



ISSN: 2141 – 3290

## ANALYTICAL METHODS FOR HYDROCARBONS CONTAMINATED SOIL IN THE TROPICS

**OKOP, I. J.**

*Department of Chemistry  
Akwa Ibom State University, Mkpato Enin,  
P.M.B. 1167, Uyo, Akwa Ibom State  
imehokop@yahoo.com*

**ABSTRACT:** Petroleum and gas exploration has contributed immensely to the economic growth of Nigeria, but over the past few decades, the Niger Delta of Nigeria has suffered human health risk and ecosystem degradation as a result of oil spillage. In this study, soil samples from a major crude oil spill site were investigated. Samples from spill site located at Ikot Ada Udo, in Akwa Ibom State, Nigeria and uncontaminated site (controls) were collected at 0-15 cm, 15-30 cm and 30-60 cm depths and analysed using gas chromatography fitted with a flame ionisation detector (GC-FID). Hydrocarbon ranges of C<sub>5</sub>-C<sub>9</sub>, C<sub>10</sub>-C<sub>26</sub> and C<sub>26</sub>-C<sub>40</sub> through the soil layers were assessed to determine the penetration and clustering of these compounds in contaminated area. The results revealed elevated levels of hydrocarbons in the soil when compared with the reference sites. The hydrocarbon concentrations levels varied from 17-319±7 mg kg<sup>-1</sup> topsoil, 15-429±11 mg kg<sup>-1</sup> subsoil to 13-183±21 mg kg<sup>-1</sup> at the greatest depth measured. This paper provides informative guidelines to target the types of remediation processes, careful monitoring and the need to conduct more post-spill studies by competent remediation professionals.

### INTRODUCTION

Crude oil refineries and oil exploration industries all over the world are becoming much aware of the risks and hazards created by spillage, disposal, indiscriminate storage, leakage and dumping of petroleum wastes to human, plant and animal lives. It is conventional that environment around petroleum exploration areas and regions constantly affected by oil spillage has inevitably received considerable amount of petroleum hydrocarbons over the few decades (Vanem *et al.* 2008). Spills put pressure on marine habitats and pose chronic urban and industrial contamination threats. Undoubtedly, soil contamination by petroleum spillage and most often by oil exploration activities has suddenly gained significant environmental attention (Okop and Ekpo, 2012 ; ITOPF, 2012; Edward and Paul, 1993).

Different analytical techniques have been employed in the analysis of organic contaminants as well as trace element contents of petroleum and crude oil contaminated soils. GC-FID methods for the determination of petroleum hydrocarbons in soil have been developed based on modifications of methods (API, 1992; Van Delft *et al.*, 1994; DRO, 1992b. Analytical methodology was sometimes lacking in dealing with crude oil contamination of soil resulting from this regional oil spillage. The choice of GC-FID over other detectors such as Photo Ionisation Detector (PID) is based on the following advantages:

- (i) FID can cope with high humidity and equally handle very wet samples than PID.
- (ii) In FID, the flame is capable of ionising large range of volatile organic and petroleum Hydrocarbons than PID, thereby detecting a wide range of Hydrocarbons.
- (iii) FID is very useful in detecting lower concentrations volatile organics because of its lower detection limits (ppm levels).

However, FID limitations include its ability to destroy the sample and detect volatile hydrocarbons from non-petroleum matter and organic material such as methane and peat.

The aim of this work was to develop and implement validated and traceable chromatographic methodology for qualitative and quantitative assessment of petroleum contaminants in soils of Niger Delta under tropical weather conditions. This was achieved by:

- (i) Developing an optimized GC-FID method for the analysis of Petroleum hydrocarbons of crude oil contamination in soil.
- (ii) Evaluating the concentration range of these contaminants in the spilled site.
- (iii) Comparing the penetration levels of hydrocarbon contamination at different depths at each location.
- (iv) Exploring the possibilities of grouping the TPH contaminants into chemically similar characteristics based on Chemometric Cluster observation analysis for the purpose of remediation and preventive actions for the oil Industries and the Government.

### MATERIALS AND METHOD

Certified reference standards used were BTEX Mix (benzene, toluene, ethylbenzene and xylene) for Gasoline Range Organics (GRO), catalog No. 47993 supplied by Supelco Analytical, Bellefonte, PA, USA; Kit. This was employed for the chromatographic determination of hydrocarbon content in soil according to DIN ISO 16703 and in waste according to EN 14039. It comprise of the following: Standard solution for the determination of the retention time window (RTW), cat No.67583, Mineral Oil standard mixture type A and B for DIN EN 14039 and ISO 16703 (cat No. 69246) and Alkane standard mixture (cat No. 68281) used for the assay of the system efficiency of GC's (C<sub>10</sub>-C<sub>40</sub>); Heptane, Puriss. p.a (cat. No. 51745) and Dual layer Florisil<sup>®</sup>/Na<sub>2</sub>SO<sub>4</sub> SPE Tube, 2g/2g/6mL (Cat. No 40080-1ea-F) all supplied by Fluka Analytical, Sigma Aldrich.

Diesel Range Organics (DRO) Mix (Tennessee/Mississippi), catalog No. 31214, Lot No. AO62141 was supplied by Restek, PA, USA. Hydrocarbon verification standards (C<sub>10</sub>, C<sub>11</sub>, C<sub>14</sub>, C<sub>15</sub> and TCD) prepared in the laboratory were all HPLC and of analytical reference grades.

### Sample Collection

The crucial step in the analysis of organic contaminants in soils and sediments of our environment starts with sampling (Draft, 1999; Alain *et al.*, 2006; Tadeusz *et al.*, 2002). The study site is located at Ikot Ada Udo, in Akwa Ibom State. Akwa Ibom State is located in the South-South of the Niger Delta of Nigeria. At this site, soil and water have been repeatedly subjected to petroleum spillages and crude oil leakages from Shell marginal oil corked well. Three sub-samples were collected at each sampling points at the designated depths. Soil auger (Nickel-plated carbon steel, 3'' diameter) was used to collect soil samples from the site by taking about 6-10 auger borings at random grid at sampling points to depths of 0 to 15 cm (top or surface soil), 15 to 30 cm (sub-surface soil) and bottom level of 30 to 60 cm. About 500g of petroleum contaminated soil samples were collected into zipped plastic bags, labeled and put into a glass jar sealed with Teflon lined cap. Control samples taken on the same day prior to actual field samples were obtained to determine the background levels of petroleum hydrocarbons in the unaffected soil for comparison with the contaminated site(s). The auger was cleaned with de-ionized water and rinsed with methanol (99%) after each sampling point.

### Sample Preparation, Preservation and Transportation

The entire sampling exercise was carried out in one day. All the real and control samples were placed in icebox and transported to the laboratory. Storage was done at 4°C until analysis was completed in two weeks. The average ambient temperature was 28°C with the task of sampling accomplished same day. The soil samples were homogenised using mortar and pestle to obtain finer texture and to remove sticks, pebbles and rock particles. The samples were thereafter transported to United Kingdom for analysis by the chemical shipping agent with full special shipping procedures (ASTM, 2005) for transporting and handling these types of samples.

### Sample Extraction

Soxhlet extraction using a Brinkmann Büchi 461 automated extraction apparatus was used in this work. Soxhlet extraction is a USEPA (USEPA, 1996) and ASTM (ASTM 2005) approved method for semivolatile and non-volatile organic contaminants from solid materials such as soil. This procedure involves extraction of the petroleum contaminants from about 10g weight of dry oil-spilled soil with a suitable solvent. Soxhlet extraction really ensures intimate contact of the sample matrix with the extraction solvent and a reasonably large amount of 2-20g sample could be used to allow quantitative extraction. Soxhlet technique has been proposed by many agencies (ISO (1995); Berst et al. (1991) as a method of choice for extraction of non-polar organic contaminants. In this work, dichloromethane (DCM, 99.8%) was used as the extracting solvent and was supplied by Sigma Aldrich.

The choice of this extraction method includes its peculiar application, availability in the laboratory and the ease of setting up with minimal or no cost. Its drawbacks include delayed extraction period and use of appreciable volume of solvent.

Optimum extraction time of about 2.5 hours was established using dichloromethane DCM after comparing with other solvents such as methanol, hexane, acetone, toluene and ethyl benzene or the mixture. DCM proved to be the most suitable solvent over hexane, acetone, toluene and ethyl benzene for this extraction due to its consistency, efficiency and ability of not interfering with BTEX retention time window (RTW) - C<sub>5</sub>-C<sub>9</sub>. This was indicative that Tropical soil in south-south Niger Delta favoured efficient extraction with DCM as solvent.

### Sample Clean-up

Sample clean-up was done to remove moisture, polar hydrocarbons, colour interferences and any impurities before subjecting the samples to GC column analysis. This was achieved by filtering the extract under applied pressure through dual layer 6 mL glass Florisil<sup>®</sup>/Na<sub>2</sub>SO<sub>4</sub> SPE Tube 2g/2g (Figure 1). This is aimed at removing moisture, polar hydrocarbons, colour interferences and impurities. The clean-up procedure effectively removed hydrocarbons of natural origin and did not have any significant effect on the amounts of petroleum hydrocarbons present.

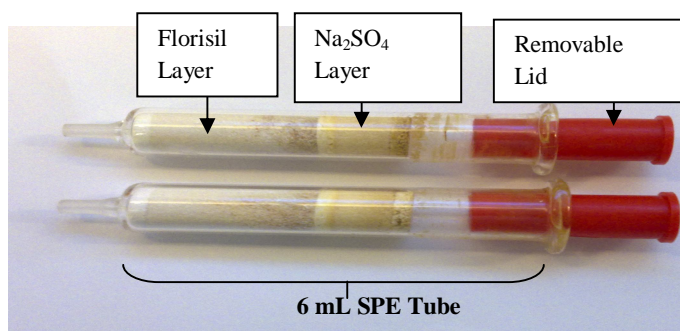


Figure 1: A pictorial representation of used Dual layer Florisil<sup>®</sup>/Na<sub>2</sub>SO<sub>4</sub> tube for sample clean-up to remove moisture, polar hydrocarbons, colour interferences and impurities.

### Analytical Procedure

A Varian BV, CP-3800 gas chromatograph coupled to the FID detector and equipped with an automatic sampler CTC Analytics CombiPAL and the 1177 split/splitless injector was used. The GC capillary (WCOT) column was a non polar, CP-Sil 8 CB Low Bleed/MS polymer; 30m long, 0.25mm inside diameter (id), 0.39mm outside diameter (Od), 0.25µm film thickness, coating of 95% methyl, 5% phenylpolysiloxane. All samples were taken into 2 mL chromatographic vial and 1µL injected in the Varian Chrompack capillary column. The developed and optimized method was tested and used for analysis of the reference and laboratory Standards, real and control samples. The instrument was now programmed under the established optimum method (Table 1).

Table 1 Summary of Instrumentation parameters of the optimized GC-FID method.

GC-FID Parameters	
Carrier gas	Helium (99.99%)
Column flow rate	1.0 mLmin <sup>-1</sup>
Sample injection volume	1 µl
Start/Initial column temperature	30°C
Initial Holding time	3 min
Temperature ramp	8°C min <sup>-1</sup>
Final column temperature	320°C
Final Holding time	15 min
Total time of analysis	51.75 min
Split ratio	1:25
Rear Injector (Varian1177) temp.	300°C
Detector (FID) temperature	320°C
Transfer line temperature	300°C
Hydrogen flow rate	30 ml min <sup>-1</sup>
Air flow rate	300 ml min <sup>-1</sup>

### RESULTS AND DISCUSSION

The analytical method developed and employed in the identification and quantification of the samples were based on the comparison of the chromatographic data with the reference standards mix, (Diesel Range Organics (DRO), waste Oil Organics (WOO)). The average peak values of all the samples were recorded and their standard deviation and % RSD calculated at 95% confidence level (Table 2). This indicated that a reasonable and acceptable degree of precision was established in the results

The analysis of the solvent blank (DCM), thimble extract and control samples taken from similar geographical non-spilled areas, randomly collected and analyzed as the standards along side with other samples had no indication of trace of hydrocarbons or other contaminants since appropriate controls were carried out (Figures 2 & 3).

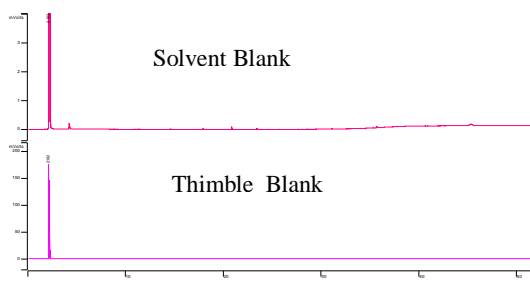


Figure 2: Chromatograms of blank solvent and thimble with no contaminants except the peak shown by the extraction solvent (DCM).

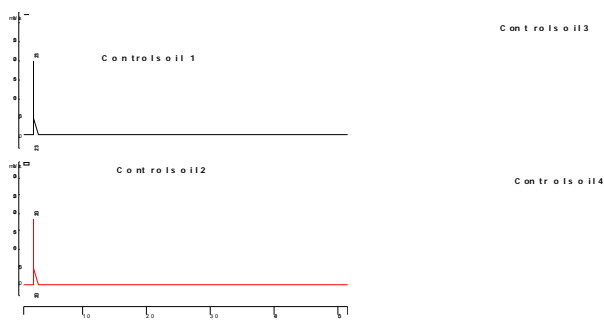


Figure 3: Chromatograms of the four control samples had no significant indication of contamination by liquid hydrocarbons. Extraction solvent peak at 2.1 minute elution time.

Table 2: Chromatographic information of reference standards- DRO, (C<sub>10</sub>-C<sub>26</sub>) and WOO (C<sub>26</sub> and above) fully separated and validated.

Name	Standard Mixture for n- Alkanes even C <sub>10</sub> -C <sub>40</sub>			AV. PK. Area MEAN	STDEV	%RSD	95% CL	
	Ret. Time (mins)	PEAK AREAS (Counts)						
		1	2	3				
n-Decane (C <sub>10</sub> H <sub>22</sub> )	11.82	3750	3751	3752	3751.00	1.00	0.03	3.04
n-Dodecane C <sub>12</sub> H <sub>26</sub>	16.17	3498	3501	3499	3499.33	1.53	0.04	4.65
n-Tetradecane, C <sub>14</sub> H <sub>30</sub>	19.95	3876	3879	3878	3877.67	1.53	0.04	4.65
n-Hexadecane, C <sub>16</sub> H <sub>34</sub>	23.29	4236	4239	4237	4237.33	1.53	0.04	4.65
n-Octadecane, C <sub>18</sub> H <sub>38</sub>	26.29	4048	4051	4047	4048.67	2.08	0.05	6.33
n-Eicosane, C <sub>20</sub> H <sub>42</sub>	29.00	3463	3465	3466	3464.67	1.53	0.04	4.65
n-Docosane, C <sub>22</sub> H <sub>46</sub>	31.48	2987	2990	2989	2988.67	1.53	0.05	4.65
n-Tetracosane, C <sub>24</sub> H <sub>50</sub>	33.75	2265	2267	2268	2266.67	1.53	0.07	4.65
n-Hexacosane, C <sub>26</sub> H <sub>54</sub>	35.84	2247	2251	2249	2249.00	2.00	0.09	6.09
n-Octacosane, C <sub>28</sub> H <sub>58</sub>	37.88	1792	1794	1795	1793.67	1.53	0.09	4.65
n-Triacontane, C <sub>30</sub> H <sub>62</sub>	40.33	1794	1792	1790	1792.00	2.00	0.11	6.09
n-Dotriacontane, C <sub>32</sub> H <sub>66</sub>	43.62	1688	1690	1689	1689.00	1.00	0.06	3.04
n-Tetratriacontane, C <sub>34</sub> H <sub>70</sub>	48.29	1494	1491	1493	1492.67	1.53	0.10	4.65

DRO Mix (16 Components)								
DRO Mix	Ret Time	Mean Av. Peak counts	(3 REPLICATES PEAK. AREA)			St Dev	%RSD	95%CL
C10 Decane	11.76	49875.00	49873	49877	49875	2.00	0.00	6.09
C11 Undecane	14.02	46776.67	46776	46781	46773	4.04	0.01	12.30
C12 Dodecane	16.11	39223.00	39221	39225	39223	2.00	0.01	6.09
C13 Tridecane	18.06	33386.00	33382	33390	33386	4.00	0.01	12.17
C14 Tetradecane	19.87	28682.33	28684	28681	28682	1.53	0.01	4.65
C15 Pentadecane	21.61	24687.00	24688	24689	24684	2.65	0.01	8.05
C16 Hexadecane	23.23	20679.00	20676	20682	20679	3.00	0.01	9.13
C17 Heptadecane	24.77	17668.00	17668	17670	17666	2.00	0.01	6.09
C18 Octadecane	26.23	15425.00	15422	15429	15424	3.61	0.02	10.97
C19 Nonadecane	27.62	12557.00	12553	12561	12557	4.00	0.03	12.17
C20 Eicosane	28.95	10376.67	10377	10374	10379	2.52	0.02	7.66
C21 Heinecosane	30.22	8341.00	8338	8345	8340	3.61	0.04	10.97
C22 Docosane	31.44	6581.67	6585	6579	6581	3.06	0.05	9.30
C23 Tricosane	32.6	5108.00	5106	5110	5108	2.00	0.04	6.09
C24 Tetracosane	33.72	3887.67	3883	3892	3888	4.51	0.12	13.72
C25 Pentacosane	34.8	2885.00	2883	2887	2885	2.00	0.07	6.09

In order to ensure proper functioning of the instrument, reproducibility and repeatability of the analysis, column conditioning and routine operational checks were performed. The overall concentration of total petroleum hydrocarbon (TPH) of each sample depth at the site were established and presented in Table 3.

Table 3: Concentration (mg kg<sup>-1</sup>) of Petroleum Hydrocarbons at each level of sample spot

Sample Location	Three depths	Hydrocarbon Concentration (mg kg <sup>-1</sup> )		
		TS	MS	BL
<b>Site</b>		<b>Soil Levels</b>		
1	3	34±11	96±11	77±13
2	3	119±5	123±2	89±7
3	3	135±12	75±9	53±9
4	3	29±12	86±13	13±8
5	3	94±3	113±12	152±4
6	3	121±4	169±7	213±9
8	3	19±5	24±23	17±7
9	3	215±4	123±3	127±3
10	3	138±21	429±11	91±15
11	3	143±6	61±16	49±2
12	3	53±8	64±13	172±11
13	3	17±24	29±20	16±19
14	3	214±13	219±8	183±21
15	3	75±3	65±13	11±21
16	3	319±7	315±4	276±4
17	3	203±8	118±9	113±2
18	3	123±19	94±14	63±13
		<b>Control Samples</b>		
19	3	0.00	0.00	0.00
20	3	0.00	0.00	0.00
21	3	0.00	0.00	0.00
22	3	0.00	0.00	0.00

The concentrations of the total petroleum hydrocarbon (TPH) of each sample depth at the site are presented in Table 3. It shows the overall level of TPH recorded in the petroleum contaminated site spans from 11±21 to 429±11 mg kg<sup>-1</sup> TPH concentration for the top soils (15 cm depth) covered 17±24 to 319±7 mg kg<sup>-1</sup>. The middle or sub-soils (30 cm depth) had a concentration range of 24±23 to 429±11 mg kg<sup>-1</sup> and a range of 11±21 to 276±4 mg kg<sup>-1</sup> was recorded for the 60 cm depths measured. Sample No.10 had highest TPH concentration (429±11) with the middle soil (15-30 cm depth) and sample No. 16 had the higher value of TPH (319±7 mg kg<sup>-1</sup>) in the top soil followed by 276±4 mg kg<sup>-1</sup> of the same sample at the 60 cm base level. No significant level of TPH was recorded for the control soil samples (Nos. 19, 20, 21 & 22) taken from similar geographical non-spilled areas. The samples showed elevated concentration of TPHs when compared with control samples in all the sites.

The high levels of TPH contamination observed in this study for spilled soils far exceeded the fifty parts per million (50 mgkg<sup>-1</sup>) compliance baseline limit set for petroleum industries in Nigeria (DPR. 1991). The concentration of TPH at the mid/sub-soil (15-30 cm) depth was higher than the concentration range reported by Okop *et al.* (2012), Ekundayo and Obuekwe (2004), Adeniyi and Afolabi (2002) for oil spilled soils of other parts of Niger Delta. High concentration levels of hydrocarbons present in contaminated sites could pose a health risk to humans, plants and animal lives.

The hydrocarbon content for each sample was computed (USEPA, 2003). All samples, references and controls were analysed several times to assess the reproducibility of the chromatographic method. A statistical analysis was performed on the sample to determine whether any significant level of variation existed during the analysis. Reference standard mixtures were analysed after every ten samples and their retention time shown on the chromatogram (Figure 4). The peaks and retention times established by the two standards in figure 4 were compared with each other and confirmed by running the standards prepared in the laboratory. Tentative identification of analyte occurs when a peak from the sample extract falls within the daily retention time window (RTW).

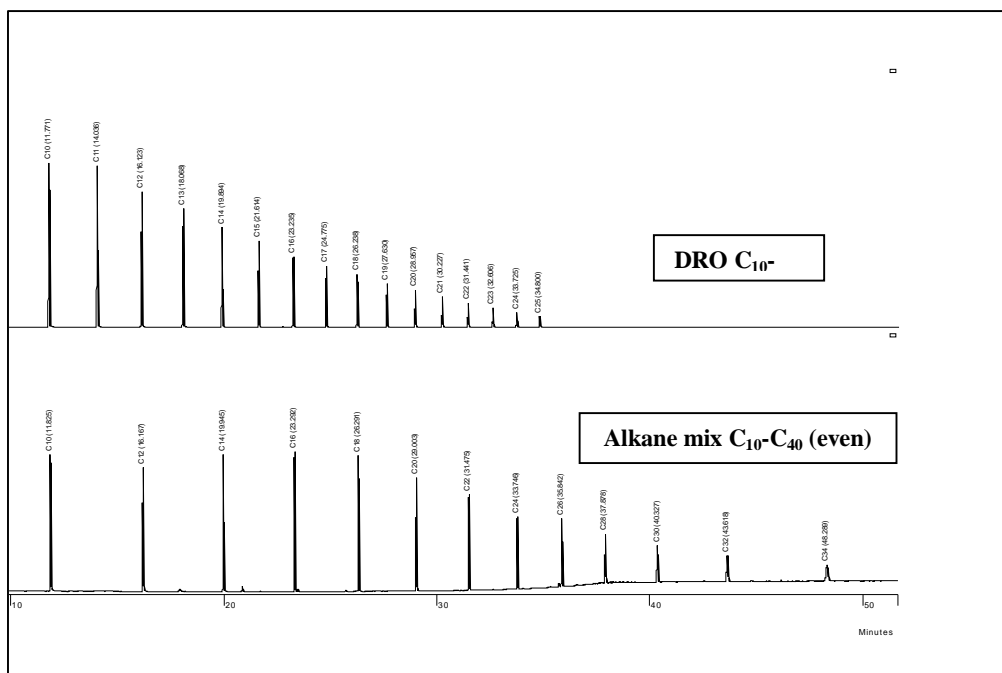


Figure 4: Chromatograms of the reference standards. Above: DRO mix (16 hydrocarbons, C10-C25) Below: Alkane mix (16 separated Hydrocarbons, C10 –C34), even number of carbons only

Confirmation is made by further analysis using the other reference standards and the ones prepared from the laboratory as shown in figures 5. The peaks eluted from all the five standards C<sub>10</sub>, C<sub>11</sub>, C<sub>14</sub>, C<sub>15</sub> and the reference standard, DRO (C10-C25) were analyzed concurrently in order to ascertain the reproducibility of the chromatographic optimization process. The three reference standards – BTEX, DRO and alkane mix and were analysed with the sample at the same time using the optimised method (Figure 6). The sample, chromatogram 3, had no trace of BTEX at the volatile Gasoline range. The inability to detect elevated levels of BTEX peaks in the sample could be attributed to their solubility in soil water, atmospheric temperature, type and extent of contamination (Mohammed, 2004) and evaporation (Hokstad, 2000) of the light crude oil on exposure for sometime before sampling and analysis.



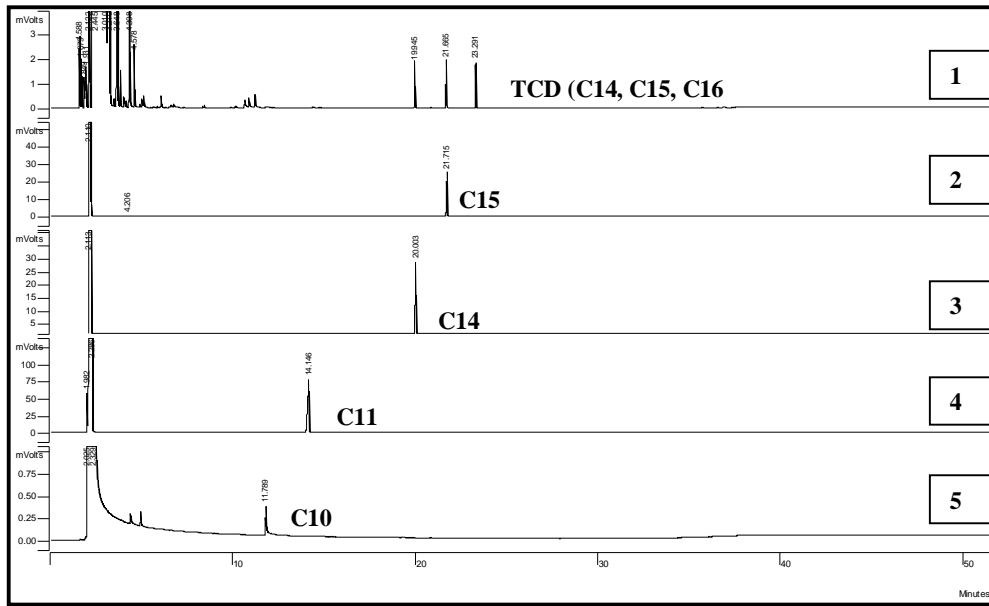


Figure 5: Chromatograms of standards prepared in the laboratory. 1) = TCD (thermal conductivity detector mix), 2) = Pentadecane ( $C_{15}H_{32}$ ), 3) = Tetradecane ( $C_{14}H_{30}$ ), 4) = Undecane ( $C_{11}H_{24}$ ), 5) = Decane ( $C_{10}H_{22}$ ).

Figure 5: The peaks and retention times established by the two standards in figure 4 were compared with each other and confirmed by running the standards prepared in the laboratory such C10, C11, C14, C15 and the TCD. Their retention times conformed to that of the reference standards

Standard solution (C10 & C40) for the determination of the retention time widow (RTW) was injected to calibrate and fix RTW from C10 and C40 before the sample measurements as part of the method validation. Two certified reference standards (alkane standard mix & DRO) and TCD (Thermal Conductivity Detector) of known composition were simultaneously analysed and their retention times compared and overlaid (Figure 6).

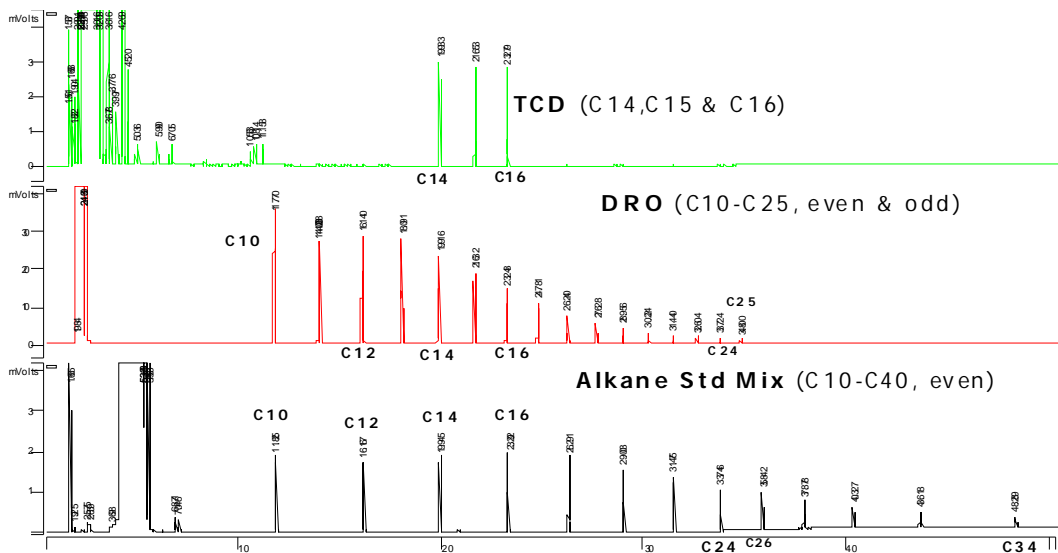


Figure 6: Retention times of Alkane standard mix, DRO and TCD were established, compared and overlaid after the RTW validation.

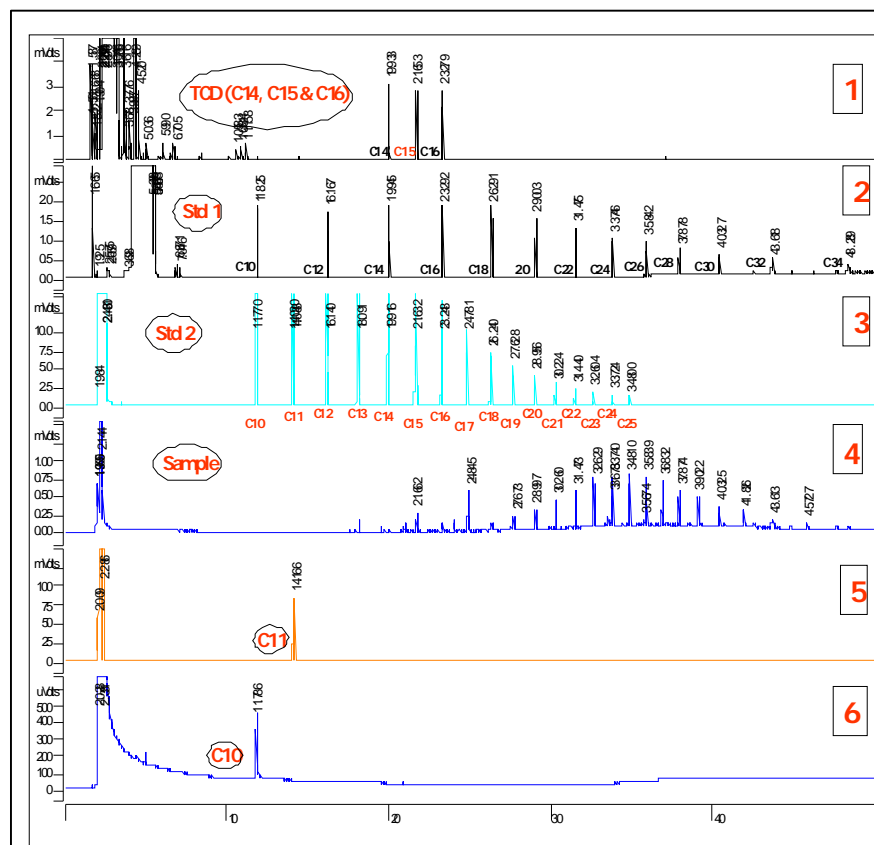


Figure 7: Alkane standard mix (chromatogram 2, std 1), DRO (chromatogram 3, std 2) overlaid with lab standards, C10, C11, C14, C15 and C16 to confirm the identity and retention times of the standard hence the corresponding samples (chromatogram 4). Chromatogram of the Alkane mix was prepared in hexane, hence the interference in retention time at C5-C8. TCD was similarly prepared in heptane while all lab samples were prepared with DCM-the extraction solvent.

Gasoline Range Organics (GRO, encompassing BTEX) were not detected at the final sample analysis (Chromatogram 4). This result is consistent with the observation by Craig *et al.*, (2007) that very low concentrations of organic pollutants (gasoline components) were found in soil and water after Katrina.

### CONCLUSION AND RECOMMENDATION

The sampling method, sample preparation and optimized extraction were carried out. The GC-FID analysis of the petroleum contaminated soil extracts using the developed, validated and optimized methods yielded higher concentration of petroleum hydrocarbons than the control soil samples. Hydrocarbon reference standards were used to assess the level of contamination in the soils of the study site. The least concentration of hydrocarbon was recorded in the deepest level of soil measured while highest concentration occurred in the middle soil level. The results revealed elevated levels of hydrocarbons in the soil when compared with the reference sites and the finding provides informative guidelines to target the types of remediation processes, careful monitoring and the need to conduct more post-spill studies by competent remediation professionals.

### ACKNOWLEDGMENT

The author thanks the University of Manchester, Manchester, United Kingdom for providing the research facility for carrying out this work.

## REFERENCES

- Adeniyi, A. A. and Afolabi, J. A. (2002). Environment International. 28,79-82.
- Alain, H., Silvia, L, Damia, B. (2006). Sampling of water, soil and sediment to trace organic pollutants. *Anal. Bioanal, Chem.* 386: 1075-1088.
- API (1992). *Methods for the Determination of Petroleum Hydrocarbons in soil*. Revision 1. American Petroleum Institute. Washington, DC.
- ASTM (2005). Annual Book of ASTM Standards Extraction of solid waste samples for chemical analysis using Soxhlet extraction, environmental assessment, hazardous substances and oil spill responses, Practice for D5369; 11.04: pp 196-201.
- ASTM (2005). Annual Book of ASTM Standards Preserving and Transporting Soil Samples, Practice for D 4220 (04.08), pp. 513-516 & 523.
- Berst, J. D, Ejem, M, Holzer, R. and Lischer, P. (1991). *Analytica Chimica Acta.* 383: 263-275.5
- Adams, C., Witt, E. C., Wang, J., Shaver, D. K., Summers, D., Filali-Meknassi, Y., Shi, H., Luna, R. and Anderson, N. (2007). Chemical quality of depositional sediments and associated soils in New Orleans and Louisiana Peninsula following hurricane Katrina. *Environ. Sci. Technol.* 41(10): 3437-3443.
- DPR (1991). Environmental Guidelines and Standards for the Petroleum Industry in Nigeria, Department of Petroleum Resources, Ministry of Petroleum and Mineral Resources, Lagos, Nigeria. (1999). Sampling Protocols and Analytical Methods for Determining Petroleum Products in Soil and Water. Prepared by the oil Industry Environmental Working Group.
- DRO (1992b). Tennessee method for the determination of Diesel Range Organics The State of Tennessee Department for Health Laboratory Services, UST program.
- Edward, J. C. and Paul, T. K. (1993). Principles and Practices for Petroleum Contaminated Soils. Boca Raton: Lewis Publishing;
- Ekudanyo, E. O. and Obuekwe, O. O. (2004). Environmental Monitoring and Assessment. Springer Netherlands. 60, (2), 235-249.
- Hokstad, J. N, Faksness, L. G. and Daling, P.S. (2000). SPE Paper 61468, presented at SPE Int. conf. On health, Safety & Environment in oil & gas exploration & production, Stavanger, Norway, pp. 26-28.
- ISO (1995). Draft International Standard ISO/DIS 13877.
- ITOPF (2012). International Tanker Owners Pollution Federation, [www.itopf.com](http://www.itopf.com).
- Mohammed, M. A (2004). Treatment techniques of oil-contaminated soil and water aquifers. International conference on water resources and arid environment. P. 2.
- Okop I. J. and Ekpo, S. E. (2012). Determination of Total Hydrocarbon Content in Soil after Petroleum Spillage, Lecture notes in Engineering and Computer Science. 3: 1722-1726.
- Okop, I. J, Okorie, F. S, Obadimu, C. O. (2012). Quantitative Evaluation of the spatial Distribution and Penetration of Liquid Hydrocarbons in Petroleum spilled Soil. *Global Advanced Research Journal of Environmental Science and Toxicology*, Vol. 1(6) pp. 152-161.
- Tadeusz, G. and Jacek, N. (2002). Trends in Analytical Chemistry, (21) 4: 276-291.
- U.S. EPA Method 3540C (1996). Soxhlet extraction. Revision 3. December, 1996.
- U.S.EPA (2003). New test methods 8000C for determinative chromatographic separations. March 2003.
- Van Delft, R. J, Doveren, A.S.M.J, Snijders A.G. (1994). *Fresenius Journal of Analytical Chemistry.* 350: 638-641.
- Vanem, E. Endresen, O. and Skjong, R. *Reliability Engineering & System Safety*, 2008, 93: 1354-1368.