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RESEARCH ARTICLE

SOURCE DETERMINATION OF TAR BALLS ON IBENO BEACH, NIGER DELTA REGION OF NIGERIA USING PRISTANE/PHYTANE RATIO

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ABSTRACT

The appearance of tar balls on the coastline is an indication of oil spill although natural seeps also contributes to this. Problems do ensue between the host communities and the oil producing companies as a result of this. Tar balls picked from Ibeno Beach, Akwa Ibom State in the Niger Delta Basin of Nigeria were analyzed to trace their origin using GC/FID. The parameter used was pristane/phytane ratio, (Pr/Ph), The results obtained from the tar ball analyses revealed that in most of the tar balls analyzed, pristane and phytane were absent as a result of extensive weathering; however, in those tar balls that still contained some amount of pristane and phytane there was a predominance of pristane over phytane giving a pr/ph ratio of more than unity (>1). Comparing this result with those obtained from the unaltered crude oil sourced from some selected oil wells in the Niger Delta which were also analyzed, revealed that the tar balls could be from Niger Delta oil wells. These oil wells Idoho Bravo, W/24, EST. 25, Soku FS, Utorugu 55 and Umuechem Pumpline. However, in four tar ball samples, a predominance of phytane over pristane was observed; an indication that such tar balls are foreign to Niger Delta environment. This study revealed that, Pr/ph ratio cannot be conveniently used to trace tar balls back to their origin because during weathering most of the isoprenoids especially pristane and phytane are altered; some even completely disappear with extensive weathering. However, the pr/ph ratio of some of the tar balls did not match those of the Niger Delta oil wells analyzed. They are suspected to be from neighboring West African countries like Gabon and Congo Brazzaville etc which may have been transported by ocean currents and left stranded on the Nigerian coast line. The significance of these study is that pristane/phytane ratio alone cannot be used to trace petroleum residue back to its source.

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INTRODUCTION

Black asphaltic bitumen (tar balls) are frequently found stranded on Nigerian beaches. Although natural seeps could contribute to the appearance of tar balls on the coastline; their presence is used as an indicator of marine pollution by oil producing communities of the Niger Delta Region. This has always led to several cases of litigation between the producing companies and the host communities. Such litigation and subsequent claims run into millions of dollars besides being time consuming (Ukpabio *et al*., 2000; NOAA, 2006). When oil is discharged into the marine environment, it undergoes weathering (physical and chemical reactions which include evaporation, photochemical and biochemical degradation); and may result in the formation of residual tars or tar balls (Henry *et al*., 1993). These dense sticky, black spheres may linger in the environment, washing up on shorelines long after a spill (Urdal *et al*., 1986; Volkmann *et al*., 1983). Chronic beach oiling is potentially degrading to the ecological and socioeconomic interest of our coastal environment. Their presence indicates that oil had been spilled or released during the recent past resulting in negative impact on marine resources (Henry *et al*., 1993), like commercial and sport fishing, recreational uses such as sun bathing and surf fishing. Oil pollution is a particular threat to immature marine animals i.e., eggs, larvae and juveniles.

The occurrence of tar balls on beaches is not new. In Ibeno, the study area, indigenes interviewed mentioned that at a certain time of the year, when many tar balls are left stranded on the shoreline by the ocean current, fishermen pick them and use to

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caulk their boats. Natural sources of oil such as riverine and ocean seeps have been releasing petroleum into the marine environment for millions of years, this fraction is not enough to be transported and deposited on coastal shorelines. It is the anthropogenic activities such as petroleum transportation, onshore and offshore exploration and production that are the major culprits, (Henry *et al*., 1993).

Tracing the sources of these petroleum hydrocarbons in the marine environments long after contamination had not been very easy especially as the oil could be so altered making correlation effort difficult. This poses a challenge to Geochemists and Analytical Chemists (Wang, 2003). However there are geochemical methodologies for identifying petroleum contamination and determining their sources long after impact that provides scientifically proven, court admissible evidence in environmental legal disputes (Mckirdy and Chivas, 1992). Tars are ideally suitable for establishing sources of hydrocarbons in the marine settings, months even years after the contamination in marine environments.

Developing an oil fingerprint, uniquely identifying oil and providing forensic evidence in oil spill cases to prove or disprove a vessel as the source of a spill has been the subject of scientific study for many years. Several studies have been carried out on crude oil and refined products in an attempt to justify this. For complex hydrocarbon mixtures or extensively weathered and degraded oil residue, there is no single technique which can unambiguously identify the source or sources of unknown spills and quantitatively allocate hydrocarbons to their respective sources (Wang, 2003, Olajire, 2006). A successful study that can trace the origin of spilled oil long after the spill has occurred and provide a forensic evidence to prove or disprove a culprit would go a long way to settle legal disputes between the host communities and the oil producing companies.

MATERIALS AND METHODS

Tar balls were collected from Ibeno beach and stored frozen at – 4^0C until they were ready for laboratory analysis. Five sample locations were chosen; based on the beach accessibility, human activities and tidal time table. The sample sites chosen based on the above qualification are given in Table 1.

Table 1. Sample Sites

S.No.	Sites Code no.	Sample sites	Geo locations
1	SS01	Okposo 1	04^0 32'36.5"N 008^0 15' 5.6"E
2	SS02	Itak Idim	04^0 32' 37.4"N 008^0 11' 59.2 E
3	SS03	Nnekpe New Barrack (Ine Atia)	04^0 32' 43.4"N 008^0 09' 27.7"E
4	SS04	Itak Ifa	04^0 32' 42.8"N 008^0 06'09.1"E
5	SS05	Mkpanak	04^0 32' 43.8"N 008^0 01' 22.8"E

Tar balls were collected systematically on each station. The tar balls collected were wrapped separately with aluminium foils and stored in a cooler with ice packs. Each tar ball was logged with a unique identification number e.g. SS0101-SS0105 were for samples from site SS01 which represented samples that were collected from Okposo1; five tar balls samples from each site were randomly picked for analyses. A total of 25 tar balls were selected for chemical analysis.

Sample Preparation

In preparation for the analyses the frozen tar balls were allowed to thaw for about 24 hours, after which each sample was split open to expose the fresher oil beneath the exterior. 4.0g of each of the tar ball samples was first dissolved in dichloromethane (DCM) to separate the petroleum residue from other impurities like sand, particulates etc. Although DCM is a poor solvent for dissolving wax hydrocarbon, it was used in this context as a polar solvent to open up the organic pore structure in the tar balls by disrupting the non- covalent interaction within the host kerogene matrix and to allow the release of the bulk polar component according to Huang *et al.* (2003). The DCM solution was filtered through glass wool to remove the impurities and then concentrated by solvent reduction.

The concentrate was separated into asphaltenes and maltenes by n-alkane precipitation. The maltenes were then separated into saturates and aromatics by liquid column chromatography according to Vasquez and Mansoori (2000); Aske (2002); Auflem (2002). In this method, 2.5g of the extract was added to 40ml of hexane; the solution was agitated and left for about 24 hours to allow the asphaltenes residuum to precipitate according to Ukpabio, (1992); Henry *et al.* (1993); Ecker, (2001); Thomas *et al.* (2004). The insoluble asphaltenes (the precipitate) was removed by centrifuging and decanting the soluble portion (the maltenes). The precipitated asphaltenes were recovered by filtration through Whatman Ashless 12.5cm filter papers. The filter paper was washed several times with *n*-hexane until the hexane washing was clear. The asphaltenes on the filter paper were then washed with dichloromethane until the washing was clear. The hexane and dichloromethane solutions were evaporated and weighed before fractionating into saturates, aromatics and resins filtrates

1g of the recovered asphaltene was dissolved in approximately 5ml of dichloromethane (DCM) and introduced into the column (46 cm long and 3 cm in diameter). A portion of the saturates, (hexane soluble) was injected into a Hewlett- Packard capillary gas chromatograph (model 6890-N) with dual flame ionization detectors (FID). The analyte was separated and detected by a gas chromatograph flame ionization detector (GC/FID). Sample responses were then compared to the calibration curve to derive the concentration of each analyte in each sample. Prior to the analysis of tar, a five-point calibration curve was establish for each analyte to determine the corresponding sensitivity and confirm the linear range of the GC/FID system. A calibration curve was established by analyzing each of the calibration standards and fitting the data to a straight line using the least square technique. For each analyte, a response factor (RF) was determined for each calibration level.

Fresh crude oil from Nigerian oilfields was analyzed. This acted as a reference point. This comparison is expected to determine the possible source of the tar balls. Six samples of unaltered crude oils samples were analyzed. Four were of a terrigeneous origin (onshore), while two were of marine origin (offshore). These were used as reference points.

Fig. 1. Tar ball sample on Ibeno beach

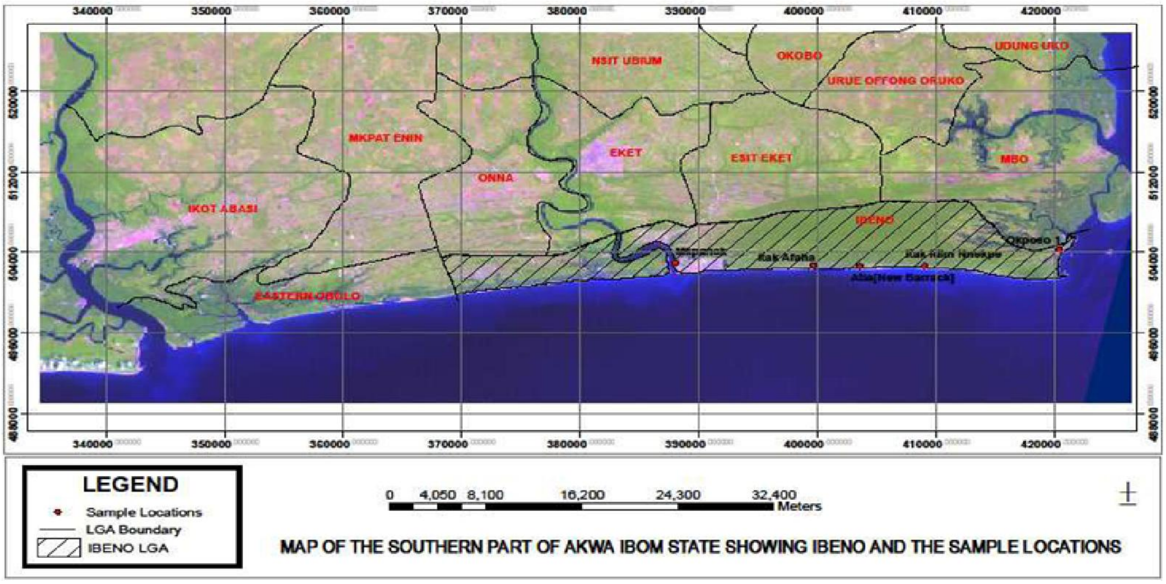

Fig. 2. Map of the Southern part of Akwa Ibom State showing Ibeno and the Sample Locations

Table 2. Pristane to Phytane ratios of the tar balls from Ibeno beach

S.No.	Sample Identity	Pristane	Phytane	nC_{17}	nC_{18}	Pr/Ph	nC_{17}/Pr	nC_{18}/Ph
1	101	BDL	BDL	BDL	BDL	BDL	BDL	BDL
2	102	BDL	BDL	BDL	BDL	BDL	BDL	BDL
3	103	BDL	BDL	0.81±3.23	0.87±5.96	BDL	BDL	BDL
4	104	8.90±0.01	8.50±0.003	BDL	BDL	1.10	BDL	BDL
5	105	BDL	0.78±2.66	BDL	0.26±6.58	BDL	BDL	0.30
6	201	8.80±0.01	8.50±0.003	BDL	BDL	1.00	BDL	BDL
7	202	11.75±0.26	12.25±0.50	BDL	12.70±0.001	1.00	BDL	1.00
8	203	BDL	BDL	BDL	BDL	BDL	BDL	BDL
9	204	8.90±0.01	8.90 ±0.001	BDL	9.98±0.34	1.00	BDL	1.10
10	205	BDL	BDL	BDL	BDL	BDL	BDL	BDL
11	301	BDL	BDL	BDL	BDL	BDL	BDL	BDL
12	302	BDL	BDL	BDL	BDL	BDL	BDL	BDL
13	303	BDL	BDL	BDL	BDL	BDL	BDL	BDL
14	304	BDL	0.60 ±2.78	BDL	BDL	BDL	BDL	BDL
15	305	BDL	BDL	BDL	BDL	BDL	BDL	BDL
16	401	13.00±0.59	14.00±1.14	BDL	BDL	0.60	BDL	0.04
17	402	12.00±0.32	23.00±8.52	BDL	BDL	0.50	BDL	0.02
18	403	25.00±10.35	36.00±30.89	20.50±4.94	34.00±18.67	0.70	0.80	0.90
19	404	12.50±0.44	14.80±1.52	29.00±15.67	27.00±8.37	0.80	2.3	1.80
20	405	BDL	BDL	BDL	BDL	BDL	BDL	BDL
21	501	BDL	BDL	BDL	BDL	BDL	BDL	BDL
22	502	BDL	BDL	BDL	BDL	BDL	BDL	BDL
23	503	BDL	BDL	BDL	BDL	BDL	BDL	BDL
24	504	131.00±615.90	92.00±288.63	220.00±184433.13	236.00±2075.20	1.40	1.70	2.60
25	505	BDL	BDL	BDL	BDL	BDL	BDL	BDL

BDL = Below Detectable Level

Vanadium and Nickel were analyzed with Atomic Absorption Spectrophotometer (AAS) while Vanadyl (VO^{2+}) and Nickel (Ni^{2+}) porphyrins were analyzed using UV spectrophotometer (Spectronic 21D) for source correlation.

RESULTS

A summary of the results of the pristane, phytane and other saturates and their ratios in the tar balls picked from Ibeno beach are given in Table 2. A summary of the results of the pristane, phytane and other saturates and their ratios in the unaltered crude oil from selected oil wells in the Niger Delta basin of Nigeria are presented in Table 3 The chromatograms of the tar balls picked from Ibeno beachare presented in Appendix 1, the Chromatogram of Crude Oil from Selected Nigerian oil fields in Niger Delta basinare presented in Appendix 2,: The Chromatogram of Crude Oil from other Nigerian oil fields are shown in Appendix 3, while Appendix 4 showed the Chromatogram of Foreign Crude Oils.

crude oil samples from Mgbede -20 oil impacted site in the Niger Delta basin of Nigeria, came up with an average pristane/phytane ratio of 0.39 (<<1.0); which does not correlate with the pristane/ phytane ratios of the samples mentioned above. Looking at the unaltered crude oil taken from some selected oil wells in the Niger Delta basin of Nigeria, a predominance of pristane over phytane was observed; their pristane /phytane ratio was very high (>>1.0) (See Table 2, appendix 2 and 3).

Comparing crude oils from other fields still in the Niger Delta basin in Nigeria, like Imo river, Egbema, Bonga etc, a predominance of pristine over phytane was observed) (see Appendix 3). Therefore these tar balls samples may be residues of crude oil from Niger Delta basin of Nigeria. But in sample nos. SS 202, and SS 402 a predominance of phytane over pristane was observed (pristane/ phytane ratio of less than unity <1.0) The source is suspected to be from a reducing environment and foreign to Niger Delta oils (see Appendix 3).

Table 3. Pristane to Phytane ratios of the unaltered oil from Niger Delta oil fields

S.No.	Sample Identity	Pristane	Phytane	nC_{17}	nC_{18}	Pr/Ph	nC_{17}/Pristane	nC_{18}/Phytane
1	Idoho Bravo	1320.50	1270.30	1280.80	1260.20	1.04	0.97	0.99
2	CAWC1 Pumpline	4215.41	2281.75	2885.36	2792.36	1.80	0.68	1.22
3	Esc 25	2498.88	1575.12	4428.82	3324.45	1.60	1.80	2.10
4	Soku FS	4027.28	1923.53	4421.20	4045.71	2.10	1.10	2.30
5	Utorugu 55	4159.21	1932.56	5678.29	4989.54	2.20	1.40	2.60
6	Umuechem pumpline	4729.62	2836.21	3375.91	4238.91	1.70	0.71	1.50

DISCUSSION

Pristane/Phytane ratio

Pristane/phytane ratio (pr/ph) is a parameter used to determine the possible depositional environment of petroleum. The ratio of the isoprenoids, pristane and phytane is associated with the nature of the redox conditions prevailing in the depositional environment. A pristane/phytane (pr/ph) ratio of less than unity (<1) is an indication that the crude oil originates from an anoxic (reducing) environment, because according to Tissot and Welte (1984), Huang *et al.* (2003), very low values of pristane /phytane ratios (<<1.0) suggest that the crude oil samples were deposited in a less oxic (reducing) environment. Pristane is a product of decarboxylation and as such pristane/phytane ratio tend to be high in a more oxidizing environment such as peat swamps and lower in strongly reducing environment (Powell and Mckirdy, 1973; Huang *et al*., 2003).

The tar balls picked from Ibeno Beach were so altered that most of the isoprenoids, pristane and phytane were completely biodegraded. However, in some of the tar balls that pristane and phytane still remained, a predominance of pristane over phytane was observed; an indication that these tar balls might have originated from a less reducing environment because according to Tissot and Welte (1984), there is a predominance of pristane over phytane in a less reducing environment due to decarboxylation of phytol or phytanic acid. The pristane/ phytane ratios of tar balls Nos. SS104, SS403, SS404, SS504 were found to be >1.0. This suggests that, the geologic origin of these samples may be a less reducing (oxic) environment (see Appendix 1and 2). Osuji *et al*. (2006), working on spilled

Akinlua *et al.* (2007) classified Niger Delta Basin of Nigeria as a less reducing transitional environment. Therefore tar balls nos. SS104, SS403, SS404, SS504 can be traced to oil fields in Niger Delta basin of Nigeria. Looking at the foreign oils, the chromatogram of one of the crude oil sample from Gabon shows a predominance of phytane over pristane. Comparing the pristane and phytane peaks in Appendix 3 and 4, it is suspected that tar balls nos. SS202 and 402 may be residue of crude oil from Gabon oil field (see Appendices 3 and 4). Most of the tar balls were so weathered that almost all the n-alkanes had disappeared. This made correlation with pristane/phytane ratio very difficult. However, there are other parameters that are degradation resistant that could be used in conjunction with pr/ph ratio to determine the source of these tar balls. These are trace metal ratios and porphyrins ratios.

Conclusion

Pristane/phytane ratio (pr/ph) is a parameter used to determine the possible depositional environment of petroleum, but where weathering sets in it makes correlation difficult because most of the isoprenoids are destroyed especially with extensive weathering; therefore Pr/ph ratio alone cannot be conveniently used to trace tar balls back to their origin.

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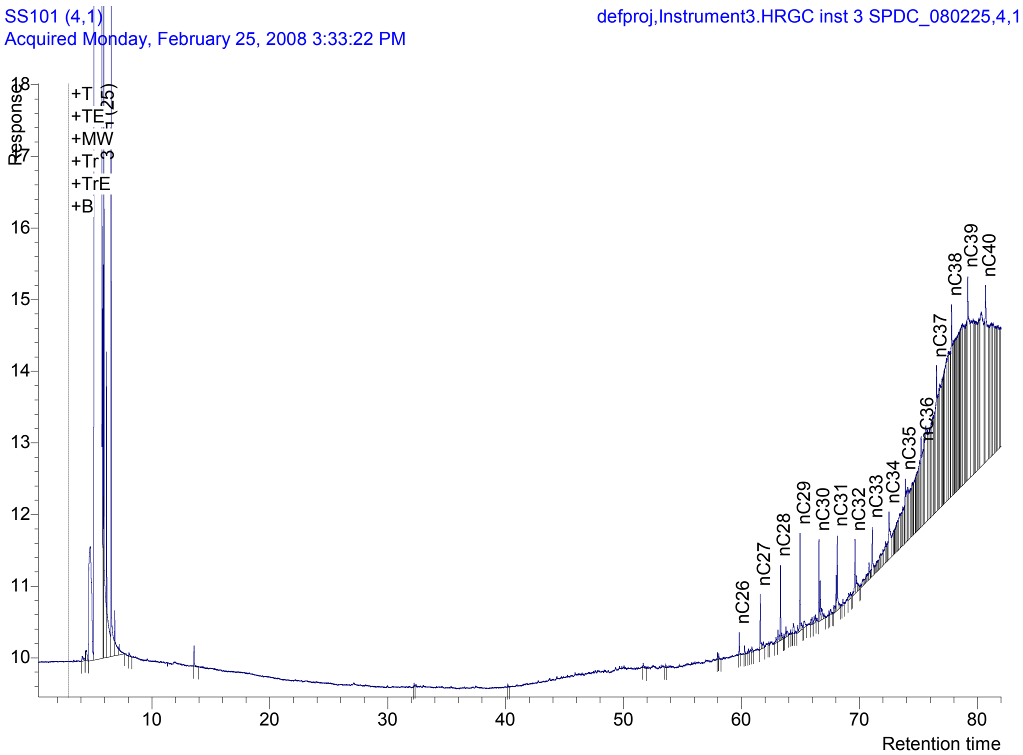
Appendix

Appendix 1: The Chromatograms of tar balls picked from Ibeno beach



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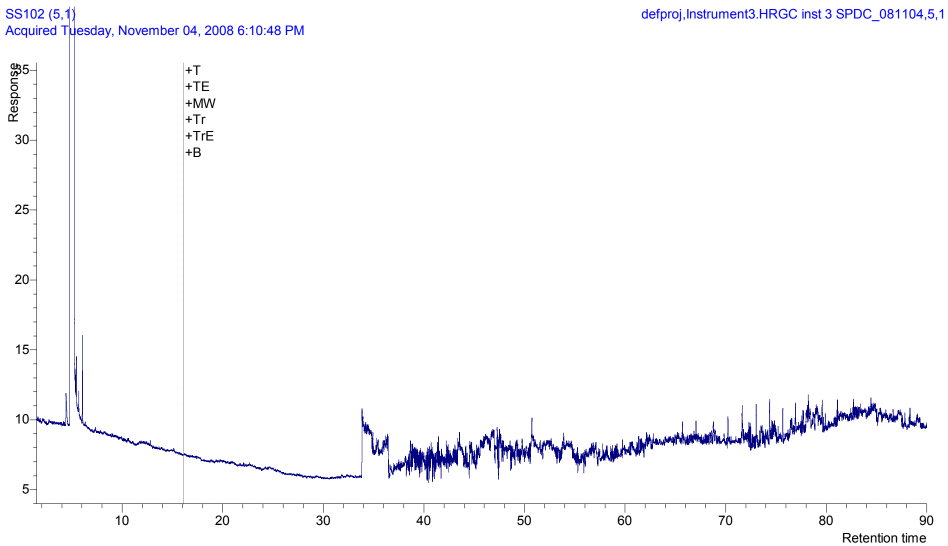

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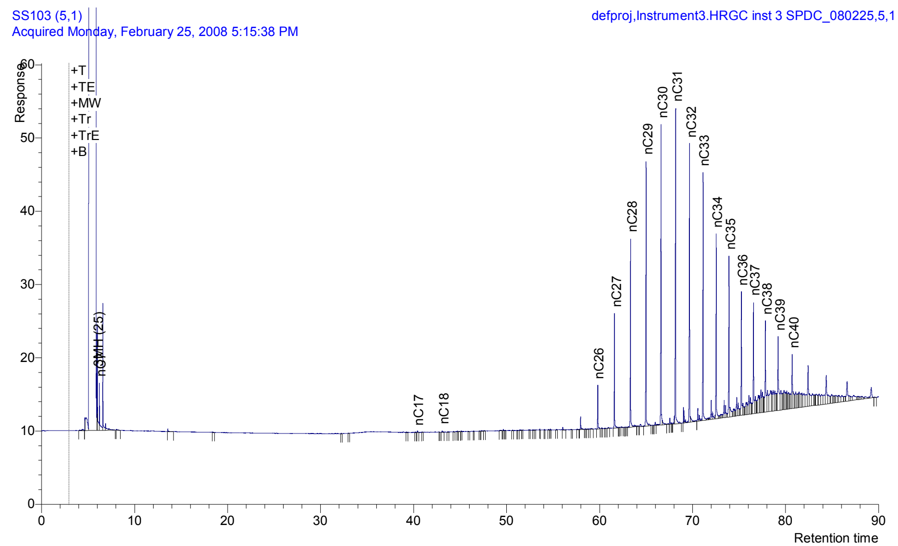

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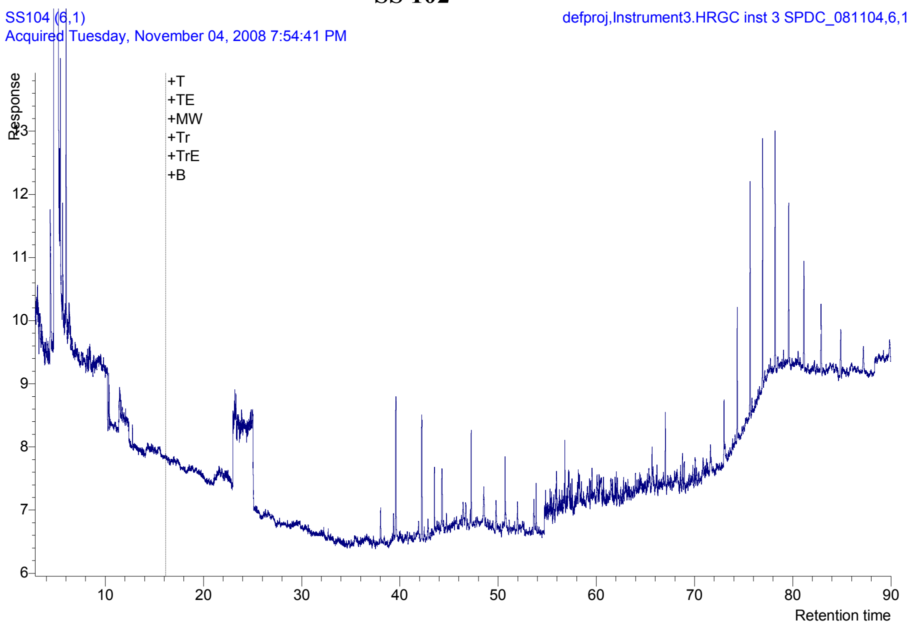

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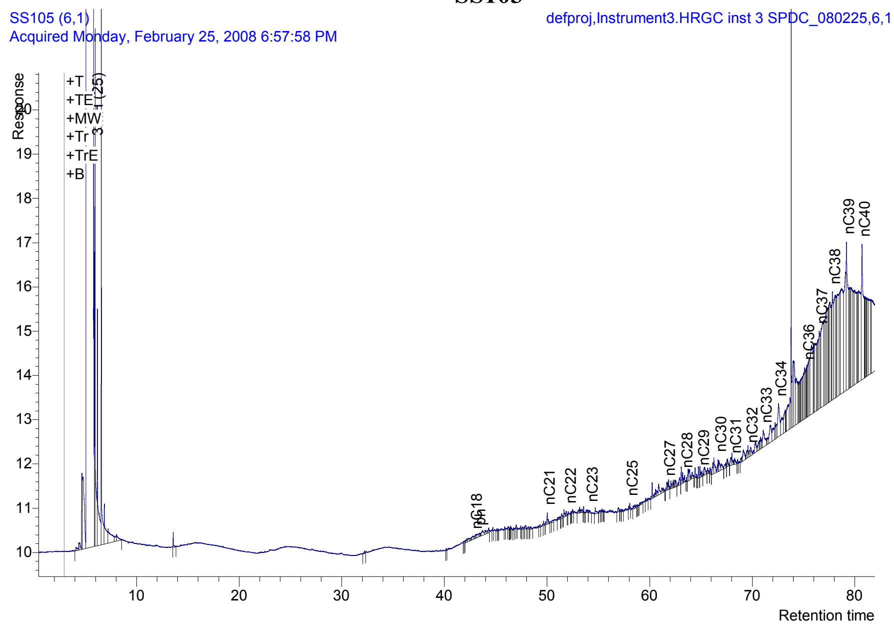

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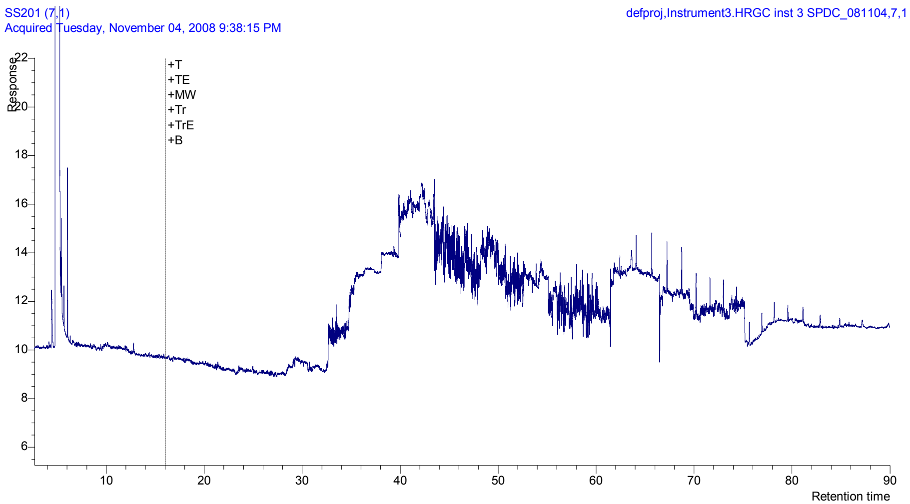

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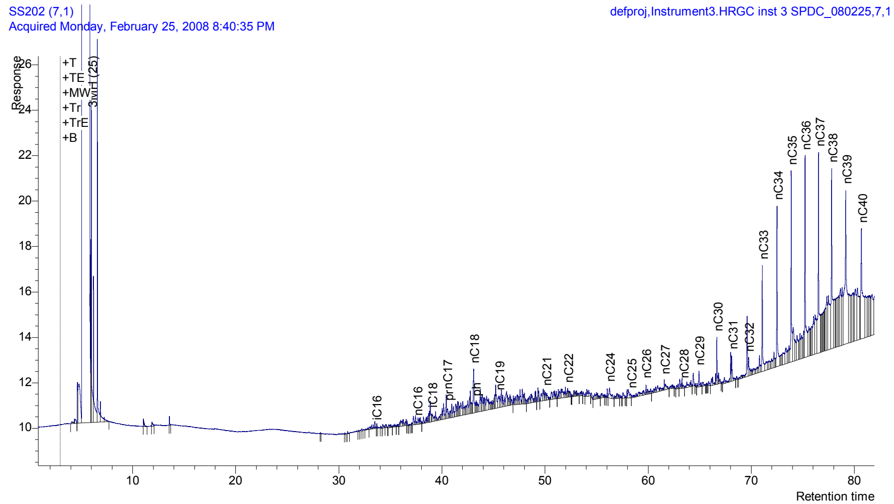

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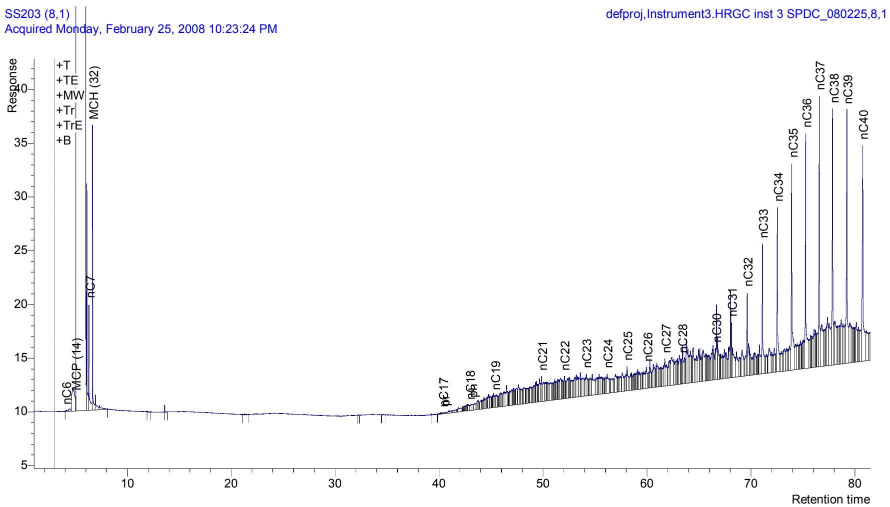

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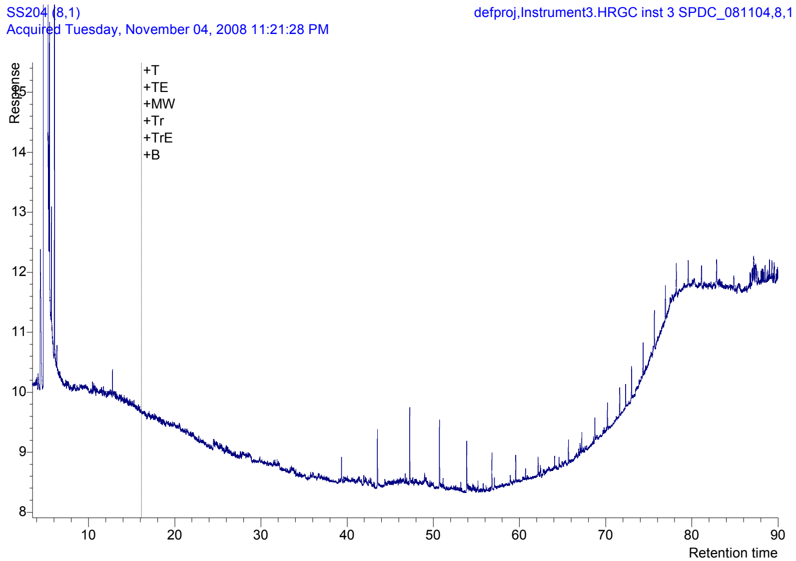

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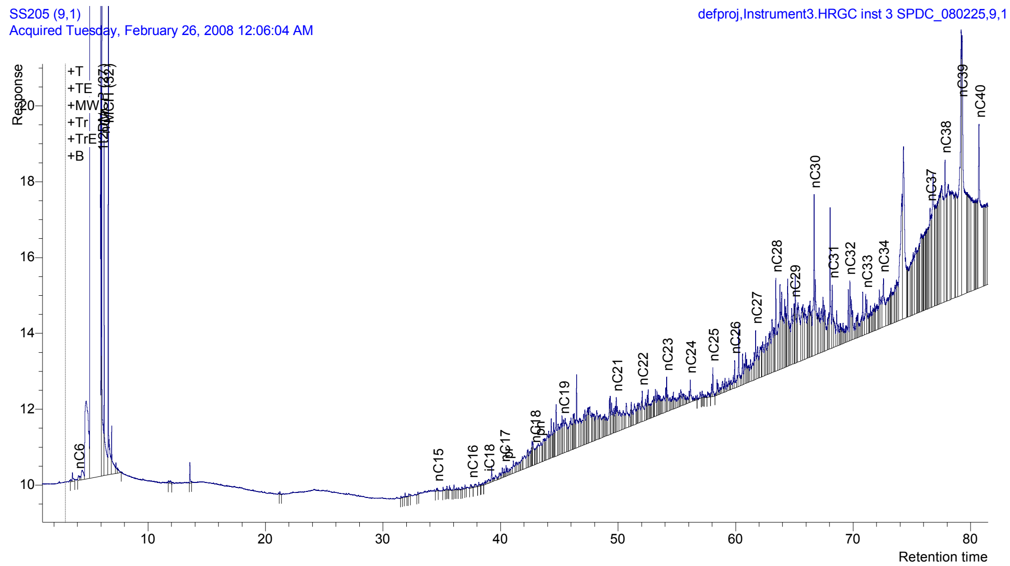

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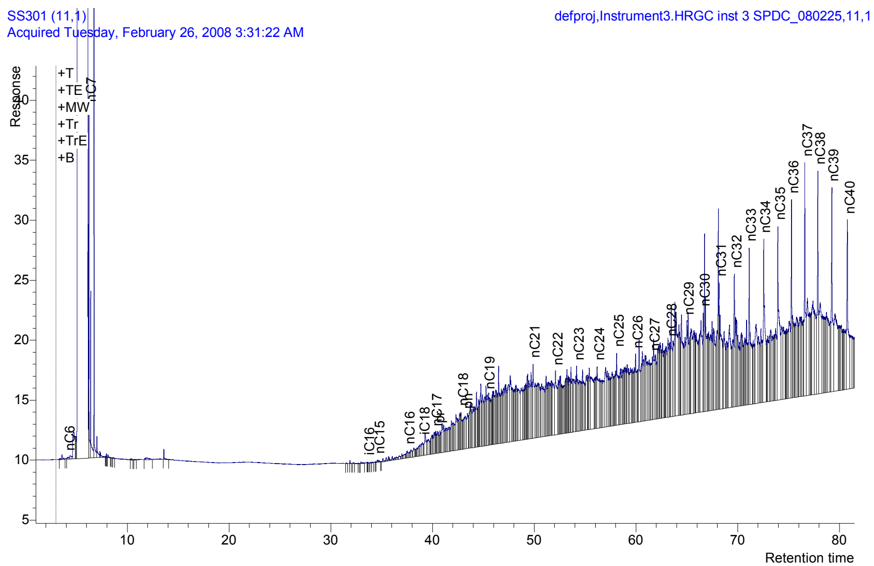

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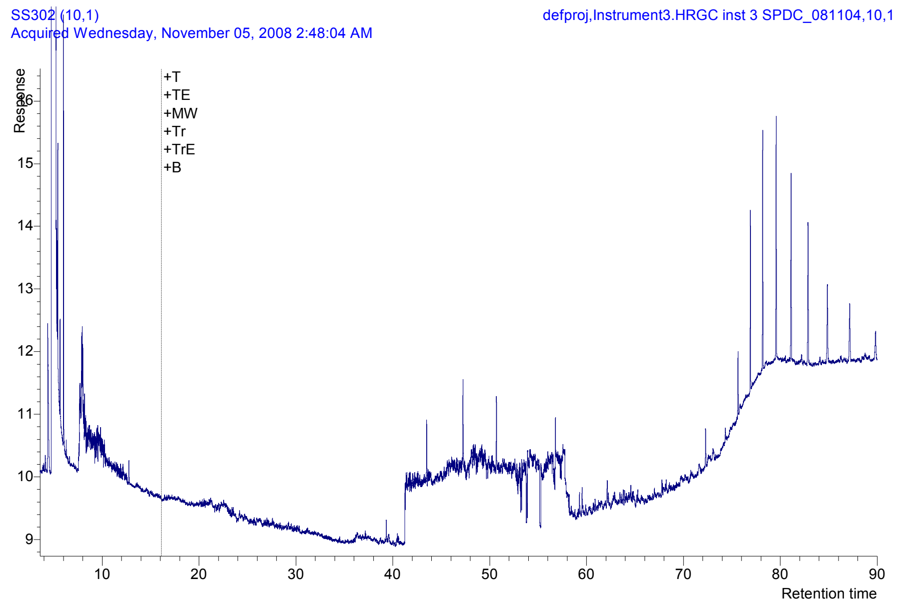

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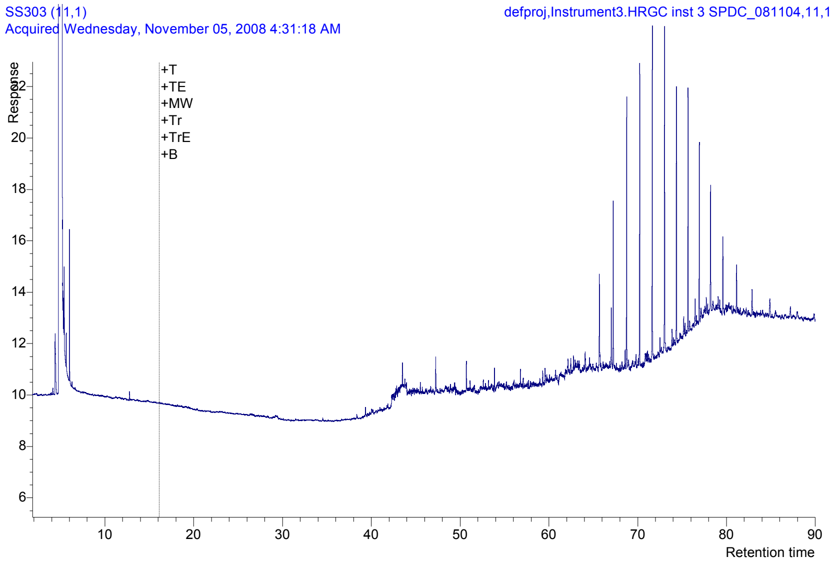

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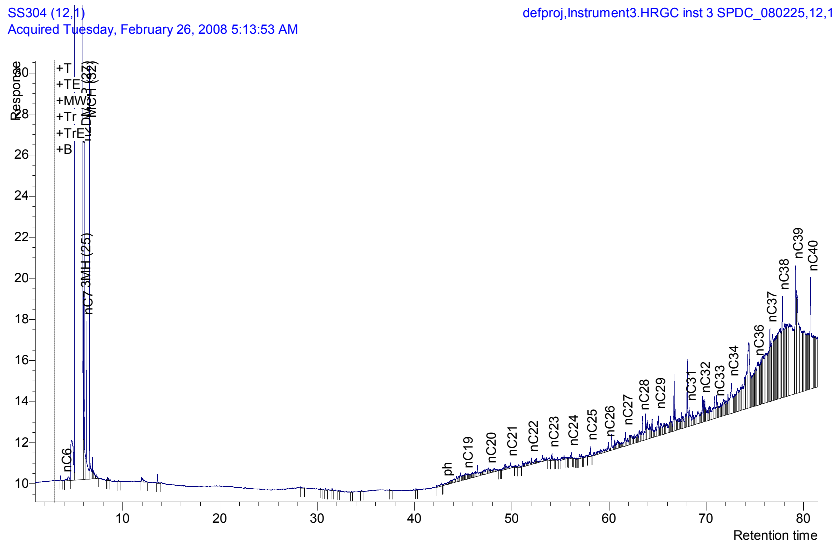

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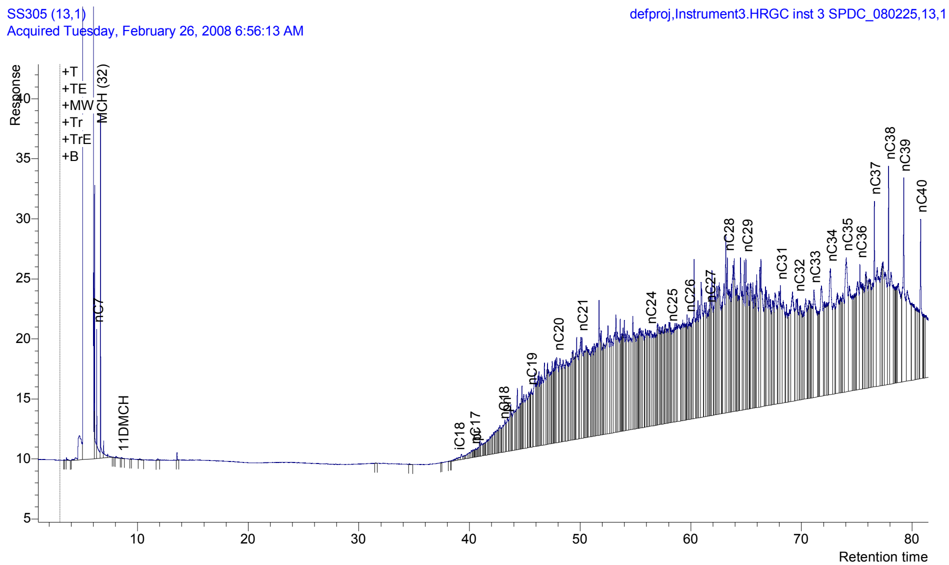

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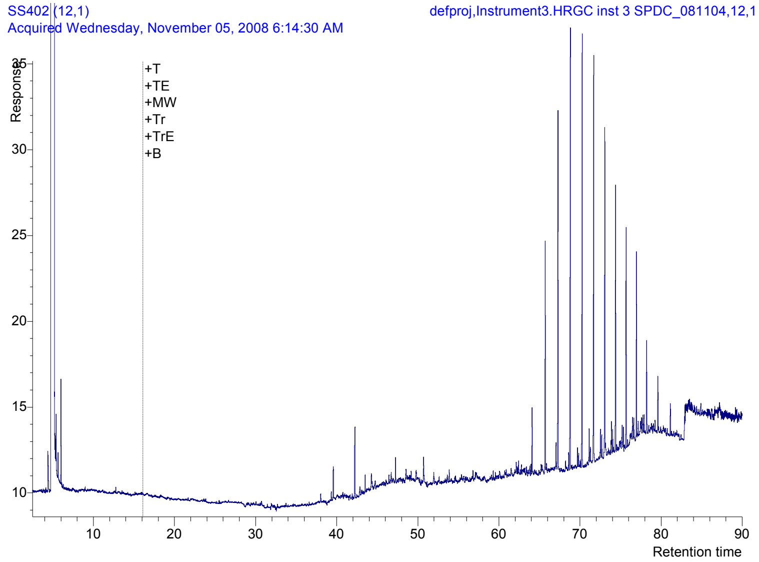

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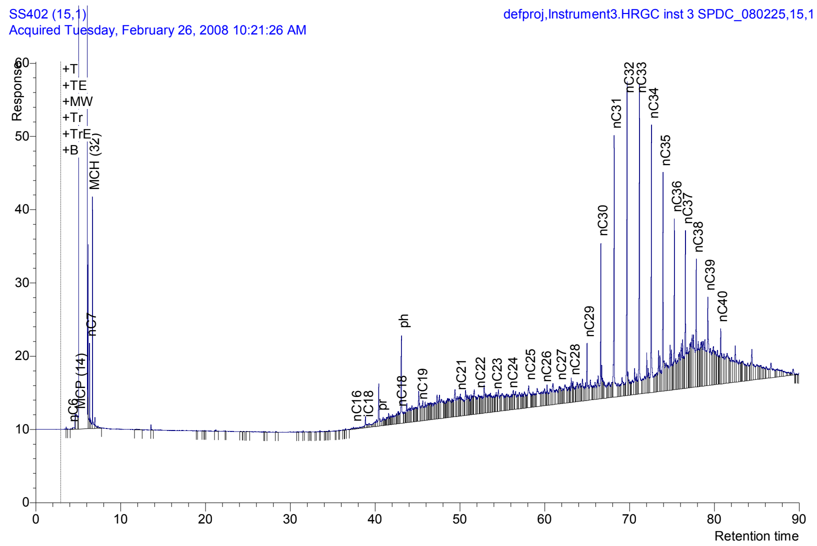

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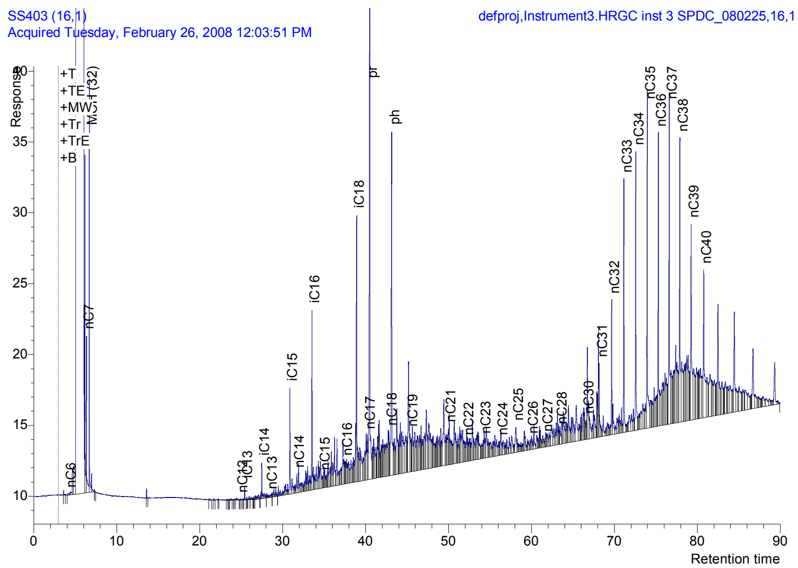

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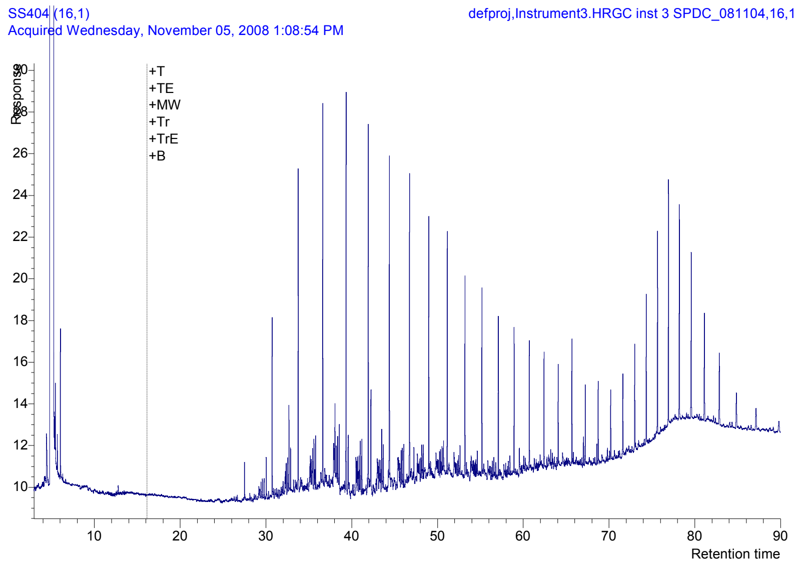

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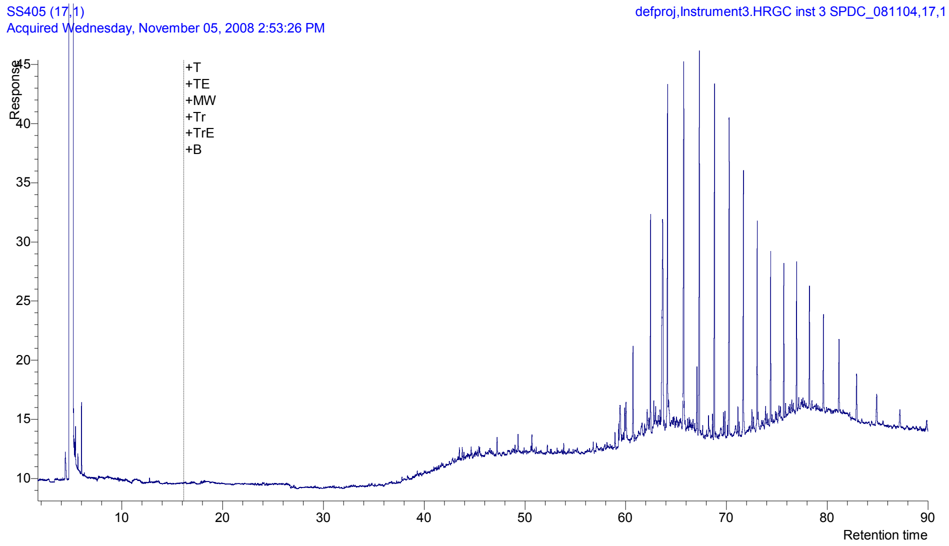

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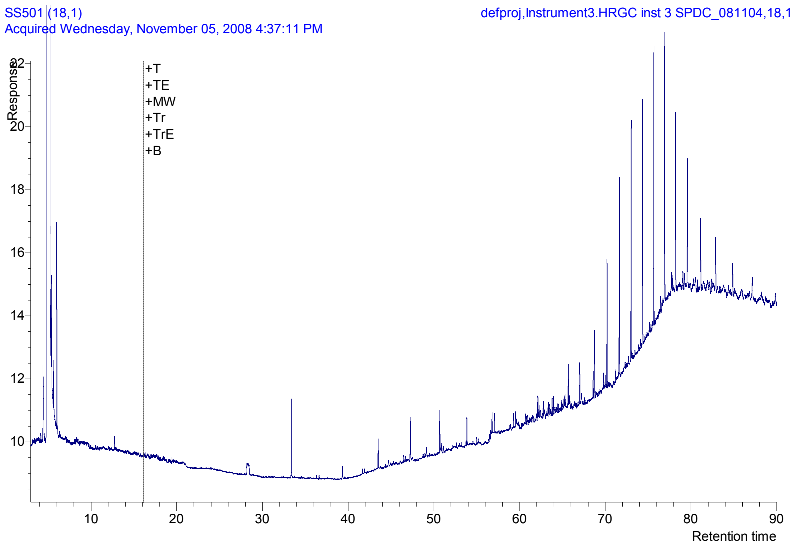

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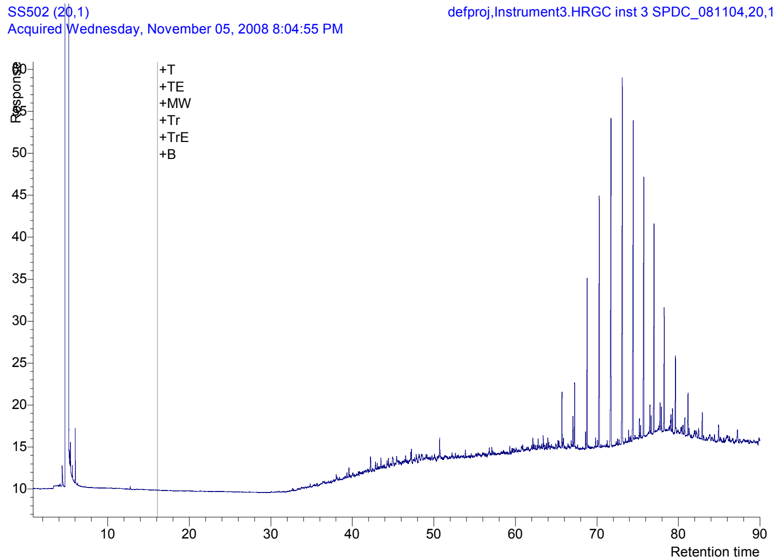

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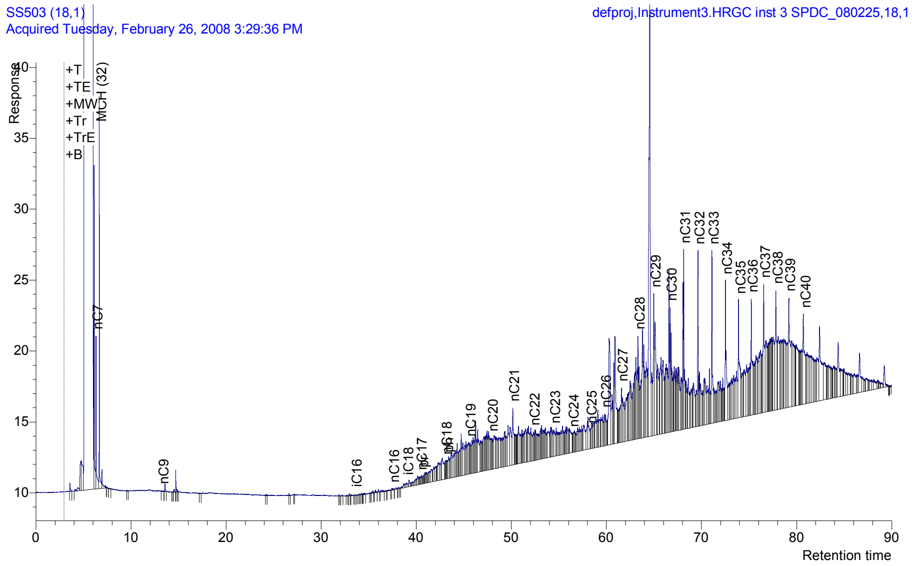

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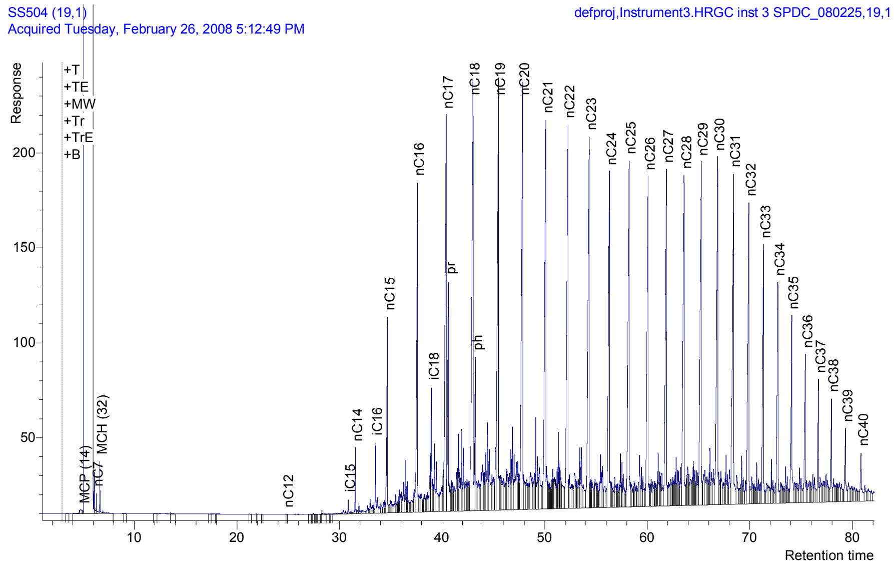

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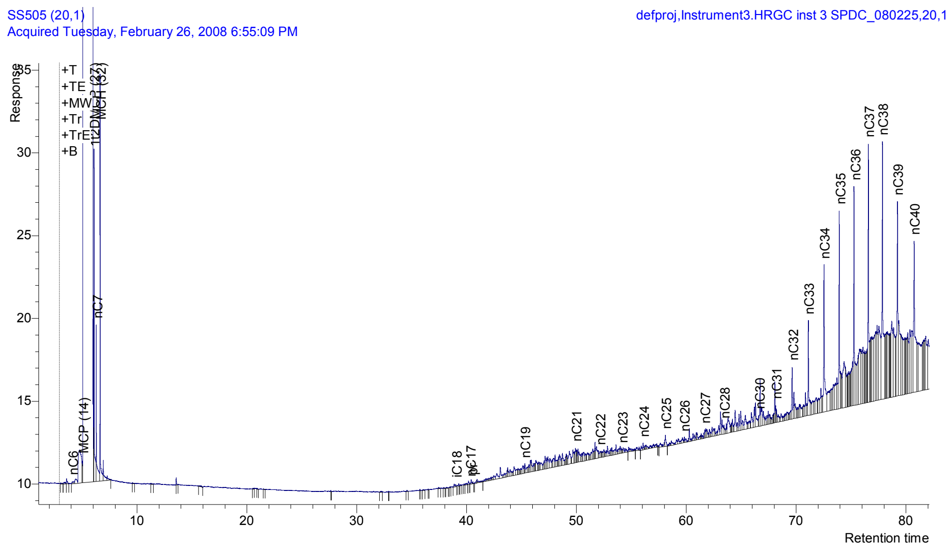
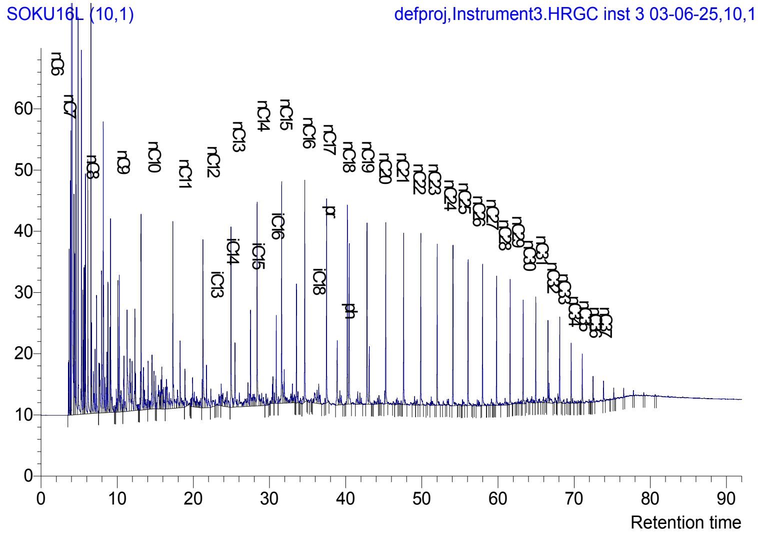
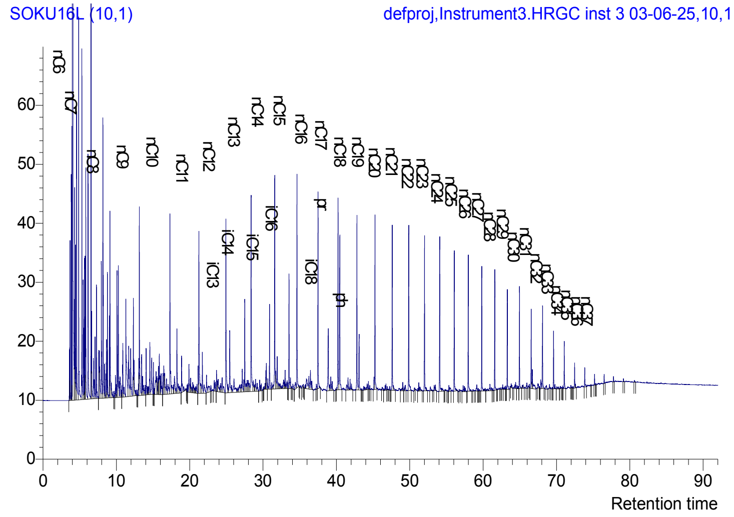


SS505

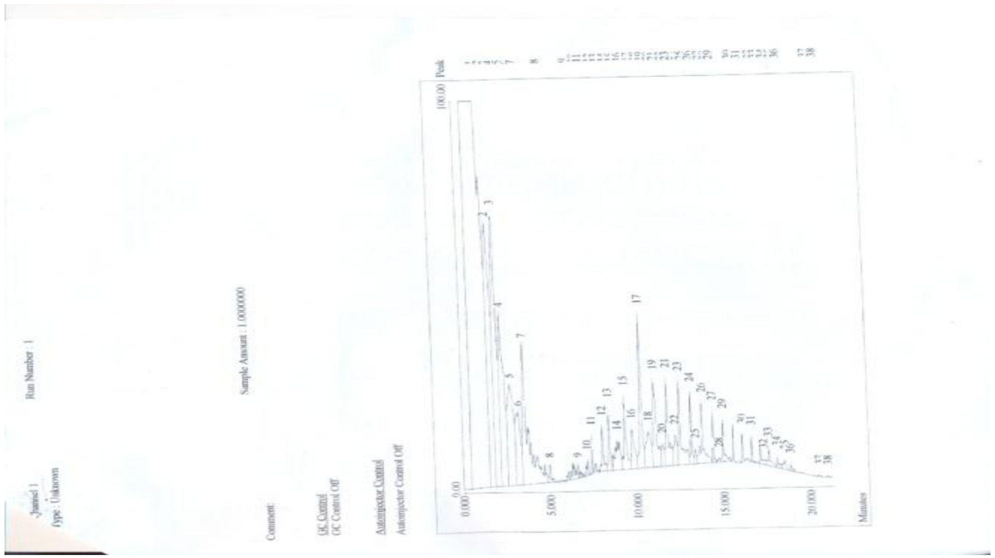
Appendix 2. The Chromatogram of Crude Oil from Selected Nigerian oil fields in Niger Delta basin



Soku FS



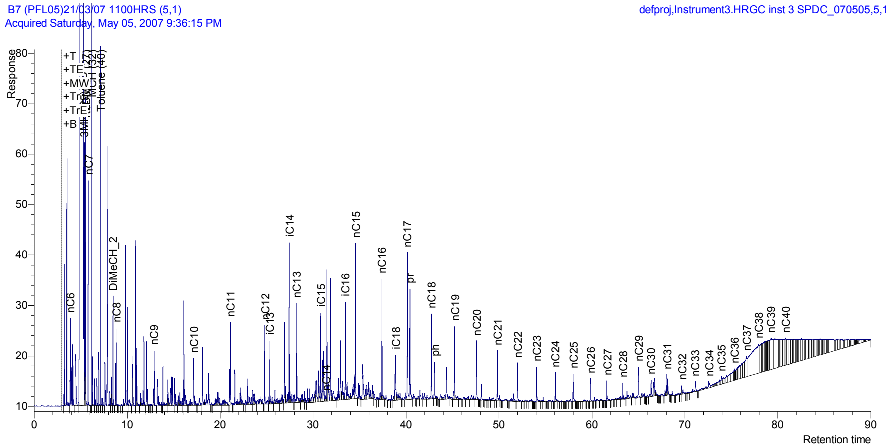
Umuechem Pumpline



Idoho Bravo

Appendix 3. The Chromatogram of Crude Oil from other Nigerian oil fields

Bonga Crude Oil



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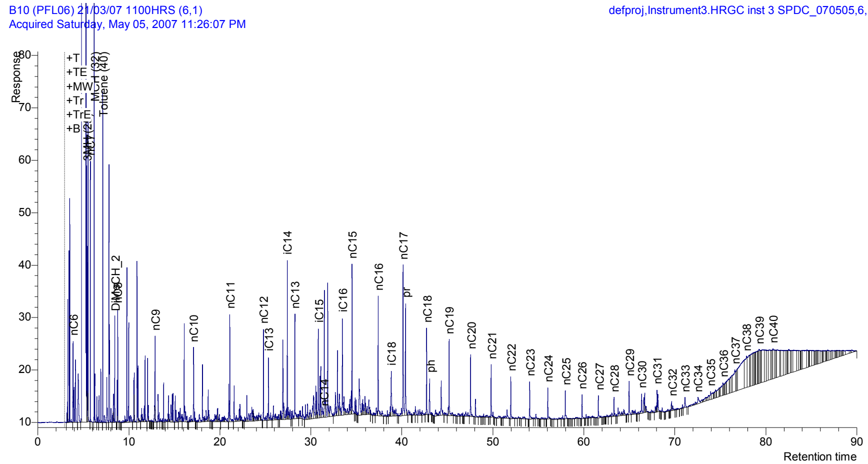
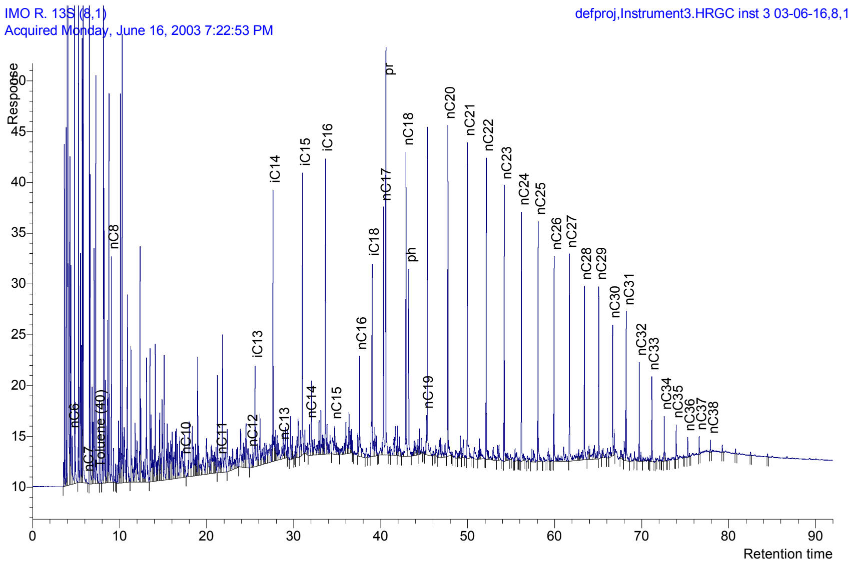
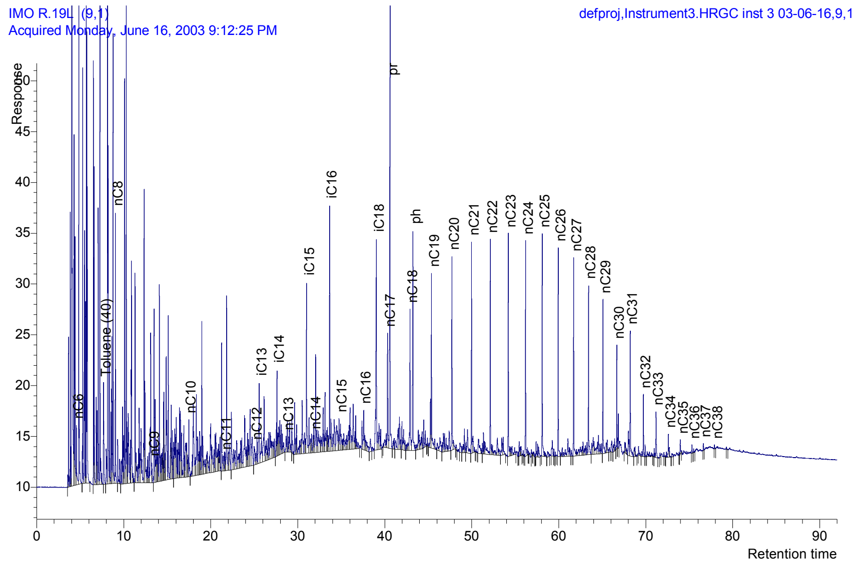


B10 (PFL06) 21/03/2007 1100HRS

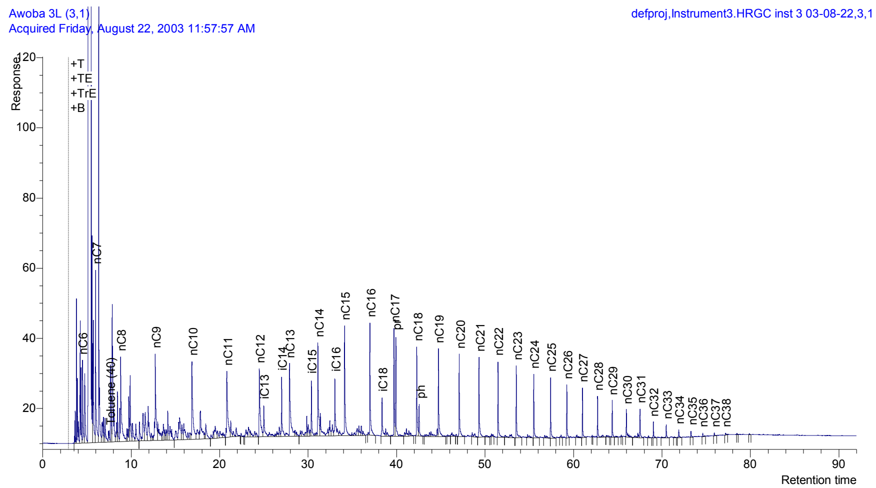


Imo River 13S

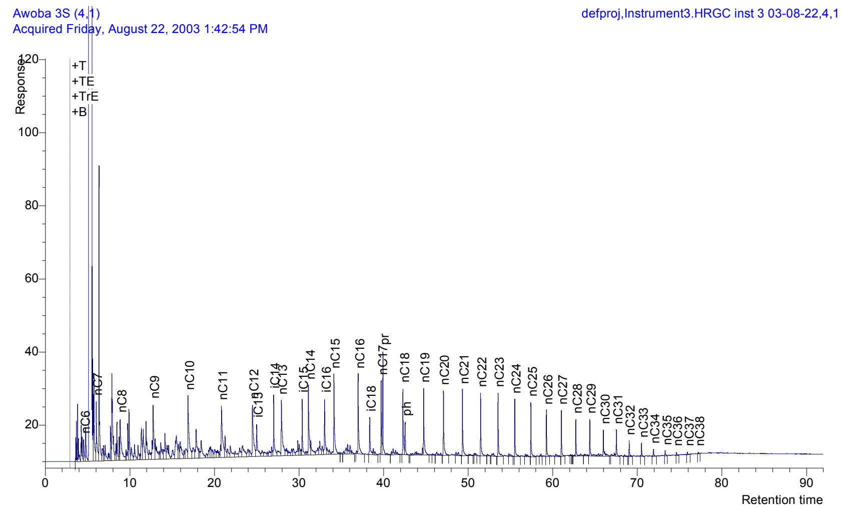


Imo River 19l

Awoba field

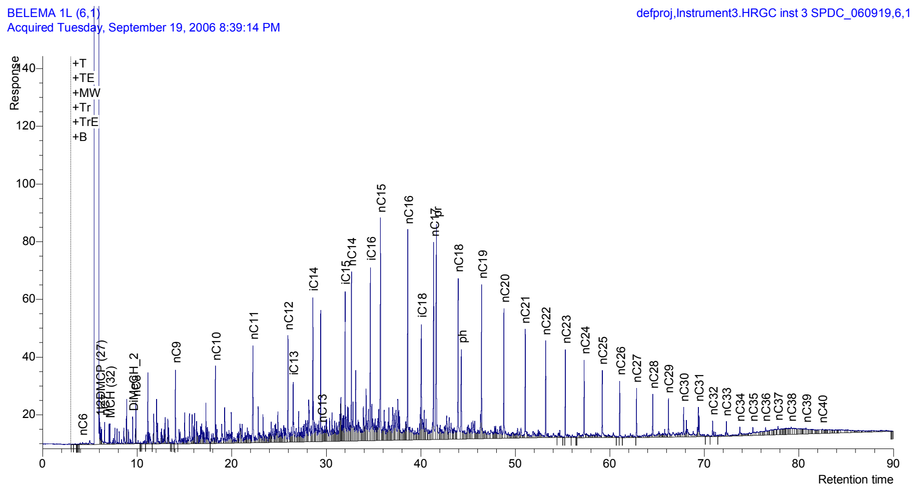


Awoba 3S

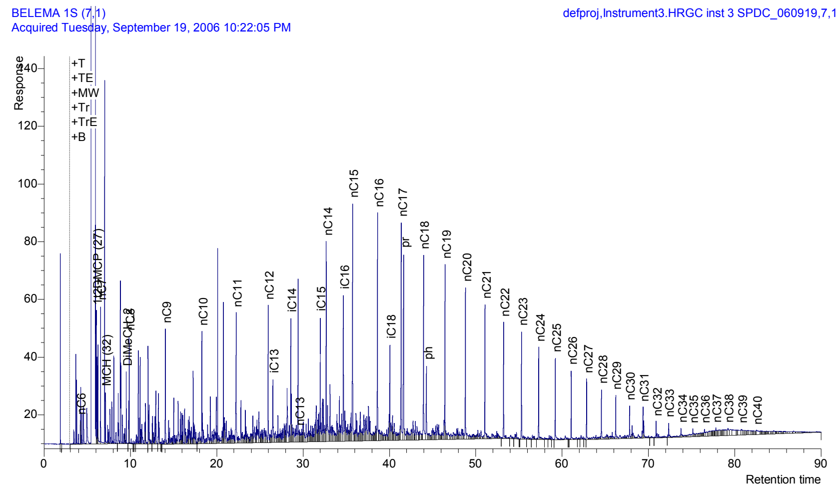


Awoba 3L

Belema field

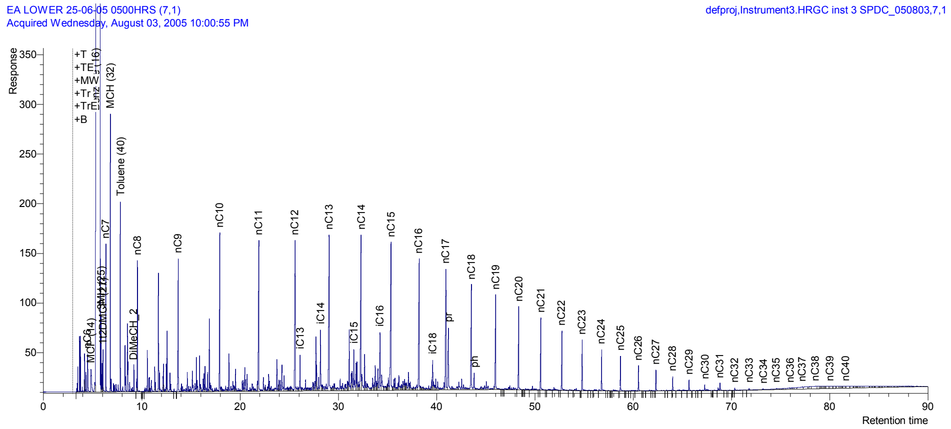


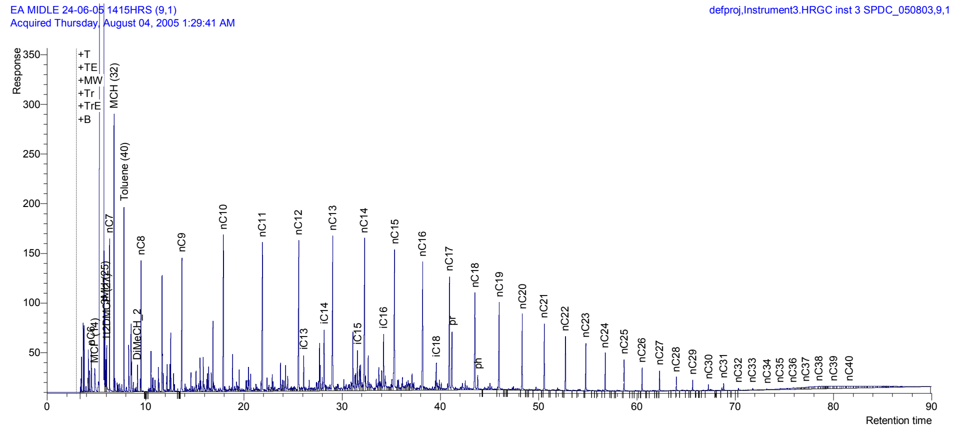
Belema 1S



Belema 1l

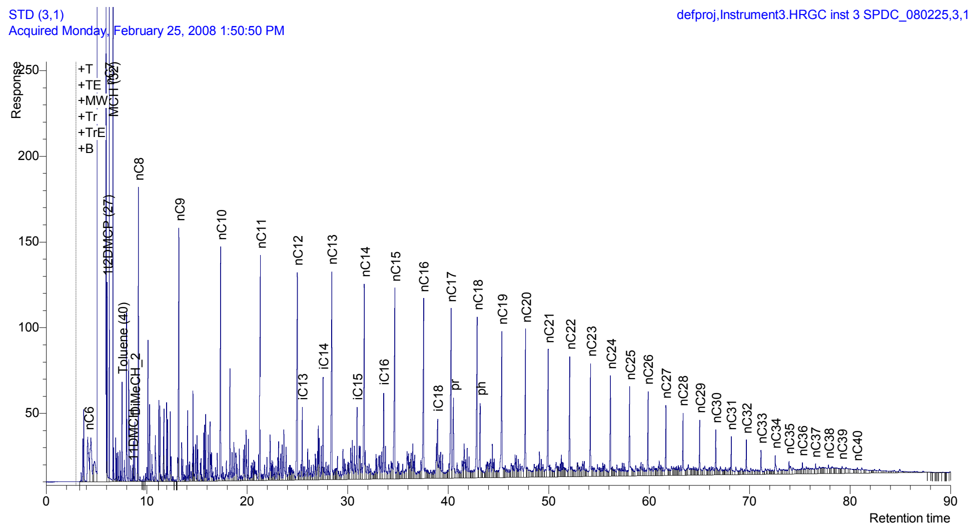
EA SAMPLES

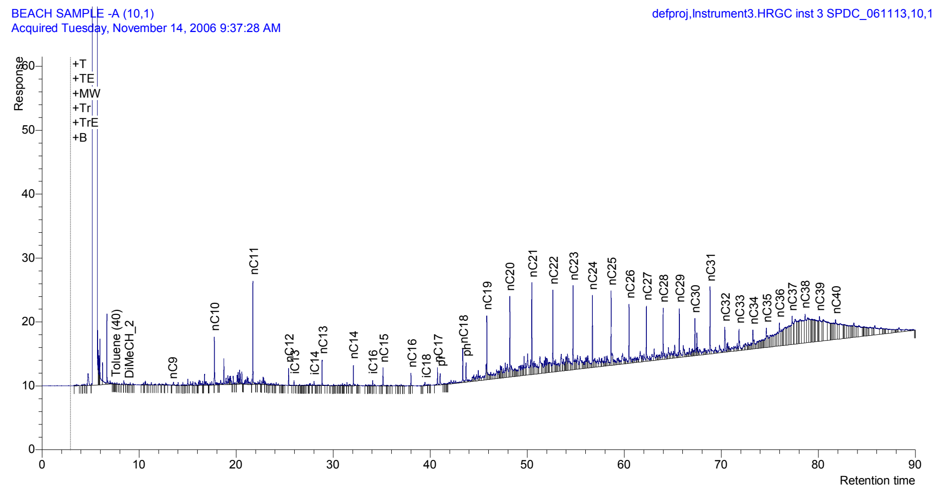




EA MIDLE 24-06-05 1415HRS **EA LOWER 25-06-05 0500HRS**

Appendix 4: The Chromatogram of Foreign Crude Oils





North Sea Oil (Standard Oil) **Gabon Oil - Beach Sample –A**

Source: SPDC

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