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Study of Some Physical and Chemical Properties of the Rock Samples Selected from Wells N 18 in the Field of Nasiriya and its Oil

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Absract
This study was based on that hydrocarbon compounds originating in the oil can be leaked from the reservoir of and oil rising to the surface through the different layers. This study followed up relied change concentrations of these compounds and concentrations of elements associated with the change as a way to track it's path rises of such material in a Well 18 (Al- Nasiriya Field) through rock samples taken from various depths along the column of the Well trying to find some kind of comparison between the change 1 Qw2`\`W2\ of focus and depth of the Well.The quantitative and qualitative analyses have been conducted of trace metals in the organic extract from the rock samples using Atomic Absorption Spectroscopy and these elements are sodium, potassium, chromium and nickel. Samples were digested using a mixture of nitric acid concentration of 20% and 20% HCl concentration and by (2:1) volume ratio. The organic content extracted from rock samples contains a compound N- Ethyl Carbazole only, as is clear from the analysis of chromatographic (GC) of the samples. Carbazole rise to the top of the well's column. Some physical and chemical properties of crude oil such as: specific gravity, specific weight API, water content and salt content were measured. Through these properties were found that the oil is considered of medium quality oils and relatively close to the earth's surface and thus it can be extracted with little cost.
Keywords: Crude Oil, Trace metals, Ethyl carbazole

1 -Introduction

Petroleum (Crude oil) represents a complex mixture containing both organic and inorganic chemical species, hydrocarbons, metals and hetro organic compounds (Duyck et al., 2007). Petroleum is a mixture of a very large number of different hydrocarbons; the most commonly found species are alkanes (paraffins), cycloalkanes (naphthenes), aroma-tic hydrocarbons, or more complicated chemicals like asphaltenes (Crude Oil Category, 2011; Okop and Ekpo, 2012). Each petroleum variety has a unique mix of species, which define its physical and chemical properties, like color and viscosity (Tissot and Welt, 1988; Aldboni, 1991; North, 1985)

Many molecular markers based on aliphatic and aromatic hydrocarbons are pro- ven to be well suited for the characterization of oil families and assignment of source faces, thermal maturity level, degree of preservation, and migration. On the other hand hetero compounds (nitrogen, oxygen, and sulphur, NSO compounds) that make up a small portion of most crude oils (Tissot and Welt, 1988) have significant implications in petroleum exploration, because their greater structural diversity results in greater variations of their physicochemical properties. Consequently, hetero compounds can provide useful geochemical clues that trace petroleum molecules back to their biological precursors (Valkovic,1978).

Organic nitrogen compounds occur in crude oils in small amounts, with an average content of 0.1% by weight(Baxby et al.,1994). Most nitrogen compounds in crude oil are in heterocyclic aromatic structures and are concentrated in the high molecular weight and high boiling point fractions(Tissot and Welte, 1988; Baxby et al.,1994; Ball et al.,1951). There are two classes of nitrogen compounds; basic (pyridinic type),and non-basic (Pyrrolic type structures), and in most cases, non-basic predominates over basic nitrogen (Varma and Naicker, 1999; Dorbon et al.,1984; Richter et al.,1952; Wilhelms et al., 1992). The pyrrolic nitrogen compounds, particularly the carbazole derivatives, exist in source rocks and crude oils, and have been reported to show great promise as potent geochemical parameters that might play a significant role in exploration and production for crude oil (Broscorkov and Drapkin, 1987).

The nature and characteristics of nitrogen compounds in petroleum have long been documented by petroleum geologists and geochemists. Especially in recent years, the polarity character of aromatic heterocyclic nitrogen compounds (non-basic nitrogen compounds form hydrogen bonds by their nitrogen atoms, and

adsorption takes place between basic nitrogen compound and medium by ionic linkages or hydrogen bonds) has been suggested as a characteristic to study petroleum migration for hydrocarbon exploration (Broscorkov and Drapkin, 1987; Min et al., 2004; Yao et al., 1998; Li, 2000). During migration, polar nitrogen compounds in petroleum will undergo reactions with the surfaces of country rocks (e.g. pores, fractures and faults). Therefore, with increasing migrating distance, the amount of nitrogen compounds in petroleum should decrease, with separation from crude oil and adsorption on country rocks along the migration paths.
The concentration of the different elements in the crude oil produced in various different parts of the world vary greatly (Filby, Shah, 1975),and the measurement of heavy metal ions (such as vanadium, nickel, iron, copper,...etc.) in heavy crude oil as linked metals organically(Fish et al., 1984) and find out information about these elements is very important not only in oil production and refining, but also to determine the prices of crude oil(Al-Swaidan, 1993; Wallace, 2003).

The aim of the study: (1)Find a relationship between the physical and chemical properties of the soil sections with physical and chemical properties of crude oil, (2) Find a relationship between the concentrations of some hydrocarbons in soil and it's depths, (3) Find a relationship between the change in the concentrations of some elements in the soil and it's depth.

2- Geological setting

Nasiriyah field is located in the governorate of Dhi Qar, and is just 38 km northwest of Nasiriyah city between latitudes east (61.10 '- 57.50') and a linear north (34.80 '-34.60') degree. It has been proven through exploratory wells:

Nasiriya-1, Nasiriya-2, Nasiriya-3, Nasiriya-4, Nasiriya-5 in the previous period and the presence of oil in the three major reservoirs (Al Moshref, Al Yamamah, Nahar Omar) with the possibility to enter Zubair and Alrtaui evaluation of the reservoir.

Located Nasiriya oil field in the range unstable Arabian Platform (Levovsrnu, 1967) in the scope of the alluvial plain, specifically in the belt of the Euphrates tectonic (Al-Hashemi,1985) ,which is characterized by the presence of folds and domes under the surface along with a general variable from the north-south to the north-west south-east with folds along with a non-depending on a large seismic surveys 1987-1988 that proved that the installation is a convex fold unaffected by cracks proportions (30*10 km), and represents the field of Nasiriyah fold convex slope with a few (2-1) degrees toward the foothills northeast-southwest, depth ranges from rocks where the base between (10-9) km.

3-Experimental and Samples

3-1 Samples:

Soil samples were taken at different depths of the Well column samples were of two types:
-Cutting samples, which is about gestures close to the surface and the depths were 0, 250, 500, 750, 1000 m.
-Core samples,. A sampling of the reservoir near the oil has been taken from the depths 2000.2190 m.
These samples milled to precise sizes 50 µm.

3-2 Extract the organic content

Extraction and the creation of models for analysis by **GC** technique, was according to the reference (Shah et al., 1970) .Used with the Cutting samples Agilent 6890N chromatography device provider with flame ionization detector (FID and the column type is HP-35, a length of 30 meters. And using the nitrogen as gas carrier. The Column temperature may use thermal program begins elementary degree heat 40°C for 2 minutes and then gradually rise by 2°c per minute to a final temperature of 190°c for 15 minutes, and the temperature Detector 325°c when the temperature of the injection port at 275°c.

The Core samples from a different device type (GC 2014 Shimadzo) and column type of user INTRTCAP MS, a length of 30 meters. Use as thermal program begins with an elementary degree heat to 60°c final degree heat 280°c for 30 minutes. It also proved temperature Detector 330°c when the temperature Injection Port at 290°c. Speed the flow of gas 30 ml per minute.

3-3 Quantitative and qualitative analysis of the mineral components

The creation of models for measuring technology **AAS** According to the reference (Brunori et al., 2005)Samples were digested using a mixture of nitric acid concentration of 20% and HCl concentration of 20% and by (2:1) volume ratio.

3-4 Measurement of the properties of crude oil

3-4-1 API gravity and Specific gravity:

100 ml of crude oil and measured it and according to standard methods, according to the reference (ASTM

D1298 b12, 2012).

3-4-2 Water content:

100 ml of crude oil is added to 400 ml of xylene and then measured by standard methods, according to the reference (ASTM D4006 e1, 2012).

3-4-3 Salt content:

100 ml of crude oil with 70 ml of Toluene and 25 ml of a mixture of 10% acetone and 15% ethanol and placed in a conical flask left to boil for (15-20 minutes) and then measured him by standard methods, according to the reference (ASTM D512, 2004).

4- Results and Discussion

4-1 Diagnosis and hydrocarbon separation by GC technique

The results of chromatographic analysis of the content hydrocarbon soil samples to the presence of a compound N-ethylcarbazole From the reservoir up to the surface, and figures from 1 to 8 illustrate chromatograms up related models studied.

Note the different time and detention compound N-ethylcarbazole in the chromatograms Noting his appearance at the time 3minutes in the chromatograms while cutting samples found at 6 minutes in chromatograms the core samples, and the reason is due to the use of two different GC for analysis and the circumstances of different analytical.

The overall figure of the curve N-ethylcarbazole refers to the increasing focus toward oil reservoir, where keeping the curve on the case of escalation along the column excluding the region between 750 and 1000 m there a sharp decline in the value of focus, and this is due to the nature of the soil at those depths where soil that is characterized by high porosity so it doesn't keep the organic matter and allow to migrated it through which to the top, table 1 shows the concentration of N-ethylcarbazole in soil depths studied, table (l) shows the concentration of N-ethylcarbazole in soil depths studied, table l shows the concentration of N-ethylcarbazole in soil depths studied .

The quantitative analysis of the content of hydrocarbon for rock samples taken from the well-studied suggests the possibility of using the concentration of Ethyl carbazole with a high abundance of crude oil to predict the distance that separates the area of drilling and reservoir oil. The results were with a good accordance with the study of R.R. Singh and P. Sivan which pointed to the possibility of the use of quantitative analysis of nitrogen compounds as an indicator of the presence of oil wells (Sivan et al., 2008)**.**

As many researchers have found that the geochemical study of the distribution of carbazole compounds provides very useful information about the petroleum geochemistry, especially, about the possibility of studying the migration of crude oil, its direction and the accumulation of oil and composition of the well (Chen, 1995; Larter et al., 1996; Hwang et al., 2002).

Some studies have shown that the distribution of carbazole compounds controlled by depositional environment and organic nature of the study area has made a lot of researchers to discuss the impact of maturity warming on the concentration of these compounds (Li et al., 1997) and provided convincing evidence on the control of thermal maturation source and proved that the concentration of carbazole compounds increases with maturity (Clegg et al., 1998).

The migration of compounds hydrocarbon from the oil reservoir to areas near the surface may be due to the transformation of these compounds into the gaseous state by heat and pressure influence on the source rocks and moves with the water associated with the Formation water, as that migration is also the result of cracks and fissures in through layers of rock in this region and can hydrocarbon compounds with a molecular weight of the low that passed through layers of rock cover after it dissolves in water associated with crude oil (Donovan et al., 1970).

The N-ethylcarbazole of compounds is relatively stable because the nitrogen atom in it be constrained by the group Ethyl associated with them and this makes it a non-interaction with other organic compounds do not tend to the formation of complex compounds with heavy elements (Broscorkov and Drapkin, 1987).

Transmitted hydrocarbons when passing through layers allow it Going through the zone of high pressure to areas with a pressure lower and continue these compounds in their migration across the porous rocks unless objected to the way an obstacle until it reaches the surface (Khansi, 2006), and because the oil Nasiriyah from oils near the surface of the earth, these hypothesis is possible to get.

4-2 Concentration of elements

This study focused on the quantification of the elements nickel, chromium, sodium and potassium because these elements of correlation with the presence of oil. The Previous studies have suggested that these elements exist in acceptable quantities in crude oil either in form dissolved organic complexes or in the form of dissolved salts.

4-2-1 The crude oil

The contents of the oil well, which made it the study of the elements sodium and potassium, nickel, chromium,

shown in the table (2).

4-2-2 Organic extract

Concentration of elements; sodium, potassium, chromium, and nickel in the organic extract of the rock samples.

Trace elements will shade the origin and migration of oil (Valkovic, 1978) Dunnington has been suggested in an earlier study focused on the ways migration of crude oils in Iraq and the countries of the Middle East that this region of origin and one has migrated From geological rock bottom to geological rock upper (Dunnigton, 1967). To find a correlation between the distance from the oil reservoir and the concentration of the ingredients to be an important process in the exploratory tests being one of the early stages in identifying new areas for exploration and must rely on oil components with high stability and up to the surface in the exploratory tests (Barker, 1982). Table (3) shows the results of the analysis, which shows where the acceptable amounts of these elements in the samples studied.

To follow the general behavior of the concentrations of elements change with the change of distance from the oil reservoir variation result were presented on figures 9-13, it can infer the following:

1 - There is a continuous increase by the content of elements in rock samples from the surface as we head towards the top of the oil reservoir where the measured values at their highest levels.

2 - The analysis shows that more elements presence in rock samples studied in a well no. 18 were the sodium, its concentration was 937.5 ppm in the surface areas, while to 3102 ppm in the near of the reservoir oil, followed by potassium, chromium and nickel.

The symmetry in the general trend of the relationship of concentration to raise (drilling depth) elements in the cases of N-ethylcarbazole indicates that thread together their presence being the one out of a relationship and the emergence of the presence of oil (Zeki and Barbooti, 1989).

The values of the elements and the content of compound hydrocarbon studied in the area of drilling in 18 wells located depth between 500 and 1000 meters, show that it is not affiliated with the general trend (increasing values of focus toward the oil reservoir). In order to identify the reasons that may be behind the appearance of this result has been back to the column laminar to this well (and this is what has been studied and presented in the introduction), where common to all configurations column being made up of rocks, calcareous lax in some of the medium hardness in others can be seen the first evidence oil in the formation of Khasib depth at 2150 meters.

That it is apparent that the region where there is a sharp decline does not retain mineral and hydrocarbon components and these components move through the region of the lower to the upper area. The failure of the detention class of hydrocarbon materials and components due in part to the low porosity of the anhydrite rocks as the cracks in the rocks consistent with the vertical migration and therefore they do not retain material passing through them.

4-3 The properties of crude oil

4-3-1 API gravity and Specific gravity

Values were measured API gravity and specific gravity standard methods (Table4) shows the results of measuring the specific gravity and the API before and after the degasification of gases in the field and being isolated from the gas oil produced by the pump in export pipelines .

The results of the relative density and the value of the API that we have obtained show that the oil Nasiriyah is one of the oils medium to light any of the good varieties compared with Dubai crude, which is the global standard (density quality 0.871g / cm^3 and the API has 31°) to the Middle East countries and the continent Asia General (McCain, 1990).

This can be seen a difference in the values of the results before and after the degasification and the reason is due to the process of isolating the gas then sends oil to refining units. And are isolation and washing in insulators, as the process of degasification to reduce the pressure to atmospheric pressure and reduce the speed of the flow of crude oil to get separated stable, depending on the amount of pressure reducing some of the hydrocarbon compounds light oil will be lost to the gas and hydrocarbons light is methane CH4 and ethane C2H6 and Propane C3H8, so is the station degasification is the first stage in a long series of stages for crude oil processing so as to allow for the larger section of the gas to be free of these hydrocarbon compounds and then increase the oil recovery (Rameshni, 2000).

Because of this process has been part of the basic components of crude oil, and this means a decrease in the value of the raw intensity and then increase the value of the API to it, and this is what was observed in the results above.

4-3-2 Water content

Found that crude oil in the field of Nasiriyah is a dry type as the percentage of water is 0.02, and this is one of the advantages of oil Nasiriyah, because this means that the proportion of salt in it and then a few lesser proportion of the erosion of pipes carrying units and refineries. Table (5) The percentage of water in the crude oil to the field of Nasiriyah before and after degasification

4-3-3 Salt content

It's found that the percentage of salt in the crude oil well 18, which is often a chlorides, are a small percentage does not exceed 6 ppm, and this result is pre-degasification but after the degasification and washing will be the proportion of salt zero, because the oil Nasiriyah from the oils dry and this is what sets it apart because the proportion of salt affect the price of crude oil, as the presence of salts in the oil leads to the formation of deposits in the pipes carrying him and a drop in pressure, also affects the functioning of the pumps and cause corrosion of equipment (McCain, 1990).

Subject of oil after the degasification to the processing of many before it is sent to the refining units and these processors are the washing process and are washing in the special units are washing the oil with water free of salts to remove any traces of salts and then transferred to other units for the removal of water from it. Table (6) shows the proportion of salt in the rough by the process of degasification and washing and beyond.

5- Conclusions

1 - The results of this study and through the measured properties of the crude oil to the field of Nasiriyah is of medium quality oils as the high value of the API and viscosity and density of the relatively low salt content is very small and the water content of the non-existent.

2 - The presence of a compound N-ethylcarbazole in rock samples near the surface (similar to its existence in the rock samples near the reservoir oil) refers to the possibility of leakage of some components of crude oil to the surface.

3 - The results of the quantitative analysis of hydrocarbon compounds and elements Cr, K, Na and Ni concentrations that tend to increase the greater the depth of drilling toward the oil reservoir.

4 - Indicate the results obtained from this study in the light of data qualitative analysis of the extract organic samples of rock taken from different depths of the well 18 to the field of Nasiriyah to the existence of a relationship between the content of hydrocarbons for rock samples and content of hydrocarbons of crude oil, there is this relationship is evident in the presence of N-ethylcarbazole in both cases.

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Table1: shows the concentration of N-ethylcarbazole in soil depths studied.

Depth (m)	Concentration (ppm)
0	0.0038
250	0.0045
500	0.0109
750	0.0133
1000	0.0050
2000	0.3820
2190	0.3860

Table 2: Concentration of elements in the crude oil wells 18

Petroleum elements	Concentration ppm
Na	81.335
K	30.521
Ni	10.286
Cr	25.225

Table3 .The concentration of sodium, potassium, chromium and nickel in rock samples from different depths

Depth (m)	**Concentration (ppm)**			
	Na	**K**	**Cr**	**Ni**
0	937.5	210	8.75	6.5
250	1362.5	250	21.5	7.75
500	1005	55	6.5	10
750	700	85	6.0	9.5
1000	825	77.50	10	11.2
2000	2878.50	345	27.5	12.70
2190	3102.50	475	28.75	15.25

Table 4 The results of measuring the specific gravity and the API before and after degasification

Property	**Before degasification**	**After degasification**
API	**23.5°**	**27.8°**
Sp. Gr.	**0.9113 gr/cm^3**	**0.893 gr/cm^3**

Table 5 The percentage of water in the crude oil to the field of Nasiriyah before and after degasification.

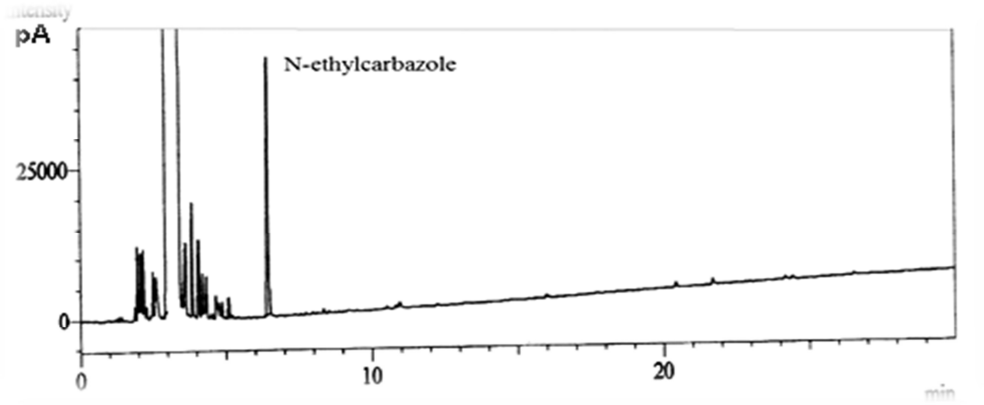
Before degasification	**After degasification**
0.02	**0**

* These results are the average of three readings.

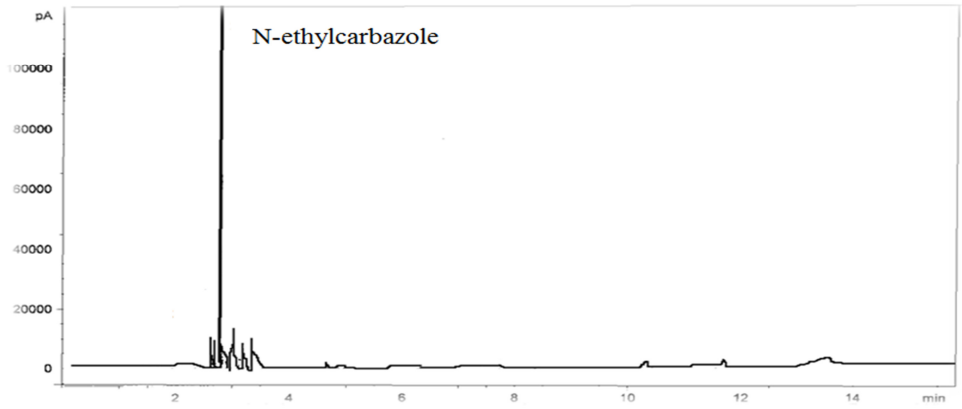
Table 6 the amount of the salt content of the Nasiriyah oil field

Before degasification	**After degasification**
6 0ppm	**6 ppm**

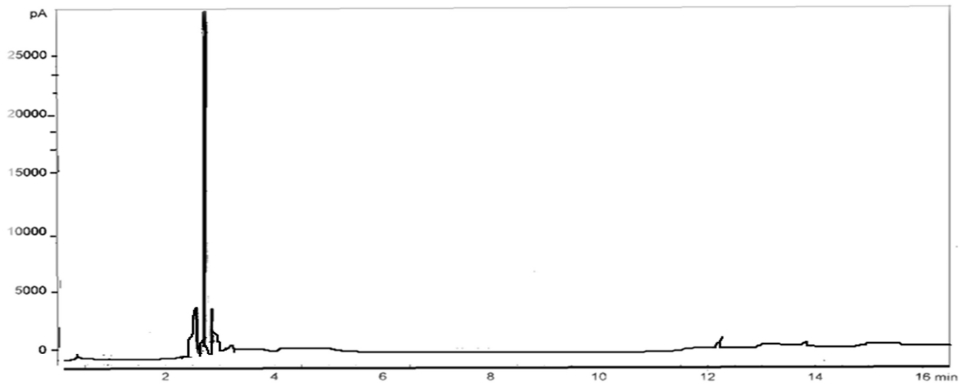
* These results are the average of three readings.



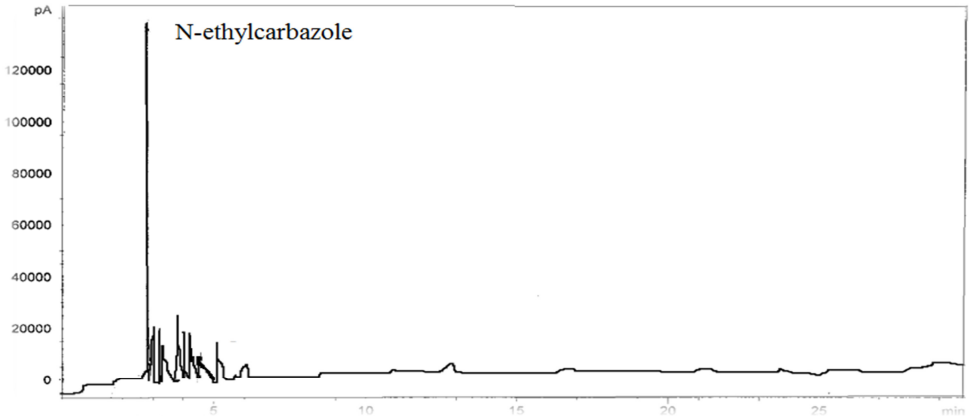
Figure(1) Chromatogram of standard N-ethylcarbazole



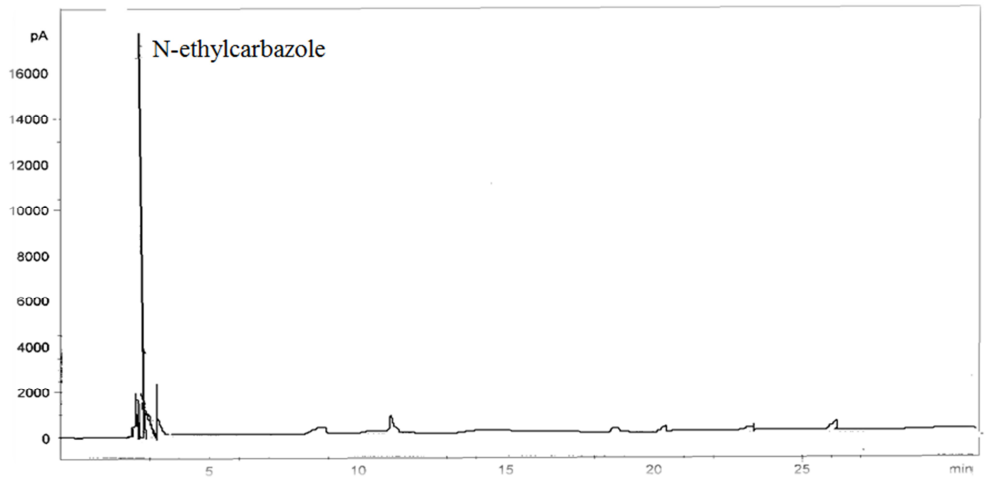
Figure(2) Chromatogram of soil extract sample, from a depth of 0 m



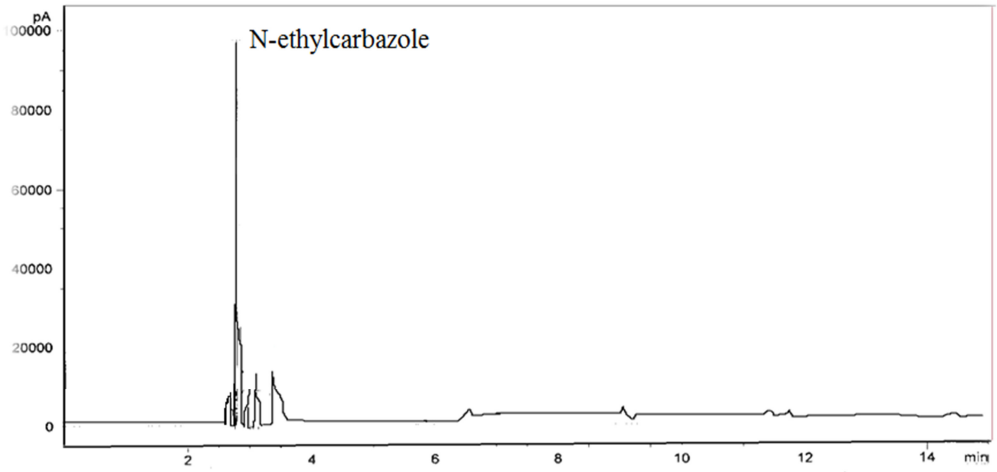
Figure(3) Chromatogram of soil extract sample, from a depth of 250 m



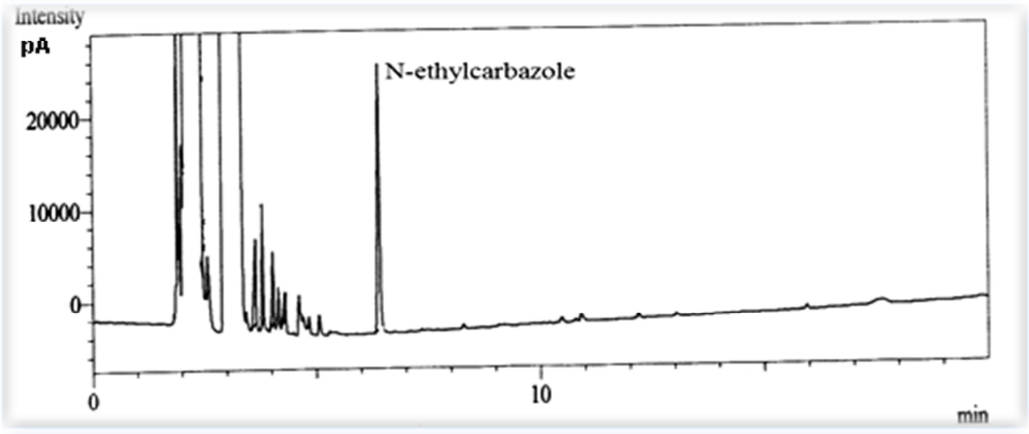
Figure(4) Chromatogram of soil extract sample, from a depth of 500 m



Figure(5) Chromatogram of soil extract sample, from a depth of 750 m



Figure(6) Chromatogram of soil extract sample, from a depth of 1000 m



Figure(7) Chromatogram of soil extract sample, from a depth of 2000 m

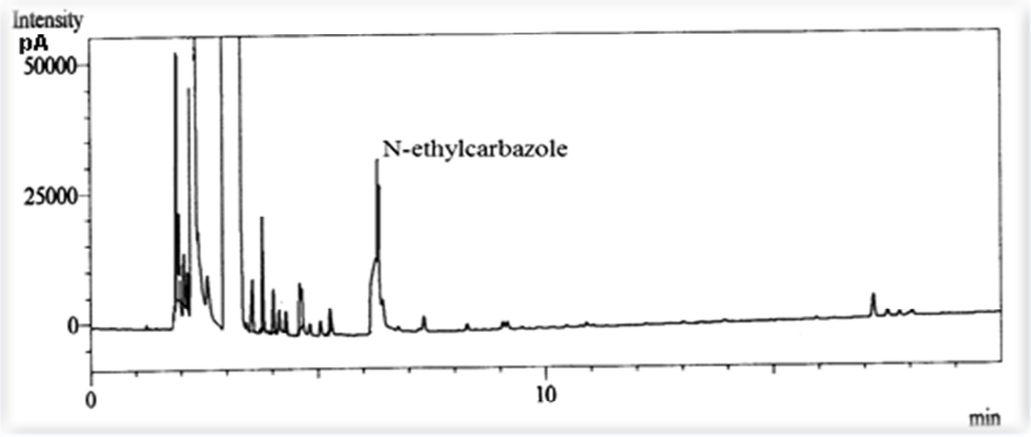


Figure (8) Chromatogram of soil extract sample, from a depth of 2190 m

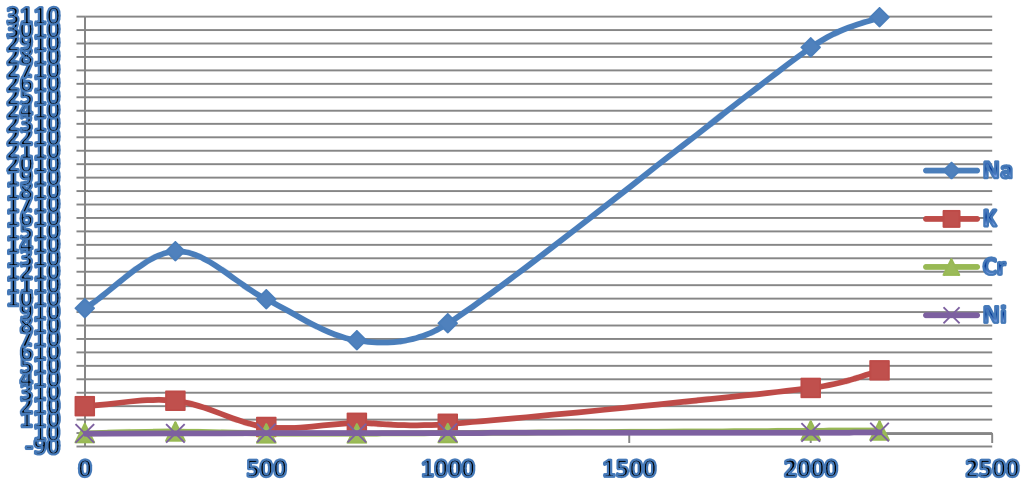


Figure 9 .The relationship between the concentration of the elements and the depth

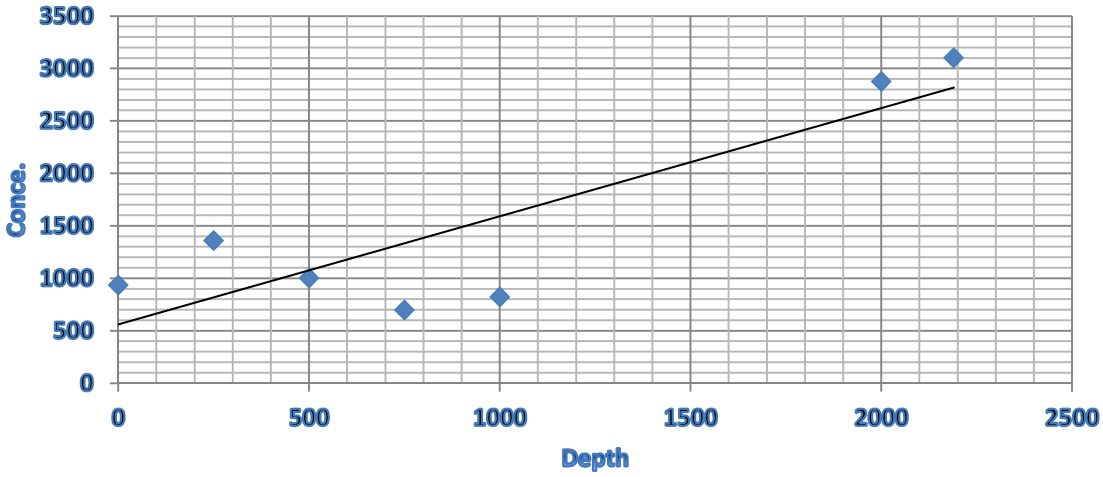


Figure 10 .The relationship between sodium concentration and the depth

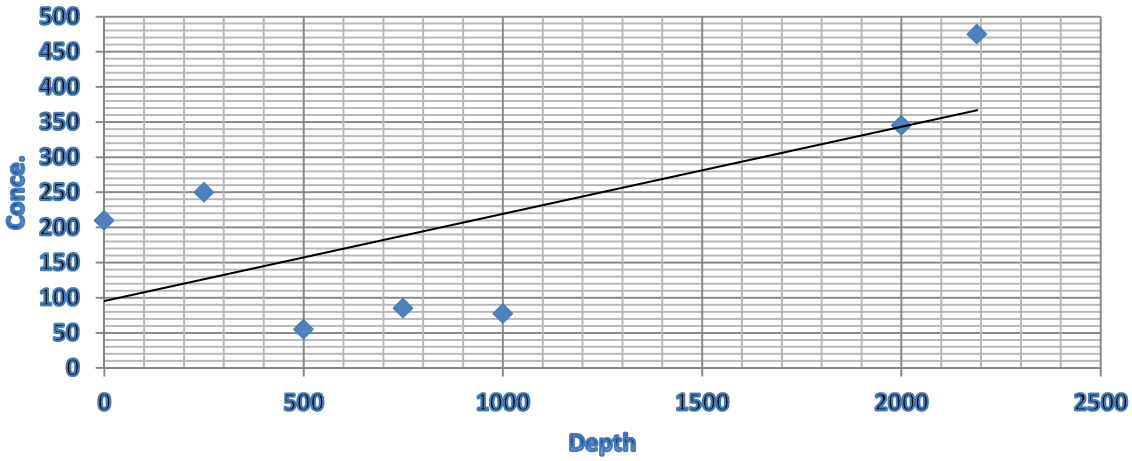


Figure 11 .The relationship between the concentration of potassium and depth

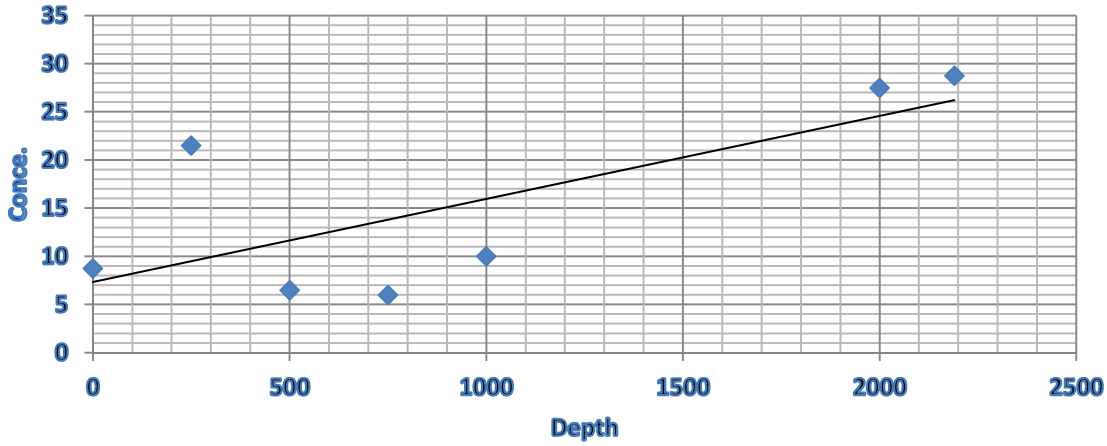


Figure 12 .The relationship between the concentration of chromium and depth

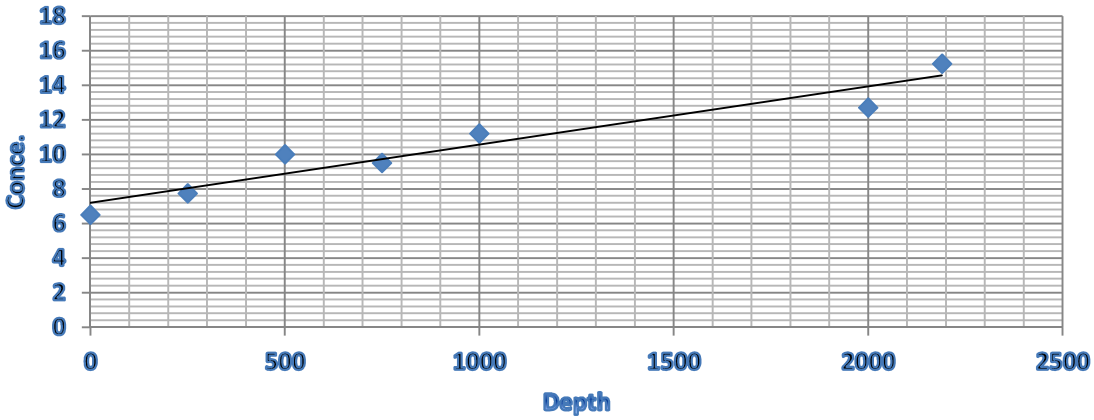


Figure 13 .The relationship between the concentration of nickel and depth

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