thermally stable compounds. It involves the partitioning/distribution of the analytes between a stationary phase (solid adsorbent or liquid coated/bonded on a solid adsorbent) and a gaseous mobile phase. The rate of distribution is different from one analyte to the other which creates a separation during the elution by the mobile phase after which the separated analytes are detected and quantified individually. Figure 8.1 is a schematic diagram of a typical gas chromatography. The set-up is the same for all GC with the difference being only the detector.

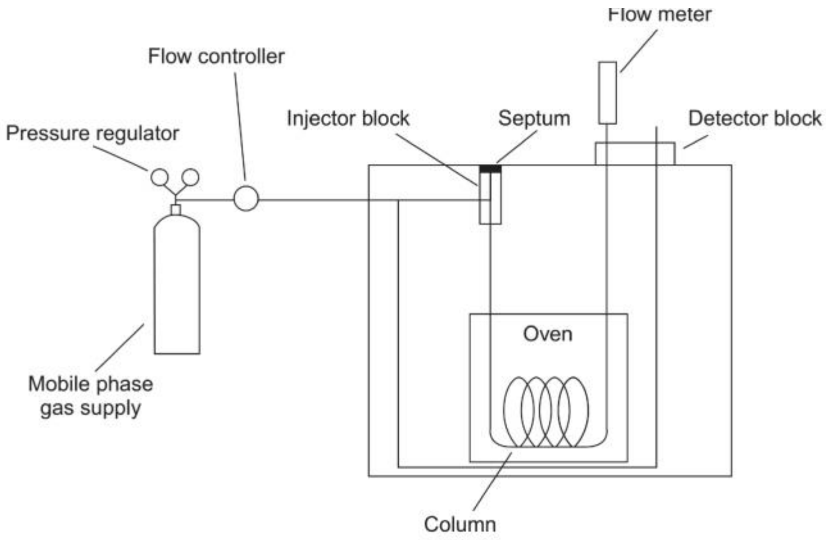

Figure 8.1: Schematic diagram of a typical Gas Chromatography

3.2.1.1GC-FID

The quantification the extracted samples from the crude oil polluted areas to know the quantity of the individual pollutants as against the gross measure of pollution earlier discussed can be carried out on a gas chromatograph equipped with a flame ionization detector (GC-FID) or a mass spectrometer (GC-MS to be discussed in the next section). The most common GC models are the Agilent Technologies Co. instrument but there are many other models like Perkin Elmer, Shimadzu among others. The components of the GC are: column (often capillary or packed); the oven where the column is located for temperature programming; the autosampler or manual injector; the detector (which in this case is FID). There are other detectors beside FID and MS but are not suitable for monitoring hydrocarbons which is the main component of crude oil. The details of the injection and mobile phase and temperature programming of GC are often the same as discussed in the next section. Some mobile phases may not however be suitable for some detectors. The detection method of FID is with the use of retention time of the analytes compared to the detection time of the standard using the same instrumental running conditions. Though FID is a sensitivity instrument, mass spectrometer detector (MSD) exhibit better sensitivity (lower limit of detection –LOD) compared to it. Analytes' identification is also relatively easier in MSD than FID. FID response to carbons attached to hydroxyl groups and amine groups is low but MSD will detect is better.

3.2.1.2GC-MS

Gas chromatography mass spectrometer **(**GC – MS) instrumental method of analysis is often performed in GC instrument of any model available (single or triple quadrupole). The instrument is controlled by computer software. A typical GC is equipped with capillary column of various dimension such as 30 m x 0.25 mm x 0.25 µm, the columns are often coated fused silica. The mobile phase (carrier gas) is often an inert gas such as helium, argon or nitrogen and at a typical flow rate of 1 mL per min. Inert gases such as helium and argon are more expensive than nitrogen and may influence the choice of the type of gas to use as mobile phase. Light carrier gasses (like He and H_2) have superior performances than the heavy ones (like N_2 and Ar). The oven temperature is oven ramped (temperature programming). An example of such oven temperature programming is to set at 50 ^oC for the first minute and heated to 310 ^oC at a rate of 10 ^oC/min and maintained for 5 min. The injection of the cleaned up sample is through the injection port. The injection can be split or splitless depending on the analyte concentration in the sample. The injected samples can be taken through a transfer line temperatures were maintained at 270-280 ^oC to remove the solvent used in diluting the sample and to concentrate the sample before taking it through the column. The MS source and Quad was set at 230 °C and 150 °C respectively . The GC-MS analysis can be carried out in auto scan mode or in selected ion monitoring mode (SIM). Each of these modes has its advantages and disadvantages and the choice is based on the aim of the analysis. SIM gives better detection limits and improved selectivity but auto scan gives better identification because all analytes present will be detected as against selective detection. The individual analytes discussed in Unit 8.3 can then be detected using the matching of their molecular ion mass number and fragmentation with a library of the instrument software. The quantification can be carried out using either external or internal standardization (to be discussed in Unit 8.5)

3.2.2 Liquid Chromatography Methods

Liquid chromatography more often called High-performance liquid chromatography (HPLC) operates in some ways similar to GC with the major difference of liquid being the mobile phase. It is used for thermal labile and non-volatile analytes. It is based on the principle of two immiscible phases (stationary and mobile) in contact with one another to effect the separation of the analytes. LC allows for a variety of phase systems (different solvent mixtures and elution modes) and wide range of selectivity which makes it versatile in application. A typical HPLC instrumentation will have the following components:

- A pump or pumps which is used to force the mobile phase (being liquid) through the system. The pump must be fitted with suitable pressure gauges and flow meters to control the solvent flow rate and pressure build-up in the system.
- Sampling valves and loops which must be located just at the head of the separation column. The valves and loops are used to inject the sample into the mobile phase after which it is driven though the column for separation by the pump.
- A separation column in which the sample components are separated into individual peaks before elution.
- A detector and readout device to detect the presence of solutes in the mobile phase and record the resulting chromatogram.

The section will discuss the operations of three LC systems in identification and quantification of organic pollutants.

3.2.2.1HPLC-FD

High-Performance Liquid Chromatography-Fluorometric Detector (HPLC-FD) instrument is a version of liquid chromatography which uses fluorometer or spectrofluorometer as detector for analysis of samples and provides excellent selectivity and sensitivity. Fluorometer is used if the detector is exclusively for a specific task and the chromatography is fairly clean but spectrofluorometer is best for all other different purposes. The analytes must be able to fluorescence or modified to fluorescence for it to be detected by this method. All species that absorb light (UV-visible) do not necessarily fluoresce. Thus, a wide variety of derivative-forming reagents have been developed to extend the realm of fluorescent detection to non-fluorescing compounds. The choice of mobile-phase must ensure that there are no compounds can quench fluorescence (compounds such as chlorinated hydrocarbons and salts that include heavy atoms - Br, I, and Cl, and heavy metals). Methanol, acetonitrile, or hexane and aqueous buffers are suitable for this method. Fluorescence detection is also limited if background light is presence; if various types of light scattering components are present; if there luminescence from the flow cell walls; and if there are emission from impurities in the solvent. These will increase with excitation intensity and produce fault signal and inaccurate results. A key advantage of fluorescence method over absorption method is that two or more solutes may absorb at the same wavelength, but emit at different wavelengths (or some may not emit) which enhances selectivity.

3.2.2.2HPLC-UV

The identification and the quantification of the analytes may be carried out in ultraviolet- visible detectors as against Fluorometric Detector if the analyte is UV-visible active. The solvent (mobile phase) is often degassed in a degassing chamber to avoid fake peak by the gasses dissolved in the solvent; the instrument should also be purged with the solvent for some time to remove trapped gases in the system. Sample injection is often carried out with autosampler but can be done by manual injection. Auto injection is more reproducible than manual injection. The injection volume is always small (typically 10 µL). The injected sample and the solvent will be forced through a column. There are different types of column but the most often used for reversed-phase LC are the bonded-phase supports which are made from micro-particulate silica bonded or coated with organic compounds (C-18 etc). The columns are also made in different dimensions. For example, a C18 reverse phase column may be of 150 x 4.6 mm, 5µm which implies 150 mm long, 4.6 mm internal diameter and 5 µm bond phase adsorbent's particle size.

The solvent systems of the mobile phase are of various types depending on the chemistry of the analytes. The mobile phase may be binary to quaternary solvent system. A typical binary solvent system may consists of solvent A (Water of HPLC grade with 0.1% formic acid or phosphate buffer) and solvent B (100% CH_3CN or CH_3OH of HPLC grade also). The application of the solvents is always with gradient programme using typical programme as follows: 0–10 min, 10% B; 10–15 min, 30% B; 15–20 min, 60% B; 20–30 min, 90% B; 10% B for final washing and equilibration of the column for the next run. The solvent flow rate is determined by the configuration of the column. The longer the column and the larger the particle size of the adsorbent in the column the higher the flow rate can be otherwise there will be pressure build-up in the system. A typical solvent flow rate can be 0.5 mL/min (Agunbiade and Moodley (2014, 2016). After elution of the sample and separation of the analytes the different analytes are detected in a ultraviolet- visible detector which could be diode array detector (DAD) or variable-wavelength detector; fixed-wavelength detector among other to give the chromatogram. The signals (peaks' heights or areas) are directly proportional to concentrations of the analytes. The signal/concentration of the standards is interpreted to know the concentration unknown (this will be discussed in details in section 8.5.

3.2.2.3LC-MS

The third alternative to the identification and the quantification of analytes is the use of mass spectrometer detector (MSD). This is a robust detection method because the analyte need not be UV-visible active as is the case with UV-Visible detector or modified to fluorescence as is the case with fluorescence detector. The solvent (mobile phase) system is similar to all the other HPLC process described above except that phosphate buffers and most ion-pairing agents are unfortunately incompatible with LC-MS method. Trifluoroacetic, formic, and acetic acids are the preferred acids for preparing buffer in mobile phase system. The analytes' identification and the quantification may are carried out with different types of MS which include tandem mass spectrometry (HPLC–MS/MS), Quadrupole time-of-flight (Q-TOF) mass spectrometer among others. These mass spectrometers use either electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) methods. The triple quadrupole (QqQ) mass spectrometer (MS) has excellent sensitivity (low limit of detection), specificity, and dynamic linear range when operated in the selected reaction monitoring (SRM) mode. Thus, the QqQ MS has become the instrument of choice in researches and environmental monitoring. However, even with tandem mass spectrometry, there is a need for chromatographic separation of the analyte from endogenous compounds. Mass spectrometer detector (MSD) preferred to all the other methods.

3.3 Quantification Methods

Quantification of analyte concentration is based on the relationship between the measured signal, (from the instruments in this case) and the absolute amount of analyte. The signals in chromatographic methods can be either peak area, peak height or response factor as the case may be. The relationship can be expressed as $S_A = kC_A + S_B$ where S_A and S_B are the signals of the analyte and blank respectively and C_A is the concentration of the analyte. This quantification can be carried out using external or internal standardization or standard addition method. The course will discuss external and internal standardization.

3.3.1 External Standardization

External standardization is the preparation of standard curve using standard reagents of the analytes being studied which are prepared in different concentrations. The standard curves, also referred to as calibration curves, are always prepared with the dissolution of the standard reagents in water or any other suitable solvent. The different concentrations of these standard reagents are then subjected to the instrumentation required for the analysis to obtain the signal S_A for the corresponding concentration C_A. External standardization can be by a single point standardization or by multiple point standardization. A single standard containing a known concentration of analyte, C_A, can be prepared and its signal, S_A, obtained. The value of k in the equation is calculated by the ratio of the signal to the concentration: $k = {}^{S_A}\!/_{C_A}$. The use of single-point standardization is not desirable for accurate standardization because all experimental errors, are carried over into the calculated value for k. Any uncertainty (error) in the value of k increases the uncertainty (error) in the analyte’s concentration. Thus, a multiple-point standardization which is often prepared from the signals of five standard concentrations (prepared in increasing order) is more preferable. A plot of five signals (S_A) versus the concentrations (C_A) is the calibration curve. The exact standardization, or calibration relationship, is determined by the use of an appropriate curve with the line of best fitting. Calibration curve has a region called the linear range. The region should be used for the determination of the unknown and not otherwise. A demerit of external standardization is that it does not account for matrix effect (Figure 8.2). In this example presented in Figure 8.2, using a normal calibration curve will result in a false reporting (i.e. error). For instance, the matrix of a soil and sediment is different from matrix of clean water used in preparing the standard and can result in false results as presented in Figure 8.2. When matrix problems are expected, an effort is made to match the matrix of the standards to that of the sample. This is known as matrix matching.

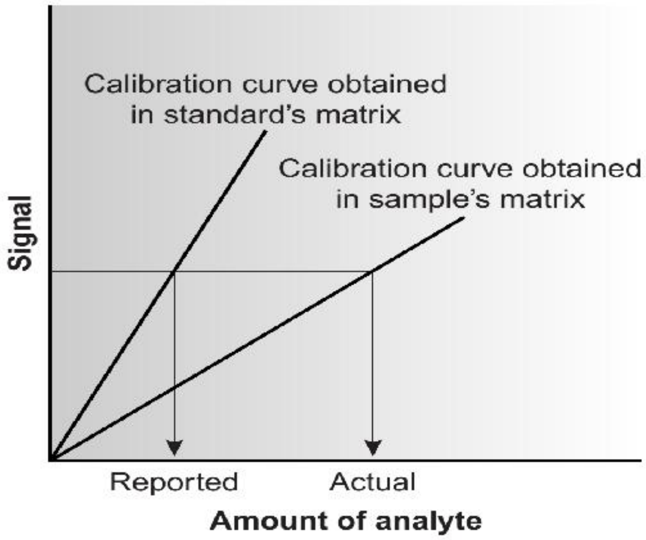

Figure 8.2: Illustration of the negative impact of matrix effect (Harvey, 2000).

3.3.2 Internal Standardization

There is the problem of samples and standards reproducibly due to matrix effects with the use external standardization. The procedure in external standardization makes it difficult to control the extent to which all samples and standards are treated to be equal. This impacts negatively on the accuracy and precision of the standardization. In another instance, a volatile solvent used to dissolve analytes will increase in concentration if some solvent is lost to evaporation and will present false results. Therefore, if the sample and a standard are in identical environment, with similar concentrations and signals, they will both experience the same loss of solvent, same matrix effects and their signals will continue to be identical. This is the basis for internal standardization. In this process a standard is added which must be different from the analyte. This standard is called an internal standard. The analyte and internal standard in any sample or standard are made to receive the same treatment which makes the ratio of their signals to be unaffected by any lack of reproducibility in the procedure. The ratio of their signal is called response factor. Thus, the determination of the unknown can be carried out with one point internal standardization or multiple points' internal standardization similar to the external version. In the single point internal standardization signal (S)-concentration (C) expression applied is as follows: $S_A = k_A C_A$ and $S_{IC} = k_{IC} C_{IC}$ where A is the analyte and IC is the internal standard. The ratio of the signal of analyte S_A to that of the internal standard S_{IC} is the response factor:

$$\frac{S_A}{S_{IC}} = \frac{k_A}{k_{IC}} \times \frac{C_A}{C_{IC}} = K \times \frac{C_A}{C_{IC}}$$

In application of internal standardization, the standard reagents solution of the analytes with the addition of the internal standard is injected into the instrument for analysis, this is done also for the sample extract containing the unknown quantity of the analytes. The response factor, ratio of the analytes and the known concentrations of the analyte standard and the internal standard signals, is used to determine the value of K for each analyte and the K used to determine the concentration of the unknown:

$$K = \frac{S_A}{S_{IC}} \times \frac{C_{IC}}{C_A}$$

For multiple point standardization using internal standard, a plot of the response factor versus concentration of the analyte’s standard is made as expressed in the equation below.

$$\frac{S_A}{S_{IC}} = \frac{K}{C_{IC}}(C_A)$$

4.0 SUMMARY

The various methods of analysis of individual compounds such as volatile organic compounds (VOCs) and polynuclear aromatic hydrocarbons (PAHs) in crude oil polluted environments were taught in this section. Gas and liquid chromatographic methods with different detectors are the most often applied modern analytical tools from this purpose. The quantification of these compounds in the samples can be achieved either by external or internal standardization.

5.0 CONCLUSION

The monitoring, detection and quantification of the specific compounds in crude oil polluted environment is very important to obtaining information about toxic effects, exposure risk tendency, the best clean-up/remediation approach, policy formulation among others. This unit has discussed the use of hyphenated chromatographic methods to selectively and sensitively identify and quantify these compounds.

6.0 TUTOR MARKED ASSIGNMENTS

1. Describe the application of gas chromatography mass spectrometer (GC-MS) for the determination of polynuclear aromatic hydrocarbons (PAHs).
2. Discuss the following quantification methods:
    a. Single point external standardization
    b. Multiple points external standardization
    c. Single point internal standardization
    d. Multiple points internal standardization

3. Write short notes on the following analytical tools for the determination of organic contaminants in the environment:
   a. Gas chromatography Flame Ionization Detector (GC-FID)
   b. Liquid chromatography mass spectrometer (LC-MS)

7.0 REFERENCES AND OTHER RESOURCES

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UNIT 3 OIL TAGGING AND USE OF BIOMARKERS IN OIL POLLUTION MONITORING

CONTENTS

1.0 INTRODUCTION

Unit 9 is dedicated to introduce you to the concept of petroleum tagging and monitoring of crude oil pollution using biomarkers. The unit starts with the explanation of what biomarkers are. Then an outline of common biomarkers compounds was provided and the relevance or information provided by the biomarker. The method of analysis of biomarkers and their applications were also discussed.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- explain what biomarkers are;
- identify common biomarker compounds used in petroleum tagging;
- describe the method of analysis of biomarkers and the importance in oil tagging and pollution monitoring.

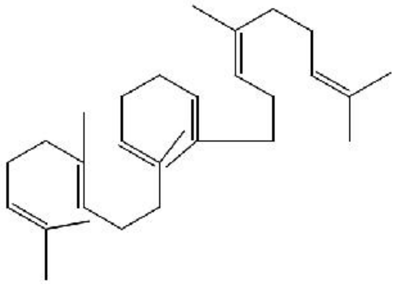
3.0 MAIN CONTENT

3.1 What are Biomarkers?

Biomarkers are compounds often hydrocarbons that are found in crude oils that are chemical signature of the organism from which they were produced. They are also found in other components like rock, soil and sediment extracts. These biomarkers are often complex organic molecules whose chemical structures remained unchanged during the metabolic processes of diagenesis for oil generation. This retention of the chemical structures becomes useful in the tracing of the crude oil source to molecules of the living organisms in which they were sourced. Biomarkers are often referred to as molecular fossils. They also provide information of the transformation process, the deposition environment's geochemistry, geological history and the migration path of the crude oil among others. Typically, biomarkers in crude oil may lose the functional groups but retain virtually all the original carbon skeleton of the source materials making the structural similarity as factor explored for source apportionment. Moreover, there are those biomarkers which are ubiquitous and prolific in many organisms and others that are only found in specific types of organisms. Hence, these are used as markers for source apportionment. Some biomarkers only appear in parent organism after they have evolved. The presence of such biomarker compounds are used as marker for the diagnostic age of the crude oil. Additionally, some biomarkers are structurally stable in certain environments than others. This type of biomarkers when abundant can be used to make inference on depositional or migration environments of the oil. In some cases subtle chemical transformation from one structure to another may occur due to high temperature and the biomarker ratio to its transformed version used as a marker for maturity. Biomarkers may also contain heteroatoms like sulphur during early diagenesis under anoxic, marine condition; organic acids are a by-product of microbial degradation, and porphyrins containing nitrogen and metals are common biomarker in low maturity oils.

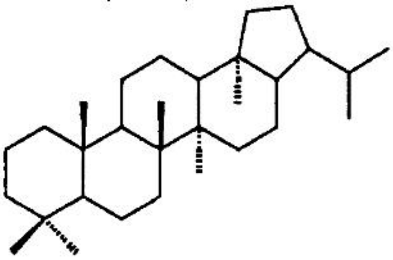
3.2 Common Biomarker Compounds

The following are some of the common biomarkers used in crude oil exploration and pollution monitoring and the implications of their presence in making inferences:

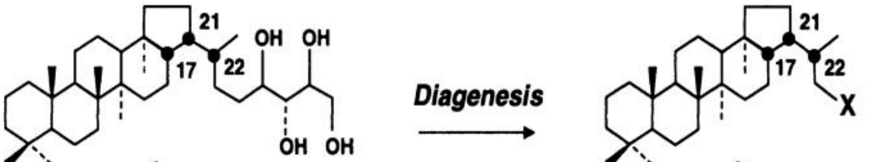


Squalene: Squalene is a C30 isoprenoid (compound I) and a common precursor for other biomarkers. Bacteria can use reactions that do not require the presence of oxygen to cyclize squalene into diploptene. This pentacyclic triterpanoid can be further modified to produce wide array of biochemicals. Eukaryotic organisms use oxygen and synthesize tetracyclic steroids instead of triterpanoids. These are used to produce other biomarkers.

Squalene can be transformed into hopane. **Hopane** (compound II) is an indication that the oil is derived from a source rock deposited in an anoxic (low or no oxygen) environment and can also be used to indicate that the source rock carbonate in nature. The conversion process involved action of prokaryotic organisms.



II



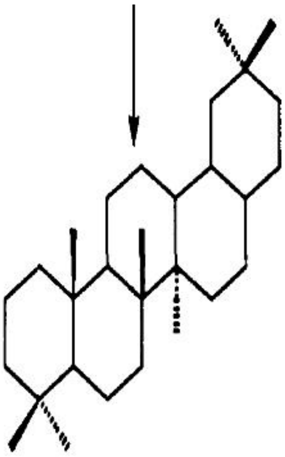
1

Bacteriohopanetetrol in Prokaryotic Organism

2

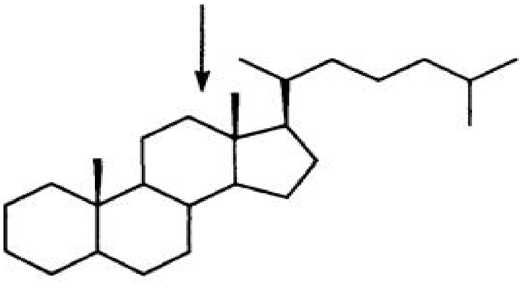
Hopane in Sediment (Biological Configuration) ββ22R

The presence of these compounds in samples from oil pollution areas can be used as indicator of the source of the pollution and the biogeochemical process the pollutants have been subjected to.



III

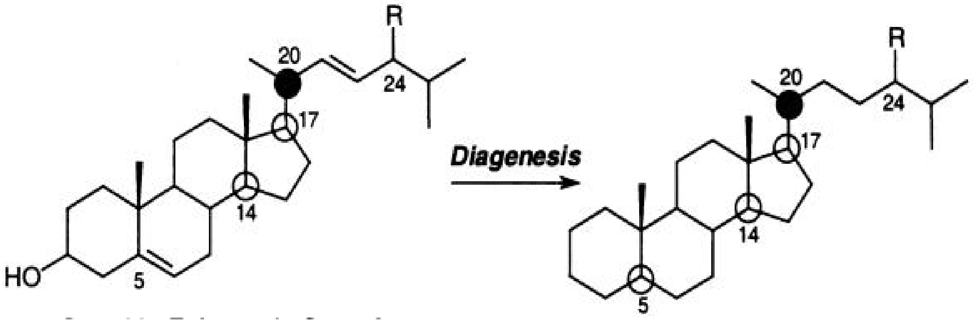
Oleanane (compound III) is another biomarker that is synthesized and retains the main structure of squalene. Oleanane is an indication of higher, flowering plant as the raw material source and the source rock being aged source rock.



IV

Cholestane (compound IV) is another product biomarker from squalene. Any oil in which cholestane is ubiquitous is an indication that the oil is derived from a marine source rock.

Steranes (compound V) are another class of biomarker that are ubiquitous in most oils and rock extracts. It is diagnostic for specific biota. Dinosteranes for example are produced by dinoflagellates, n-propylcholestane by chrysophyte marine algae. The value of the information gleaned from steranes is not from their occurrence but from their relative distribution to hopanes. For example. the ratio of hopanes-to-steranes can serve as an indicator of source. Low ratios were found in marine sources, while high ratios were observed for lacustrine and terrigenous sources. This can be used to monitor the well and the field from where the oil pollution occurred.



V

Sterol in Eukaryotic Organism → transformed Sterane in Sediments (crude oil)
R = H; CH_3; C_2H_5; C_3H_7

3.3 Petroleum Tagging and Biomarker Analysis

The conversion processes of the biological origins of the crude oil have ensured that the majority of the components have been extensively converted into organic compound (majorly hydrocarbon). Moreover, biomarkers are generally minor components of a crude oil or rock extract. Therefore, highly selective and sensitive methods of analysis employing gas chromatography – mass spectrometry (GC-MS) are necessary for their measurement. Gas chromatography (GC) is being used for biomarker analysis, particularly for n-alkanes, branched alkanes and acyclic isoprenoid hydrocarbons. The individual biomarkers are much low in abundance (concentrations ranging from 1 to 500 ppm) compared to fractions such as the regular paraffin and aromatics but they are some of the most abundant structurally defined compounds used in tagging petroleum. Typically a crude petroleum sample is separated into a saturate and aromatic fraction during the sample preparation stage prior to biomarker analysis and then both fractions are analyzed independently. The most common GC analysis method is the GC-MS alternative because of the need for structural elucidation and comparison. In the transformation process, the biomarkers are in different isomers and the separation of individual isomers is achieved in the capillary columns of the GC with nonpolar stationary phases which is sufficient to resolve many of the biomarkers of interest. The separation into saturate and aromatics in the sample preparation stage provides the desired greater resolution, reduces the effects of interference and allows for the determination of biomarker concentrations down to the low ppm and ppb levels. It is typical for a single biomarker analysis to monitor several hundred biomarkers. Thus, mass spectrometer (MS) is most useful for the detection, providing a molecular "fingerprints" from the ionization and fragmentation of the biomarker into their characteristic fragmentation pattern. That helps to better and selectively identify the eluted biomarker compounds. The MS uses Electron impact (typically 70 ev) as the most common ioniziation technique. When available, a tandem mass spectrometry technique (GC-MS/MS) is used to analyze and distinguish biomarkers further because of its additional selectivity which is essential when resolving more complex biomarker distributions. The GC-MS method of analysis and quantification is the same as the ones explained in Unit 8.

3.4 Application of Biomarkers in Petroleum Tagging

Biomarkers in crude oils can be used to assess the thermal maturity of the source rocks. This is because there are changes in the relative abundances of certain biomarkers in crude oil as the maturity of the source rocks changes. Therefore, variations in the biomarker parameters can be used to identify and characterize the source rock maturity and for analysis of the migration of the oil. These biomarker maturity parameters can be formulated from the ratio of one biomarker to another which are indicator of its use of processes that occur during source rock maturation. The processes such as: Cracking (breaking large molecules into smaller molecules); Isomerization (changing the structural arrangements of atoms in the molecules); Aromatization (formation of aromatic rings by loss of hydrogen from naphthenes). These processes create associated relative changes in the biomarker in crude oil.

In the applications of biomarkers for petroleum maturity or oil tagging, there are some limiting factors or considerations must be kept in mind:

- It must be known that the exact relationship between a biomarker parameter and the source maturity is dependent on heating rate; source rock geology, and source organic matter’s chemistry (kerogen type). As a result, the exact maturity associated with a given value for a biomarker parameter can change from basin to basin.
- Furthermore, the relationship between a biomarker maturity indicator and source rock maturity is generally non-linear.
- With increasing maturity, many biomarker maturity indicators reach terminal values; hence, a given biomarker parameter is applicable only over a specific maturity range.

- The concentrations of biomarkers in petroleum decrease with thermal maturity.

Despite these limitations, biomarker indicators of source maturity can be extremely useful. An example of biomarker parameters that can be used are those based on compounds that are highly resistant to biodegradation, such as:

$$\frac{\text{Triaromatic}}{\text{Monoaromatic + Triaromatic steroids}}$$

3.5 Application of Biomarkers in Oil Pollution Monitoring

Crude oil pollution monitoring using the presence of individual organic compounds like VOCs, PAHs may be misleading because some of these compounds may be released into the environment from other sources other than crude oil. Thus, the application of biomarkers as indicator of oil pollution associated with crude oil is very important. This is carried out by the use of GC-MS in the investigation and quantification of these biomarker compounds listed in section 9.4. These compounds are characteristic of crude oil and their presence in the environment is considered a strong inference of crude oil related pollution. There are also other statistical measures like principal component analysis (PCA) that can be used to model other parameters thus far discussed (both aggregate and individual) together with the biomarkers to evaluate the extent of their correlation and use that to also draw inferences on the source of pollution in crude oil pollution monitoring.

4.0 SUMMARY

Biomarkers which are compounds that retain the chemical signature of the materials from which crude oil were derived are useful in identifying the source material, the source rock, the maturity of the crude oil, the migration path and other information about the oil. They are best analysed with sensitive analytical tools like GC/MS or GC/MS-MS because of their low concentration and the advantage of the analytical tool in providing the chemical fingerprint of the compounds. This unit has briefly describes the usefulness of biomarkers in petroleum tagging and in the monitoring of crude oil related environmental pollution.

5.0 CONCLUSION

Biomarkers are valuable compounds in exploration and characterization of petroleum because of the information they provide. A more detailed knowledge of these compounds and their application will add value to the knowledge of geochemist, environmental specialist and chemist in general. This unit has provided briefly introduction to the concept of biomarkers and concludes that they are valuable compounds in crude oil tagging and environmental monitoring.

6.0 TUTOR MARKED ASSIGNMENTS

1. Discuss what biomarkers are and highlight the common biomarker compounds used in crude oil tagging.
2. Describe the method of analysis of biomarkers.
3. Outline the importance of biomarker in:
   a. Petroleum tagging
   b. Crude oil pollution monitoring

7.0 REFERENCES AND OTHER RESOURCES

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