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New Methodology for Preconcentration and Detection of Ultra Trace Amount of Naphthalene and Anthrasene as Markers of Predict to Exploration of Petroleum Reservoir by Cloud Point Extraction Combined with Deferent Techniques

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Abstract: This study is an attempt to use two compounds (Naphthalene, NAPH and Anthrasene, ANTH.) which were to recognize the leakage from petroleum reservoir to surface. This a phenomenon was using such as proximity indicator for petroleum deposits. Productive oil wells (Maysan-Iraq) were chosen with the soil and water samples to case study. The ultra-trace amounts of NAPH and ANTH were extracted by cloud point extraction (CPE) combined with UV-VIS and GC-MS techniques. The conditions of optimization for CPE were conducted with using Triton 114 (TX 114) as non-ionic surfactants. These conditions were of, of the conditions of separation used for the determination of NAPH and ANTH by GC-MS were the same conditions of CPE- UV-VIS. The results indicated that the retention times were of 6.75 and 13.72 min. After applying CPE method for NAPH and ANTH the concentration range was 0.003-2, 0.002-2 µg mL^{-1}, LOD value was 0.2154×10^{-2}, 6.842×10^{-4} µg mL^{-1}, LOQ value was 7.1082×10^{-3}, 2.2578×10^{-3}, preconcentration factor was 33.33, 20 and enrichment factor was 115.1941, 26.516 respectively. Analysis of PAHs

compounds concentrations in organic extract showed that the amounts of these compounds were different depending on many factors like depth, type of sample and location of sample. For example, the concentration of NAPH in Maysan Governorate near Halfaya well (1000 m) was of 1.8796 µg mL^{-1}, while it has a value of 1.6719 µg mL^{-1} at 750 m and not detected at 500 and 250 m depth. The experimental results of this study indicated that the analysis of PAHs 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, Naphthalene, Anthrasene, cloud point extraction, UV-VIS, GC-MS, Triton X-114.

INTRODUCTION

Crude oil represents a complex mixture containing both organic and inorganic chemical species, hydrocarbons, 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 (naphthalene), 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 [5-7]

The determination of PAHs in aqueous samples is rather difficult as their concentration in water is extremely low due to their low solubility. Besides, because PAHs tend to adsorb on walls and surfaces with they come into contact, serious losses often occur during sampling and storage[7-10] 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[11,12]. Consequently, hetero PAHs compounds can provide useful geochemical clues that trace petroleum compounds back to their biological precursors[13]. 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[14]. 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[15-19].

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)[20,21]. However, it is a long time 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[22]. 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[23]. 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[24].The cloud-point temperature (CPT), or equivalently the lower critical consolute temperature, is the specific temperature at which the clear micellar solution of a weakly polar surfactant, such as nonionic or zwitterionic surfactant, becomes turbid upon heating or cooling[25-27]. Explicitly for nonionic surfactants, at temperatures above the cloud point, the homogeneous surfactant solution separates into two immiscible phases with well-defined composition, one of which contains much of surfactant, called surfactant-rich phase or coacervate phase, whereas the other, called water phase, is almost free of micelles and has a surfactant concentration near its critical micelle concentration (CMC)[27,28]. In general, nonionic surfactants are utilized in most CPE processes

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 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 $^\circ$C ,injection mode was splitless, pressure was 100 kPa,, column flow was 1.33 mL/min, ion source temperature was 200 ℃, interface temperature was 280 ℃, ionization mode was EI, start was 35.00 m/z and ending was 500.00 m/z . The oven temperature programmed as 100 ℃ for 3 min, 200 ℃ for 3 min, and 250 ℃ for 3 min .

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 (Naphthalene, and Anthracene) 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).
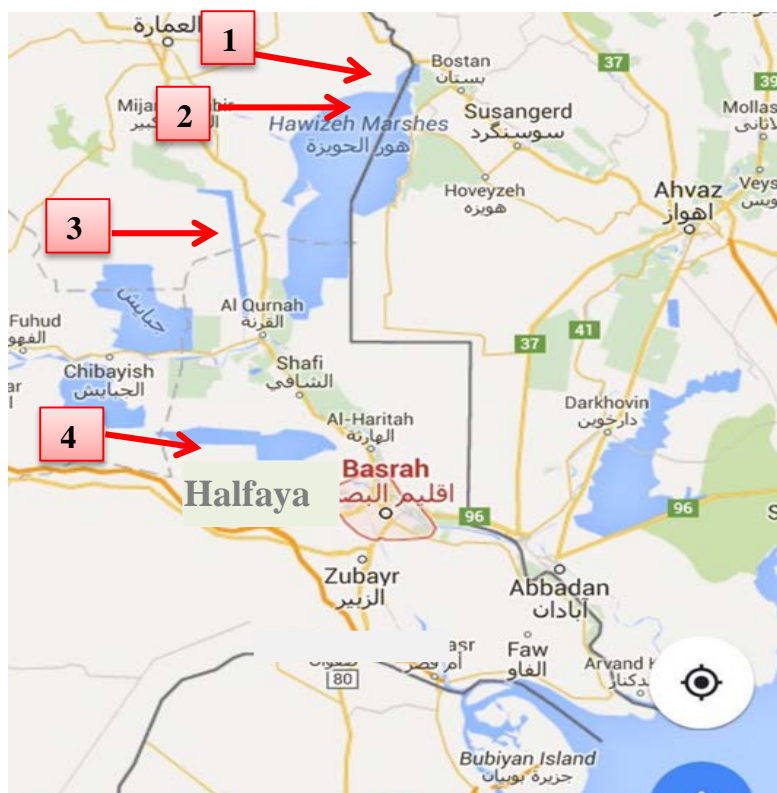
2.3 Preparation of samples:

2.3.1 Cutting samples: Cutting 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[29]. 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 (0-4ºC) 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

Figure 1: map of sample's location where (1) Marsh of Om Nia'aj, (2) Marsh of Al-Disyme, (3) trocar beside petro china company and (4) Halfaya oil wells.
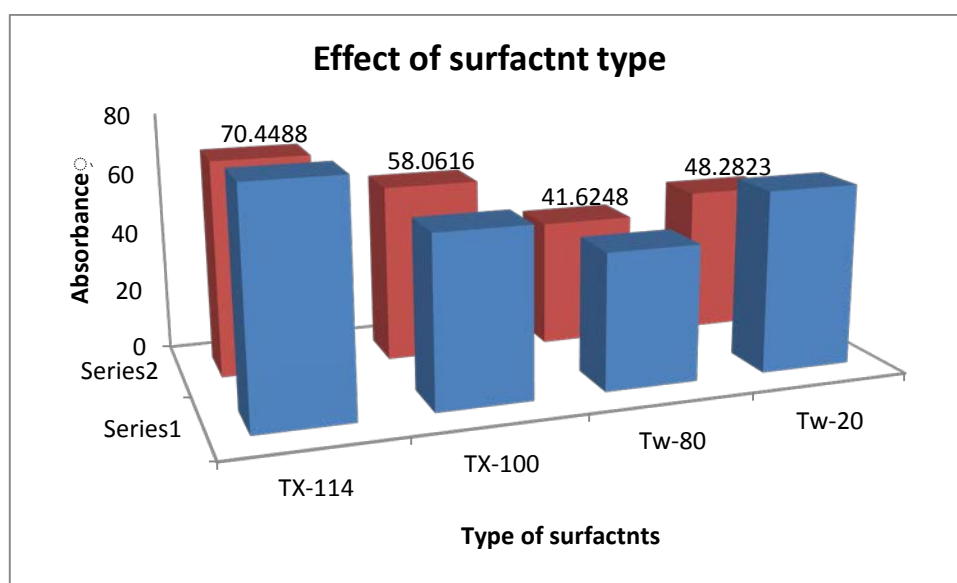
2.4 General CPE Procedure: To an aliquot of 10 mL of a solution containing known amount of Naphthalene or Anthracene standard (0.3-3 ppm), were taken into a series of 10 mL graduated centrifugal tubes. 2mL of 0.5M of Lithium Chloride and (0.3-0.6 mL) of 10% (v/v) Triton X-114 were added and diluted to mark with water. The content of each tube was transferred to water bath at (55-65°C) for (15-20) 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, it 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 it was measured of each solution containing the analyte by UV-VIS and GC-MS techniques

RESULTS AND DISCUSSION

3.1 Optimization 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-at-time (OFAT) procedure for improving the recovery of extraction, sensitivity and detection limit for the determination of each compounds[30,31].
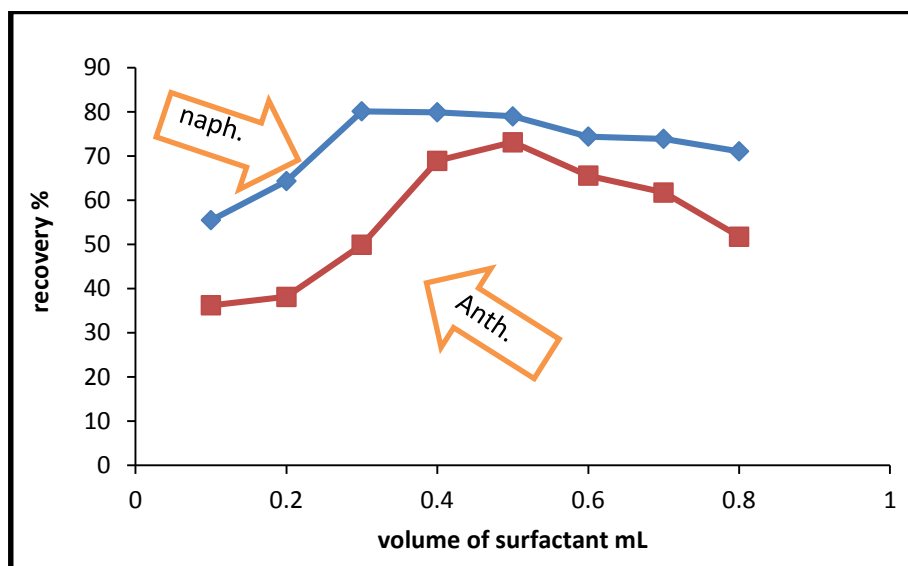
3.1.1 Effect of surfactant Type: In this study, four types of non-ionic surfactants, such as TX-114, TX-100, Tween-80, Tween-20 were tested. The experiments were conducted with 10 mL solution containing of 2µg mL^{-1} of each target analytes and 0.5mLof 10% of each surfactant followed the general CPE procedure. The results are depicted in **Figures 2 and 3**. It can see that the best recovery was obtained with TX-114 for all analytes 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 2: surfactant for NAPH and ANTH

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 precent recovery. Thus the effect of TX-114 amount on the percent recovery of each target analyte was carried out with 10 mL solution containing $2\mu g.mL^{-1}$ of Naphthalene, and Anthracene, 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 0.3 and 0.5 mL of 10% TX-114 for Naphthalene and Anthracene 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 0.3 and 0.5 mL of 10% TX-114 were chosen as optimal for Naphthalene and Anthracene respectively.
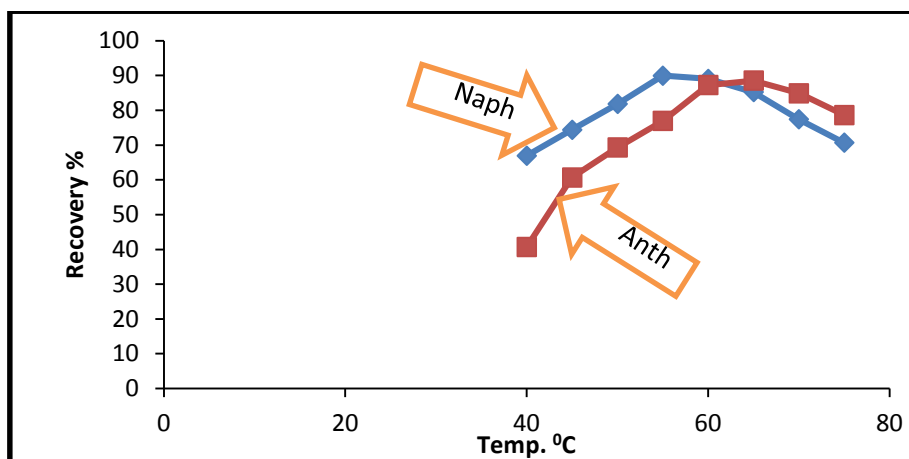

Figure 3: effect of surfactant amount

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 20 min in a search of optimum value and the results showed in **Figure 6**.

The findings revealed that the optimum temperature for the extraction of target organic compounds Napthalene and Anthracene, was of 55, 65 ℃ respectivly. This gave maximum percent recovery, indicating a good quantitative extraction for analytes. At higher temperature than optimal, the recovery decreases perhaps due to the gradually thermal decomposition of the compounds. Thus 55, 65 ℃ at 20 min was selected as operating equilibrium temperature in this study.

Figure 4: effect of equilibration temperature on CPE

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[32]. The time of incubation was varied from 5-30 min at other optimum parameters as shown in **Figure 8.** It can be seen that optimum heating time to achieve maximum recoveries was 15, 20 min for extraction of Naphthalene and Anthracene respectively, indicating the better thermodynamic equilibrium for CP formation with smaller volume, higher viscosity of surfactant-rich phase and better partition of each analyte between two phases.
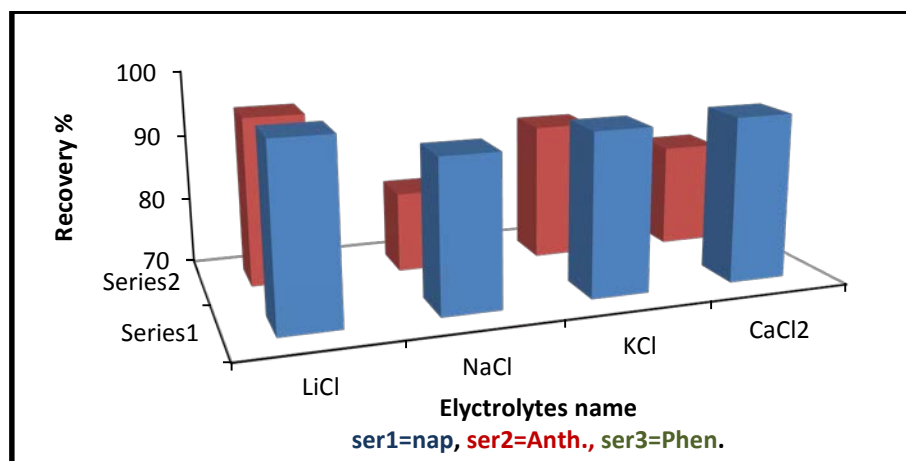

Figure 5: effect of incubation time on CPE

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[33].
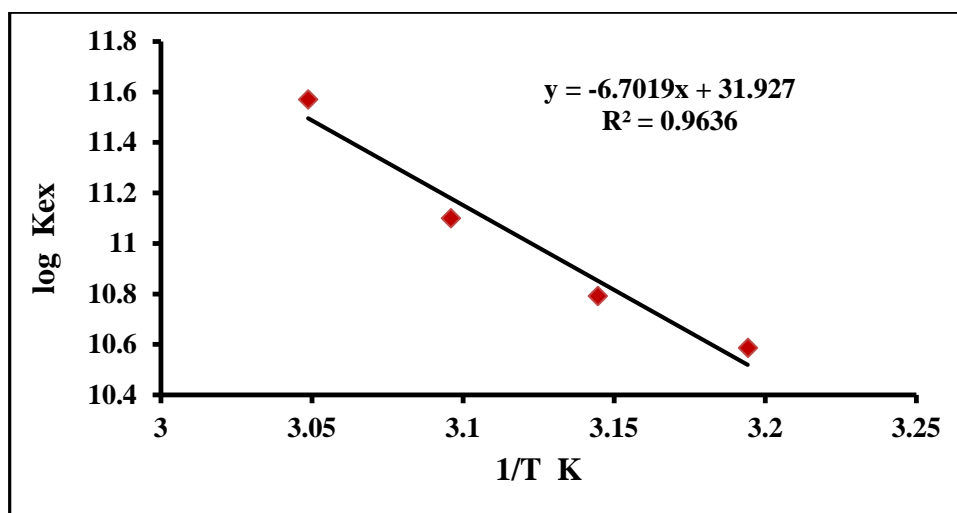
The effect of the selected electrolytes on the CPE of solutions containing each analyte at concentration of 2 μg mL^{-1} was studied keeping other parameters constant. It is observed that the addition of electrolytes, including LiCl, NaCl, KCl, and CaCl$_2$, to micellar solutions decreases the cloud-point temperature[34,35].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[36]. Nevertheless, the addition of these salts make the separation of the two phases easier, because it increases the density of the bulk aqueous phase[37]. 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 same degree[38]. 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[39,40]

Figure 6: effect of electrolytes on CPE

3.2 Thermodynamic study: The equilibrium extraction constants (K_{ex}) and thermodynamic parameters for the extraction of analyte during the cloud point using Triton X-114 as a mediated extracting agent at various temperatures for Naphthalene and Anthracene were determined. The equilibrium constants (K_{ex}) at the selected temperature were calculated and the results of naphthalene and Anthracene are shown in **Table (1, 2)** and **Figures (7,8)**.
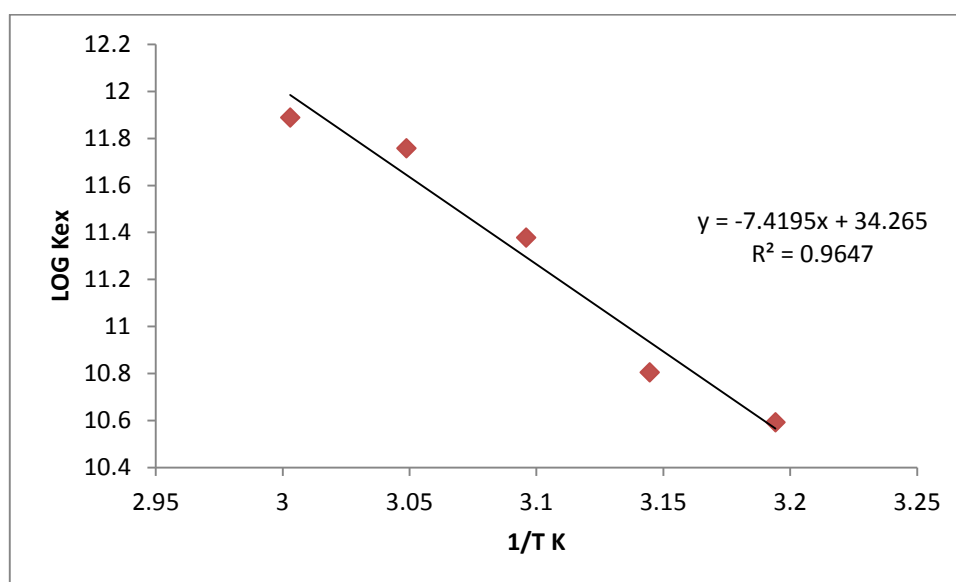

Figure (7): Effect of the equilibration extraction temperature on NAPH by CPE.

Table 1: Thermodynamic parameters of NAPH

T °K	ΔH_{ex} (KJ.mole^{-1})	ΔG_{ex} (KJ.mole^{-1})	ΔS_{ex} (J.mole^{-1}.K^{-1})
313		- 62.0937	323.9831
318	0.1256	- 64.3078	327.8263
323		- 67.1849	333.6031
328		- 71.1148	342.4142

y = -7.4195x + 34.265
R² = 0.9647

Figure 8: Variation of equilibrium constant with temperature during CPE for ANTH.

Table 2: Variation of thermodynamic parameters with temperature during CPE for ANTH.

T °K	ΔH_{ex} (KJ.mole^{-1})	ΔG_{ex} (KJ.mole^{-1})	ΔS_{ex} (J.mole^{-1}.K^{-1})
313		-3.0226	12.3571
318		-3.0295	12.2274
323	0.0027	-3.0352	12.0971
328		-3.0403	11.9692
333		-3.0448	11.8443
338		-3.0486	11.7266

3.3 Methods validation for measurement of NAPH and ANTH:

3.3.1 UV-VIS method: Under the conditions of optimization of NAPH and ANTH, 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. The calibration data are listed in **Table 3 and 4**.
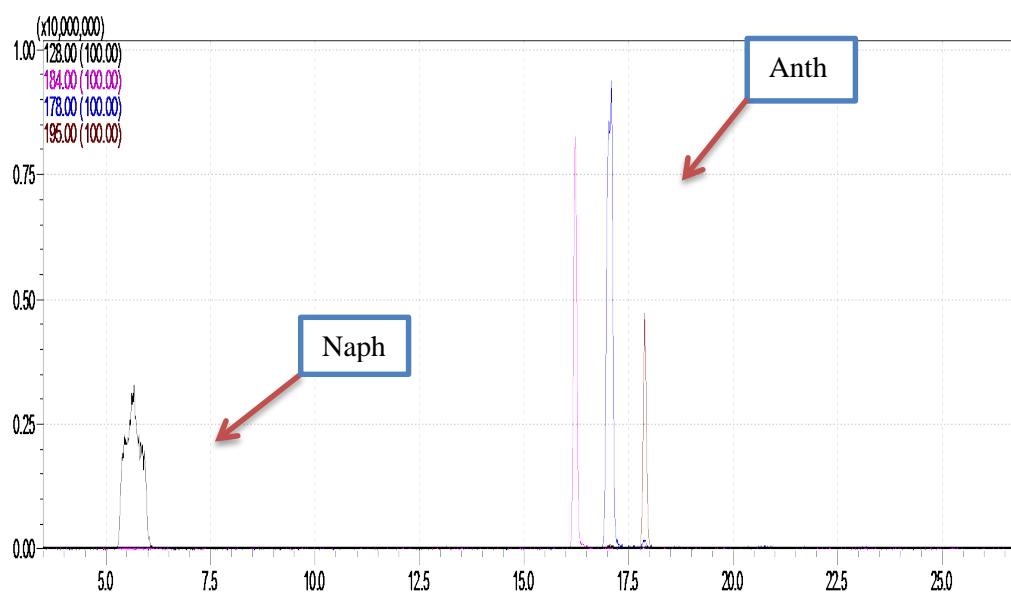
Table 3: statistical calculations of calibration curve of Naphthalene after CPE by UV

o.	Parameters	Value
1	Regression equation y=bx +a	y= 1.0717x – 0.0094
	Correlation coefficient (r)	0.9991
	Linearity percentage (r^2 %)	99.83
	Dynamic range ppm	0.1 – 2 ppm
	Molar absorptivity Ɛ ($L.mol^{-1}.cm^{-1}$) Ɛ=(A/b×c ppm)×m.wt.×1000	13.85×10^4
	Slop b ($mL.\mu g^{-1}$)	1.0717
	Intercept a (a = y - bx)	0.0094
	Standard deviation Sd	3.4014×10^{-4}
	Percentage Relative standard deviation RSD %	0.0627
0	Limit of detection LOD ($\mu g.ml^{-1}$)	9.8174×10^{-3}
1	Limit of quantitation LOQ ($\mu g.ml^{-1}$)	0.0323
2	Sandells sensitivity ($mg.cm^{-2}$)	9.2418×10^{-4}
3	Preconcentration factor	33.33
4	Enrichment factor	26.4613

Table 4: Statistical calculation of Anthracene after CPE by UV

o.	Parameters	Value
	Regression equation y=bx +a	Y=1.9063x-0.0011
	Correlation coefficient (r)	0.9996
	Linearity percentage (r^2 %)	99.93
	Dynamic range ppm	(0.06 – 1.2) ppm
	Molar absorptivity Ɛ ($L.mol^{-1}.cm^{-1}$) Ɛ=(A/b×c ppm)×m.wt.×1000	34.2614×10^4
	Slop b ($mL.\mu g^{-1}$)	1.9063
	Intercept a (a = y - bx)	0.0011
	Standard deviation Sd (n=3)at 0.5ppm	2.3358×10^{-5}
	Percentage Relative standard deviation RSD %	2.4389×10^{-3}
0	Limit of detection LOD ($\mu g.ml^{-1}$)	4.5×10^{-3}
1	Limit of quantitation LOQ ($\mu g.ml^{-1}$)	14.85×10^{-3}
2	Sandells sensitivity ($mg.cm^{-2}$)	5.1953×10^{-4}
3	Prconcentration factor	20
4	Enrichment factor	32.4666

3.3.2 GC-MS method: The retention time of two compounds is 6.75 min to NAPH and 13.72 min to ANTH. Calibration curves five-points (0.03 to 2 µg.mL^{-1}), procedural blank, check standard and sample duplicates were carried out for every set of samples (**Table 3** and **Figure 9**). The relative standard deviation (RSD) values of 0.78 was showed acceptable to response factors of the five-point calibration curve for individual compounds.

Figure 9: Chromotogram of standard Naphthalene, and Anthracene by GCMS

Table 5: Statistical parameters of Naphthalene after CPE by GCMS

o.	Parameters	Value
1	Regression equation y=bx +a	y= 6943442x-3639.2
	Correlation coefficient (r)	0.9987
	Linearity percentage (r^2 %)	99.75
	Dynamic range ppm	0.003 – 2 ppm
	Slop b (mL.µg^{-1})	6943442
	Intercept a (a = y - bx)	3639.2
	Standard deviation Sd (n=3)at 1ppm	5.8 x 10^3
	Percentage Relative standard deviation RSD %	0.7896
	Limit of detection LOD (µg.ml^{-1})	0.2154 x10^{-2}
0	Limit of quantitation LOQ (µg.ml^{-1})	7.1082x10^{-3}
1	Preconcentration factor	33.33
	Enrichment factor	115.1941

Table 6: statistical calculation of Calibration graph of Anthracene after CPE by GCMS

no.	Parameters	Value
1	Regression equation y=bx +a	y= 516751x +6253.4
2	Correlation coefficient (r)	0.9984
3	Linearity percentage (r^2 %)	99.69
4	Dynamic range ppm	0.002 – 2 ppm
5	Slop b (mL.µg^{-1})	516751
6	Intercept a (a = y - bx)	6253.4
7	Standard deviation Sd (n=3)at 1ppm	2.5341×10^2
8	Percentage Relative standard deviation RSD %	4.6345×10^{-2}
9	Limit of detection LOD (µg.ml^{-1})	6.842×10^{-4}
10	Limit of quantitation LOQ (µg.ml^{-1})	2.2578×10^{-3}
11	Preconcentration factor	20
12	Enrichment factor	26.516

3.3.3 chromotogram for selected samples containing NAPH and ANTH:

Figure 10: sample no.9 Naphthalene and Anthracene

Figure 11: sample no. 12Naphthalene & Anthracene

Figure 12: sample no. 15 Naphthalene & Anthracene

Figure 13: sample no. 22 Naphthalene & Anthracene

Figure 14: sample no. 27 Naphthalene & Anthracene

3.3.4 Mass Spectrum of NAPH and ANTH 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 15 and 16 [41,42].

Figure 15: Mass spectrum of Naphthalene (Library; IS=78)

Figure 16: Mass spectrum of Anthracene (Library; IS=71)

3.4 Results of application by UV-VIS Spectrophotometry after CPE

Table 7: UV-VIS application results of Naphthalene and Anthracene

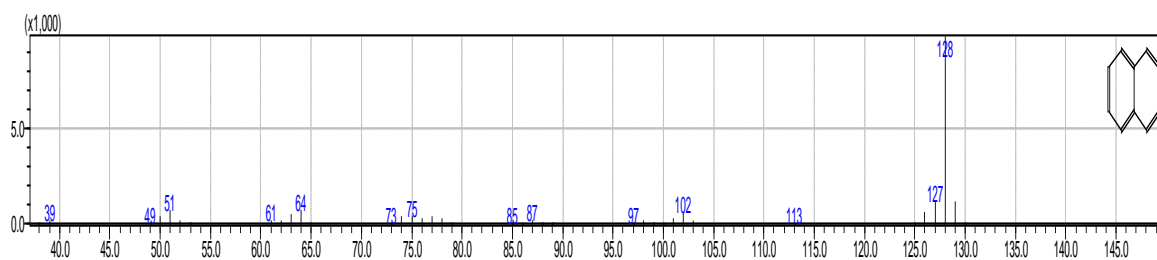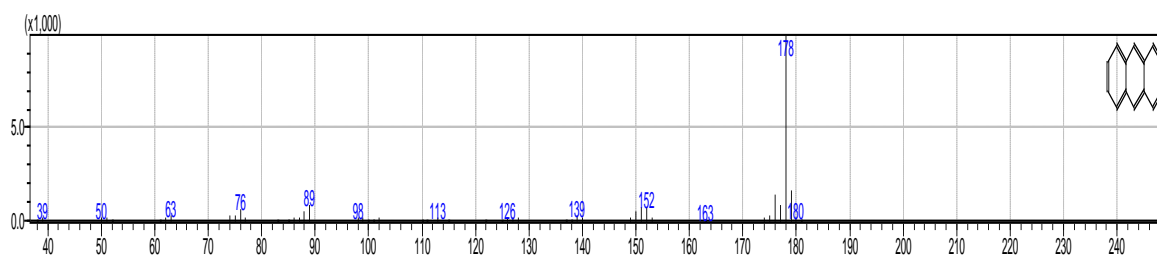|	Name	Naphthalene		Anthracene	
	λ_{max}	223		253	
	Sample name,no. and depth	Abs. nm	Conc. /ppm	Abs. nm	Conc./ ppm
	HF002-M001H/halfaya well 250m	Nd	Nd	Nd	Nd
	HF002-M001H/halfaya well 500m	nd	nd	Nd	Nd
	HF002-M001H/halfaya well 750m	Nd	Nd	Nd	Nd
	HF002-M001H/halfaya well 1000m	0.321 9	1.198 7	Nd	Nd
	HF060-M067ML/halfaya well 250m	Nd	Nd	Nd	Nd
	HF060-M067ML/halfaya well500m	Nd	Nd	Nd	Nd
	HF060-M067ML/halfaya well 750m	0.087 4	0.330 2	Nd	Nd
	HF060-M067ML/halfya well 1000m	0.134 4	0.504 1	Nd	Nd
	HF007-JK007/ halfya well 250m	0.411 6	1.529 4	Nd	Nd
0	HF007-JK007/ halfya well 500m	0.533 2	1.981 2	Nd	Nd
1	HF007-JK007/ halfya well 750m	0.443 8	1.650 2	Nd	Nd
2	HF007-JK007/ halfya well 1000m	Nd	Nd	Nd	Nd
3	HF007-N007/ halfya well 250m	0.329 6	1.227 1	Nd	Nd
4	HF007-N007/ halfya well 500m	Nd	Nd	Nd	Nd
5	HF007-N007/ halfya well 750m	0.183 6	0.696 8	0.072 6	0.189 8
6	HF007-N007/ halfya well 1000m	0.211 3	0.801 9	Nd	Nd
7	Om nia'aj marsh/soil	Nd	Nd	Nd	Nd
8	Om nia'aj marsh/water	Nd	Nd	Nd	Nd
9	Om nia'aj marsh/soil	Nd	Nd	Nd	Nd
0	Om nia'aj marsh/water	nd	Nd	Nd	Nd

1	Om nia'aj marsh/soil	0.351 9	1.329 7	Nd	Nd
2	Om nia'aj marsh/water	0.137 3	0.489 9	Nd	Nd
3	Desaym marsh/soil	Nd	Nd	Nd	Nd
4	Desaym marsh/water	Nd	Nd	Nd	Nd
5	Desaym marsh/soil	0.265 4	0.989 3	Nd	Nd
6	Desaym marsh/water	0.346 5	1.279 5	Nd	Nd
7	Petro china trocar/soil	0.118 69	0.445 7	0.064 7	0.169 9
8	Petro china trocar/water	Nd	Nd	Nd	nd
9	Petro china trocar/soil	Nd	Nd	Nd	Nd
0	Petro china trocar/water	Nd	Nd	Nd	Nd

Table 8: GCMS application results of Naphthalene and Anthracene

	Name	Naphthalene		Anthracene	
	RT/min	6.75		13.72	
	Sample name,no. and depth	Peak area	Conc. /ppm	Peak area	Conc. /ppm
	HF002-M001H/halfaya well 250m	Nd	Nd	Nd	Nd
	HF002-M001H/halfaya well 500m	Nd	Nd	Nd	Nd
	HF002-M001H/halfaya well 750m	9365 781	0.185	12937 166	0.072
	HF002-M001H/halfaya well 1000m	73014 81	1.241	8325 5	0.048
	HF060-M067ML/halfaya well 250m	Nd	Nd	Nd	Nd
	HF060-M067ML/halfaya well500m	17324 832	0.317	Nd	Nd
	HF060-M067ML/halfaya well 750m	13281 753	0.250	6135 262	0.037
	HF060-M067ML/halfya well 1000m	28449 412	0.502	Nd	Nd
	HF007-JK007/ halfya well 250m	Nd	Nd	5864 872	0.035
0	HF007-JK007/ halfya well 500m	Nd	Nd	2510 661	0.018
1	HF007-JK007/ halfya well 750m	98941 977	1.671	1638 187	0.014
2	HF007-JK007/ halfya well 1000m	11146 0	1.879 685	14187 58	0.078
3	HF007-N007/ halfya well 250m	72653 821	1.235	Nd	Nd
4	HF007-N007/ halfya well 500m	Nd	Nd	Nd	Nd
5	HF007-N007/ halfya well 750m	45873 50	0.791	15099 26	0.083
6	HF007-N007/ halfya well 1000m	42064 30	0.728	10773 06	0.061

#	Sample	NAPH area	NAPH conc	ANTH area	ANTH conc
7	Om nia'aj marsh/soil	Nd	Nd	136779	0.012
8	Om nia'aj marsh/water	Nd	Nd	Nd	Nd
9	Om nia'aj marsh/soil	Nd	Nd	5338173	0.033
0	Om nia'aj marsh/water	Nd	Nd	Nd	Nd
1	Om nia'aj marsh/soil	80379007	1.364	8298361	0.048
2	Om nia'aj marsh/water	2921308	0.515	Nd	Nd
3	Desaym marsh/soil	Nd	Nd	Nd	Nd
4	Desaym marsh/water	Nd	Nd	531807	0.033
5	Desaym marsh/soil	6114893	1.044	Nd	Nd
6	Desaym marsh/water	7717279	1.310	15152531	0.083
7	Petro china trocar/soil	2569572	0.456	7334415	0.043
8	Petro china trocar/water	Nd	Nd	Nd	nd
9	Petro china trocar/soil	565116	0.124	690136	0.006
0	Petro china trocar/water	1451726	0.271	Nd	Nd

CONCLUSIONS

Analysis of NAPH and ANTH concentration in organic extract of petroleum origin has shown that magnitudes of these compounds increase with depth. For example, the concentration of NAPH near surface was not detected while it has a value of 1.8796, 1.6719 µg mL^{-1} at 1000,750 meters respectively. These results can be used to predict the presence of petroleum deposit. On the other hand, our findings support the identification of potential risks of the environment and human health. The concentration of NAPH in water sample as example it was 1.9812µg mL^{-1}.The developed methods for the detection of ultra-trace quantities of NAPH and ANTH in the studied samples using CPE 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 detect of concentration for these compounds especially ANTH, due its very low concentrations in both of soil and water samples. The method of CPE 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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