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Research Paper

Extraction and identification of aliphatic hydrocarbons in Marine sediment samples at Benghazi city and Dyriana town coasts (Libya)

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Abstract
This study aimed to identification and extraction of aliphatic hydrocarbon compounds of some sediment samples collected from different locations along Benghazi city and Dyriana town coasts (Libya).The GC-Mass analysis method was used to estimate the hydrocarbon compounds. The results recorded presence different types of aliphatic hydrocarbons .Different contents were recorded in the studied samples. The major aliphatic hydrocarbon compounds were (C9 – C20), the study showed that most of these compounds sources are mainly due to the effect of petroleum activity , or human activity (as fishers) at the studied locations.

Key words: *Aliphatic Hydrocarbons, Sediment samples, Benghazi , Libya*

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I. Introduction:

Aliphatic hydrocarbons are hydrocarbons based on chains of carbon atoms. There are three types of aliphatic hydrocarbons. **Alkanes** are aliphatic hydrocarbons with only single covalent bonds. **Alkenes** are hydrocarbons that contain at least one C–C double bond, and a**lkynes** are hydrocarbons that contain a C–C triple bond. Occasionally, we find an aliphatic hydrocarbon with a ring of C atoms; these hydrocarbons are called ***cycloalkanes***(or *cycloalkenes* or *cycloalkynes*). Because alkanes have the maximum number of (H) atoms possible according to the rules of covalent bonds, alkanes are also referred to as **saturated hydrocarbons**. Which divided into three main groups according to the types of bonds they contain: alkanes, alkenes, and alkynes. Alkanes have only single bonds, alkenes contain a carbon-carbon double bond, and alkynes contain a carbon-carbon triple bond(Jensen ,2009).Aliphatic compounds can be saturated, joined by single bonds (alkanes), or unsaturated, with double bonds (alkenes) or triple bonds (alkynes). Besides hydrogen, other elements can be bound to the carbon chain, the most common being oxygen, nitrogen, sulfur, and chlorine. The least complex aliphatic compound is methane (CH_4) (*Smith&*March,*2007).*

Aliphatic compounds may be saturated or unsaturated. Saturated hydrocarbon contains mainly of alkanes which are open chain hydrocarbons containing carbon-carbon single bond. Most of the time the bond exists in the form of a covalent bond. These compounds are inert in nature and do not readily react with acid, bases or other reagents. Hydrocarbon molecules which have no double bonds in them are called saturated. This simply means that there are as many hydrogen atoms aspossible in the molecule, and no more can be added. Unsaturated hydrocarbons are alkenes and alkynes which have one carbon-carbon double bond and one carbon-carbon triple bond respectively. Unsaturated hydrocarbons are more reactive than saturated hydrocarbons, and they usually fewer hydrogen atoms can be seen in bond with carbon atoms (Albaiges,1997).

Most aliphatic hydrocarbons are flammable. These compounds are used as fuels.Aliphatic compounds can be cyclic or acyclic meaning they can contain close chains or rings of carbon atoms in their molecule.Boiling point and melting point .The small difference between the electro negativities of carbon and hydrogen means that the bond between them is only very weakly polar. Chain branching causes a decrease in the area of contact. So if two alkanes have the same molecular weight the more highly. branched one will have the lower boiling point. The melting points of aliphatic hydrocarbons also increase with size but in a less regular manner.Solubility and density: As the hydrocarbons are non-polar they tend to be insoluble in water and other

polar solvents. They prefer to dissolve in non-polar solvents such as benzene and diethyl ether. Thus, hydrocarbons cab be described as hydrophobic or lipophilic. The hydrocarbons are less dense than water meaning that they float on the surface of water (Morrison and Boyd ,1992).

Extraction of Aliphatic Hydrocarbons:

Aliphatic compounds can be extracted by the process known as Pressurized Fluid Extraction or (PFE) where organic and aqueous extraction solvents are used. Water which is converted to hot steam can also be used to extract aliphatic hydrocarbons mostly from solid and semi-solid environmental samples.(IUPAC,1997).Very little use has been made of aliphatic hydrocarbons as solvents in conventional flame spectrometry. Pentane, methyl cyclepentane and cyclohexane have been tested as solvents for the determination of nickel in an oxygen cyanogen flame. These solvents appeared to offer no striking advantages, although excellent sensitivity was obtained when pentane was used in AAS. Heptane, cyclohexane and cyclohexene have been investigated as possible solvents for the determination of beryllium by AFS. In both the oxygen acetylene and the nitrous oxide acetylene solutions. Alphatic hydrocarbons are occasionally used as diluents for other solvents. The Table (1) give the names,the formula and the physical state of the simple and some tall chain of aliphatic Hydrocarbons.(IARC,1983).

Table (1): The classification of aliphatic hydrocarbons:

Alkane	Formula	Physical State
Methane	CH_4	(gas)
Ethane	C_2H_6	(gas)
Propane	C_3H_8	(gas)
Butane	C_4H_{10}	(gas)
Pentane	C_5H_{12}	(liquid)
Hexane	C_6H_{14}	(liquid)
Heptane	C_7H_{16}	(liquid)
Octane	C_8H_{18}	(liquid)
Nonane	C_9H_{20}	(liquid)
Decane	$C_{10}H_{22}$	(liquid)
Undecane	$C_{11}H_{24}$	(liquid)
Dodecane	$C_{12}H_{26}$	(liquid)
Pentadecane	$C_{15}H_{32}$	(liquid)
Hexadecane	$C_{16}H_{34}$	(liquid)
Heptadecane	$C_{17}H_{36}$	(liquid)
Icosane	$C_{20}H_{42}$	Solid
Triacontane	$C_{30}H_{62}$	Solid
Tetracontane	$C_{40}H_{82}$	Solid
Pentacontane	$C_{50}H_{102}$	Solid

The most important source of alkanes is natural gas and crude oil. Alkanes are separated in an oil refinery by fractional distillation and processed into many different products *(*Sephton and Hazen,2013).

Resource of hydrocarbon:

Hydrocarbon resources are resources that contain hydrocarbon molecules which means it consists both hydrogen and carbon that can take the form of a solid, liquid, or gas . Hydrocarbons are the main components of fossil fuels, also known as nonrenewable energy resources, including coal, oil, and natural gas The natural sources of hydrocarbons include coal, petroleum, and natural gas. Fossil fuels are a category of fuels that are made by slow geological processes acting on dead organisms that are hundreds of millions of years old their remains have become deposited and transformed into sediment as a result of the great heat and pressure in the earth's crust. They are used as fuels, burnt to release heat and other forms of energy. They are reformulated into gasoline, diesel fuel, and heating oil . Coal is a solid fuel, petroleum is a dark and viscous liquid fuel (otherwise called crude oil), and natural gas is a gaseous fuel Hydrocarbon resources are the largest source of primary energy, contributing to over 85% of the world's primary energy (Ravindra et al.,2008).

Fossil fuel:

Resources are simply hydrocarbon resources, given a different name .Therefore, due to the time it takes for them to form, fossil fuels are not considered a renewable energy source. The most common types hydrocarbon resources include : Coal Oil , Natural gas and petroleum. Figure (1.1) describe the types of fossil fuel.(Krom et al., 1989).

Natural gas:

It is a traditional energy resource, which is a resource that is nonrenewable. It is a combustible mixture of gaseous hydrocarbons, the primarily compound being methane, a naturally occurring colorless, odorless, nontoxic, and flammable gas. Natural gas accumulates in sedimentary rocks beneath the surface of the earth. These layers of rock trap the natural gas as it attempts to float to the surface, and the natural gas molecules become trapped in holes and cracks throughout rock formations .Natural gas is used to generate electricity, heat buildings, fuel vehicles, heat water, and power furnaces in industrial facilities. Nearly 50 percent of U.S. homes use natural gas, mostly for space and water heating, as well as for appliances like ovens, stoves, and lighting fixtures. Additionally, chemicals derived from natural gas, such as hydrocarbon gas liquids, are used to produce plastics, pharmaceuticals, and other products (Botts et al., 2015).

Petroleum

It is a broad term that groups together a combination of organic liquids and gases that is formed after kerogen is heated and compressed over long periods of time. This mix can be fairly complex, but the main gaseous component of petroleum is natural gas - largely methane - whereas the main liquid component is crude oil. Crude oil itself is a complex mixture of hydrocarbons,so the exact composition of petroleum is never the same. Secondary fuels such as gasoline, kerosene, heating oil, and dieselfuel are all included in the definition of "petroleum". Petroleum traps energy, first originating from the Sun, that was captured by photosynthetic lank ton in ancient oceans. Just like coal, petroleum is a type of fossil fuel.(Lipiatou et al., 1997).

Coal :

Coal is composed primarily of carbon along with variable quantities of other elements, chiefly hydrogen, sulfur, oxygen, and nitrogen. Coal is the largest source of energy for the generation of electricity worldwide, as well as one of the largest worldwide anthropogenic sources of carbon dioxide releases (Natural Resources Canada ,2011). When coal is used for electricity generation, it is usually pulverized and then combusted (burned) is an a furnace with a boiler. The furnace heat converts boiler water to steam, which is then used to spin turbines which turn generators and create electricity.(Gordan Research Conference,2015).

Coal is an important feedstock in production of a wide range of chemical fertilizers and other chemical products. The main route to these products is coal gasification to produce syngas. Primary chemicals that are produced directly from the syngas include methanol, hydrogen and carbon monoxide, which are the chemical building blocks from which awhole spectrum of derivative chemicals are manufactured, including olefins, acetic acid, formaldehyde, ammonia, urea and others. The versatility of syngas as a precursor to primary chemicals and high-value derivative products provides the option of using relatively inexpensive coal to produce a wide range of valuable commodities(Del vanto and Dashs , 2002).

Industrial activities in the coastal region of Libya:

Industrial activities in the coastal region of Libya is confined to large cities, like Tripoli, Misurata and Benghazi, with some centers of specialized industrial complexes (petrochemicals, oil and gas refineries, steel industry), The petrochemical complex in Abukammash (near Farwa Lagoon in the west) is a continuous risk to the marine environment, even if no pollution crises have been reported to date, (Saleh ,2012).

The oil refineries on the coastal area, including those in Zawiya, RasLanouf, Brega, Zwitina and Tobruk, are another source of potential oil pollution; as is the steel and iron company in Misuratah. In fact, most of the state owned companies have contingency plans for accidental pollution incidents, developed in collaboration with the EGA and Mediterranean Action Plan (MAP), over the past 20 years In the present study, some marine sediment samples is taken as bioindicator for contamination of hydrocarbon compounds: The main aims of this study can summarized in the following points, Identification and determination of aliphatic and hydrocarbons in some marines sedimentattempt to study the origin of the hydrocarbons in the investigated area .

II. Materials and Methods:

Description of the studied area :

Benghazi region , lies on the southern coast of the east Mediterranean , north of the coast of Libya. It is one of the most important center for fishery in Libya Benghazi is a major seaport and the second-most populous city in the country, as well as the largest city in Cyrenaica. Benghazi has wonderful weather; Summers are hot and rainless, the studied area is extended from Benghazi city to Dyriana town.

Sampling and Preparation of Samples:

Two main region were selected in this study Benghazi city and Dyrianatown.Where the sediment samples were collected in polyethylene bags , then dried and grinded by mortar, then transfer to the laboratory to use the other steps.

Determination of hydrocarbon :

Hydrocarbons have been determined in marine sediment according to (UNEP , 1991) . The sample were analyzed for aliphatic hydrocarbons following different steps including : extraction , cleaning up and fractionation , instrumental analysis and quality control .

Extraction Step of hydrocarbons for fish Sample :

Five grams of wet weight of sediments sample were treated with 30 g of anhydrous sodium sulfate and the mixture was blended at high speed for 5 min. Then the mixture was extracted using a soxhlet with 200 ml of methanol for 8 hrs. 20 ml of 0.7 M KOH and 30 ml of distilled water were added to the flask and the reflux was continued for 2hrs to saponify the lipids. The content of the extraction flask was extracted three times in a separating funnel with 80 ml hexane. The three extracts were combined, dried with anhydrous sodium sulfate and filtered through glass wool. The hexane fraction was concentrated with a rotary evaporator down to about 15 ml at 300^0C and concentrated down to a volume of 1 ml with nitrogen gas stream and then subjected to cleaning up and fractionation(El Nemr et al ., 2007).

Cleaning up and Fractionation:

Cleaning up and fractionation were performed by passing the concentrated extract through a silica/aluminum oxide column. The chromatography column was prepared by slurry packing 20 ml of hexane containing 10 g of silica, followed by 10 ml containing 10 g of aluminum oxide and finally 1 g of anhydrous sodium sulfate. The hydrocarbon sample extract (1 ml) was sequentially eluted from the column with 25 ml of hexane for the saturated aliphatic fraction (F1), and then 60 ml of hexane and dichloromethane (80:20) was used for the elution of the unsaturated aromatic fraction (F2). F1 and F2 were concentrated using gentle stream of nitrogen for instrumental analysis. 2µL of each sample of unsaturated aromatic fraction was injected in the split less mode and purge time was 1 min. the response factor of individual hydrocarbon compounds to the internal standard was measured and calculated at least three times (at the beginning, in the middle, and at the end for each batch of GC injections). Identification and quantification of hydrocarbon compounds were based on matching their retention time with a mixture of hydrocarbon standards.

Instrumentation and Analysis Conditions:

The GC-MS instrument is combined of two parts: The gas chromatograph (GC) that separates the chemicals in the sample and the mass spectrometer (MS) that identifies and quantifies the chemicals. When the sample has been properly cleaned it is injected into the GC inlet where it is vaporized and transferred by an inert gas (mobile phase), normally helium, through a column with a special polymer coating on the inner surface, (stationary phase). The molecules separate according to their volatility, the smaller ones travelling faster compared to larger molecules, as well as adsorption to the stationary phase. The time when the molecule comes out of the column is called retention time. At the end of the column the molecules are ionized which is important because the molecules must be charged to travel through the filter (mass analyzer)inthe mass spectroscope. The filter separates the ions according to mass to charge ratio (m/z) related properties depending upon the analyzer that is used. When the analysis is performed, mass to charge ratio (m/z) is measured. The most commonly used mass filter is quadruple as used in the current study, whereas other filters such as sector field (SF) and time of flight (ToF) are also common. After the ions have been separated they pass through a detector that counts the number of a specific mass. Thisinformation is fed into a computer that records all the data produced and plots a mass spectrum (Ravindra et al., 2008). All the experiment methods were carried out at (Alexandria University), Central laboratory of Oceanography and Fishers High institute .

III. Results:

The obtained results which recorded in this study are described as following:

Aliphatic hydrocarbons :

The Tables of (2) showed the results of aliphatic hydrocarbons in the samples.

Table (2) : the concentration (µg/g) of aliphatic hydrocarbons in sedimentmeasured by GC/MS .

Sample	Marine sediment		Average
	Benghazi	Draryanah	
C-9	752.55	662.99	**707.77**
C-10	33.02	26.77	**29.895**
C-11	10.46	9.31	**9.885**
C-12	57.51	64.17	**60.84**

C-13	38.77	23.16	**30.965**
C-14	62.21	74.09	**68.15**
C-15	22.95	24.05	**23.5**
C-16	42.04	50.28	**46.16**
C-17	15.28	16.49	**15.885**
C-18	27.08	30.11	**28.595**
C-19	8.44	8.1	**8.27**
C-20	16.51	16.01	**16.26**
Total	**1086.82**	**1005.53**	1046.175

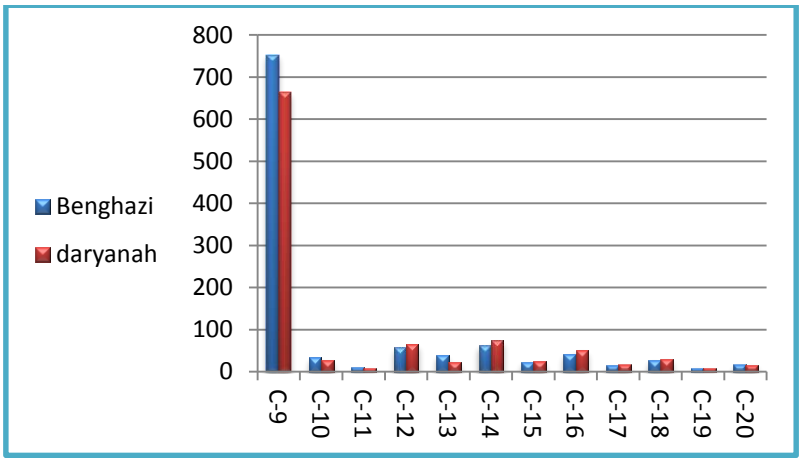
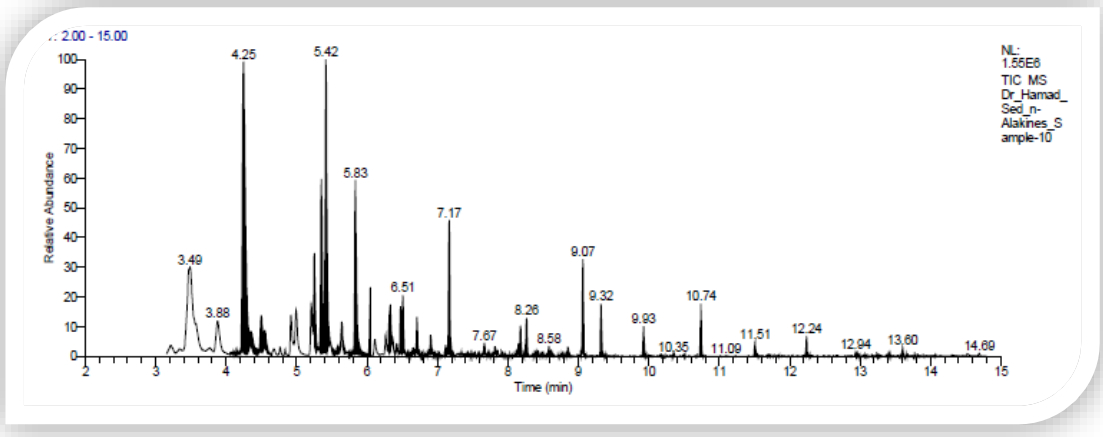
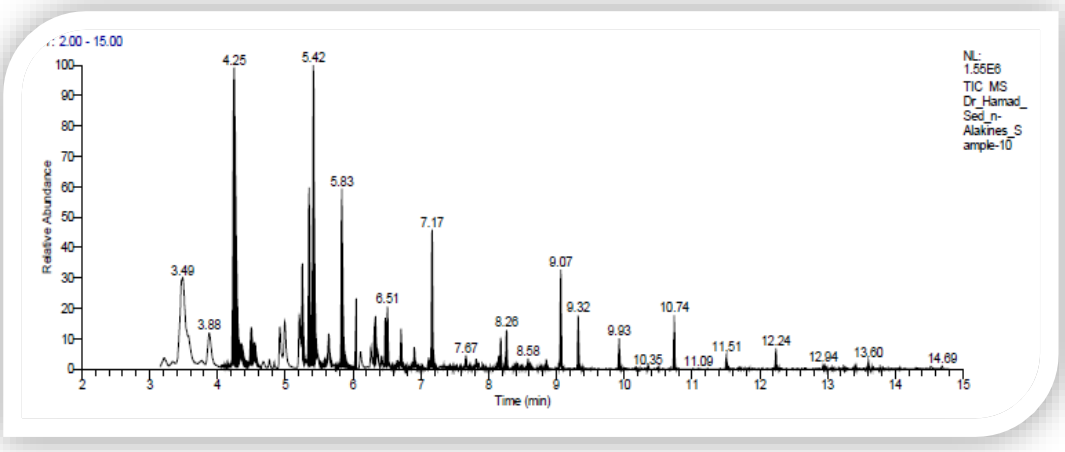


Figure (1): Distribution the concentrations (µg/g) of aliphatic hydrocarbonsof Marine sediment**.**



Figure(2):The GC mass analysis for marine sediment sample of Daryanah



Figure(3) :The GC mass analysis for Marine sediment sample of Benghazi city coast .

IV. Discussion:

Aliphatic hydrocarbons:

The concentrations of aliphatic hydrocarbons in the sediment samples are shown in the Table of (2) and represented in Figures of (1-3). The results showed that the types and the n-alkanes compounds containing the aliphatic hydrocarbons of C_9 to C_{20}. The concentrations were fluctuated between (8.27 - 707 µg/g). These values are lower than those data which recorded in some Alexandria organism (451 – 1148 µg/g) , also lower than the values of (El – Sikaily et ., al 2002) (180 µg/g) at some Mediterranean coasts and in harmony with results of (Neussrey , 2013) study (100 µg/g) , and lower than data of at EasternHarbor of Alexandria (1782 µg/g) (Emara and shridah ,2008).The high concentrations of the detected aliphatic hydrocarbons was (1451.04 , 1697.88 and 1975.86 µg/g) is related to C_9 compound in the fishes and (1415.54 µg/g) sediment marine samples , respectively .This was less than the recorded levels for clean urban sites in Scotland, UK; with an average value of 3003 µg/g (wet weight) (Mackie et al., 1980), however it is less than the recorded level for black sea which was ranged from (1200 – 24000 µg/g) of sediment (Readman et al., 2002). Most of hydrocarbon are related to the human activities as fishers and / or petroleum industry , Benghazi is one of the most cities around the Mediterranean sea coast which have high activates at Benghazi Harbour , beside that the water current may be increase the contents of hydrocarbon compounds at the studied samples,

Correlation coefficients between individual aliphatic hydrocarbons concentrations were found to positively high relation ($r > 0.9$) for most of the parent components except for C_9 which gave high to medium negatively correlation ($r = -0.8$ to $- 0.4$) in the sample.Correlation coefficients between different types of tissues revealed that gills present positively high relation

V. Conclusion:

According to the results obtained in this study , the selected samples of sediment containing different types of aliphatic hydrocarbons, the main sources of the detected hydrocarbon compounds mainly due to the effect petrol industry activities.

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