

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 of a 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 by cloud point extraction (CPE) combined with UV-VIS and GC-MS techniques. The optimization of conditions of CPE was conducted with UV-VIS and using Triton 114 (TX 114) as non-ionic surfactants. These conditions were of 0.4-0.6 mL of TX-114, equilibration temperature of 65 °C, incubation time of 20 min and 0.5 M LiCl chosen as the best electrolyte for CPE. The conditions and statistical analysis of measurement by UV-VIS and GC-MS techniques to DBT and CARB are λ_{max} at 231 and 237 nm, concentration range of Beer's law was (0.3-3, $\mu\text{g mL}^{-1}$), molar absorptivity of 5.9892×10^4 and $5.6523 \times 10^4 \text{ L mol}^{-1} \text{cm}^{-1}$, LOD values were of 0.0021 and $0.251 \mu\text{g mL}^{-1}$, and LOQ values were 0.00693 and $0.8283 \mu\text{g mL}^{-1}$ respectively. The conditions of separation used for the determination of DBT and CARB by GC-MS were the same conditions of CPE-UV-VIS. The results indicated that the retention times were of 16.22 and 17.88 min, concentration range of (0.01-2, 0.05-2 $\mu\text{g mL}^{-1}$) for DBT and CARB respectively. LOD value of DBT was $0.0074 \mu\text{g mL}^{-1}$, while for CARB was $0.00388 \mu\text{g mL}^{-1}$. Analysis of hydrocarbon 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 $1.1953 \mu\text{g mL}^{-1}$, while it has a value of $0.4802 \mu\text{g mL}^{-1}$ at 750 m and $0.163 \mu\text{g mL}^{-1}$ 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, Dibenzothiophene, 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, hetero 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 aliphatic hydrocarbons 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 or hydroorganic mobile phase, etc. [18]. The aim of this study is the 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 cell was 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 PIO 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 0.25 μ m, Length 30m, Internal Diameter 0.25mm), injection temperature was 250 $^{\circ}$ C, injection mode was splitless, pressure was 100 kPa, column flow was 1.33 mL/min, ion source temperature was 200 $^{\circ}$ C, interface temperature was 280 $^{\circ}$ C, ionization mode was EI, start was 35.00 m/z and ending was 500.00 m/z.

The oven temperature programmed as 100 $^{\circ}$ C for 3min, 200 $^{\circ}$ C for 3min, and 250 $^{\circ}$ C for 3min.

2.2 Chemicals

All of the materials and reagents which used in this work are of high purity. The HPLC grade water were used in the preparation of the solutions and double distilled water for washing glass wares. The PAHs (dibenzothiophen 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 the general 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 0.45 μ m Whatmann filter paper and of each sample stored in refrigerator at (0-4 $^{\circ}$ C) until use. Each water sample was subjected to the general CPE procedure.

2.3.3 Sites of the Sampling

All soil 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 of Om nia'aj.
- 2- Marsh of Al-Disyme.
- 3-Trocar beside petro china company and.
- 4- Halfaya oil wells

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 $\mu\text{g mL}^{-1}$ of DBT and CARB and different 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.

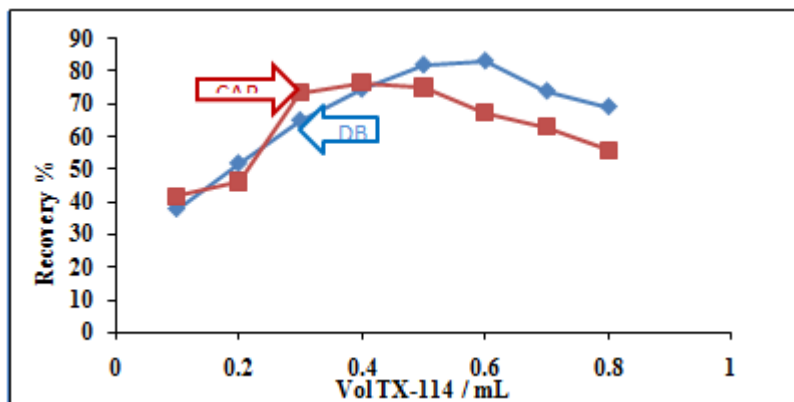


Figure 4: Relation between volume of surfactant and recovery for each of DBT and CARB

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 °C to 75 °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 °C. 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 °C at min was selected as operating equilibrium temperature in this study.

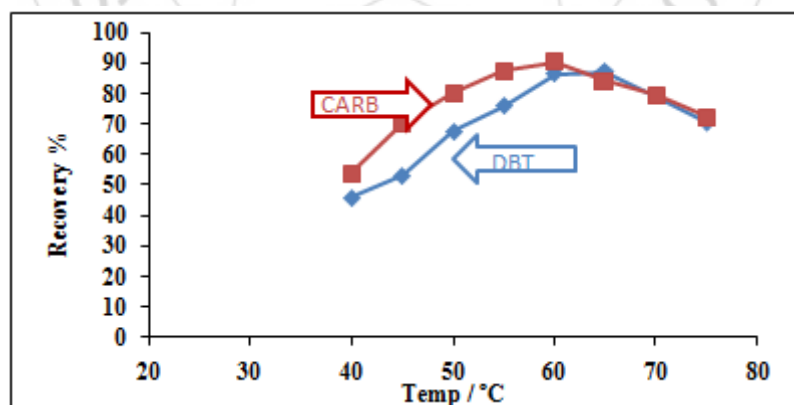


Figure 5: Effect of temperature on recovery of DBT and CARB

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.

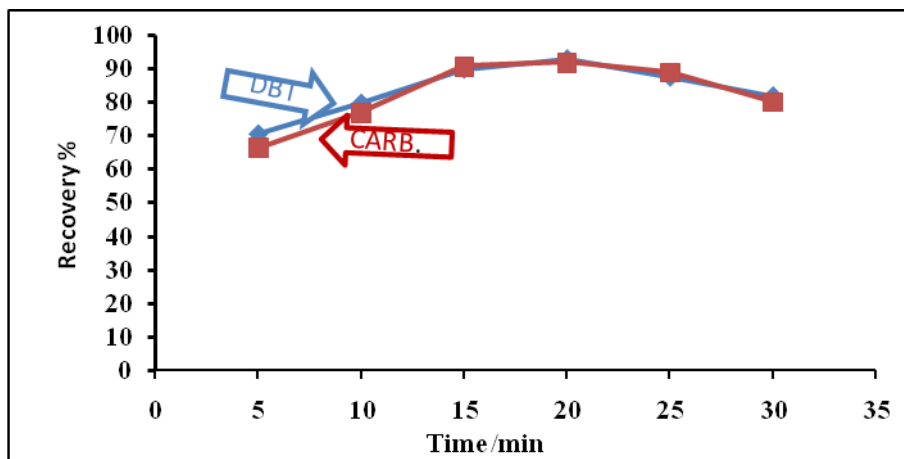


Figure 6: Effect of the incubation time on the recovery of DBT and CARB

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 $\mu\text{g mL}^{-1}$ 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].

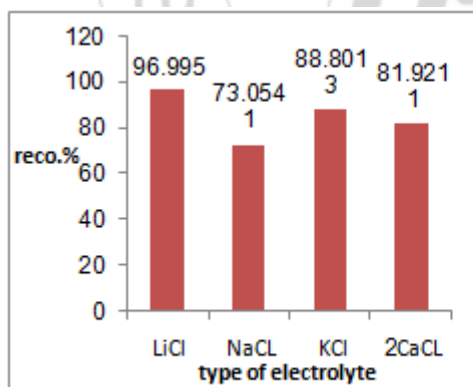


Figure 7: Effect of electrolyte on DBT

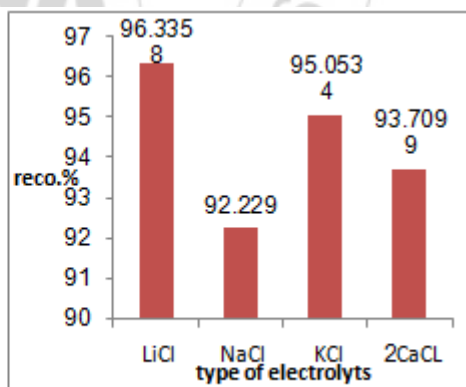


Figure 8: Effect of electrolyte on CARB.

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 $\mu\text{g.mL}^{-1}$	0.3 – 3
Molar absorptivity ϵ ($\text{L.mol}^{-1}.\text{cm}^{-1}$) $\epsilon=(A/b \times c \text{ ppm}) \times \text{m.wt.} \times 1000$	5.9892×10^4
Slop b ($\text{mL}.\mu\text{g}^{-1}$)	0.3045
Intercept a ($a = y - bx$)	0.0098
Standard deviation Sd (n=5) at 1 $\mu\text{g.mL}^{-1}$	2×10^{-4}
Percentage Relative standard deviation RSD %	4×10^{-5}
Limit of detection LOD ($\mu\text{g.mL}^{-1}$)	2.1×10^{-3}
Limit of quantitation LOQ ($\mu\text{g.mL}^{-1}$)	6.93×10^{-3}
Sandells sensitivity (mg.cm^{-2})	3.0721×10^{-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 $\mu\text{g.mL}^{-1}$	(0.3 – 3) $\mu\text{g.mL}^{-1}$
Molar absorptivity ϵ ($\text{L.mol}^{-1}.\text{cm}^{-1}$) $\epsilon=(A/b \times c \text{ ppm}) \times \text{m.wt.} \times 1000$	5.6523×10^4
Slop b ($\text{mL}.\mu\text{g}^{-1}$)	0.3275
Intercept a ($a = y - bx$)	0.0031
Standard deviation Sd (n=5) at 1 $\mu\text{g.mL}^{-1}$	3.2×10^{-5}
Percentage Relative standard deviation RSD %	9.846×10^{-3}
Limit of detection LOD ($\mu\text{g.mL}^{-1}$)	0.251
Limit of quantitation LOQ ($\mu\text{g.mL}^{-1}$)	0.8283
Sandells sensitivity (mg.cm^{-2})	3.0783×10^{-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 $\mu\text{g.mL}^{-1}$), 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.

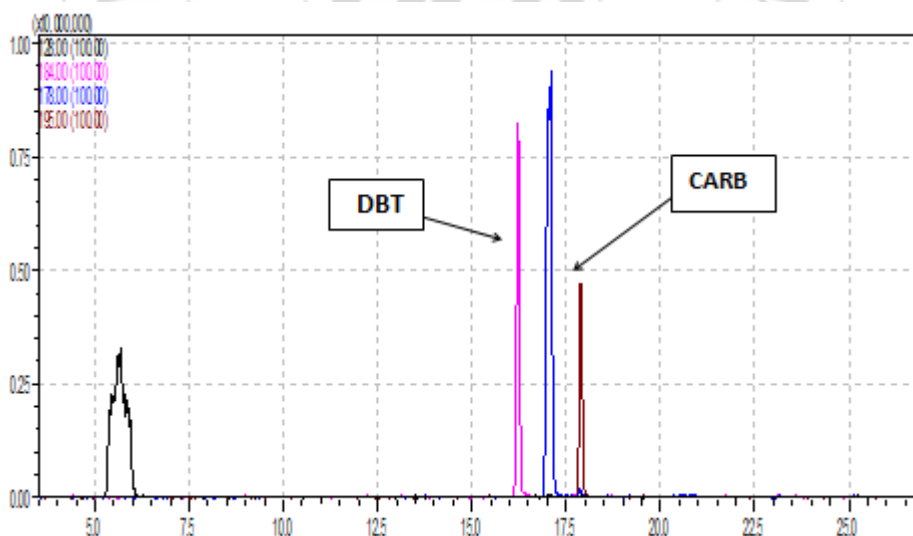


Figure 9: chromatogram of standard DBT and CARB by GC

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 $\mu\text{g.mL}^{-1}$	0.01 – 2 $\mu\text{g.mL}^{-1}$
5	Slop b ($\text{mL.}\mu\text{g}^{-1}$)	52885
6	Intercept a ($a = y - bx$)	355.55
7	Standard deviation Sd ($n=3$)at 1 $\mu\text{g.mL}^{-1}$	3.451×10^2
8	Percentage Relative standard deviation RSD%	0.6250
9	Limit of detection LOD ($\mu\text{g.mL}^{-1}$)	0.74×10^{-2}
10	Limit of quantitation LOQ ($\mu\text{g.mL}^{-1}$)	2.442×10^{-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 $\mu\text{g.mL}^{-1}$	0.005 – 2 $\mu\text{g.mL}^{-1}$
5	Slop b ($\text{mL.}\mu\text{g}^{-1}$)	24974
6	Intercept a ($a = y - bx$)	2834.2
7	Standard deviation Sd ($n=5$)at 1 $\mu\text{g.mL}^{-1}$	0.201
8	Percentage Relative standard deviation RSD%	7.0402×10^{-4}
9	Limit of detection LOD ($\mu\text{g.mL}^{-1}$)	0.388×10^{-2}
10	Limit of quantitation LOQ ($\mu\text{g.mL}^{-1}$)	1.2×10^{-2}

3.2.3-Chromatogram for Selected Samples Containing DBT and CARB

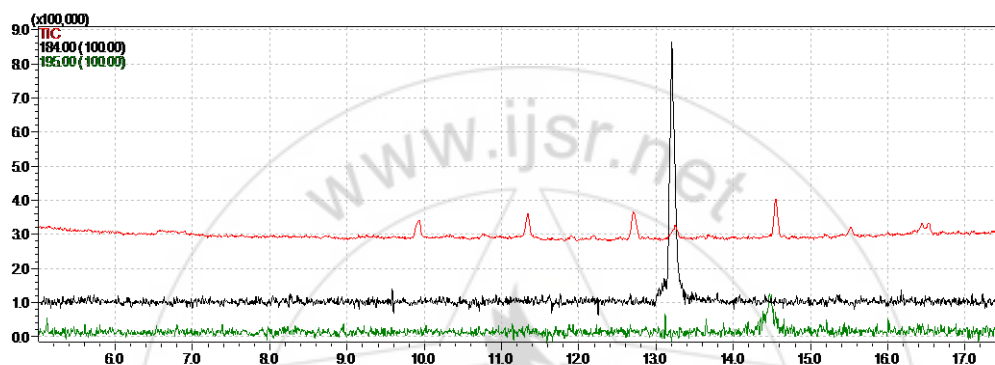


Figure 10: Sample 9/DBT and CARB

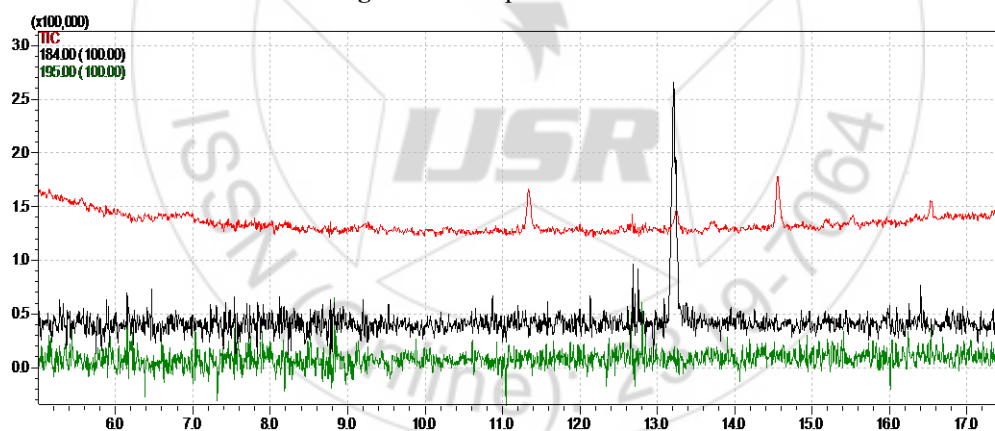


Figure 11: Sample 15/ Dibenzothiophene and 9-Ethylcarbazole

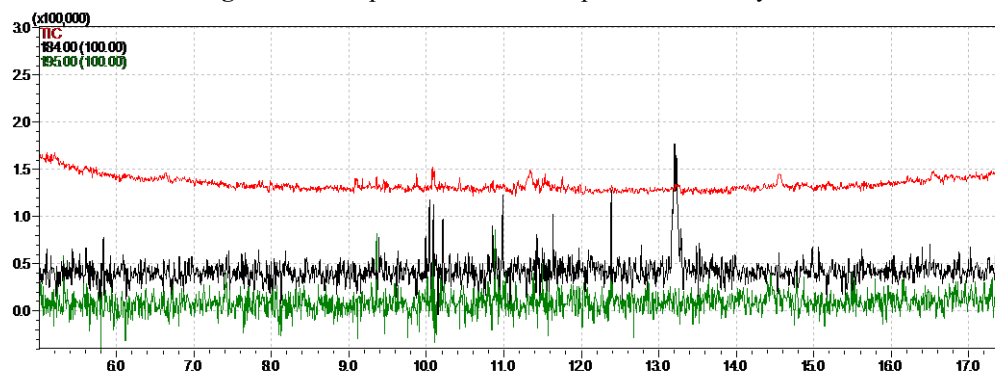


Figure 12: Sample 22/ Dibenzothiophene and 9-Ethylcarbazole

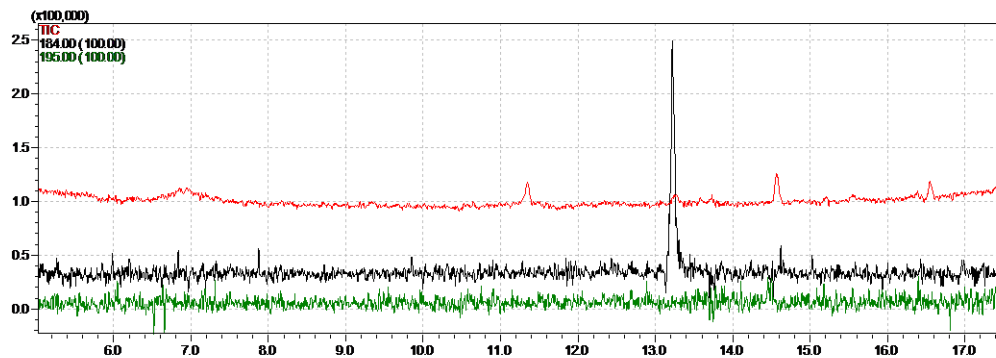


Figure 13: Sample 27/Dibenzothiophene and 9-Ethylcarbazole

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.

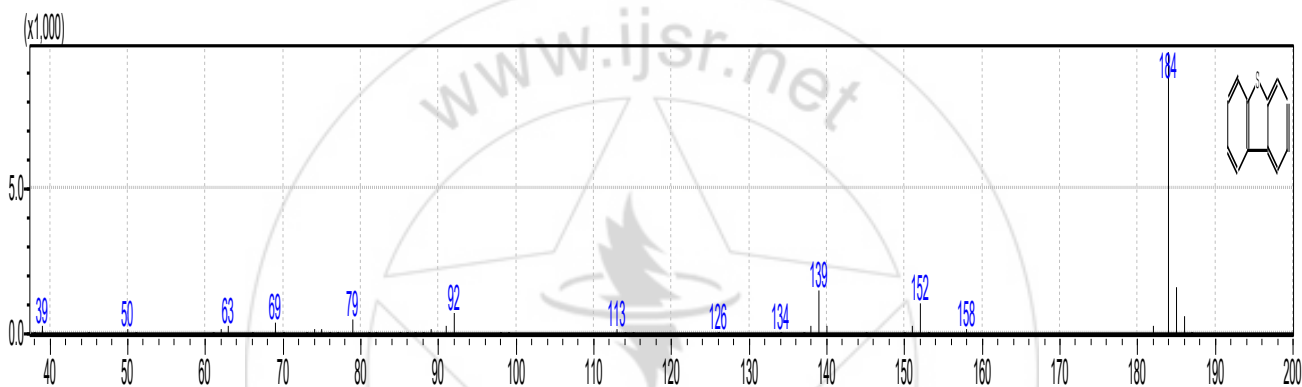


Figure 16 Mass spectrum of DBT (Library; IS=62)

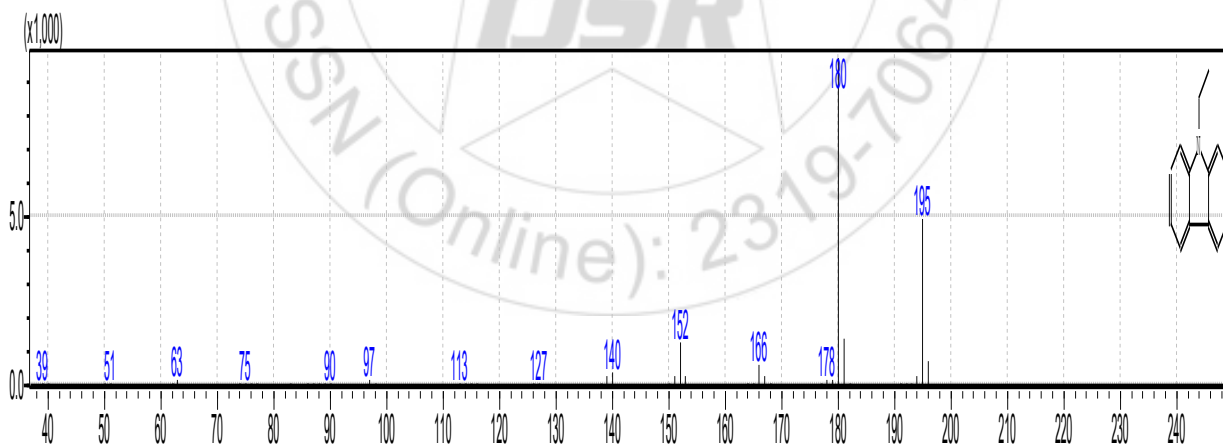


Figure 17 Mass spectrum of CARB (Library; IS=58)

3.3 Results 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 $0.4802 \mu\text{g mL}^{-1}$ while it has a value of $1.1953 \mu\text{g mL}^{-1}$ 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 $0.011523 \mu\text{g mL}^{-1}$.

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, rapid and very suitable to measure successfully of the two target compounds and it can be used for the assay of these compounds or other similar compounds in presence of interfering matrices without environmental contamination..

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