
بسم الله الرحمن الرحيم

THE FRACTIONATION OF CRUDE PETROLEUM USING CHROMATOGRAPHY, EXTROGRAPHY AND SUPERCRITICAL FLUID EXTRACTION

by

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DECLARATION

I hereby declare that this work has not already been accepted for any degree and is not being concurrently submitted in candidature for any degree.

Signed.....Candidate

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I hereby that the work described in this thesis is the result of my own investigations except where otherwise indicated.

Signed .....Candidate

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ABSTRACT

The accurate and reliable analysis of crude oil, weathered oil and oil-spill-related environmental samples is extremely important in view of the distribution of oil pollution in the environmental. In this work the fractionation selectivity of column chromatography, extrography and supercritical fluid extraction was compared.

Column chromatography with a silica gel as stationary phase provided a means of fractionating a standard mixture of saturated and aromatic hydrocarbons and crude oils such that the aromatic profile could be determined by GC-MS. The recoveries of saturated, aromatic and polar compounds from crude oil are in the range of 60.6-70.3 %, 12.9-19.8 % and 7.1-9.4 % respectively, with relative standard deviations under 6 %.

The potential of extrography on silica gel as a fractionation technique of crude oil has been evaluated in terms of reproducibility and selectivity of separation. The recoveries of saturated, aromatic and polar compounds from crude oil are in the range of 59.3-72.0, 13.6-21.0 and 7.5-10.5 % respectively, with relative standard deviations under 6 %. The overlapping effects between the adjacent fractions were evaluated using GC-MS. It was found that extrographic fractionation produced a better separation than the column chromatographic technique.

The supercritical fluid extraction parameters determined in this study using spiked samples have shown to be effective starting conditions for fractionation of crude oil samples. These studies have shown that under optimized SFE conditions (density 0.75 $g.cm^{-3}$ and temperature 40 ^{0}C) crude oil can be selectively fractionated into saturated and aromatic compounds.

Comparatively, it was found that SFE provided an effective extraction within 56 minutes while the chromatography and extrography methods required 8-10 and 4-6 hours respectively. The total recovery of crude oils for column chromatography, extrography and SFE are in the range of 83.4-90.5 %, 89.4-95.9 % and 77.7-99.9 % respectively. The capability of SFE to fractionate mixtures containing homologous compounds with narrow molecular weight ranges has shown to be more effective than can be achieved with column chromatography and extrographic techniques.

Studies into the SFE of spiked aqueous matrices performed utilizing a liquid extraction cell showed that crude oil could be fractionated into saturated and aromatic compounds under the optimized conditions of pressure $\approx$ 3000 Psi and 40 ^{0}C with a 15 minute extraction time and 2 cm^{-3} min^{-1} flow rate.

Abbreviations

AFID	Alkali- Flame- Ionization Detector
API	Atmospheric Pressure Ionization
bbl	Barrel
b/d	Barrel per day
BP	Boiling Point
CI	Chemical Ionization
CP	Critical Point
CSD	Critical Solvent Deashing
DC	Direct Potential
DCM	Dichloromethane
DNA	Deoxyribonucleic acid
ECD	Electron Capture Detector
EI	Electron Ionization
PVC	Ethylene Polyvinylchloride
FI	Field Ionization
FID	Flame Ionization Detector
FPD	Flame Photometric Detector
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
GC/MC	Gas Chromatography/ Mass Spectrometry
GLC	Gas Liquid Chromatography
GSC	Gas- Solid Chromatography
HP	Hewlett Packard
HPLC	High Performance Liquid Chromatography
HR-MS	High Resolution-Mass Spectrometry
IR	Infrared Spectroscopy
LC/MC	Liquid Chromatography/ Mass Spectrometry

L-V	Liquid-Vapor-Like System
LC	Liquid Chromatography
MFRC	Marine Fisher Research Center
MS	Mass Spectrometry
MS-MS	Tandem Mass Spectrometry
m/z	Mass to charge ratio
NCB	National Coal Board
NMR	Nuclear Magnetic Resonance
NPD	Nitrogen- Phosphors Detector
ODS	Octadecyl Bonded Silica
PAHs	Polycyclic Aromatic Hydrocarbons
Pc	Critical Pressure
PCBs	Polychlorinated Biphenyl's
ROSE	Residuum Oil Supercritical Extraction
RT	Retention Time
SCD	Sulfur chemiluminescence Detector
SFC	Supercritical Fluid Chromatography
SFC/MS	Supercritical Fluid Chromatography/ Mass Spectrometry
SFE	Supercritical Fluid Extraction
SF	Supercritical Fluid
SPE	Solid Phase Extraction
SCOT	Support Coated Open Tubular (column)
Tc	Critical Temperature
TIC	Total Ion chromatograms
TMS	Trimethylchloro silane
TCD	Thermal Conductivity Detector
TIC	Total Ion Chromatogram
TLC	Thin-Layer Chromatography
T-P	Temperature- pressure
TPH	Total Petroleum Hydrocarbon
UNEP	United Nation Environmental Pollution

USDA	The U.S. Department Of Agriculture
UV	Ultra-Violet
WCOT	Wall Coated Open Tubular

Chapter 1

1.1 GENERAL INTRODUCTION

The term petroleum was first used by Agricola [1] in 1546. Derived from the Latin words Petra (rock) and Oleum (oil), it is used to describe all three phases of extractable organic compounds found in the earth, although the three phases can each have separate names. Gaseous petroleum is normally called natural gas (associated or non - associated with oil). Liquid petroleum as extracted is known as crude oil to distinguish it from refined oil which is derived from crude oil. The semi-solid or solid forms of petroleum are called asphalt, tar, bitumen, or pitch. The name petroleum is only applied to secondary organic matter, that is the matter that has been produced by the thermal breakdown of kerogen [2].

Petroleum differs from the class of materials to which coal belongs in three important respects, unlike coal, it is usually liquid at room temperature, completely soluble in organic solvents such as benzene and carbon disulphide, and on combustion it leaves much less ash than coal [3].

Most petroleum types are complex mixtures that are difficult to characterize in detail, and therefore the many definitions used to describe petroleum and its products lack precision. The Concise Oxford Dictionary [4] defines petroleum as a " mineral oil found in rocks or on the surface of water, used for illumination and mechanical power". Legally, petroleum has been called a mineral [5], but this usage does not satisfy the common geological definition of a

mineral as an inorganic substance with chemical and physical properties either uniform or varying within narrow ranges[6].

1.2 History and uses of petroleum

The history of petroleum use and related materials such as bitumen, goes back to the dawn of civilization [7]. It was first observed almost 6000 years ago as oil and asphalt seepage. The use of petroleum has also been documented in many places on the earth such as in Romania, Iran, Italy, Egypt, Iraq, India, Cuba, and later in the United States.

The early civilization that developed in the great river valleys of Mesopotamia used asphalt obtained from hand-dug pits in building construction as flooring, building cements and water proofing materials, for ornamental purpose, and to caulk their boats. Petroleum oil derived from seepage was used for jewel-setting, preservation of mummies [8] and for medicinal purposes ("Syrian oil" or "green oil") in ancient Egypt and in the early Roman Empire. After the decline of the Roman Empire the knowledge of the properties of petroleum reappeared in the Arab countries [9], who developed the first distillation process which they introduced into Western Europe through Spain. The lighter oils obtained were used to fill porous pots which could be ignited by fuses and gunpowder. These early incendiary devices were reported in battles dating from the seventh century.

The birth of the modern oil industry has just entered its second century. The first modern commercial drilling and production of oil is usually said to have

began in 1859 in the US, when "Colonel" Edwin Drake sunk a well in Pennsylvania near some natural seepage's, to a depth of 69.5 ft, with production of about 25 barrels per day [10].

Since this first commercial oil well, crude oil output in the United States has increased from approximately 200 barrels in 1859 to 10,000,000 bbl in 1874. In 1990 world petroleum consumption was at a rate of a bout 65 million barrels per day [11].

In 1861 the first cargo of oil contained in wooden barrels was sent across the Atlantic to London, and by the 1870 s, refineries, tankers, and pipelines had become characteristic features of the industry. Throughout the remainder of the nineteenth century the United States and Russia were the two areas in which the most striking developments took place and very rapidly became an international large scale activity [12].

Crude oil as it comes from the ground has little or no direct use, it is merely a raw material. Its value as a commodity is only realized when its many different hydrocarbon components are separated out, broken down or combined with other chemicals to provide products that can be marketed. A crude oil's value, therefore, is directly related to the yield of useful products each barrel will produce as it is passed through a refinery.

Today, a modern refinery can distill thousands of barrels of oil a day through continuously operating distillation towers that are based on the same

principle as Sillimans distillation [9]. The basic principle of the refining processes can be divided into three different areas:

1. Separation, that is division of the feedstock into various streams (or fractions) depending upon the nature of the crude material.

2. Conversion, that is the production of saleable material from the feedstock by skeletal alternation, or even by alternation of the chemical type of the feedstock constituents.

3. Finishing, that is purification of the various product streams by a variety of processes that remove impurities from the product.

Tens of thousands of different products can be derived from crude oil as shown in Table 1.1. What can be extracted economically from a crude oil varies according to its particular individual qualities, and the processing facilities of a particular refinery. In general, crude oil yields three basic groups of products which are produced when it is broken down into cuts or fractions:

1. Gas and gasoline.

2. Middle distillates.

3. Fuel oil and residual cut.

The gas and gasoline cuts form the lighter products of a tower are some times referred as "white products". These provide domestic gases, aviation fuel, motor fuel and raw material or feedstocks for the petrochemical industry. Naphtha

is extracted from both the light and middle distillate cuts forming a basic feed stock for other products particularly those involved in the improvement of gasoline quality for car engines and feedstocks for the petrochemical industry.

The middle distillates refers to products from the middle of a tower such as kerosene, light gas oil, heating oil, diesel oils, lubricating oils, and some waxes. The actual proportion of light, medium and heavy fractions that exist naturally in a barrel varies enormously from one crude to another. For instance, light North African crude from Algeria or Libya [13] has a high yield of light and middle distillates, while other crudes may yield almost no light products, with heavy fuel oil and residue accounting for over 80 % of a barrel in certain cases.

Petroleum is also a highly suitable raw material from which to obtain hydrocarbon monomers which can be used to form polymers. The polymerization process is illustrated by the synthesis of polyethylene (polythene) $[-CH_2-CH_2-CH_2]_n$ from ethylene [14]. Polyvinylchloride (PVC) $[CH_2CH(Cl)-]_n$ is made by substituting alternate hydrogens on one side of the polythene chain with chlorine.

Modern chemical technology can synthesize a huge range of these substituted hydrocarbon polymers containing chlorine, oxygen, sulphur and other elements. Such products have become part of our household vocabulary and include: paints, insulating plastic such as PVC, Perspex, Bakelite and synthetic fibbers [15] etc.

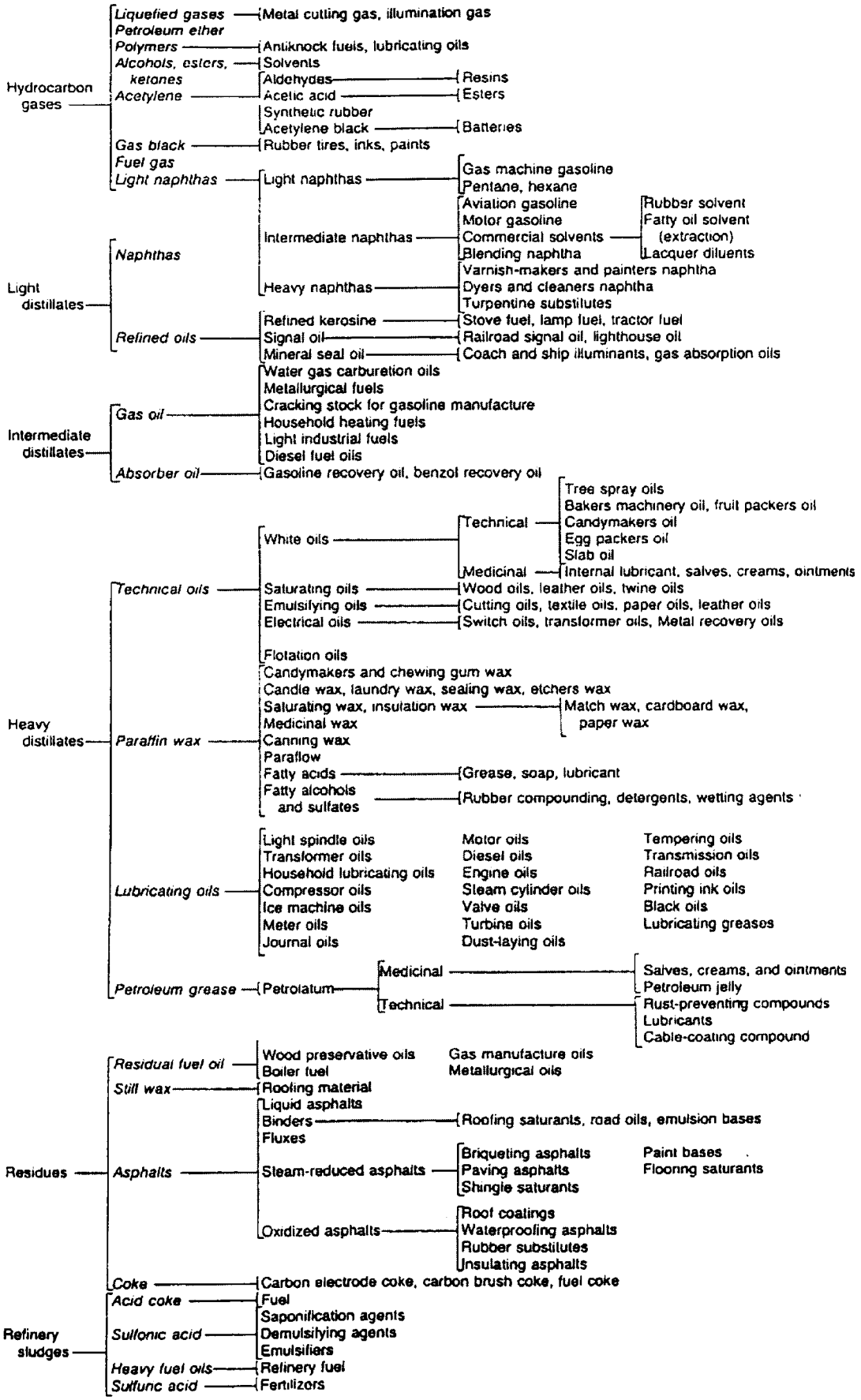


Table 1.1. Crude petroleum and some of its products [15].

1.3 Discovery of oil in Libya

Libya has an area of about 1.76 MM sq. km, of which 62 % is occupied by sedimentary basins. Traces of oil and gas had been found in occasional water wells for many years, although there have been no reports of surface "shows". The search for oil in Libya may be considered the shortest and most successful in the history of oil. Systematic exploration for oil began for the first time in 1954, and within three years commercial accumulations from the Sirte Basin were discovered[16].

The exploitation of oil is governed by a petroleum law of 1955, when the first concession was granted. General control is in the hands of the Secretariat (formerly ministry) of petroleum. The first oil was discovered in Libya by ESSO Standard Oil of Libya in January, 1958 in its Atshan No. 2 well .This well is located in concession 1 in Western Libya . It produced oil at the rate of 508 barrels per day on the test [17].

Production for export began in 1961 and expanded rapidly, to take Libya into fourth place among Middle East and Mediterranean producers in 1973 and eighth place in the world. Proven recoverable reserves were quoted at 23 billion barrels in 1981. Figure 1.1 illustrates the oil and gas production during the period 1983-1993. Oil production in 1993 averaged about 1.38 million bpd verses 1.48 million bpd in 1992. Libyan production averaged about 1.37 bpd in 1994 [17]. The major oil fields, pipe line system and export terminals of Libya are illustrated in Figure 1.2.

The proximity of Libyan ports to European markets, and the lightness and low sulphur content of most Libyan crude's are factors which have encouraged an extraordinarily rapid expansion of oil output, unequaled any where in the World. The price of Zweteena and Brega light crude to established customers rose from $12.32 a barrel in 1975 to $ 26.27 and $ 41 a barrel in early 1981. Principle markets are in Western Europe and North America. Total oil revenues were $ 15.22 billion in 1979 and $ 22.53 billion in 1980. There are five export terminals in the Gulf of Sirte and sixth is planned in the west. The Libyan tanker fleet, one of the biggest in Africa [18], comprised 13 units of total capacity of 1.2 million tons. Six refineries have been built since 1970 and three more are planned to a total capacity of one million b/d.

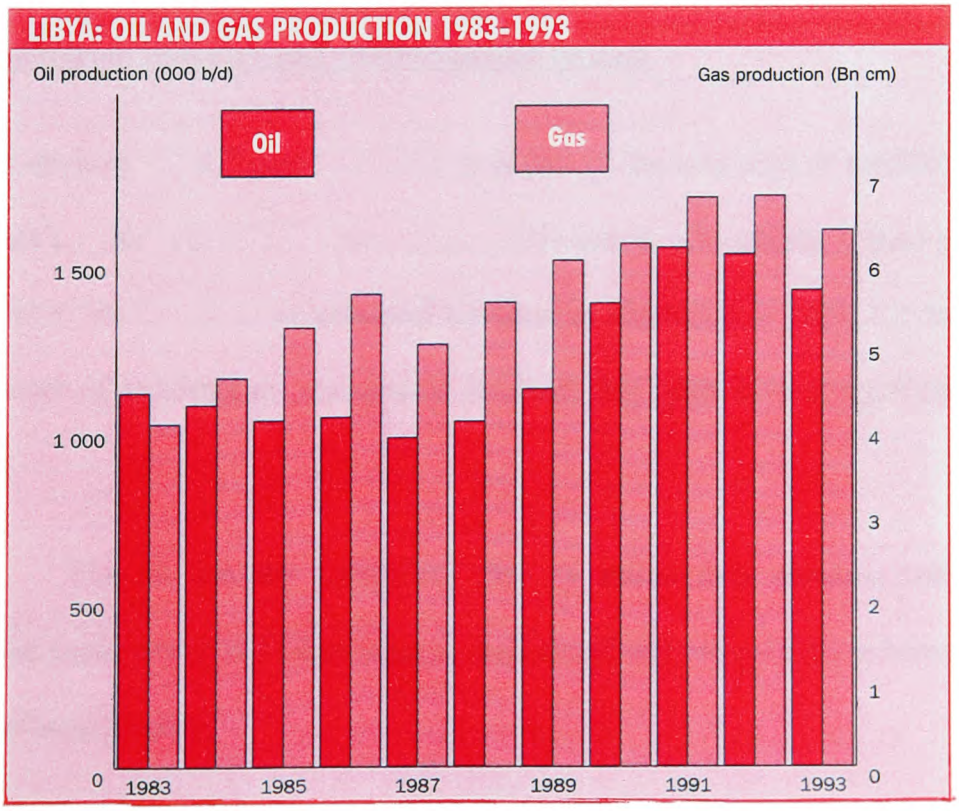


Figure 1.1. Oil and Gas Production In Libya [19].

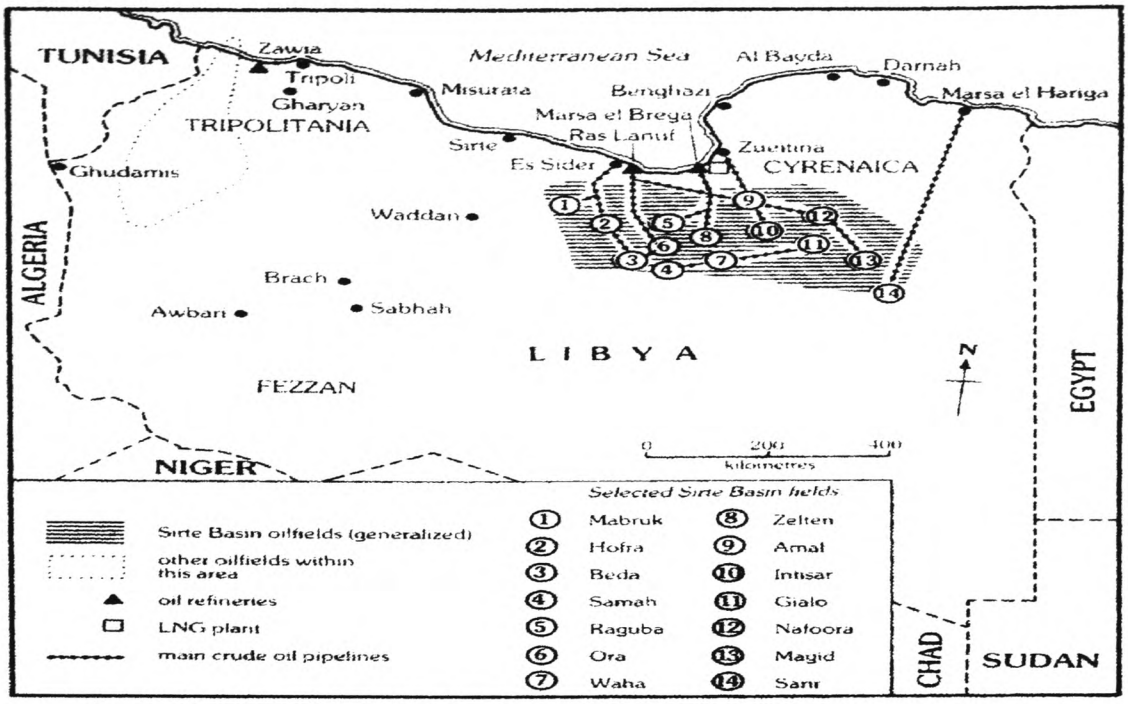


Figure 1.2. Libyan hydrocarbon resources and installations [17]

1.4 The petroleum industry and environmental impact

The environmental " cost " of industry is part of the total cost of satisfying human wants by producing goods and services. This covers not only the impact on land, air, and water from routine industrial activities as illustrated in Table 1.2. but also the chance of accidents or unexpected incidents that might have a significant local effect.

The oil industry recognizes that its action may produce some change in the environment and takes steps to understand and measure the influence of all area of its operation.

The International Convention for the prevention of pollution from ships, 1973 (MARPOL 73/78) defines oil in Annex 1 as " oil means petroleum in any

form including crude oil, fuel oil, sludge, oil refuse and refined products (other than petrochemicals) [20].

Table 1.2. Environmental impacts of oil [21].

Environment	Exploration	Extraction Production Processing	Transmission	Use and disposal
Atmosphere	Emissions of H_2S and hydrocarbons as a result of a blowouts	Refinery emissions of SO_2, H_2S, CO_2, No_x, and hydrocarbons	—	Emissions of SO_2, CO_2, and hydrocarbons
Hydrosphere	Blowouts and spills from exploratory wells at sea, leading to oil contamination	Blowouts and spills brine and drilling chemicals disposal Refinery effluents	Tanker accidents, leading to oil contamination	Groundwater contamination by leaking tanks
Lithosphere	Blowouts and spills from on land	Blowouts and spills sludge disposal	Pipeline construction and spills Damage to permafrost	Used oil disposal
Human impacts	Disruption of life style	Interference with fisheries	Interference with fisheries or land use Disruptions of life style during construction	Hydrocarbons and polynuclear aromatic hydrocarbons from combustion

1.4.1 Oil pollution in the Mediterranean sea

Concern about the presence of oil in the marine environment is not a new phenomenon in the Mediterranean Sea. Natural seepage has existed over geological times, particularly in north-eastern parts. However, the oil pollution of

anthropogenic origin is substantial and considerable amounts are frequently observed, mainly as lumps of tar on beaches or off- shore often together with surface film contamination

Since the 1960 s, the Mediterranean has acquired the reputation of being one of the most polluted seas in the world. Millions of tons of pollutants, both natural and synthetic, are spilled into this sea every year. Philippe Le Lourd, former Director of the regional oil combating center in Malta, estimates that somewhere between 500,000 and one million tons of oil (and oil related products) are flushed into the Mediterranean every year. Most of this pollution comes from routine shipping operations and tanker traffic through the discharge of dirty ballast waters, bilge slops, and oily wastes.

Today, around 600 million tons of petroleum products are shipped into and through the Mediterranean every year (Figure 1.3) About half of this amount ends up at 18 ports scattered around the coastline [22].

In the mid-1970s, the Mediterranean was covered with so much oil that scientists trying to study marine life often pulled in nets filled with tar balls instead of fish. In 1977, during a research cruise in the Eastern Med. scientists from the International Atomic Energy Agency's Laboratory at Monaco made the following observation; "between Crete and Libya a 30 minute neuston sampling period (surface) two filled 100 cm^3 collecting jars with tar balls. In other areas, as much as 500 litters of tar per sq. km of water surface have been found in the Ionian Sea off Libya and between Libya and Sicily [23].

The protection of the Mediterranean sea has become a priority following the United Nations Conference on the Human Environment held in Stockholm in 1972. Since that time enormous efforts have been made by the United Nations and specifically by UNEP, in the organizing of expert consultation and intergovernmental meetings necessary to establish and carry out the "Action plan of the Med. sea" which was approved by conference of Plenipotentiaries in Barcelona in February 1976. These two initiatives may improve in some respects the oil pollution situation in the Mediterranean.

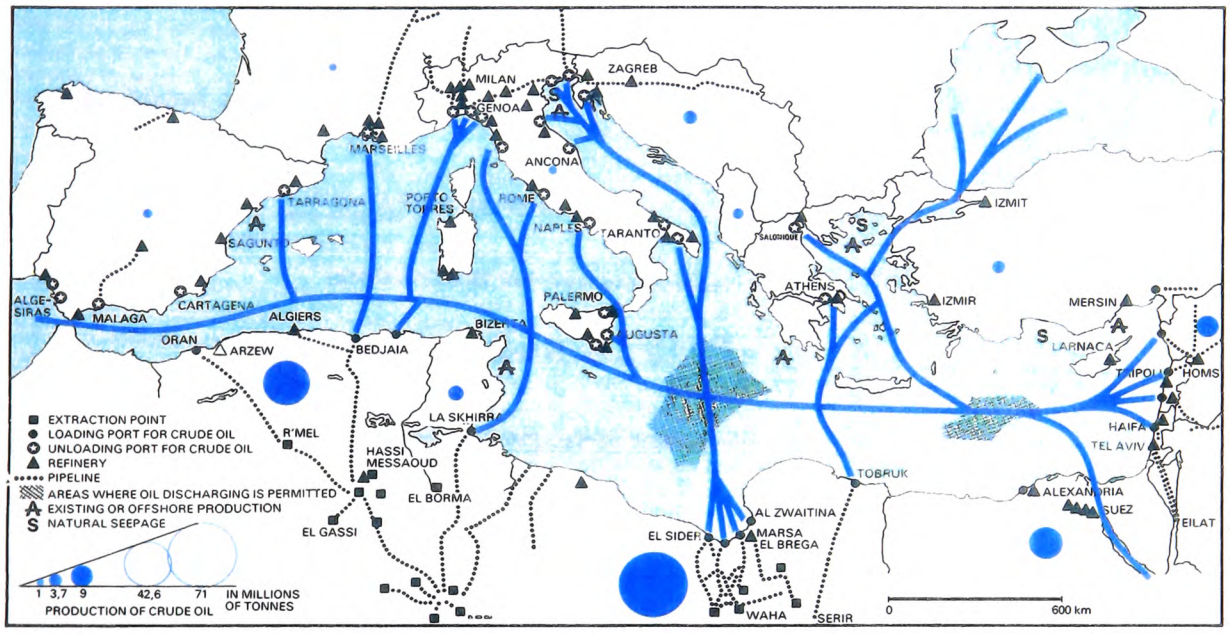


Figure 1.3. Production areas and transported paths of oil in the Mediterranean region [24].

The main source of the oil pollution in the Mediterranean sea can be classified as the following [22]:

1. Major sources

1.1 Ballasting / deballasting operations of tankers

1.2 Discharge of oily bilge - water

1.3 Tank washing

1.4 Refinery effluents

1.5 Discarded lubricants and other oils.

2. Minor sources are

2.1 Accidents to tankers and other vessels (small annual contribution but each can pose a major local problem)

2.2 Offshore exploration and exploitation

2.3 Accidents to pipelines and terminals

2.4 Natural seepage

2.5 Atmospheric rain - out.

Once this " complex chemical soup" has entered the sea its subject to a subsequent series of physical, chemical and biological processes which define the biogeochemical cycle of oil at the sea.

Some natural processes lead to disappearance of oil from the sea surface, whilst others cause it to persist. Spilt oil is eventually assimilated by the marine

environment unless the oil is first blown ashore. Natural processes affecting oil are evaporation, emulsification, dispersion, sedimentation, dissolution, photooxidation and biodegradation. Figure 1.4. illustrates these processes and Figure 1.5. illustrates what is considered to be their relative importance with time.

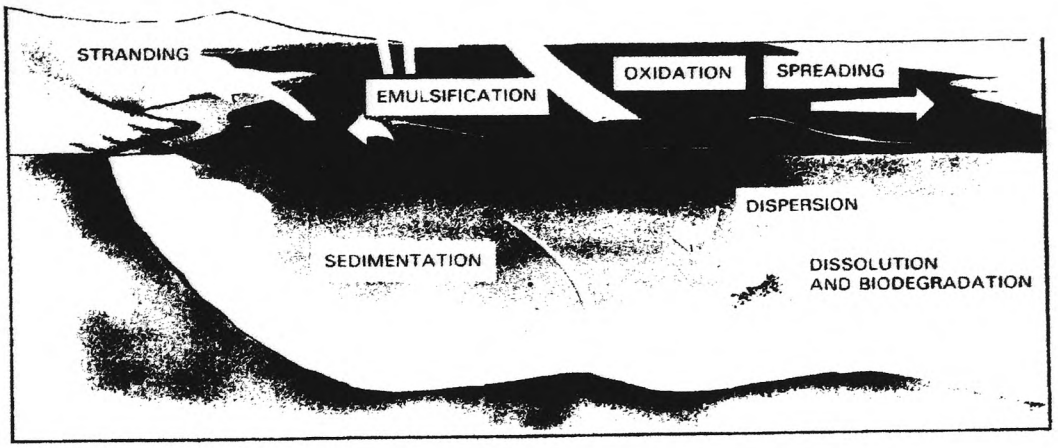


Figure 1.4. Fate of spilt oil including the main weathering processes [25].

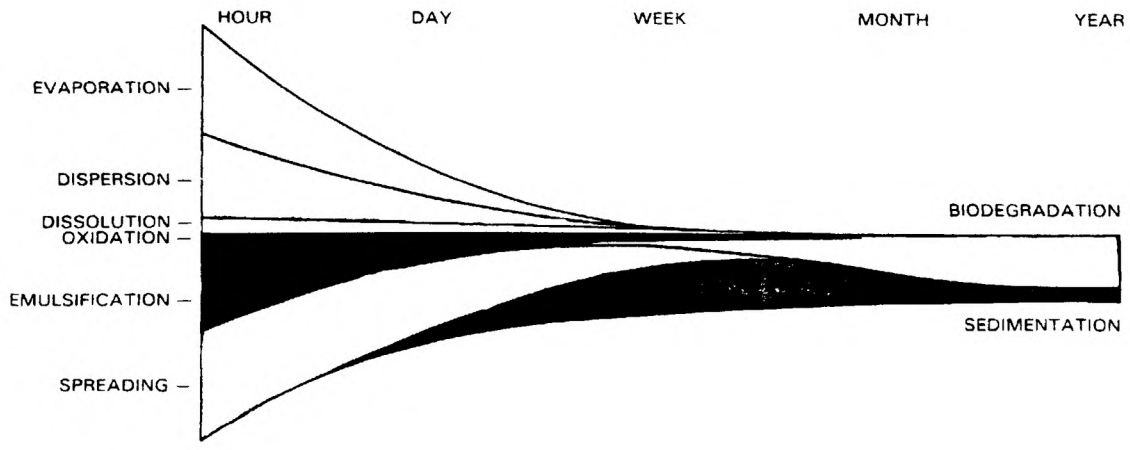


Figure 1.5. A schematic representation of the relative importance of spill processes at various times [25].

Meanwhile dynamic processes such as currents, waves and tidal movements have also a pronounced effect on the oil spill as they, together with the wind, control the advective and dispersive behaviour of oil in the sea. Most of these processes are controlled by the oil properties. The main physical properties that affect the behaviour of a spilt oil at sea are specific gravity, distillation characteristics, viscosity and pour point [26].

The understanding of the transport and fate of their environmental consequences and particularly for evaluating the capacity of the receiving waters to accept wastes without detrimental effects, identification of a potential source of oil pollution and the degree of weathering can some times give an approximate indication of the length of time that has elapsed since the oil was spilt.

The Bouri (the first Libyan off-shore oil field development) crude oil behaviour has been studied using sophisticated computer modeling [27, 28].The fate of oil in Libyan waters as illustrated from Marine Fisheries Research Center (MFRC) report [29] " the water coastal currents and the meteorological conditions tend to deposit oil on the seashore or to concentrate it on some preferential points, no matter whether oil comes from offshore sources or from land ones. In summertime, this movement is reinforced by winds that wash ashore oil, particularly the residues. Tar balls are then deposited along the Libyan coastline where they accumulate".

1.4.2 Oil Spill Impact

The complete range of marine life is affected by any oil released at sea, including phytoplankton, zooplankton, fish, birds and mammals. The effects of the oil depend greatly on the oil itself and upon the type and condition of the receiving environments. The harmful effects on living organisms may be divided into those that are primarily physical and those that are primarily chemical.

Life forms at the water surface, such as marine birds and mammals are subject to physical effects caused by oil coating the organisms or their immediate environment. This is very clearly seen when water birds become covered with oil. By matting the feathers, the oil destroys their insulative capacity, reduce buoyancy in the water and prevents flight. In other organisms oil coating may cause death by asphyxiation. Oil films on the surface water reduce light transmission and, hence, photosynthetic primary production. It also reduces oxygen uptake by water and so cause a lower dissolved oxygen concentration and the death of many organisms.

The chemical effects of oil can be related to the components involved. The low boiling saturated hydrocarbons have until quite recently, been considered harmless to the marine environment. It is now been found that this fraction, which is rather insoluble in sea water, produces at low concentrations anesthesia and narcosis and at greater concentrations cell damage and death in a wide variety of lower animals. It may be especially damaging to the young forms of marine life. The low boiling aromatic hydrocarbons are the most toxic fraction. Benzene, toluene and xylene are acute poisons for man as well as for other organisms;

naphthalene and phenanthrene are even more toxic to fishes than benzene, toluene and xylene. These hydrocarbons and substituted one-, two-, and three- ring hydrocarbons of similar toxicity are abundant in all oils and most especially, the lower boiling oil products. Low boiling aromatics are more water soluble than saturated compounds and can kill marine organisms by direct contact. Olefinic hydrocarbons, intermediate in structure and properties, whilst absent in crude oil do occur in refining products, (e.g. gasoline, cracked products) and are in part responsible for immediate toxicity [30].

Numerous other components of crude oils such as cresols, xylenols, naphthols, quinoline, pyridines are of special concern because of their great toxicity and their solubility in water. 3, 4-Benzopyrene and 1, 2-benzanthracene are believed to be the main carcinogens in petroleum and in industrial products. They cause mutations either by direct covalent bonding with Deoxyribonucleic acid (DNA) or by wedging themselves into the DNA helix (intercalation). and inhibit blood cell formation in bone marrow or depress the central nervous system[31].

High boiling point saturated and aromatic hydrocarbons may not exert much direct toxicity but may interfere with the responses of aquatic organisms to chemical stimuli (e.g. sex attractants) with equally serious consequences.

1.5 THE GENESIS OF PETROLEUM

The problem of petroleum genesis has long been a topic of research interest. The many theories proposed in the past to explain the origin of petroleum are based on two major concepts inorganic versus organic (biogenic) origin. The inorganic hypothesis [32,33,34] assumes that oil forms from the reduction of primordial carbon or its oxidized form at elevated temperatures deep in the earth. The organic (biogenic) theory [35,36,37] is based on the accumulation of hydrocarbons from living things plus the formation of hydrocarbons by the action of heat on biologically formed organic matter. Engler [38] in 1910 was the first author to postulate that an organic substance other than coal was the source material of petroleum. He showed that waxes and fats could be converted into petroleum-like products at a temperature of about 400 ^{0}C. Later on, many investigators did similar experiments [39] with many different organic materials.

It is now widely accepted that petroleum has a biogenic origin, being derived from the remains of plants and animals deposited together with fine grained minerals at the bottom of the sea. The great similarity between the chemical structures of compounds present in petroleum and those of compounds in living organisms strongly supports this idea. Development of modern techniques such as gas chromatography, nuclear magnetic resonance, spectroscopy and mass spectrometry has permitted the isolation and identification of many of these compounds. From the analysis of the extracts of recent and ancient sediments and

of petroleum it can be seen that petroleum is a product of the partial conversion of the original organic matter [40].

The origin and maturation of petroleum is shown in Figure 1.6 and follows two pathways from living material. The first pathway, on the left of the figure, provides 10-20 % of petroleum which is formed directly from the hydrocarbons synthesized by living organisms or from other biological molecules, which are readily converted to hydrocarbons. Most of these early formed hydrocarbon molecules contain more than 15 carbon atoms, most possess easily recognized biological structures.

The second pathway, on the right suggests, that lipids (fats), proteins, and carbohydrates are converted into the organic matter (kerogen) of sedimentary rocks. When kerogen is buried deeper at higher temperatures, it cracks to form a bitumen that breaks down further to form petroleum. Some hydrocarbons are also formed at this stage. At higher temperatures, and lower levels petroleum can further break down in two ways, one leading to increasing smaller hydrogen-rich molecules and the second leading to larger hydrogen-deficient molecules [41].

The accumulation of petroleum is believed to involve three steps:

1. The generation of oil.

2. The primary migration (the movement of oil from source to reservoir rock).

3. The secondary migration (the redistribution of oil within the reservoir rock to form a pool).

The kinds and amounts of petroleum that are generated in the earth are influenced by three factors:

1. The nature of the remains of living organisms preserved in the sediments.

2. The abundance of this organic matter.

3. The extent to which it has been heated.

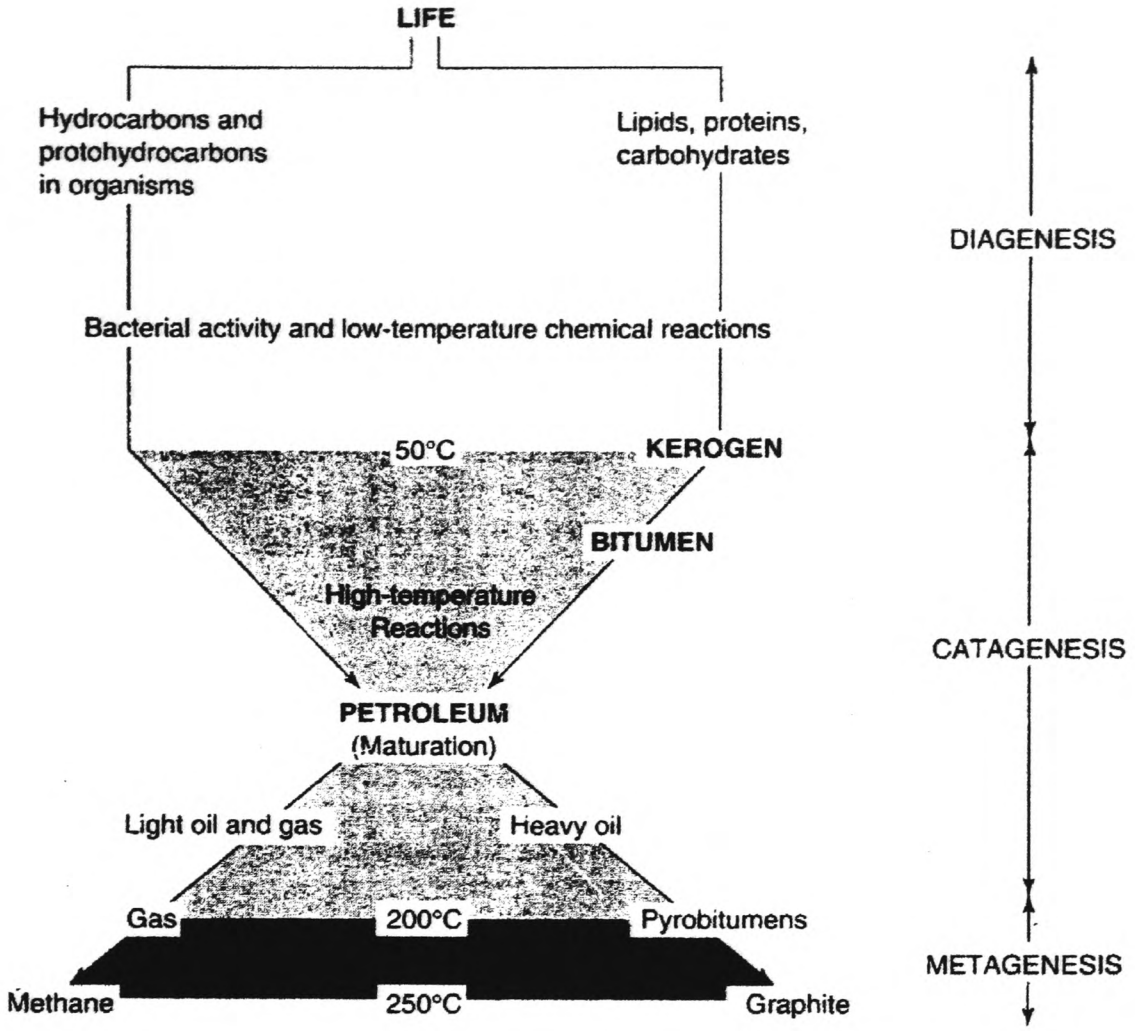


Figure 1.6. The origin and maturation of petroleum [37] .

1.6 COMPOSITION OF CRUDE OIL

Petroleum, generally referred to as crude oil, is defined as " a mixture of hydrocarbons that existed in the liquid phase in natural underground reservoirs and remains liquid at atmospheric pressure after passing through surface separating facilities" [42] . The constituent molecules, as the term suggests comprise predominantly of atoms of carbon and hydrogen in varying abundance, arranged and linked together in many different ways.

Variations in the ratio of these hydrocarbons are principally responsible for differences in the chemical and physical properties of crude oils. In appearance, crude oils vary from straw yellow through a series of green and brown to black. They also vary in both density and viscosity. Although crudes consist of mixtures of the same series of compounds, the relative proportions of each of such series vary so giving rise to differences between crudes. North sea crude is low in sulphur content while all Middle East crudes are high in sulphur. Venezuelan crude tends to be dominantly naphthenic and contains relatively high amounts (30 ppm) of vanadium and nickel. Crude oil is a complex mixture comprising tens of thousands of molecules from volatile gases to waxy residues, many of which have not yet been characterized. For example, despite 50 years of research on Ponca city crude, only 60 % (w/w) has been characterized [43] .

The principle elements of crude oil, as mentioned earlier, are carbon and hydrogen with lesser amounts of sulphur, nitrogen, oxygen and metals. These elements are combined to form a complex mixture of organic compounds that range in molecular weight from 16 (methane) to several thousands (asphaltenes). Between these two extremes are many thousands of compounds having simple to very complex structures.

Hydrocarbons constitute the most important fraction in any crude oil. Their proportion can vary significantly from 30-40 % and up to100 % in gas condensates[2]. These hydrocarbons are usually separated by fractional distillation.

The principle fractions obtained from distillation of some Libyan crudes are categorized as in Table1.3 [44]

Table 1.3. Fractions obtained from distillation of some Libyan crude oils.

fractions	Distillation Range ^{0}C	Yield wt %			
		Sertica Crude	Sedra Crude	Zwetena Crude	Bouri Crude
Gases	Gas	3.6	2.1	1.4	0.2
Straight Run Naphtha	C5-175	29.2	22.2	27.2	12.1
Kerosene	175-235	10.0	9.3	11.1	7.0
Gas Oil	235-350	20.8	21.0	21.7	20.1
Vacuum Gas Oil	350-560	23.	29.9	25.6	35.3
Vacuum residue	560 +	12.6	15.5	12.7	25.1

Constituent components of crude oil may be divided into groups based on chemical classification.

1. Saturated hydrocarbons: comprising normal, isoalkane (paraffins) and cycloalkanes (naphthenes).

2. Aromatic hydrocarbons: including pure aromatic, cycloalkanoaromatic (naphthenoaromatic) molecules, and usually cyclic sulfur compounds. The latter are most frequently benzothiophene derivatives.

3. Resins and asphaltenes: high molecular weight, polycyclic, polyfunctional compounds containing nitrogen, sulphur and oxygen.

4. Organometallic compounds.

1.6.1 Saturated hydrocarbons (Alkanes)

Each of the three classes of saturated hydrocarbons:- normal alkanes, isoalkanes, and cycloalkanes have been found in petroleum. The smallest alkane present is methane and the largest are waxy materials of very high molecular weight (up to C_{100}). The proportions of the three classes vary greatly between crudes. Above about C_{10}, the saturated hydrocarbons are characterized more easily if they are separated from the other components before analysis. In petroleum terminology, the three classes are often called normal n-paraffins, isoparaffins and cycloparaffins (naphthenes) respectively. The word paraffin is derived from the Latin parum affinis, which means " of slight affinity"

1.6.1.1 n - Alkanes

Normal alkanes are defined as straight chain hydrocarbons, and form the bulk of most crude oils. They may be found up to C_{80}. This makes them the most easily identifiable compounds in petroleum, because there is only one isomer for each carbon number and they tend to show well-defined regularly spaced peaks in a gas chromatogram. All other compound classes contain many different isomers, so identification is more difficult. Table 1.4. shows some of these hydrocarbons identified in the Libyan crude oils [44].

The normal paraffin's are relatively inert towards strong acids, bases, and oxidizing agents. Sulphuric acid, for example, is used to remove impurities from n-alkanes so that they may be used for medicines and as coatings for food containers, seeds, spores, and leaves (for protection during storage, and to reduce water loss from plants growing in dry desert areas).

Table1.4. Normal Paraffins Isolated From Sarir Libyan Crude Oils.

Compound	% (wt/wt)
n-Butane	0.76
n-Pentane	1.23
n-Hexane	2.34
n-Heptane	2.33
n-Octane	2.39
n-Nonane	2.45

1.6.1.2 Isoalkanes

This hydrocarbon class consists of branched chain molecules (Fig. 1.7) that exist in a wide range of different concentrations. Individual isoalkanes are not isolated and identified as easily as are n-alkanes, for as the carbon number increases so does the possible number of structural isomers. It is theoretically possible to have more than a million branched chain structures for C_{25}.

Table 1.5. lists the number of possible isomers for the series corresponding to the formula C_nH_{2n+2} [46] . Isobutane is the first member of this series. A number

of isoprenoide have been identified for example, pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane) are frequently found at sufficient concentration as to appear in a gas chromatogram as distinct peaks alongside the peaks of the C_{17} and C_{18} n-alkane. Table 1.6. Shows Iso-alkanes and some other branched alkanes isolated from Sarir Libyan crude oils [44].

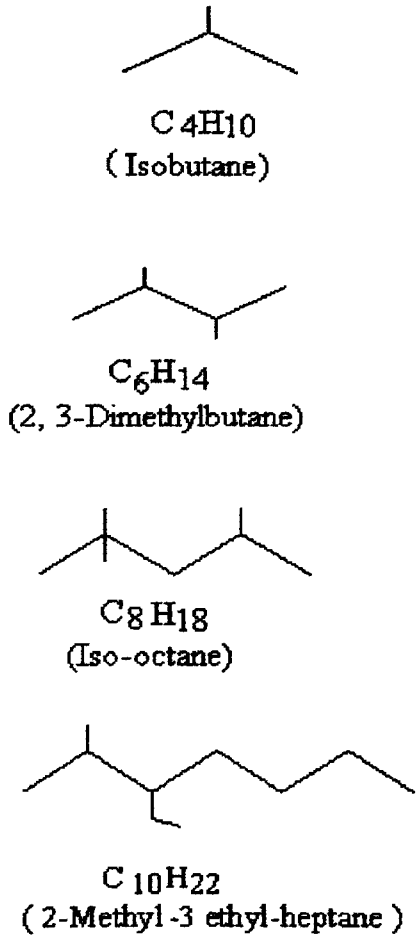


Figure 1.7. Example of isoalkanes occurring in petroleum [46].

Table 1.5. The possible number of alkane isomers for each size of molecule [2].

Size	Isomers	Size	Isomers
C_1, C_2, C_3	1 each	C_{10}	75
C_4	2	C_{11}	159
C_5	3	C_{12}	355
C_6	5	C_{13}	802
C_7	9	C_{15}	4, 347
C_8	18	C_{18}	60, 553
C_9	35	C_{25}	36, 797, 588

Table 1.6. Iso-alkanes and some other branched alkanes isolated from Sarir crude oils [44].

Compounds	% (wt/wt)
Iso-Butane	0.76
Iso-Pentane	1.0
Iso-Hexane	1.12
2-Methyl hexane	0.88
3-Methyl hexane	1.10
2,3,4-Trimethyl pentane	0.20
2,3-Dimethyl hexane	1.04
2-Methyl heptane	1.52
4-Methyl heptane	0.10
3-Methyl heptane	0.29

1.6.1.3 Cycloalkanes

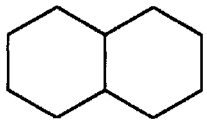
These are a series of saturated hydrocarbons with the general formula C_nH_{2n} that contain a " ring" structure with five, six, or seven carbon atoms. The petroleum industry generally refers to this series as the napthenes. It is now generally believed that oil fractions contain chiefly five and six members rings because (a) Only naphthenes with five and six membered rings have been isolated from the lower boiling fractions. (b) Thermodynamic studies show that naphthene rings with five and six carbon are the most stable. (c) The naphthenic acids contain chiefly cyclopentane as well as cyclohexane rings [47].

As shown in Figure 1.8, these are cyclic paraffins (or alicyclics) and polycyclics. Naphthenes can have substituent groups attached to the rings, e.g. methyl cyclohexane, or they can consist of two or more naphthene rings fused together as in decline. A gas-liquid chromatography (GLC) analysis of cycloalkane compounds present in gasoline fraction obtained from Sarir Libyan crude oil [44] is given in Table 1.7.

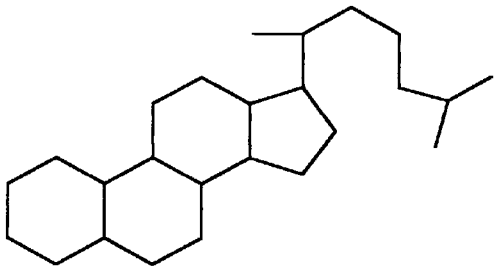
Naphthenes are liquids at normal temperature and pressure, they are insoluble in water and generally boil at temperatures 10 to 20 ^{0}C higher than corresponding carbon number alkanes. They make up about 50 % of both light and heavy crude oils with the quantities increasing in the heavier fractions and decreasing in the lighter fractions.

C_5H_{10}
(Cyclopentane)

C_6H_{12}
(Cyclohexane)



$C_{10}H_{18}$
(Decalin)



$C_{27}H_{48}$
(Cholestane)

Fig. 1.8. Example of cycloalkanes occurring in petroleum [46].

Table 1.7. Cycloalkanes Isolated From Sarir Libyan crude oils [44].

Compound	% (wt/wt)
Cyclopentane	0.06
Methy cyclopentane	1.86
Cyclohexane	1.36
1,1-Dimethyl cyclopentane	1.98
1,3- Dimethyl cyclopentane	1.39
1,2- Dimethyl cyclopentane	0.23
1,1,3-Trimethyl cyclopentane	0.66
Methylcy clohexane	4.68
1,1-Dimethyl cyclohexane	2.58
Ethyl cyclopentane	0.82
1-Methyl-2-Ethyl cyclopentane	0.33

1.6.2 Unsaturated hydrocarbons

1.6.2.1 Aromatic Hydrocarbons

The amount of aromatic material varies considerably between crudes ranging from about 10 % to 50 % or even higher. These molecules comprise hydrocarbons containing one or more benzene rings. They tend to be concentrated in the heavy fractions of petroleum such as gas oil, lubricating oil and in residue in which the quantity often exceeds 50 %.

Aromatic hydrocarbons may be divided into monoaromatics such as benzene, toluene, and the xylenes and polycyclic aromatic hydrocarbons containing several rings with two or more carbon atoms shared between rings as shown in Figure 1.9. Accordingly, aromatics can be subdivided into two main groups: (a) The first group are the alkylaromatic hydrocarbons which possess only aromatic rings and aliphatic substituents. The most widely occurring homologous series in this instance are those of alkylbenzene, alkylnaphthalenes, alkyl phenanthrenes, alkyl chrysenes and alkyl picenes. (b) The second, and no less important group of aromatic hydrocarbons are those molecules with naphthenoaromatic structure i.e., those containing both naphthenic and aromatic rings such as tetralin and indane.

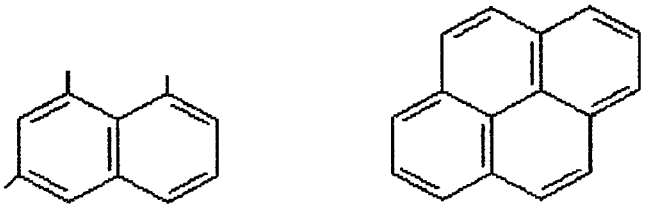
Aromatic hydrocarbons are liquids at normal temperature and pressure (the boiling point of benzene is 80.5 ^{0}C). Toluene ($C_6H_5CH_3$) is the most common aromatic component of crude oil, followed by the xylenes (C_6H_4 $(CH_3)_2$), benzene (C_6H_6) and naphthalene ($C_{10}H_8$).

Aromatics have the highest octane ratings of the hydrocarbon types, so they are valuable constituents in gasoline blends. However, they are undesirable in the lubricating oil range because they have the highest change in viscosity with temperature of all the hydrocarbons.

Aromatics

(C_6H_6)
Benzene

(C_7H_8)
Toluene



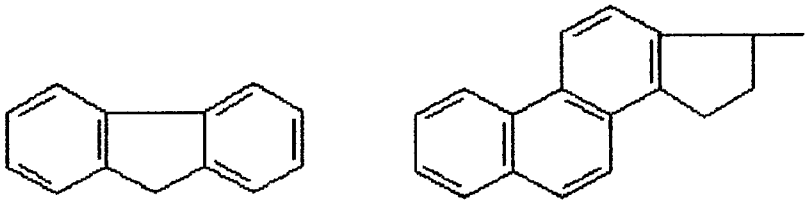
($C_{13}H_{14}$)
Trimethyl-naphthalene

($C_{16}H_{10}$)
Pyrene

Naphthenoaromatics

($C_{10}H_{12}$)
Tetralin

(C_9H_{10})
Indane



($C_{13}H_{10}$)
Fluorene

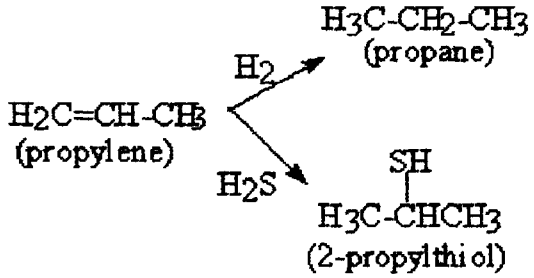
($C_{18}H_{16}$)
Methycyclo-pentanophenanthren :

Figure 1.9. Examples of aromatics occurring in petroleum [46].

1.6.2.2 Alkenes

These are known as the olefins, which are unsaturated cyclic, open or branched chain compounds. Those with 2-4 carbon atoms are gases at room temperature while those containing 5 or more carbon atoms are usually liquids.

Olefins are uncommon in crude oil due to their relative high reactivity. They are readily reduced to paraffin's with hydrogen or to thiols with hydrogen sulfide in the sediments [48]. Propylene for example forms propane with hydrogen or 2-propylthiol with hydrogen sulfide as shown below:



Alkenes are not present in significant quantities (if at all) in crude oils, some early work reported the presence of low molecular weight alkenes in a Pennsylvania crude but at insignificant concentrations [49]. Alkenes however, are formed in the refinery processes. Cracking produces alkenes as a result of radical reactions. They undergo alkylation reactions under acidic conditions for example isobutene reacts with isobutane in the presence of sulphuric acid to produce 2,2,4-trimethyl pentane. Furthermore, olefins are polymerised to give higher molecular weight molecules [49].

Figure 1.10. shows a number of olefins found in oils. In general, they are more toxic than alkanes, but less toxic than aromatics [50]. Alkenes are the major starting materials for many petrochemical processes.

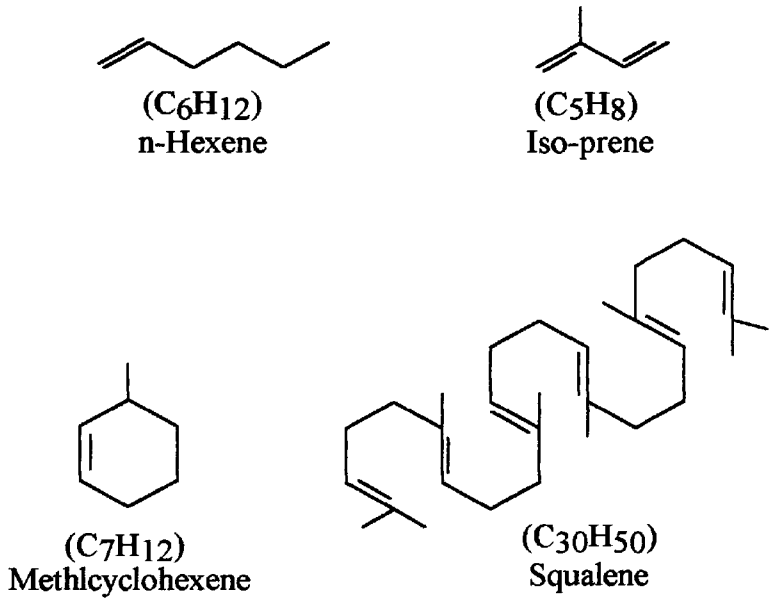


Fig.1.10. Some alkenes hydrocarbons found in oils [51].

1.6.3 Nonhydrocarbon compounds

Crude oils contain appreciable amounts of organic non-hydrocarbon constituents. These are mainly sulphur-, nitrogen-, and oxygen-containing compounds and, in smaller amounts, organometallic compounds in solution and inorganic salts in colloidal suspension. These constituents appear throughout the entire boiling range of the crude oil but tend to concentrate mainly in the heavier fractions and in the non volatile residues. Although concentrations of non hydrocarbons in any one fraction may be relatively small, their influence can be

important. To cite some examples, acidic components such as thiols and carboxylic acids promote corrosion of metal equipment. Reforming catalysts employed in the production of motor gasoline are seriously deactivated by sulphur compounds. Trace metals (V, Ni) can passivate or poison catalysts used for desulphurization of fuel oil or in catalytic cracking of heavy distillates. Clearly, knowledge of the presence and characteristics of these non-hydrocarbons is important to the petroleum technologist and geochemists.

1.6.3.1 Sulphur compounds

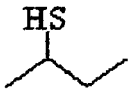
The structures of some sulphur compounds that occur in petroleum are listed in Figure 1.11. Sulphur compounds occur naturally in crude oils in different forms:

1. Free sulphur (S)
2. Hydrogen sulfide (H_2S)
3. Ethanethiol (C_2H_5SH),and in general, mercaptic sulphur(RSH)
4. Diethyl sulfide ($C_2H_5C_2H_5$)
5. Diethyldisulfide ($C_2H_5S_2C_2H_5$)
6. Polysulfides
7. Benzo-and di-benzothiophenes
8. In some cases oxidized forms such as sulfoxides and sulfones.

In general, crude oils with higher density (or lower API gravity) have higher sulphur contents. The total sulphur in crude oil varies from perhaps 0.04 % in light naphtha to about 5.0 % in some heavy oil cuts. The presence of sulphur compounds in finished petroleum products often produce harmful effects in terms of equipment corrosion, environmental pollution and unacceptable odour. Sulphur compounds in gasoline for example, are believed to promote corrosion of engine parts, especially under winter conditions when water containing sulphur dioxide from the combustion may accumulate in the crankcase. Mercaptans in solution cause the corrosion of copper and brass in the presence of air. Free sulphur is also corrosive as are sulfides, disulfides and thiophenes, which are detrimental to the octane number response to tetraethyllead. In diesel fuels, sulphur compounds increase wear and can contribute to the formation of engine deposits and although a high sulphur content can sometimes be tolerated in industrial fuel oils, the situation for lubricating oils is that a high content of sulphur seems to lower resistance to oxidation and increases the deposition of solids.

Combustion of fuels that contain sulphur produces sulphur dioxide (SO_2) and sulphur trioxide (SO_3) which form sulphuric acid when exposed to water vapour or water. When deposited on surfaces sulphuric acid causes white spots (on lamp glass), evil smells and badly damages forests through acid rain. It can also causes acute health hazards to people and animal life and produce property damage [50].

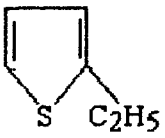
Thiols (2-Butanethiol)



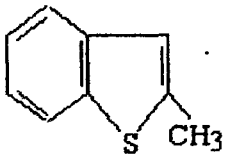
Sulfides (2-Thiabutane)

Sulfides (Thiacyclohexane)

Thiophenes (Ethyltiophene)



Thiophenes (Methylbenzothiophene)



Thiophenes (Dimethyidibenzothiophene)

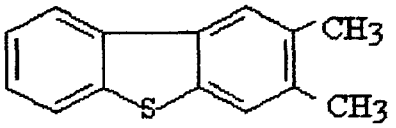


Figure1.11. Examples of sulphur compounds in crude oils [2].

1.6.3.2 Nitrogen compounds

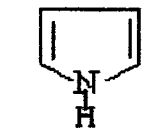
The nitrogen content of crude oil is low and generally falls within the range 0.1-0.9 %, although early work indicates that some crudes may contain up to 2 %. The highest known nitrogen content in the United States oils is found in certain California crudes, where a maximum of 0.82 % has been reported [52].

The majority of nitrogen compounds in crude oils is found in the higher boiling fractions of the oil, and often 95 % of all of these compounds are found in residues with boiling points over 300 ^{0}C at 30 mm Hg pressure. Nitrogen in petroleum may be classified arbitrarily as basic and nonbasic as shown in Figure.1.12. The basic nitrogen compounds, are composed mainly of pyridine homologues. The nonbasic nitrogen compounds are usually of pyrrole, indole and carbazole types.

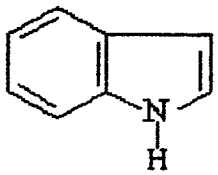
The presence of nitrogen in petroleum is of much greater significance in refinery operations than might be expected from the small amounts present. In gasoline nitrogen compounds can be responsible for the poisoning of cracking catalysts, discoloration, engine fouling, poor lubrication and they also contribute to gum formation in such products as domestic fuel oil.

The petroporphyrins structure (fig. 1.13) are closely connected with those of chlorophyll and hemoglobin hence they are "biological markers" and provide powerful evidence in support of a biogenic origin of petroleum [53].

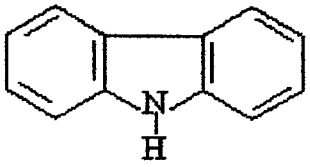
Non basic



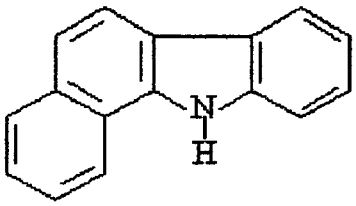
(C_4H_5N)
Pyrrole



(C_8H_7N)
Indole

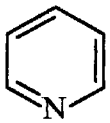


$(C_{12}H_9N)$
Carbazole

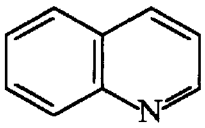


$(C_{16}H_{11}N)$
Benzocarbazole

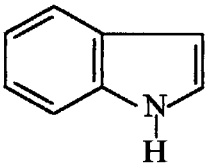
Basic



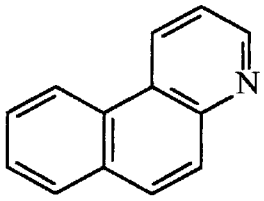
(C_5H_5N)
Pyridine



(C_9H_7N)
Quinoline



(C_8H_9N)
Indoline



$(C_{13}H_9N)$
Benzoquinoline

Figure 1.12. Example of organic nitrogen compounds in crude oils [12].

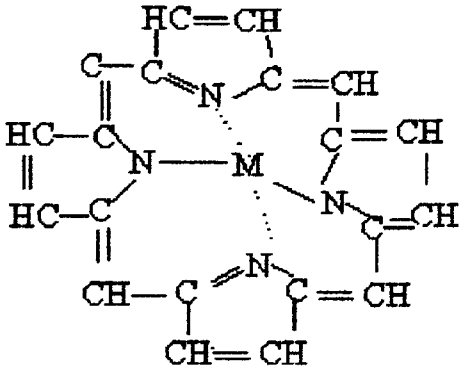


Figure 1. 13. Structure of petroporphyrins.

1.6.3.3 Oxygen compounds

The total oxygen content of crude oils is generally less than 2 %, ranging from 0.1 to 4.0 %. Compounds are principally phenols and carboxylic acids as shown in Figure 1.14. The phenols comprise cresols and higher boiling alkylphenols, the acids include straight chain and branched chain acids, and cyclopentane and cyclohexane derivatives. There is also some indication of the presence of acids containing aromatic rings (mono and dinuclear).The identification of steroid carboxylic acids in some crudes presents a further indication of the biochemical contribution to the formation of petroleum [54].

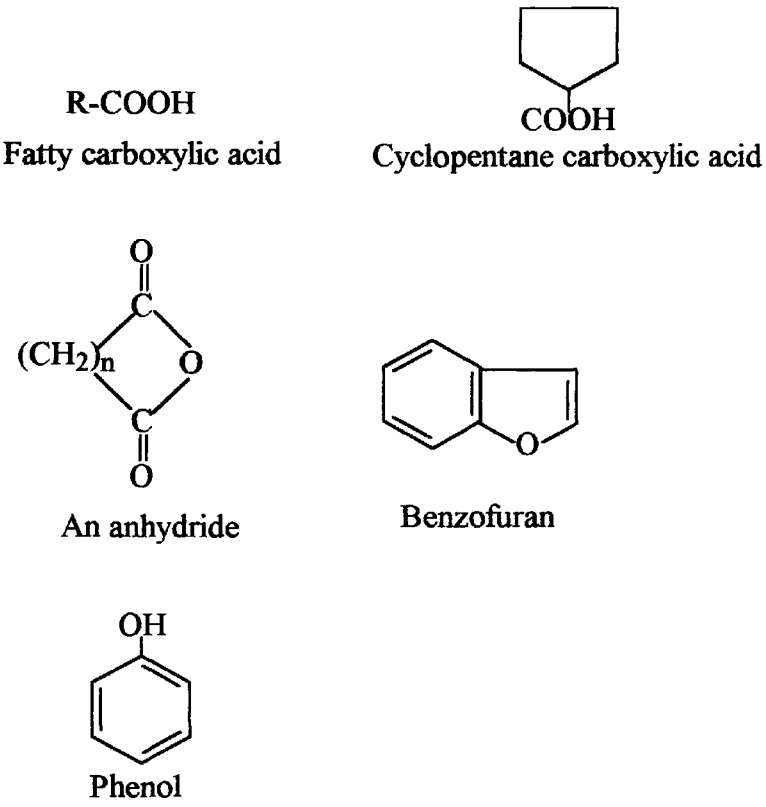


Figure 1.14. Typical oxygen compounds from crude oil [51].

1.6.3.4 Asphaltics

High molecular weight constituents of crude oil usually consists of N, S, O, containing compounds. They are referred to as resins and asphaltenes. These are complex structural arrangements made of polycyclic aromatic or naphthenoaromatic nuclei, with chains and hetroatoms. They constitute the heavy ends of petroleum and have to be considered as the natural high molecular weight members of the aromatic and naphtheno-aromatic series.

Heavy (low API gravity) crude oils invariably contain more nitrogen and sulphur as shown in Figures 1.15 and 1.16. These are the approximate ranges for nitrogen and sulphur for a variety of total crudes. Oxygen follows the same trend, with residues frequently containing more than 5 % oxygen.

Resins and asphaltenes are usually distinguished on the basis of their separation procedure. Precipitation by pentane separates resins and asphaltenes from remainder of the crude, while addition of n-heptane separates the soluble resins from the insoluble asphaltenes. The asphaltenes are dark brown to black, amorphous solids. The resins may be light to dark colored, thick, viscous substances to amorphous solids.

The main use of asphaltene is given in the previous section (1.2). Asphalt contents as high as 50 % have been reported for some Middle East and South American curdes, although most crudes contain less than 15 %.

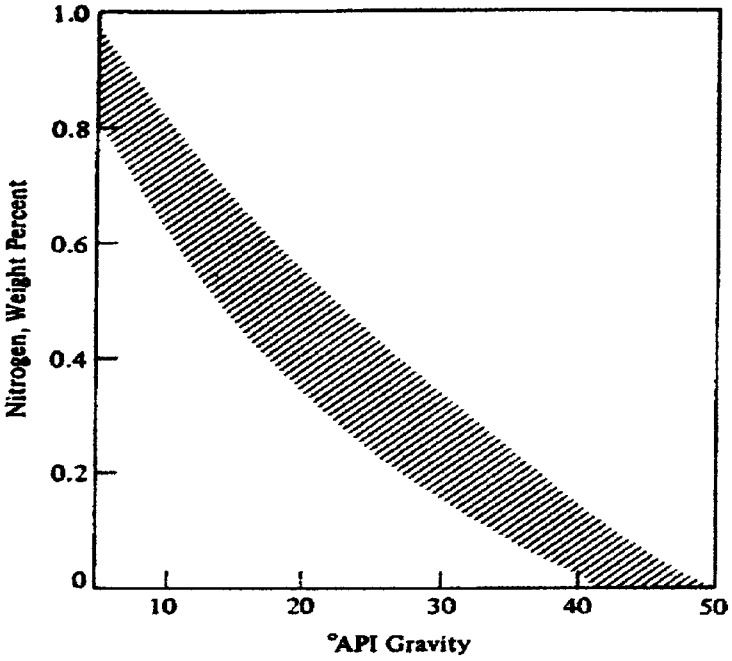


Figure 1.15. Variation in nitrogen content with ^{0}API gravity for crude oils [2].

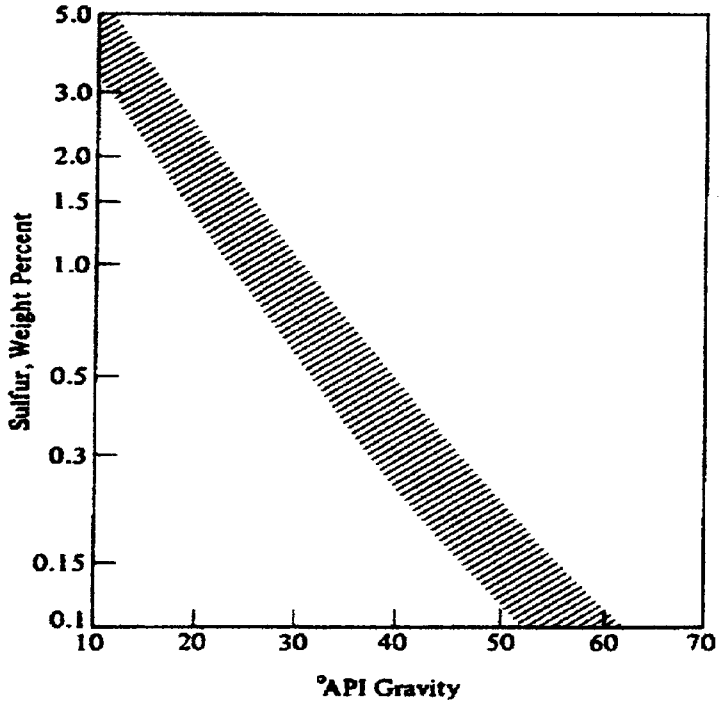


Figure 1.16. Variation in sulphur content with ^{0}API gravity for crude oils [2].

1.6.3.5 Organometallic compounds

Numerous " trace" elements have been detected in crude oils. About 0.01-0.05 % by weight (table 1.8) is the normal range, as determined by all tests. The occurrence of metallic constituents in crude oil is of more considerable interest to the petroleum industry than might be expected from the very small amounts present. Even small amounts of some of these metals such as nickel and vanadium in the charging stocks for catalytic cracking affect the activity of the catalyst and result in increased gas and coke formation and reduced yield of gasoline. In high temperature power generators, such as oil fired gas turbines, the presence of metallic constituents, particularly vanadium, may lead to ash deposits on the turbine rotors, thus reducing clearances and disturbing their balance. Most particularly, damage by corrosion may be very severe. Most of these elements are found in sea water and may have been derived from it, either as compounds in colloidal suspension or as materials secreted by algae and other marine organisms, which may also have provided the material from which the petroleum was formed.

Table 1.8. Range of principal trace elements found in petroleum [12].

Element	Range in petroleum (ppm)	Element	Range in petroleum (ppm)
Cu	0.2-12.0	Ga	0.001-0.1
Ca	1.0-2.5	Ti	0.001-0.4
Mg	1.0-2.5	Zr	0.001-0.4
Ba	0.001-0.1	Si	0.1-5.0
Sr	0.001-0.1	Sn	0.1-0.3
Zn	0.5-1.0	Pb	0.001-0.3

1.7 Crude oil identification

The composition of petroleum varies markedly according to its geographical source. Since the chemical composition significantly influences the properties of crude oil, it is necessary to understand the composition of a particular oil prior to its use in refining processes.

The physical and chemical composition of a feed stock is much truer indicator of refining behaviour. They play a large part not only in determining the nature of the products that arise from the refining operations but also in determining the means by which a particular feed stock should be processed. As indicated previously, petroleum is an exceedingly complex mixture consisting predominantly of hydrocarbons and containing sulphur, nitrogen, oxygen, and metals as minor constituents. The physical and chemical characteristics of crude oils and the yields and properties of products or fractions prepared from them vary considerably and are dependent on the concentration of the various types of hydrocarbons and minor constituents present. Some types of petroleum have economic advantages as sources of fuels and lubricants with highly restrictive characteristics because they require less specialized processing than that needed for production of the same products from many types of crude oils. Others may contain unusually low concentrations of components that are desirable fuel or lubricant constituents, and the production of these products from other crude oils may not be economically feasible [55].

The history of analysis of the constituents in petroleum started over 100 years ago, when in 1865 La Rue and Miller [56] identified several aromatic

hydrocarbons in a Burma petroleum, and the German chemist K. Shorlemmer [57], discovered n-butane, n-pentane and n-hexane in Pennsylvania (USA) crude oil. From that time, and especially over the last 50 years, the rapid advances in analytical techniques have allowed the identification of large numbers of petroleum constituents.

In the last forty years the whole field of chemical analysis has developed at an extremely rapid pace. Detection and estimation of single components in very complex mixtures of natural products, like petroleum fractions, are nowadays carried out as a matter of routine in plant laboratories with very accurate results. Two main factors account for this change: the development of new analytical/separation techniques, particularly chromatographic methods. Notably gas-liquid chromatography and high pressure liquid chromatography and developments in spectroscopic and hyphenated techniques [58].

Inspite of all these advances, knowledge of the constituents of some petroleum fractions is still very sparse, particularly in the region of residual oils and asphalt materials. Generally, the approach is to analyze and profile oils based on the relative proportions of the major classes of hydrocarbon- alkanes , cycloalkane and aromatics. The abundance of analytical techniques that can be applied to the characterization of oils is most apparent. No single analytical protocol can however, withstand the scientific and economical constraints of a universal fingerprinting technique.

When an oil spill is discovered, whether at sea or on a coastline, there are various reasons making it necessary to ascertain the source of the spill. These reasons may include a wish to prevent further spillage, to prosecute the offender, to obtain compensation or to prove the innocence of a suspected offender. Importantly, having a reliable, scientific method of identifying offenders should act as a deterrent to others who might have caused oil spills to accrue in further pollution, either intentionally or through negligence [59]. A wide variety of analytical techniques have been applied to the problem of oil characterization ranging from the measurement of bulk parameters, to the identification of individual components. The characterization of crude oils usually involves the determination of a set of parameters for a specific portion of the oil. These methods are known collectively as fingerprinting techniques [60].

In the past, research has focused primarily on the determination of the low molecular weight (less than 300) aliphatic and olefinic hydrocarbons because of their relative ease of analysis by gas chromatography. Of more recent interest are the PAHs because of their possible carcinogenic and mutagenic properties. The current increase in the use of fossil fuels and investigations into the potential use of liquefied coal and shale oil requires the development of a monitoring system for PAHs in the environment [60, 61].

The fingerprinting of crude oil spills is a very complex problem which has been addressed [62-69] Whilst aliphatic hydrocarbons have been the most widely studied chemical markers this does present a number of disadvantages. Firstly, n-

alkanes may be quickly degraded in sea water by chemical and biochemical processes [66]. Secondly, Iso-and cycloalkanes when used alone do not allow the identification of the origin of crude oil spills with certainty [67]. Better results were obtained using PAHs with more than two rings. These have a substantial lifetime in sea water and may be identified even after a long period of weathering [68]. The complexity of such samples necessitates the combination of several chromatographic techniques to achieve separations [69].

Our work has centered on the fractionation selectivity of Libyan crude oils using column chromatography, extrography and supercritical fluid extraction (SFE), with subsequent analysis using gas chromatography-mass spectrometry (GC-MS).

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Chapter 2

2 Chromatographic and Mass Spectrometric analysis of Petroleum

2.1 Introduction

The present state of the technology of petroleum processing and the need for oil spill identification makes demands upon the control of analysis processes. Such processes are well fulfilled by the modern methods of chromatography and spectrometry. The advantages of these methods consist in the minute sample amounts required for analysis, relatively accurate results, elimination of subjective errors, and increased speed of analysis.

Petroleum is formed by a complex and incompletely understood series of chemical reactions from organic materials laid down in previous geological eras. The composition of petroleum varies depending on the source and geological history of each deposit. Many hydrocarbon compounds in petroleum are similar in chemical and physical properties and thus, in the analysis of multi-component crude oils it is still difficult to separate every component, even with high-resolution capillary chromatography columns.

Chromatography is a very elegant non-destructive technique which can provide analytical and preparative separations of substances with similar structures, including molecules with identical or similar molecular weights, isotope mixtures, positional isomers, diastereoisomers and enantiomers. It can also be applied to mixtures containing molecules with widely different molecular weights, from simple light gases to biopolymers of molecular weights of over several thousands.

Analysis of a matrix for a particular component or group of components is a formidable task. This is especially so if the matrix is composed of a highly complex

mixture of hydrocarbons as well as oxygen, nitrogen, and sulfur containing compounds, and trace amounts of metals. This is precisely what is required of analytical chemists in the petroleum industry.

Gas chromatography has been used to examine the aliphatic compounds present in oil particularly the distribution of normal and branched alkanes [1]. In addition, the use of specific detectors (e.g., nitrogen and sulfur) enables the distribution of compounds containing these elements to be studied [2,3].

Basically, chromatography is a separation technique, or a differential migration process, where the sample components are selectively retained by a stationary phase. It involves separation due to the difference in equilibrium distribution of sample components between two immiscible phases; a moving or mobile phase and a stationary phase. The term chromatography stems from the Greek words Khromatos-colour and graphos-written, and was the first used in 1903 by the Russian chemist, M. Tswett, who demonstrated the separation of the pigments in green leaves on a calcium carbonate adsorbent [4]

Chromatography methods as shown in Figure 2.1 can be classified according to the type of mobile and stationary phases selected. Gas chromatography [5] includes those methods in which the mobile phase is a gas, liquid chromatography, in which the mobile phase is liquid includes liquid-liquid (partition), Liquid-solid (adsorption), and ion exchange as well as gel permeation chromatography.

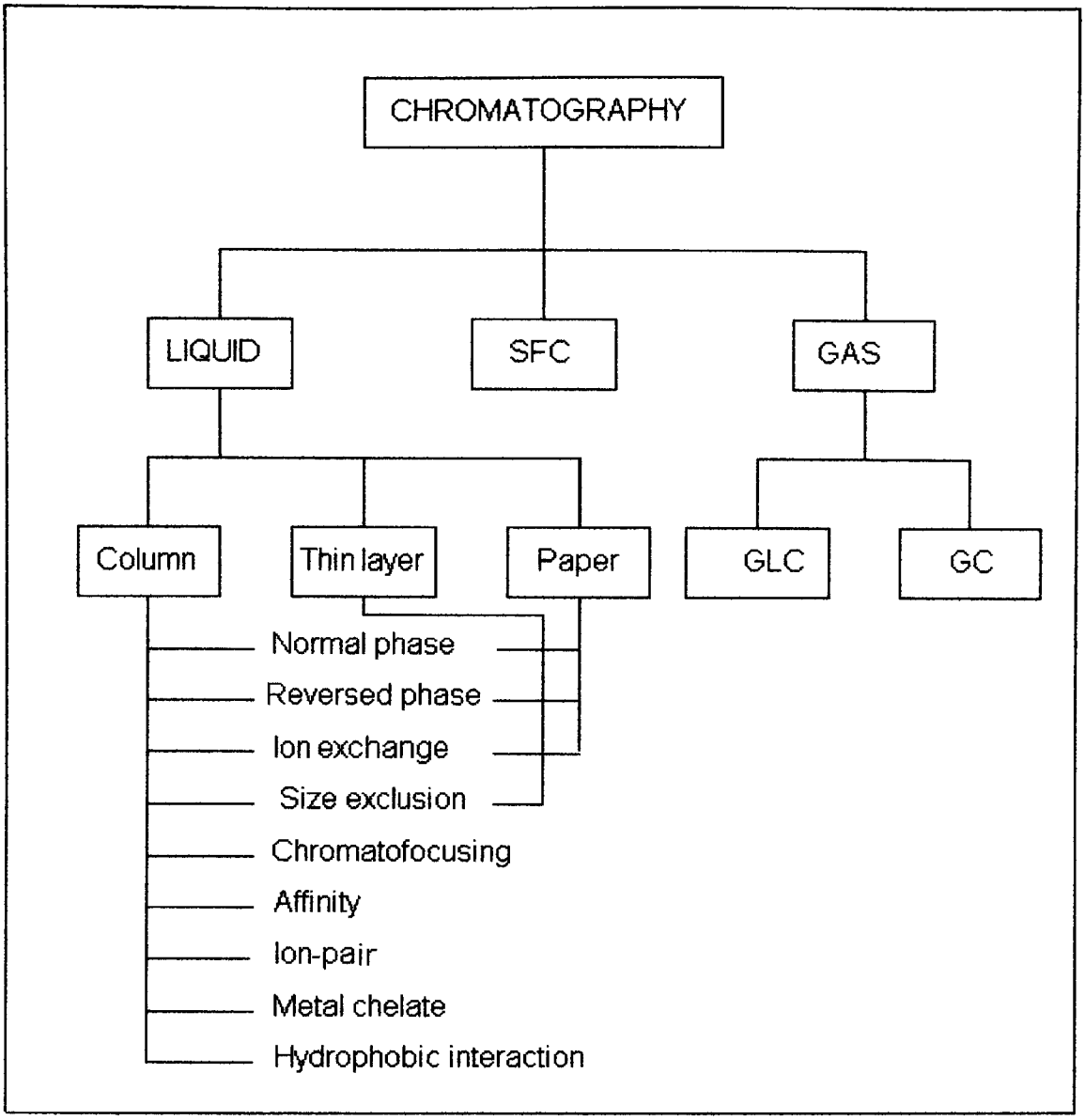


Fig. 2.1. Types of chromatography [5].

2.2 Gas chromatography

The most frequently used chromatographic technique is gas chromatography (GC) for which instrumentation was first offered commercially in 1955 [6]. GC offers a rapid and highly efficient qualitative and quantitative analysis of a wide variety of compounds which have boiling points up to about 350 ^{0}C.

characterization of spilled oils, often in conjunction with a number of other techniques.

The use of GC enables the partial resolution of the oil into individual components, especially when high resolution glass capillary columns are used. The advantages of GC are its specificity for particular compounds, the small sample amount required and the fact that the technique can give information on the weathering processes that the oil has undergone and hence, its age. Gas chromatographic analysis of a fraction of a microliter of a petroleum cut routinely provides qualitative and quantitative data for some hundred compounds in a couple of hours, often automatically since gas chromatography readily lends itself to automation. However, a major limitation of GC is that compounds which are to be separated must be volatile to some extent or else they will not elute from the column. In addition, as most separations require the column to be heated, compounds being introduced into the GC column must be thermally stable or they will decompose. This may require the compounds to be derivatised, i.e. transformed into a species which is both volatile and thermally stable [7].

The technique has proved to be an exceptionally versatile method for the analysis of compounds present in the light fractions of petroleum. However, the use of the technique for direct component analysis in the heavy fractions of petroleum is not only difficult but also subject to many limitations. For example, the number of possible components of a certain molecular weight range increases with increasing molecular weight. Further more, there is a corresponding sharp decrease in physical property differences (e.g. volatility) between isometric structures as the molecular weigh increases. Thus, it is very difficult, and / or

occasionally almost impossible to separate and identify single components in the heavier fractions of petroleum by gas chromatography [8].

The essential components of a gas chromatograph is shown in a schematic diagram Figure 2.2.

1. Sample introduction devices;
2. Column and column oven;
3. Detector;
4. Gas supply unit for carrier and auxiliary gases;
5. A means of visualizing the detector response.

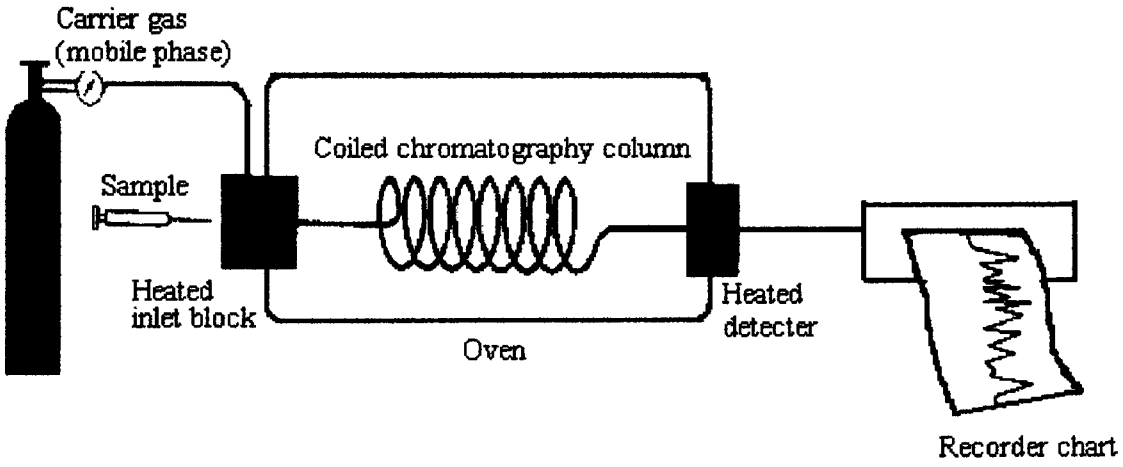


Fig. 2.2. Schematic representation of a gas chromatography [9].

Generally, the sample is injected into the column in solution, via a heated injection port. The purpose of the injection port is to vaporize the sample. The vaporized material is then purged through the column by a continuous stream of inert carrier gas, such as helium or nitrogen, which flows through the column at a uniform rate. The flow rates normally range from 50 to 100 $cm^3.min^{-1}$ for ¼ in. o.d. columns, from 15 to 50 $cm^3.min^{-1}$ for 1/8 in. o.d. columns, and from 1 to 5 $cm^3\ min^{-1}$ for capillary columns.

Sample inlets fall into two main categories, one for packed-column and the other for capillary-column devices. For packed columns, all material injected is carried by the mobile phase onto the column. The inlet is usually an open tube, but sometimes, albeit rarely, the inlet itself may be packed to inssure that the first centimeters of the column do not become contaminated with degradation products or nonvolatile materials that may affect the efficiency of the column.

Capillary columns require increased care in injection because of the much smaller capacity of the column. There are four different inlet designs: direct, split/splitless, programmed-temperature vaporization, and cool on-column injectors. Capillary columns generally operate under split, splitless, and on-column modes. The purpose of the split injector is to allow injection of a relatively large volume of sample, then to split this after injection so that a smaller portion is delivered to the column and hence will not overload the capillary column, which has relatively low sample capacity [6].

The column is perhaps the most important feature of a GC instrument. It contains the stationary phase medium and thus effects the separation of the components in a mixture. The column may be made of glass or aluminium and is typically 2-6 mm ID and 1-3 m in length when packed with stationary phase material or 0.2-0.5 mm ID and 10-100 m long if in the form of a capillary column.

In GC the sample mixture is subject to a competitive distribution between a mobile gas stream and a stationary solid or liquid. There are two main separating mechanisms;

1) Adsorption or Gas Solid Chromatography (GSC)

2) Partition or Gas Liquid Chromatography (GLC)

In GSC the stationary phase usually consists of a powdered adsorbent. Common examples are molecular sives (calcium aluminum silicate), silica gel (SiO_2), alumina (Al_2O_3) and charcoal. As the sample molecules are swept through the column they are continuously adsorbed/desorbed in and out of the stationary phase. The flow rate of each component depends upon its affinity for the stationary adsorbent and it is by this mechanism the separation is attained. The analysis of inorganic gases and low molecular weight hydrocarbons are the main application of GSC [8].

The stationary phase in GLC consists of an inert powder known as the support, which is coated with a thin film of an involatile liquid. The mechanism of separation is a competitive partitioning of sample molecules in and out of the liquid coating, as they are swept through the column by the mobile gas stream. Many types of stationary liquid phases are commercially available, each designed to optimize the separation of various classes of compounds.

The rapid development of GC may be mainly attributed to the speed at which complex analytical separations can be carried out. However the most dramatic advance in speed and efficiency of separation has occurred following the introduction of open tubular or capillary columns.

In capillary GC the liquid phase is coated in the form of a thin film on the inside surface of the columns, which are therefore known as wall coated open tubular or WCOT columns. The internal diameter of the tubing normally ranges from 0.2 to 1.0 mm. However it is not the narrowness of diameter but the "openness" of tube bore which is effective in producing an enhancement of about two orders of magnitude in separating power over traditional packed columns. The unrestricted flow path for the carrier gas makes it possible to construct

columns of great length. Typically, columns are manufactured in coils up to 50 meters, and without prohibitive pressure drops very high efficiency is obtained.

The earliest capillary columns were made of stainless steel, but these were quickly replaced by glass to give much improved performance. A major drawback of glass columns is that they are very fragile. Fused silica columns possess extreme flexibility and are currently the most popular choice.

The separated components emerge from the end of the column and enter a detector which produces an electrical signal. The electrical signal generated by the detector represents the detector response to a change in the composition of its contents. The result is the familiar series of gaussian peaks, with each peak indicating the arrival of a solute at the detector. The electrical signal is then amplified and passed into a recorder or data handling device. The most commonly used GC detectors are a Flame Ionization Detector (FID), Electron Capture Detector (ECD), Thermal Conductivity Detector (TCD), Flame Photometric Detector (FPD), Nitrogen-Phosphorus Detector (NPD), Alkali-Flame-Ionization Detector (AFID), Mass spectrometer Detector (MSD).

There are numerous approaches to both qualitative and quantitative analysis using gas chromatography. The simplest qualitative approach makes use of the characteristic value for the retention time, t_r. Numerous factors affect this value and careful control of many parameters is required for absolute identification because of the large number of parameters which affect t_r, including column characteristics, the nature of the stationary phase, the carrier gas flow rate and the column temperature.

Quantitative analysis requires measurement of the peak height or peak area. Using a regular standard curve one can obtain the amount of the unknown.

Peak heights are easy to measure and thus are frequently used. However, the peak height diminishes in relation to the length of time required for elution. This means that measurement of peak height for components with long retention times is less sensitive than for components with short retention times. Peak area is independent of broadening effects caused by the variables as column temperature, eluent flow rate, and rate of sample injection. Many modern chromatographic instruments are equipped with electronic integrators that provide precise measurements of relative peak areas.

The method of standard additions is a useful technique for calibrating, especially for occasional samples. One or more aliquots of the sample are spiked with a known concentration of standard, and the increase in peak area is proportional to the added standard. This method has the advantage of verifying that the retention time of the unknown analyte is the same as that of the standard.

A more important method of quantitative analysis is the use of internal standard. The sample and standard are spiked with an equal amount of a solute whose retention time is near that of that of the analyte. The ratio of the area of the standard or analyte to that of the internal standard is used to prepare the calibration curve and determined the unknown concentration. This method compensates for variations in physical parameters, especially inaccuracies in pipetting and injecting microliter volumes of samples.

2.3 Gas Chromatography-Mass Spectrometry

Mass spectrometry has gained wide acceptance in petroleum chemistry as a means of providing structural data on the constituents of petroleum mixtures. Gas chromatography-Mass spectrometry (GC-MS) has provided a powerful tool in the analysis of many types of compounds and for these reasons will continue to be of great importance. The early application of analytical mass spectrometry was developed to large extent by workers in the petroleum industry, during and immediately after World War II. These early developments included the analysis of gaseous mixtures of hydrocarbons [9].

The combination of gas chromatography with mass spectrometry results in an extremely useful hybrid instrument for the analysis of petroleum, petrochemical raw materials and products. It is very powerful technique in environmental analysis where many toxic substances at trace level may be determined within complex samples [10]. The two techniques are highly complementary. Chromatography provides an excellent method for separating the components of a mixture into a set of individual substances. However, it provides little information regarding the identity of the compound so separated. Furthermore, identification of the compounds by gas chromatographic methods alone often requires matching with authentic pure samples which are either difficult to prepare or very expensive. The mass spectrometer, on the other hand, is an instrument capable of giving detailed information about the identity and structure of an organic unknown, provided that the unknown is pure. In the event that the analyte is a mixture, then the qualitative analytical powers of the instrument are severely compromised.

In GC-MS the separated compounds eluting from the GC column enter an ion source in which they are bombarded by a high energy electron beam. Here, the compounds are ionized producing a series of fragment ions. These ions are then accelerated through a mass analyzer where they are separated according to their mass/charge ratio (m/z) before being detected and processed by the MS data system. Complete spectra can be collected in this way, allowing for the identification of individual compounds by comparing the recorded spectra against library spectra or authentic standards [11] .

Organic mass spectrometry has been an analytical tool for about 40 years, and it has been applied to environmental research over the past three decades, mainly in conjunction with gas chromatography. Mass spectrometric techniques such as chemical ionization (CI-MS), high resolution (HR-MS), mass spectrometry, field ionization and desorption mass spectrometry (FI-MS), tandem mass spectrometry (MS-MS) and pyrolysis GC-MS, all with the associated online computers and processor are providing ways to tackle the analytical problems associated with the analysis of complex organic mixtures. The overall field of mass spectrometry has been extensively reviewed [12].

2.3.1 Mass Spectrometric Instrumentation

The mass spectrometer functions as a group of subsystems as illustrated in Figure 2.3.b each of which performs an operation on the sample in the following serial order: vaporization of the sample, ionization of the sample vapours, mass analysis of the ions, detection the mass analyzed ions, and recording of the detected signal .There are two additional subsystems that support the overall operation of the instrument: the vacuum and data systems. The interface between the GC and MS components should be capable of sustaining a large pressure drop

from about 1 atm in the GC to below 10^{-6} torr in the ion source (except where chemical ionization conditions are employed). Most modern GC-MS systems simply have a heated transfer line through which the end of the capillary column is inserted directly into the MS. Several types of interface, or separator, have been developed commercially for use with packed columns.

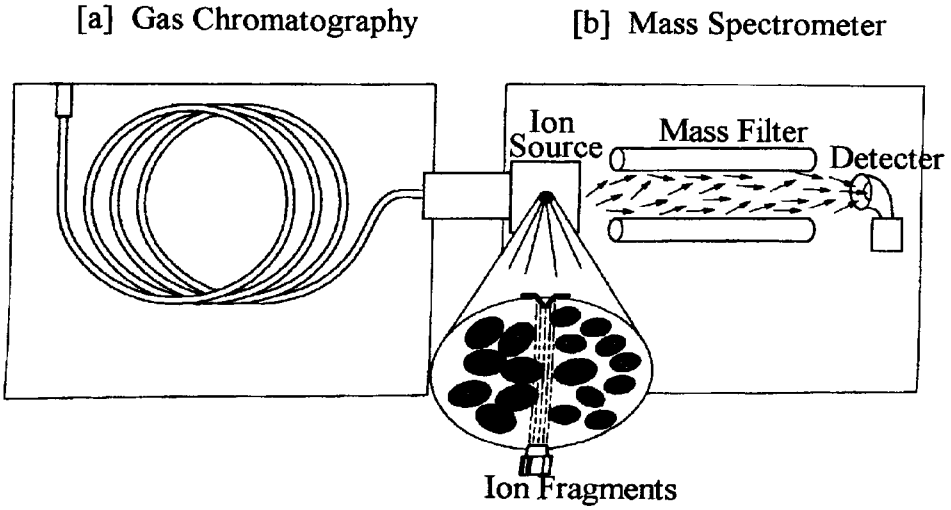


Fig. 2.3 Schematic representation of a GC-MS system [13].

The choice of the ionization method is of great relevance to achieving proper analysis of an unknown organic compound. The ionization of organic molecules may be achieved in many ways, for example: Electron impact (EI), Chemical ionization (CI), Atmospheric pressure ionization (API), laser desorption, and Californium-252 plasma desorption. Of these methods, EI, CI, and to a lesser extent, API are the techniques most frequently used [14].

Electron impact (EI) gives reproducible and characteristic spectra sufficient for identification of many classes of compounds. Typically a rhenium or tungsten cathode, the filament, is heated by an electric current, causing the emission of electrons. The electrons are accelerated by a potential difference of

5-100 volts between the cathode and the ion source. Ions are formed by the exchange of energy during the collision of the electron beam and sample molecules. The positive ions are then extracted from the ionization chamber by a repeller or pusher element in the chamber, held at a small positive potential, or by field penetration from the accelerating voltage. The ions are then accelerated by a high voltage potential towards the analyzer. The lower the ionization potential, the higher the filament heating current required to maintain a constant electron emission current.

Many compounds do not give a molecular ion in an EI system because of the excess ionization energy imported to the molecules during the EI process. The chemical Ion ionization (CI) technique was developed to solve this problem. The quasi-molecular ions produced in CI may have only 50-80 K cal/mole of excitation energy [15]. CI produces ions by ion-molecule reactions between neutral sample molecules and a high pressure (0.2-2 torr) reagent gas ion plasma, usually methane or isobutane. The mixture is subject to electron bombardment, when the reagent gas is ionized. Thus methane gives rise to the species $CH_4^{\cdot+}$ and CH_3^+. At the relatively high source pressure used, collision and ion molecular reactions with the reagent gas occurs leading to the formation of secondary ions CH_5^+ and $C_2H_5^+$

$$CH_4^{\cdot+} + CH_4 \longrightarrow CH_5^+ + CH_3^{\cdot}$$

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2$$

with only a small excess of internal energy. When these secondary ions collide with sample molecules, the latter may be ionized. Thus reactions which involve abstraction of a hydride ion with formation of a $M\text{-}1^+$ ion, or addition of a proton leading to a $M+1^+$ ion, are most commonly observed.

Several factors contribute to the popularity of electron impact ionization: ease of operation, simple source construction, precise beam intensity control, relatively high efficiency of ionization, and narrow kinetic energy spread of the ions formed.

Generally, two types of mass analyzer are conventionally used for GC-MS, the quadrupole mass filter and the ion trap. The quadrupole mass filter is characterized by fast scanning of the Direct Potential (DC) ramp and linear mass scale.

The quadrupole mass analyzer consists of a set of four round or hyperbolic rods in a quadrant formation. Opposite rods are electrically connected together and a voltage applied which consists of a d.c. and r.f. (1-2 MHz) component. Thus an oscillating field is set up between the rods and when an ion moves into this quadrupole field it will oscillate between the electrodes. If the mass of the ion is such that these oscillations are stable then the ion will move through the analyzer to the electron multiplier. Ions of other m/e value will undergo unstable oscillations of increasing amplitude until they move out of the quadrupole field. Since there is no force along the axis of the rods an ion accelerating potential of 20-30 v only is required. Scanning is achieved by varying the magnitudes of the d.c. and r.f. voltages; however, by keeping the ratio constant, a linear mass spectrum is produced.

Single focusing magnetic analyzers with a resolution of 500-3000 are commonly used in organic analysis. The ions formed are accelerated through the source slit into a homogeneous magnetic field and then follow a curved path, the radius (R) of which is determined by the accelerating potential (v) and magnetic field strength (B). the mass/charge ratio (m/e) of an ion is given by:

$$m/e = B^2 r^2 / 2V$$

Since the radius is fixed in the design of the instrument, varying either B or V will result in ions of varying m/e values falling on the detector. Varying B at a fixed accelerating potential is commonly used to scan through the mass range. The resolution of magnetic analyzers is principally determined by the radius of curvature and also by the width of the source and detector slits, which can be controlled by the operator.

High resolution magnetic instruments use both electric and magnetic fields to focus the ions. This double focusing allows the masses to be measured accurately, and this permits molecular formulae to be deduced. High-resolution instruments scan more slowly than low-resolution instruments, and this can cause problems when high-resolution capillary columns are used for the GC [16].

In addition to the above, quadrupole instruments are preferred over magnetic-sector mass spectrometers for performing CI /GC-MS experiments because of the absence of large accelerating potentials in the former. Thus, the tendency for high- voltage arcing that can occur in magnetic sector instruments is not a problem with quadrupoles. Nevertheless, magnetic- sector instruments can provide analytical capabilities that are not otherwise available [17].

2.3.2 Fragmentation associated with hydrocarbons

The petroleum industry has made extensive use of mass spectrometry [10], so the mass spectral behavior of hydrocarbons is well known. In a mass spectrometer, only ionic species can be separated according to their masses and the separation must be achieved under a vacuum. Some compounds may not give molecular ions because either: the activation energy for decomposition is very low

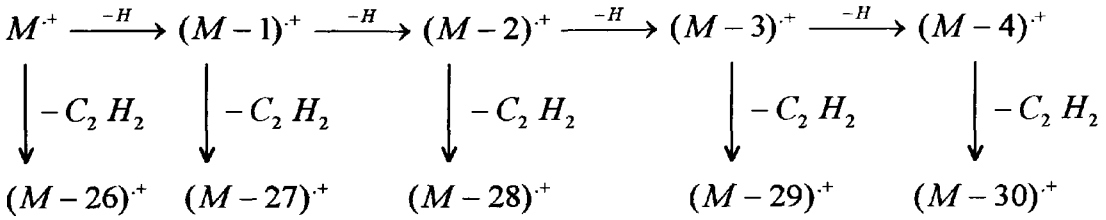
or zero (so that no M^+ ions survive to reach the collector) or the sample decomposes thermally prior to ionization.

The molecular ion will normally be seen in the mass spectra of the lower n-alkanes, but its intensity falls off with increased size. For long straight chain molecules, ions will be observed at increments of 14 mass units (CH_2). At each of these prominent peaks will be a smaller peak one unit higher for C^{13} and peaks one and two units lower corresponding to the loss of hydrogen atoms.

In highly branched molecules, random rearrangements (migration of hydrogen atoms) are common but not intense. Formation of tertiary carboniun ions is favored in primary fragmentation, so that often no molecular ion (M^+) peak occurs. An increasing number of double bonds favors the formation of more intense molecular ion peaks. Thus, in normal paraffinic hydrocarbons, the major ions of interest occur at the parent (molecular weight) mass and at lower masses resulting from cleavage of successive C-C bonds.

Cycloalkanes give spectra very similar to those of linear alkanes except that the molecular ions are more intense. Once a cycloalkane ring has broken, the residual ion behaves like the ions of linear alkanes, again giving ions 14 mass units apart. For cycloalkanes the principal fragment ions occur at m/z $C_nH_{2n+1-2r}$ where r is the number of rings.

The EI mass spectra of PAH are characteristically simple [20], featuring an intense molecular ion and low intensity ions resulting from the expulsion of protons and C_2H_2. This common PAH fragmentation pattern is depicted below:



Alkyl aromatics produce a characteristic homologous fragment ion series, in the case of alkyl benzene corresponding to $C_6H_5(CH_2)_n^+$ (m/z 91, 105, 119,...etc., for n = 1 or more) and the molecular ion is normally observed. The presence of intense fragment ions at m/z 118, 133, 147..etc., indicates either extensive branching or multiple alkyl substitution while intense ions at m/z 91 and 92 indicate n-alkyl substitution generally. The even electron benzylium ion $C_7H_7^+$ at m/z 91 has shown to undergo rearrangement to form the stable even electron tropilium ion, a cycloheptatriene ion which can yield a homologous series of ions by alkyl substitution as seen in Figure 2.4. More highly condensed alkylated aromatic hydrocarbons exhibit similar behavior to alkyl benzene in that intense ion series are observed normally beginning with an ion corresponding to the methyl derivative of the aromatic nucleus less one hydrogen, at successive CH_2 additions. The presence of hetroatoms in aromatic structures is due mainly to furanic, phenolic, thiophenic, pyrrolic, and pyridinic groups. It is useful to remember the changes in general formulas related to the addition of such groups to aromatic structures.

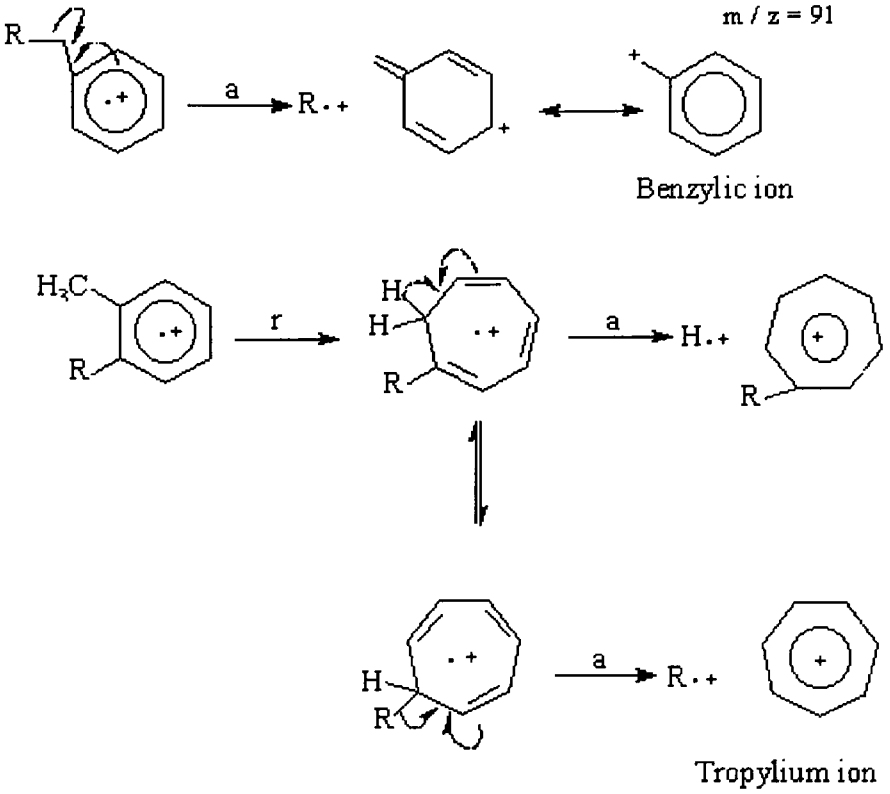


Fig. 2.4. Rearrangement Of The Benzylic Ion To Form A Tropylium Ion From An Alkyl Substituted Benzene [21].

2.3.3 Derivatisation

Molecules unsuitable for gas chromatographic analysis because of their instability, low volatility or high polarity may be converted into a derivative whose properties are more compatible with instrumental requirements. This step of sample preparation is often referred to as derivative preparation. In many cases, compounds which are insufficiently volatile for GC analysis can be successfully eluted following derivatization. Derivatization methods may be classified into three groups according to the reagents used and the reaction achieved, namely silylation, acylation and alkylation. In many cases the derivatives are formed as soon as the sample dissolves, few require heating. Silylation [19] is the most widely used derivatization technique. It involves the replacement of an acidic hydrogen

replacement of an acidic hydrogen on the sample molecule with an alkylsilyl group, e.g.$SiMe_3$. Trimethylchloro silane(TMS):

$$R\text{-}OH + Ci\text{-}SiMe_3 \longrightarrow R\text{-}O\text{-}SiMe_3 + HCl$$

The derivatives are generally less polar, more volatile and more thermally stable.

2.4 Fractionation of crude oil by liquid-solid (column) chromatography

2.4.1 Principles of column chromatography

Elution chromatography (liquid-solid) was discovered at the beginning of the 20th century, but developed rapidly only after the development of a theoretical explanation of liquid-liquid elution chromatography during the forties and particularly after the discovery of elution gas chromatography in the fifties. Liquid chromatography or column chromatography is one of the simplest and most used chromatographic methods as in Tswetts original experiments.

Elution adsorption chromatography has frequently been applied to the study of the constituents of petroleum. The separation of the several distinct hydrocarbon classes using silica gel was noted by Clerc [22]; this was followed by Charlets [23] who pioneered the combination of elution chromatography (from alumina) with spectroscopic analysis (UV) for the characterization of a cracked gas oil. Later, more detailed studies of the composition of both cracked [24] and straight run gas oil samples also featured the use of elution adsorption chromatography using silica gel or alumina as adsorbents. Chromatographic separation has been used to separate petroleum base samples into fractions of sufficiently limited compositional range to permit complete analysis by spectral (Mass, UV, IR) techniques. The analysis of the fractions obtained has in turn

provided information on the separation capabilities of these chromatographic methods.

Separation by adsorption chromatography essentially commences with the preparation of a porous bed of finely divided solid, the adsorbent. The adsorbent is usually contained in an open tube (chromatography column); the sample is introduced at one end of the adsorbent bed and induced to flow through the bed by means of a suitable solvent. As the sample moves through the bed the various components are adsorbed to a greater or a lesser extent depending on the chemical nature of the compound. Thus, those molecules that are strongly adsorbed spend considerably more time on the adsorbent surface than in the mobile phase, components that are weakly adsorbed move through the bed more rapidly.

Numerous factors affect the process of migration through a bed, and in fact the total distance traveled in a given time by different molecules of the same material is not constant. Nevertheless, the suitable choice of stationary and mobile phases allows adequate separation of even multi component mixtures to be achieved [25].

Liquid chromatography is frequently used to fractionate a sample on the basis of polarity differences, differences in molecular size or difference in ion-exchange capacity after solvent extraction. Either column or thin-layer techniques may be use, but column methods are generally preferred as the sample recovery is more straight-forward. Adsorption chromatography can also be used as a concentration technique by applying the sample to the column in a large volume of a non eluting solvent and then eluting the adsorbed sample components with a small volume of a strong eluting solvent.

The most widely employed adsorbents for liquid-solid chromatography are silica gel, alumina, florisil (synthetic magnesium silicate), carbon, and diatomaceous earth's.

The sample is applied to the column in small volume of a weak solvent and the separation is effected by eluting with a series of solvents of increasing polarity . The components of interest are eluted in a number of fractions. The dimensions of the column used are dictated by the size of the sample and the resolution required. Wide columns are used for large samples and long columns for difficult separations. The magnitude of absorbent activity, and therefore retention is referred to using the Brockmann scale [26], and can be controlled by the addition of known amounts of water to the dry adsorbent followed by equilibration in a closed container prior to use and by pre-drying the extract with e.g. anhydrous sodium sulfate, prior to applying the extract to the column [27,28].

The fractionation of petroleum components by adsorption on such material as fullers earth, animal charcoal, and various types of clay dates back to the beginning of the century. These materials effect an arbitrary separation of the material into a number of fractions that have variously been described as oil and resins (hard and soft). Prior to fractionation using adsorption chromatography, petroleum must be treated in order to remove asphaltenes. This is necessary insofar as they are usually difficult to remove from the earth or clay and may actually be irreversibly adsorbed on the adsorbent. Silica or alumina pre-treated with chemical reagents such as concentrated sulfuric acid, sodium hydroxide, or silver nitrate can be used to change the selectivity of the column. The combination chromatography has been reported using alumina and silica gel arrangement in

arrangement in column chromatography to separate coal-derived products, shale oil and crude oil into compound classes [31-36].

2.4.2 Fractionation of crude oil

The accurate and reliable analysis of crude oil, weathered oil, and oil-spill samples is extremely important in view of the wide distribution of oil and oil pollution in the environment. During the last decade, advances have been made in the methods used for oil spill cleanup [29] including physical, chemical, and biodegradative techniques. In order to provide an effective cleanup strategy and to minimize environmental damage, detailed compositional and structural information of the petroleum is required. Other important areas of application include oil and petroleum processing and enhanced oil recovery processes, where detailed information regarding crude oil composition is necessary for rational process design[30]. The fractionation of aromatics using silica gel is important since it provides a direct guide to the progress of refining operations, such as solvent extraction, hydrogenation or acid treatment. Other uses of the method are in monitoring the tailoring of feed stocks to make special products, and determining final product quality.

The complexity of petroleum crude oils as explained in chapter one demands very sophisticated analytical schemes for characterization. Because of the sheer number and variety of compounds present, these materials defy analysis by a single technique. In particular, techniques such as gas chromatography and mass spectrometry, which respond to individual compounds, produce results too complex to be routinely and easily interpreted. It is therefore desirable to simplify the analysis by first performing a rapid coarse fractionation, hopefully providing the analyst with less complex mixtures.

2.4.3 Fractionation of Libyan crude oil

Our initial studies centered on a comparison of the performance of adsorption chromatography with extrography for the fractionation of Libyan crude oil.

A liquid chromatographic method was developed for the fractionation of Libyan crude oil. The efficiency and reproducibility of the method were demonstrated by using a standard mixture containing saturated and aromatic hydrocarbons. Reference samples of Libyan crude oil namely Bouri, Sirte, Sidra, Zwetena, and Messla were then separated using the method. Each was fractionated into saturates, aromatics and resins. Characterization and identification of individual aliphatic and aromatic compounds was accomplished using GC-MS.

2.4.4. Compound-class separation by adsorption chromatography

A chromatographic glass column (12.5 mm i.d.400 mm length) was plugged with Pyrex glass wool and serially rinsed with methanol, hexane and dichloromethane, and allowed to dry. The column was dry-packed with 60 g. of activated silica gel (0.13-0.25 mm) and topped with about 0.5 cm sand. To obtain an even packing density and ensure stability during packing, the silica gel was poured from a funnel attached to the top of the column, vibrational and rotational agitation of the column was used. The column was conditioned with 20 ml hexane, and the eluent was discarded.

The irreversible adsorption of asphaltenes onto the column packing material can cause chromatographic inconsistencies [37]. Because of this, asphaltenes were removed by precipitation from hexane, prior to each sample

being loaded onto the column. The asphatic content of each crude is illustrated in Figure2.5.

A 2 cm^3 aliquot of the hexane soluble portion of a crude (or standard) was transferred to the top of the column using an 10 cm^3 hexane to complete the transfer. An elutropic series of chromatographic grade solvents were then used to develop the column to give five fractions as shown in Table 2.1.

Hexane (150 cm^3) was used to elute saturated hydrocarbons (F1), 220 cm^3 of 36 % benzene in hexane was used to elute aromatic hydrocarbons (F2), subsequent washes with 225 cm^3 chloroform (F3), 300 cm^3 of 95 % chloroform in diethyl ether (F4) and 325 cm^3 of 93 % chloroform in ethanol (F5) were used to elute the resin fractions.

All fractions were separately blown to dryness with nitrogen and the residue weights recorded. This procedure was performed in duplicate. The percentage composition of the saturated, aromatic and polar aromatic compounds in the crude oils were then calculated.

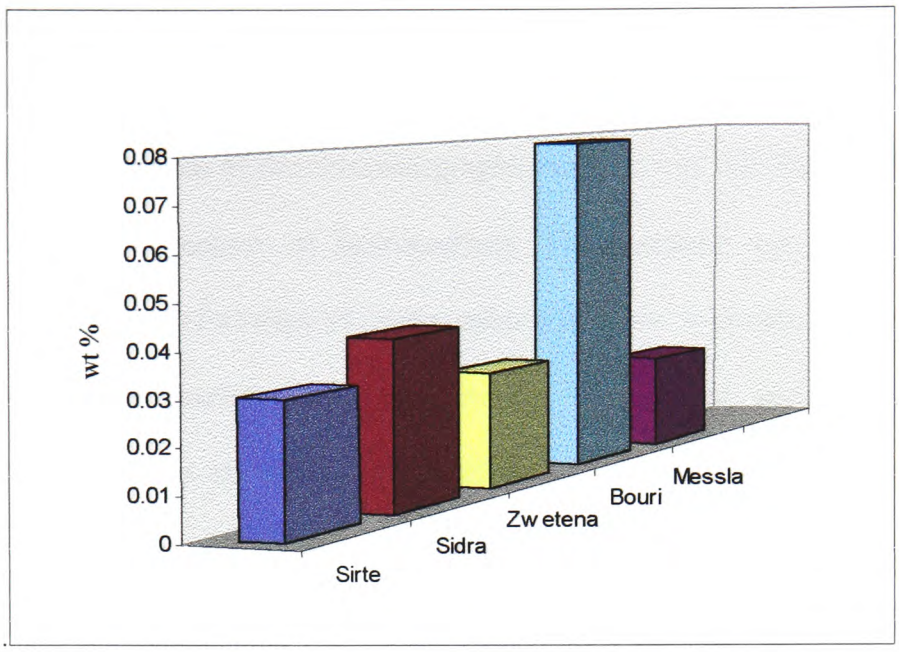


Fig. 2.5. Asphaltene content in Libyan crude oils under investigation.

Table. 2.1. Eluotropic series of solvents used to develop compound-class fractions:

Fraction	Solvent	Elution volume (ml)
F1	n-hexane	150
F2	64% n-hexane+36% benzene	220
F3	chloroform	225
F4	95% chloroform+5%diethylether	300
F5	93% chloroform+7% ethanol	325

The final analysis of target hydrocarbons was performed on an Hewlett Packard (HP) Model 5890 GC equipped with a Model 5971 Mass Selective Detector (MSD). Using an HP1 (cross linked Methyl Silicone GUM) column with dimensions of 50 m x 0.32 mm i.d. (0.17 um film). Data acquisition was achieved with an HP G 1034 C MS chem. Station (DOS series). The chromatographic conditions and experimental details are described in chapter 5.

2.4.5 Results and Discussion

2.4.5.1 Fractionation the hydrocarbon standard

The performance of the chromatographic method was initially investigated using the authentic mixture of hydrocarbons. The standard was prepared by mixing 100 ppm each of a range of hydrocarbons in 2 cm^3 n-hexane. It contained nine saturated hydrocarbons ranging from C_{12} to C_{20} and seven polycyclic aromatic hydrocarbons of molecular weight range of 128 to 228. The mixture was then fractionated using the chromatographic method. Figures 2.6 and 2.7 show the GC-MS total ion chromatograms (TIC) of fractions F1 and F2 containing saturated and aromatic hydrocarbons respectively.

Here, the high fractionation efficiency of the chromatographic method is indicated by the absence of contamination or overlap between the two types of hydrocarbon.

The total recovery of saturated and aromatic hydrocarbon standard was 83.3 % and 85.7 % respectively. The recovery of individual saturates varied according to their molecular weight whilst no such trend was apparent for aromatic components. Recovery for individual saturated hydrocarbons ranged from between 6.7 % to 15.4 % and for the aromatic compounds were 9.1 % to 20.2 % as shown in Tables 2.2 and 2.3 respectively.

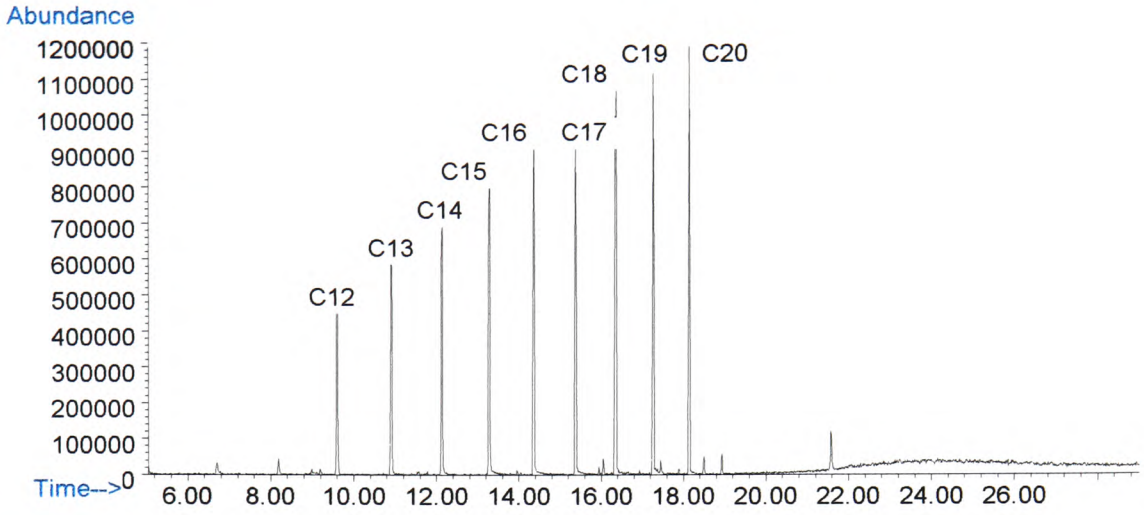


Fig. 2.6. TIC of Saturated hydrocarbon fraction (F1) of standard solution.

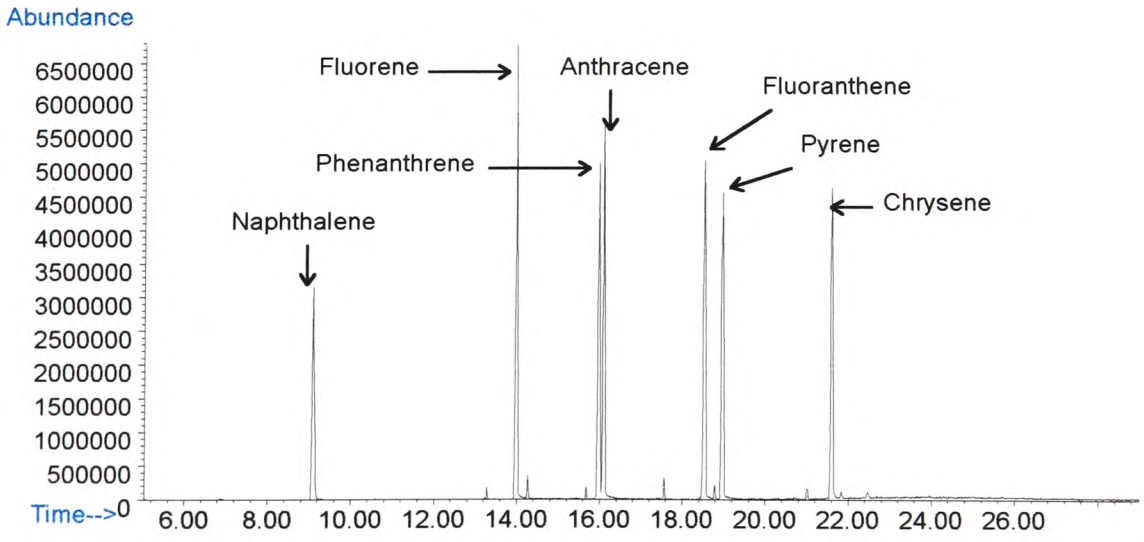


Fig. 2.7. TIC of PAH fraction (F2) of standard solution.

Table 2.2 Retention time, molecular weight and recovery of standard saturated hydrocarbons using silica gel column fraction.

Pk	Saturated compound	RT(min)	Carbon No.	MW	(%)
1	Dodecane	9.6	C12	170	6.7
2	Decane	10.9	C13	184	8.4
3	Tetradecane	12.1	C14	198	8.7
4	Pentadecane	13.3	C15	212	10.8
5	Hexadecane	14.4	C16	226	12.1
6	Heptadecane	15.4	C17	240	12.3
7	Octadecane	16.4	C18	254	15.4
8	Nonadecane	17.3	C19	268	12.7
9	Eicosane	18.1	C20	282	12.9

Table 2.3 Retention time, molecular weight and recovery of standard aromatic hydrocarbons using silica gel column fraction .

Pk	Aromatic compound	RT(min)	Carbon No.	MW	(%)
1	Naphthalene	9.1	C10	128	9.1
2	Fluorene	14.1	C13	166	15.3
3	Phenanthrene	15.9	C14	178	13.6
4	Anthracene	16.1	C14	178	13.1
5	Fluoranthene	18.6	C16	202	14.8
6	Pyrene	19.0	C16	202	13.9
7	Chrysene	21.6	C18	228	20.2

2.4.5.2 Fractionation of crude oil

Having established the efficiency of the chromatographic fractionation procedure our studies continued with crude oil. Five varieties of Libyan crude oil namely, Sirte, Sidra, Zwetena, Bouri and Messla, were obtained from several production companies. These were separated on silica gel into five fractions using the previous optimized protocol. Each fraction was analyzed by GC-MS. The aim of this study was to compare the efficiency and reproducibility of separation of aromatic compounds present in these oil samples using column chromatography with the other fractionation procedures that we planned to develop in future phases of the project. The procedure was successfully applied to the fractionation of saturated hydrocarbons (F1) from aromatic compounds (F2) in five Libyan crude oil samples.

Analysis of F1 using GC-MS demonstrated that there was no saturated / aromatic overlapping and that complete fractionation had been achieved. These observations are consistent with the previous results obtained for the standard saturated-aromatic mixture. Table 2.4 shows that there is no significant differences between the saturated hydrocarbon content of the five samples of crude oil (Sirte, Sidra, Zwetena, Bouri and Messla). In each case the percentage of saturated hydrocarbon were in excess of 60 % of the total. These findings are in agreement with the US Bureau of Mines Method of Classification. Libyan crude oil is classified as paraffinic, bordering on paraffin-intermediate base (Crude Assay Report, Petroleum Research Center, 1987). The composition of saturated hydrocarbon in different cuts is generally always more than double the amount of the aromatic and polar compounds in Libyan crude oil samples [40].

Table 2.4. Saturated hydrocarbons present in five different crude oil samples *.

Crude oil	Extract yield (mg)	%
Sirte,	61.9	74.2
Sidra,	68.9	76.0
Zwetena,	65.1	74.9
Bouri	60.6	67.5
Messla	70.3	77.7

* Average of two replicates

The distribution of the saturated hydrocarbons may often give a good indication as to specific type of oil being investigated. Figures 2.8 and 2.10 to 2.13 shows the TIC of the five different Libyan crude oils. These chromatograms indeed, show that the constituent distribution pattern varies with the type of crude oil.

Figure 2.8 shows the TIC of fraction (F1) of Bouri crude oil. The saturated hydrocarbons ranged from C_{10} to C_{26}. The identification of individual straight-chain saturated hydrocarbons by GC-MS is usually quite straight forward, since the smooth and equal retention spacing of the peaks is characteristic of homologous hydrocarbon series. Figure 2.9 shows a typical mass spectrum obtained from Bouri crude (F1) corresponding to an n-alkane heptadecane $C_{21}H_{44}$. In this case, the relative abundances of the ions are also typical, showing maximum abundance around $C_4H_9^+$, $C_5H_{13}^+$ and $C_6H_{13}^+$. The intense peaks occur with the general formula, C_nH_{2n+1} (m/e = 57, 71, 85, 99, etc.). For long straight chain molecules, additional peaks will be observed at increments of 14 mass units (CH_2).

Table 2.5 shows the retention time and identification of seventeen saturated hydrocarbons as well as the extract yield of individual compounds from Sirte crude. The separation of saturated (F1) and aromatic (F2) hydrocarbons in crude oil was achieved. Analysis of F1 and F2 demonstrated that there was no compound class overlap between saturates and aromatics.

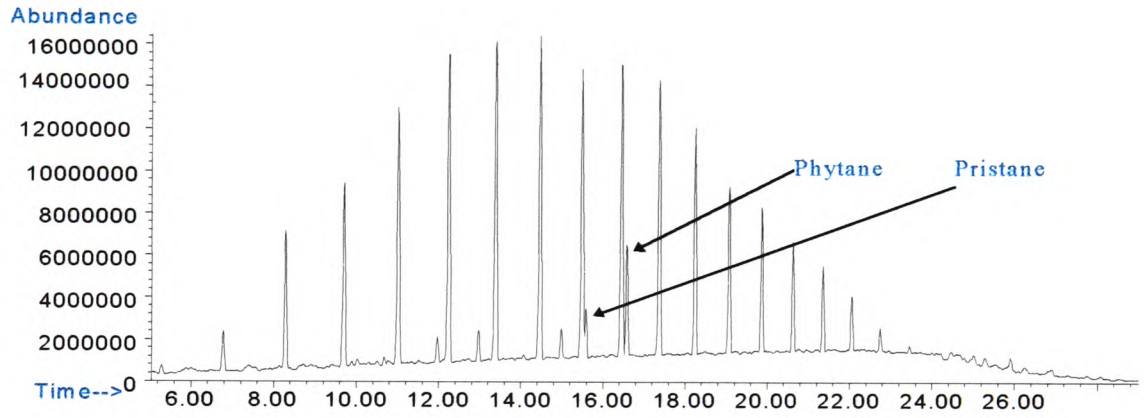


Fig. 2.8. GC-MS TIC of saturated hydrocarbon fraction (F1) of Bouri crude oil.

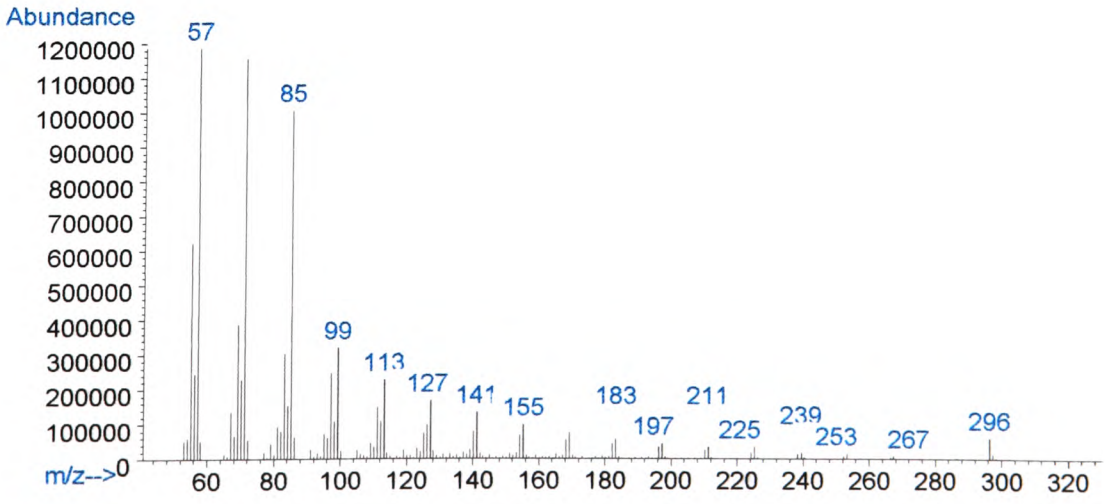


Fig. 2.9. Mass spectrum of Heptadecane [scan 1228 (19.085 min)] obtained from Figure 2.8 of Bouri crude (F1) showing the typical distribution of fragment ions for n-alkanes.

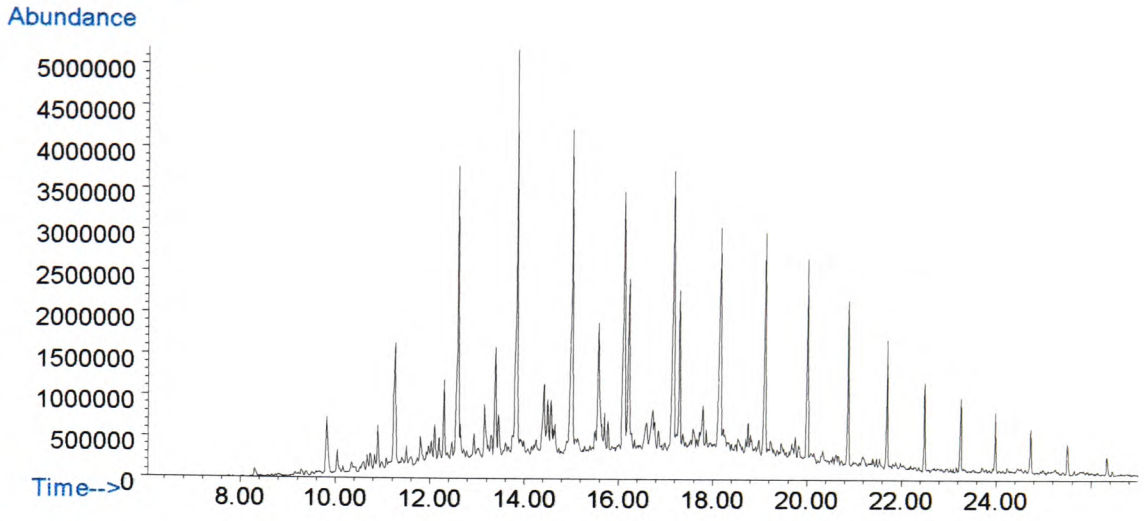


Fig. 2.10. GC-MS TIC of saturated hydrocarbon fraction (F1) of Zwetena crude oil.

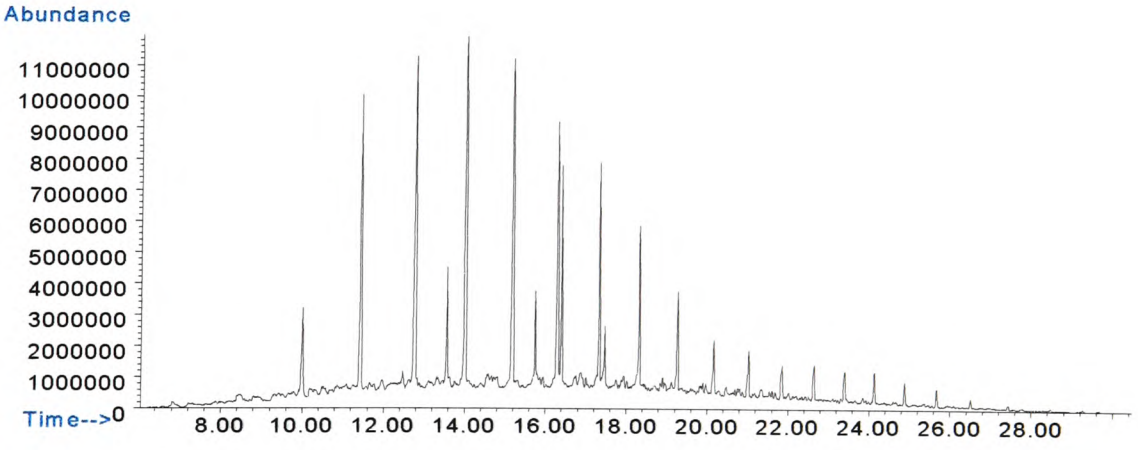


Fig. 2.11. GC-MS TIC of saturated hydrocarbon fraction (F1) of Sidra crude oil.

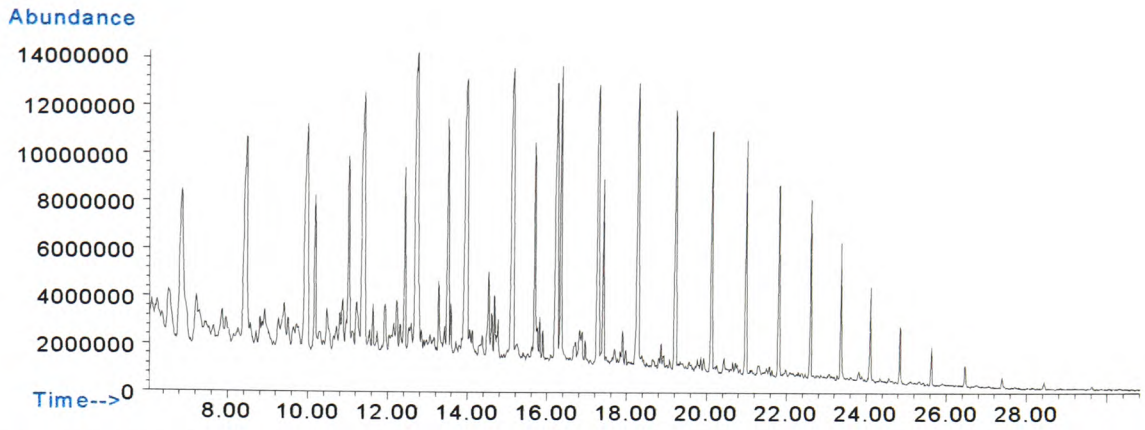


Fig. 2.12. GC-MS TIC of saturated hydrocarbon fraction (F1) of Messla crude oil

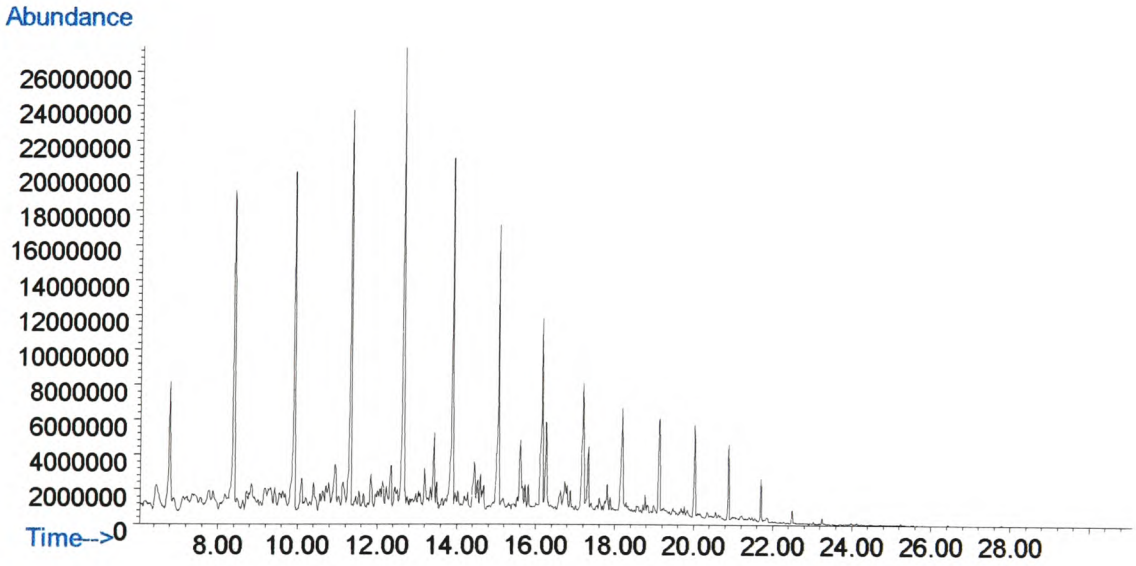


Fig. 2.13. GC-MS TIC of saturated hydrocarbon fraction (F1) of Sirte crude oil

Table 2.5. Retention time, identification and % extract yield of some saturated hydrocarbons from Sirte crude oil.

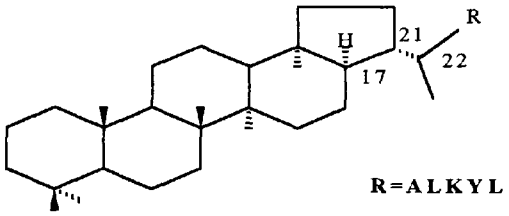
PK#.	Saturated hydrocarbon	RT	MW	Extract yield (mg)*
1	Decane	6.78	142	0.7
2	Undecane	8.29	156	2.0
3	Undecane	9.71	156	3.0
4	Tridecene	11.02	184	4.1
5	Undecane, 2, 3-dimethyl-	12.26	184	5.0
6	Pentadecane	13.40	212	5.1
7	Docosane	14.48	310	5.0
8	Heptadecane	15.51	240	4.1
9	Docosane	16.46	310	4.2
10	Tridecane, 7-hexyl-	17.39	254	4.3
11	Docosane	18.25	310	3.6
12	Eicosan	19.07	282	2.9
13	Docosane	19.87	310	2.5
14	Pentatriacontane	20.63	493	1.8
15	Tetratriacontane	21.36	493	1.2
16	Tetratriacontane	22.05	479	0.8
17	Hexacosane	22.74	336	0.1
Total				50.4

Extract yield for individual saturated hydrocarbon = GC $_{\text{Area \%}}$ X weight of saturated hydrocarbon extract.

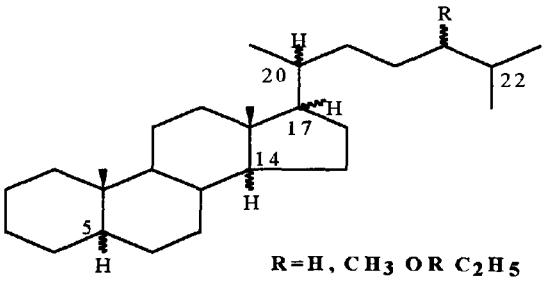
Studies on the separation and identification of biomarker compounds in oil samples have greatly increased in resent years [44,45]. Biomarker compounds are important because of their usefulness in recognition of oil source and in oil correlations. Among the various types of biomarkers, triterpanes and steranes are the best choice for identification purposes because of their high molecular weights, high stability and relatively high concentrations in crude oil. It has been found that hopanes have a very high resistance to photochemical and microbial degradation in comparison with the saturated and aromatic compounds[46].

For oil spill fingerprinting purposes the distribution of "biomarker" compounds, including the steroidal and triterpenoidal alkane (steranes and

triterpanes) is important [41]. Figure 2.14 shows representative structures of pentacyclic triterpanes and steranes. By using GC-MS it is possible to study their distribution [42], variations of which form the basis of the mass spectrometric fingerprinting technique [43]. Under Electron impact Ionization (EI) conditions these compounds produce characteristic fragment ions including m/z 217, 218, and m/z 191, (diagnostic for the steranes and triterpanes respectively). Figures 2.15 to 2.17 shows the distribution profile of triterpane compounds at m/z 191 and sterane compounds at m/z 217 and 218 in Bouri crude oil (F1). Representative spectra of these species obtained from Bouri crude are given in Figures 2.18 and 2.19. Mass chromatograms showing the distribution of steranes and triterpanes in Libyan crude oil from different geographical locations illustrating their different fingerprints are shown in Figures 2.20 to 2.25.



17∝ (H), 21β (H)



C27 - C29 regular steranes

Fig.2.14. Sterechemistry of the pentacyclic triterpanes and steranes.

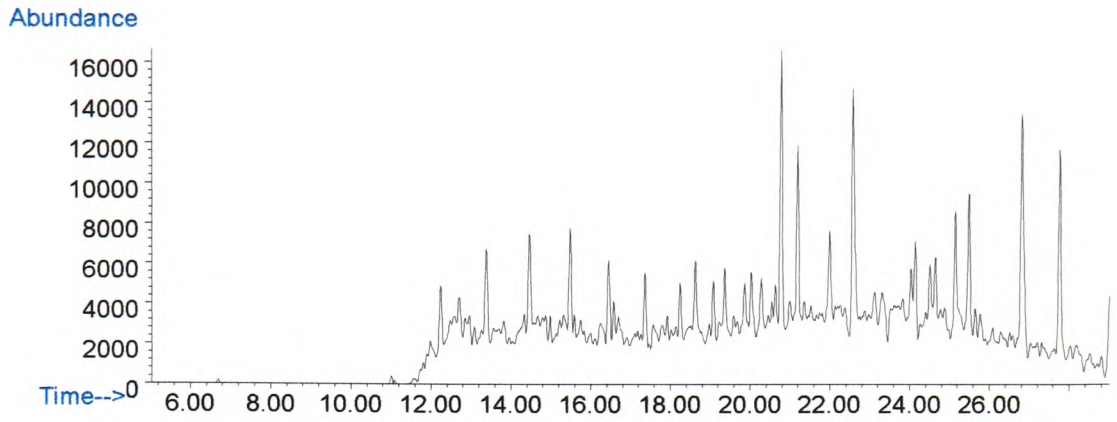


Fig. 2.15. Distribution profile of triterpanes (m/z 191 mass chromatogram) in Bouri crude oil.

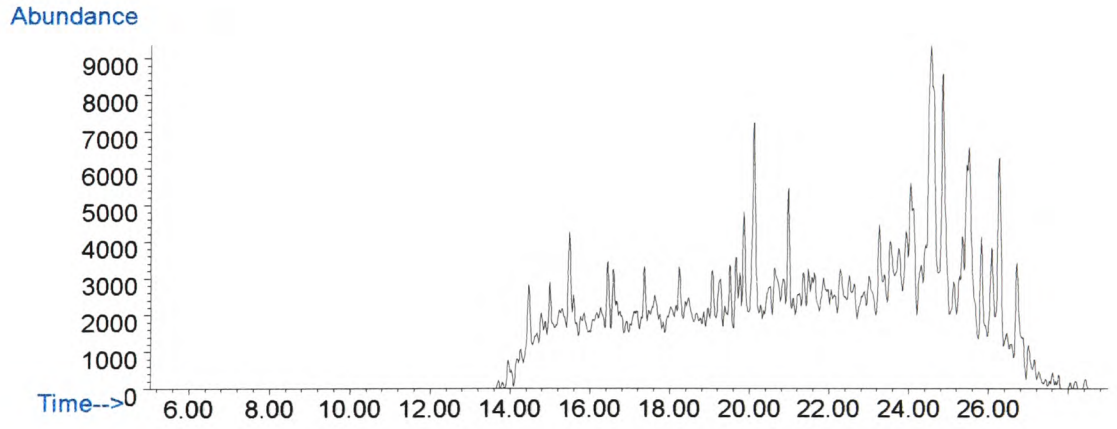


Fig. 2.16. Distribution profile of steranes (m/z 217 mass chromatogram) in Bouri crude oil.

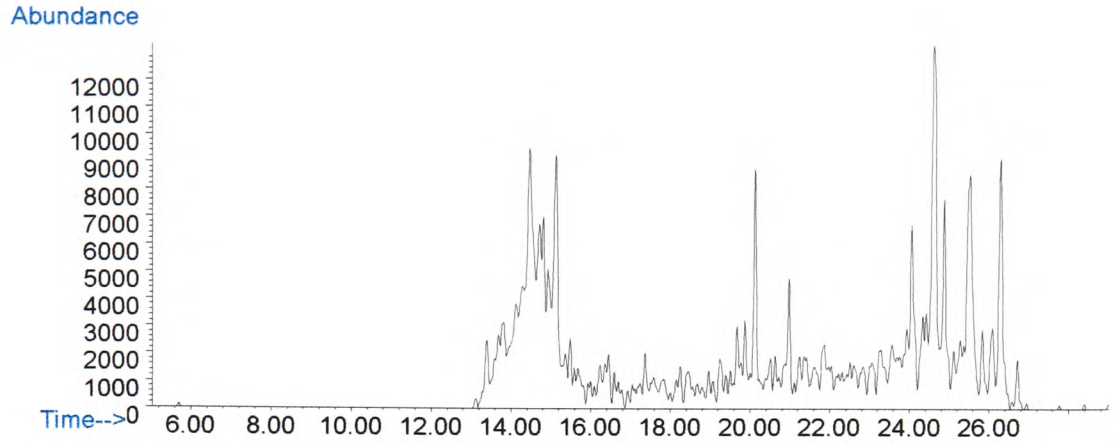


Fig. 2.17. Distribution profile of steranes (m/z 218 mass chromatogram) in Bouri crude oil.

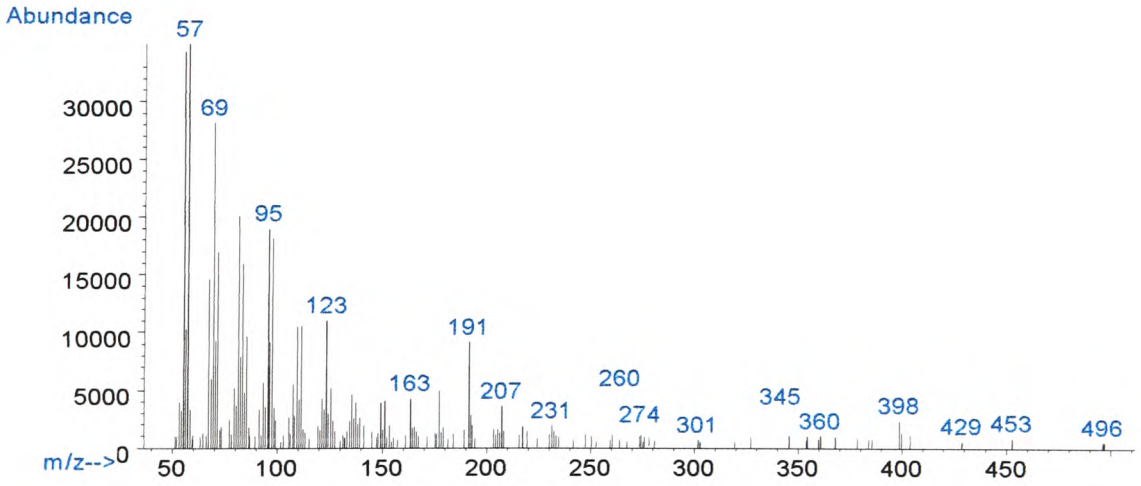


Fig.2.18. Mass spectrum of sterane (scan # 1636, 24.651min) obtained from Bouri crude (fig 2.8).

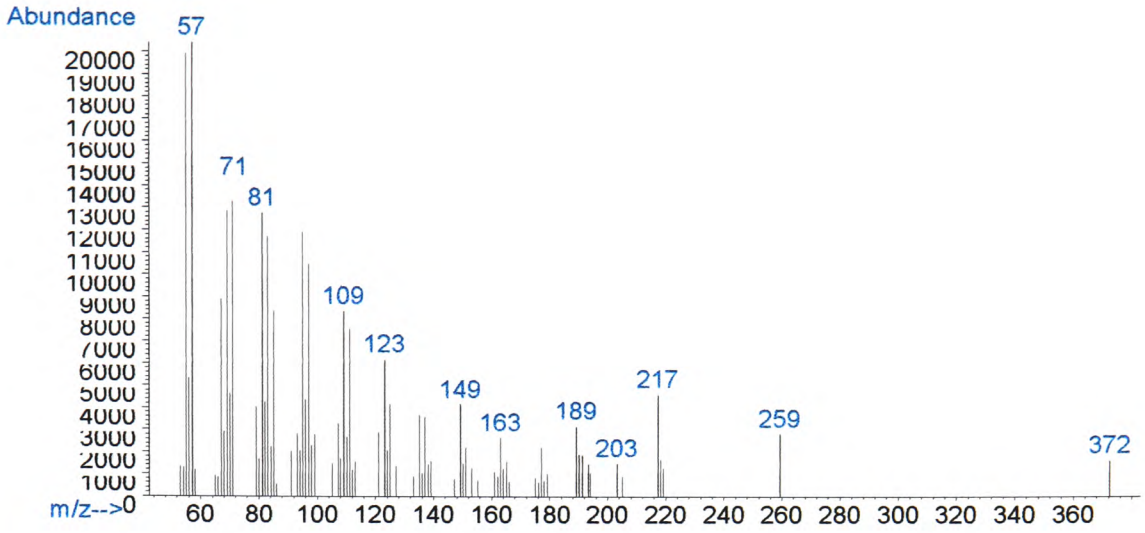


Fig.2.19. Mass spectrum of hopane (scan #1885, 27.989 min) obtained from Bouri crude oil figure 2.8.

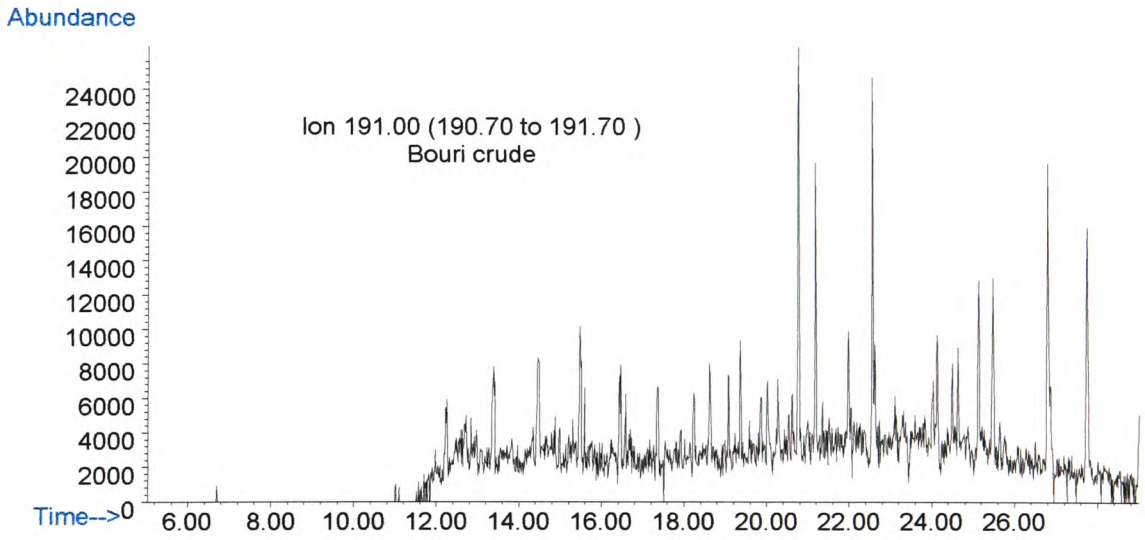


Fig. 2.20. GC-MS triterpanes fingerprint of Bouri crude oil.

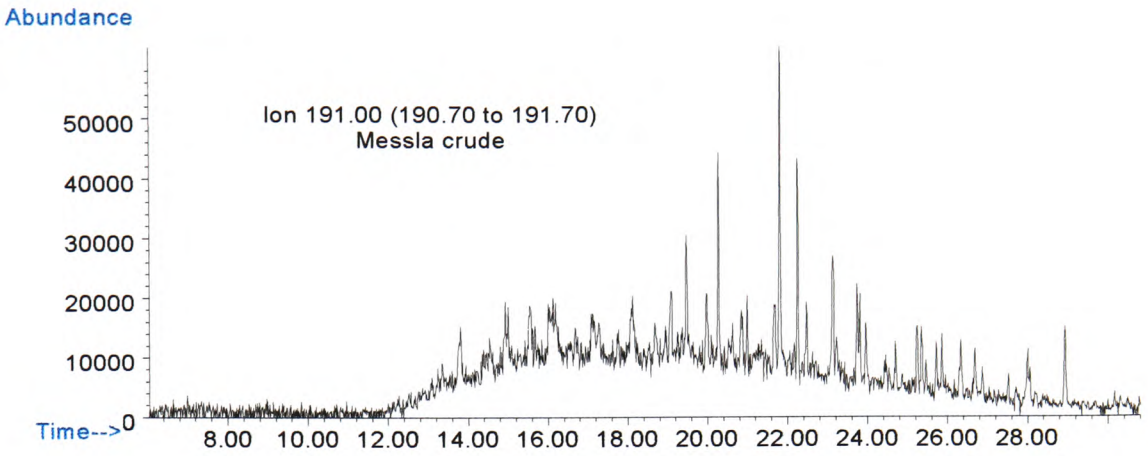


Fig. 2.21. GC-MS triterpanes fingerprint of Messla crude oil.

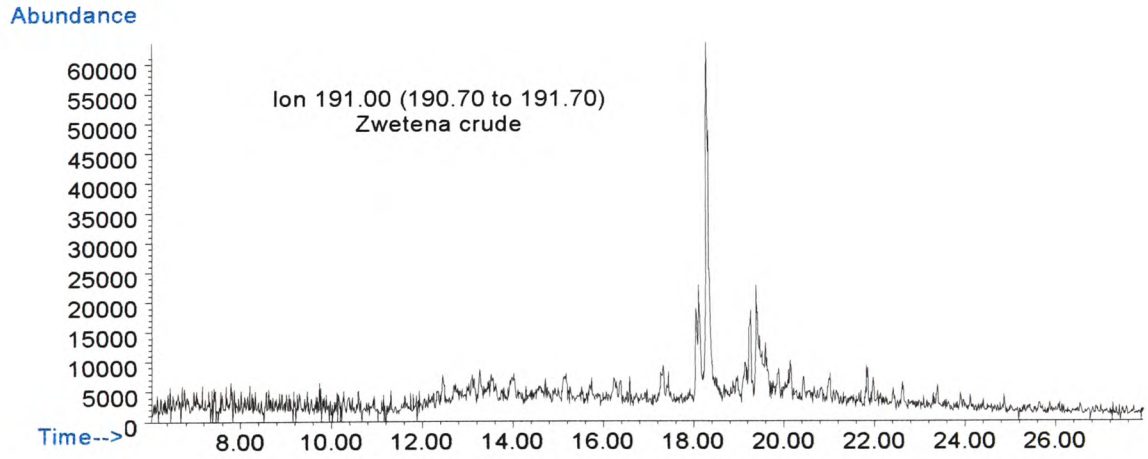


Fig. 2.22. GC-MS triterpanes fingerprint of Zweteena crude oil.

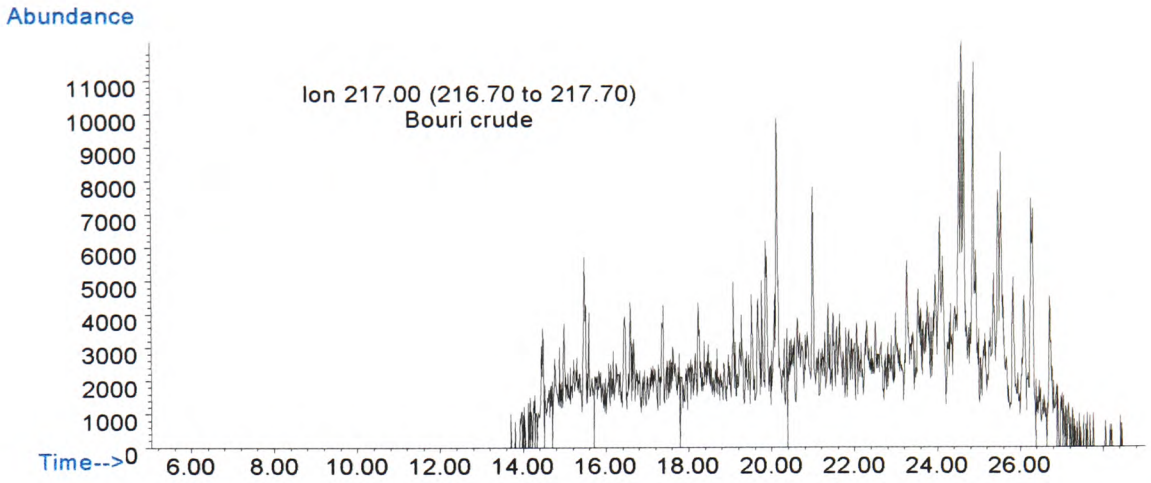


Fig. 2.23. GC-MS sterane fingerprint of Bouri crude oil.

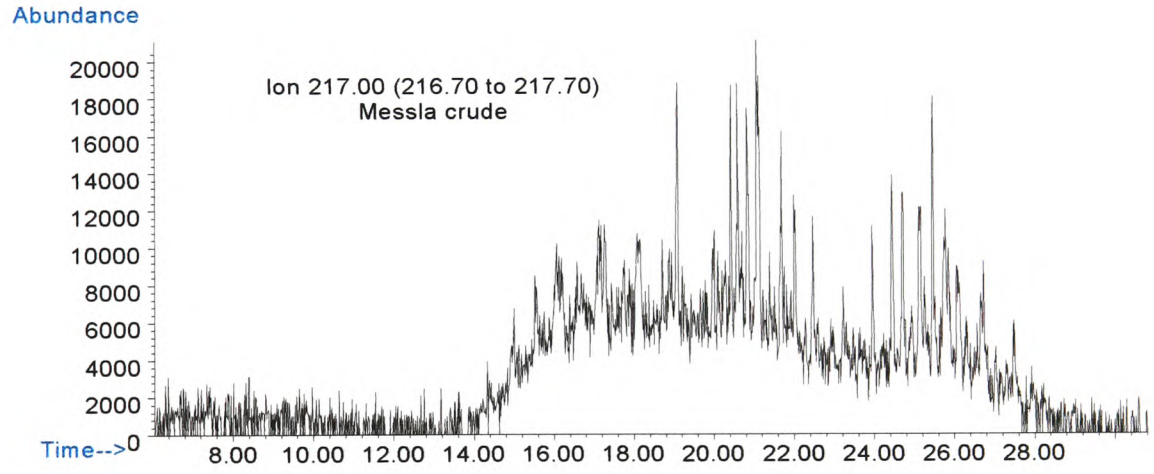


Fig. 2.24. GC-MS sterane fingerprint of Messla crude oil.

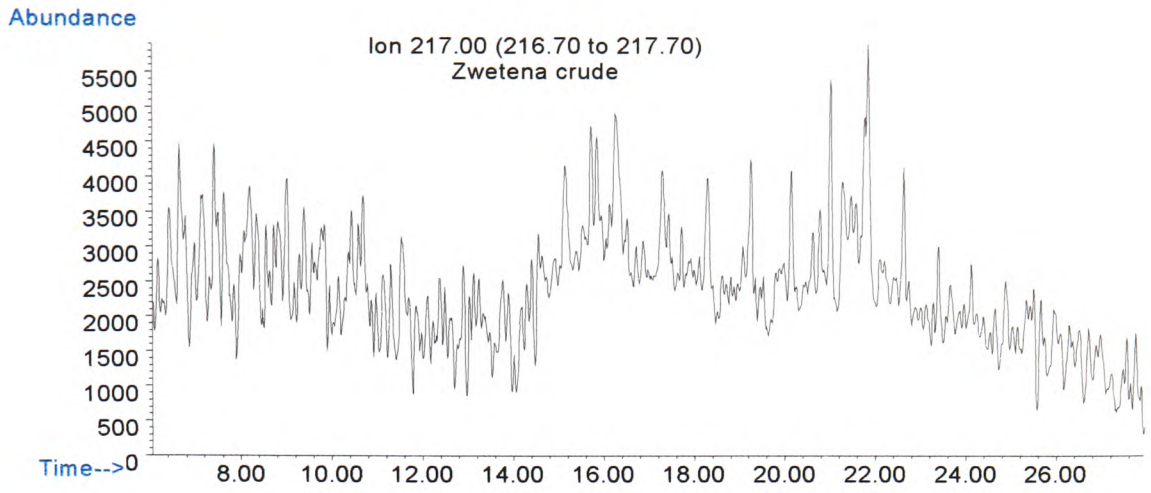


Fig. 2.25. GC-MS sterane fingerprint of Zweteena crude oil.

The fingerprinting of crude oil may also be achieved using PAHs as markers. Generally the technique is based on some form of fractionation by column chromatography in order to obtain a solution of total PAHs. In our work a complete separation of PAHs in crude oil was achieved. Figures 2.26 to 2.30 show the GC-MS total ion chromatograms of fraction F2 for five Libyan crude oils. Tables 2.6 to 2.10 lists aromatic hydrocarbons identified from F2 of the five oils. The TIC obtained by GC-MS analysis of the polycyclic aromatic hydrocarbon fraction (F2) of the Bouri crude oil is shown in Fig.2.26. Peaks labeled refer to the actual molecular weight of the compounds present. The mass spectrum for scan # 1694, retention time of 24.6 min is shown in Figure 2.31 and indicates the presence of series of larger aromatic species with masses of 252, 276 etc. Note also that compounds with MW at m/e 252, are likely to indicate the most carcinogenic PAHs, these are present at very low levels as compared to other components.

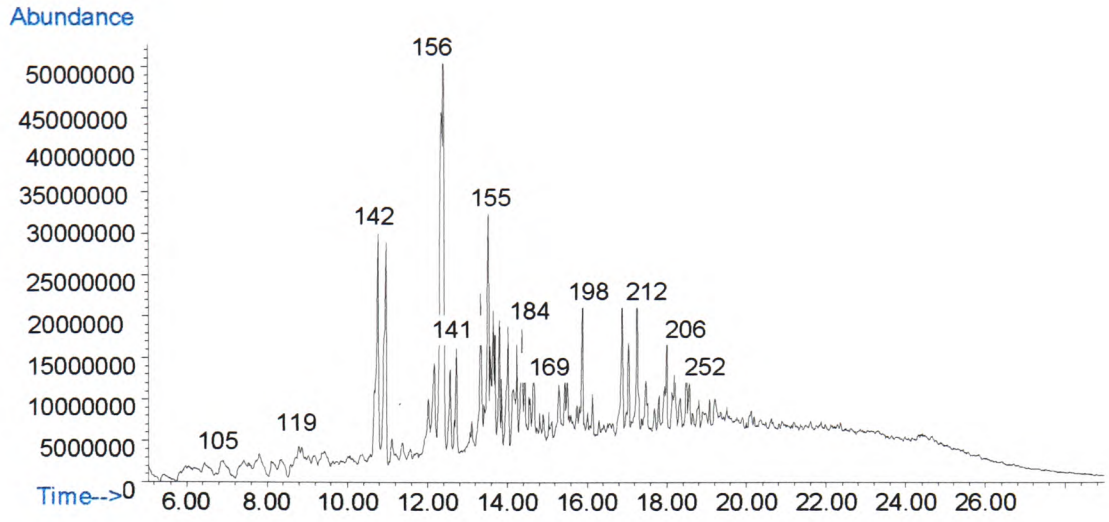


Fig. 2.26. Total ion chromatogram obtained from the GC-MS analysis of the polycyclic aromatic hydrocarbon fraction (F2) of Bouri crude oil. Peak labels refer to the actual MW of the compounds.

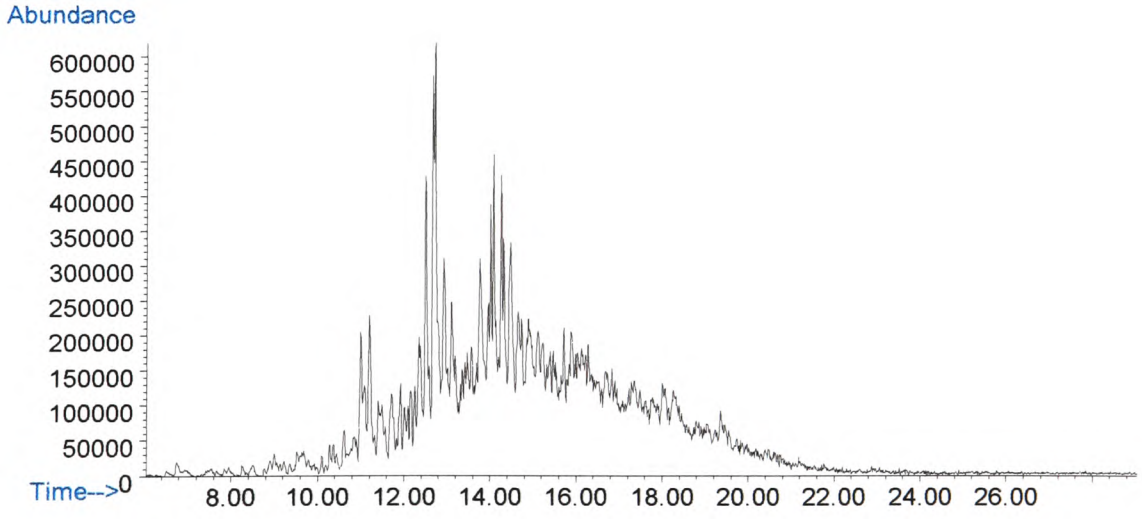


Fig.2.27. GC-MS TIC of aromatic hydrocarbons fraction (F2) of Sidra crude oil.

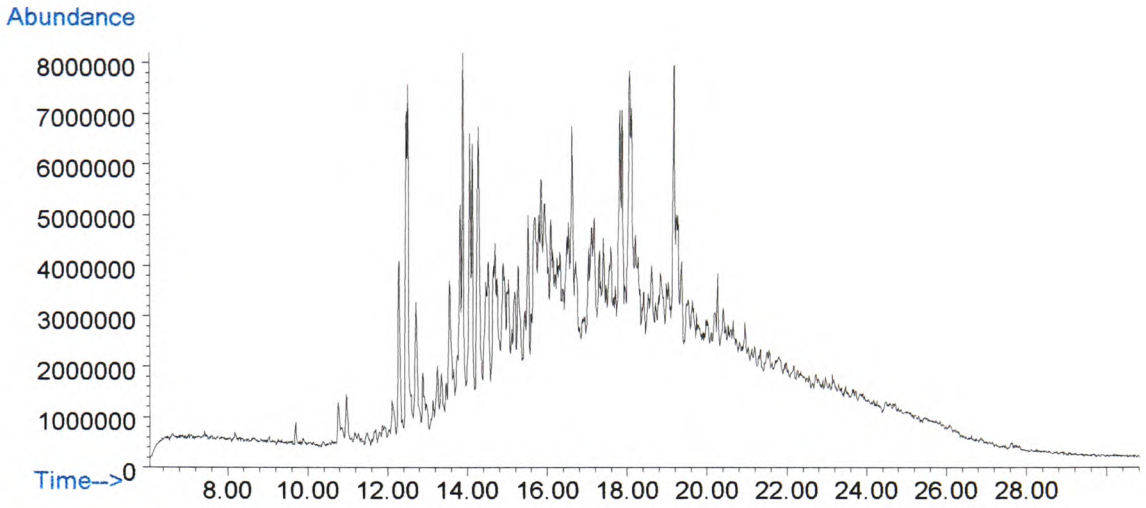


Fig.2.28. GC-MS TIC of aromatic hydrocarbons fraction (F2) of Sirte crude oil.

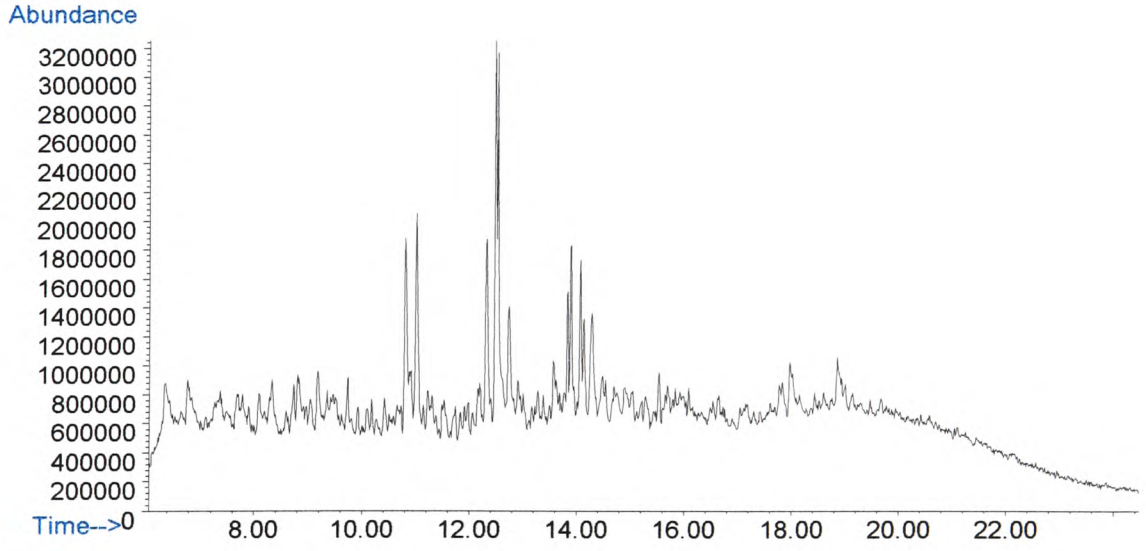


Fig.2.29. GC-MS TIC of aromatic hydrocarbons fraction (F2) of Messla crude oil.

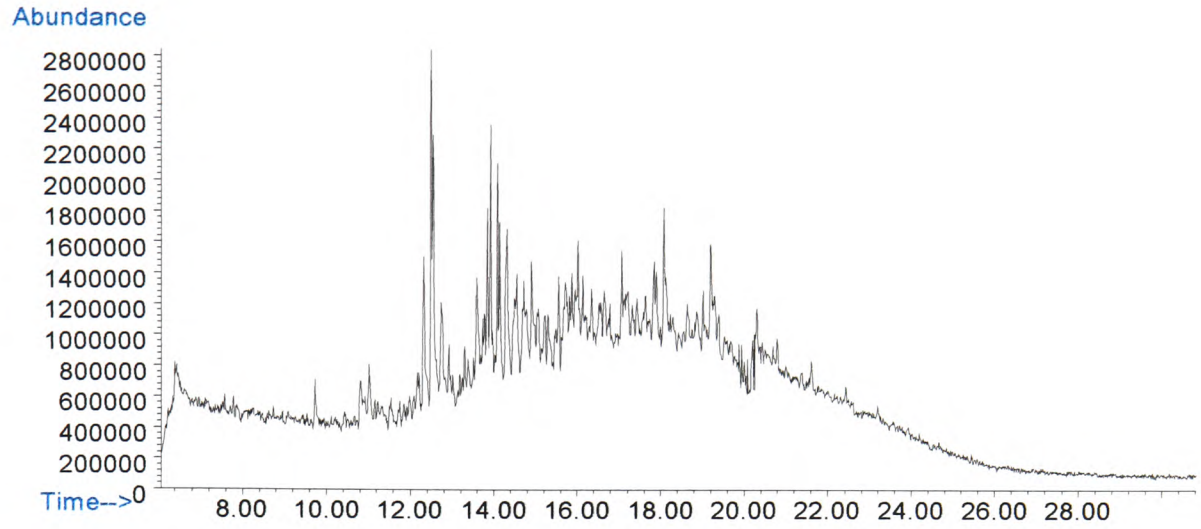


Fig.2.30. GC-MS TIC of aromatic hydrocarbons fraction (F2) Zwetena crude oil.

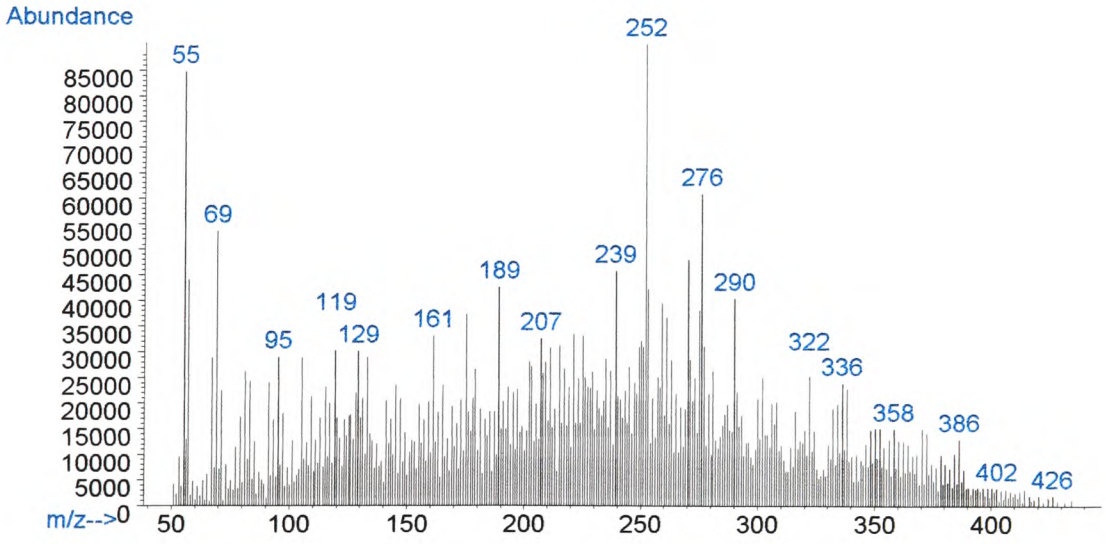


Fig 2.31. Mass spectrum of large aromatic species from Bouri crude oil at (scan # 1694, 24.6 min).

Table.2.6. Aromatic hydrocarbons(F2) isolated from Bouri crude oil using silica gel column fractionation and GC-MS data analysis.

PK#	RT	Library/ID	MW	Carbon No
1	7.42	Benzene,2-ethyl-1,3-dimethyl-	134	C10
2	8.35	Benzene,4-ethyl-1,2-dimethyl-	134	C10
3	10.68	Naphthalene,2-methyl-	142	C11
4	10.78	Naphthalene,1-methyl	142	C11
5	10.97	1H-indene,1-ethylidene	142	C11
6	11.12	Naphthalene,1,2,3,4-tetrahydro-1,	142	C11
7	12.01	Naphthalene,2-ethyl-	156	C12
8	12.18	Naphthalene,1,5-dimethyl-	156	C12
9	12.36	Naphthalene,2,6-dimethyl-	156	C12
10	12.41	Naphthalene1,6-dimethyl-	156	C12
11	12.58	Naphthalene,1-ethyl-	156	C12
12	12.73	Naphthalene,2,7-dimethyl-	156	C12
13	12.34	Naphthalene2,3,6-trimethyl-	170	C13
14	13.42	Naphthalene1,6,7-trimethyl-	170	C13
15	13.52	Naphthalene1,4,6-trimethyl-	170	C13
16	13.58	Naphthalene1,4,5-trimethyl-	170	C13
17	13.66	Naphthalene,2,3,6-trimethyl-	170	C13
18	13.69	Benzene,ethylpentamethyl-	176	C13
19	13.81	Naphthalene1,4,6-trimethyl	170	C13
20	13.86	Naphthalene1,6,7-trimethyl	170	C13
21	14.02	Naphthalene1,4,5-trimethyl-	170	C13
22	14.16	Naphthalene1,3,6-trimethyl-	170	C13
23	14.25	Naphthalene1,4,5-trimethyl-	170	C13
24	14.36	Naphthalene,2-methyl-1-propyl- -	184	C14
25	14.43	Benzo[b]thiophene,2-ethyl-5,7-dim	184	C14
26	14.66	Azulene,7-ethyl-1,4-dimethyl-	184	C14
27	15.30	Azulene,7-ethyl-1,4-dimethyl	184	C14
28	15.32	Phenol,3,4,5-trimethoxy-	184	C14
29	15.44	9H-Fluorene,4-methyl-	187	C14
30	15.45	9H- Fluorene,1-methyl-	180	C14
31	15.50	Naphthalene,1-methyl-7-(1-methyle-	184	C14
32	15.89	Naphthalene,2-(1,1-dimethyl)-	184	C14
33	16.65	Dibenz[c,e]oxepin	194	C14
34	16.14	Phenanthrene	198	C14
35	16.87	Benzene,1-fluoro-3-(2-phyenylethenyl)-	198	C14
36	17.05	Benzen,1,1-oxybis[4-methyl--	198	C14
37	17.26	benzene,1-fluro-3-(2-phenylethen-	192	C14
38	17.73	Benzenethiol,4-1,1-dimeth-	192	C14
39	17.47	Phenanthrene,tetradchydro-	192	C14
40	17.48	Anthracene,1-methyl-	192	C14
41	17.80	Naphtho[2,3-b]thiophene,2,9-dimet-	212	C14
42	17.94	Naphtho[2,3-b]thiophene,4,9-dimethyl-	212	C14
43	18.00	Naphtho[2,3-b]thiophene,2,9-dimet-	212	C14
44	18.14	2,8-dimethyldibenzo[B,D]thiophene-	212	C14
45	18.20	2,8-dimethyldibenzo[B,D]thiophene	212	C14
46	18.33	2[3H]-phenanthrenone-	212	C15
47	18.48	Phenanthrene,2,3-dimethyl--	206	C16

Table.2.7. Aromatic hydrocarbons(F2) isolated from Sirte crude oil using silica gel column fractionation and GC-MS data analysis.

PK #	RT	Library / ID	MW	Carbon No.
1	8.40	Benzene, 1, 2, 3, 4-tetramethyl-	134	C 10
2	8.79	Benzene, (1-azido-1-methyethyl)-	134	C10
3	9.50	Benzene, 1,4-dimethyl-2-(2-methylprop-	146	C11
4	9.58	Benzene, ethyl-1,2,4-trimethyl-	148	C11
5	10.16	Benzene,4-(2-butenyl)-1,2-dimethyl-,	160	C12
6	10.26	Benzaldehyde,4-butyl-	162	C11
7	10.50	Benzene, (3-methyl-2-butenyl)-	146	C11
8	10.71	Benzene, dimethyl[(2-methylpropoxy)-	192	C13
9	10.88	Naphthalene, 1-methyl-	143	C11
10	10.94	Naphthalene, 1-methyl-	142	C11
11	11.08	Naphthalene, 2-methyl-	142	C11
12	11.29	Benzene, 4-(2-butenyl)-1,2-dimethyl-	160	C12
13	11.37	Naphthalene,1,2,3,4-tetrahydr-1,4	160	C12
14	11.91	4-Quinolinol, 2-methyl-	159	C10
15	11.98	Acenaphthene	154	C12
16	12.04	1H-Indene, 2,3-dihydro-	174	C13
17	12.26	Naphthalene, 2-ethyl-	156	C12
18	13.35	Toluene, 3-(2,2-dicyanoethenyl)	168	C11
19	13.45	Naphthalene, 1-ethyl-	186	C12
20	13.90	Naphthalene, 1,6,7-trimethyl-	170	C13
21	13.96	Naphthalene, 1,4,5-trimethyl-	170	C13
22	14.13	Naphthalene, 2,3,6-trimethyl-	170	C13
23	14.20	Naphthalene, 1,4,6-trimethyl-	170	C13
24	15.00	[1,1-biphenyl]-4methanol	184	C13
25	15.52	Naphthalene, 1-methyl1-7-(1-methylethyl-	184	C14
26	15.60	Azulene, 7-ethyl-1,4-dimethyl-	184	C14
27	15.73	Benzenmethanol,2-methyl-	198	C14
28	16.06	Dibenzofuran, 2- methoxy-	198	C13
29	17.12	Phenanthrene, 9,10-dihydro-1-methyl-	194	C15
30	17.17	4-Phenanthrenol, 1,2,3,4-tetrahydro-	212	C15
31	17.22	9H-Fluorene, 2,3-dimethyl-	194	C15
32	17.26	4-Imidazolidinone, 5,5-diphenyl-	238	C15
33	17.96	Anthracene, 1-methyl-	192	C13
34	19.25	Phenanthrene, 2,5-dimethyl-	206	C16
35	19.35	Phenanthrene, 2,3-dimethyl	206	C16

Table.2.8. Aromatic hydrocarbons(F2) isolated from Messla crude oil using silica gel column fractionation and GC-MS data analysis.

PK #	RT	Library / ID	MW	Carbon No.
1	11.00	Naphthalene, 1-methyl-	142	C11
2	11.14	Naphthalene, 2-methyl	142	C11
3	11.61	Naphthalene,1,2,3,4-tetrahydro-	175	C13
4	11.84	Triazolo3,4-pyridine	161	C9
5	12.07	Benzene, 1,2,3,4-tetramethyl-	174	C13
6	12.16	Quinolinone, 1-methyl-	159	C10
7	12.42	Naphthalene, 1,5-dimethyl	156	C12
8	12.58	Naphthalene, 1,7-dimethyl	156	C12
9	12.62	Naphthalene, 1,3-dimethyl	156	C12
10	12.84	Naphthalene, 2,6-dimethyl	156	C12
11	13.01	Naphthalene, 2,7-dimethyl	156	C12
12	13.33	Benzenemethanol,-	132	C9
13	13.38	Toluene, 3-(2,2-dicyanoethenyl)	168	C11
14	13.49	Pyrazine, 2-chloro-	156	C7
15	13.59	Isoquinoline, 1-butyl-	185	C13
16	13.77	Naphthalene, 2,3,6-dimethyl	170	C13
17	14.00	Naphthalene, 1,4,6-dimethyl	170	C13
18	14.17	Naphthalene, 1,6,7-dimethyl	170	C13
19	14.65	Naphthalene, 1,4,5-dimethyl	170	C13
20	15.00	[1,1-Biphenyl]-4-methanol	184	C13
21	15.23	Phenol, 4-chloro-5-methyl-	184	C10
22	15.63	4,6-Pyridinedione-	154	C13
23	15.70	benzene,[(2-bromorthoxy) methyl]-	134	C10
24	15.90	1H-Azepine, (1-chloro-2,2-dimetyl-	184	C9
25	15.93	9H-Fluorene, 4-methyl-	180	C14
26	16.64	Benzenamine, 5-chloro-2-methyl-	141	C7
27	16.74	Anthracene	178	C14
28	16.82	1,2,4-Triazolo-pyridine-	195	C12
29	17.14	9H-Fluorene,2,3-dimethyl-	194	C14
30	17.21	Phenanthrene, 9,10-dihydro-1-methyl-	194	C15
31	17.25	Dibenzo[c,e]thiepin	210	C14
32	17.51	Dibenzothiophene, 3-methyl-	198	C13
33	17.81	9H-Carbazol, 1-3 amine-	210	C14
34	17.92	Phenanthrene, 4-methyl-	192	C15
35	17.99	1H-Indene, 1-phenyl-	192	C15
36	18.16	1H-Indene, 2-phenyl-	192	C15
37	18.72	Silanthrene,5,10-dihydro-	212	C12
38	18.83	Dibenzo[b,f]-diazocine-	224	C15
39	19.27	Phenanthrene, 2,7-dimethyl-	206	C16
40	19.38	Phenanthrene, 2,5-dimethyl-	206	C16
41	20.37	Phenanthrene, 2,3,5-dimethyl-	220	C17

Table.2.9. Aromatic hydrocarbons(F2) isolated from Sidra crude oil using silica gel column fractionation and GC-MS data analysis.

PK #	RT	Library / ID	MW	Carbon No.
1	10.28	Benzene,1-(2-butenyl)-	160	C12
2	10.61	Benzene, (2-methyl-2-butenyl)-	160	C12
3	11.00	Naphthalene, 1-methyl-	142	C11
4	11.20	Naphthalene, 2-methyl-	142	C11
5	11.41	Naphthalene,1,2,3,4-tetrahydro-	160	C12
6	11.72	Naphthalenediol,1,2,3,4-tetra-	178	C11
7	12.02	Indan,1,1,6.7-tetramethyl-	174	C13
8	12.26	Naphthalenol, 3-methoxy-	174	C11
9	12.35	Naphthalene, 1-ethyl-	156	C12
10	12.51	Naphtalene, 2,6-dimethyl-	156	C12
11	12.68	Naphtalene, 1,5-dimethyl-	156	C12
12	12.72	Naphtalene, 1,3-dimethyl-	156	C12
13	12.93	Naphtalene, 1,6-dimethyl-	156	C12
14	13.11	Naphtalene, 2,7-dimethyl-	156	C12
15	13.31	1H-Inden-1-ol,2,3-dihydro-	134	C9
16	13.36	Benzimidazole, 2-ethyl-1	188	C12
17	13.77	Naphthalene, 1,4,5-trimethyl-	170	C13
18	14.02	Naphthalene, 2,3,6-trimethyl-	170	C13
19	14.27	Naphthalene, 1,6,7-trimethyl-	170	C13
20	14.48	Naphthalene, 1,4,6-trimethyl-	170	C13
21	15.12	Azulene, 7-ethyl-1,4-diethyl-	184	C14
22	15.23	Quinolinecarbonitrile, 4-methyl-	184	C11
23	15.47	1,2-Benzenediamine-	184	C12
24	15.99	9H-Fluorene, 1-methyl-	180	C14
25	16.04	9H-Fluorene, 2-methyl-	180	C14
26	16.83	Anthracene	178	C12
27	17.29	Phenanthrene, 9,10-dihydro-1-methyl-	194	C15
28	18.01	Anthracene, 1-methyl-	194	C15
29	18.07	Phenanthrene, 4-methyl-	192	C15
30	18.26	Anthracene, 1-methyl-	192	C15
31	19.36	Phenanthrene, 2,5-dimethyl-	206	C16

Table.2.10. Aromatic hydrocarbons(F2) isolated from Zweteena crude oil using silica gel column fractionation and GC-MS data analysis.

PK #	RT	Library / ID	MW	Carbon No.
1	10.82	Naphthalene, 1-methyl-	142	C11
2	10.91	Benzene, 1-(2-butenyl)-2,3-dimethyl-	142	C11
3	11.02	Naphthalene, 2-methyl-	142	C11
4	11.54	Benzeneethanamine,-	160	C10
5	11.85	Benzene,(3-cyclopentylpropyl)-	152	C9
6	11.99	Benzaldehyde, 3-(trifluormethyl)-	174	C8
7	12.21	1H-Inden-1-one-	160	C11
8	12.32	Naphthalene, 1,7-dimethyl-	156	C12
9	12.54	Naphthalene, 1,3-dimethyl-	156	C12
10	12.74	Naphthalene, 2,3-dimethyl-	156	C12
11	12.92	Naphthalene, 1,6-dimethyl-	156	C12
12	13.51	Quinolinecarbonitrile,-	188	C10
13	13.78	Naphthalene, 1,4,6-trimethyl-	170	C13
14	13.91	Naphthalene, 2,3,6-trimethyl-	170	C13
15	14.14	Naphthalene, 1,4,5-trimethyl-	170	C13
16	14.30	Naphthalene, 1,6,7-trimethyl-	170	C13
17	14.71	Benzoxazepine, 2-carbonitrile,	184	C11
18	15.30	Azulene,7-ethyl-1,4-dimethyl-	184	C14
19	15.81	9H-fluorene,2-methyl-	180	C14
20	15.86	9H-Fluorene, 4-methyl-	180	C14
21	16.51	Dibenzo[b,d]pyran-	198	C13
22	16.56	Aniline, phenethyl-	197	C14
23	16.64	Anthracene	178	C14
24	17.13	9H-Fluorene,2,3-dimethyl-	194	C15
25	17.43	Dibenzothiophene,3-methyl-	198	C13
26	17.83	1H-Indene,2-phenyl-	192	C15
27	18.07	9H-Fluorene,9-ethylidene-	192	C15
28	18.29	Dibenzo[a,e]cyclooctene,-	208	C16
29	18.86	Naphtho[2,3]thiophene-	212	C14
30	19.06	2H-Thiopyran, 3-phyenyl-	206	C16
31	19.18	Phenanthrene,2,7-dimethyl-	206	C16
32	19.29	Phenanthrene,3,6-dimethyl-	206	C16
33	19.38	Phenanthrene,2,3-dimethyl-	206	C16
34	19.52	Phenanthrene,2,5-dimethyl-	206	C16
35	20.08	Thiazolo[5,4] pyrimidine-	205	C5
36	20.19	2-Imidazolidinone,1-(2,6-dimethyl)-	220	C12
37	20.29	4H-1-Benzopyran-	276	C16
38	20.42	Phenanthrene,2,3,5-trimethyl-	220	C17
39	20.51	2-Methyl-1-phenyltryptamine	250	C17

Fig 2.32 shows the mass spectrum of scan number # 970 (16.144 min) for either anthracene or phenanthrene (MW = 178); both give essentially identical mass spectra. Standard relative retention times (RRT) was needed to determine identity. in this case. This was facilitated by comparing the retention time of a standard mixture containing seven polycyclic aromatic hydrocarbons of molecular weight range of 128 to 228 Table 2.3 with that of the unknown at scan number 970 (16.14 min) analyzed under the same conditions. Figures 2.32 and 2.33 shows mass spectra of Bouri crude oil (F2) and PAH standard at scan number 970 (16.144 min) and 986 (16.140 min). Both show a compound with MW = 178. In this manner it was determined that the hydrocarbon isolated in the Bouri crude oil (F2) at scan number # 970 (16.144 min) was anthracene.

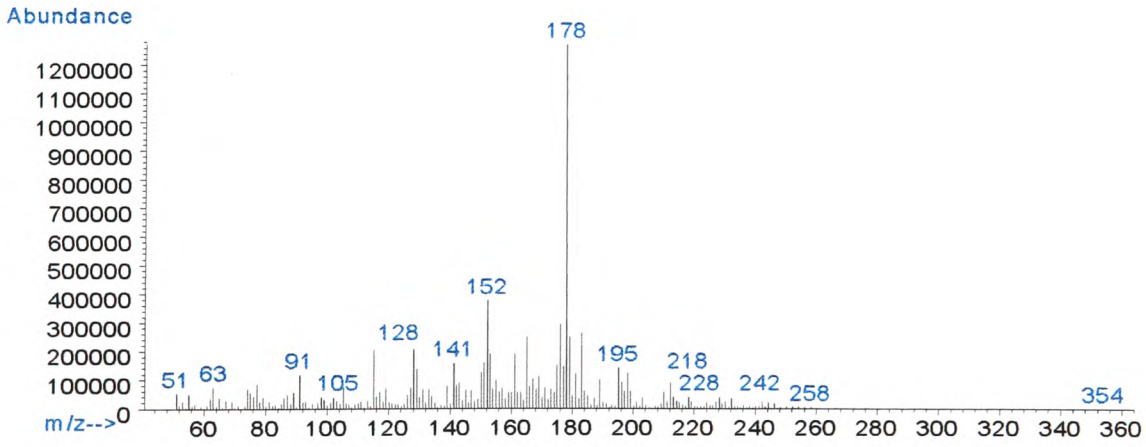


Fig. 2.32. Mass spectrum of Bouri crude oil (F2) of scan # 970 (16.144 min) which represents anthracene (MW=178).

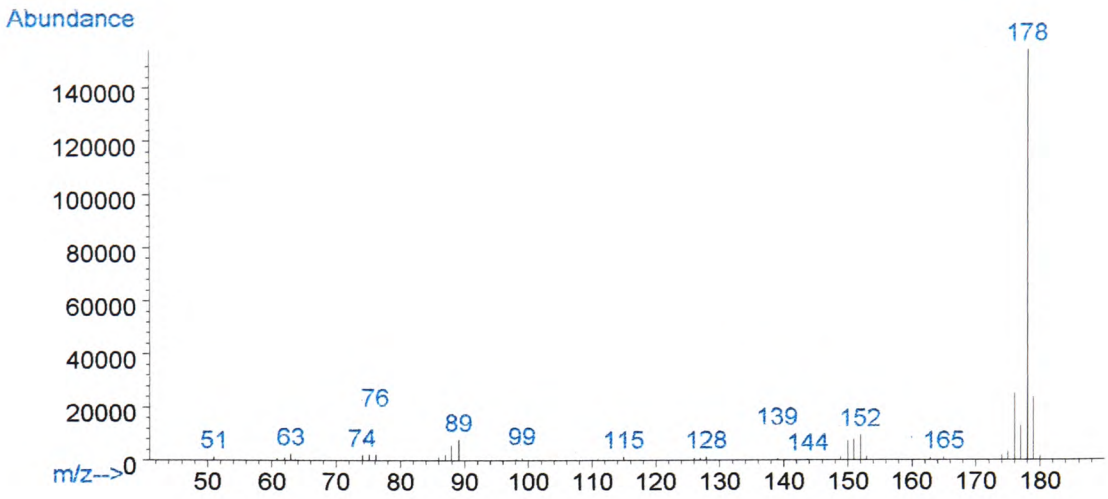


Fig.2.33. Mass spectrum of aromatic standard of scan 986 (16.140 min) which represent anthracene (MW 178).

The GC-MS extracted ion profiles of alkyl homologues of naphthalene, phenanthrene, dibenzothiophene, biphenyl and alkylbiphenyls and fluorine in Bouri crude oil are show in Figures 2.34 to 2.38. It is apparent that aromatic hydrocarbons are dominated by alkylbenzene and alkylnaphthalene homologues. The ions found at m/z 128, 142, 156, 170, 184, belonging to the alkylnaphthalenes, are one the most significant. Anthracene/Phenanthrene and the corresponding methylated compounds could be detected by m/z values of their molecular ions: 178, 192, 206, 220, and 234 and fluorenes and alkyl fluorenes with m/z values of 166, 180, 194, 208 etc.

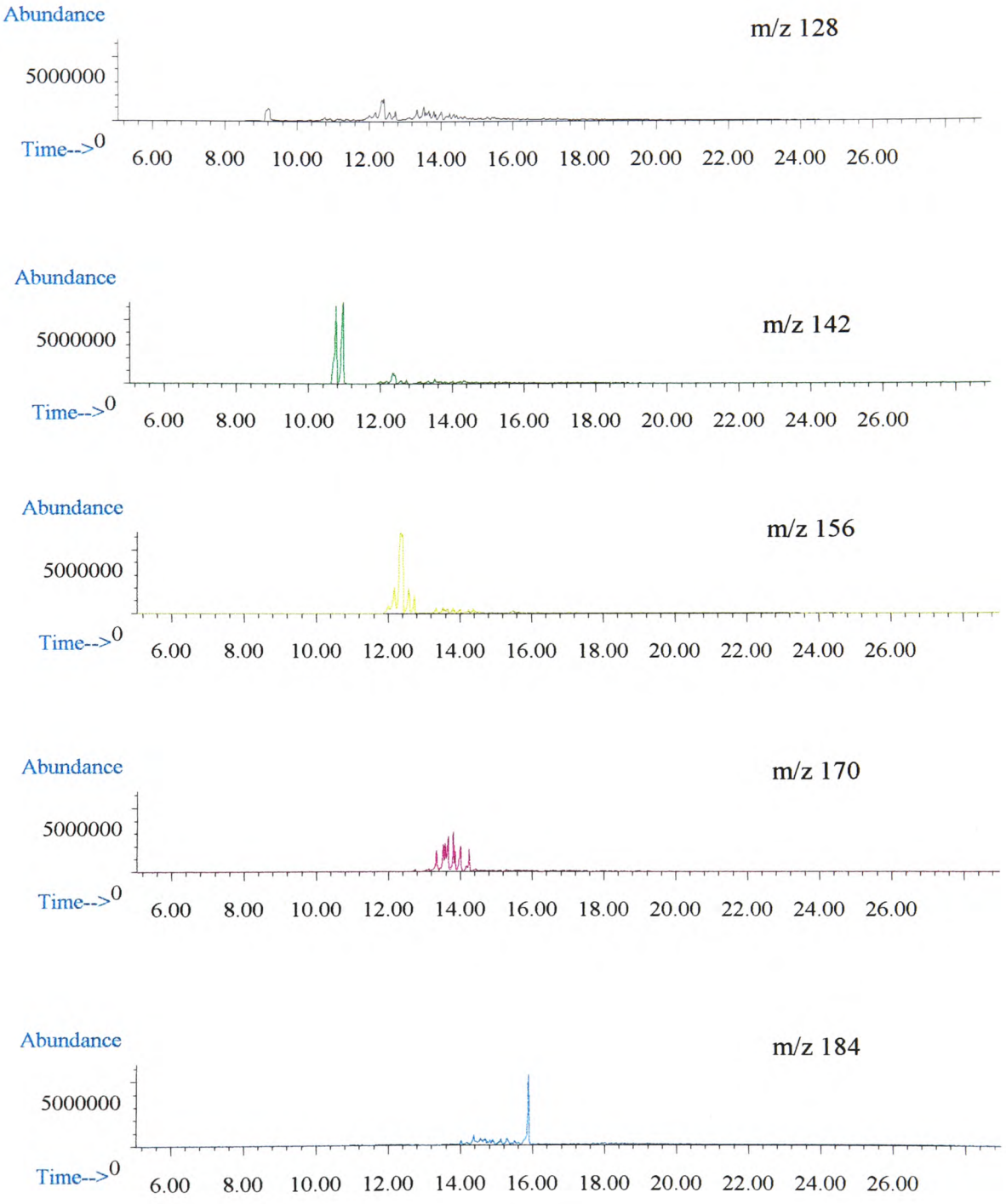


Fig. 2.34. GC-MS extracted ion profile of alkyl homologues of naphthalene in Bouri crude oil.

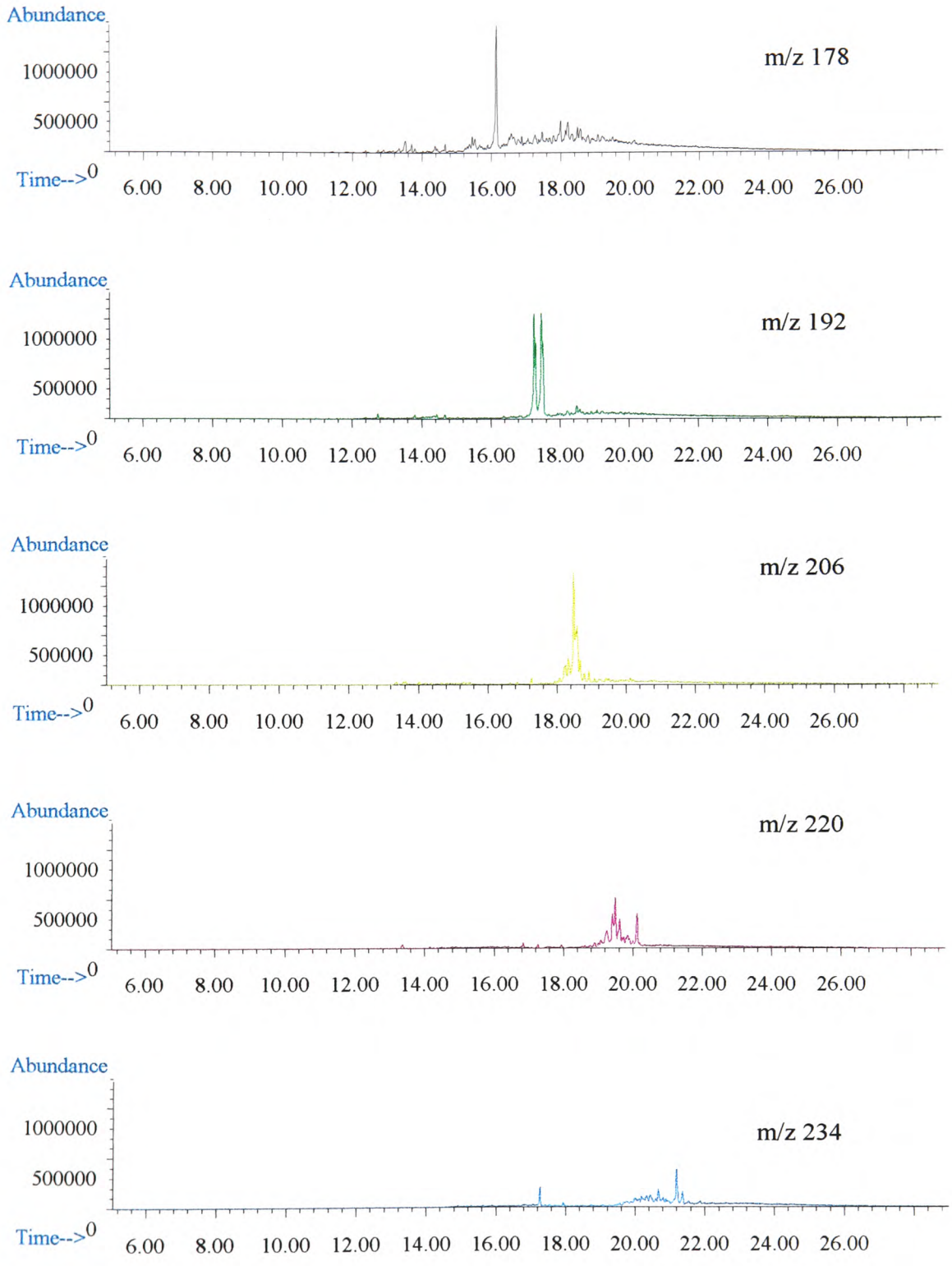


Fig.2.35. GC-MS extracted ion profile of alkyl homologues of anthracene / phenanthrene in Bouri crude oil.

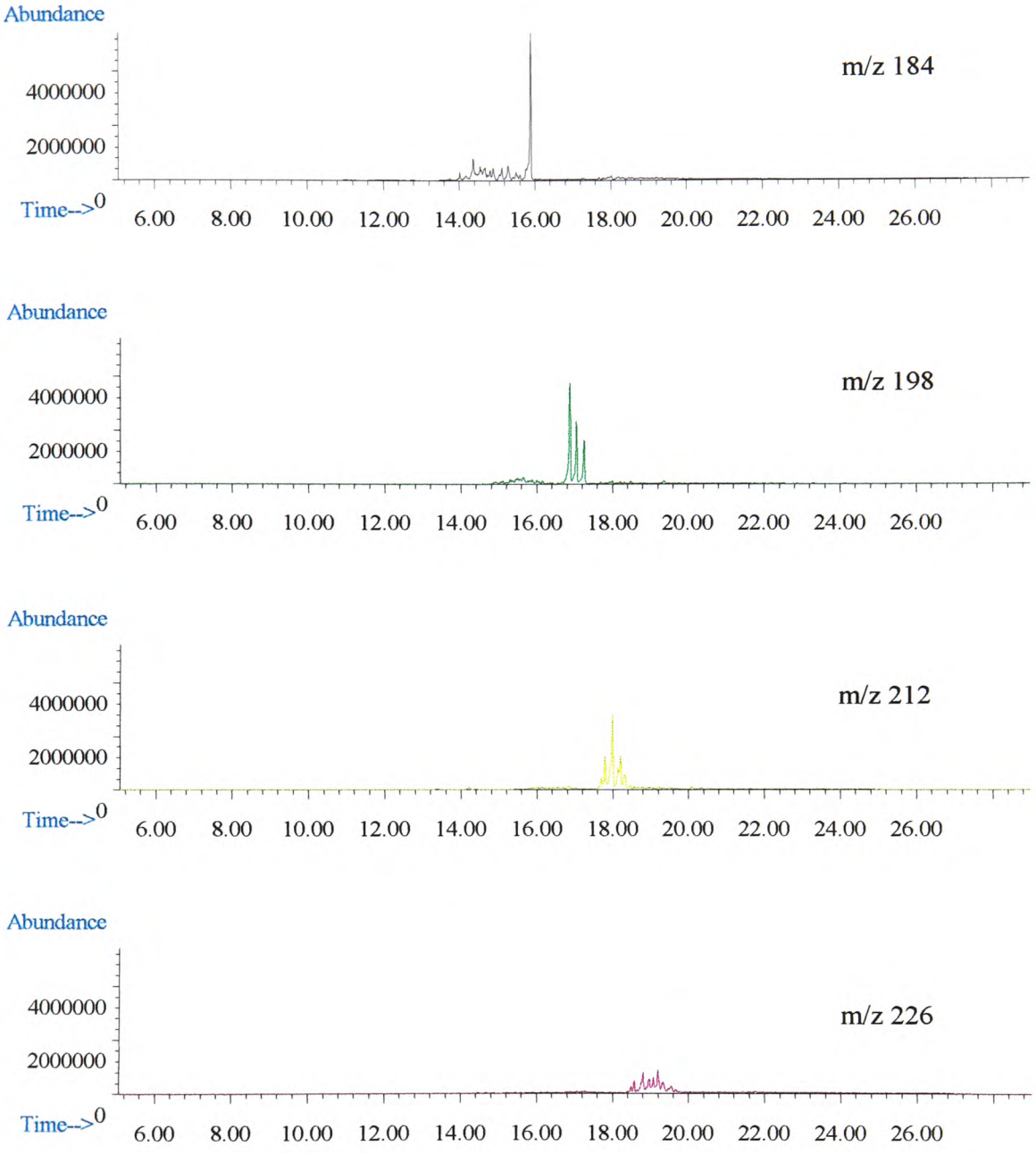


Fig. 2.36. GC-MS extracted ion profiles of alkyl homologues of dibenzothiophene in Bouri crude oil.

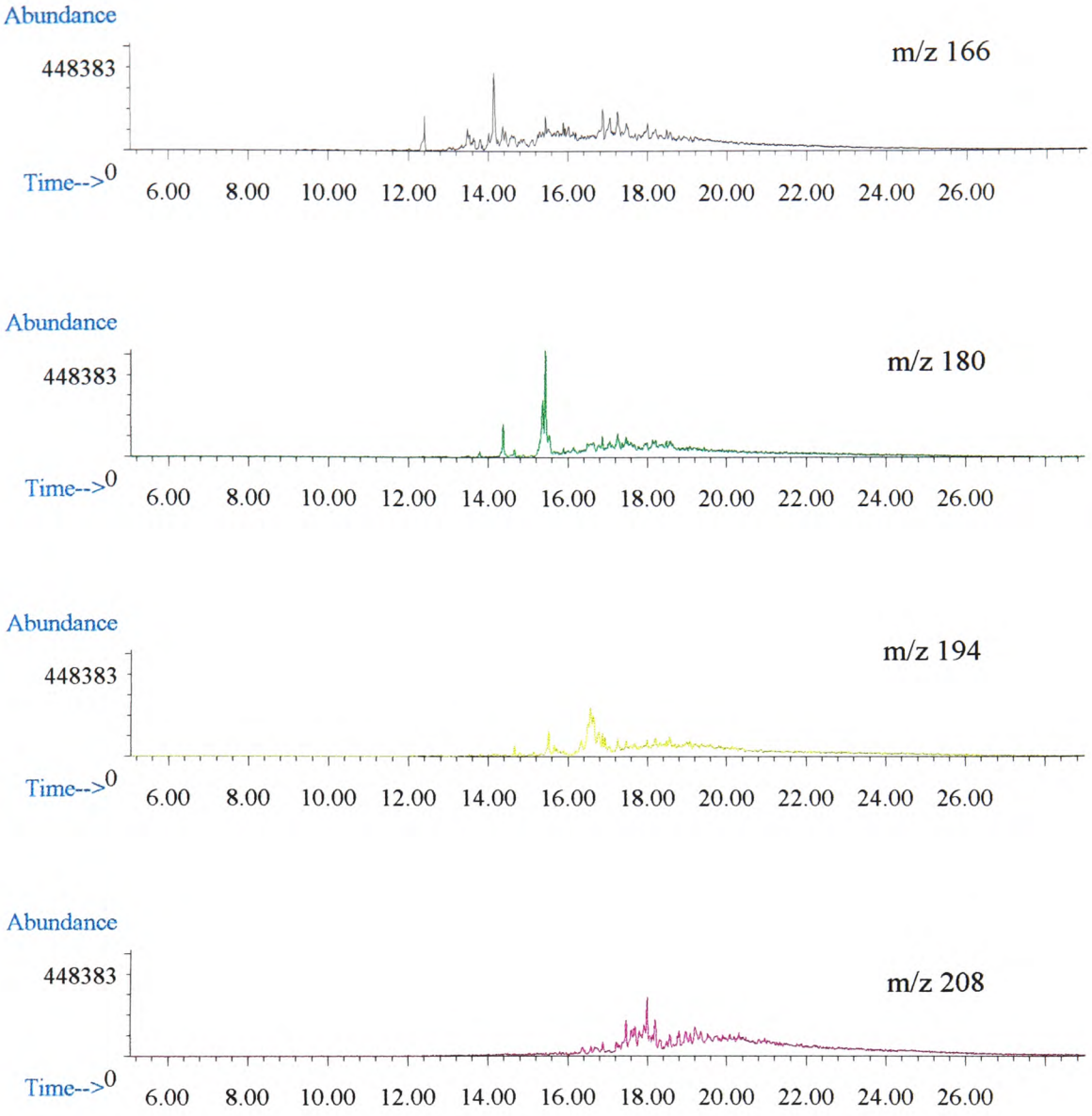


Fig. 2.37. GC-MS extracted ion profiles of alkyl homologues of fluorene in Bouri crude oil.

2.4.5. 3 Quantitation of major components in crude oil

There are many factors that could affect analytical precision and accuracy [47]. In order to achieve analytical precision and accuracy, the following refinements were implemented in addition to the routine quality control procedures:

1. Sample pre-injection volume was accurately controlled.

2. A more rigorous calibration check standard was implemented to improve analytical precision.
3. The same analyst used one GC-MS instrument throughout the analytical procedure.

Quantitative results for the distribution of the three major hydrocarbon classes within Libyan crude oil samples are summarized in Table 2.11 and Figure 2.38. The weight percent average of duplicate fractions recovered for saturated, aromatic and polar hydrocarbons was in the range of 83.4 - 90.7 wt % with a relative standard deviation of under 6 %. It is evident in all cases that the saturate content is high. This classifies each crude as a paraffinic base. These findings are in agreement with the Libyan crude oil classified as paraffinic, bordering on paraffin-intermediate base (crude assay report, Petroleum Research Center, 1987).[40]

Table 2.11. Compound-class analysis (wt %) of Libyan crude oil using the column fractionation method:

Crude oil	Saturates	Aromatics	Polars	Recovery
Sirte	61.9	13.2	8.3	83.4
Sidra	68.9	14.2	9.4	90.7
Zwetena	65.1	14.7	7.1	86.9
Bouri	60.6	19.8	9.4	89.8
Messla	70.3	12.9	7.3	90.5

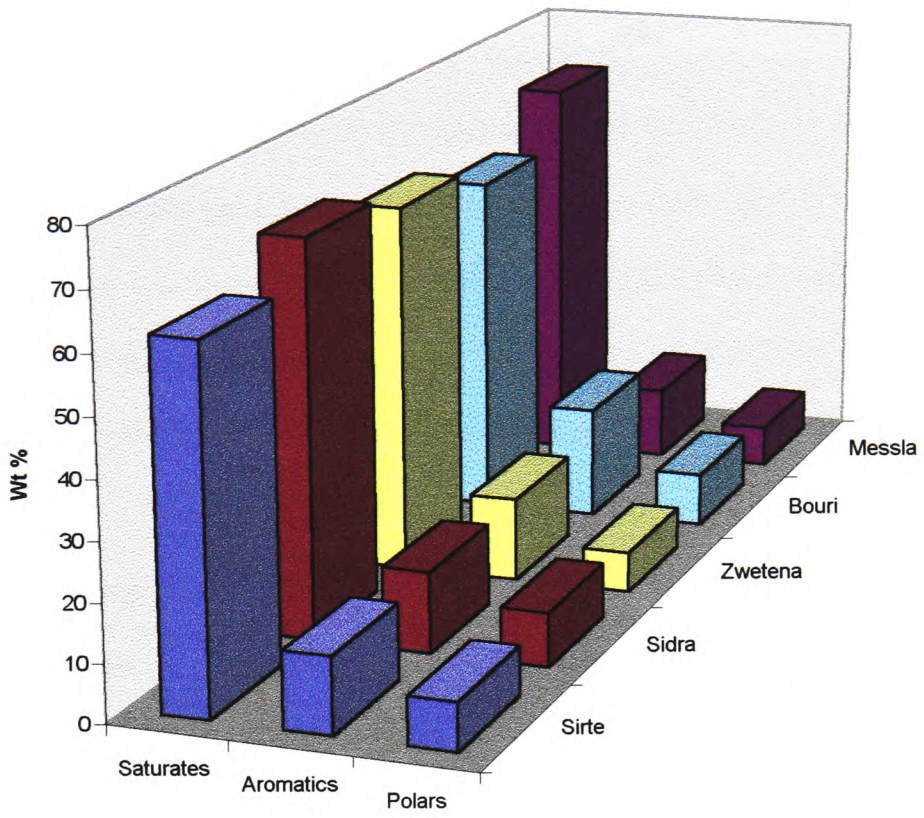


Fig.2.38. Column Chromatography fractions distribution of Crude Oil.

2.5 Development of an Extrographic Separation Technique for Fractionation of Libyan crude oils

Whilst chromatographic methods are generally used for hydrocarbon fractionation, other approaches can be successful. Solvent extraction techniques have been widely used for pitch characterization, but these can be problematic because of co-solubilization effects which make it possible to find the same compounds in both the soluble and the insoluble fractions [48,49] . Preparative liquid chromatography has also been extensively used for the fractionation and characterization of coal and petroleum derived products. It provides good separation into classes according to their functionality, but some overlapping of

aromatics with saturates occurs [50,51] and usually preparative Liquid chromatography (LC) is tedious and time consuming [52].

Extrography is an alternative technique first described by Halasz [53] in 1979 which provides good fractionation in a relatively short time. It has been used under different conditions for the fractionation of low volatile residues from oil distillates, coal tar and petroleum pitches [54]. However, the technique has not been shown to be effective for the fractionation of more volatile matrixes including crude oil.

The simplicity and superior reproducibility of the technique suggests that it could become a standard method for coal-tar and petroleum pitch characterization. The technique combines extraction and chromatography. The mechanisms of separation involves an orderly adsorption of compounds onto active centers of silica gel followed by a gradual desorption by sequential elution with solvents of increasing polarity.

The yield and composition of any fraction obtained by extrographic fractionation is thought to be influenced by the sample to sorbent ratio. A low ratio of 1:15 for the extrographic fractionation of coal extracts has been shown to possess the following positive features [55]:

1. Increased separation selectivity
2. Asphaltene pre-precipitation unnecessary
3. Separation of relatively simple components
4. Low operational costs
5. Relatively wide choice of solvents.

Our studies continued in order to determine the applicability of the approach for the fractionation of crude oil samples. Our aim was to develop and

optimize a extrographic procedure and compare its performance with the previous chromatographic protocol.

2.5.1 Efficiency of extrography in the fractionation of Libyan crude oils

Since the introduction of extrography several publications have appeared where the sample is coated onto an inert or polar support before the commencement of the actual separation [56]; a similar procedure was adapted for this work. Both the extrographic technique and the fractionation procedure are described in detail in chapter 5. Briefly, 2 grams of crude oil was accurately weighed and dissolved in 100 cm^3 of dichloromethane in a 250 cm^3 round-bottom flask. 40 grams of activated silica gel was then added to the solution, the solvent was then removed using a rotary evaporator and the loaded silica (ratio 1:20) was then vacuum dried at 80 °C and 2 kpa. Extrography was performed in a glass column of 12.5mm i.d and 400 mm long. The arrangement of the adsorbent within the column is shown in Figure 2.39. 60 grams of unloaded silica gel was placed at the base of the column to avoid fraction overlap [57]. To obtain an even packing density and ensure stability during packing, an experimental device was used in which the silica gel was poured into a vertical column from a funnel attached to the top of the column, this utilized a device which produced both vibrational and rotational movements of the column. A sequence of five solvents was used for extrographic development as shown in Figure 2.40. The flow rate was approximately 2 cm^3 min^{-1}. Solvent was pumped into the system by a plunger pump. The solvent was removed from the collected fractions using a rotary evaporator and the residues were blown to dryness with nitrogen. The residues were weighed to determine yield of saturates, aromatics and polars. GC-MS of

each fraction was carried out using HP (5890 B) GC coupled to HP 5971 A mass spectrometer. The conditions for the analysis are given in chapter5.

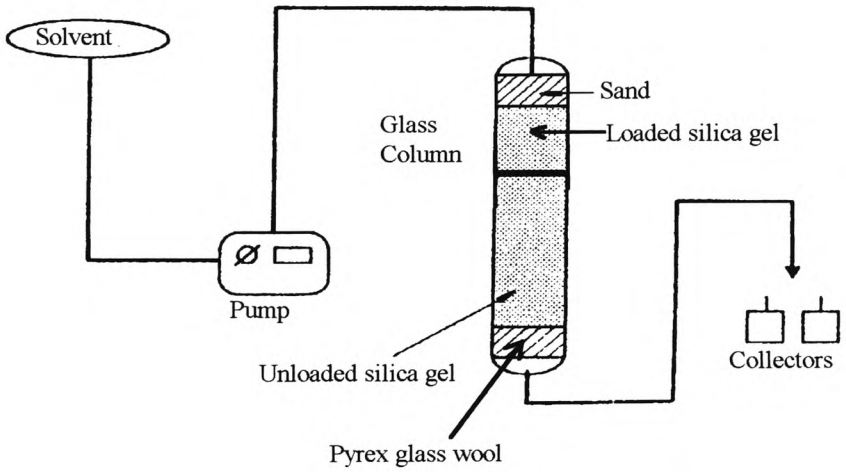


Fig. 2.39. System for extrography fractionation [57].

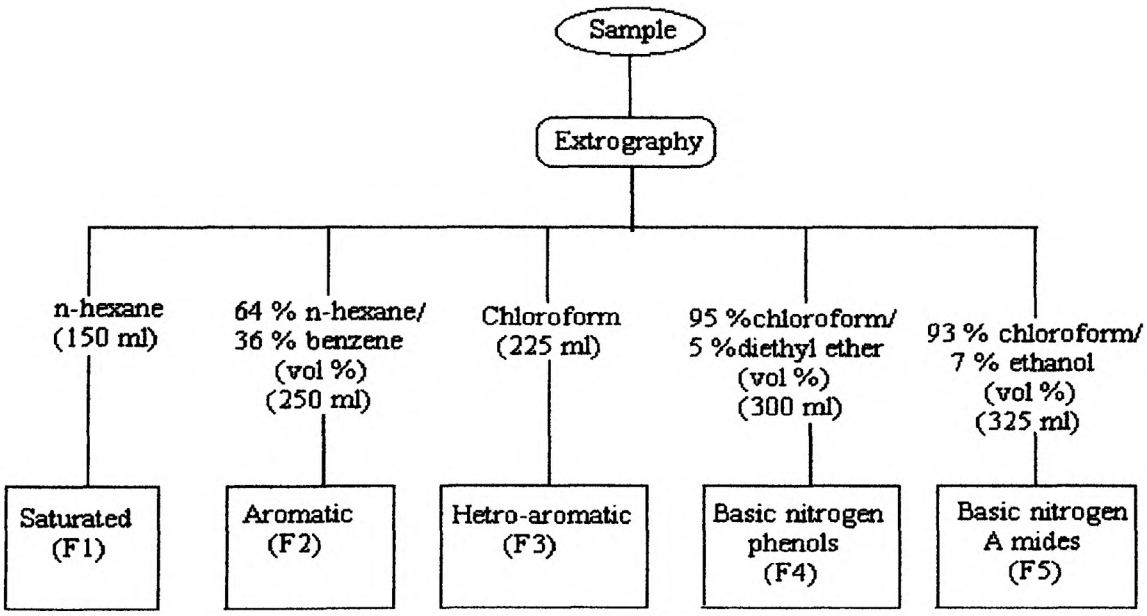


Fig. 2.40. Extrographic Fractionation Scheme [52].

2.5.2 Results and Discussion

According to Halasz [53,54], extrographic separations arise from the orderly adsorption of the components of the sample, together with selective extraction by solvents of increasing polarity, with the least polar compounds being retained in the pores of the adsorbent. Therefore, the sample to adsorbent ratio and the resulting degree of relative silica gel activity should be critical.

The sample/adsorbent ratio varies greatly, according to different authors. Recently Moinelo et al. [53] found compound class overlap between fractions at sample to adsorbent ratio greater than 7:100, although this value will depend on the composition of the sample. In our case, separations were obtained with a ratio of 1:20, which is less than that used by Halasz and Blumer et al [56].

This separation procedure was successfully applied to five Libyan crude oils in duplicate. The results are shown in Figure 2.41 and Table 2.12. These results demonstrate that the weight percent average of duplicate fractions recovered for saturated, aromatic and polar was in the range of 93.8 - 95.9 wt % with a relative standard deviation of under 6 %. Figure 2.42 illustrates the recovery of compound classes using column chromatography and extrographic technique. Table 2.13 shows the mean recovery and standard deviation using both the chromatographic and extrographic methods, to be less than 6 %.

Table.2.12. Compound class analysis (wt %) of Libyan crude oils by extrographic fractionation method.

Crude oil	Saturates	Aromatics	Polars	Recovery
Sirte	67.5	14.4	7.5	89.4
Sidra	69.4	17.3	9.3	95.9
Zwetena	69.8	17.2	8.0	95.1
Bouri	59.3	20.9	10.5	90.7
Messla	72.0	13.6	8.2	93.8

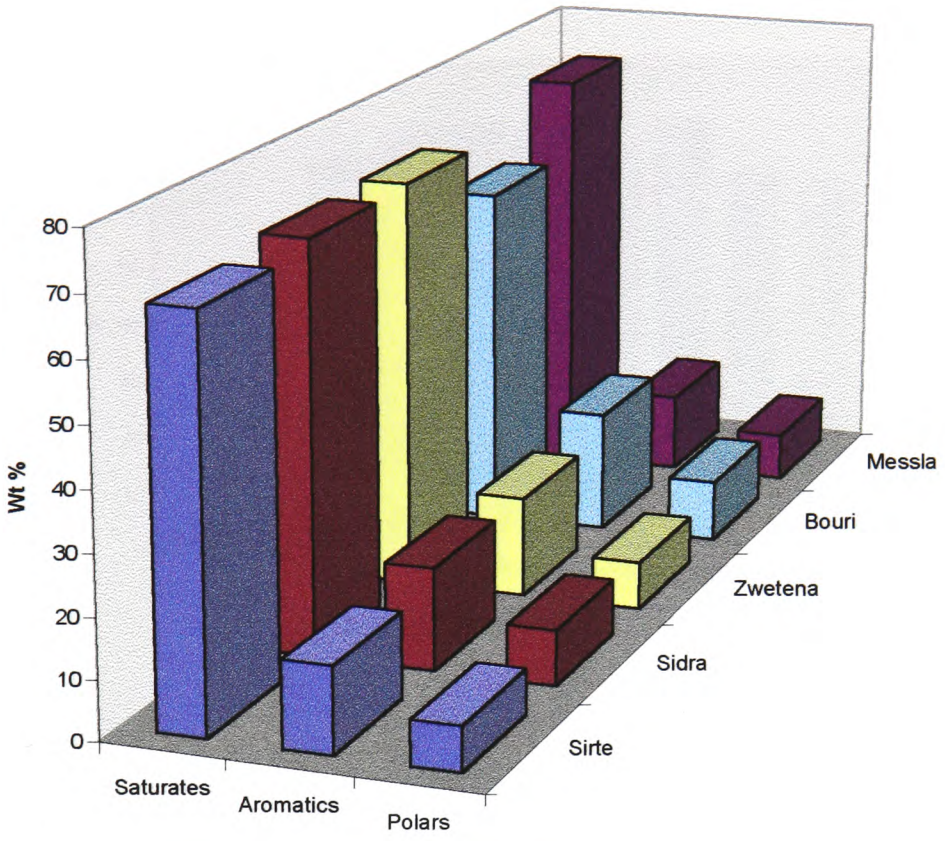
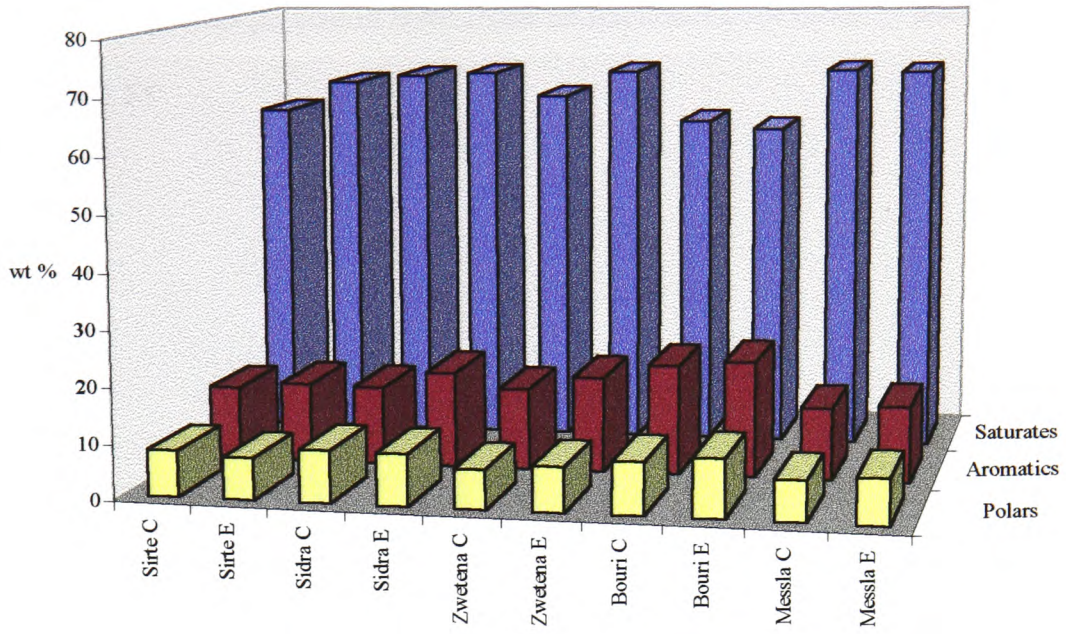


Fig.2.41. Extrographic fraction distribution of Crude Oil.

Table 2.13. The mean and standard deviations of wt % average recovery using chromatographic and extrographic method.

Crude oil		Saturates wt %	Aromatics wt %	Polar wt %	Recovery
Sirte	C*	61.9	13.2	8.3	83.4
	E*	67.5	14.4	7.5	89.4
mean ± s.d.		64.7 ± 4.0	13.9 ± 0.9	7.9 ± 0.6	86.4 ± 4.3
Sidra	C	68.9	14.2	9.4	90.7
	E	69.4	17.3	9.3	96.0
mean ± s.d.		69.1 ± 0.4	15.7 ± 2.2	9.3 ± 0.1	93.3 ± 3.7
Zwetena	C	65.1	14.7	7.1	87.0
	E	69.8	17.2	8.1	95.1
mean ± s.d.		67.5 ± 3.3	15.9 ± 1.7	7.6 ± 0.6	91.0 ± 5.7
Bouri	C	60.6	19.8	9.4	89.8
	E	59.3	20.9	10.5	90.7
mean ± s.d.		59.9 ± 1.0	20.4 ± 0.8	10.0 ± 0.8	90.3 ± 0.6
Messla	C	70.3	12.9	7.3	90.5
	E	70.0	13.6	8.2	93.8
mean ± s.d.		70.2 ± 0.2	13.2 ± 0.5	7.6 ± 0.6	92.1 ± 2.3

- C: column chromatography and E: extrographic technique.



C: Column chromatography, E: Extrographic technique

Fig.2.42 Column chromatography and extrographic fraction distribution of crude oil

In all cases final analysis was performed by GC-MS. The total ion chromatograms of F1 fraction of five Libyan crude oils are shown in Figures 2.43 to 2.47. In all cases, fraction one contained n-alkanes from C_{10}-C_{30} together with pristane, and phytane. C_{12}-C_{23} n-alkanes, being the most abundant. GC-MS analysis also indicated that the n-hexane fractions F1 were composed totally of saturated hydrocarbons. The absence of co-extracted aromatics therefore indicates that extrographic fractionation was effective.

GC-MS analysis of the F2 fractions isolated from the Libyan crude oils are shown in Figures 2.49 to 2.53. The complex character of each chromatogram is mainly due to the presence of large numbers of methyl- and poly-alkylated PAH as clearly seen in Table 2.14. It is apparent that aromatic hydrocarbons are dominated by alkyl benzene and alkyl naphthalene homologues at m/z 117, 131, 145, 159 and

m/z 128, 141, 155, 169, 183, respectively, as shown in Figures 2.53 and 2.54. The most prominent compounds present in Sirte crude oil fraction F2 are listed by peak number in Table 2.14.

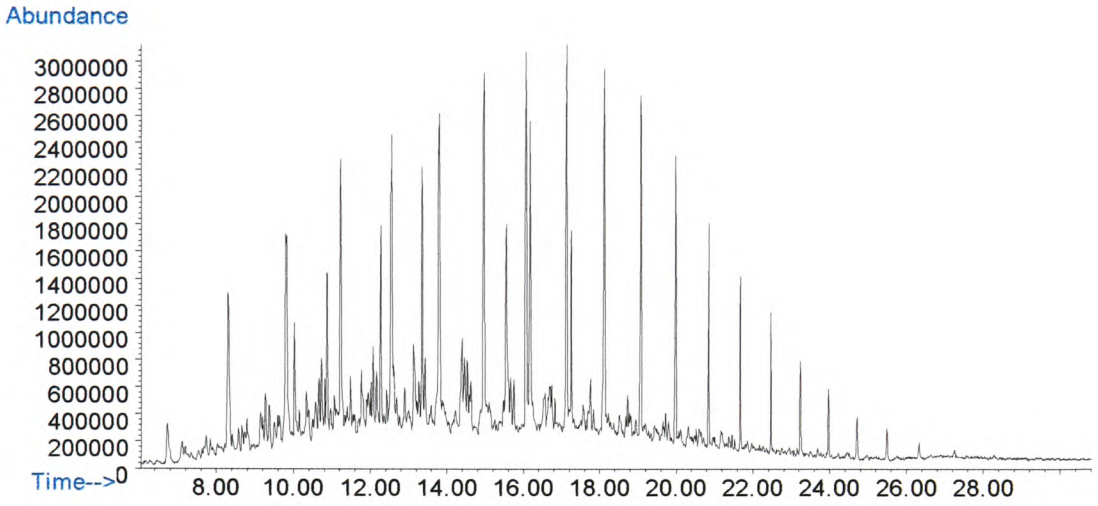


Fig. 2.43.GC-MS TIC of saturated hydrocarbon fraction (F1) of Sirte crude oil

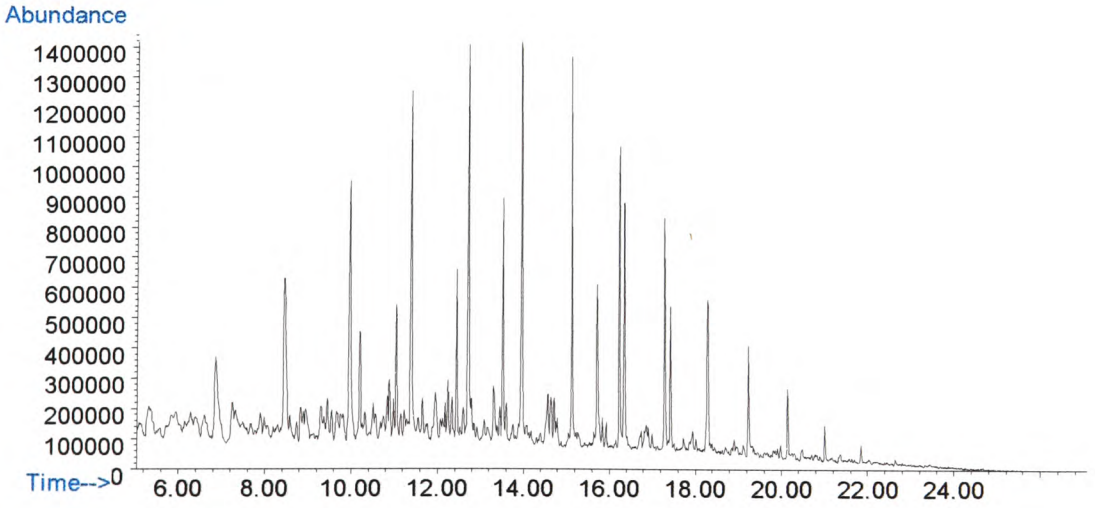


Fig. 2.44.GC-MS TIC of saturated hydrocarbon fraction (F1) of Sidra crude oil.

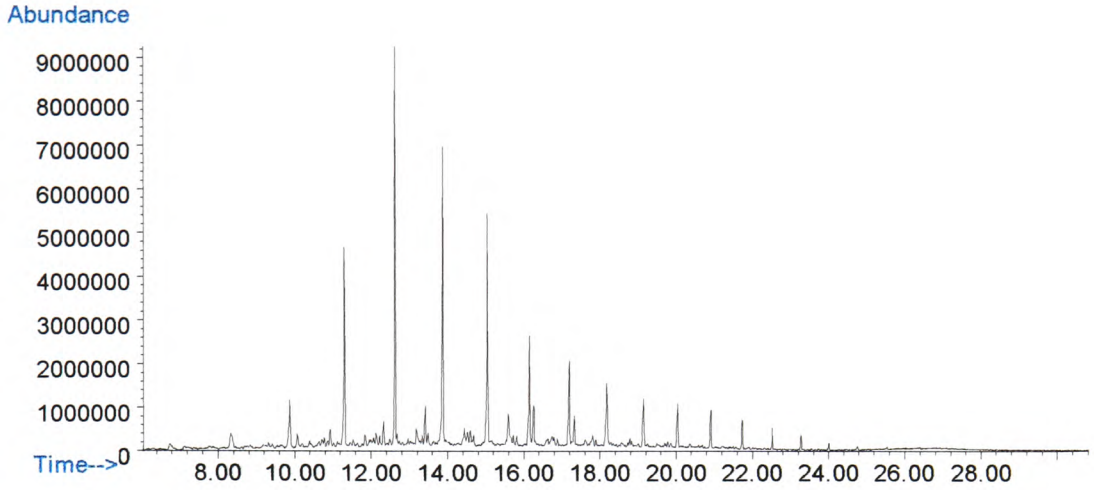


Fig. 2.45.GC-MS TIC of saturated hydrocarbon fraction (F1) of Zwetena crude oil.

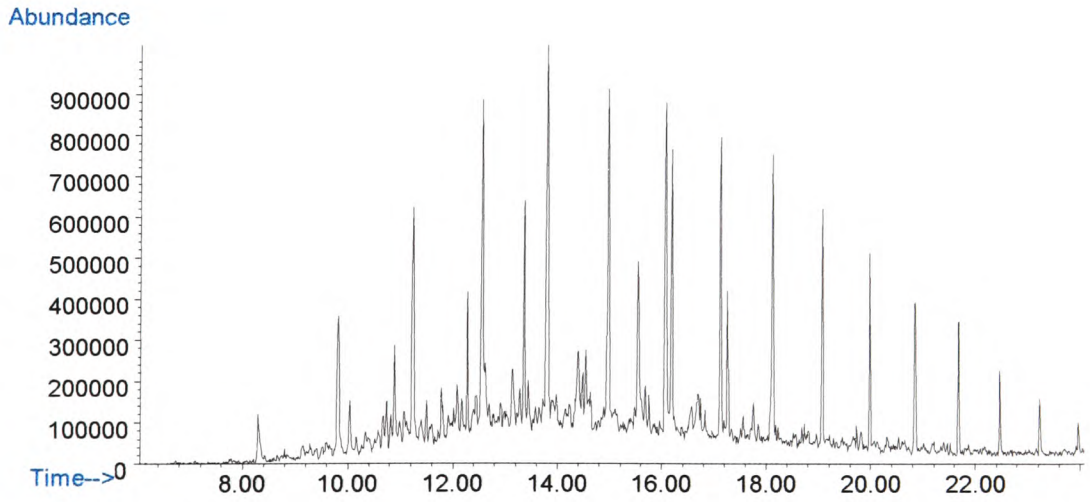


Fig. 2.46.GC-MS TIC of saturated hydrocarbon fraction (F1) of Messla crude oil.

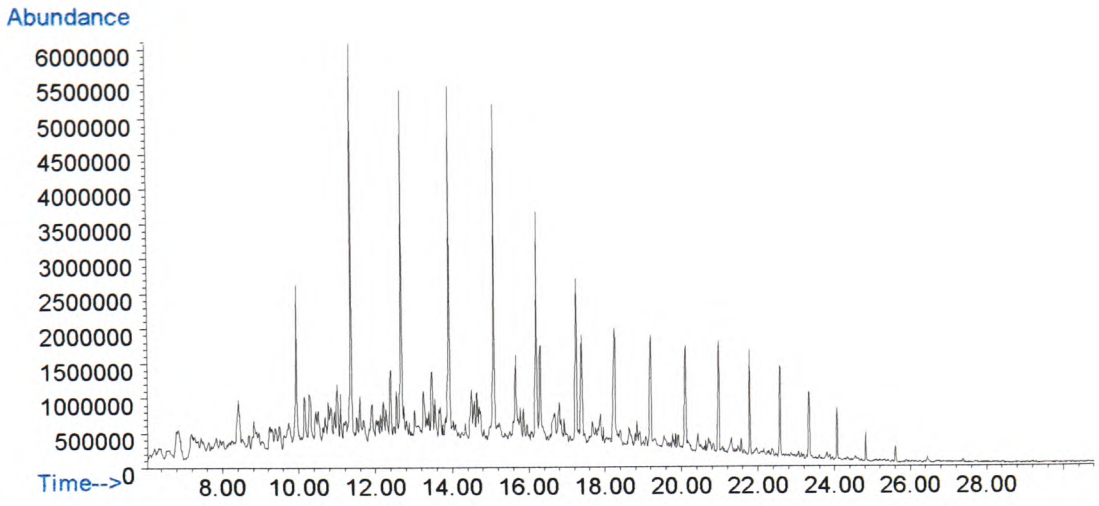


Fig. 2.47.GC-MS TIC of saturated hydrocarbon fraction (F1) of Bouri crude oil.

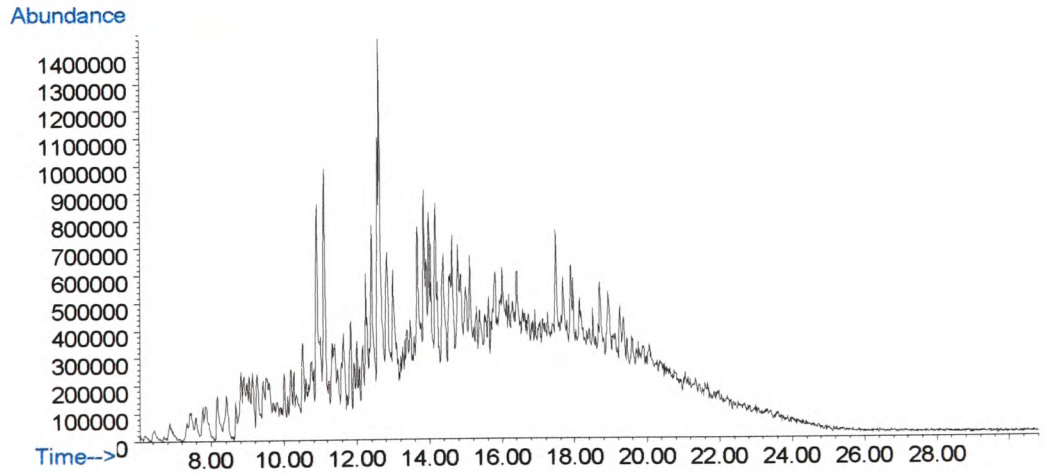


Fig. 2.48. GC-MS TIC of aromatic hydrocarbon fraction (F2) of Bouri crude oil.

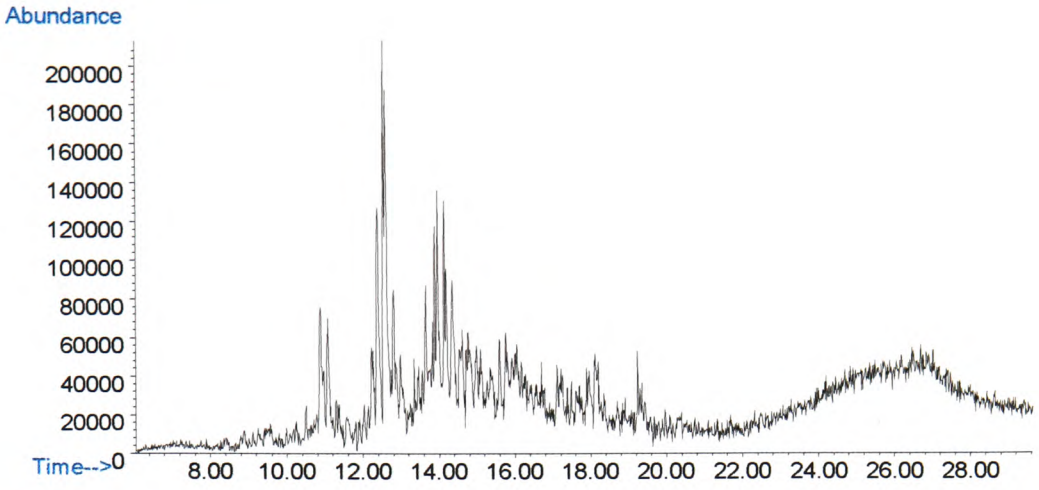


Fig. 2.49. GC-MS TIC of aromatic hydrocarbon fraction (F2) of Zwetena crude oil.

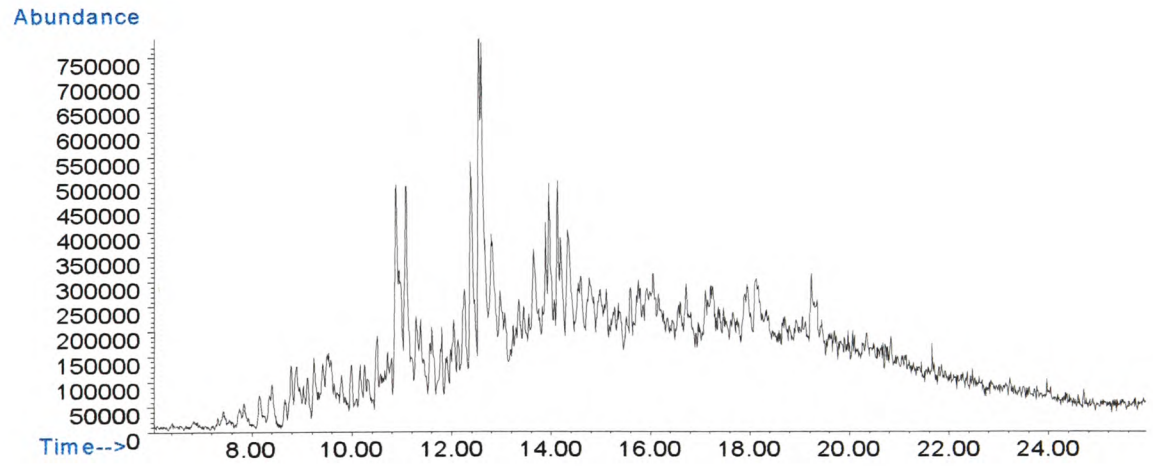


Fig. 2.50. GC-MS TIC of aromatic hydrocarbon fraction (F2) of Sirte crude oil.

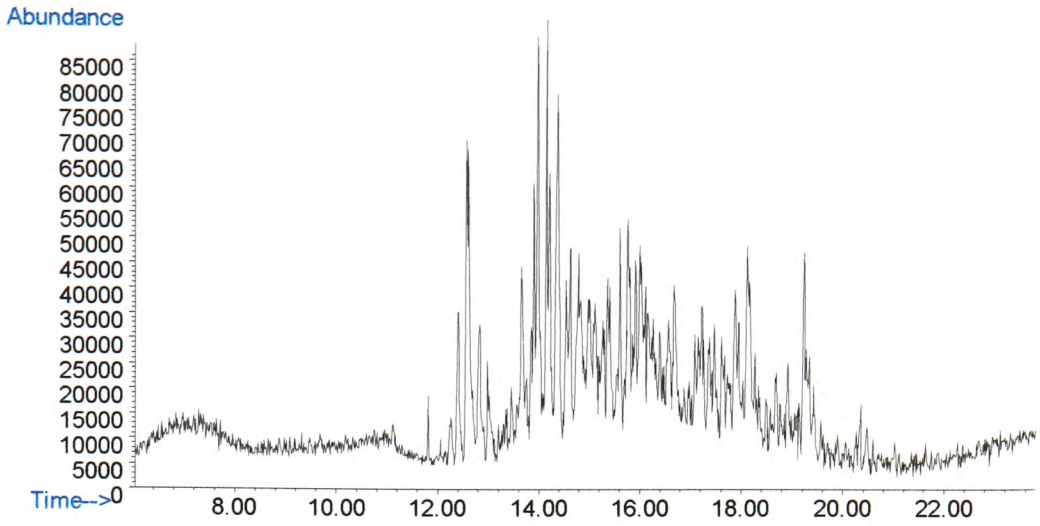


Fig. 2.51. GC-MS TIC of aromatic hydrocarbon fraction (F2) of Sidra crude oil.

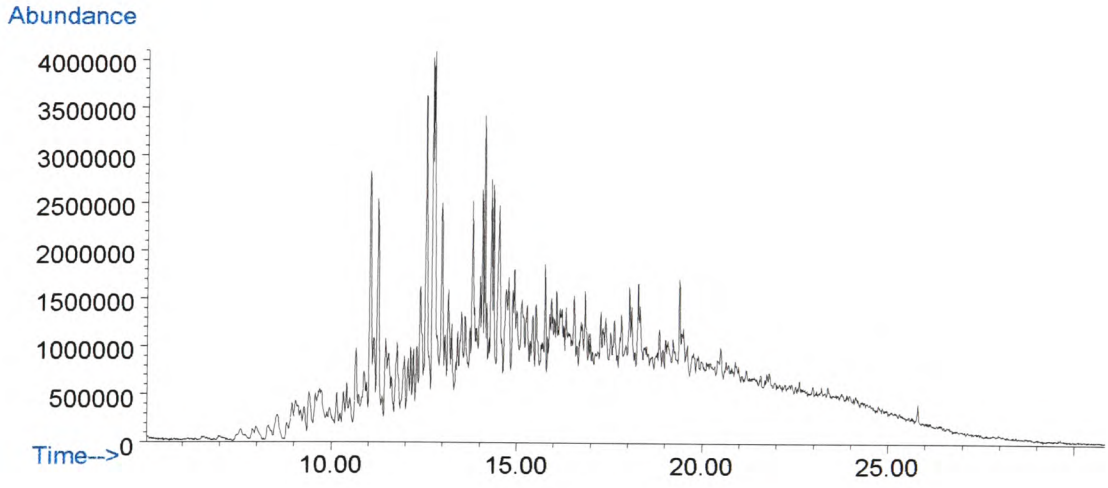


Fig. 2.52. GC-MS TIC of aromatic hydrocarbon fraction (F2) of Messla crude oil.

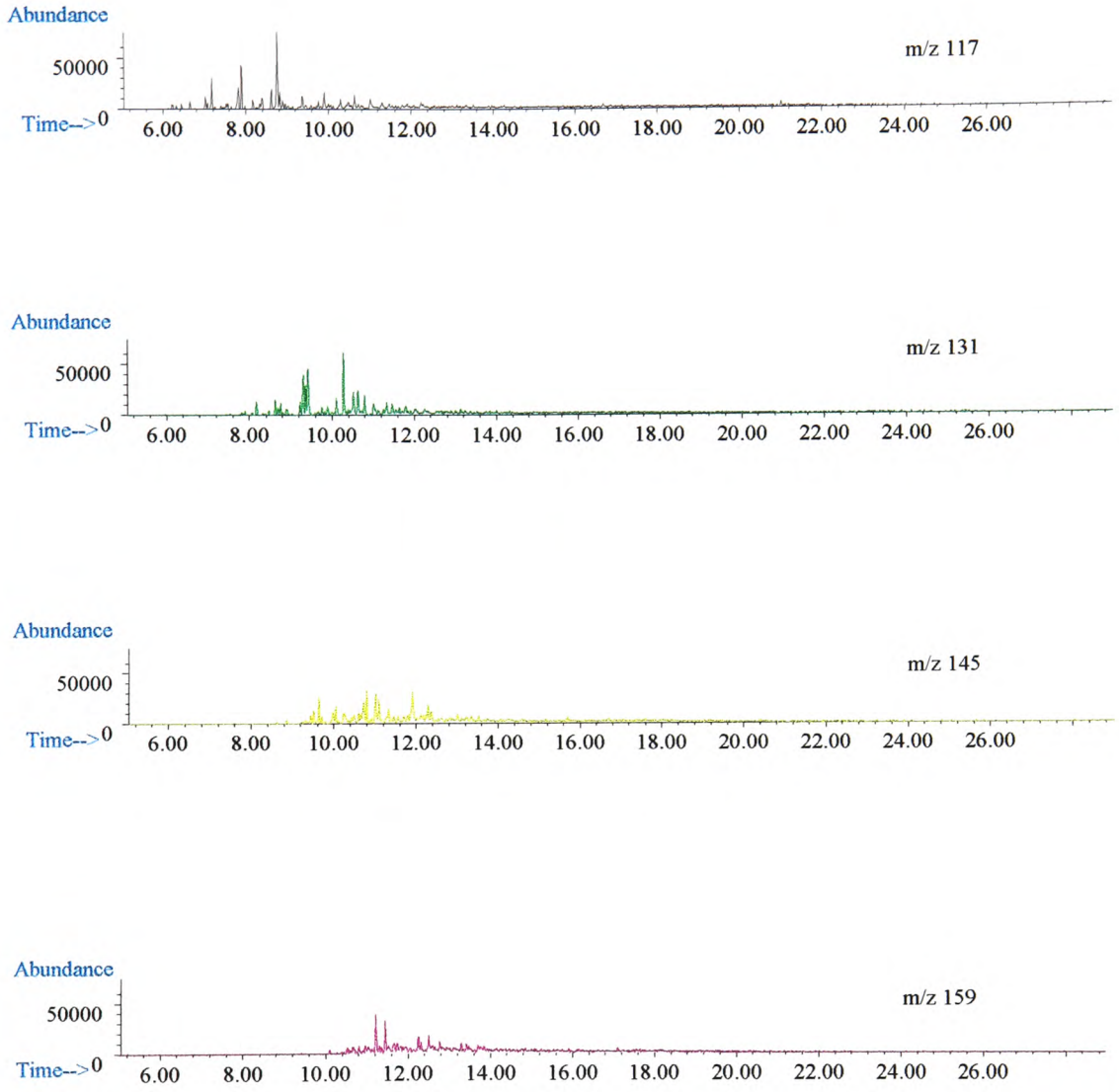


Fig. 2.53 GC-MS extracted ion profiles of alkyl homologues of Benzene in Sirte crude oil.

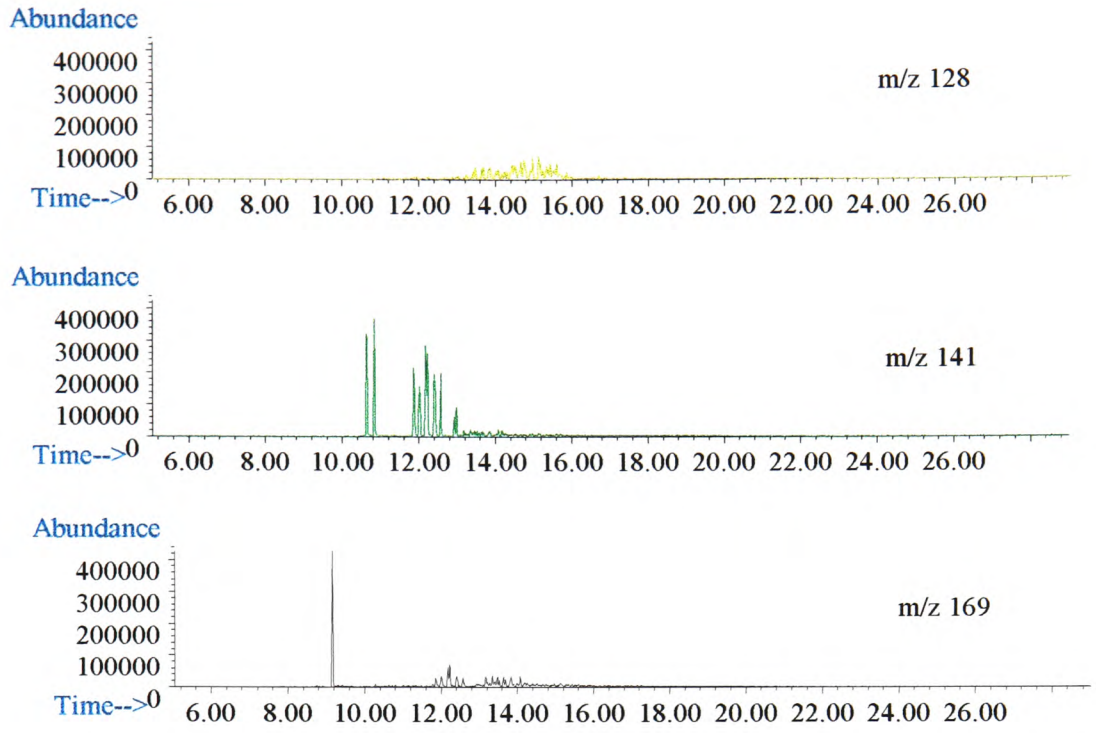


Fig. 2.54. GC-MS extracted ion profiles of alkyl homologues of naphthalene in Sirte crude oil.

The simplicity of the TICs of fractions F3, F4, and F5, indicated that they contained limited numbers of compounds amenable to GC-MS analysis. This is clearly seen from a comparison between the recovery of these fractions and that for fractions F1 and F2. Figures 2.55 to 2.57 show the chromatograms of fractions F3, F4, and F5 from Sirte crude oil. The distribution of some of the identified polycyclic aromatic hydrocarbons are given in Tables 2.15 to 2.17. The chemical formulae and structure of some of the identified compounds given in appendix. Compounds in fraction F3 are mainly nitrogen heterocyclic aromatics.

Fraction F4 is mainly composed of phenolic and basic nitrogen compounds. The major compounds identified in this fraction are shown in Table 2.16. The nitrogen content of fraction (F5) is considerably higher than that of fraction (F4), it is deduced that most species present contain more than one

nitrogen atom. In addition, the oxygen content is also considerably higher. The principle compounds identified in this fraction are illustrated in Table. 2.17.

Table. 2.14. Recovery of some aromatic hydrocarbons (F2) from Sirte crude oil using Extrographic fractionations and GC-MS analysis.

PK#	RT	Library/ID	MW	Carbon No
1	12.26	Naphtalene,1-ethyl-	156	C12
2	12.42	Naphtalene,1,5-dimethyl-	156	C12
3	12.59	Naphtalene,1,3-dimethyl-	156	C12
4	12.64	Naphtalene,2,3-dimethyl-	156	C12
5	12.85	Naphtalene,2,6-dimethyl	156	C12
6	13.02	Naphtalene,1,7-dimethyl	156	C12
7	13.11	Benzen,[1-(cyclohexen-1-yl)ethyl)-	186	C14
8	13.27	Benzen,(1-ethylhexen)-	190	C14
9	13.38	1,1-Biphyenyl,4-methyl-	168	C13
10	13.48	Naphthalene,1-(2-propenyl)-	168	C13
11	13.60	Naphthalene,1,4,5-trimethyl	170	C13
12	13.68	Naphthalene,1,4,6-trimethyl	170	C13
13	13.88	Naphthalene,1,6,7-trimethyl	170	C13
14	13.94	Naphthalene,2,3,6-trimethyl	170	C13
15	14.01	Naphthalene,1,4,6-trimethyl	170	C13
16	14.19	Naphthalene,1,6,7-trimethyl	170	C13
17	15.12	Azulene,7-ethyl-1,4-dimethyl-	184	C14
18	15.16	Azulene,7-ethyl-1,4-dimethyl	184	C14
19	15.24	Azulene,7-ethyl-1,4-dimethyl	184	C14
20	15.96	9H-Fluorene,2-methyl-	180	C14
21	16.74	9H-Fluorene,9-methylene-	180	C14
22	17.28	9H-Fluorene,2,3-dimethyl-	180	C14
23	17.42	Phenanthrene,9,10-dihydro-1methyl-	194	C15
24	17.70	1H-Indene,2phenyl-	192	C15
25	17.93	Anthracene,2-methyl-	192	C15
26	17.99	Anthracene,4-methyl	192	C15
27	18.16	Phenanthrene,4-methyl-	192	C15
28	19.28	Phenanthrene,2,5-methyl	206	C16
29	21.47	Pyridine,5-ethenyl-2methyl-	119	C8

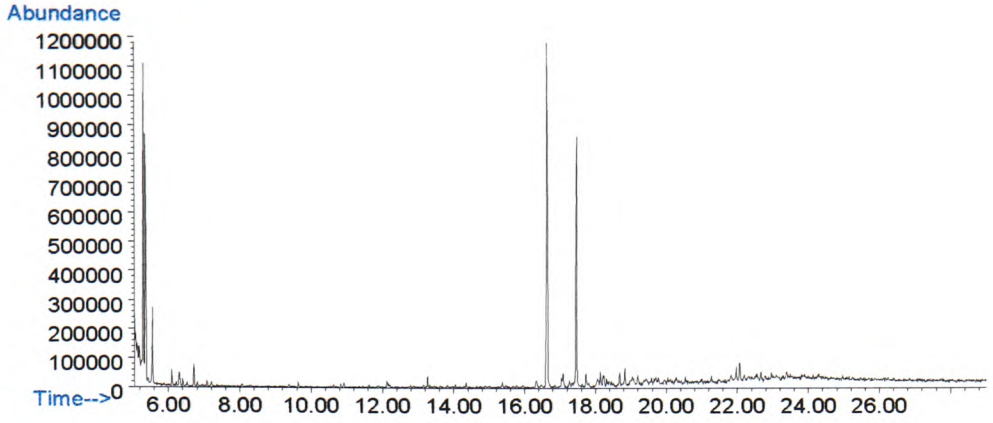


Fig. 2.55. GC-MS scan chromatograms of Sirte crude oil Fraction (F3).

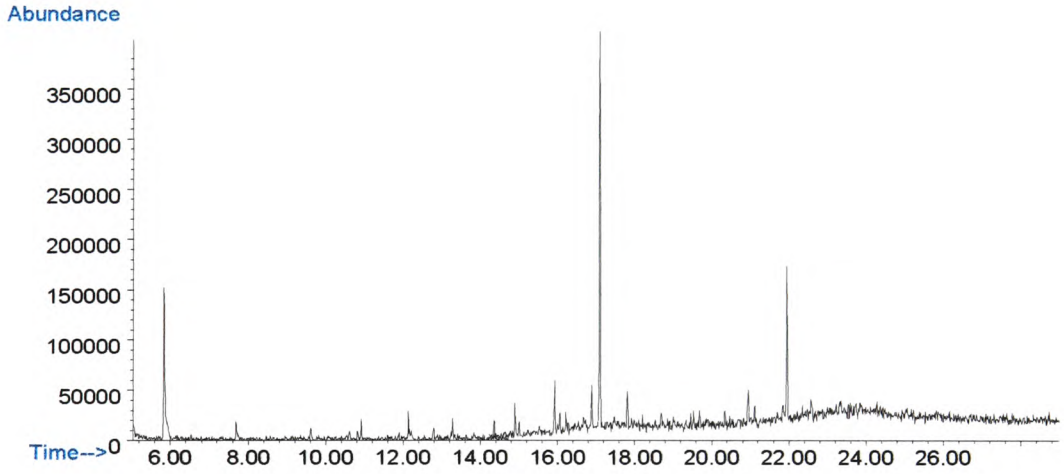


Fig. 2.56. GC-MS scan chromatograms of Sirte crude oil Fraction (F4).

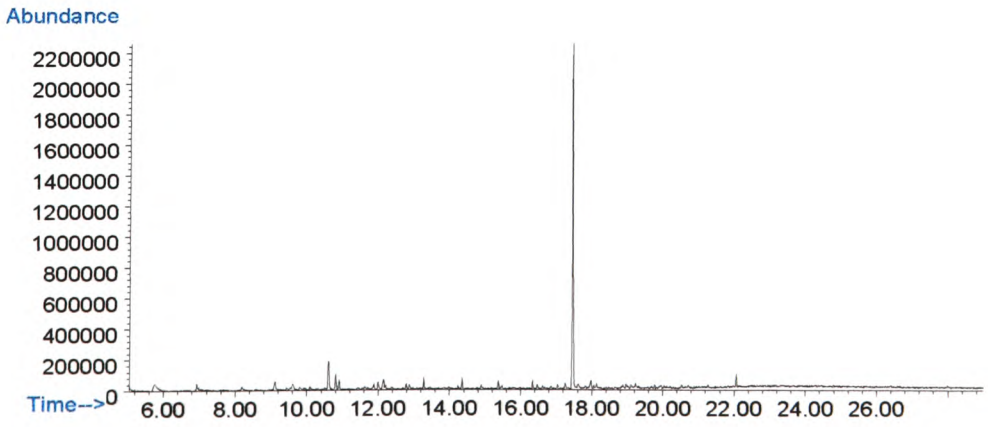


Fig. 2.57. GC-MS scan chromatograms of Sirte crude oil. Fraction (F5).

Table 2.15. Principal compound classes identified in fraction (F3).

PK	Library / ID	MW	Formula
1	1-MethylIcarbazole	181	$C_{13}H_{11}N$
2	9H-Carbazole, 2methyI-	181	$C_{13}H_{11}N$
3	9H-CarbazoIe	181	$C_{13}H_{11}N$
4	TrimethyIcarbazoIe	209	$C_{15}H_{15}N$
5	9H-CarbazoIe,9-ethyl-	195	$C_{14}H_{13}N$
6	N-MethyI-1-(methylamino)carbazole	210	$C_{14}H_{14}N_2$
7	1H-Indole,5-mehthyl-2-phenyl-	207	$C_{15}H_{13}N$
9	1H-Indole,1-methyI-2phenyI-	207	$C_{15}H_{13}N$
9	3-Methyl-2-phenylindole	207	$C_{15}H_{13}N$
10	1-Methyl-2-phenylbenzimidazole	208	$C_{14}H_{12}N_2$
11	Benzonitrile, m-phenethyl	207	$C_{15}H_{13}N$
12	1-Phenyl-1H-indole	193	C14H11N
13	2-Phenylbenzimidazole	194	C13H10N2
14	1,2,5-trimethyl-9H-carbazole	209	C15H15N

Table 2.16. Principal compound classes identified in fraction (F4).

PK	Library / ID	MW	Formula
1	Quinoline, 2 - ethenyl-	155	$C_{11}H_{13}N$
2	1 H-Indole, 5 methyl- 2 - phenyl -	207	$C_{15}H_{13}N$
3	Phenol, 2, 2 -[(1- methy- 1, 2- ethanediyl) -	282	$C_{17}H_{18}N_2O_2$
4	2-Methyl-7-phenylindole	207	$C_{15}H_{13}N$
5	Benzene, (ethoxymethyl)-	136	$C_9H_{12}O$
6	Phenanthridine, 5, 6, dihydro-	181	$C_{13}H_{11}N$
7	2-Methyl-2-phenylindole	207	$C_{15}H_{13}N$
8	2,3-dichlorophenol	163	$C_6H_4NCl_2O$
9	2-Phenylphenol	170	$C_{12}H_{10}O$
10	Dimethylphenol	122	$C_8H_{10}O$
11	Dibenz(a,h)acridine	279	$C_{21}H_{13}N$
12	Phenanthridine	179	$C_{13}H_9N$

Table 2.17. Principal compound classes identified in fraction (F5).

PK	Library / ID	MW	Formula
1	Quinoline, 4-phenyl-3-oxide	222	$C_{14}H_{10}N_2O$
2	1, 2-Benzenediamine, N-phenyl-	184	$C14H_{10}N_2O$
3	Thiazole, 2-(phenylthio)-	193	$C_9H_7NS_2$
4	Phenanthrenamine	193	$C_{14}H_{11}N$
5	Benzo(f)quinoline, 3- methyl-	193	$C_{14}H_{11}N$
6	Anthracenamine	193	$C_{14}H_{11}N$
7	Quinoline,-3-Bromo-	207	C_9H_6BrN
8	3-phenylindole	193	$C_{14}H_{11}N$
9	6-methylquinoline	143	$C_{10}H_9N$
10	2-Quinolinol	108	C_9H_7NO
11	Quinoline	129	C_9H_7N

2.6. Conclusion:

The fractionation of saturated and aromatic hydrocarbons by column chromatography presented several problems. For example, the retention characteristics of the adsorbents used with non polar mobile phases were strongly influenced by the water content of the adsorbent. Variations in the water content resulted in non reproducible separations. The high adsorptivity of the adsorbents can result in the loss of trace components and the tailing of late-eluting components, causing overlap of compound class bands.

In this work, a fractionation procedure for crude oil has been developed using inexpensive, silica gel micro glass column chromatography. The efficiency and reproducibility of the method were demonstrated by the separation of a standard mixture of saturated and aromatic hydrocarbons. Using this method, Libyan crude oil samples were effectively separated into saturated and PAH fractions. The recoveries of saturated, aromatic and polar hydrocarbons are in the range of 61.9 -70.3 %, 12.9-19.8 % and 7.1-9.9 % with relative standard

deviations under 6 %. The dominant aromatic hydrocarbons in Libyan crude oils are alkyl homologues of benzene, naphthalene, and phenanthrene

An extrographic procedure has been successfully developed and applied to the separation of Libyan crude oil samples into five fractions of increasing polarity using the given elutropic sequence of solvents. The recoveries of saturated, aromatic and polar hydrocarbons are in the range of 59.3-72.0 %, 13.6-21.0 % and 7.5-10.5 % with relative standard deviations under 6 %. The procedure provides a clean rapid separation of crude oil. The method combined with GC-MS can be used for the identification, characterization, and quantitation of hydrocarbon mixtures.

The yield and nature of compounds identified by GC-MS within the individual fractions derived from the chromatographic and extrographic approaches indicate that the yield of the chromatographic fractionation is higher in the first two fractions. On the other hand, the extrographic method gave good yield in the more polar fraction. The yields and compounds identified in n-hexane F1 fractions from the two methods were almost the same. Hence the performance of the two techniques with respect to these fractions can be considered to be similar.

However, the aromatic fractions produced by the chromatographic technique were shown to be contaminated with hydroxyl and pyrrolic-type compounds whereas the corresponding fractions produced by the extrographic technique provides an aromatic fraction almost free of class overlap. Fraction (F3) mainly corresponds to NH groups. The structure of these compounds is illustrated in the appendices. The presence of neutral nitrogen heterocyclic compounds has been confirmed by mass spectrometry. Fraction (F4) is composed

of phenolic and basic nitrogen compounds. Fraction (F5) is characteristic of amidic compounds. The column chromatography was largely unsuccessful when applied to fractionation of high polarity compounds the last three fractions. The strong brown coloration of these fractions probably arise from the presence of involatile resin species.

The sample to adsorbent ratio in extrography plays an important role in achieving a good separation of components. In the present study, successful separations were obtained using a sample to adsorbent ratio of 1:20.

Overall, these results suggest that extrography might be the most suitable technique for fractionating crude oils with a view to characterization, because of its limited requirements in time and materials as well as its simplicity. To make this possible, extrography should be able to provide a given number of fractions of well-defined chemical composition.

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Chapter 3

3 Fractionation of crude oil using SFE

3.1 Introduction

For the majority of analytical protocols, it is the sample preparation step that can be the most time consuming and labour intensive. Almost all contemporary preparation techniques including soxhlet extraction, distillation, preparative liquid chromatography and liquid extraction present certain disadvantages. All use large amounts of hazardous solvent, further sample clean -up is usually necessary, the desired solvent may not be strong or selective enough or it may be difficult to remove after the extraction. The resultant solution must usually be concentrated by evaporation prior to final analysis. Furthermore, as a result of the Montreal Protocol, many traditional solvents will be banned in the near future [1].

Supercritical-fluid extraction (SFE) is a hybrid operation utilizing the advantages of both distillation and liquid extraction. It has the benefit that slight changes in the temperature and pressure of a supercritical fluid can cause extremely large changes in the fluid's density and thus its solvating power. In comparison with conventional approaches, supercritical fluid extraction offers considerable flexibility for extraction by variation of pressure, temperature, choice of supercritical fluid and the use of solvent modifiers (entrainers).

Historically, the critical point (de la tour point) of a substance was first observed in 1822 by Baron Cagniard de la Tour, who stated that above a certain temperature, single substances do not condense or evaporate, but exist only as fluids. Later Hannay and Hogart reported that solid substances such as metal halides

are soluble in supercritical ethanol and carbon tetrachloride [2-4]. Francis in 1954 reported the solubility of 261 different compounds in near supercritical CO_2[5].

The phenomenon of solubility enhancement in dense gases was discovered in the late 1870 s when the effect of pressure on the solubility of potassium iodide in ethanol were observed [2]. The next development was the discovery of the effects of supercritical water in geological processes [6], and methane in the formation and migration of petroleum [7]. The real starting point for SFE as an industrial process was probably the work of Zosel at the Max Planck institute for Coal research [8].

Several instrument manufactures produce bench-top SFE systems that make the study of supercritical fluid separation relatively easy and inexpensive. Some systems are readily adapted for preparation-scale operation.

The potential advantages offered by SFE include:

1. Reduced extraction times.
2. Controllable extraction conditions.
3. Reduced risk of contamination.
4. Potential for fractionation.
5. Compatibility with on-line methods of analysis (e.g., chromatography).
6. Flexibility for off-line analysis (e.g., spectrophotometry)
7. Class selective extraction by solubility discrimination at different densities.
8. Supercritical fluid solvents are more easily removed from the extraction material.
9. Concentration of trace substances is possible, since CO_2 is volatile at room temperature.

10. Running costs are low and it can be automated.

11. Use of non toxic solvents.

12. Environmentally friendly.

The limitations of the SFE are:

1. The choice of SF tends to be limited to those substances which have low critical points.
2. Potentially more dangerous than conventional extraction methods due to operation at elevated pressures.

3.2 Application of supercritical fluid extraction

The application of supercritical fluids in separation processes is a rapidly developing area of research and there is an immense potential for industrial application. The main initial interest in supercritical fluid extraction came from the petroleum industry where the need for improvements to existing petroleum technology led to the investigation of supercritical fluid extraction as a means of refining coals and oils [9]. The deasphalting of petroleum oils using supercritical fluids was patented in 1947 [10]. Subsequently, a number of related processes have been developed for example the removal of ozocerite from ores [11], recovery of lighter oil products from residues obtained after crude oil distillation [12] and the extraction of lanolin from grease using supercritical methane. More resent developments in the fuel industry have included the extraction of liquid fuel constituents from coal using mixtures of supercritical toluene and xylene or supercritical pentane / isopropanol, or supercritical ethanol [13] and the remove of oil from tar sands and lignite tars in cases where distillation has proved unsatisfactory.

Other SFE processes being investigated include the separation of petroleum pitch into fractions with a supercritical solvent such as toluene, using temperatures

up to 657 K and pressures to 4900 Psi. Petroleum pitch has considerable potential as an inexpensive raw material for the economical production of high performance carbon fibers. The temperature and pressure are selected to give a liquid-like solvent density that dissolves the pitch in a single phase. Inorganic and coke particulates in the pitch are insoluble in this phase and precipitate from the solution. These impurities are removed from the bottom of the column, and the purified-solvent extract is fractionated in the next series of stages. Equilibrium phase compositions have been reported for the toluene / Ashland A - 240 pitch system at temperatures of 595, 634, and 674 K and pressure ranging from 406 to 1064 Psi. The molecular weight distributions of the extracted fractions show that the process is effective in separating pitch by molecular weight[14] .

Berry and et al.[15], studied the fractionation of petroleum and coal derived oils into hydrocarbon classes using SFE with CO_2 and 10 % methanol as modifier. Extractions were performed at increasing densities ranging from 0.25 $g.cm^{-3}$ to 0.95 $g.cm^{-3}$ (40 ^0C). They found > 90 % cyclic, branched and normal alkanes were extracted below 0.60 $g.cm^{-3}$. 90 % of aromatic species were extracted at densities between 0.65 - 0.95 $g.cm^{-3}$. Sulphur, oxygen and nitrogen heterocyclics together with phenolic compounds were present in fractions obtained at densities > 0.85 $g.cm^{-3}$.

The ability of SFE to provide rapid and quantitative recovery of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl's (PCBs), pesticides, and hydrocarbons, from a variety of environmental samples including diesel exhaust particulate, urban dust, fly ash and sediment has been reported [16,17]. SFE has been reported to give better PAH recoveries in 30-60 min than those generally obtained with several hours of liquid solvent extraction using either a soxhlet apparatus or

sonication [18]. The technique has also been used for the determination of total petroleum hydrocarbons (TPH) in real-world fuel spill samples containing heavy fuel oil, diesel fuel, light crude oil, gasoline or kerosene [19].

The SFE approach has also been applied in the food and pharmaceutical industries. The decaffeination of coffee using supercritical extraction processes has been operating in Germany science 1978, and more recently, supercritical carbon dioxide has been used to produce concentrated hop extracts and acid extracts from hops, which are used to give beer its characteristic taste [20,21].

In addition to this the U.S. Department Of Agriculture (USDA) has been assessing the use of supercritical carbon dioxide for the extraction of oils, particularly triglycerides, from soybean flake and corn germ. This process can provide an oil which is low in phosphorus compounds [22]. The approach is also being used to produce low oil content snack food, such as defatted potato chips, providing improved nutritional value. Other studies have shown supercritical carbon dioxide to be very useful in the extraction of biologically active compounds from complex matrixes in very high purity.

The elimination of lipids from the pancreas has been investigated [23] using SFE with CO_2 as a pretreatment prior to full pancreatic extraction, here, resulting extracts contained only 0.1 % of lipids and showed much higher enzymatic activity than those obtained by conventional solvent extraction. Amino acids and carboxylic acids have been extracted from biomasses and waste water (from pulp production) using CO_2 containing a solvent entrainer [24]. Supercritical fluids have the potential to extract drugs from plants, without the side effects and chemical decomposition that can result from extraction with organic liquid solvents [25].

3.3 Fluid properties in SFE

A supercritical fluid is a substance with both gas-and liquid-like properties. It is gas-like in that it is a compressible fluid that fills its container, and is liquid - like in that it has comparable densities (0.1-1g.cm^{-3}) and solvating power.

The phase change of a substance from a gas to a liquid depends upon the temperature and pressure applied to the system. Above a certain temperature, called the critical temperature (Tc), a substance cannot be liquefied, regardless of the applied pressure. The minimum pressure required to liquefy a substance at its critical temperature is the critical pressure (Pc). The critical temperature and pressure combined to define a unique point on the phase diagram known as the critical point as shown in Figure 3.1. When a substance is subjected to pressures and temperatures above its critical point, a highly compressed gas known as a supercritical fluid is formed. However, the converse is not always true- pressures and temperatures above the critical values do not always result in a supercritical fluid. At very high pressure (>10^8 Pa) the freezing curve can rise into the supercritical fluid region and so both solid and supercritical phases can exist [26].

Figure 3.1 shows the temperature-pressure (T-P) phase diagram of a pure substance, in which the regions corresponding to solid, liquid, and gas phases are indicated. The evaporation curve starts at the triple point (TP) and ends at the critical point. The melting curve starts at the triple point and rises steeply with increasing temperatures and pressures. In the region where the temperatures and pressures are below the critical point (CP), two or three of the phases (i.e., solid, liquid, and gas) coexist in equilibrium along the evaporation, melting, and sublimation curves. In the region above the critical temperature, the substance cannot be liquefied by increasing the pressure at a constant temperature, and there is

no such phase transition from gas to liquid, or vice versa. The substance in the supercritical region is neither a liquid nor a gas however, it is generally referred as a fluid irrespective of the fluid density

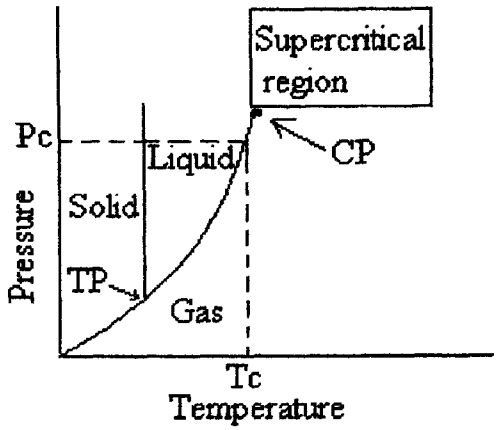

Fig. 3.1 The critical point and the supercritical region [26].

A comparison of the average values of important physical properties of the three common states illustrated in Table 3.1. The diffusivity of a supercritical fluid is higher than that of a liquid by a factor of several hundred. Which means that mass transfer in a supercritical fluid is faster than in the liquid by the same factor.

The viscosity also shows a significant difference from that of a liquid- approximately 100 times lower, though the density is similar to that of a liquid. The combination of these properties is that a supercritical fluid penetrates a material as though it was a gas, but with the very important difference that it has solvent properties approaching that of liquid. These gas like transport parameters contribute to improve rates of mass transfer thus resulting in faster extraction.

Table 3.1. Properties of Supercritical Fluids vs. Gases and Liquids [27].

Property	Gas	Liquid	SF
Density ($g.cm^{-3}$)	10^{-3}	1.0	0.1 - 1.0
Diff. Coeff. (cm^2s^{-1})	10^{-1}	$<10^{-5}$	10^{-3} - 10^{-4}
Viscosity ($g.cm^{-1}s^{-1}$)	10^{-4}	10^{-2}	10^{-3} - 10^{-4}

Safety considerations and the critical properties of supercritical fluids greatly restrict the choice of a fluid in practice. Table 3.2 shows the critical parameters of some potentially useful compounds. Many of those listed would not be suitable due to their unfavorable physical properties, cost, or reactivites. For example, water is an unsuitable choice for SFE because of the high temperature and pressure (Tc = 74.4 °C, Pc = 3205 Psi) required for it to become supercritical. Ammonia is very unpleasant to work with. A fume hood or other venting precautions are needed to keep it out of the laboratory atmosphere, it is also greatly restricted by its strongly corrosive effects. Nitrous oxide has been used extensively. It is polar and has reasonable values of critical temperature and pressure. However, there is evidence of violent explosive reactions between nitrogen oxide and oils and fats. The hydrocarbons pose fire and explosion hazards.

Table 3.2. Properties of some chemicals that may be suitable for chromatography with supercritical fluid phases [28]:

Compound	Tc (^{0}C)	Pc (Psi)	ρc (g.cm^{-3})	bp (^{0}C) at 1 atm
Carbon dioxide	31.3	1070.4	0.448	-78.5
Ammonia	132.3	1646.2	0.24	-33.4
Water	374.4	3208.2	0.344	100
Methanol	240.5	1173.4	0.272	64.7
Ethanol	243.4	926.1	0.276	78.4
Isopropanol	235.3	690.9	0.273	82.5
Ethane	32.4	707.8	0.203	-88
n-propane	96.8	617.4	0.220	-44.5
n-butane	152.0	551.3	0.228	-0.05
n-pentane	196.6	489.5	0.232	36.3
n-hexane	234.2	435.1	0.234	69.0
2,3-dimethyibutane	226.8	455.7	0.241	58.0
Benzene	288.9	710.0	0.302	80.1
Dichlorodifluoromethane	111.7	579.2	0.558	-29.8
Dichlorofluoromethane	178.5	749.7	0.522	8.9
Trichlorofluoromethane	196.6	612.3	0.554	23.7
1,2-Dichlorotetrafluoroethane	146.1	521.9	0.582	3.5
Chlorotrifluoromethane	28.8	720.8	0.58	-81.4
Nitrous oxide	36.5	1050.1	0.457	-89
Diethyl ether	193.6	533.6	0.267	34.6
Ethyl methyl ether	164.7	638.0	0.272	7.6

A good solvent for extraction should exhibit the following properties:

1. It should be selective, because the object is to separate an analyte from a matrix, the solvent should be able to dissolve the desired material better than it dissolves other constituents.
2. Should also have a high capacity for the analyte. This helps minimize the volume and time required to extract quantities sufficient for analysis.
3. Solvent should be stable and unreactive to the proposed system (i.e. inert to both solute and matrix and stable under the condition of the processes).

4. From the economic perspective, a desirable solvent should not be corrosive to the equipment, should be relatively inexpensive and should be friendly to the environment.

When all of these constraints are taken into account, carbon dioxide becomes the medium of choice because it possesses favorable properties including: low critical temperature (31.1 °C), moderate critical pressure (103.2 Psi), can be operated at a low density of ca. 0.1 $g.cm^{-3}$ up to nearly 1 $g.cm^{-3}$, non-explosive, odorless, non-flammable, high purity at relatively low cost, non toxic, and low reactivity. However, the major limitation of CO_2 is its inability to extract polar analytes at typical working pressures (1134.8 - 8511.3 Psi). The extraction of polar analytes requires the addition of modifiers or entrainers to the CO_2 such as methanol or acetonitrile. In some cases derivatization will serve the same purpose of enhancing the extractability.

3.4 SFE instrumentation

Several instrument manufactures [29] now offer a variety of commercially available bench-top SFE systems that vary in design, operation and features. The basic components of an SFE system [30] are shown in Figure 3.2. The main features of the instrumentation are a pump to pressurize the gas to above critical pressure, an extraction vessel to hold matrix to be extracted, a fixed or variable restrictor to control the density of supercritical fluid, an analyte collection device, temperature control systems for several zones, and an overall system controller. In addition, a supply of high purity CO_2 is required. The pump used in the SFE system must be able to maintain a high pressure, typically 3500-10,000 psi, at constant reproducible flow rates.

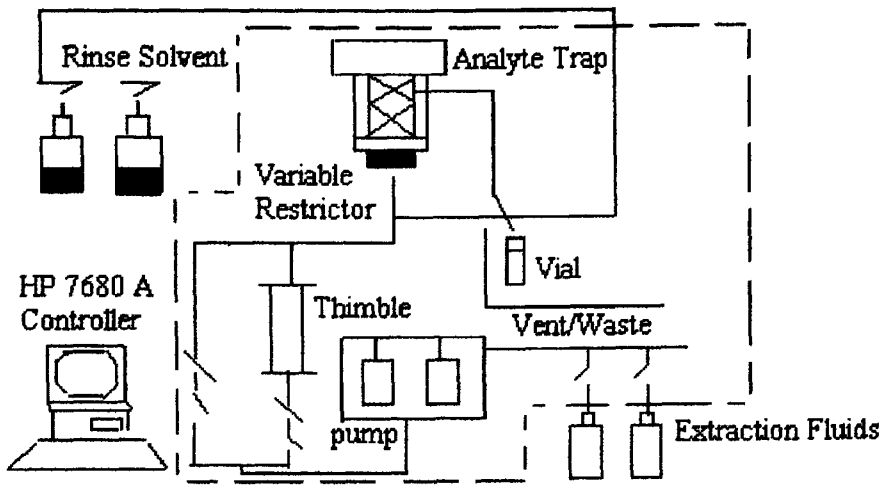

Fig. 3.2. Flow diagram of Hewlett-Packard SFE Model 7680 A [30].

Analytical SFE is typically performed using syringe pumps that are similar or identical to those used for supercritical fluid chromatography (SFC), although alternatives are available as pneumatic and reciprocating pumps are used. Reciprocating pumps require additional cooling to prevent cavitation.

The pressurized CO_2 is used to extract the analyte from its matrix contained in a sample cell. Sample cells typically range in size from 150 ul-50 cm^3 and are constructed from stainless steel or similar inert material. The effect of extractor cell geometry and packing of the sample [29] in a the extraction cell has been investigated in a series of papers. The extraction thimble must be able to withstand the high pressure that will be used in the system, up to 15000 psi in some cases. The temperature of the extraction cell is controlled using a thermostatic heater.

SFE manifests its best advantage when extracting analytes from solids and semisolids, rather than from liquids, fluids and gases. The primary limitation in extracting analytes from liquid or fluid sample matrices is the result of the extraction

thimbles design, this approach is discussed in chapter four. Generally, to extract liquid samples by SFE the sample must first be mixed with a solid phase support material such as silica gel or alumina, so the sample is no longer free flowing[30].

Extraction's can be performed in two distinct ways: (i) static (ii) dynamic, and both can be carried out separately or as part of a combined technique. Dynamic SFE is carried out by flushing the sample continuously with supercritical fluid (ca. 0.1- 4 cm^{-3} min^{-1}). It is widely used off-line but even more so in on-line methods. Static SFE is less frequently used than dynamic SFE. It is useful for solubility measurements and can be applied as a pre-optimizing method for dynamic SFE.

Pressurization of the system is achieved using a fixed or variable restrictor. The design of the restrictor can very from a simple fixed device comprising a piece of fused silica (fixed device) to a computer-controlled dynamic orifice (variable device). The restrictors used in SFE are usually deactivated fused silica capillaries or metal capillaries with a crimped end. Restrictors that are narrowed at the end keep the analyte solubility (fluid density) unchanged all the way to the restrictor exit. The variable restrictor design is preferred because the fixed restrictor is susceptible to blockages.

The collection of resulting extracts can be performed in two ways, on-line or off-line. Figure 3.3 summarizes the concept of using both modes of SFE in conjunction with a myriad of analytical techniques [32]. With off-line SFE, analytes are often collected in either a few milliliters of a liquid solvent, and analysis of the extract is conducted as it would be for any conventional liquid solvent extraction, or the extracted analytes can be collected by passing the supercritical fluid through a column packed with chromatographic material [33], bubbling the condensed fluid

through a small amount of solvent [34] or allowing the supercritical fluid containing sample to expand into an empty container with or without cryogenic cooling [35].

The on-line coupling of SFE can increase overall sensitivity, as the entire extract can then be analyzed without sample splitting, and intermediate sample handling steps are eliminated. An on-line interface must provide a quantitative transfer of analyte between the SFE system and the final system/detector.

On-line SFE using high pressure flow cells has recently shown promise as a means of eliminating the collection solvent as well as the need for flow restrictors[36]. Table 3.3 compares the practical aspects of off - and on-line SFE with conventional 16 h liquid solvent extraction for determination of PAHs in an urban air particulate sample [36].

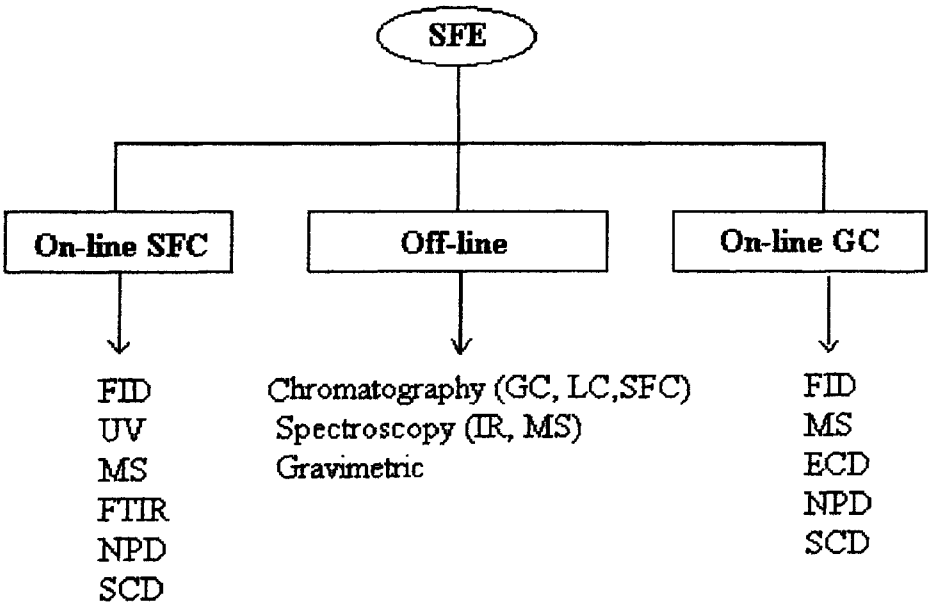

Fig. 3.3 Compatibility of different modes of SFE with chromatography detectors[32].

Table 3.3 Comparison of off-and on line SFE with conventional techniques for the quantitation of PAHs in urban dust [36].

Parameter	Conventional	Off-line SFE	On-line SFE
Sample size	1000 mg	20 mg	2 mg
Extraction time	48 h	1 h	15 min
Extract concentration time	3 h	0-10 min	0 min
Liquid solvent required	450 ml	3 ml	0 ml
Analysis time for extraction/concentration	16h	20 min	20 min
Shortest possible total analysis time(one sample)	3 days	2 h	1 h

The first report of a direct coupling of SFE with chromatography was in 1976 by Stahl and Schiltz [37]. They combined SFE with Thin-Layer Chromatography (TLC) in a study of natural products. Since then, SFE has been coupled on-line with techniques, such as High Pressure Liquid Chromatography (HPLC) [38], Supercritical Fluid Chromatography (SFC) [39], Gas Chromatography (GC) [40], Infrared Spectroscopy (IR) [41]. The direct introduction of SFE extracts into a Mass Spectrometer (MS) has also been reported [42]. Even though many different hyphenated systems have been applied, the most popular coupled SFE techniques continue to be SFE-GC and SFE-SFC.

On-line SFE-GC has been applied to variety of samples including sediments, soil, animal and plant tissues [43]. Flame ionization is the usual method of detection. Electron-capture detection and mass spectrometry are useful when specific information is needed about analytes and MS is always required when identification must be reliable. On-column SFE-GC yields the best sensitivity possible with small

samples (ppb sensitivity with 1 mg samples) because sample transfer is very efficient. Split SFE-GC is capable of dealing with large samples (up to 15 g) [44].

SFE-SFC has been mostly applied to the analysis of polymers and polymer additives, although PAH, polychlorinated biphenyl and pesticide analysis has been reported.

3.5 Optimizing SFE Conditions

Instrumentation used in analytical SFE continues to mature and evolve. The results obtained from SFE are very dependent on the operational parameters used during the extraction. These parameters include temperature of the oven, extraction pressure, flow rate, fluid composition, extraction time, analyte collection (packed bed or solvent trapping), sample pre-treatment (including grinding, addition of drying agents, and dispersants, etc.), static or dynamic procedures. An important consideration of any extraction is to determine the nature of the sample analyte-matrix combination. Low and moderately polar compounds such as hydrocarbons, alcohol's, esters show a high solubility in supercritical CO_2 at relatively low densities (0.2 - 0.4 $g.cm^{-3}$). Increasing polarity and molecular weight results in a drop in solubility of the analyte. This is can be over come by using either higher densities, more polar supercritical fluid or to enhance the solvent strength of CO_2 by the addition of a modifier [29].

The rate of extraction is primarily influenced by the rate of diffusion of the supercritical fluid through the sample matrix. As such particle size is a major consideration and freeze drying, grinding and sieving may be utilized inorder to increase the surface area of a solid sample. For liquid samples, the particle size of the solid phase support material can be significant [45].

The density or pressure of extraction medium is generally the most effective variable and should be optimized first. The threshold pressure is a term developed by Giddings. et al. [46] to describe the point where the analyte becomes soluble in the fluid. It is desirable to extract slightly above the threshold pressure to minimize the extraction of unwanted co-extractions.

The selectivity of the extraction can be controlled by the solvent strength and hence the SF density. If there is sufficient difference between the target analytes solubilities, a stepwise increase in the supercritical density will allow selective extraction to be achieved. This is dependent on the analyte solubility, and as a result the selective extraction of a series of compounds is possible.

Extraction recoveries are quite often improved by raising the temperature well above the critical temperature of the fluid being used. With increasing temperature the diffusion coefficient of supercritical fluid increases and as result the mass transfer will increase, producing a faster extraction. An increase in the fluid flow results in an increase in the volume of fluid passed through the extraction cell and thus an increase in the diffusion.

3.6 Crude oil fractionation using SFE

For our studies, a HP 7680 A SFE extractor was used. A schematic diagram of the system is shown in Figure 3.2.

For a typical extraction, a weighed amount of sample is placed in a high-pressure extraction vessel (thimble), which is housed in the extraction oven. The extraction fluid is delivered to the thimble by a cooled dual-piston reciprocating pump. The pump and oven temperature are used to control the SF density. Extract flows from the thimble to the analyte trap (the receiver), where the SF fluid vaporizes and leaves the concentrated analytes behind. A rinse solvent is used to

dissolve and transfer analytes to out-put collection vials. The choice of rinse solvent depends on the anaylte properties and the requirement of the analyzing device. A schematic of the extraction process is shown in Figure 3.4.

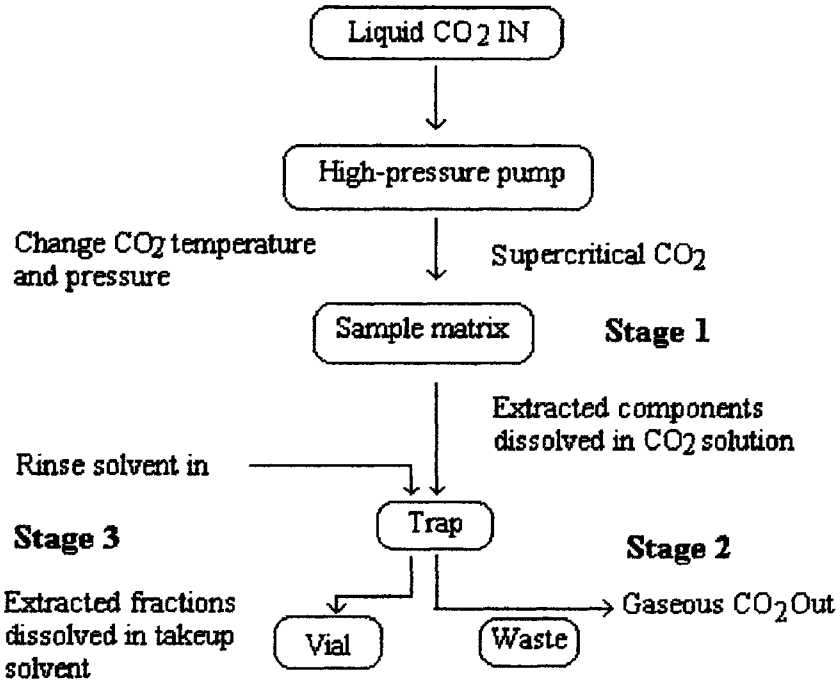

Fig. 3.4 Extraction process for one extraction step [30].

3.7 Sample Preparation For SFE

3.7.1 Preparation of standard mixture sample

The aim of these investigations was to determine if SFE could offer a means of hydrocarbon class fractionation of crude oil prior to GC-MS analysis.

SFE extraction and collection conditions were established using a authatic standard mixture containing saturated and polycyclic aromatic hydrocarbons. The standard mixture was placed on a solid phase support. 2 cm^3 of the standard solution was placed in a 250 cm^3 round-bottom flask containing 50 cm^3 of

dichloromethane and activated silica gel (60-120 mesh, BDH, England, activated in vacuo for 16 hours at 130 ^{0}C) was then added to the solution in the ratio of 1:15 (sample/silica gel). The solvent was removed from the mixture under reduced pressure. The sample was then forwarded for SFE fractionation.

3.7.2 Preparation of crude oil samples

Crude oil samples (0.5 - 1.5 g) were placed in a 250 cm^3 round-bottom flask. The mixture was dissolved in dichloromethane (50-100 cm^3), activated silica gel was then added to the solution in the ratio of 1:15, 1:33 and 1:45 (sample/silica gel). The solvent was removed under reduced pressure. The crude oil sample was then forwarded for SFE fractionation.

For SFE 2.0 g of loaded silica (standard mixture or crude oil) was placed in the extraction thimble. A layer of fine sand was placed on top of the silica to help prevent fines and small particles from clogging the system. The thimble was then placed into the extraction chamber of the system.

3.7.3 Supercritical Fluid Extraction profile

In order to optimize the extraction conditions two sets of experiments were performed. The first set of experiments involved the sequential extraction of an individual sample at different densities (0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85, 0.95 g. cm^{-3}), as shown in Figure 3.5.

The second set of experiments involved extraction of the sample at one set density within the range list as shown in Figure 3.6.

Other than density, all extractions within each set of experiments were performed under identical conditions which are given in Table 3.4. Each sample was soaked for 2 minutes at the set experimental density. This step can be considered to

be an "equilibrium period" or a "static extraction phase". The samples were then extracted dynamically at the specified density for a given time (x) which determined a constant sweep volume (3.0 cm^3). After leaving the thimble, the extract was decompressed onto a sample trap containing Octadecyl bonded silica (ODS) support material. The temperature of the trap was set at 20 ^0C in order to effect efficient cryotrapping of the precipitating analytes. After the decompression period the ODS trap was purged with dichloromethane. The dichloromethane containing extracted components was then collected in pre-weighted vials. The extracts were evaporated to dryness, re-weighted and then analyzed by GC-MS. The instrumental parameters are given in chapter 5.

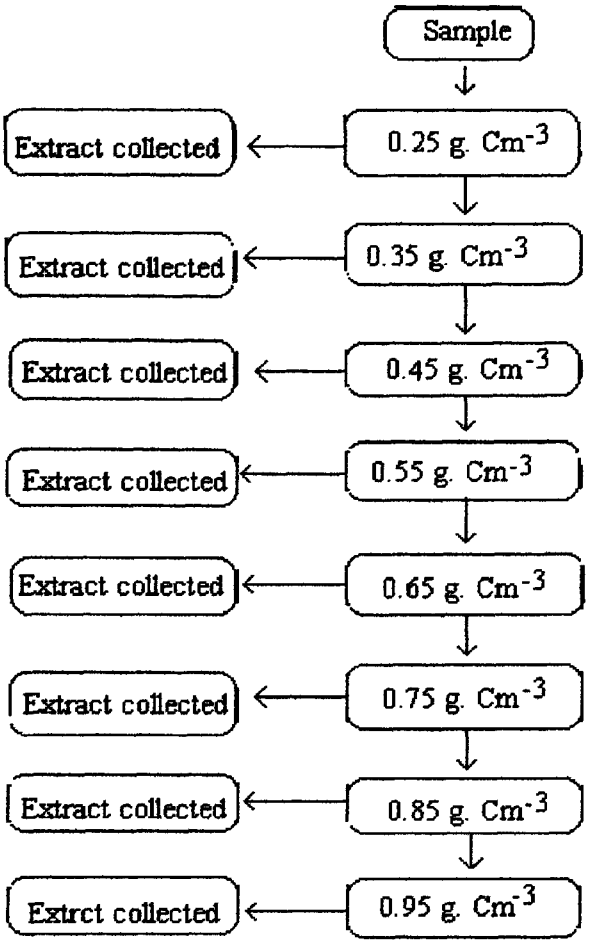

Fig. 3.5 Experiment Type 1.

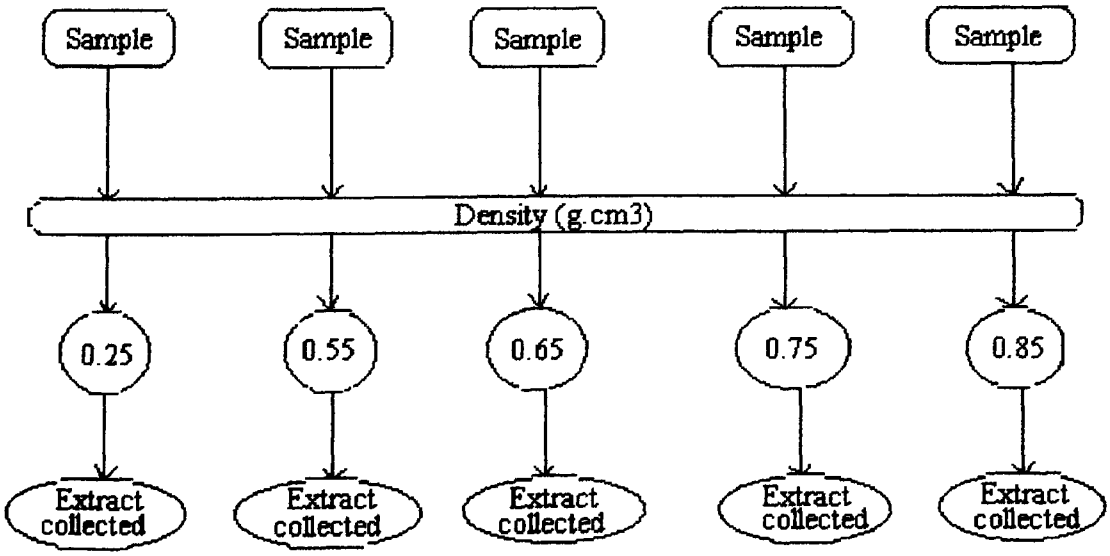

Fig.3.6 Experiment Type 2.

Table 3.4. SFE Conditions used:

Extraction step Fluid Delivery				
Density	Variable			
Pressure	Variable			
Flow rate	1.0 cm^{-3}. min^{-1}			
Extraction fluid	CO_2			
Extraction Chamber				
Chamber temperature	Variable			
Equilibrium time	2.0 minuets			
Extraction time	Variable			
Thimble size	7.0 cm^3			
Thimble volume swept	3.0 cm^3			
Analyte Trap(containing ODS support material)				
Nozzle temperature	40 ^0C			
Trap temperature	20 ^0C			
Void volume compensation	1.0 cm^3			
Fraction output				
Rinse Solvent	Volume cm^3	Rate $cm^{-3}.min^{-1}$	Nozzle Temp.	Trap Temp
Dichloromethane	1.0	2.0	45	40

3.8 Result and discussion

3.8.1 Standard mixture of saturated and aromatic hydrocarbons

The results from our studies using the authatic standard mixture were very encouraging. The selective extraction capability that was achieved as a function of fluid-pressure is illustrated in the GC-MS total ion chromatograms shown in figures 3.7 to 3.14.

Overall the results reveal that at higher pressures, the carbon number distribution significantly shifts toward heavier end. These results were also corroborated by the color differences of the extracted samples. At higher pressure,

the samples were darker. It was clear that at higher pressure, much heavier hydrocarbons partitioned into the extract phase. The first extractions (up to density 0.55 g. cm^{-3}) were colorless, suggesting that if anything was extracted, it was limited to the saturated hydrocarbons. Extractions at a density of 0.65 $g.cm^{-3}$ produced a pale orange extracts. This suggests that some of the less volatile more polar compounds were extracted. The extractions at a density of 0.95 $g.cm^{-3}$ produced a much darker orange color. Color differences between extracted samples provided visual evidence of compositional variations.

The extraction experiments were conducted at 40 °C and at pressures of 1117, 1223, 1284, 1355, 1508, 1937, 3058 and 5560 Psi that corresponded to densities of 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85, 0.95 $g.cm^{-3}$ respectively, with a flow rate of 1 cm^{-3} min^{-1} for (5 min/dynamic)

Figures 3.7 to 3.9 shows the TIC obtained at densities of 0.25, 0.35, 0.45 $g.cm^{-3}$. Mass spectral analysis of these fractions indicate the presence of cyclic, branched and normal alkanes only. It was therefore concluded that the selective fractionation of saturated hydrocarbons could be achieved at densities below 0.65 $g.cm^{-3}$.

Mass spectral analysis can be further refined by performing single ion scans for ions (m/z 57, 71, 85) which characteristic of particular saturated hydrocarbons. These results indicate the trends of recoveries of saturated hydrocarbons at low densities. It is evident that all cyclic, branched and normal alkanes were extracted at densities below 0.65 $g.cm^{-3}$.

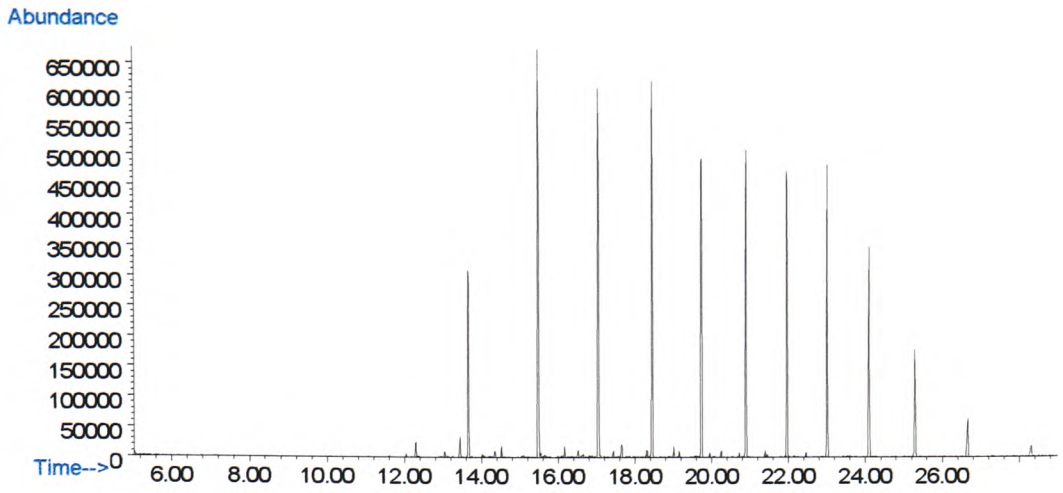

Fig. 3.7 TIC of standard mixture of saturated and aromatic hydrocarbons extracted by SFE at density 0.25 g. cm^{-3}. GC conditions chapter 5.

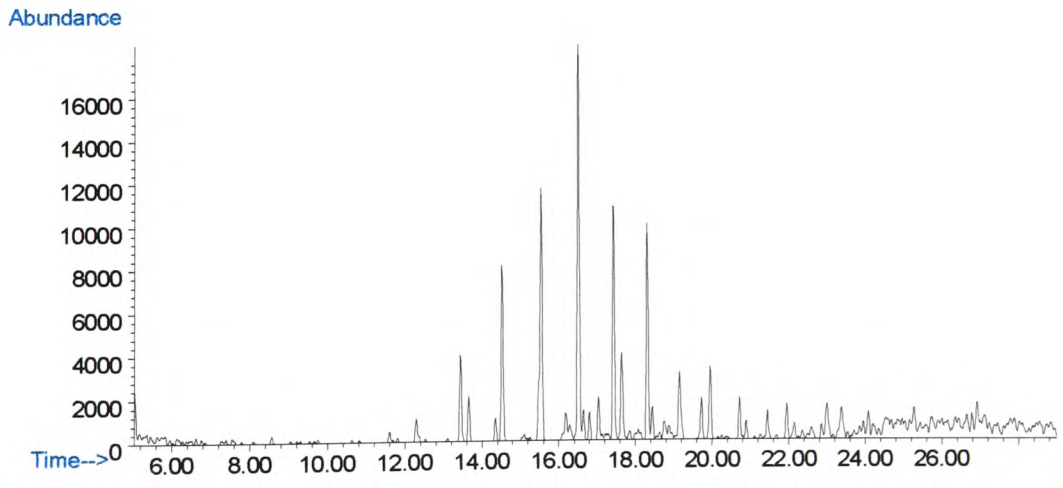

Fig. 3.8 TIC of standard mixture of saturated and aromatic hydrocarbons extracted by SFE at density 0.35 g. cm^{-3}. GC conditions chapter 5.

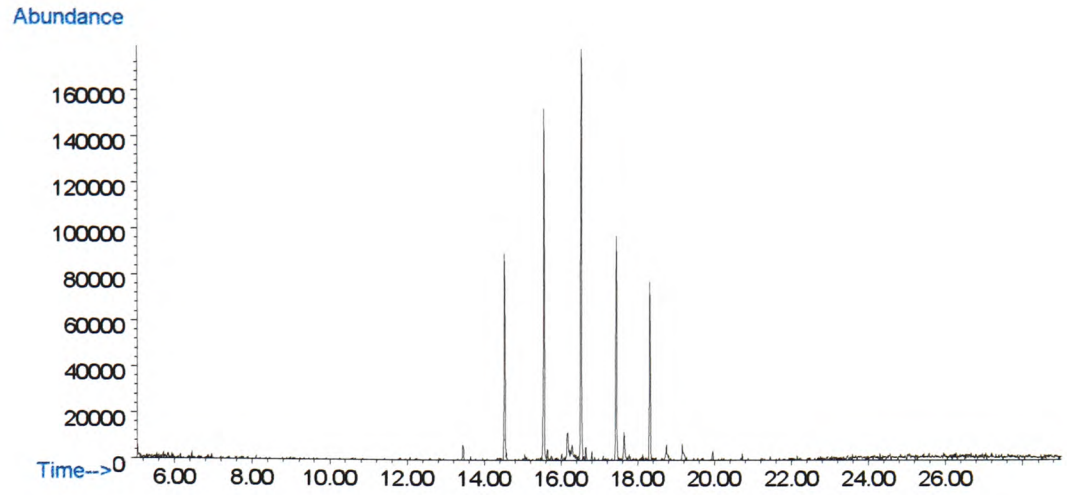

Fig. 3.9 TIC of standard mixture of saturated and aromatic hydrocarbons extracted by SFE at density 0.45 g. cm^{-3}. GC conditions chapter 5.

A major aim of the investigation was to optimize (if possible) the selective fractionation of PAHs from other endogenous hydrocarbons. It was decided to use relatively short extraction times (5 min dynamic) so that the recovery enhancements by increasing pressure could be observed. Figures 3.10 to 3.14 shows typical GC-MS total ion chromatograms of PAH fractions recovered at densities of 0.55, 0.65, 0.75, 0.85, 0.95 g. cm^{-3}. It is evident that PAHs start to become extracted at 0.55 $g.cm^{-3}$. Examination of these chromatograms reveals that at densities of 0.55 and 0.65 $g.cm^{-3}$ extracts are contaminated with some saturated hydrocarbons however, these are present at significantly reduced quantities. The rate of extraction is limited by the solubility of the compounds in the fluid and the volume of fluid used in the extraction. Thus, samples with higher component concentrations require longer extraction times (larger fluid volumes) or a stronger extraction fluid for complete extraction. With increasing pressure, e.g. up to 5553 Psi (density = 0.95 $g.cm^{-3}$) the recoveries of PAHs are seen to increase. This can be explained by the increasing

density. As expected, progressively higher molecular weight material was extracted with the higher density extraction fluid as clearly seen in figure 3.15.

Figure 3.15 shows the components of extracted PAHs under various densities. When the extraction was conducted at a density of 0.55 $g.cm^{-3}$, essentially the naphthalene was the major component extracted. At the next extraction (density = 0.65 $g.cm^{-3}$) essentially all the naphthalene was exhausted and anthracene and fluorene, (three ring aromatics) were the major components extracted along with a significant quantity of fluoranthene and pyrene.

At densities of 0.75, 0.85, 0.95 $g.cm^{-3}$, the higher homologues fluoranthene and pyrene were recovered. Recoveries were increased gradually from 14.2 % to 21.91 % for fluoranthene and 13.08 % to 18.84 % for pyrene, although high levels of the low homologues were also still present.

At the higher experimental density of 0.85 and 0.95 $g.cm^{-3}$ only chrysene (four ring aromatic) was recovered (2.28 and 6.20 %) respectively.

It was concluded that SFE using these conditions could provide a class selective fractionation of hydrocarbons. Thus, our studied continued inorder to investigate the applicability of the method for the fractionation of crude oil samples.

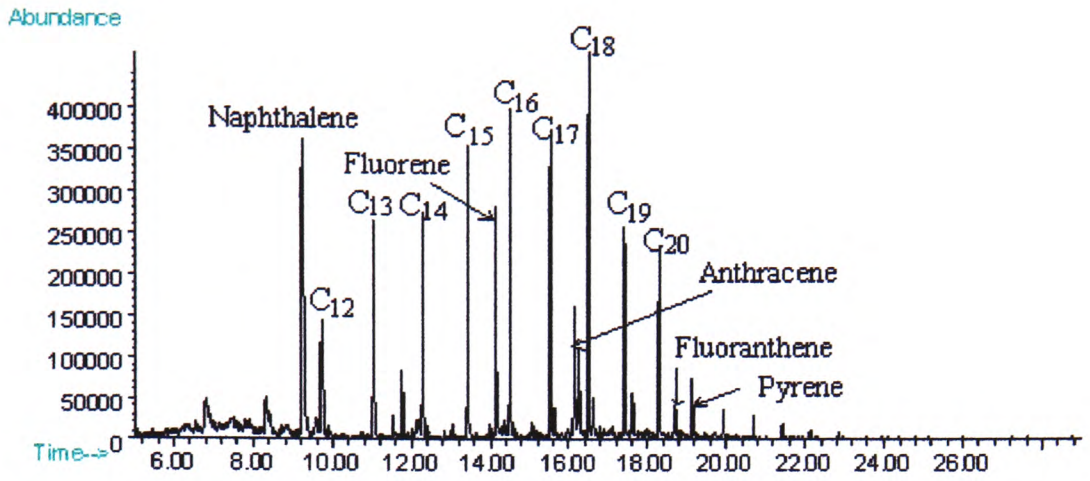

Fig. 3.10 TIC of standard mixture of saturated and aromatic hydrocarbons extracted by SFE at density 0.55 g. cm^{-3}. GC conditions chapter 5.

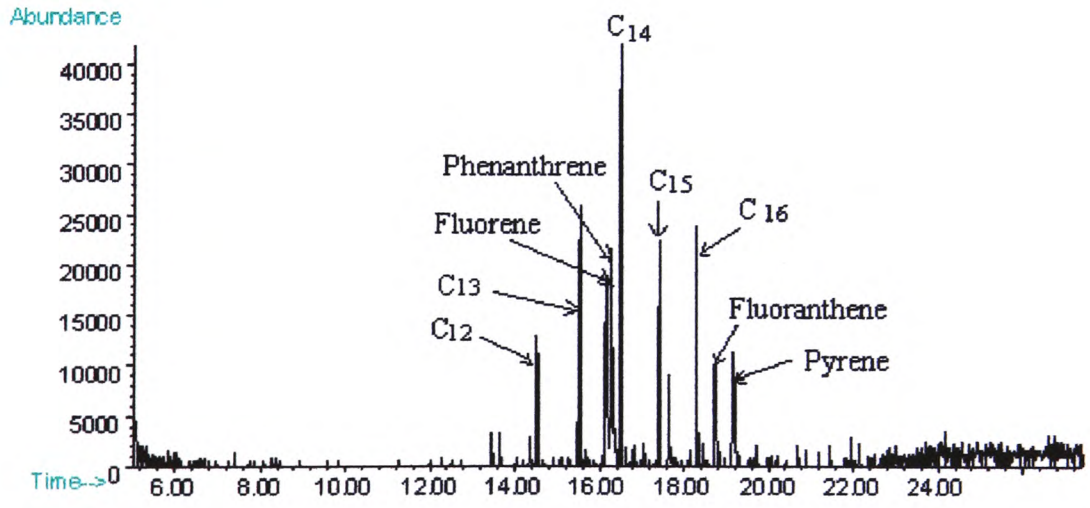

Fig. 3.11 TIC of standard mixture of saturated and aromatic hydrocarbons extracted by SFE at density 0.65 g. cm^{-3}. GC conditions chapter 5.

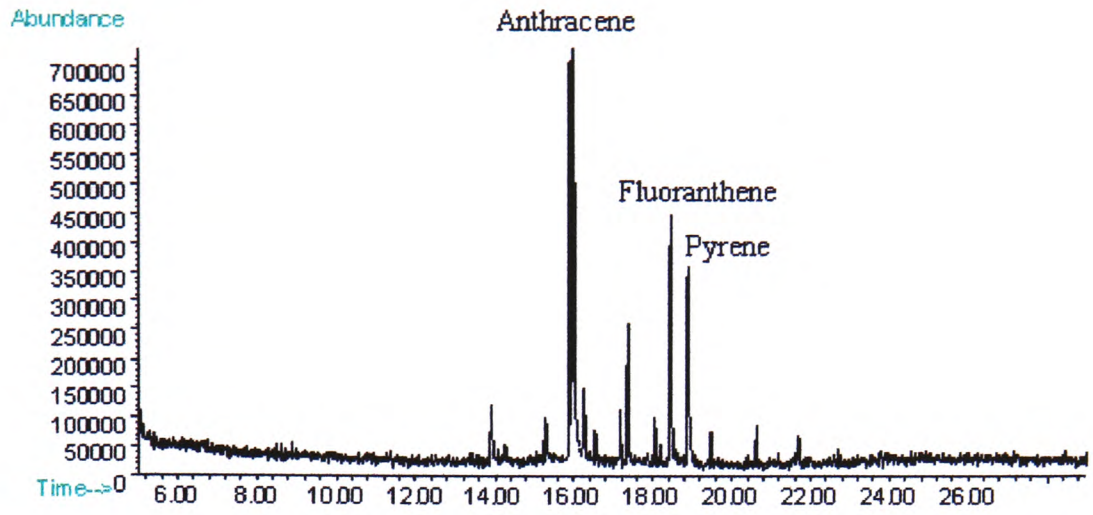

Fig. 3.12 TIC of standard mixture of saturated and aromatic hydrocarbons extracted by SFE at density 0.75 g. cm^{-3}. GC conditions chapter 5.

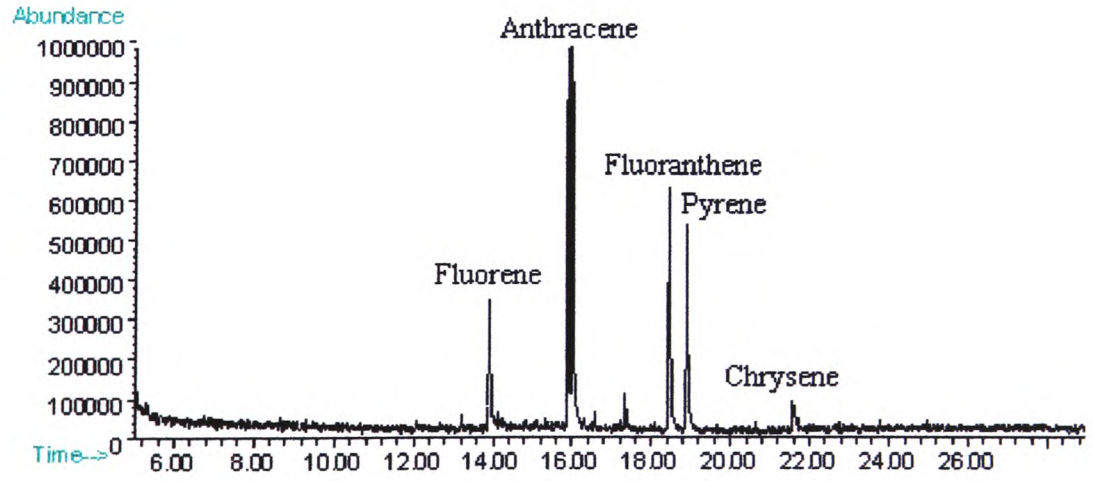

Fig. 3.13 TIC of standard mixture of saturated and aromatic hydrocarbons extracted by SFE at density 0.85 g. cm^{-3}. GC conditions chapter 5.

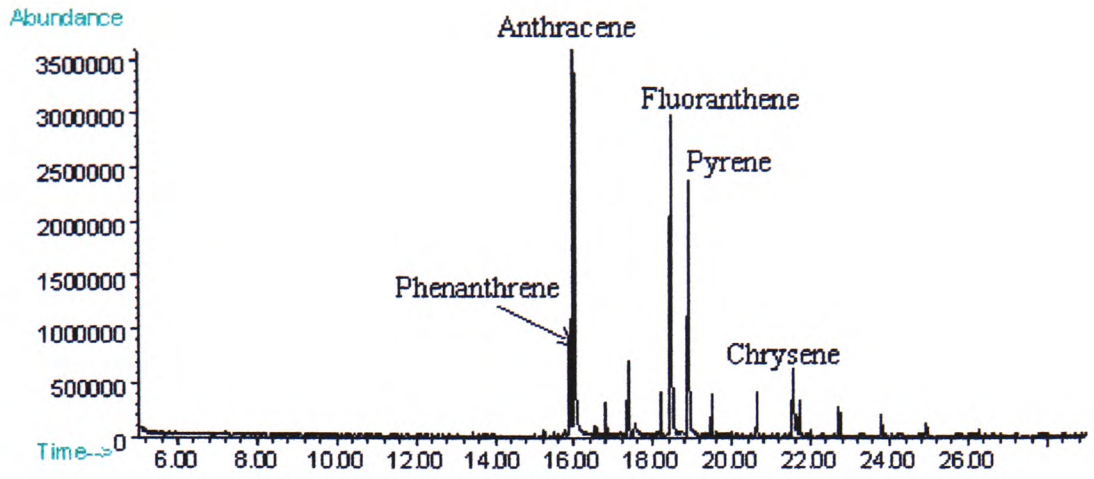

Fig. 3.14 TIC of standard mixture of saturated and aromatic hydrocarbons extracted by SFE at density 0.95 g. cm^{-3}. GC conditions chapter 5.

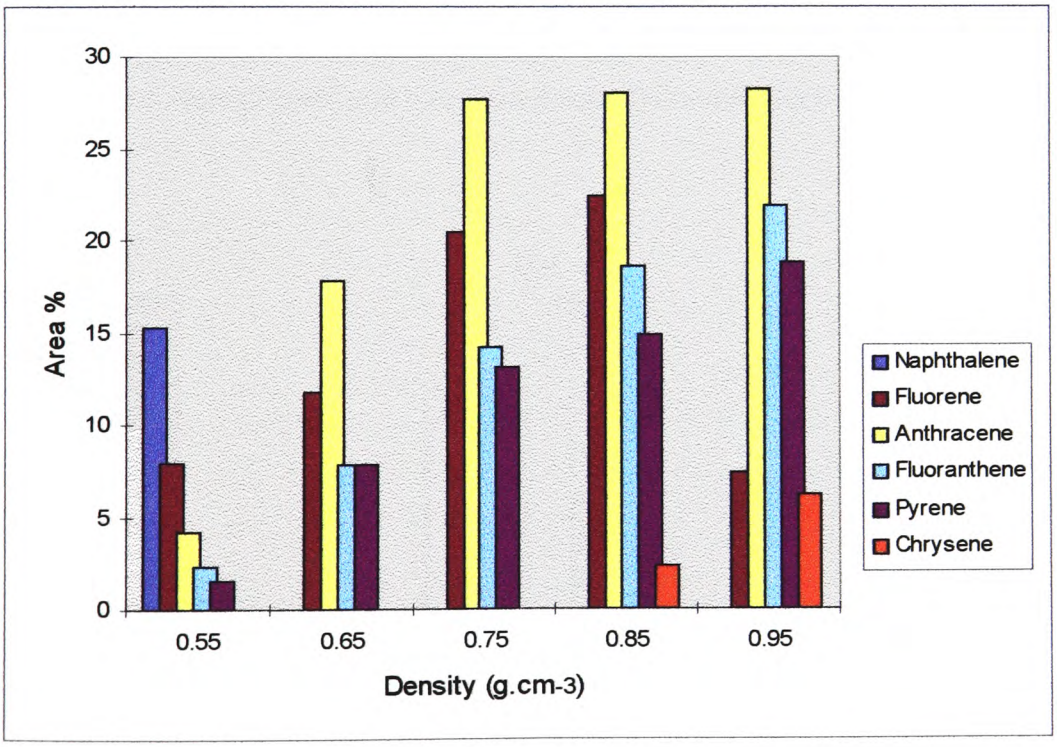

Fig. 3.15 Percent amount (Area %) of extracted PAHs vs. density ($g.cm^{-3}$) of standard mixture of saturated and aromatic hydrocarbons.

3.8.2 Crude oil

3.8.2.1 Optimizing density

Investigations into the class selective fractionation of crude oil were initially performed using exactly the same protocol as used for standard mixture analysis.

Figures 3.16 to 3.19 show the GC-MS analysis of extracts obtained at low densities of 0.25, 0.35, 0.45 and 0.55 g.cm^{-3}.

The equal spacing of the chromatographic peaks is characteristic of homologous hydrocarbon series. The identification of individual straight- chain by mass spectrometry is quite straight forward, since they produce smooth envelopes of major peaks at intervals of 14 mass units (i.e 43, 57, 71, 85, ... etc) corresponding to ions of the type $CH_3\ CH_2\ CH_2^+$, $CH_3\ CH_2\ CH_2\ CH_2^+$, etc. as shown in figure 3.20. Analysis of these chromatograms revealed that no aromatic compounds were present and that class fractionation has been achieved.

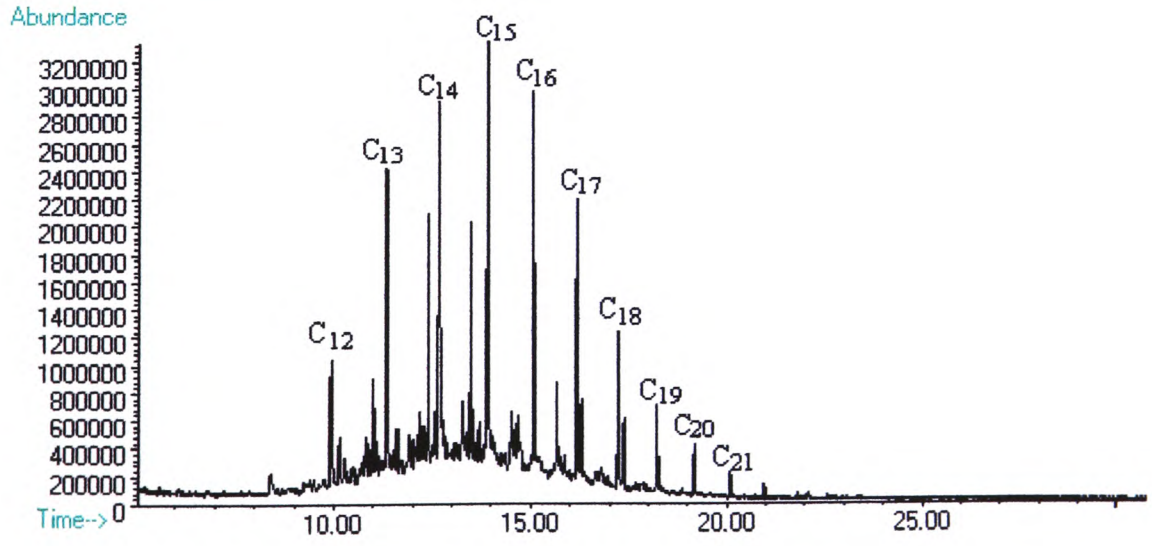

Fig. 3.16 TIC of Bouri crude oil extracted by SFE at density 0.25 g. cm^{-3}. GC conditions chapter 5.

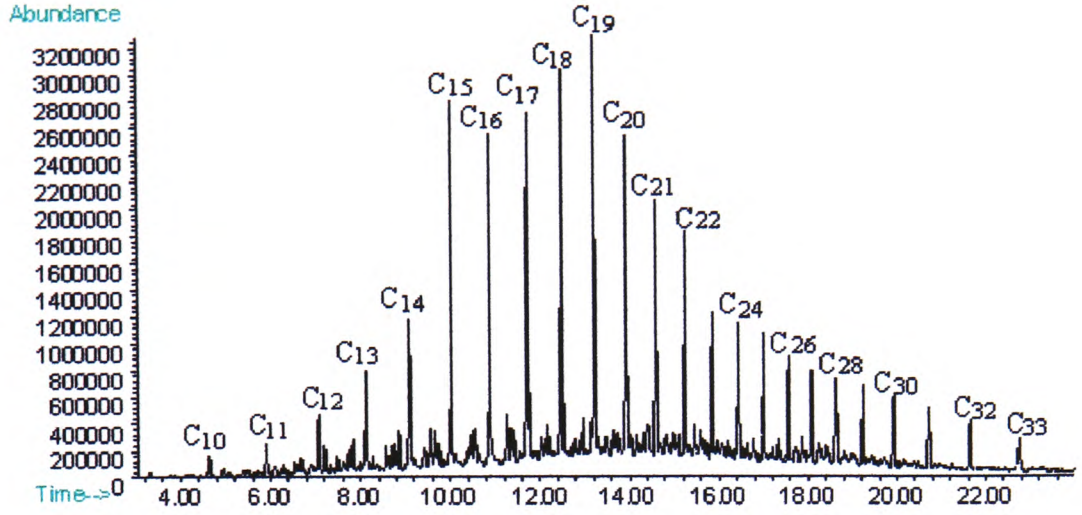

Fig. 3.17 TIC of Bouri crude oil extracted by SFE at density 0.35 g. cm^{-3}. GC conditions chapter 5.

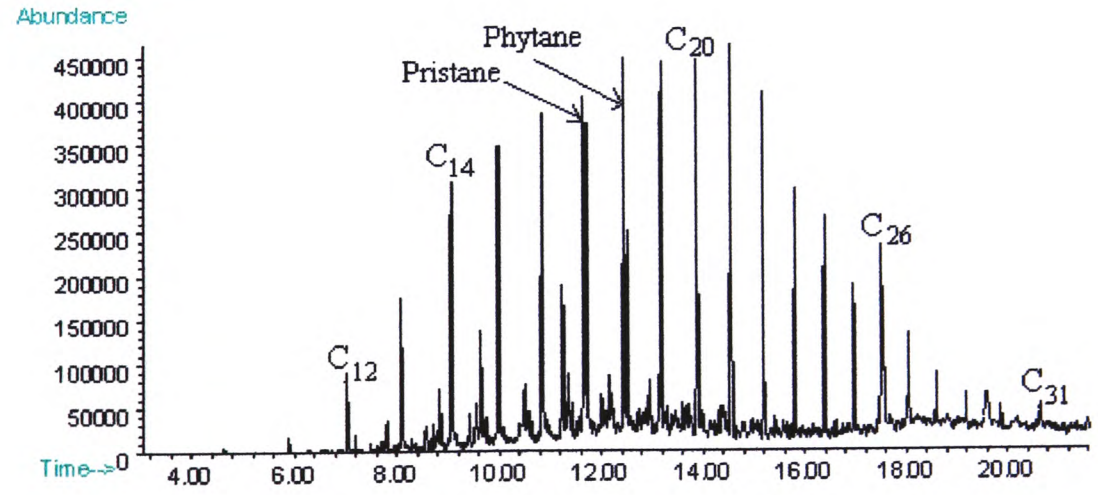

Fig. 3.18 TIC of Bouri crude oil extracted by SFE at density 0.45 g. cm^{-3}. GC conditions chapter 5.

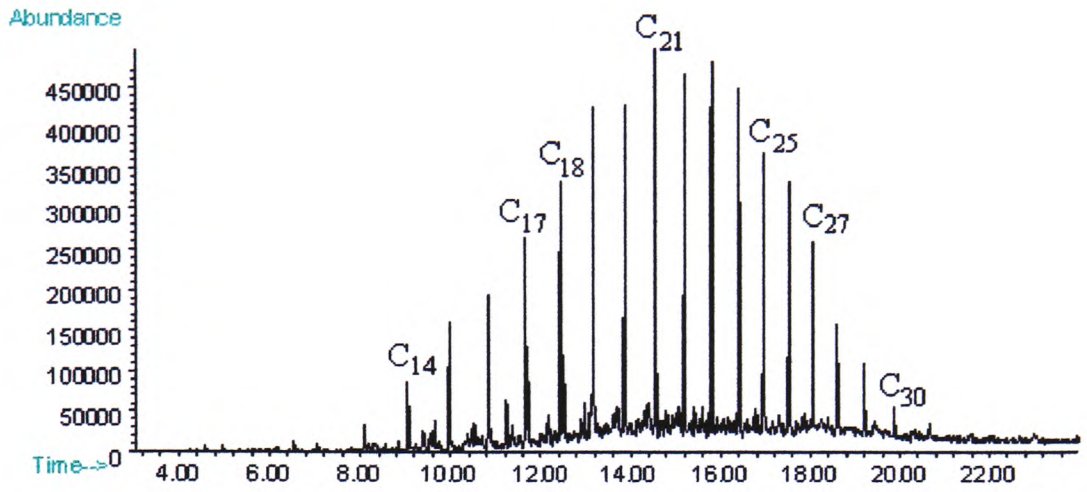

Fig. 3.19 TIC of Bouri crude oil extracted by SFE at density 0.55 g. cm^{-3}. GC conditions chapter 5.

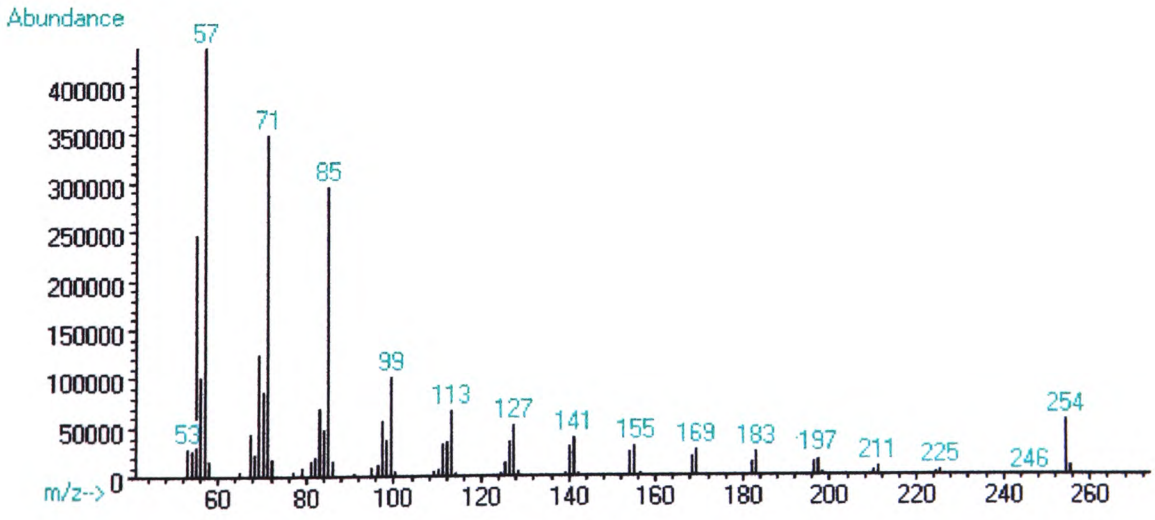

Fig.3.20 Mass spectrum of scan # 838 (12.495 min) at density 0.35 g. cm^{-3} which represent Octadecane ($C_{18}H_{38}$).

Figure 3.21 shows the GC - MS analysis of the fraction obtained at 0.65 $g.cm^{-3}$. Examination of this data revealed that the fraction did contain PAHs however, there was some saturated hydrocarbon present. These results are consistent with observations obtained during standard analysis.

Figures 3.22 to 3.24 show the GC-MS analysis of fractions obtained at 0.75, 0.85 and 0.95 g. cm^{-3} respectively. It can be seen from these TIC, that saturated hydrocarbons are not present in these fractions as evident by the absence of chromatographic envelopes of homologous series. Further analysis of the data indicated fraction contents dominated by alkylated series of 2, 3, 4 and 5 ring PAHs. Figures 3.25 to 3.28 represent homologous series of alkylated naphthalene, phenanthrene, pyrene and chrysene respectively.

The major constituents identified in the later two fractions (0.85, 0.95 $g.cm^{-3}$) were alkalated pyrene, benz (a) anthracene, triphenylene, 1H-indole, chrysene, and fluoranthene.

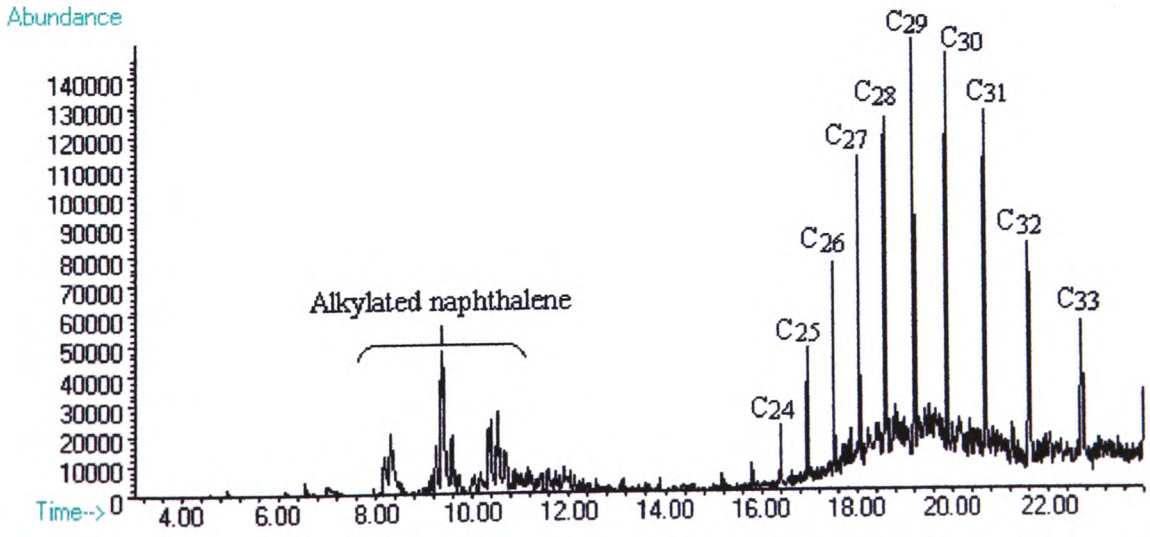

Fig. 3.21 TIC of Bouri crude oil extracted by SFE at density 0.65 g. cm^{-3}. GC conditions chapter 5.

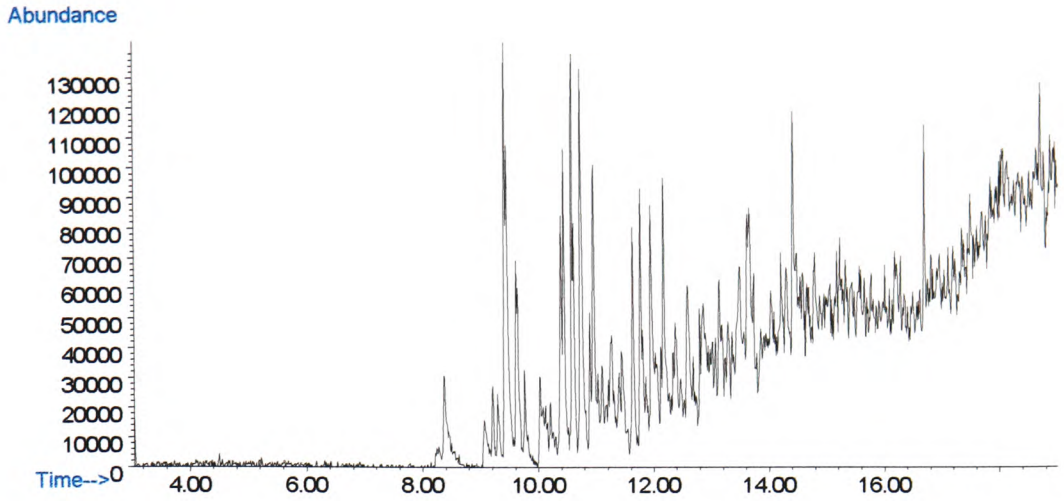

Fig. 3.22 TIC of Bouri crude oil extracted by SFE at density 0.75 g. cm^{-3}. GC conditions chapter 5.

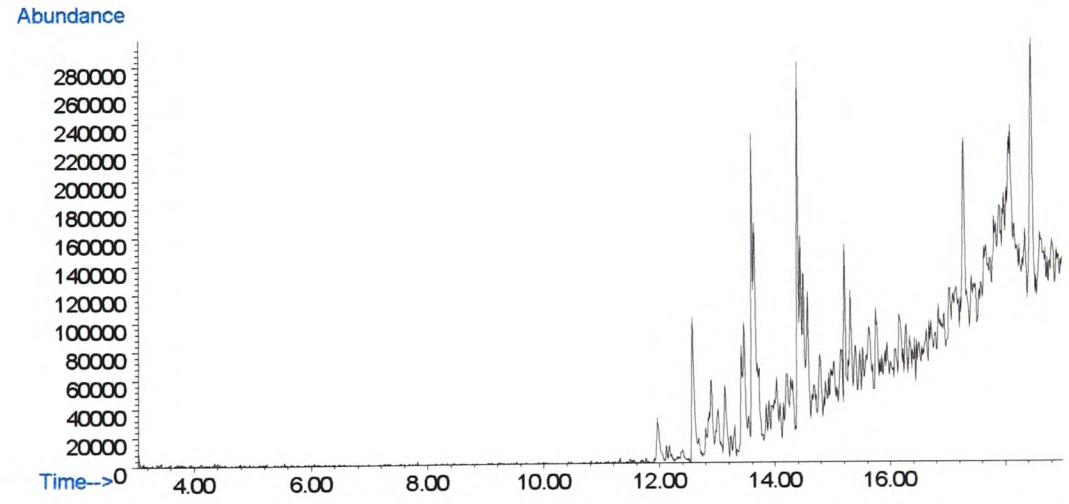

Fig. 3.23 TIC of Bouri crude oil extracted by SFE at density 0.85 g. cm^{-3}. GC conditions chapter 5.

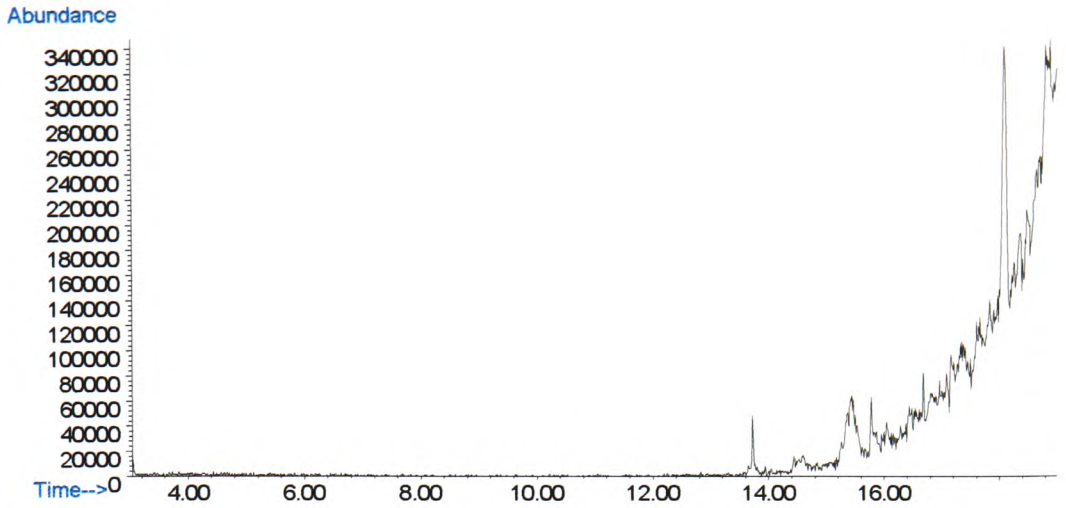

Fig. 3.24 TIC of Bouri crude oil extracted by SFE at density 0.95 g. cm^{-3}. GC conditions chapter 5.

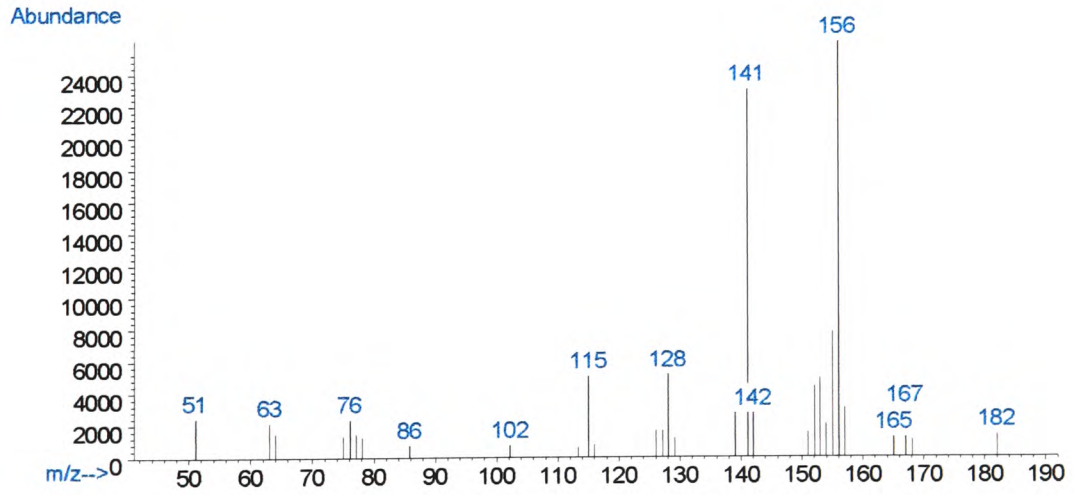

Figure 3.25 Mass spectra of alkyl naphthalene scan # 567 (m/z 156) obtained from Bouri crude oil at density 0.75 g. cm^{-3} (fig.3.22).

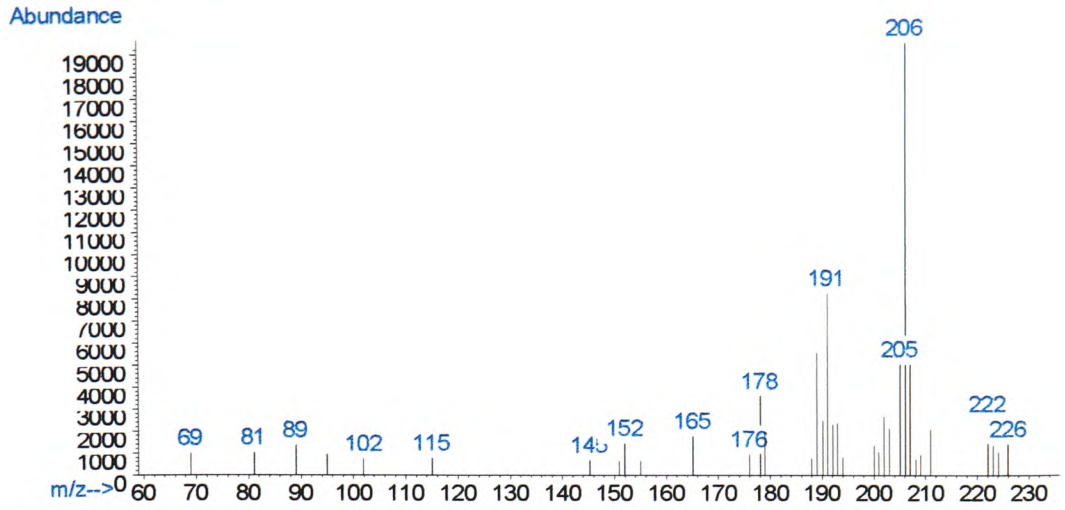

Figure 3.26 Mass spectra of alkyl phenanthrene scan # 1016 (m/z 206) obtained from Bouri crude oil at density 0.85 g. cm^{-3} (fig.3.23).

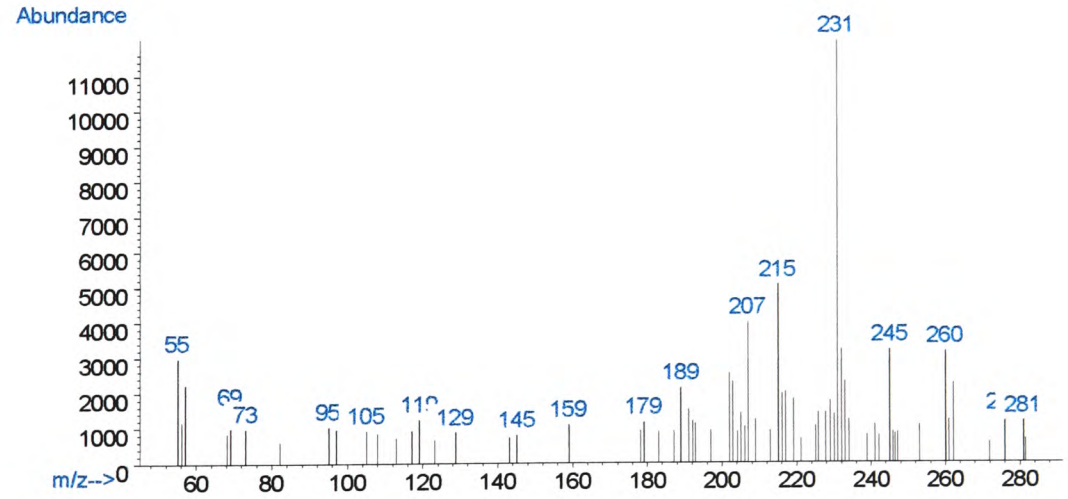

Figure 3.27 Mass spectra of alkyl pyrene scan # 1234 (m/z 231) obtained from Bouri crude oil at density 0.85 g. cm^{-3} (fig.3.23).

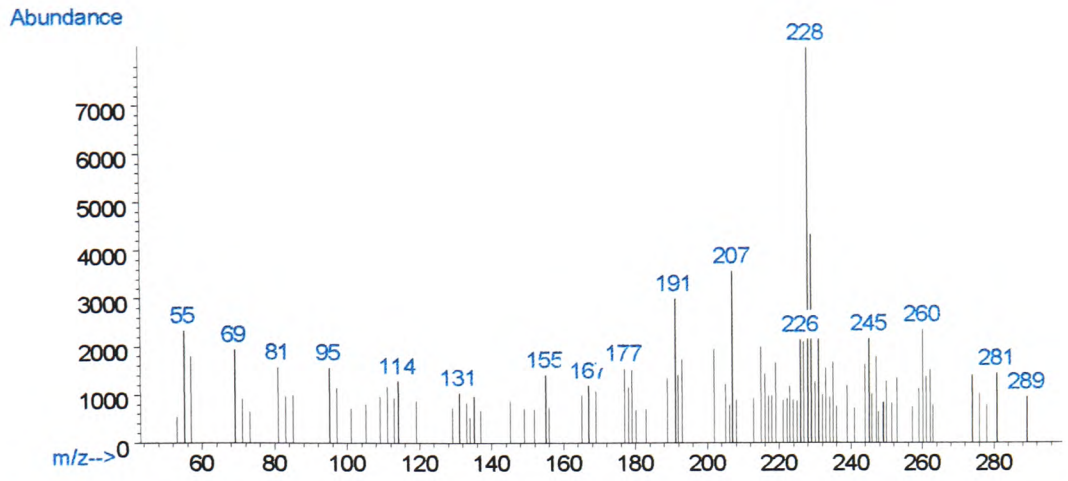

Figure 3.28 Mass spectra of alkyl chrysene scan # 1234 (m/z 228) obtained from Bouri crude oil at density 0.85 g. cm^{-3} (fig.3.23).

A further series of extraction tests, using Bouri, Sidra and Zweteena crude oils were performed at densities of 0.45-0.85 $g.cm^{-3}$ while keeping the temperature at 40 ^0C and CO_2 flow 1 cm^3 min^{-1} as illustrated in Table 3.4. The extraction results (fig 3.29) suggest that for a 5 min extraction, the percent oil removed is the lowest at 0.45 $g.cm^{-3}$ and the highest at densities of 0.65 and 0.75 $g.cm^{-3}$. Density of 0.85 $g.cm^{-3}$ produces a slight decrease in recovery.

This observation is consistent with our studies using the standard mixture. With increasing density the solvating power is increased, but at higher densities the diffusion coefficient is decreased. This can cause lower recoveries as a result of the slower rate of the extraction processes [47]. Another explanation is that trapping may be inefficient at higher pressure.

Overall, it was concluded that class selectivity of crude oils could be achieved using the described protocol. Saturated hydrocarbons being extracted at densities below 0.65 $g.cm^{-3}$ and aromatics above this value. However, there was some co-extraction at 0.65 $g.cm^{-3}$.

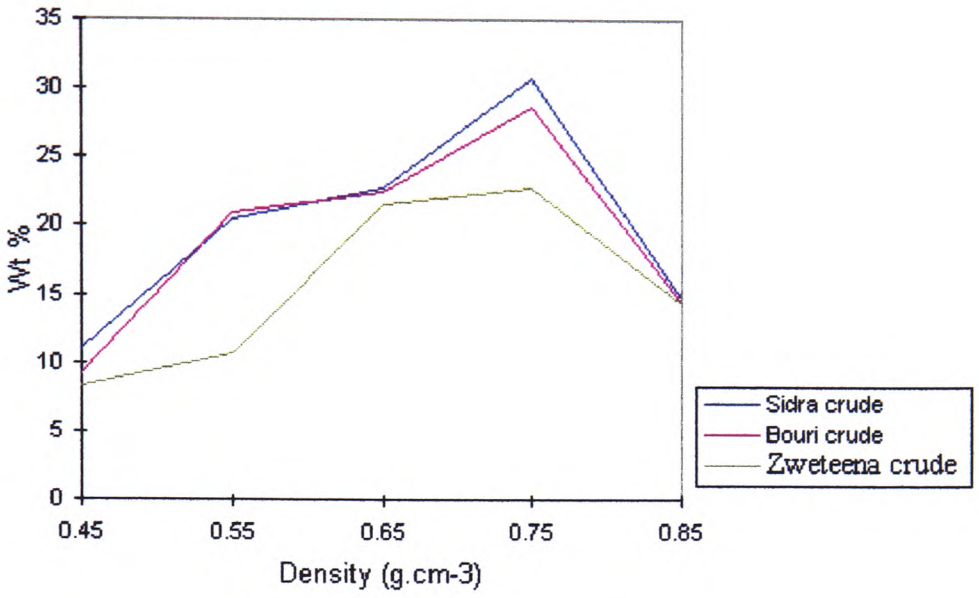

Fig. 3.29. Effect of density on the recovery (%) of crude oils.

A second set of experiments (type 2, figure.3.6) were performed to ascertain if the actual protocol (experiment type 1 or 2) could effect fractionation efficiency. For instance, a cumulative density extraction (experiment type 2) may produce a different extraction profile of crude oil than direct single density extraction. For this, samples were extracted at one particular density keeping all other conditions identical to those used in the experiment 1.

Examination of the GC-MS analyses obtained for fractions of Bouri crude obtained at 0.65, 0.75 and 0.85 $g.cm^{-3}$ indicate that saturated hydrocarbons are co-extracted with PAH at all densities as shown in Figures 3.31 to 3.33. And that class selectivity could not be achieved using the single density extraction approach. Based on these findings it was decided to adopt the experiment type 1 protocol for further investigations.

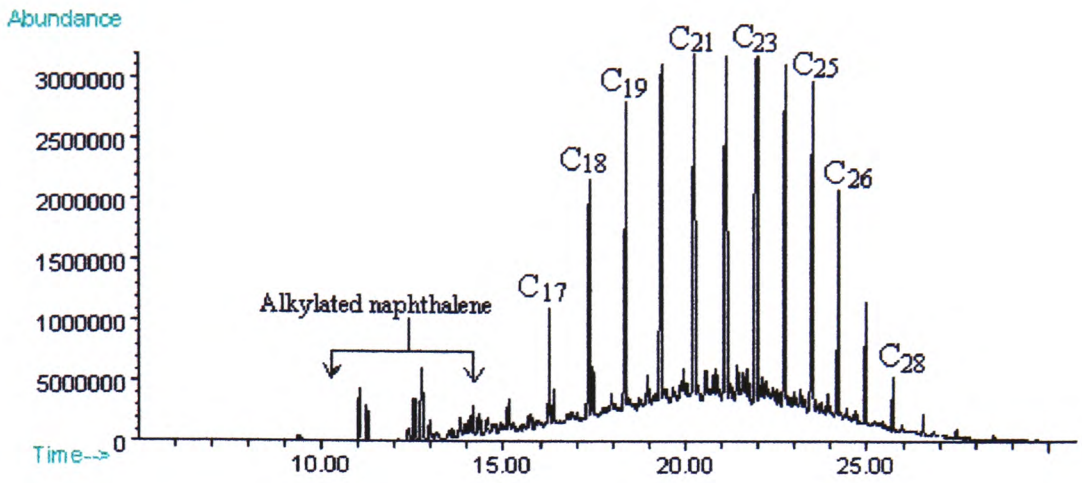

Fig. 3.31 TIC of Sirte crude oil extracted by SFE (experiment type 2) at density 0.65 g. cm^{-3}. GC conditions chapter 5.

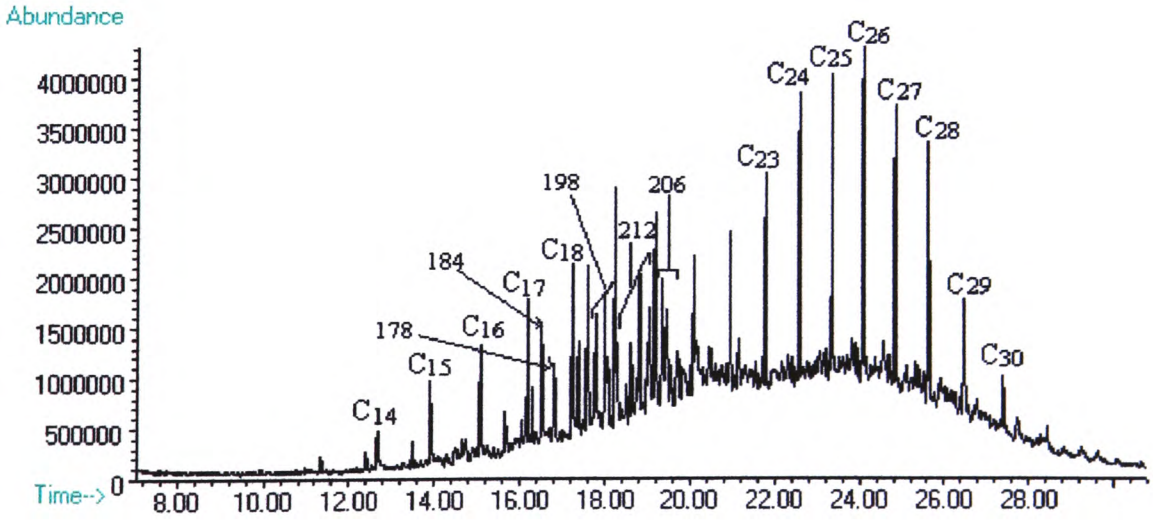

Fig. 3.32 TIC of Bouri crude oil extracted by SFE (experiment type 2) at density 0.75 g. cm^{-3}. GC conditions chapter 5.

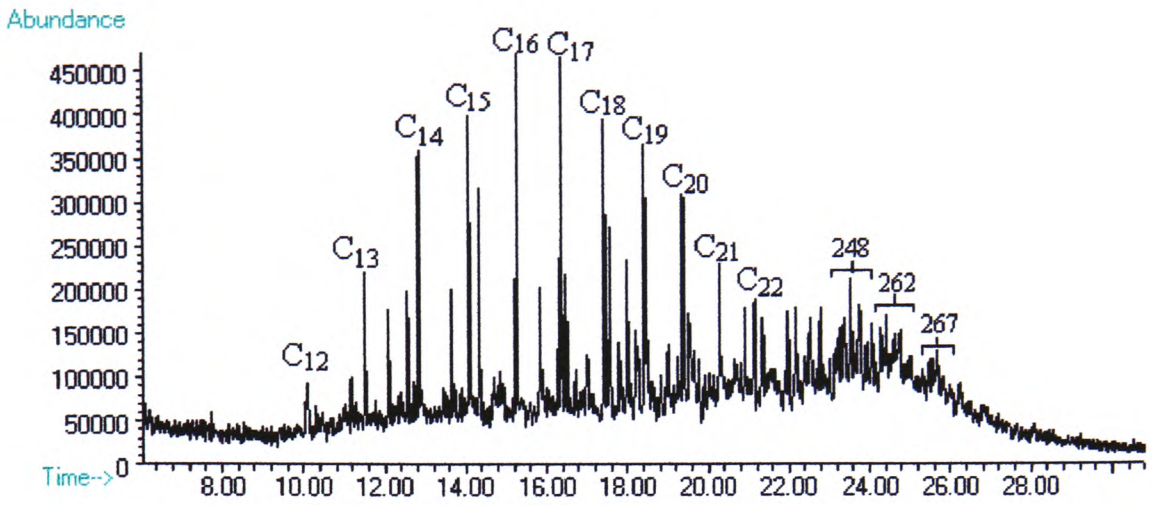

Fig. 3.33 TIC of Bouri crude oil extracted by SFE (experiment type 2) at density 0.85 g. cm^{-3}. GC conditions chapter 5.

3.8.2.2 Effect of temperature

The second SFE parameter that was investigated was the extraction temperature. Temperature is a very important factor to consider for the optimization of extraction conditions. In general, supercritical fluids are more effective extracting agents when the extraction is performed at a temperature above the melting point of the analyte. Raising the temperature can add thermal energy to the system and increase partial pressure. Mass transfer of the solute in the SF is improved as cohesive forces of the solid decreases, knowledge of the vapor pressure of solute as a function of temperature can have a profound effect on both the recorded solubility and the separation factors that are obtained in a multi-component solute separation scheme [48].

Earlier investigations demonstrated that raising the temperature of the extraction cell from 50 to 200 ^0C using pure CO_2 can dramatically increase the recoveries of PAHs and PCBs from environmental solids despite the fact that the

density of the CO_2 drops dramatically [49]. To determine if this effect can be used to increase fractionation efficiency of PAHs from saturated hydrocarbons in crude oil, samples of Bouri crude oil were extracted at 40, 60, 80, and 100 ^{0}C. All other parameters were identical to those used previously (Experiment type 1).

Step 1.

The first set of experiments involved extraction using pure CO_2 at eight different densities; 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85, and 0.95 g.cm^{-3} at temperature of 40 ^{0}C. As expected, progressively higher molecular weight compounds were extracted with increase in density as previously established.

Step 2.

Next, SFE was repeated using the same conditions as for step 1, except the extraction temperature was increased to 60 ^{0}C. In this case the maximum upper density limit obtained was 0.85 g. cm^{-3}.

Examination of the total ion chromatograms obtained for Bouri crude at this temperature (60 ^{0}C) revealed that PAHs were only present in the extract obtained at 0.65 g.cm^{-3} as shown in Figures 3.34 to3.36. All fractions obtained contained saturated hydrocarbons and overall oil recoveries were below that at lower temperature (fig. 3.40). It has been reported [49] that a significant reduction in oil recovery will result if CO_2 is used at elevated temperatures. The phase transition at this temperature appeared to shift from a liquid-liquid (L-L) -like system to a liquid-vapor (L-V)-like system at the higher temperature. This observation can be explained by the sharp decrease in CO_2 density corresponding to the extraction performance. It is known that the L-L system exhibits considerably greater oil extraction capability than the L-V system, the behavior is also consistent with a marked drop in the reduced density of CO_2 at the higher temperature [50].

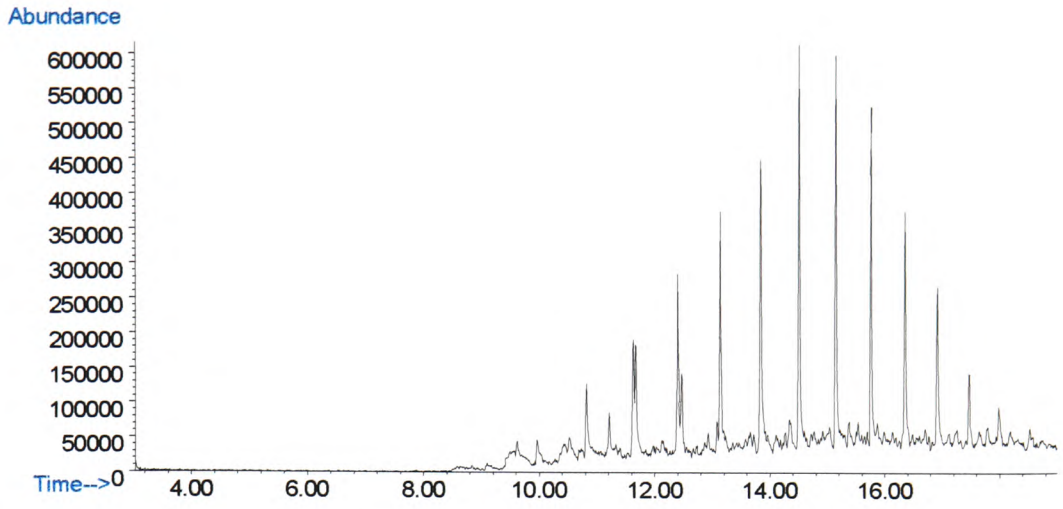

Fig. 3.34 TIC of Bouri crude oil extracted by SFE at density(0.65 g. cm^{-3}) and temperature(60 ^{0}C). GC conditions chapter 5.

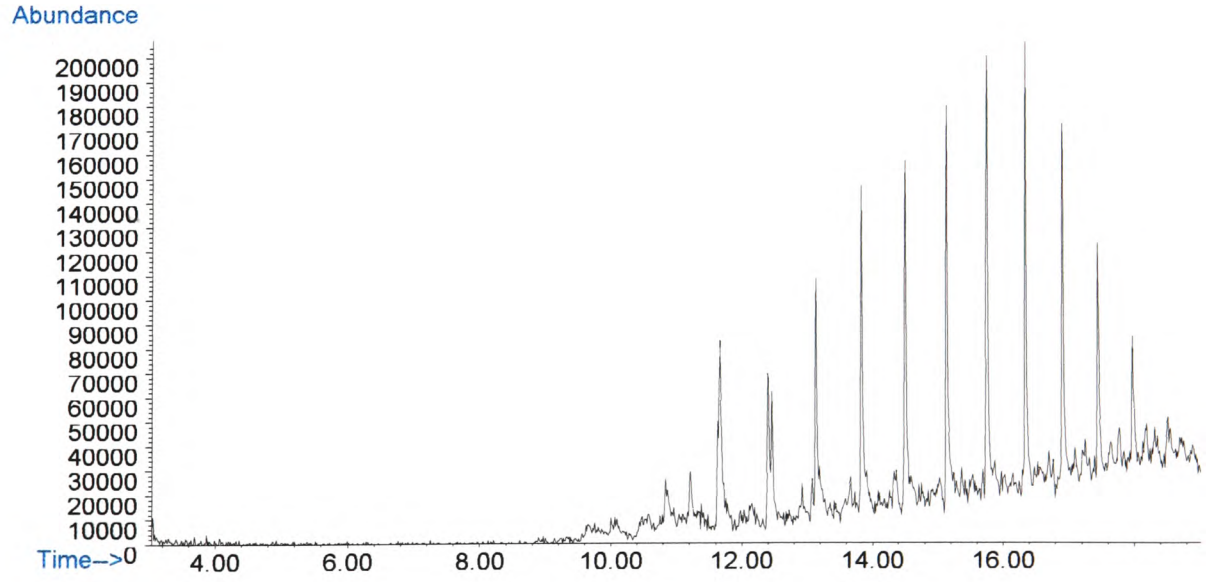

Fig. 3.35 TIC of Bouri crude oil extracted by SFE at density(0.75 g. cm^{-3}) and temperature(60 ^{0}C). GC conditions chapter 5.

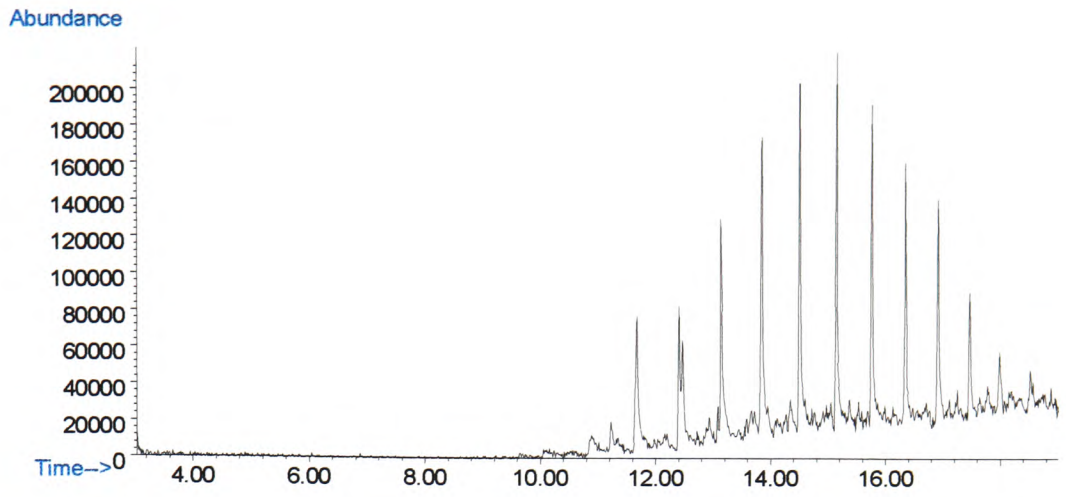

Fig. 3.36 TIC of Bouri crude oil extracted by SFE at density(0.85 g. cm^{-3}) and temperature(60 ^{0}C). GC conditions chapter 5.

Step 3 and 4 :

Extractions were repeated, again using the same conditions but at temperatures of 80 and 100 ^{0}C. In both cases the maximum density achieved were 0.75 g.cm^{-3} and 0.65 g.cm^{-3} respectively. Results obtained from these investigations indicate that all fractions contained exclusively saturated hydrocarbons, no PAHs were present. Figures 3.37 to 3.39 Again, the total oil recoveries were much lower than were achieved in previous studies using lower temperatures(Fig. 3.40). We think that this can be explained by the fact that a shift from a liquid-liquid (L-L) like system to a liquid - vapor (L-V) like system occurs at the higher temperature. It is known that the L-L system exhibits considerably greater oil extraction capability than the L-V system. This observation can be explained by the sharp decrease in CO_2 density corresponding to the extraction performance [50].

This behavior is too complex to be interpreted exactly, it may be regarded as due to the competing effects between the solvent density and solute volatility[51]. As temperature increases, solvent density decreases and solute volatility increases. The decrease in the solvent density decreases the probability of a given solute molecule

in the extractant phase interacting with a solvent molecule, tending to decrease solubility. Increasing solute volatility, on the other hand, increases the escaping tendency of the solute from the condensed phase, thus tending to increase solubility.

It was concluded that elevated temperatures (> 45 ^{0}C) produced inferior extraction recovery and selectivity and that low temperatures (< 45 ^{0}C) would be used in further work.

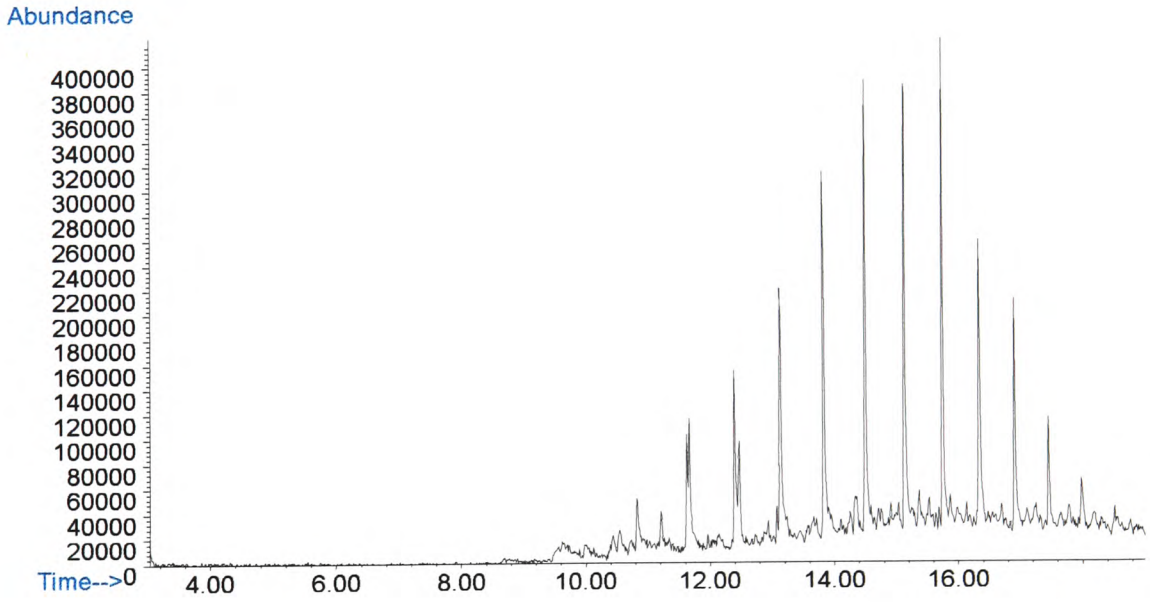

Fig. 3.37 TIC of Bouri crude oil extracted by SFE at density(0.65 g. cm^{-3}) and temperature(80 ^{0}C). GC conditions chapter 5.

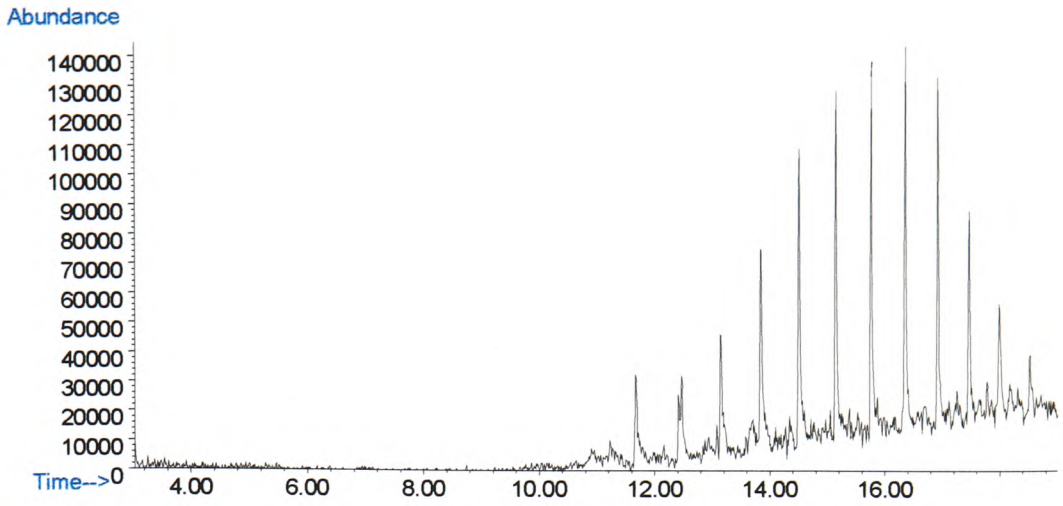

Fig. 3.38 TIC of Bouri crude oil extracted by SFE at density(0.75 g. cm^{-3}) and temperature(80 ^{0}C). GC conditions chapter 5.

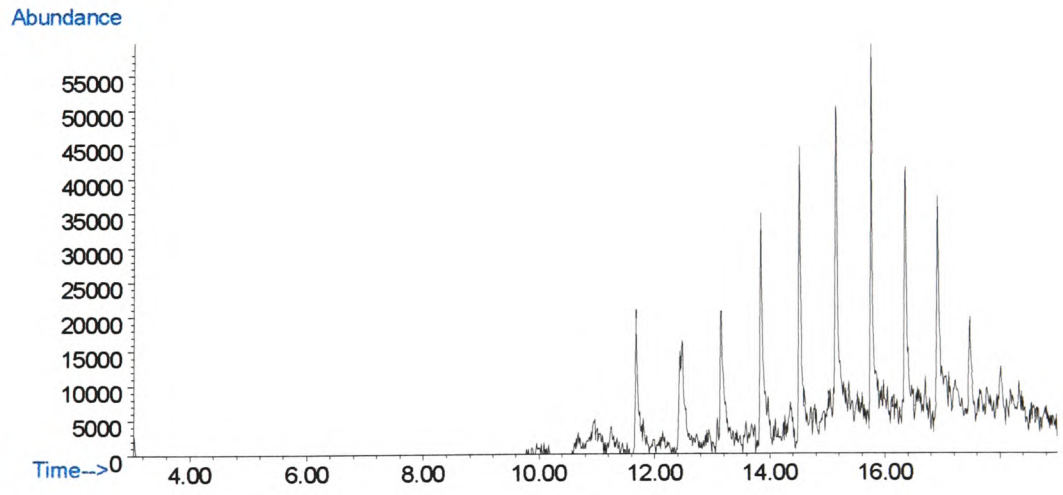

Fig. 3.39 TIC of Bouri crude oil extracted by SFE at density (0.65 g. cm^{-3}) and temperature(100 ^{0}C). GC conditions chapter 5.

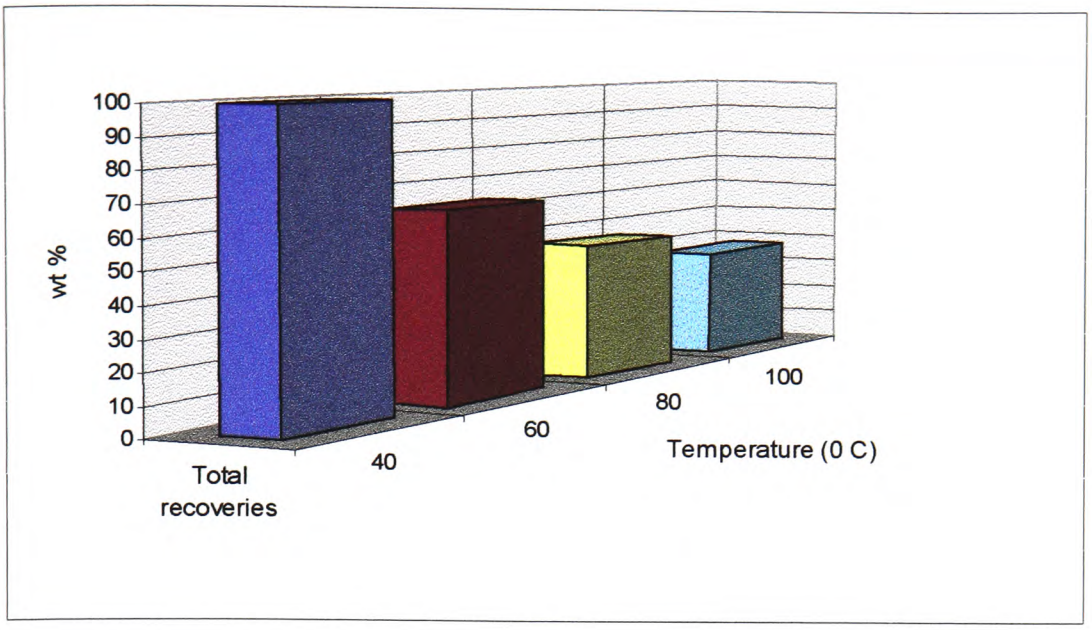

Fig. 3 40 Influence of the extraction pressure at 40, 60, 80 and 100 ^{0}C extraction temperature on the total recoveries of Bouri crude oil at density 0.65 g. cm^{-3}. GC conditions chapter 5.

3.8.2.3 Sample ratio considerations

A major variable that could significantly influence the fractionation efficiency of our protocol was that of the oil/silica ratio. The addition of too much oil to the activated silica could overload it, thus reducing the selective adsorptivity of the support and hence, the selectivity of extraction .

Our investigations continued in order to assess the effect of this ratio. A series of 3 extractions were performed using the same (experiment type 1) conditions (Table 3.4) except the silica loading was different in each case, these were: 1/45, 1/33 and 1/15 (sample/silica gel).

Figure 3.41 shows the trend of recoveries of Bouri Crude oil obtained at different sample/silica gel ratios. Inspection of the figure shows that maximum recovery for all ratios occurs at 0.75 g.cm^{-3} before decreasing at higher densities.

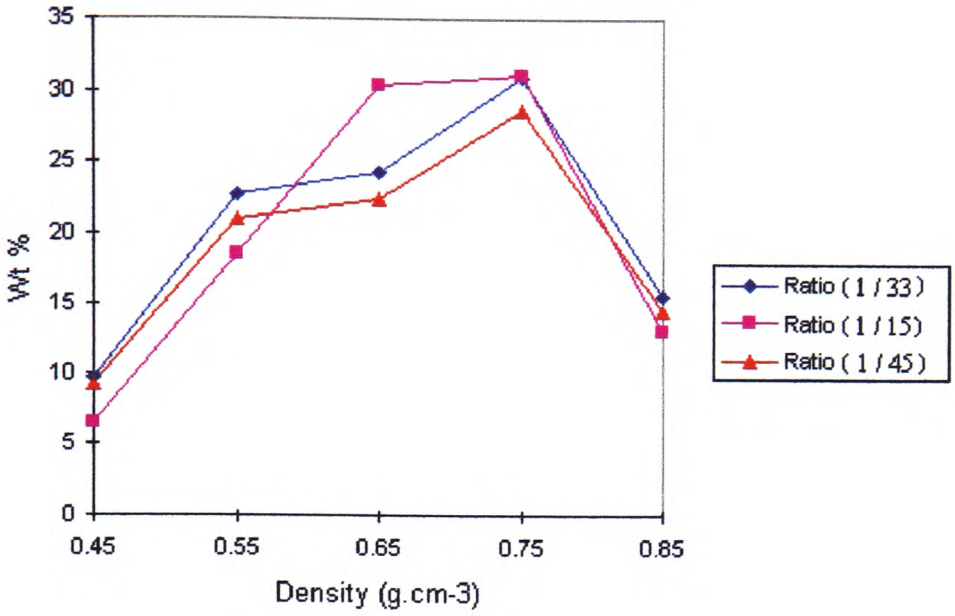

Fig.3.41 Plot of recovery (wt %) vs. Density (g. cm^{-3}) for Bouri crude oil at various sample/silica gel ratio.

Figures 3.42 to 3. 44 show the GC-MS analysis of fractions of Bouri crude oil that had been extracted at density 0.75 g. cm^{-3} with oil/silica ratios 1/45, 1/33 and 1/15 (sample/silica gel). It is evident that compound class overlap exists in fractions obtained using ratios of 1/33 and 1/45 as shown in Figures 3.42 and 3.43. However, further analysis of data obtained for the sample with a ratio of 1/15 (figure. 3.44) demonstrated that there was no saturate/aromatic overlapping in this fraction and that complete fractionation has been achieved. This observation is consistent with the results obtained using the authatic standard mixture.

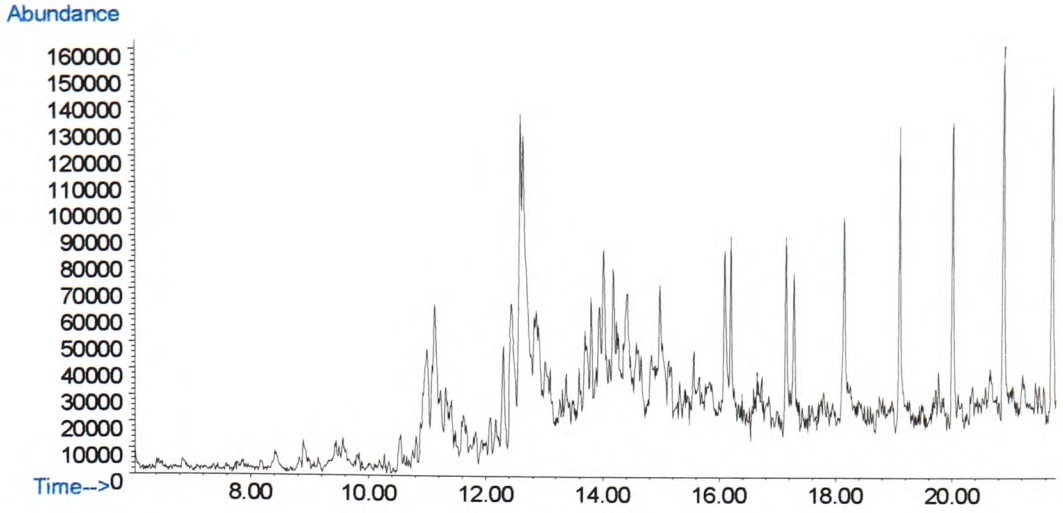

Fig.3.42 TIC of Bouri crude oil extracted by SFE at sample/silica gel ratio (1/33) and density (0.75).

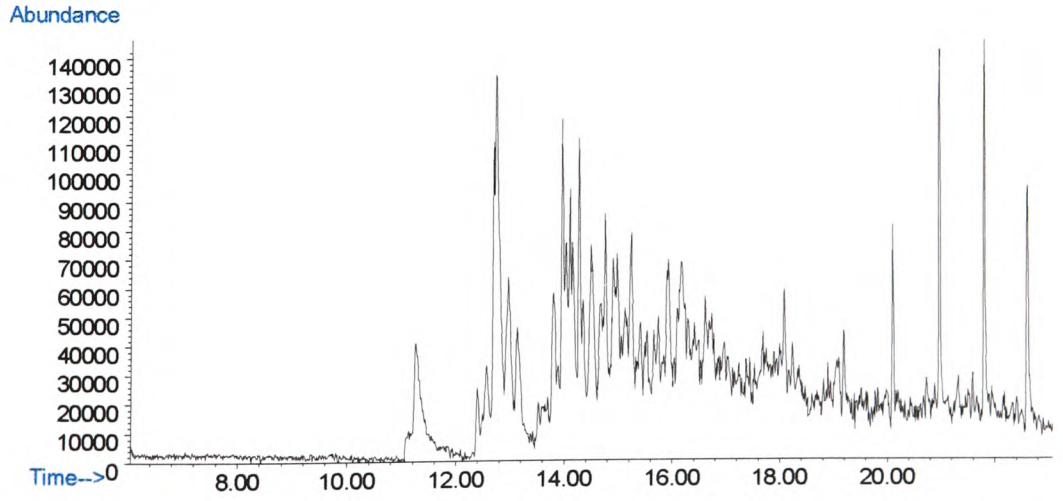

Fig.3.43 TIC of Bouri crude oil extracted by SFE at sample/silica gel ratio (1/45) and density (0.75).

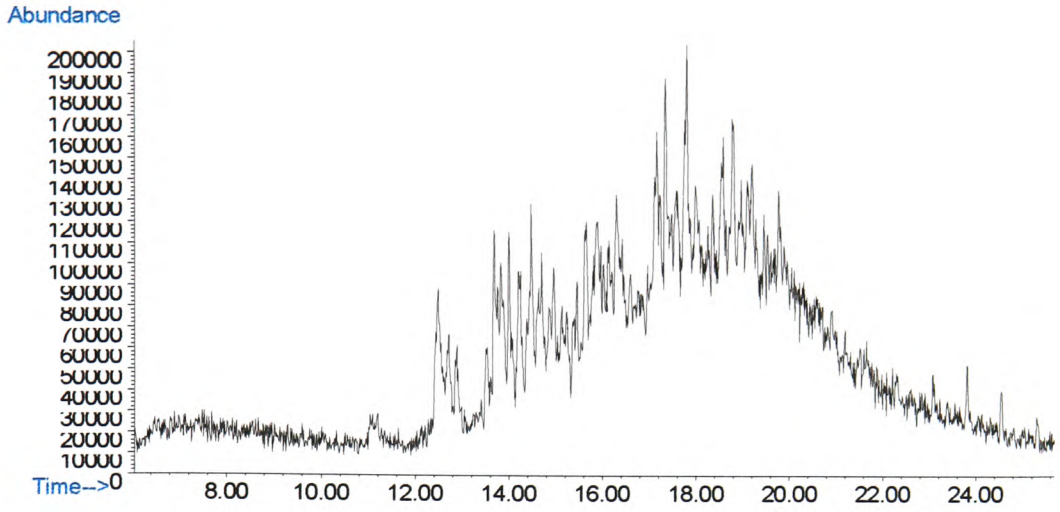

Fig.3.44 TIC of Bouri crude oil extracted by SFE at sample/silica gel ratio (1/15) and density (0.75).

3.8.2.4 Effect of modifier

100 % carbon dioxide is normally used as the extraction medium in most SFE protocols. In certain instances, however, CO_2 has limited solvating power for highly polar and moderately polar/high molecular weigh compounds, even at high density. The recovery of polar analytes requires the use of fluids more polar than pure CO_2. A useful method of increasing this solvating power is to use a solvent modifier (cosolvents or entrainers).The action of modifier in SFE is to increase the solubility of the target analyte in the medium as a whole or interact with active sites on the sample matrix, thus releasing the analyte. Table 3.5 shows a listing of the various modifiers [52] that have been used with CO_2 as the primary supercritical fluid. The most commonly used modifiers are alcohols i.e.: methanol .

Table 3.5 Modifiers that have been used in supercritical fluid technology with carbon dioxide as the primary supercritical fluid [52].

n-Butanol	Methylene chloride
Methanol	n-Pentanol
Chloroform	n-Hexanol
Diethyl ether	Isopropanol
Ethanol	Formic acid
Ethyl acetate	Carbon disulfide
n-Hexane	2-Pentanol
Acetonitrile	Tetrahydrofuran
n-Heptanol	Trichlorofluoromethane
n-Decanol	Water

In general, the solvent modifier selected should be a "good" solvent for the analyte of interest. The choice of modifier is dependent on the sample matrix and the analyte to be extracted, some times, several different modifiers can be used for a particular sample, i.e. both 10 % toluene and 5 % methanol have been show to provide maximum recovery of spiked PAHs in soil samples [53].

There are numerous methods of adding solvent modifier to the carbon dioxide. For our studies modifier was dynamically added to the supply of CO_2 using a slave Hplc pump. Modifier enters the extraction system via a thermostatic mixing tee. This tee mixes the modifier with CO_2, equilibrates the fluid in a thermostatic zone and then delivers the mixed fluid to the thimble.

A series of extractions were performed under previously optimized conditions using 5 % and 10 % addition of methanol.

Again, data analysis revealed that a significant reduction in PAHs recovrey. This could be explained in two ways, either the addition of 10 % methanol makes the supercritical CO_2 too polar thus the PAHs become insoluble in the extraction

medium or that the presence of 10 % methanol in the final extract causes a decrease in the efficiency of the SFE trap, i.e. extracted PAHs are washed off of the trap to waste. To determine if this was the case, collection and analysis of the actual waste would be necessary. Unfortunately time did not permit this. 5 % methanol has significant influences on replacing the analyte from active site is demented and the recovery are improved.

Figures 3.45 shown the actual recoveries of PAHs extracted from Bouri crude oil with carbon dioxide and 0 %, 5 %, and 10 % methanol.

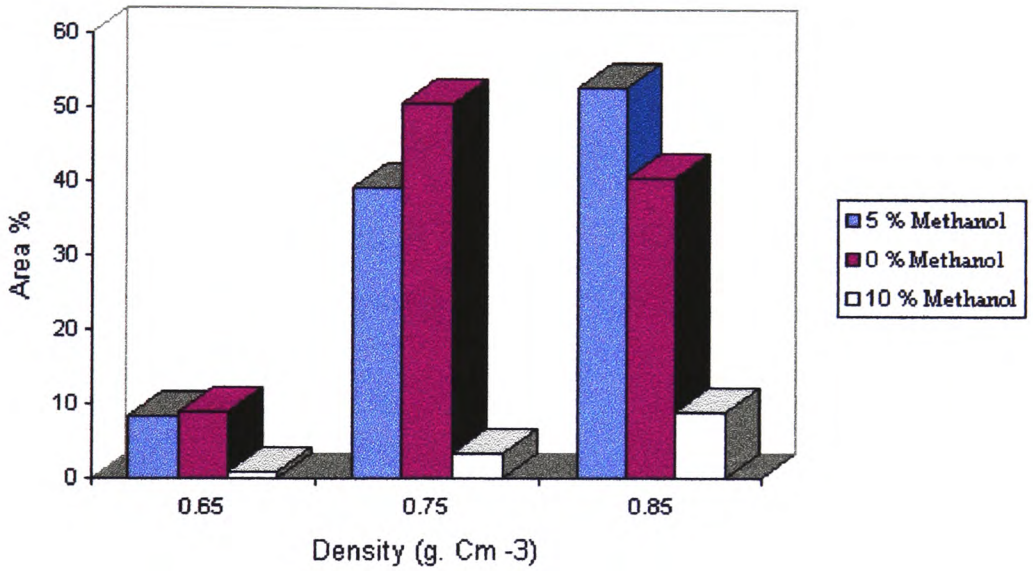

Fig.3.45 SFE efficiency comparison using CO_2 and CO_2/methanol modifier at various density.

3.8.2.5 Effect of extraction time

Our studies continued in order to investigate the influence of extraction time initial extraction on recoveries. For this, three experiments were performed at different extraction times (5, 10 and 15 min.). All other parameters were identical to those used previously as shown in Figure 3.6.

As mentioned previously the color differences between extracts can provided visual evidence of compositional variations as a function of time. Extracts obtained using shorter times were relatively colorless indicating that saturated hydrocarbons were extracted during this period. Those obtained at longer times become increasingly colored typically containing more polar, less volatile components. This was confirmed by GC-MS analysis of five Libyan crude oils, which indicated that the saturated hydrocarbons were extracted using shorter extraction times and the more polar and aromatic compounds were extracted with increasing extraction time.

The results are summarized in figure 3.46. In addition to confirming that class selectivity had be achieved the results show that an increased extraction time provides increased recoveries i.e. From 17.5 % (5 min) to 26.5 % (15 min) at 0.75 g. cm^{-3}. As can be seen from figures 3.47 to 3.49 complete class fractionation was achieved at 5 minutes.

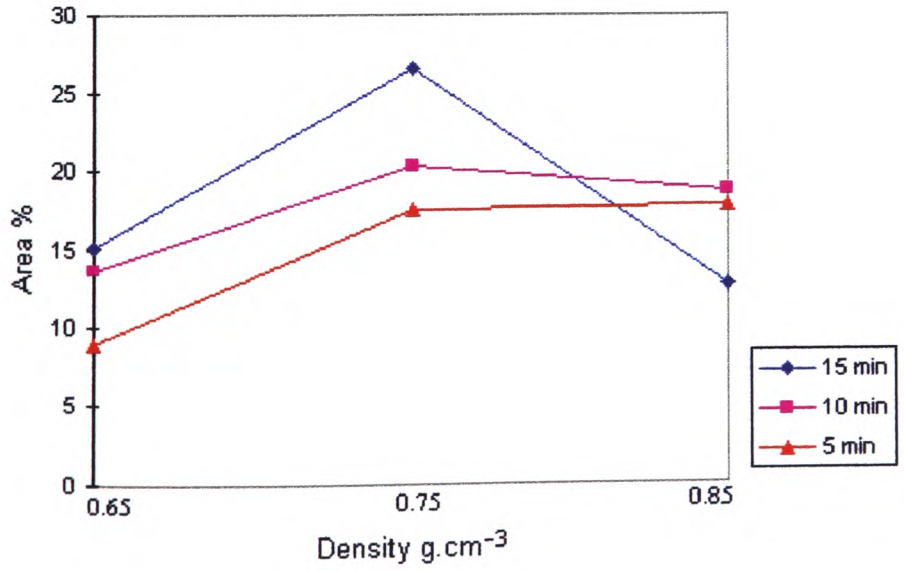

Fig. 3.46 Percent amount of extracted PAHs at various extraction time.

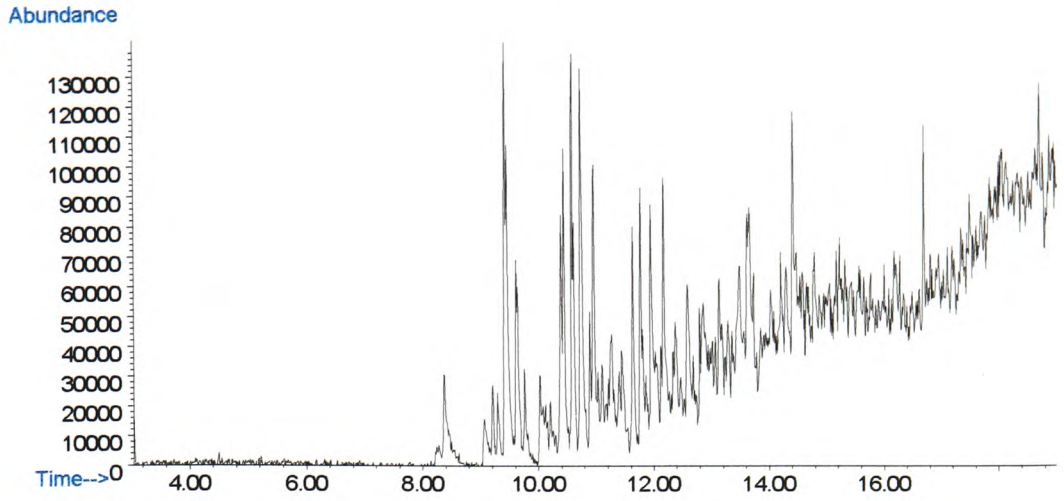

Fig. 3.47 TIC of Bouri crude oil extracted by SFE at density (0.75 g. cm^{-3}) and 5 minutes extraction time. GC conditions chapter 5.

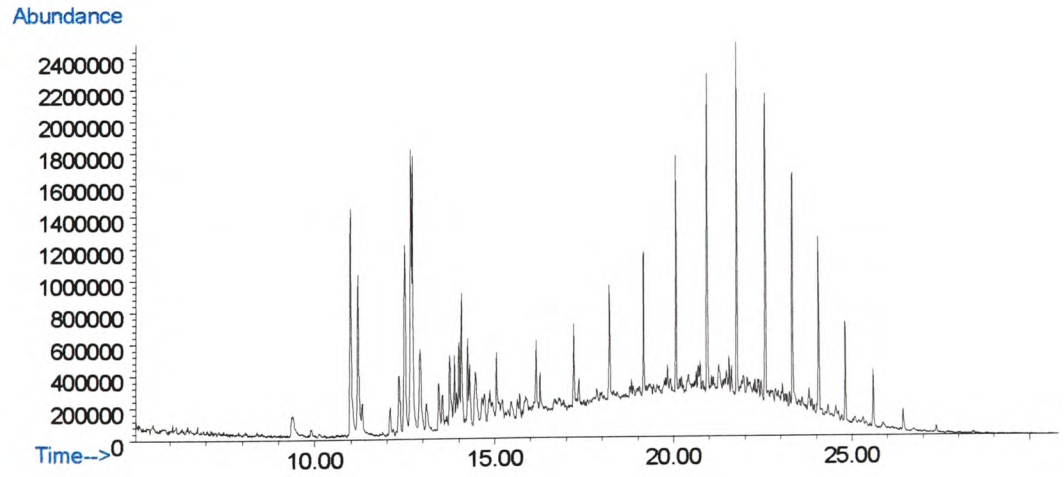

Fig. 3.48 TIC of Bouri crude oil extracted by SFE at density (0.75 g. cm^{-3}) and 10 minutes extraction time. GC conditions chapter 5.

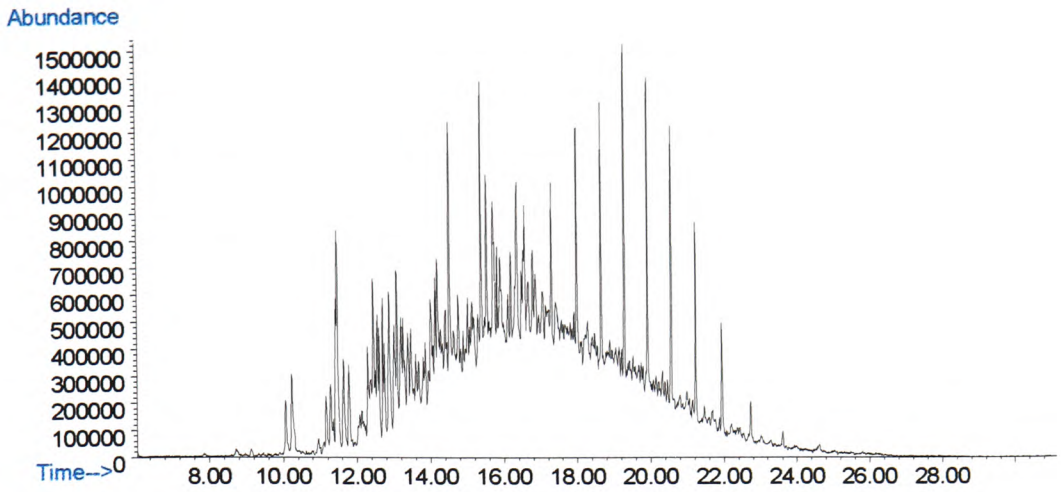

Fig. 3.49 TIC of Bouri crude oil extracted by SFE at density (0.75 g. cm^{-3}) and 15 minutes extraction time. GC conditions chapter 5.

3.9 Comparison of SFE vs. Extrography and column chromatography

The main task of sample preparation is to separate an analyte from a matrix by investing the minimum amount of effort and time necessary to provide quantitative and qualitative analysis with acceptable degrees of accuracy and precision. The traditional approaches to sample preparation are often very labour intensive and require manual manipulation of many different pieces of glass ware.

A comparison of the class selective fractionation abilities of SFE, column chromatography and extrography are presented in table 3.11 providing a summary of some of the parameters used in each approach. It is evident from these results that the time required for SFE was less than 56 minutes per sample (for eight extraction steps including equilibrium time) whilst the corresponding column chromatography took 8-10 hours and extrography took 4-6 hours.

There are a large number of steps in the traditional preparation methods (chromatographic, clean-up, evaporation etc.) whilst the SFE approach can be computer controlled and therefore lends itself to a high degree of automation.

Consumption of organic solvent is a major consideration in the development of a new analytical protocol. In SFE the amount of organic solvents used was less than 5 cm^3 for each step, CO_2 is a gas at ambient conditions, the extracted analytes are concentrated in the collection solvent while the depressurized CO_2 is simply vented away. Column chromatography and extrography required 1220 cm^3 of various solvents.

The most important factor of all was that SFE reduced the need for disposal of waste solvent, and exposure of the personnel to toxic organic solvents normally used with traditional extraction methods.

The total recoveries and class fractionation efficiencies of PAHs from saturated hydrocarbons in crude oil achieved by SFE was comparable to that obtained by the chromatographic and extrographic methods. The total ion chromatograms obtain by GC-MS analysis of the aromatic fraction of Bouri crude using all three methods are shown in Figures 3.50 to 3.52

Table 3.11 comparison of SFE with conventional fractionation techniques.

Parameter	Column chromatography	Extrography	SFE
Time	8-10 hours	4-6 hours	< 56 min
Solvent	Organic	Organic	CO_2
Concentration step	Yes	Yes	None
Clean -up	Yes	Yes	None
disposal problem	Yes	Yes	None
Environmental hazards	Yes	Yes	None
Personal exposure	Yes	Yes	None
sample size	2 cm^3	0.5-2 cm^3	0.5-1.5 cm^3
Adsorption material	60 grams	40 grams	2 grams
Total recoveries (wt %)	83.37 - 90.50	89.39 - 95.92	77.67 - 99.92
PAHs recoveries (wt %)	12.2 - 19.8	13.59 - 20.9	-

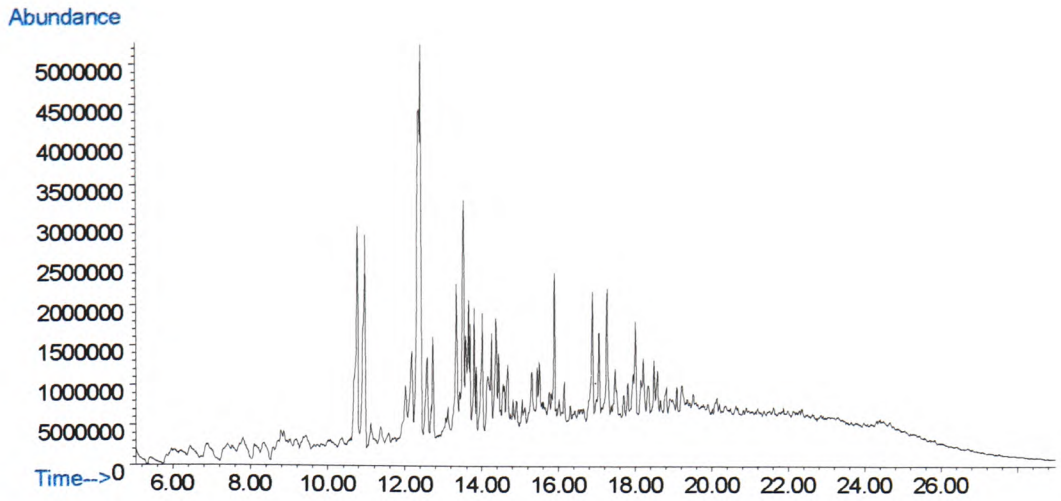

Fig. 3.50 GC-MS scan chromatogram of an aromatic hydrocarbon fraction (F2) of Bouri crude oil using column chromatography fractionation.

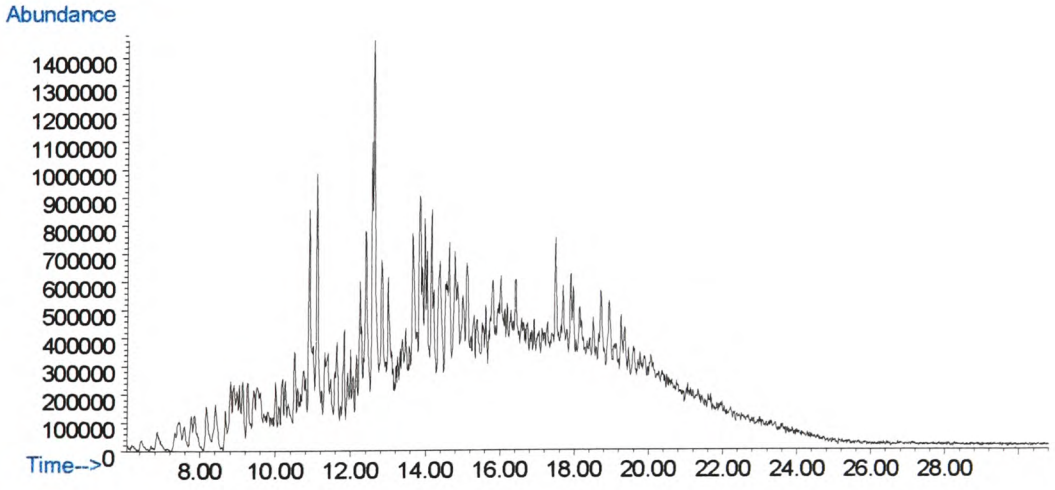

Fig. 3.51 GC-MS scan chromatogram of an aromatic hydrocarbon fraction (F2) of Bouri crude oil using extrography fractionation.

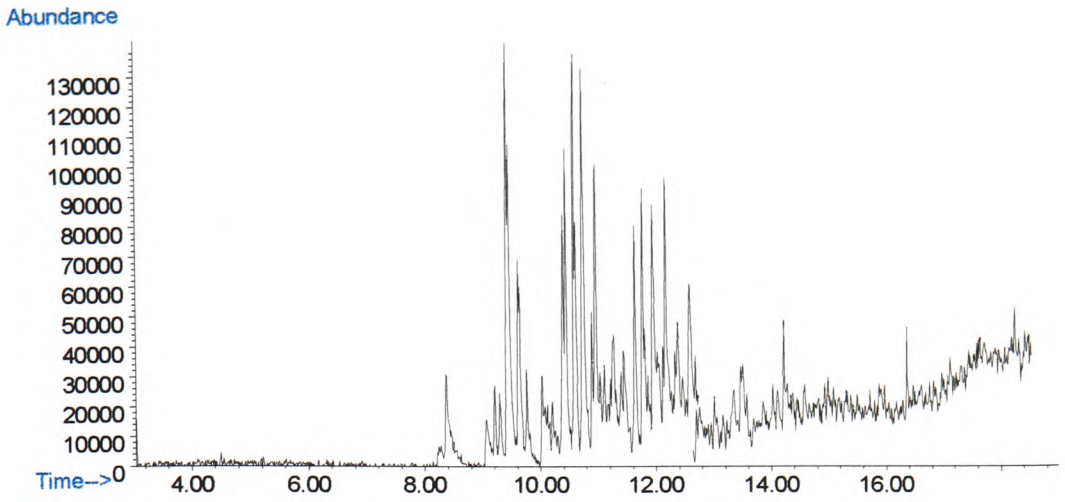

Fig. 3.52 GC-MS scan chromatogram of an aromatic hydrocarbon fraction of Bouri crude oil using SFE.

3.10 Conclusion

These studies have shown that SFE can provide a class selective fractionation of crude oil providing the effective separation of PAHs and saturated hydrocarbons from oil based matrices.

Precise control of extraction parameters is very important in providing a selective extraction. In our studies the optimized conditions for this were density < 0.65 g. cm^{-3}, temperature 40 ^{0}C, initial extraction time 5 minutes, 2 minutes equilibrium time, flow rate 1 cm^{-3} min^{-1}, nozzle temperature 45 ^{0}C, trap temperature 20 ^{0}C and trap packing Octadecyl bonded silica (ODS)

Extraction at low density (< 0.55 g. cm^{-3}) could be selectively used to remove unwanted components (saturated hydrocarbons) prior to further sample treatment or the sample could be extracted at higher densities (> 0.65 g . cm^{-3}) to obtain the PAHs.

The extraction performance was solvent density dependent. As the pressure increased, the extraction of PAHs increased. The rate of extraction was also higher

at higher densities. Near the critical temperature of CO_2 extraction was most efficient, indicating that solvent density was not the sole variable governing extraction.

Above the critical temperature of CO_2, the phase transition appeared to shift from a liquid - liquid like system to a liquid- vapor like system corresponding to a significant reduction in the amount of oil extracted.

SFE is fast, requiring only 56 minutes per sample as opposed to the 8-10 hours currently used for column chromatography fractionation. The high fractionation efficiencies of PAHs from crude oil can be obtained with 0 % modifiers. There is still the need in SFE to find a supercritical fluid with higher solvating power for high polarity molecules. It should be friendly both to the instrument (non-corrosive) and the environmental (non-toxic). However, these demands might be very difficult to meet. Working with a single fluid with no modifier would simplify the instrumentation, and the fluid-modifier phase equilibrium could then be disregarded. The heavier compounds were extracted as extraction time and pressure increased, the highest SFE efficiency for PAHs was obtained at 5 minutes. The color difference of the extracts also provided visual evidence of compositional variations as a function of time. The loading ratio of crude oil on to silica gel has been investigated, optimum fractionation efficiency was obtained with a ratio of 1/15 .

The currently available commercial instrumentation can be used with little modification. 90 % of the extraction procedures using the HP 7680 A is automated this reduces experimental error.

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Chapter 4

4 Supercritical Fluid Extraction Of Crude Oil From Water Samples

4.1 Introduction

The extraction of environmental pollutants from associated matrices is the first and the most important step in an environmental pollution study. Many different methods have been employed in order to concentrate organic components from aqueous solution such as liquid-liquid extraction, adsorption on solid adsorbents and passage through capillary polymeric columns.

To date, the vast majority of the work with SFE has centered on the extraction of analytes from solid matrices. That which has been reported for SFE of aqueous matrices has been performed on a large scale such as for waste water treatment [1,2].

Supercritical fluid extraction of aqueous samples offers a potential approach for the analysis of priority pollutants in aqueous environmental samples and drugs/drug metabolites from biological fluids [3,4]. There are two approaches for the extraction of aqueous samples by SFE: (1) Liquid matrices are first adsorbed onto a solid support (SPE) and then extracted with a supercritical fluid. (2) Direct SFE of the matrix using a special extraction cell designed for the purpose. The first approach has been discussed in chapter three. Here, the direct approach will be discussed.

There are several problems associated with the extraction of compounds from aqueous solution. The main problem is that the extraction cell must be of the correct geometry to retain the bulk of the water during the extraction process. If the analyte is present at trace levels, the volume of matrix must be large to ensure

obtaining sufficient quantities of analyte to measure. Another problem is the relatively high solubility of water in the supercritical carbon dioxide, which is approximately 0.3 % [5]. For a dynamic extraction, the removal of this small amount of water over time can cause problems such as restrictor plugging. Additionally, if the SF extract is to be collected in a non polar solvent a two-phase system can result, thereby making sampling for final analysis rather difficult. These problems have been recently partly solved, however, the SFE of organics from water is not as routine as SFE of environmental solids.

The dynamic approach appears to be preferred by most workers since complete extraction of the analyte can be expected if enough SF is passed over/through the sample. Loss of extract especially if components are highly volatile can be quit common depending upon the accumulation strategy (i.e. solvent collection, solid phase deposition, cryofocusing). With the correct choice of strategy, immobilization of the desired extractant should occur [6].

The first report on SFE of water samples appeared in the late eighties[7,8], and the first method [7] was based on the "closed loop striping" principle. Here the SF was (after pressuring of the system) recycled by a pump from the outlet of the extraction cell back into the water sample. After the equilibration of the system a sample of the supercritical phase was taken by means of a valve loop. The contents of the loop were then analyzed by supercritical fluid chromatography (SFC). This system was used for the analysis of di-isopropyl methyphosphonate at a concentration of 834 ug l^{-1} in water. The method was also used for the extraction of phenol from aqueous solutions [9].

The other approach [5] was based on a sandwich-type phase separator, in which the supercritical carbon dioxide and water phases are separated by means of a hydrophobic membrane. Two types of membrane were able to withstand the high pressure necessary: PVDF [(-CH_2-CF_2-)n] and Delrin [(-CH_2-O-)n]. A sample of the separated supercritical fluid was taken by a valve with loop for SFC analysis. Phenol and 4-chlorophenol were utilized as test compounds.

Departing from the "conventional" extraction cell design, the use of a novel phase segmentor/phase separator for the extraction of 4-chlorophenol and phenol from water has been reported [5]. On-line SFC was used for subsequent analysis. Recoveries and reproducibilities for the system were not reported. Several other organic/water mixtures have been screened by SF-CO_2 in feasibility tests. A partial list includes acetone, ethanol and formamide [10].

4.2 Extraction Cell Design

The aim of this part of our studies was to design an SFE extraction cell that would enable the (selective) extraction of crude oils from water samples.

Figure 4.1 shown the extraction vessel used for our studies was a modified form of the system used by Hedric, et. al [11,12]. Basically it was an empty preparative HPLC column (30 cm in length with an internal diameter of 8.0 mm) having a capacity of 12 cm^3. The vessel was subsequently modified for use with liquid samples in the following manner. Blind nuts on each end of the column were drilled out to a diameter of 1.59 mm. Stainless steel inlet and outlet tubes (1.59 mm i.d) were inserted into each end of the column and welded such that the ends of the tubes extended to 1.0 cm^3 from the top and bottom of the column.

A Gilson HPLC model 811 modified for SFE and SFC was used to supply CO_2 to the extraction cell via a modified HPLC pump (model 303) fitted with a cooling head. The extraction cell was placed in a PYE series 104 GC oven. Figures 4.2 and 4.3. shows the plumbing scheme [12] used, this consisted of three, '3 port' switching valves (Rheodyne) with an adjustable restrictor to control the back pressure. This was fitted with a post restrictor tube which was crimped to aid extract deposition.

For sample loading, (Fig. 4.2) the CO_2 supply line was closed from valve A. About 8 cm^3 of aqueous sample was loaded with a plastic syringe through valve B. During loading the sample valve C was opened to atmosphere such that air could be purged from the system as the sample entered. The same scheme was employed after each extraction in order to remove the 'spent' sample. Using this system configuration, the need to dismantle the extraction cell for sample introduction/removal is negated.

Valves B and C were turned into the on-line positions after loading the sample and supercritical CO_2 was supplied by opening valve A as illustrated in Figure 4.3. Dynamic extraction was performed and analytes were trapped in an organic solvent (dichloromethane) contained in sample vials.

During the extraction several problems arose which were related to the large volume of gas which is produced at the low pressure end of the restrictor. A flow of 1.0 cm^{-3}. min^{-1} of supercritical fluid corresponds to 100-500 cm^{-3} min^{-1} of decompressed gas, depending upon the density and nature of the SF used. Collection of the analyte in a liquid solvent is especially difficult. Violent bubbling

of the liquid by the gas can cause sporadic loss of analyte. The cooling of solvent and delivery tubing by the Joule-Thompson effect can also produce problems at high flow rates as co-extracted water tends to freeze at the tip of the post restrictor delivery tube causing a blockage. To overcome these problems associated with extract collection the post restriction tubing was warmed using a temperature controlled heater and the organic solvent vials were moderately heated using a water bath. To avoid loss of solvent due to bubbling, narrow neck long vials were used for sample collection as shown in Figure 4.4. The amount of solvent in these vials was not more than 1/3 of the total volume of the vial. During extraction, solvent loss due to evaporation was compensated for by adding more solvent during extraction. At the end, traces of water were removed from the extract by passing through anhydrous sodium sulfate.

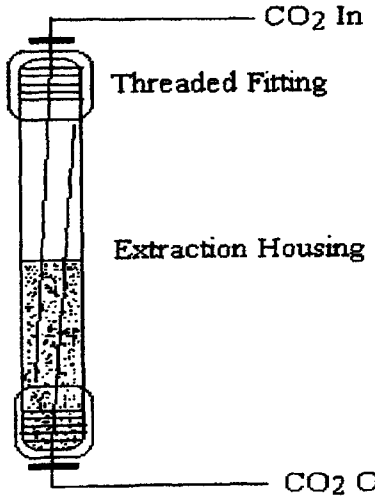

Fig.4.1.Aqueousextraction vessel [12].

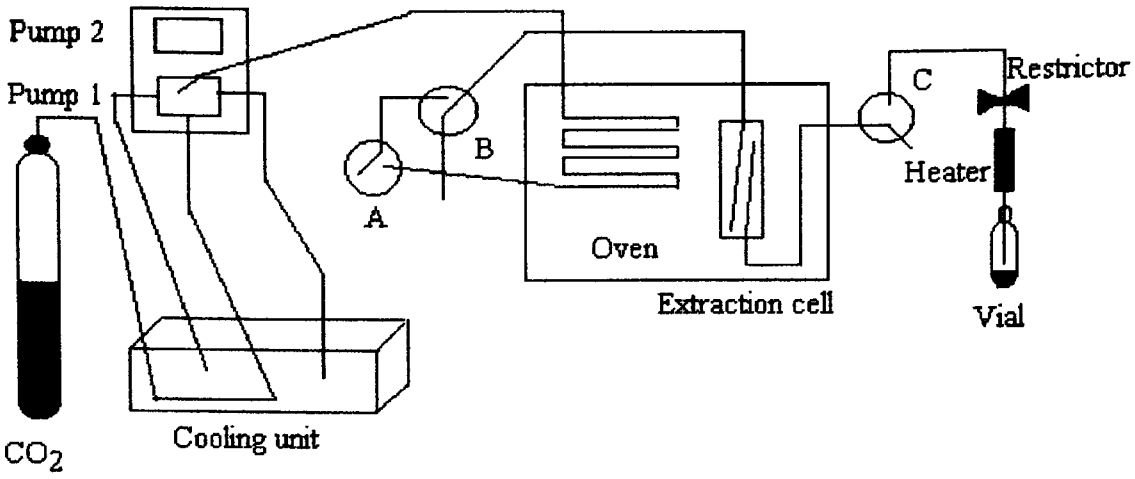

Fig. 4.2. Configuration of SFE unit -Sample loading position (A) [12].

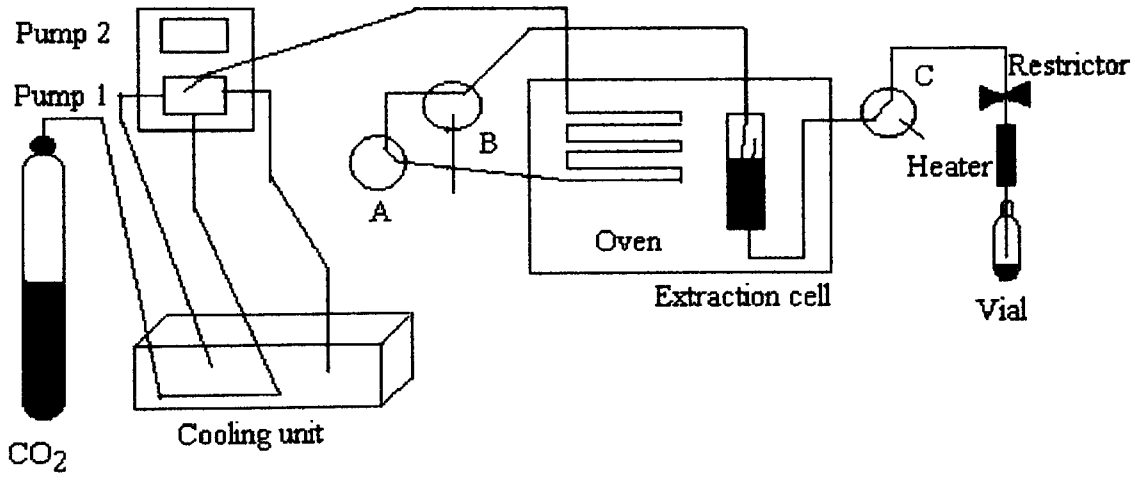

Fig. 4.3. Configuration of SFE unit -Extraction position (B) [12].

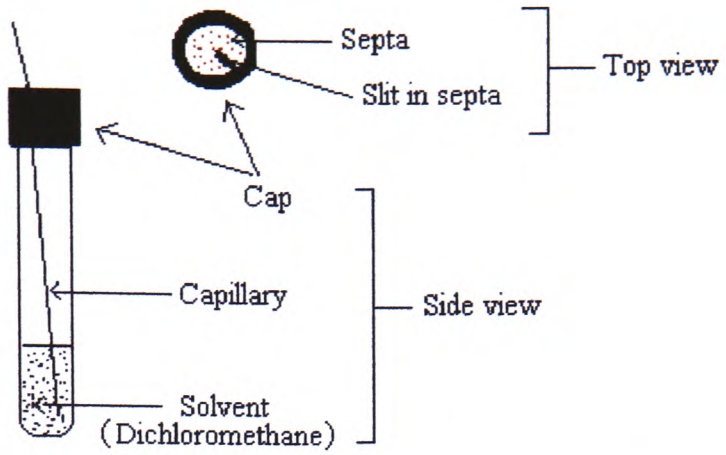

Figure 4.4 Solvent trap (slit in the septa allowed CO_2 to escape).

4.3 Fractionation of saturated and PAHs in crude oil from water

Polycyclic aromatic hydrocarbons (PAHs) are of great environmental concern due to their toxicity and wide distribution [13]. The distribution of PAH in different bodies of water is dependent on their point sources. Spillage of crude oil or refined products from a tanker, oil drilling areas, or storage areas, and terrestrial run-off rain water containing PAHs from the air and leachates them from soil, pavements, slag dumps, and coal storage piles, contribute to the accumulation of PAHs.

The usual extraction procedure for PAHs in an aqueous sample employs liquid-liquid extraction. This technique is often very tedious and time consuming. At the same time, due to the lack of selectivity in this method, it is often necessary to include an additional sample clean-up step prior to analysis. Consequently, the extraction efficiency of such a method is unsatisfactory. Furthermore, with the involvement of the additional steps, the introduction of impurities is inevitable [14].

PAHs are one of the most troublesome groups of compounds, because of their poor solubility in supercritical fluids, especially compounds with more condensed benzene rings. The recovery is also strongly dependent on the type of matrix. Recovery of PAHs usually decreases with increasing molecular weight (decreasing solubility).

Studies of supercritical extraction related to aqueous solutions of organic compounds have concentrated on a single-compound extraction. Most environmental pollutants, however, are complex chemical mixtures and each component of the mixture affects the solubility and extraction parameters of all the other components in the mixture [15].

Our studies centered on the use of supercritical carbon dioxide inorder to effect the class fractionation of PAHs and saturated hydrocarbons from crude oils in water.

For our work, 500 cm^3 of distilled water was saturated with 2 cm^3 of Bouri crude oil. Extraction studies were performed on 8 cm^3 of this spiked water. All extractions were performed with 100 % CO_2 using the modified Gilson HPLC system described previously. The resulting extracts were collected in dichloromethane (2 cm^3). After extraction the DCM containing extract was passed through anhydrous sodium sulfate and concentrated to 1.0 cm^3 under nitrogen and the was analyzed by GC-MS. The detailed experimental procedure and GC-MS conditions are given in chapter 5.

4.4 Results and Discussion

4.4.1 Effect of density

These initial studies were investigated in order to optimize the pressure, temperature and extraction time, for the recovery of PAHs from spiked water. Density is an important parameter since the solvating power of a supercritical fluid is proportional to its density. For this, SFE was conducted under the following conditions:

Pressure	2000, 2500, 2800, 3000, and 3500 Psi
Temperature	40 ^{0}C
Extraction time	15 minutes
Flow rate	2.0 cm^{-3}. min^{-1}
sample volume	8 cm^3

The extraction profile of Bouri crude oil at different pressures is shown in Figures 4.5 to 4.9. The extraction temperature was kept constant at 40 ^{0}C, the pressure was, however, changed stepwise from 2000 to 3500 Psi at 15 minute interval which maintaining a constant flow rate of CO_2 (2.0 cm^{-3} min^{-1}). According to the GC-MS profile, the extraction of the saturated hydrocarbons started at a relatively low pressure (2000 Psi) as shown Figure 4.5. Examination of this chromatogram, revealed that a few minor peaks (9 % of total area) were co-

extracted PAHs . Figures 4.6 to 4.7 show typical GC-MS total ion chromatogram of Bouri crude oil at pressures of 2500 and 2800 Psi. Data analysis of these two chromatograms revealed that PAHs start to become extracted at pressure > 2000 Psi. As expected, progressively higher molecular weight material was extracted at higher extraction fluid pressure.

The fraction obtained at 2500 Psi essentially contained alkyl benzene homologues whilst that obtained at 2800 Psi contained mainly alkyl naphthalenes.

The GC-MS analysis of Bouri crude fraction obtained at pressure 3000 Psi is shown in Figure 4.8. Inspection of the associated mass spectra revealed that a high degree of fractionation of PAHs from oil had been achieved. Figures 4.10 to 4.13, shows the m/z (128, 105, 198 and 192) searched which are corresponded to Bouri crude oil extracted at pressure 3000 Psi (fig. 4.8). The m/z values searched are specific for PAH compounds. Figure 4.9 shows the TIC of all final fraction obtained at pressure 3500 Psi. Examination of the spectra revealed the presence of some overlap.

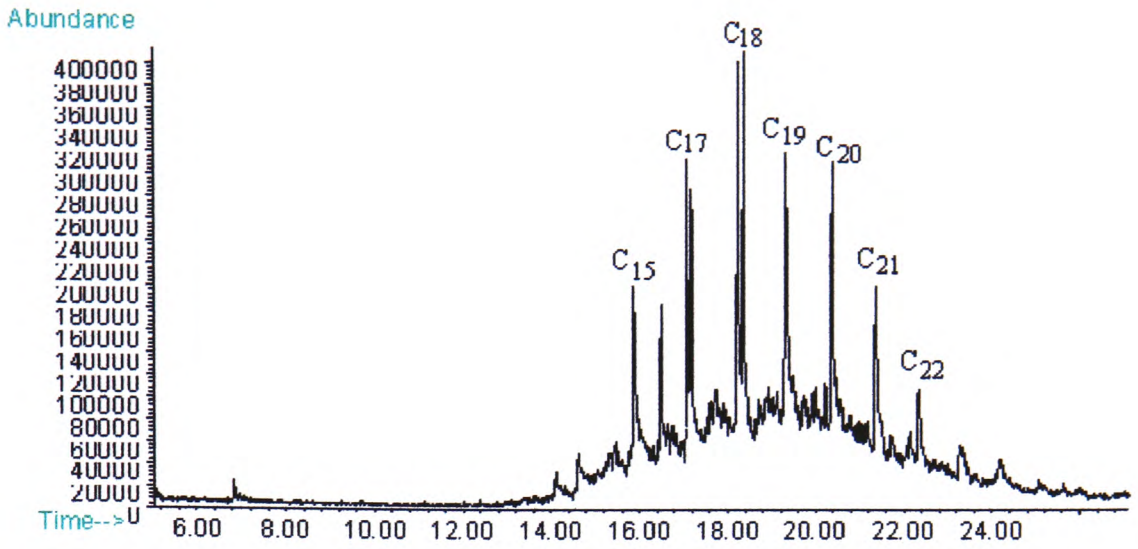

Fig. 4.5 TIC of Bouri crude oil extracted from water by SFE at pressure 2000 Psi

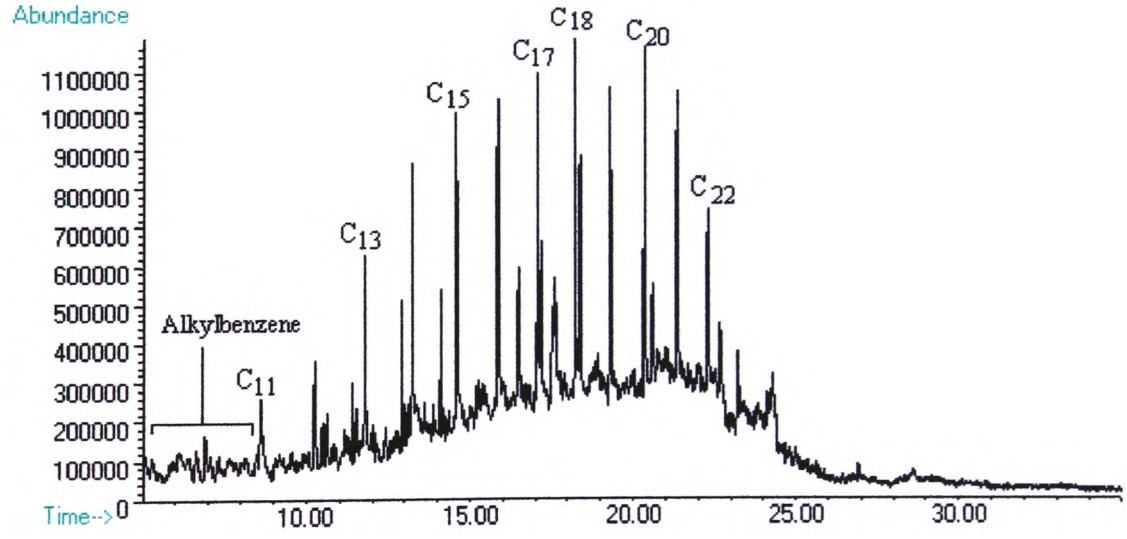

Fig. 4.6 TIC of Bouri crude oil extracted from water by SFE at pressure 2500 Psi

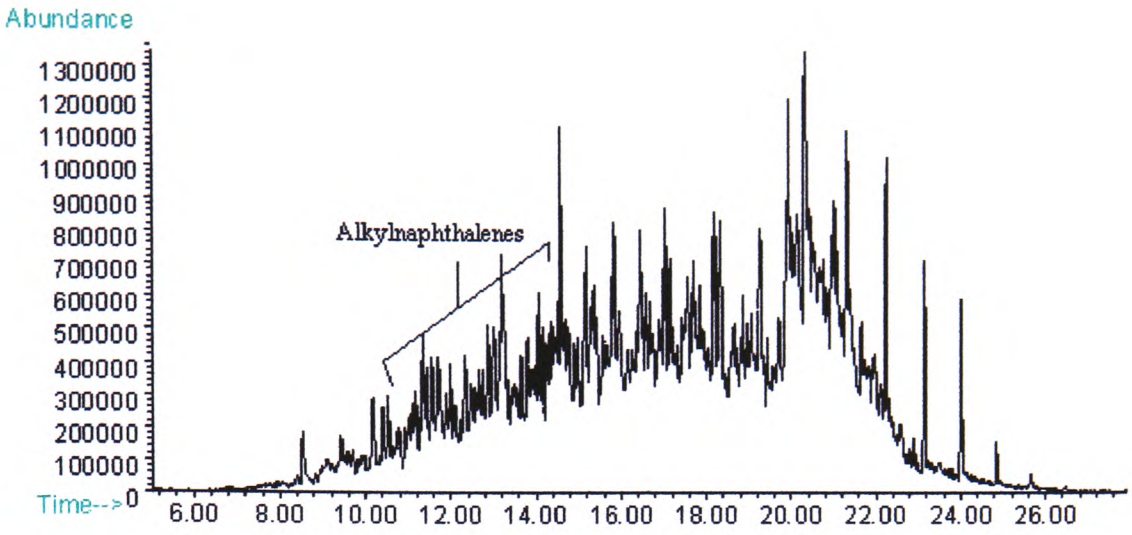

Fig. 4.7 TIC of Bouri crude oil extracted from water by SFE at pressure 2800 Psi

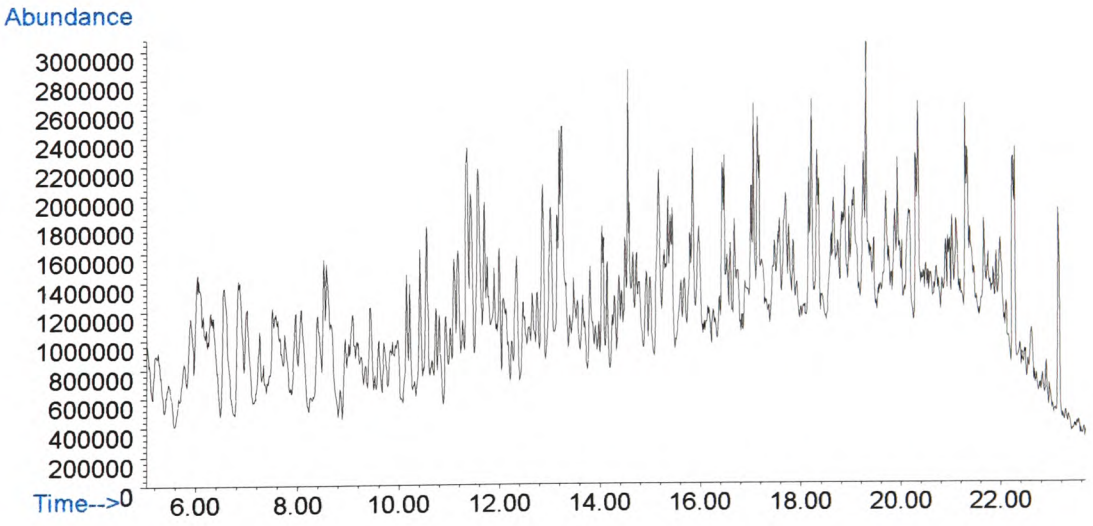

Fig. 4.8 TIC of Bouri crude oil extracted from water by SFE at pressure 3000 Psi

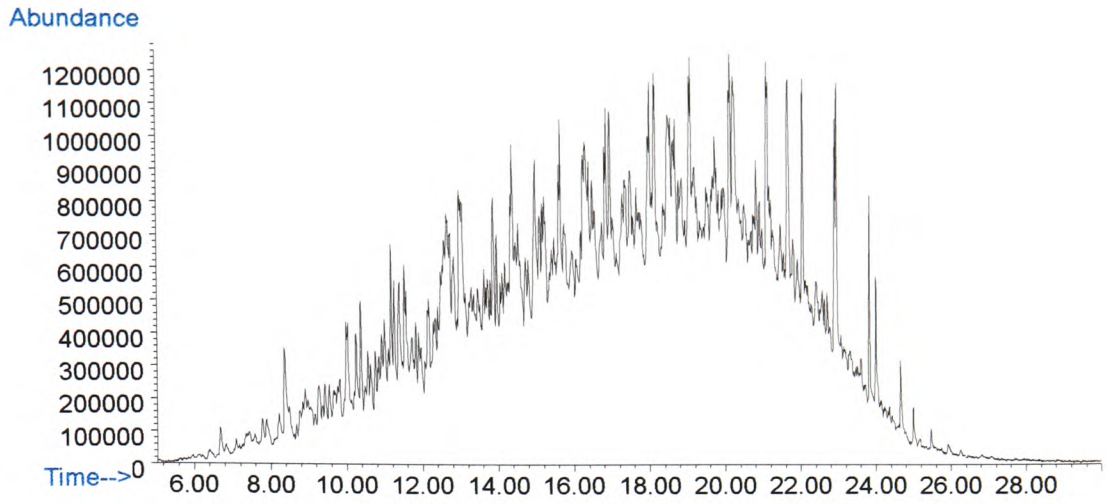

Fig. 4.9 TIC of Bouri crude oil extracted from water by SFE at pressure 3500 Psi

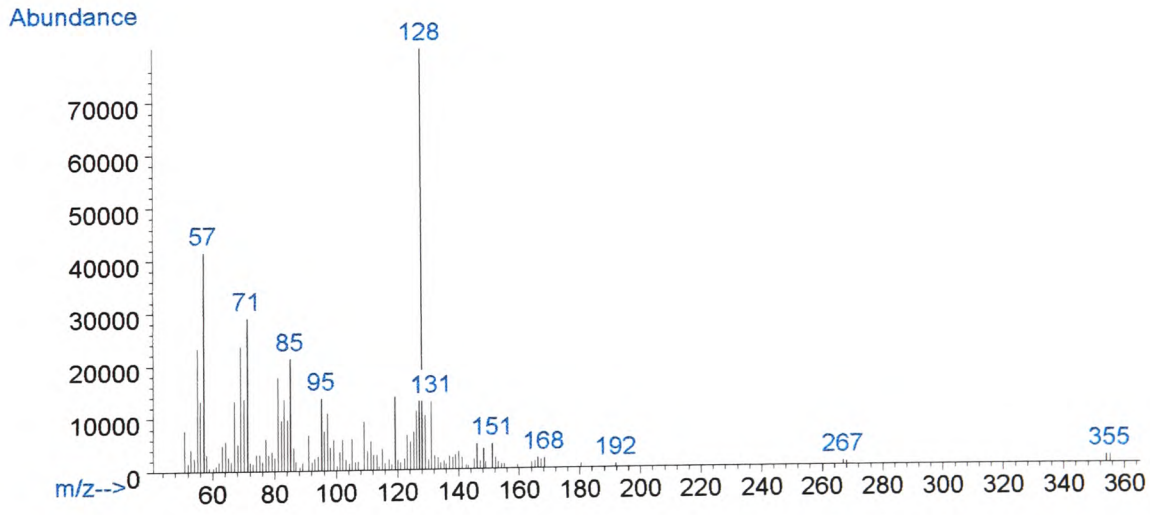

Figure 4.10.Mass spectra of scan # 504 obtained from (fig. 4.8) which represent PAH compound with MW = 128

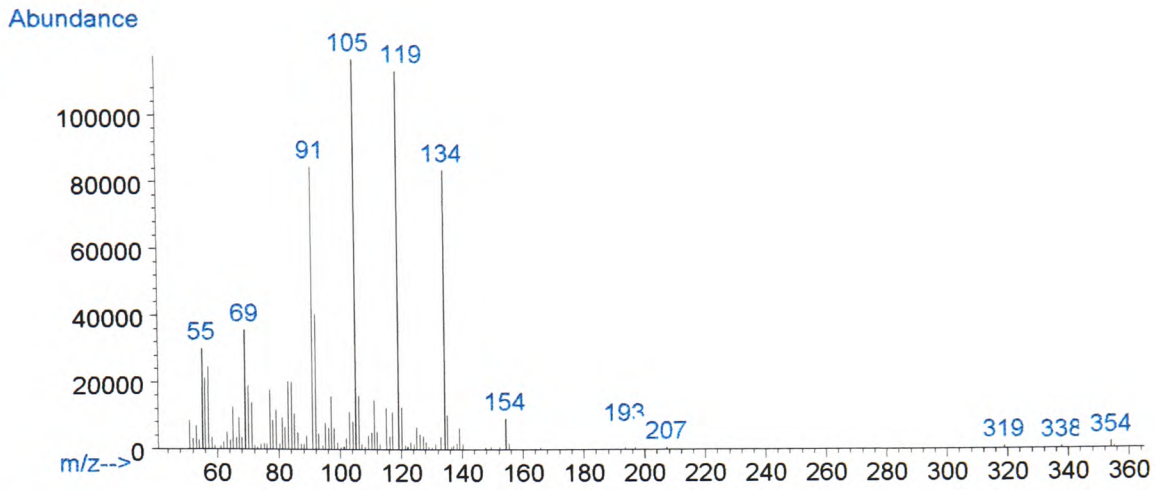

Figure 4.11.Mass spectra of scan # 227 obtained from (fig. 4.8) which represent PAH compound with MW = 105

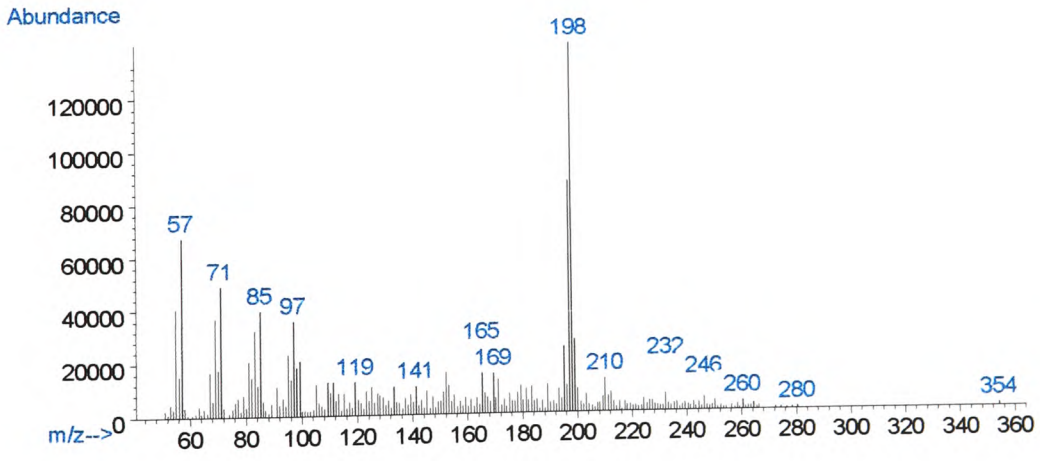

Figure 4.12.Mass spectra of scan # 1183 obtained from (fig. 4.8) which represent PAH compound with MW = 198

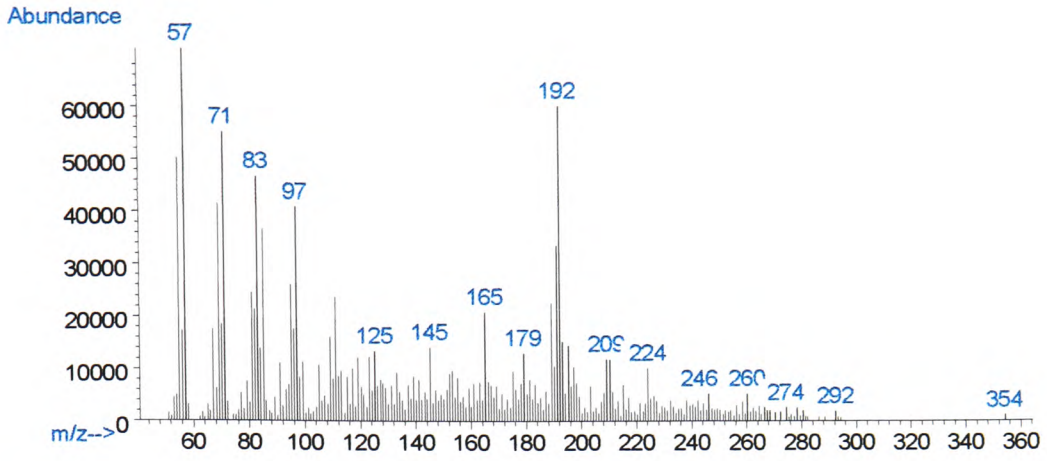

Figure 4.13.Mass spectra of scan # 1294 obtained from (fig. 4.8) which represent PAH compound with MW = 192

Figure 4.14 shows the effect of extraction pressure on the overall recovery of crude oil from water. At low pressure (2000 Psi) the rate of extraction was low; only 35.3 % of crude oil was recovered using a volume of 30 cm^3 of supercritical CO_2. Higher rates of extraction and recoveries were achieved at greater pressures using the same volume of extraction medium. Consequently, we concluded that more efficient extraction and better recoveries could be obtained at higher pressure.

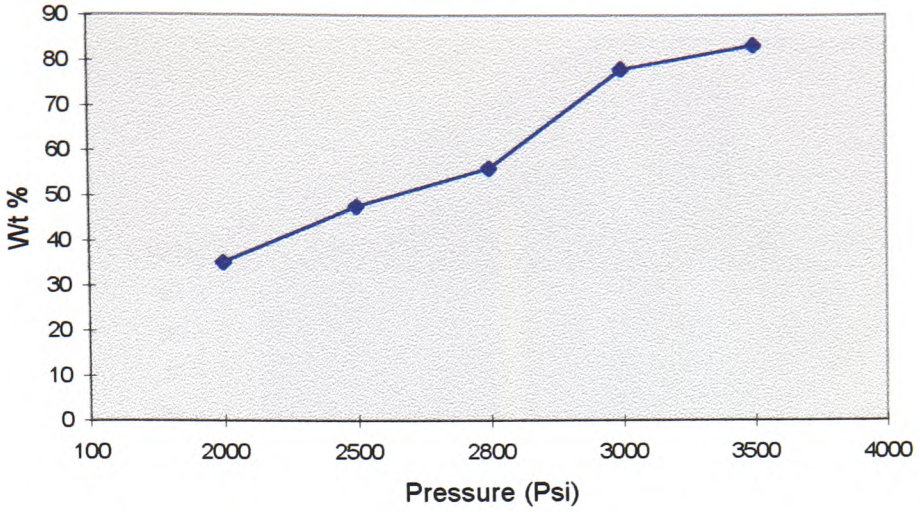

Fig. 4.14 Effect of pressure SFE of Aqueous matrix.

Figure 4.15 shown the percentage of saturate and aromatic hydrocarbons recovered at different pressures from water spiked with Bouri crude. It can be seen that the saturates are the most abundant class present in this particular crude, ranging from 38.5 to 90.8 %. The aromatic species range from 9.2 to 61.5 % overing the experimental pressure range used. It is important to note however, that the recovery maxima for each hydrocarbon class occurs at significantly different extraction pressures, thus indicating that a degree of class selectivity was achieved. From our results a pressure of 3000 Psi maximized PAH recovery and minimized saturate recovery.

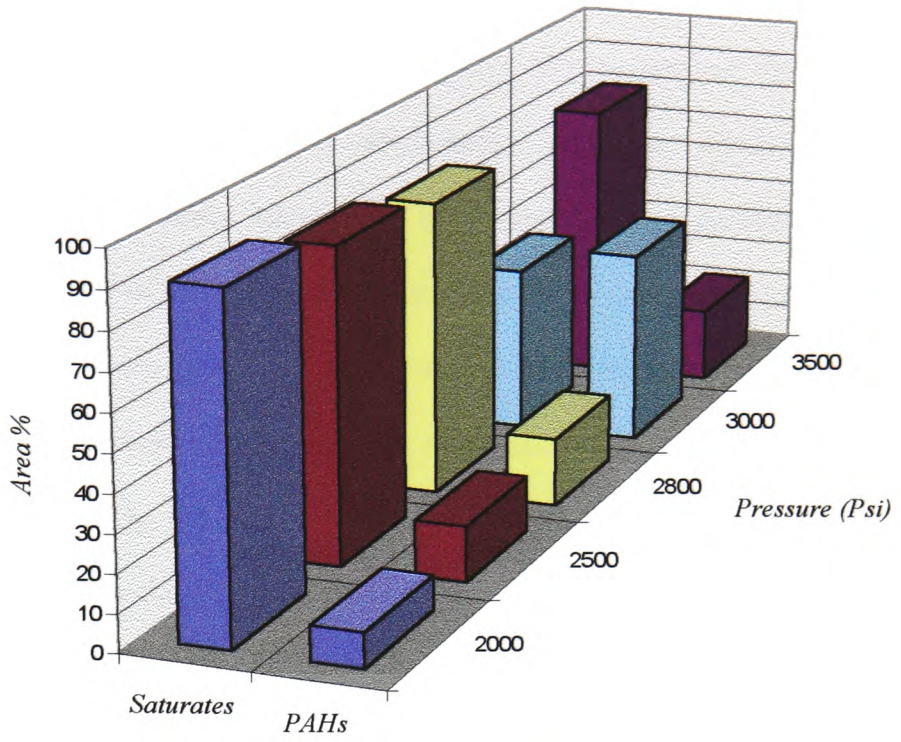

Fig. 4.15 Percent amount of saturated and aromatic of extracted Bouri crude oil at various pressure.

4.4.2 Effect of extraction temperature

The second SFE parameter that was investigated with the system was the extraction temperature. SFE was performed under the following conditions:

Pressure	3000 Psi
Temperature	40 ^{0}C, 60 ^{0}C and 70 ^{0}C
Flow rate	2 cm^{-3}. min^{-1}
Extraction time	15 minutes

The fraction obtained at a temperature of 40 ^{0}C (fig. 4.16) was shown to consist of a high percentage of alkyl aromatic species (70.6 %). However, fractions obtained at both 60 ^{0}C and 70 ^{0}C (fig. 4.17 and 4.18) were shown to

contain insignificant amounts of PAH. This behavior is too complex to be interpreted exactly, it may be due to the competing effects between the solvent density and solute volatility [16]. As temperature increases, solvent density decreases and solute volatility increases. The decrease in the solvent density decreases the solubility of a given solute molecule in the extract phase. This phase behavior of crude oil-co_2 mixture may be related to changes in partial molar volumes and intermolecular forces between hydrocarbons in the vicinity of the critical point of the CO_2, although it is difficult to evaluate these properties for mixtures as complex as this [17]. Increases in temperature produced a decrease in overall oil recovery (fig. 4.19).

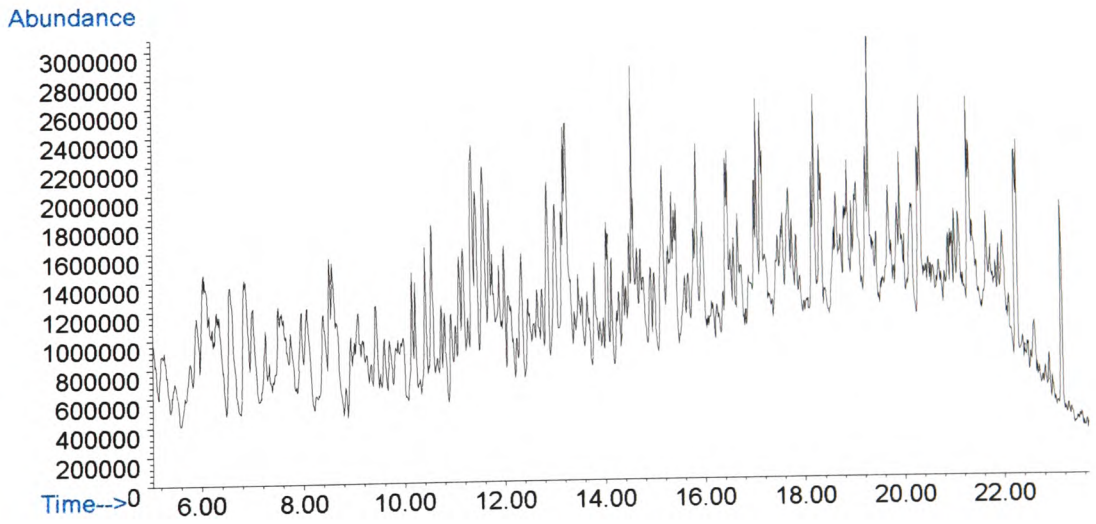

Fig. 4.16. TIC of Bouri crude oil extracted from water by SFE at temperature 40 ^{0}C and constant pressure 3000 Psi. GC conditions chapter 5.

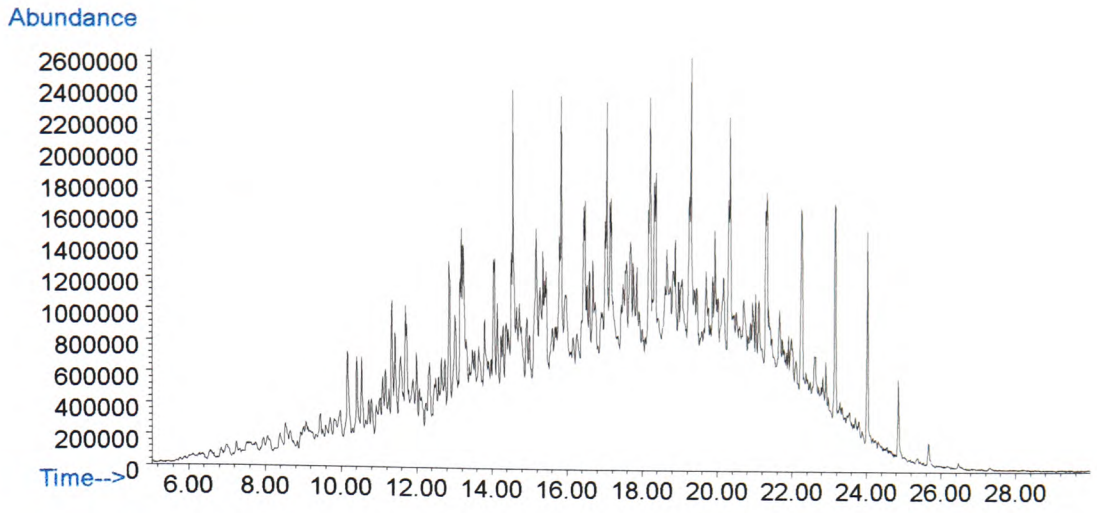

Fig. 4.17. TIC of Bouri crude oil extracted from water by SFE at temperature 60 ^{0}C and constant pressure 3000 Psi. GC conditions chapter 5.

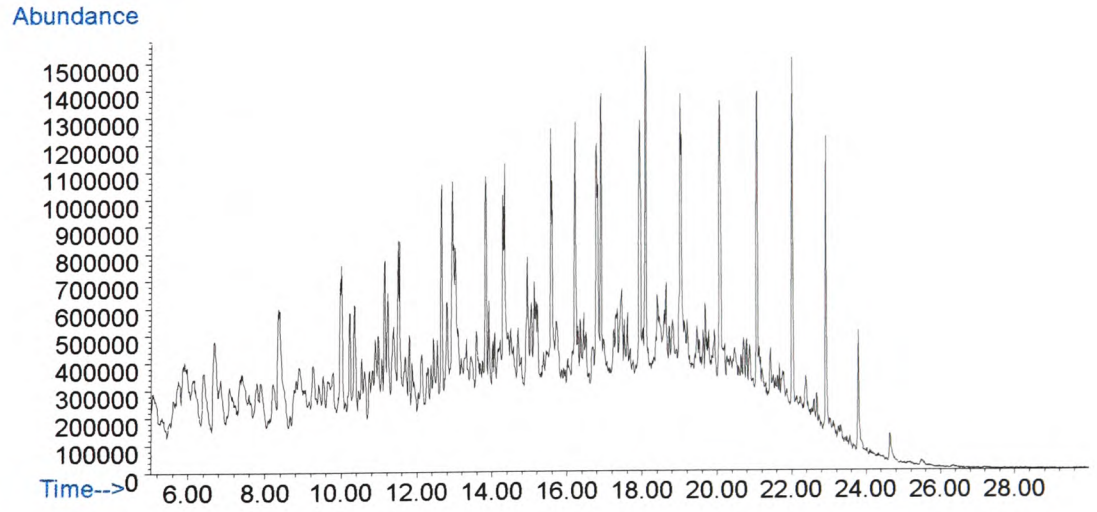

Fig. 4.18. TIC of Bouri crude oil extracted from water by SFE at temperature 70 ^{0}C and constant pressure 3000 Psi. GC conditions chapter 5.

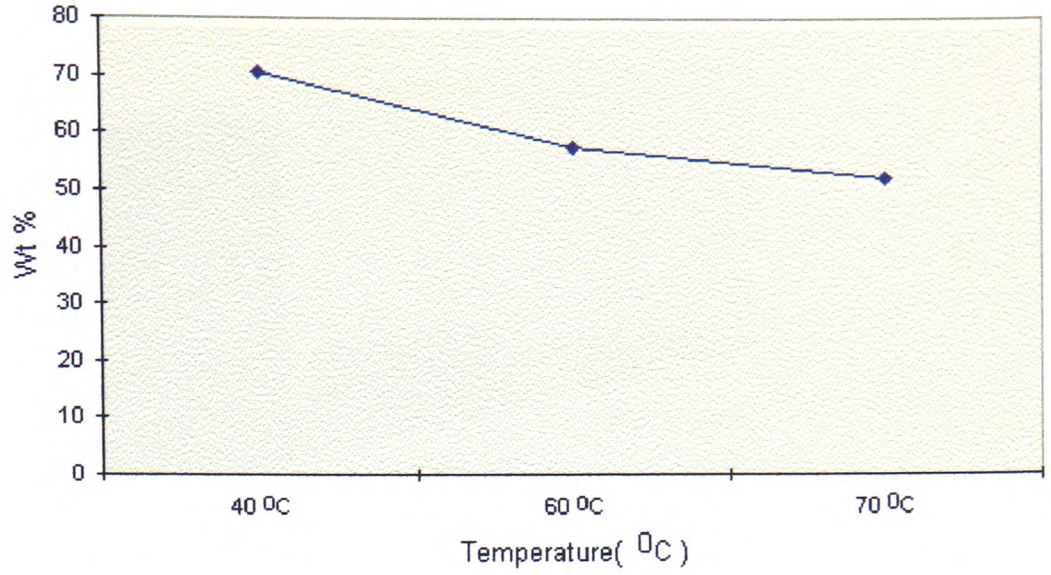

Fig. 4.19. Effect of temperature SFE of Aqueous matrix.

4.4.3 Effect of extraction time

The extraction time is an important factor in SFE. A spiked water sample was extracted for 15 minutes after which the CO_2 supply line was closed and the remaining CO_2 in the system allowed to gradually escape. The extract collection vial was then replaced with a fresh vial containing dichloromethane (2 cm^3). The cell was then re-extracted for a further 15 minutes after which the procedure was repeated once more resulting in the acquisition of 3 extraction vials containing cumulative quantities of analyte.

GC-MS analysis of the 3 resulting fractions indicated that PAH recovery maximized within the first 15 minutes of extraction as shown in Figure 4.20.

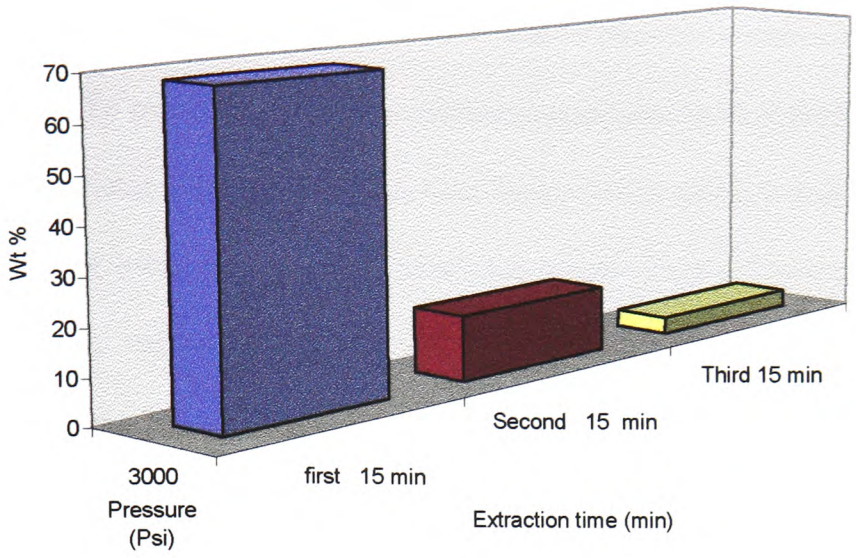

Fig. 4.20. Effect of extraction time SFE of Aqueous matrix.

4.5 Conclusion:

These studies indicate that the optimized parameters for the extraction of crude oil using our aqueous SFE system are:

Pressure	3000 Psi
Temperature	40 ^{0}C
Extraction time	15 minutes
Flow rate	2 cm^{-3}. min^{-1}

It is concluded that PAHs can be fractionated from distilled water by SFE using a liquid extraction cell. For extraction purposes, 2000 and 3000 Psi is the most suitable pressures for the class selective fractionation of saturated and

aromatic hydrocarbons respectively. Other optimized parameters are temperature and extraction time, which were 40 ^{0}C and 15 minutes respectively.

To over come the main problems associated with collecting the analytes, the restrictor plugging problems have been recently partly solved by warming the restrictor using a temperature controlled heater. To avoid loss of solvent due to bubbling, narrow neck long vial capped with septum was used for sample collection.

The initial results here indicated that the technique may have promise for analytes which are insoluble in water and also in the case where direct injection onto a liquid chromatography of aqueous media may be hazardous. Further work must center on the trapping system, the extractability of analytes at lower concentrations as well as a study of the effects of salinity on extraction behavior.

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Chapter 5

5 Experimental

5.1 Matrices studied

1. Libyan crude oils from several geographical sources namely: Bouri, Sirte, Sidra, Zweteena and Messla, were supplied from shipment tanks by several refineries and production companies.
2. Standard compounds of saturated and aromatic hydrocarbons used to evaluate the mode of separation of chromatographic, extrographic and SFE.
3. Libyan crude oil spiked into a distilled water.

5.2 Chemicals

1. Solvents:

   Dichloromethane, n-Hexane, Benzene, Chloroform, Diethylether, Ethanol, Methanol and Acetone

2. Standard compounds:

   Dodecane, Decane, Tetradecane, Pentadecane, Hexadecane, Heptadecane, Octadecane, Nonadecane, Eicosane, Naphthalene, Flourene, Phenanthrene, Anthracene, Flouranthene, Pyrene and Chrysene.

3. Reagents:

   Anhydrous sodium sulfate, Sodium chloride, glass wool and fine sand.

4. Absorbents:

   Silica gel (0.13-025 mm (60-120 mesh) supplied by BDH company.

5. Carbon dioxide:

   SFC grade (Air products U. K. and Distillers).

6. Chromatographic column:

   A chromatographic glass column (12.5 mm i.d. 400 mm length) with a Teflon stopcock and punger pump to maintain the elution rate.

5.3 Apparatus

1. Gas chromatography-Mass spectrometry (HP Model 5890 GC equipped with a Model 5971 Mass Selective Detector).
2. Supercritical fluid extractor (HP Model 7680 A)

5.4 Chromatography

In this chapter the method used covers the separation and determination of representative aromatic and nonromantic fraction from hydrocarbon mixtures using column chromatography and extrography technique.

5.4.1 Column chromatography

The chromatographic fractionation was performed using a glass column (12.5mm i.d 400 mm length) plugged with Pyrex glass wool at the base. This was serially rinsed with methanol, hexane, dichloromethane and allowed to dry. The column was dry - packed with 60 grams of activated silica gel (0.13 - 0.25 mm) that was activated in vacuo for 16 hours at 130 ^{0}C and topped with a bout 0.5 cm^3 sand . To obtain an even packing density and ensure stability during packing , vibration and rotational agitation of the column was used . The column

was conditioned with 20 ml hexane and the eluent was discarded. An aliquot (2 m^3) of the authentic mixture of saturated and aromatic hydrocarbons and or/ Libyan crude oil (2 cm^3 in hexane) was transferred onto the column using 10 ml hexane to complete the transfer . Distilled chromatographic grade solvents were used in increasing eluting strength as illustrated in table 2.1 .

5.4.2 Extrographic technique

In order to study fraction selectivity of crude oil and the standard mixture of saturated and aromatic hydrocarbons , 2 mg of crude oil were solubilized or suspended in 100 cm^3 dichloromethane in a 250 ml round-bottom flask and 40 grams of silica gel (0.13-0.25 mm) added to the solution. The silica gel was previously activated for 16 hours at 130 ^{0}C. After mixing, the DCM was removed by vacuum and dried at 80 ^{0}C and 2 kpa .The dried material was placed in a glass column (12.5 mm i.d. 400mm length). Activated unloaded silica gel (60 g) was placed into the column first to avoid fraction overlapping. The column was topped with about 0.5 cm of sand. The arrangement of the absorbent within the column is shown in Figure 2.39. A sequence of five solvents was used for extrographic development as shown in Figure 2.40.

5.4.3 Sample analysis

GC-MS Protocols for the qualification of crude oil was developed. For this purpose a GC model HP 5890 equipped with a mass selective detector (MSD) HP5971 having HP1034 CMS Chem. Station (DOS Series) data system was used.

Gas chromatography : A fused silica, 50 m x 0.32 mm i.d. HP1 (cross linked methyl silicon gum) with a film thickness of 0.17 um was used with helium as the carrier gas. Temperature programmed for crude oil and standard mixture analyze were as given below :

Injector port	250 ^{0}C
Interface transfer line	280 ^{0}C
Total run time	30 min

Temperature programmed from 60 ^{0}C (2 min hold) to 300 ^{0}C (4 min hold) at 10 ^{0}C/min. The mass spectrometer was scanned from 50 to 550 amu. and 5 min solvent delay.

5.5 Sample Preparation

Crude oil and the standard mixture were precoated on silica gel Prior to SFE.

5.5.1 Pre-coating the sample

Between 0.5-1.5 g of crude oil or 2 cm^3 of standard mixture were placed in a 250 cm^3 round-bottom flask containing dichloromethane. Activated silica gel was then added to the solution in ratios of 1/15, 1/33 and 1/45. The solvent was removed from the mixture under reduced pressure.

5.5.2 Supercritical fluid extraction

All SFE experiments were carried out using the Hewlett- Packard (HP) 7680 T and 7680 A supercritical fluid extractor. For applications requiring modifier addition, methanol (5 and 10 %) was added. The pumps were coupled to the SFE instrument as prescribed by the manufacturer.

In all cases, precoated silica gel (2.0 g) was placed in stainless steel extraction thimbles topped with fine sand which was then loaded into the extraction chamber of the HP SFE. The SFE extraction conditions used for the two sets of experiment (figs. 3.5 and 3.6) are given below :

SFE condition used for optimized density (experimental type 1).

EXTRACTION STEPS	1	2	3	4	5	6	7	8
FLUID DELIVERY								
density ($cm^{-3}.min^{-1}$)	0.25	0.35	0.45	0.55	0.65	0.75	0.85	0.95
pressure (Psi)	1117	1223	1284	1355	1508	1937	3058	5560
flow rate	$1.0\ cm^{-3}.min^{-1}$							
extraction fluid	CO_2							
EXTRACTION CHAMBER								
chamber temperature	$40\ ^0C$							
equilibration time	2.0 min							
extraction time	5.0 min							
thimble size	$7.0\ cm^3$							
thimble volumes swept	2.6	1.9	1.5	1.2	1.0	0.9	0.8	0.7
ANALYTE TRAP								
nozzle temperature	$45\ ^0C$							
trap temperature	$20\ ^0C$							
trap packing	stainless							
void volume compensation	$1.0\ cm^3$							
FRACTION OUTPUT								

Rinse substep	Solvent Name	Volume (ml)	Rate ($cm^{-3}.min^{-1}$)	Nozzel Temp.	Trap Temp.	Vial No.
1	DCM	1.0	2.0	$45\ ^0C$	$20\ ^0C$	8

SFE condition used for optimized density (experimental type 2).

EXTRACTION STEP		1	2	3
FLUID DELIVERY				
density $cm^{-3}.min^{-1}$		0.65	0.75	0.85
pressure Psi		1508	1937	3058
flow rate		$1.0\ cm^{-3}.min^{-1}$		
extraction fluid		CO_2		
EXTRACTION CHAMBER				
chamber temperature		$40\ ^0C$		
equilibration time		2.0 min		
extraction time		5.0 min		
thimble size		$7.0\ cm^3$		
thimble volumes swept		1	0.9	0.8
ANALYTE TRAP				
nozzle temperature		$45\ ^0C$		
trap temperature		$20\ ^0C$		
trap packing		stainless		
void volume compensation		$1.0\ cm^3$		
FRACTION OUTPUT				
Rinse substep	Solvent Name	Volume (ml)	Rate ($cm^{-3}.min^{-1}$)	Nozzel Temp.	Trap Temp.	Vial No.
1	DCM	1.0	2.0	$45\ ^0C$	$20\ ^0C$	3

SFE condition used for optimized temperature.

EXTRACTION STEPS	1	2	3	4
FLUID DELIVERY				
density ($cm^{-3}.min^{-1}$)	0.65	0.75	0.85	0.95
pressure (Psi)	1508	1937	3058	5560
flow rate	1.0 $cm^{-3}.min^{-1}$			
extraction fluid	CO_2			
EXTRACTION CHAMBER				
chamber temperature	40 , 60, 80, and 100 ^0C			
equilibration time	2.0 min			
extraction time	5.0 min			
thimble size	7.0 cm^3			
thimble volumes swept	1.0	0.9	0.8	0.7
ANALYTE TRAP				
nozzle temperature	45 ^0C			
trap temperature	20 ^0C			
trap packing	stainless			
void volume compensation	1.0 cm^3			
FRACTION OUTPUT				

Rinse substep	Solvent Name	Volume (ml)	Rate ($cm^{-3}.min^{-1}$)	Nozzel Temp.	Trap Temp.	Vial No.
1	DCM	1.0	2.0	45 ^0C	20 ^0C	4

SFE condition used for optimized modifier.

EXTRACTION STEP		1	2	3
FLUID DELIVERY				
density $cm^{-3}.min^{-1}$		0.65	0.75	0.85
pressure Psi		1508	1937	3058
flow rate		$1.0\ cm^{-3}.min^{-1}$		
extraction fluid		CO_2		
modifier (methanol)		5 % and 10 %		
EXTRACTION CHAMBER				
chamber temperature		$40\ ^0C$		
equilibration time		2.0 min		
extraction time		5.0 min		
thimble size		$7.0\ cm^3$		
thimble volumes swept		1	0.9	0.8
ANALYTE TRAP				
nozzle temperature		$45\ ^0C$		
trap temperature		$20\ ^0C$		
trap packing		stainless		
void volume compensation		$1.0\ cm^3$		
FRACTION OUTPUT				

Rinse substep	Solvent Name	Volume (ml)	Rate ($cm^{-3}.min^{-1}$)	Nozzel Temp.	Trap Temp.	Vial No.
1	DCM	1.0	2.0	$45\ ^0C$	$20\ ^0C$	3

SFE condition used for optimized extraction time.

EXTRACTION STEP		1	2	3
FLUID DELIVERY				
density $cm^{-3}.min^{-1}$		0.65	0.75	0.85
pressure Psi		1508	1937	3058
flow rate		$1.0\ cm^{-3}.min^{-1}$		
extraction fluid		CO_2		
EXTRACTION CHAMBER				
chamber temperature		$40\ ^0C$		
equilibration time		2.0 min		
extraction time		5.0, 10, 15 min		
thimble size		$7.0\ cm^3$		
thimble volumes swept		1	0.9	0.8
ANALYTE TRAP				
nozzle temperature		$45\ ^0C$		
trap temperature		$20\ ^0C$		
trap packing		stainless		
void volume compensation		$1.0\ cm^3$		
FRACTION OUTPUT				
Rinse substep	Solvent Name	Volume (ml)	Rate ($cm^{-3}.min^{-1}$)	Nozzel Temp.	Trap Temp.	Vial No.
1	DCM	1.0	2.0	$45\ ^0C$	$20\ ^0C$	3

SFE condition used for sample ratio optimization .

EXTRACTION STEP		1	2	3	4	5
SAMPLE RATIO			1/15	1/33	1/45	
FLUID DELIVERY						
density $cm^{-3}.min^{-1}$		0.55	0.65	0.75	0.85	0.95
pressure Psi		1355	1508	1937	3058	5560
flow rate		$1.0\ cm^{-3}.min^{-1}$				
extraction fluid		CO_2				
EXTRACTION CHAMBER						
chamber temperature		$40\ ^0C$				
equilibration time		2.0 min				
extraction time		5.0 min				
thimble size		$7.0\ cm^3$				
thimble volumes swept		1.2	1.0	0.9	0.8	0.7
ANALYTE TRAP						
nozzle temperature		$45\ ^0C$				
trap temperature		$20\ ^0C$				
trap packing		stainless				
void volume compensation		$1.0\ cm^3$				
FRACTION OUTPUT						
Rinse substep	Solvent Name	Volume (ml)	Rate ($cm^{-3}.min^{-1}$)	Nozzel Temp.	Trap Temp.	Vial No.
1	DCM	1.0	2.0	$45\ ^0C$	$20\ ^0C$	5

5.6 Aqueous extraction

Class fractionation of PAHs and saturated hydrocarbons from crude oils in aqueous matrix.

5.6.1 Chemicals

1. sample matrix : Bouri crude oil
2. Solvent : DCM
3. Reagents : Anhydrous Sodium Sulfate.
4. Carbon dioxide

5.6.2 preparation of spiked distilled waters

Aqueous solutions used for evaluation were prepared by spiking 2 cm^3 of Bouri crude oil dissolved in n- hexane into a 500 cm^3 distilled water. The mixture then mixed by ultrasound and a magnetic stirring device to saturate the aqueous solution.

5.6.3 Extraction Cell design

The extraction vessel used was modified from an empty preparative HPLC column (30 cm in length with an internal diameter of 8.0 mm) having capacity of 12 cm^3. Blind nuts on each end of the column were drilled out to a diameter of 1.59 mm. stainless steel inlet and outlet tubes (1.59 mm id.) were inserted into each end of the column and welded such that the ends of the tubes extended to 1.0 cm^3 from the top and the bottom of the column.

5.6.4 Supercritical fluid extraction system

1. Gilson HPLC (model 811) was used to supply CO_2 to the extraction cell.
2. Modified HPLC pump (model 303) fitted with a cooling head.
3. PYE Series (104 GC) oven
4. Three port switching valve (Rheodyne) with an adjustable restrictor to control the back pressure

Supercritical fluid extraction conditions :

pressure:	2000, 2500 , 2800, 3000, and 3500 psi
Temperature:	40, 60, 70, ^{0}C
Flow rate:	2.0 cm^3. min
sample volume:	8 cm^3
Extraction time:	15, 30 and 45 minutes.
Trap solvent:	Dichloromethane

GC Conditions : as given in paragraph 5.4.3.

Chapter 6

6. Conclusions and further work

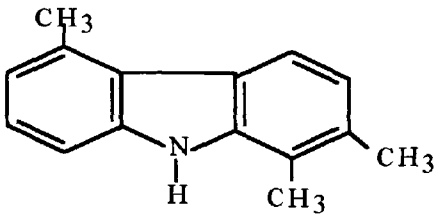
The micro-column chromatographic method developed in this work was shown to provide and effective means to fractionate crude petroleum samples into saturated, aromatic and polar hydrocarbon classes. A major disadvantage of the technique was poor reproducibility. Investigations indicated that variations in the water content of the silica adsorbent used, significantly influenced analyte retention. Future work in this area would centre on the development of a procedure that would accurately and reproducibly precondition the silica adsorbent prior to use. The extrographic method developed in this work was also shown to be an effective approach for the fractionation of crude petroleum samples. In comparison with the chromatographic method, extrography provided higher recoveries of the more polar fractions in addition to effecting a more accurate fractionation between aromatic and polar classes. This approach is promising, however, the technique needs to be applied to the analysis of "real" samples in order to assess its precision, accuracy and suitability for spill-related environmental monitoring. This would involve the systematic analysis of weathered and spilled oil samples including tar ball samples, slick residues and salt water emulsions. In addition to testing the feasibility of the technique, the results could be used to establish a data base for oil spill profiling.

These studies have shown that supercritical carbon dioxide may be used at different densities to provide a rapid fractionation of crude oil into hydrocarbon classes. The extraction of samples pre-adsorbed onto silica, using a density of 0.55 g cm^{-3} were found to selectively remove saturated hydrocarbons.

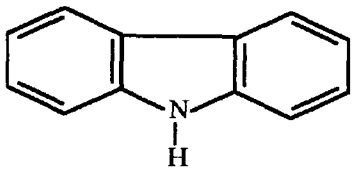
Subsequent extractions at 0.65 to 0.85 g cm^{-3} were found to remove carbocyclic aromatics. Hetrocyclic aromatics were removed at higher densities. As these studies proceeded it become apparent that fractionation efficiency is potentially dependent on many variables, other than those tested here. These include, the type of solid phase support used, sample size, choice of supercritical fluid, matrix effects, effect of and type of modifier and extract trapping technique used. In order to gain a fundamental understanding of the principles underlying the technique and provide a systematic approach for future method development, such parameters must be investigated in future studies.

The initial results for aqueous extraction indicated that the technique may have promise for the analysis of hydrocarbon types in aqueous environmental samples. To extract aqueous samples containing very low levels of petroleum bigger extraction cells are required to increase sample size. The main problem to be addressed in further studies is that of post restriction blockage. This could be over come by designing a more effective heater. Further work also must centre on the influence of salts on the extraction of organic materials from aqueous solution. With such data, one may be able to draw more general conclusions about the behaviour of an extraction system in the presence of strong electrolytes. Additionally, the effect of various SFE parameters on extraction efficiency must involve the use of "real" samples, not just spiked matrices.

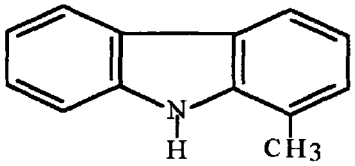
Appendixes



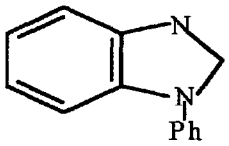
($C_{15}H_{15}N$)
1,2,5-Trimethy-9H-carbazole



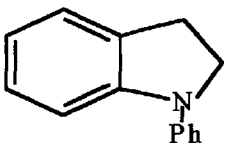
($C_{12}H_9N$)
9H-carbazole



($C_{13}H_{11}N$)
1-Methyl-9H-carbazole

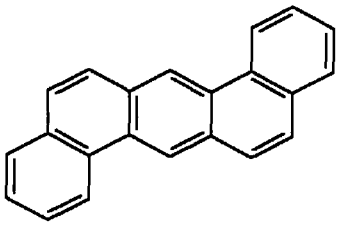


($C_{13}H_{10}N_2$)
2-Phenylbenzimidazole

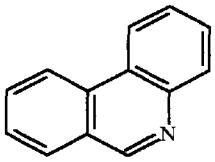


($C_{14}H_{11}N$)
1-Phenyl-1H-indole

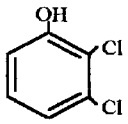
Principal compound classes identified in fraction 3



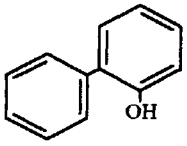
($C_{21}H_{13}N$)
Dibenz (a,h) acridine



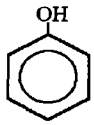
($C_{13}H_9N$)
Phenanthridine



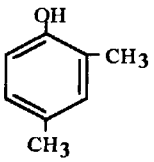
($C_6H_4N_2OCl_2$)
2,3-dichlorophenol



($C_{12}H_{10}O$)
2-Phenylphenol

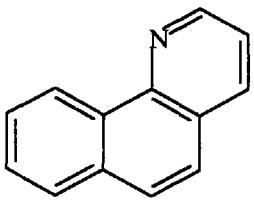


(C_6H_6O)
Phenol

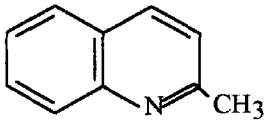


($C_8H_{10}O$)
Dimethylphenol

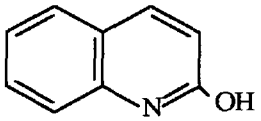
Principal compound classes identified in fraction 4



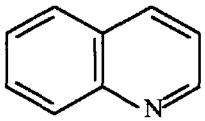
($C_{13}H_9N$)
Benzo(h)quinoline



($C_{10}H_9N$)
2-Methylquinoline



(C_9H_7NO)
2-Quinolinl



(C_9H_7N)
Quinoline

Principal compound classes identified in fraction 5