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New Approach for Detection of Ultra Trace Amounts of Organic Compounds as Markers of Predict to Exploration of Petroleum Reservoir by Cloud Point Extraction Combined with UV-VIS Spectrophotometry and GC-MS Techniques

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Abstract: ***This work is an attempt to use what is to recognize the leakage of hydrocarbons as Dienzothiophene (DBT) and N-Ethylcarbazole (CARB) from petroleum reservoir from depth to surface so as to the possibility of using such a phenomenon as proximity indicator for petroleum deposits. The soil and water samples near ofa productive oil wells(Maysan- Iraq) were chosen as a case study. The ultra trace quantities of these hydrocarbon compounds that constitute organic extracted were determined bycloud point extraction (CPE) combined with UV-VIS and GC-MS techniques.The optimization of conditions of CPE was conducted with UV-VIS and using Triton114(TX 114) as non-ionic surfactants. Theseconditions were of 0.4-0.6 mL ofTX-114, equilibration temperature of 65 ºC , incubation time of 20 min and 0.5 MLiCl chosen as the best electrolyte for CPE. Theconditions and statistical analysis ofmeasurement byUV-VIS and GC-MASS techniques to DBT andCARB are*** λ_{max} ***at 231 and237nm, concentration range of Beer's law was (0.3-3, µg mL***$^{-1}$***) ,molar absorptivity of 5.9892x10***^{4} ***and5.6523x104 L mol***$^{-1}$***cm***$^{-1}$***,LOD values were of 0.0021 and 0.251µg mL***$^{-1}$***,and LOQ values were 0.00693 and 0.8283µg mL***$^{-1}$ ***respectively. The conditions of separation used for thedetermination ofDBT and CARB by GC-MSwere the same conditions of CPE-UV-VIS. The results indicated that the retention times were of 16.22 and17.88 min, concentration range of 0.01-2,0.05-2 µg mL***$^{-1}$***) for DBT and CARB respectively. LODvalue ofDBTwas 0.0074 µg mL***$^{-1}$***, whileforCARBwas0.00388 µg mL***$^{-1}$***.Analysis of hydrocarbons compounds concentrations in organic extract showed that the amounts of these compounds were different. For example, the concentration of DBT in Maysan Governorate near Halfaya well(1000m) was of 1.1953 µg mL***$^{-1}$***,while it has a value of 0.4802 µg mL***$^{-1}$ ***at 750 m and 0.163 µg mL***$^{-1}$ ***at 500 m. The experimental results of this study indicated that the analysis of hydrocarbons which extracted from soil and water samples can be used to predict or the Remote sensing for the presence of petroleum accumulation or indicator of pollution.***

Keywords: Crude Oil, Dibezothiophene, N-Ethyl carbazole, cloud point extraction, UV-VIS, GC-MS, Triton X-114

1. Introduction

Petroleum (Crude oil) represents a complex mixture containing both organic and inorganic chemical species, hydrocarbons, hetro organic compounds, and metals [1]. Crude oil has a large number of different hydrocarbons; the most commonly found species are aromatic hydrocarbons, alkanes (paraffins), cycloalkanes (naphthenes), or more complicated compounds like asphaltenes [2, 3]. Each petroleum variety has a unique mixture of chemicals, which define its chemical and physical properties, like colour, density and viscosity [4, 5].

Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds whose carcinogenic and/or mutagenic effects are well known. These substances can be produced in anthropogenic and natural processes and they can be found in many different types of samples, both environmental and biological. For this reason, their monitoring and detection has become an important and difficult problem and this has led to develop a new analytical methods with improving selectivity and sensitivity [6, 7].

Many of organic markers based on aromatic and aliphatichydrocarbons are well suited for the characterization of oil families and estimation of source faces, degree of preservation, thermal maturity level, and migration. On the other hand hetero compounds (nitrogen, oxygen, and sulphur, NSO compounds) that make up a small portion of most crude oils have specific implications in petroleum exploration, because their greater structural diversity results in greater variations of their chemical and physical properties [5]. Consequently, hetero PAHs compounds can provide useful geochemical clues that trace petroleum compounds back to their biological precursors [8].

Organic nitrogen and sulphate compounds occur in crude oils in very small amounts, with an average content about 0.1%by weight [9]. Most nitrogen and sulphate compounds in petroleum are in heterocyclic aromatic structures and are concentrated in the large molecular weight and high boiling point fractions [5, 10].

The presence of these compounds in crude oils and rocks source have been reported to show great promise as a good geochemical parameters that might play a significant path in exploration and production for crude oil [11].

Estimation of organic pollutants identities and their low concentrations in surface water, waste water, sediments, and soil is an important and difficult topic in environmental analysis. Although many man-made organic chemicals have been detected in the aquatic environment and soil, petroleum hydrocarbons including PAHs represent some of the most common pollutants found in water from the industrial process where petroleum products are used widely [12, 13].

The preconcentration and extraction of these compounds from water and soil can be carried out by means of liquid-liquid extraction (LLE) and solid-phase extraction (SPE) techniques. LLE is a very useful technique, it has been used in the US Environmental Protection Agency (EPA) [14, 15]. However, it is a longtime consuming and requires large amounts of solvent. SPE is a less time consuming method, but it still requires more organic solvents for the elution step.

Recently, PAH extraction with surfactants based on the cloud-point phenomenon named as cloud point extraction (CPE) has been proposed [16, 17]. The use of this approach offers some advantages for the extraction of PAHs compared with traditional solvent extraction ability to concentrate PAHs with high recoveries, high preconcentration factors, safety, low cost benefits, and very small amounts of the relatively nonflammable and nonvolatile surfactant are required; suited with micellar orhydroorganic mobile phase, etc. [18]..The aim of this study isthe possibility of obtaining data for the concentration of such organic compounds and how it relates to the leaking of oil components and therefore potentially be used as indicators of the presence of petroleum, which helps to petroleum exploration or identified it as environmental contaminants.

2. Experimental

2.1 Apparatus

UV-Vis Spectrophotometer equipped with 10 mm quartz cellwas used for the scanning of the absorption spectra and absorbance measurements for the target analytes throughout this study . The shaking water bath SW23 microprocessor with PlO temperature control (JULABO GmbH, Germany) was employed during the course of CPE experiments.

A Shimadzu GCMS-QP2010 Ultra, CARY 100 Conc. Australia Double beam was used in this study. GC Column used was the Inert Cap 1MS (Thickness 0.25um, Length 30m, Internal Diameter 0.25mm , injection temperature was 250°C ,injection mode was splitless, pressure was 100 kPa, column flow was 1.33mL/min, ion source temperature was 200 ºC, interface temperature was 280 ºC, ionization mode was EI, start was 35.00 m/z and ending was 500.00 m/z . The oven temperature programmed as 100 ºC for 3min, 200 ºC for 3min, and 250 ºC for 3min .

2.2Chemicals

All of the materials and reagents which used in this work are of high purity. The HPLC gradewater were used in the preparation of the solutions and double distilled water for washing glass wares .The PAHs (dibezothiophen and N-ethylcarbazol) were supplied by Sigma-Aldrich. Triton X-114 obtained from Sigma Ultra UK. HPLC-grade acetonitrile obtained from HiMedia. Sodium chloride, lithium chloride and potassium chloride were obtained from Fluka (Germany).

2.3 Preparation of Samples

2.3.1 Soil Samples

Clay samples were taken at different depths of different Wells column samples were cutting samples, which is about gestures close to the surface and the depths were of 250, 500, 750, 1000 m, another type of soil which got from the banks of marsh. These clay samples were mixed, dried in oven and milled to precise sizes 50 micron.10 g of clay was accurately weight and taken as a test sample.The extraction of samples was carried out by soxhlet method with 250 mL methylene chloride for 8 hours.The extracted solution was concentrated in rotary evaporator to less than 1 mL, and the volume was collected and completed to 10 mL with distilled water. This sample solution was subjected to thegeneral CPE procedure.

2.3.2 Water Samples

Water sample were collected in polyethylene containers which previously cleaned with diluted chromic acid to remove materials and other contaminants according to APHA [19]. These containers were finally washed with distilled water and filled until use. In the site, the containers were rinsed well with marsh water before filling them with test samples. The containers were then marked and sealed lock immediately. The collected water samples were filtered through 0.45µm Wattmann filter paper and of each sample stored in refrigerator at (0-4°C) until use. Each water sample was subjected to the general CPE procedure.

2.3.3 Sites of the Sampling

Allsoil and water samples were collected from four different sites located at Maysan Governorate in the south of Iraq as follows and indicated in Figure 1.

1-Marsh ofOm nia'aj.
2- Marsh ofAl-Disyme.
3-Trocar beside petro china company and.
4- Halfaya oil wells

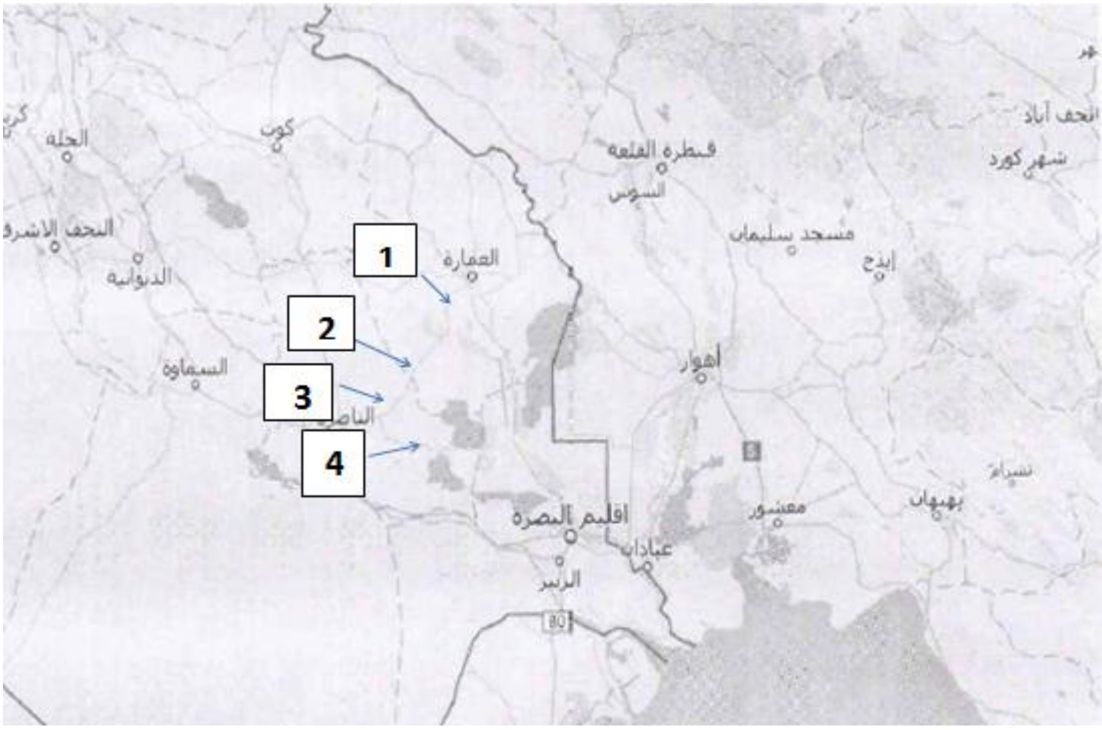

Figure 1: Map of the study area including sampling locations (Maysan-Iraq)

2.4 General CPE Procedure

To an aliquot of 10 mL of a solution containing known amount of DBT orCARB standard (0.3-3 ppm) or sample solution were taken into a series of 10 mL graduated centrifugal tubes, 0.5M of lithium chloride was added and 0.6 mL of 10% (v/v) Triton X-114 were added and diluted to mark with water. The content of each tube was transferred to water bath at 65°C for 20 min to form cloudy solution. The separation of the phases was accelerated by centrifuging at 3500 rpm for 20 min, if the weather was hot we can enhance the separation with sudden cooling with ice. After decantation of aqueous phase, the surfactant-rich phase that remained adhered to the tube was dissolved with a 1.0 mL of ethanol and the absorbance of each solution containing the analyte was measured spectrophotometrically by UV-VIS at specificλmax.

3. Results and Discussion

3.1Optimization of CPE Conditions

All of the parameters that impact on the CPE methodology such as,type of surfactant, amount of surfactant, equilibration temperature(T), incubation time (Et), and the type of electrolyte for the extraction processes were optimized by one-factor-a-time (OFAT) procedure for improving the recovery of extraction, sensitivity and detection limit for the determination of each compounds [20, 21]

3.1.1 Effect of Surfactant Type

In this study, four types of non-ionic surfactants,such as TX-114, TX-100, Tween-80, Tween-20 were tested. The experiments were conducted with 10 mL solution containing of µg mL^{-1} of each target analytes and % of each surfactant followed the general CPE procedure. The results are depicted in Figures 2 and 3. It can seen that the best recovery was obtained with TX-114 for both DBT and CARB compared to the rest of studied surfactants. It is worth mentioning the surfactant of Tween-type has shown that the cloudy layer formation needs very higher cloud point temperature than the Triton-type which it is inevitably led to dissociation of target analytes and hence poor recovery obtained. Thus the TX-114 was selected throughout this study.

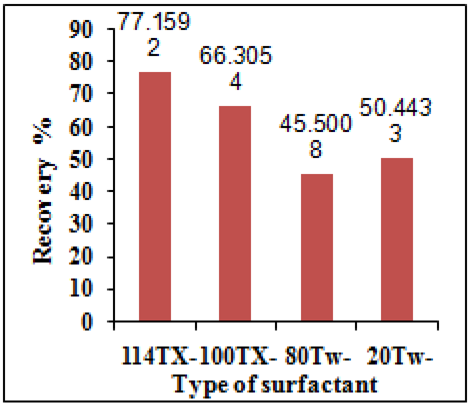

Figure 2effect of surfactant type on DBT

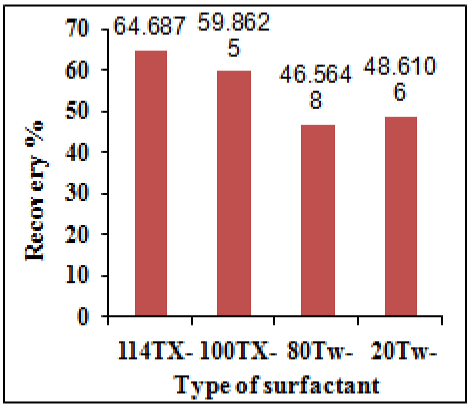

Figure 3effect of surfactant Type on CARB

3.1.2 Effect of TX-114 Amount

It is known that a successful cloud point procedure should maximize the extraction efficiency by minimizing the phase volume ratio which improve its enrichment capability and hence the percent recovery. Thus the effect of TX-114 amount on the percent recovery of each target analyte was carried out with 10 mL solution containing µg mL^{-1} of DBT and CARB anddifferent volumes of 10% (v/v) Triton X-114 ranging from 0.1-0.8 mL , keeping other conditions constant. The recovery percentage of each analyte was shown in Figure 4. It was shown that the percent recoveries increase significantly and reached maximum at 0.6 and 0.4 mL of 10% TX-114 for BDT and CARB respectively and then decrease thereafter due to the increment in overall volumes and viscosity of surfactant-rich phase leading to poor recovery. At low amount of surfactant the recovery was also poor , perhaps due to the insufficiently of micelles formation entrapping the target analyte quantitatively. Therefore, the optimum volume at 0.6 and 0.4 mL of 10% TX-114 were chosen as optimal for BDT and CARB respectively.

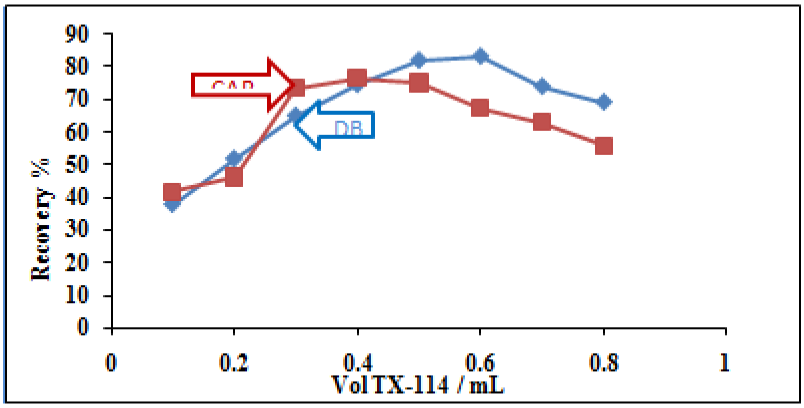

Figure 4: Relation between volume of surfactant and recovery for each of DBT and CARB

3.1.3 Effect of Temperature

Since the extraction by CPE is carried out under thermal conditions for the phases separation, an equilibrium temperature plays very important role in CPE process to ensure phases separation and complete extraction of an analyte. Thus effect of temperature was examined at previously optimized conditions and varied from 40 ^{O}C to 75 ^{O}C at min in a search of optimum value and the results showed in Figure 5. The findings revealed that the optimum temperature for the extraction of both target organic compounds was of 60 ºC. This gave maximum percent recovery, indicating a good quantitative extraction for both analytes. At higher temperature than optimal , the recovery decreases perhaps due to the gradually thermal decomposition of the compounds. Thus 60 ºC at min was selected as operating equilibrium temperature in this study.

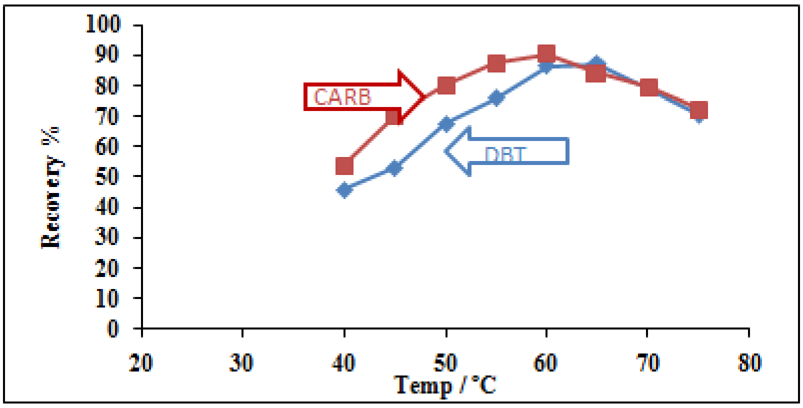

Figure 5: Effect of temperature on recovery of DBT and CARB

3.1.4 Effect of Time

The effect of incubation time also important parameter for improving the extraction by CPE process and ultimately obtaining the best recovery [22]. The time of incubation was varied from 5-30 min at other optimum parameters as shown in Figure 6. It can be seen that optimum heating time to achieve maximum recoveries was 15 min for both extraction of target analytes, indicating the better thermodynamic equilibria for CP formation with smaller volume , higher viscosity of surfactant-rich phase and better partition of each analyte between two phases.

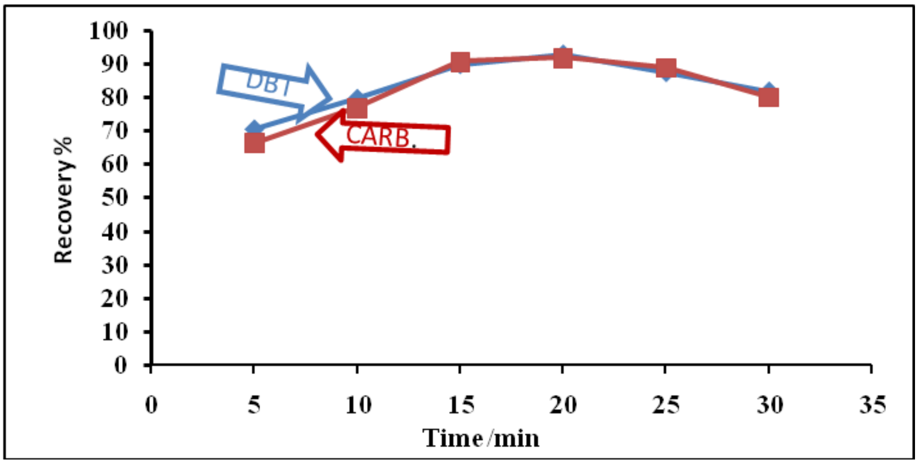

Figure 6: Effect of the incubation time on the recovery of DBT and CARB

3.1.5 Effect of Electrolytes Type

Several authors have shown that electrolytes effect led to increase or decrease the cloud-point temperature of non-ionic surfactant. The relevant electrolyte concentrations for the above effect are usually high concentrations. The observed effects of the electrolytes on the cloud-points of non-ionic surfactants have been defined in terms of salting-in and salting -out effects [23].

The effect of the selected electrolytes on the CPE of solutions containing both analyte at concentration of µg mL^{-1}was studied keeping other parameters constant . It is observed that the addition of electrolytes, including LiCl, NaCl, KCl, and $CaCl_2$, to micellar solutions decreases the cloud-point temperature [24, 25]

The results indicate that an increase in the ionic strength have not an appreciable influence on the final recovery of the extracted surfactant-rich phase [26]. Nevertheless, the addition of these salts make the separation of the two phases easier, because it increases the density of the bulk aqueous phase [27].

Depending upon the density of the surfactant-rich phase in relation to that one of the aqueous phase, the surfactant-rich phase can be either the bottom or top layer. By addition of salts to the system, the density of the aqueous phase can be adjusted to some degree [28]. In some cases, it is found to be easier and more desirable to work with an upper surfactant-rich layer, thereby minimizing the possibility of cross-contamination of components from the corresponding aqueous phase. Besides, the CPE procedure can be repeated by addition of more surfactant to the aqueous phase, in order to achieve higher extraction efficiency [29, 30].

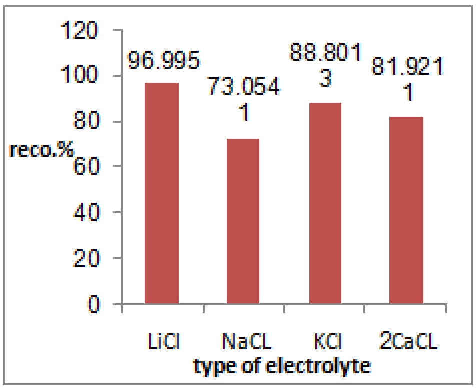

Figure 7: Effect of electrolyte on DBT

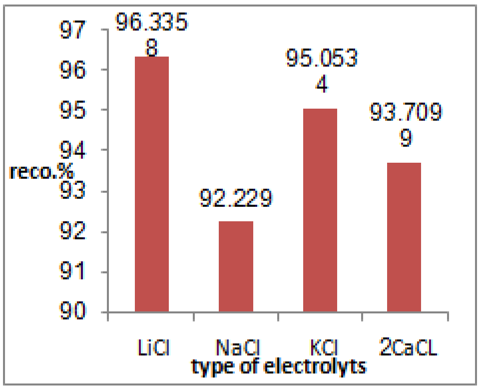

Figure 8: Effect of electrolyte on CARB.

The calibration data are listed in Table 1 and 2.

3.2 Methods validation for measurement of DBT and CARB

3.2.1 UV-VIS method

Under the conditions of optimization of DBT and CARB, the calibration graphs were constructed by plotting the absorbance signal against the concentrations of each compound subjected according to the general procedure for CPE. The solutions were transferred into the optical cell of 10-mm for the measurement of each compound spectrophotometrically at the respective absorption maxima against a reagent blank prepared under similar conditions.

Table 1: Statistical calculations of calibration curve of DBT by UV

Parameters	Value
λ $_{max}$ (nm)	231
Regression equation y=bx +a	Y=0.3045x-0.0098
Correlation coefficient (r)	0.999959
Linearity percentage (r^2 %)	0.9992
Dynamic range μg.mL^{-1}	0.3 – 3
Molar absorptivity ε (L.mol^{-1}.cm^{-1}) Ɛ=(A/b×c ppm)×m.wt.×1000	5.9892x10^4
Slop b (mL.μg^{-1})	0.3045
Intercept a (a = y – bx)	0.0098
Standard deviation Sd (n=5)at 1 μg.mL^{-1}	2x10^{-4}
Percentage Relative standard deviation RSD %	4x10^{-5}
Limit of detection LOD (μg.mL^{-1})	2.1x10^{-3}
Limit of quantitation LOQ (μg.mL^{-1})	6.93x10^{-3}
Sandells sensitivity (mg.cm^{-2})	3.0721x10^{-3}
Preconcentration factor	250
enrichment factor	29.23
Distribution ratio D	31.287

Table 2: statistical calculations of calibration curve of CARB by UV

Parameters	Value
λ max nm	237
Regression equation y=bx +a	Y=0.3275x-0.0031
Correlation coefficient (r)	0.999949
Linearity percentage (r^2 %)	0.9999
Dynamic range μg.mL^{-1}	(0.3 – 3) μg.mL^{-1}
Molar absorptivity ε (L.mol^{-1}.cm^{-1}) Ɛ=(A/b×c ppm)×m.wt.×1000	5.6523x10^4
Slop b (mL.μg^{-1})	0.3275
Intercept a (a = y - bx)	0.0031
Standard deviation Sd (n=5)at1 μg.mL^{-1}	3.2x10^{-5}
Percentage Relative standard deviation RSD %	9.846x10^{-3}
Limit of detection LOD (μg.mL^{-1})	0.251
Limit of quantitation LOQ (μg.mL^{-1})	0.8283
Sandells sensitivity (mg.cm^{-2})	3.0783x10^{-3}
Preconcentration factor	166.7
Enrichment factor	35.98
Distribution ratio	30.04

Table 2 statistical calculations of calibration curve of CARB by UV

3.2.2 GC-MS method

The retention time of two compounds is 16.22 min to DBT and 17.88min to CARB. Calibration curves five-points (**0.08 to 2 μg.ml^{-1}**), procedural blank, check standard and sample duplicates were carried out for every set of samples (table3 and figure9). the relative standard deviation (RSD) values of 0.6250 was showed acceptable to response factors of the five-point calibration curve for individual compounds.

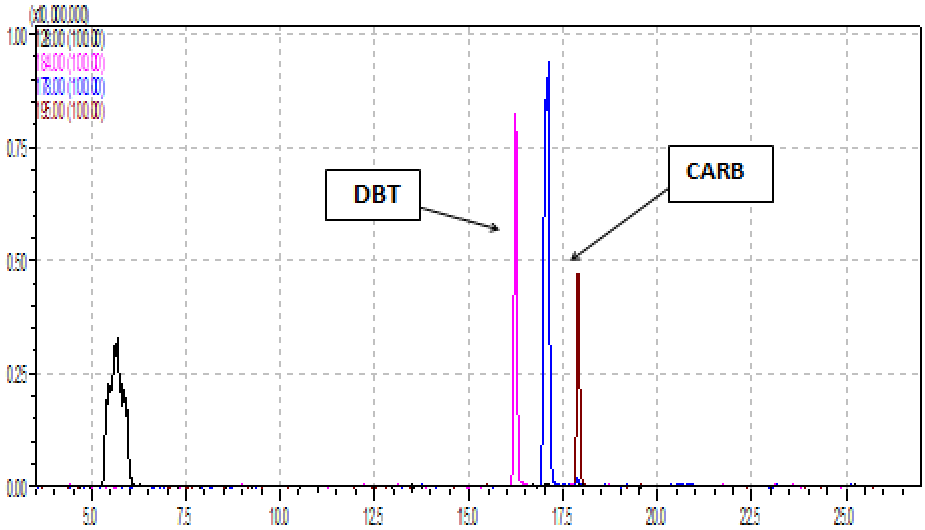

Figure 9: chromotogram of standard DBT and CARB by GC

Table 3: Statistical calculations of DBT calibration curve by GC

no.	*Parameters*	*Value*
1	Regression equation y=bx +a	y= 52885 x - 355.55
2	Correlation coefficient (r)	0.9985
3	Linearity percentage (r^2 %)	99.71
4	Dynamic range μg.mL^{-1}	**0.01 – 2 μg.mL^{-1}**
5	Slop b (mL.μg^{-1})	52885
6	Intercept a (a = y - bx)	355.55
7	Standard deviation Sd (n=3)at 1 μg.mL^{-1}	3.451 x 10^2
8	Percentage Relative standard deviation RSD%	0.6250
9	Limit of detection LOD (μg.mL^{-1})	0.74 x10^{-2}
10	Limit of quantitation LOQ (μg.mL^{-1})	2.442 x10^{-2}

Table 4: Statistical calculations of CARB calibration curve by GC

no.	**Parameters**	**Value**
1	Regression equation y=bx +a	y= 149278x – 556.11
2	Correlation coefficient (r)	0.9997
3	Linearity percentage (r^2 %)	99.96
4	Dynamic range μg.mL^{-1}	0.005 –2 μg.mL^{-1}
5	Slop b (mL.μg^{-1})	24974
6	Intercept a (a = y - bx)	2834.2
7	Standard deviation Sd (n=5)at 1 μg.mL^{-1}	0.201
8	Percentage Relative standard deviation RSD%	7.0402x10^{-4}
9	Limit of detection LOD (μg.mL^{-1})	0.388x10^{-2}
10	Limit of quantitation LOQ (μg.mL^{-1})	1.2x10^{-2}

3.2.3-Chromatogram for Selected Samples Containing DBT and CARB

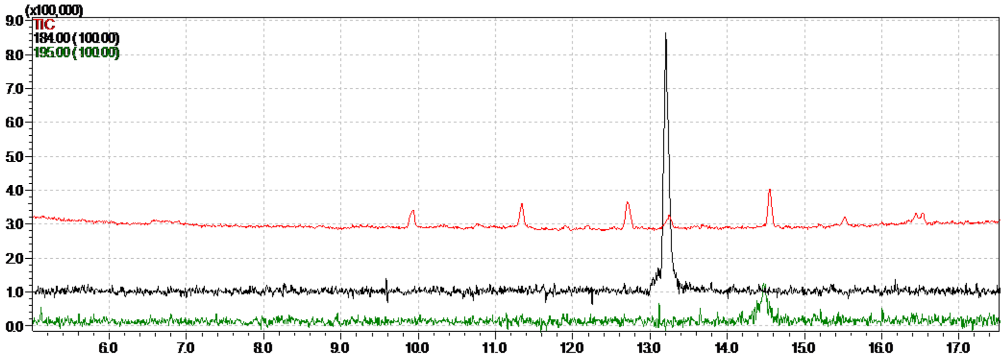

Figure 10: Sample 9/DBT and CARB

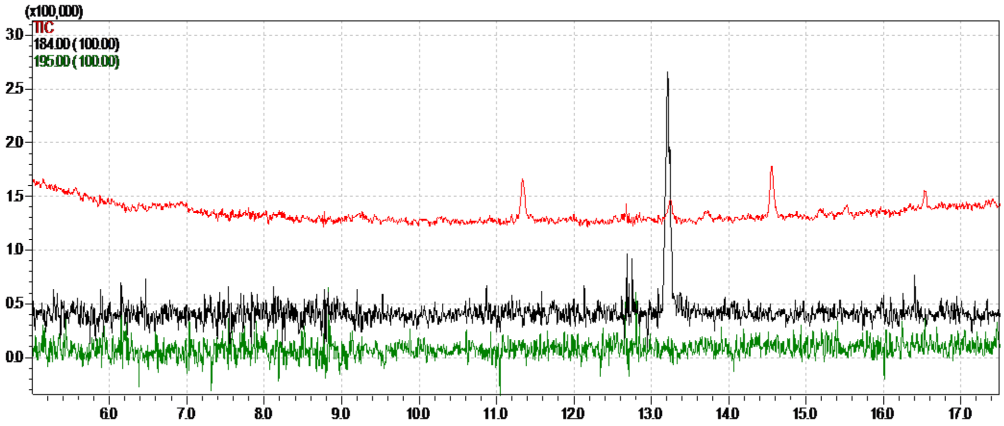

Figure 11: Sample 15/ Dibenzothiophene and 9-Ethylcarbazole

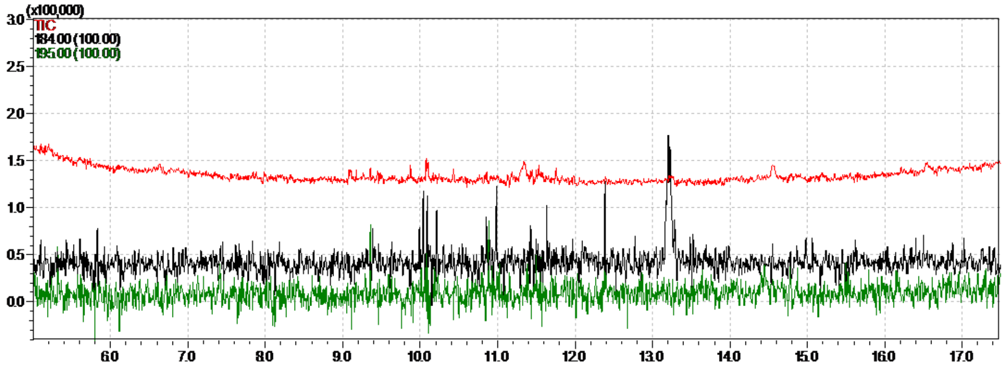

Figure 12: Sample 22/ Dibenzothiophene and 9-Ethylcarbazole

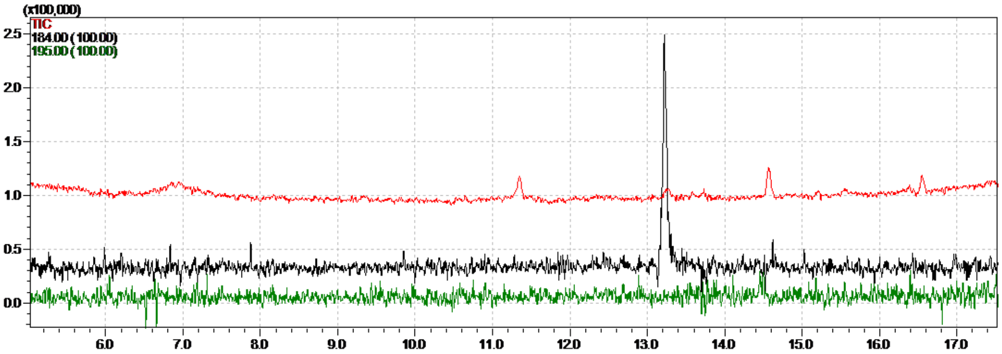

Figure 13: Sample 27/Dibenzothiophene and 9-Ethylcarbazole

3.2.4 Mass Spectrum of DBT and CARB in Samples

Mass spectra represent a very important result to prove the relation between the peak and the target compound from the library of device, and without it can't consider the peak as an evidence, especially when the compound is in complex matrix, but combining between chromatogram and spectrum to get clear view about the target analyte as shown in Figures 16 and 17.

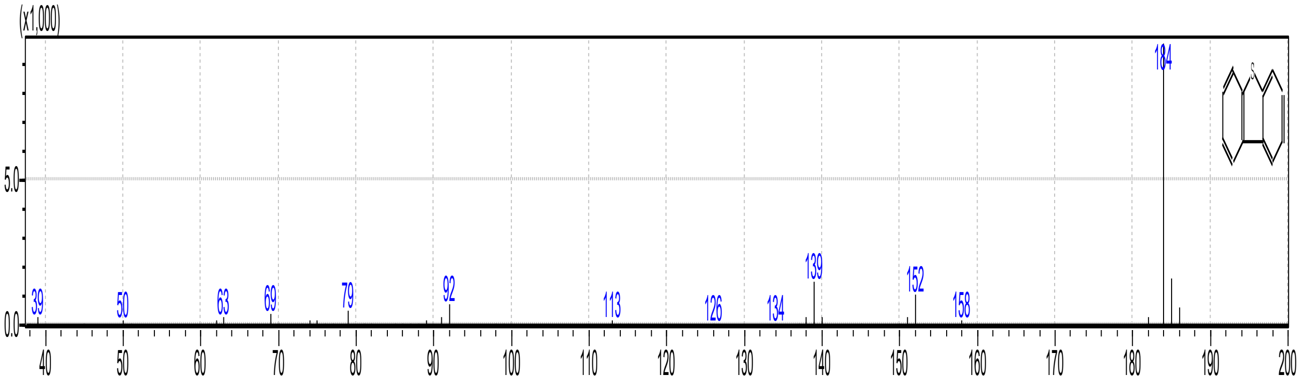

Figure 16 Mass spectrum of DBT (Library; IS=62)

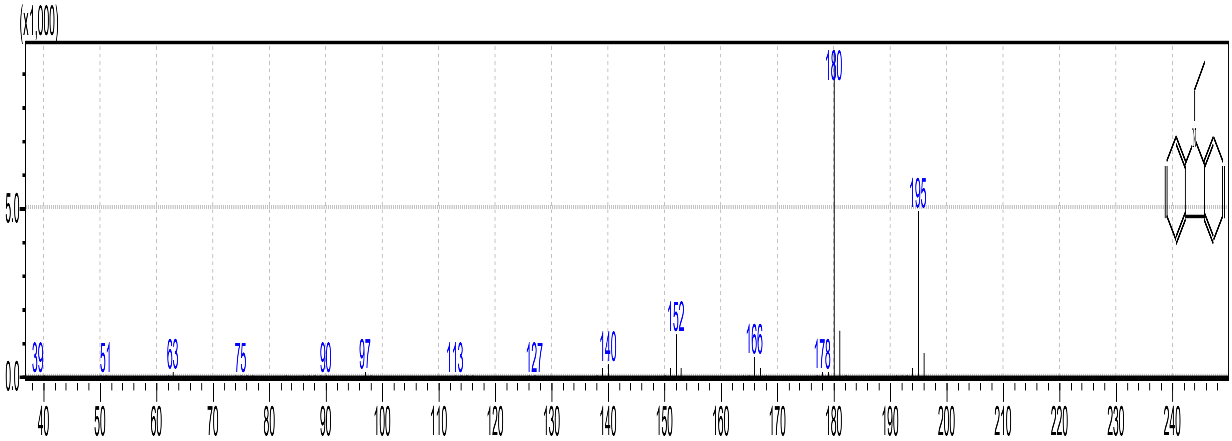

Figure 17 Mass spectrum of CARB (Library; IS=58)

3.3Results of Applications by UV-VIS Spectrophotometry after CPE

Table 5: results of UV-VIS technique

Name		DBT		CARB	
λ max		231 nm		237 nm	
Samples name, no and depth		Abs. nm	Conc. µg.mL^{-1}	Abs. nm	Conc. µg.mL^{-1}
1	HF002-M001H/halfaya well 250m	nd		Nd	nd
2	HF002-M001H/halfaya well 500m	nd	nd	nd	nd
3	HF002-M001H/halfaya well 750m	nd	nd	nd	nd
4	HF002-M001H/halfaya well 1000m	0.3737	1.1953	nd	nd
5	HF060-M067ML/halfaya well 250m	nd	nd	nd	nd
6	HF060-M067ML/halfaya well500m	nd	nd	nd	nd
7	HF060-M067ML/halfaya well 750m	nd	nd	nd	nd
8	HF060-M067ML/halfya well 1000m	nd	nd	nd	nd
9	HF007-JK007/ halfya well 250m	nd	nd	nd	nd
10	HF007-JK007/ halfya well 500m	nd	nd	nd	nd
11	HF007-JK007/ halfya well 750m	0.1560	0.4802	nd	nd
12	HF007-JK007/ halfya well 1000m	0.1713	0.5304	nd	nd
13	HF007-N007/ halfya well 250m	nd	nd	nd	nd
14	HF007-N007/ halfya well 500m	nd	nd	nd	nd
15	HF007-N007/ halfya well 750m	nd	nd	nd	nd
16	HF007-N007/ halfya well 1000m	0.171	0.5297	nd	nd
17	Om nia'aj marsh/soil	nd	nd	nd	nd
18	Om nia'aj marsh/water	0.1305	0.3966	nd	nd
19	Om nia'aj marsh/soil	nd	nd	nd	nd
20	Om nia'aj marsh/water	nd	nd	nd	nd
21	Om nia'aj marsh/soil	nd	nd	nd	nd
22	Om nia'aj marsh/water	nd	nd	nd	nd
23	Desaym marsh/soil	nd	nd	nd	nd
24	Desaym marsh/water	nd	nd	nd	nd
25	Desaym marsh/soil	nd	nd	nd	nd
26	Desaym marsh/water	nd	nd	nd	nd
27	Petro china trocar/soil	nd	nd	nd	nd
28	Petro china trocar/water	nd	nd	nd	nd
29	Petro china trocar/soil	0.1059	0.3158	nd	nd
30	Petro china trocar/water	nd	nd	nd	nd

3.4 Results of Application by GC-MS after CPE

Table 6: Results of GC-MS Technique

Name		DBT		CARB	
RT/min		6.75 min		14.46 min	
Sample name,no. and depth		Peak area	Conc./ µg.mL^{-1}	Peak area	Conc./ µg.mL^{-1}
1	HF002-M001H/halfaya well 250m	nd	nd	nd	nd
2	HF002-M001H/halfaya well 500m	nd	nd	Nd	nd
3	HF002-M001H/halfaya well 750m	7883	0.155782	nd	nd
4	HF002-M001H/halfaya well 1000m	64055	1.217936	nd	nd
5	HF060-M067ML/halfaya well 250m	nd	nd	nd	nd
6	HF060-M067ML/halfaya well500m	nd	nd	nd	nd
7	HF060-M067ML/halfaya well 750m	nd	nd	nd	nd
8	HF060-M067ML/halfya well 1000m	nd	nd	nd	nd
9	HF007-JK007/ halfya well 250m	nd	nd	nd	nd
10	HF007-JK007/ halfya well 500m	nd	nd	nd	nd
11	HF007-JK007/ halfya well 750m	24569	0.471297	1100	0 .011094
12	HF007-JK007/ halfya well 1000m	29384	0.562344	1952	0 .016802
13	HF007-N007/ halfya well 250m	nd	nd	nd	nd
14	HF007-N007/ halfya well 500m	8296	0.163592	nd	nd
15	HF007-N007/ halfya well 750m	nd	nd	nd	nd
16	HF007-N007/ halfya well 1000m	28330	0.542414	nd	nd
17	Om nia'aj marsh/soil	nd	nd	nd	nd
18	Om nia'aj marsh/water	19653	0.378341	763	0.008837
19	Om nia'aj marsh/soil	nd	nd	nd	nd
20	Om nia'aj marsh/water	nd	nd	nd	nd
21	Om nia'aj marsh/soil	nd	nd	nd	nd
22	Om nia'aj marsh/water	6205	0.124053	1135	0.011329
23	Desaym marsh/soil	8339	0.164405	nd	nd
24	Desaym marsh/water	8870	0.174445	nd	nd
25	Desaym marsh/soil	nd	nd	nd	nd

26	Desaym marsh/water	nd	nd	nd	nd
27	Petro china trocar/soil	8641	0.170115	nd	nd
28	Petro china trocar/water	nd	nd	1164	0.011523
29	Petro china trocar/soil	16970	0.327608	nd	nd
30	Petro china trocar/water	nd	nd	nd	nd

4. Conclusion

Analysis of hydrocarbon compounds concentration in organic extract of petroleum origin has shown that magnitudes of these compounds increase with depth. For example, the concentration of DBT near surface was 0.4802 µg mL^{-1} while it has a value of 1.1953 µg mL^{-1} at 1000 meters. These results can be used to predict the presence of petroleum deposit. On the another hand,our findings support the identification of potential risks of the environment and human health. The concentration of CARB in water sample as example it was 0.011523 µg mL^{-1}.

The developed methods for the detection of ultra trace amounts of DBT and CARB in the studied samples by using cloud point extraction methodology coupled with UV-VIS spectrophotometric and GC-MS techniques is for the first time . The GC-MS method was more suitable and successfully validated than UV-VIS technique to determine of these compounds especially CARB, due its very low concentrations in both of soil and water samples. The method of cloud-point extraction was simple, easy, rapidand very suitable to measure successfully of the two target compounds and itcan be used for the assay of these compounds or other similar compounds in presence of interfering matrices without environmental contamination..

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