



## SEPARATION AND INFRARED (FT-IR) CHARACTERIZATION OF AROMATIC HYDROCARBONS FROM HIGH BOILING FRACTIONS (>200 °C) OF NIGERIA CRUDE OIL (USING TRICHLOROETHYLENE AS THE ELUANT)

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**Abstract:** *The separation and characterization of aromatic hydrocarbons from high boiling fractions (>200°C) of Nigeria crude oil is reported. The crude oil was distilled under atmospheric pressure in a glass system, with the help of a paraffin bath. The bottom fraction of the crude oil was fractionated using solvent deasphalting (in which case n-heptane was used followed by filtration), and elution - adsorption chromatography. The saturates were eluted with n-heptane by liquid chromatography on silica gel while the aromatics were eluted with trichlorethylene. The I.R. analysis of the aromatic extracts showed absorption peaks at 3082.94 cm<sup>-1</sup>, 3037.06cm<sup>-1</sup>, 1584.82cm<sup>-1</sup>, 1557.09cm<sup>-1</sup>, 1497.43cm<sup>-1</sup>, 1247.97cm<sup>-1</sup>, 931.79cm<sup>-1</sup>, 907.36cm<sup>-1</sup>, 841 .53cm<sup>-1</sup>, 676.46cm<sup>-1</sup> and 629.49cm<sup>-1</sup> respectively. These absorption peaks are due to the presence of aromatics hydrocarbons.*

**Keywords:** Separation, Characterization, Infrared, Aromatic hydrocarbons, Nigeria crude oil, Trichloroethylene, Chromatography, High boiling fraction, Petroleum

### INTRODUCTION

The extraction and utilization of crude petroleum has an enormous impact on the quality of life experienced by most citizens of the industrialized world. Over the years, there have been many extensive studies directed towards the identifications and measurement of the general classes of compounds and individual components found in crude petroleum. These analyses are very important in the refining and utilization of petroleum and petroleum products, and was instrumental in the development of many widely used procedures in analytical chemistry<sup>1-4</sup>.

The understanding of the distribution of the aromatic hydrocarbons in crude oils (Nigeria crude oils), will go a long way in helping to solve some of the problems which the occurrence of aromatic hydrocarbons in crude oils have created to the oil industries and to the broad national economy. Some of these problems are coke formation, and the red oils produced in heavier fractions as encountered in crude oil processing<sup>4-7</sup>.

Also, aromatic hydrocarbons are of special value in many petroleum and petrochemical products, and produce endless list of the most versatile and important industrial organic chemicals, and is the starting point for many

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diverse products used in homes and industries<sup>8-11</sup>. Therefore as a contribution to a better understanding of the inherent properties of Nigeria crudes, this work aims at the extraction (separation) and infrared characterization of aromatic hydrocarbons from the high boiling fractions (>200 °C) of Nigeria well- head crude oil.

#### EXPERIMENTAL

A chromatographic column of length 83 cm and internal diameter 1.9 cm, Teflon stop clock (for the above chromatographic column), glass wool, rotatory evaporator, oven (capable of 160°C), wall-clock, distillation flask, round bottomed flask, 100 ml graduation cylinder, 50 ml beakers, reagent bottles, weighing balance, 100 ml beaker, vigreux fractionating column with lag, a water cooled condensers, a quick fit thermometer of -20°C to 250°C range, a Perkin receiver adapter, a receiver, fire blanket, paraffin bath, buchner funnel, glass rod, what man No. 1 paper in 12-cm, silica gel (MN-Kiesegel 60, 0.2-0.5mm/35-70mesh), baked at 150 °C for a minimum of 16 hrs, desiccators, screw-cap adapter (for the thermometer, a few fragments of unglazed porous porcelain (porous pot) to promote regular ebullition, a container for water, a wash basin, FT-IR. machine (Perkin Elmer model 1310 at fugro lab. Port Harcourt, Nigeria).

#### DISTILLATION OF THE CRUDE SAMPLE

The source of the crude oil used for this experiment is well-head sample EDO P-13-Au, got from Mobil Producing Nigerian Unlimited at Akwa Ibom State of Nigeria, from the Qua Iboe terminal Eket. 500 ml (494.3g) of the crude oil was put into a one-litre capacity round bottomed flask. To the neck of the distillation flask was connected a vigreux fractionating column, coated with a silvery material to minimize heat loss. The column was then fitted with a condenser. A quick-fit thermometer having – 20 – 250 °C range was fixed at the top of the fractionating column. The steel head adapter enabled the joining of the flask, the condenser and the thermometer to be achieved.

The condenser was connected to a Perkin receiver adapter. When the distillation flask has been charged with the crude oil, a few chips (fragments of unglazed porous porcelains) were added to the crude oil in the distillation flask. This was done to promote regular ebullition in the subsequent heating.

The flask with the whole set-up was lagged with fire-blanket and heated in a paraffin bath until the oil began to reflux. Distillation started at 38°C and reached a final range of 200°C. Further distillation to higher temperature could not be achieved due to increased bumping that resulted when this was attempted.

The distillate was collected in the receiver, and the distillation process was completed within the interval of 8 hrs. The volume of the distillate collected was 230 ml.

#### DE-ASPALTING OF THE CRUDE RESIDUE (> 200 °C)<sup>1,15</sup>.

100 ml of the bottom fraction (>200°C) were mixed with 150 ml of n-heptane, shaken and heated on a steam bath while stirring, then allowed to stand over night. This was filtered slowly through Whatman No.1 paper in 12-cm Buchner.

The asphaltenes were precipitated while n-heptane soluble fractions were recovered by filtration followed by distilling off the n-heptane solvent. The n-heptane soluble-fractions were kept for further analysis.

#### Chromatographic Separation of the n-heptane-soluble Fractions of The Crude Oil Residue (> 200°C)/The Extraction of Aromatic H.C From Crude Oil<sup>1,15,19-24</sup>.

40 ml (39.5g) of the concentrated bottom fractions was applied on to a 140.5 g silica-gel MN-Kiesegel (60,0.2-0.5 mm/35-70 mesh) column. The silica-gel was activated at 150 °C for eight (8) hours and allowed to cool in a desiccator before use. The column was packed by making a slurry of silica-gel with n-heptane which was introduced into a cleaned and dried column of length 83 cm and internal diameter of 1.9 cm, with a glass wool placed at the bottom. The slurry was added gradually with gentle



tapping of the column. While the tap was kept open, the liquid was allowed to flow out at such a rate that it never fell below the level of the adsorbent. When all the adsorbent (slurry) was added, the solvent was allowed to drain slowly until no further settling (gap in the column) of the column took place, but the level of the solvent was never allowed to fall below the top of the column. The

column was filled to two - third (50 cm) of the length of the column. Another glass wool was placed at the top of the column<sup>21-24</sup>.

The elution of the deasphalted extract began with n-heptane that eluted the saturates, 200 ml of n-heptane was used, (step I). Then the aromatic hydrocarbons were eluted with 200 ml of trichloroethylene (step II).

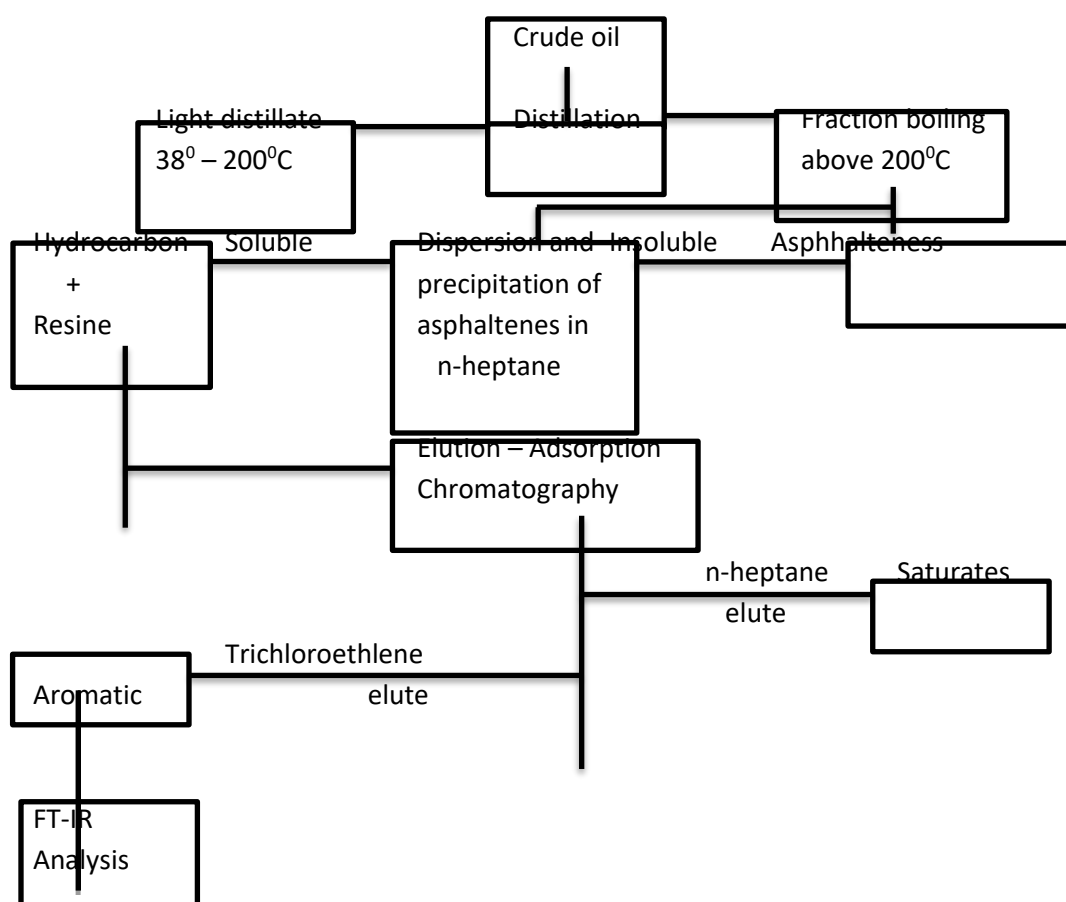


Figure 1: Separation flow chart for Aromatic hydrocarbons from high boiling fractions (>200°C) of Nigeria crude oil (Using Trichloroethylene as the Eluant).

INFRARED (FT-IR) SPECTROMETER ANALYSIS<sup>11, 25-27</sup>

A Perkin-Elmer model 1310 Fourier transform I.R spectrometer was used. The I.R analysis was performed at



PRODEC - FUGRO LABORATORY LTD. Port Harcourt, Nigeria.

In order to determine the I.R spectrum of the neat liquid sample, a capillary film of the pure dry sample is formed between a pair of sodium chloride plates (200- 500  $\mu\text{m}$  thick), by carefully placing three small drops on the polished surface of one plate, covering them with the second plate and exerting gentle pressure with a slight rotatory motion to ensure that the film contains no air bubbles. The plates with the sample were then placed in the demountable cell holder, ensuring that the gaskets were properly located. The quick release nuts were firmly screwed down (not too tightly. otherwise the liquid will exude from between the plates). The whole assembly was then located in the sample beam path of the infrared spectrophotometer. Another solution cell was filled with the pure solvent and placed in the reference beam to cancel any absorption of the solvent.

The procedure used in this analysis allowed the interfacing of microscope with Fourier transform infrared (FTIR) spectrometer. This is a useful combination allowing sample of less than 1 ng to be identified. The sample mount was oriented in an 8X beam condenser in an FTIR

spectrometer, where multiscan signal averaging technique (with the help of computer), produced a spectrum with the desired signals-to-noise ratio. The analysis time was 30 minutes. The horizontal scale is the normal infracord scale (linear in wavelength), but the spectra are marked in wave numbers for convenience. The vertical scale measures the transmittance (T). No special precautions were taken other than the polystyrene calibration checks<sup>17-23</sup>.

#### **PRECAUTIONS**

1. Salt plates are soft and easily scratched, they also cleave readily if uneven pressure is applied, the plates are best handled with rubber-tipped tweezers, and they should be stored in a desiccator.
2. Another problem is that the plates dissolve or etch when exposed to water or hydroxylic solvents. Even the moisture on ones fingers is sufficient to damage them: the polished faces should never be touched.
3. The best solvents for cleaning salts plates are carbon tetrachloride and chloroform. Because of the toxicity of these solvents with prolonged exposure they should be handled only in the hood or other well-ventilated area.

#### **RESULTS OF THE INFRARED ANALYSIS<sup>12,13</sup>**

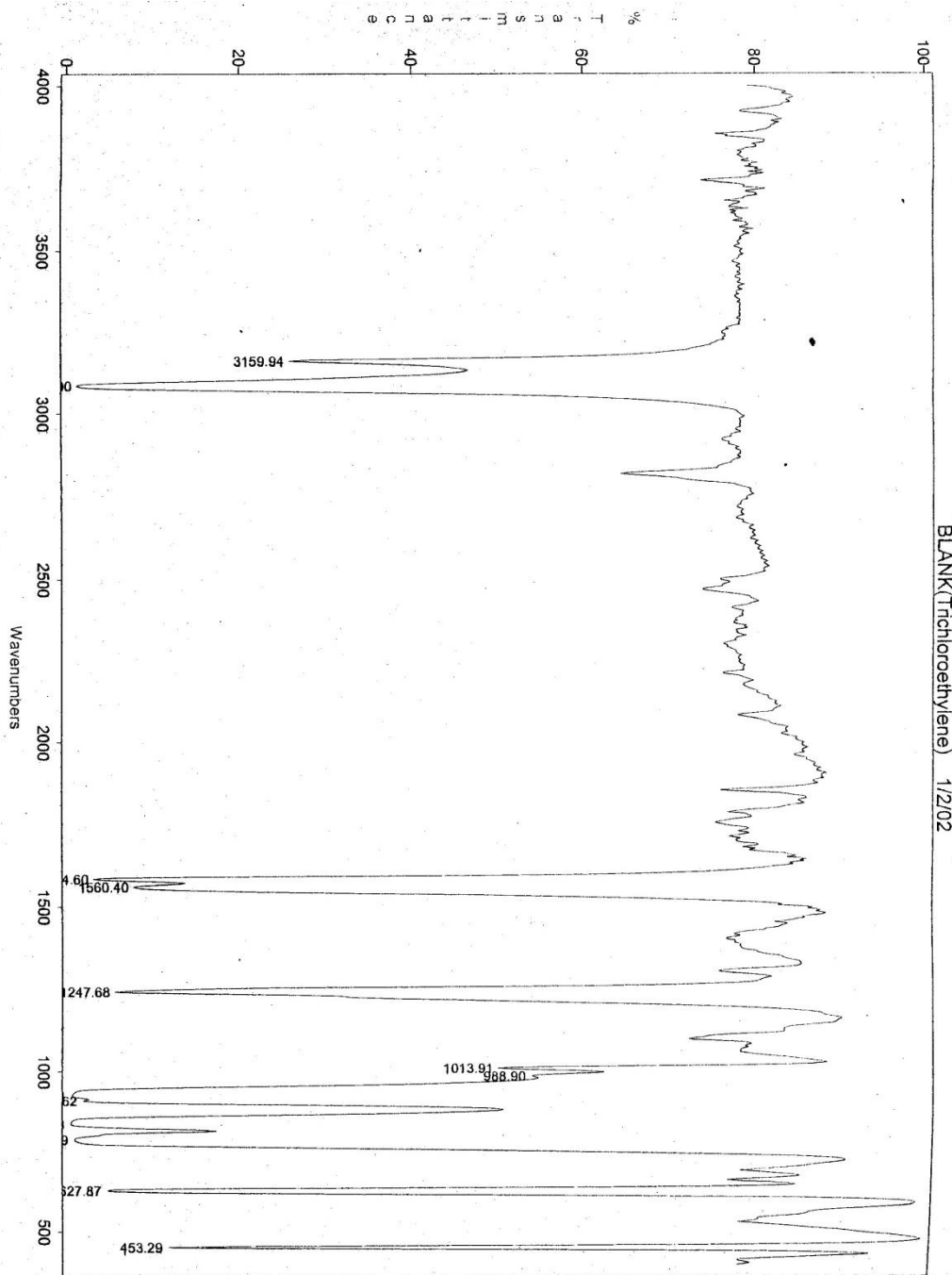


Figure 2: Blank spectrum of Trichloroethylene (FT-IR).

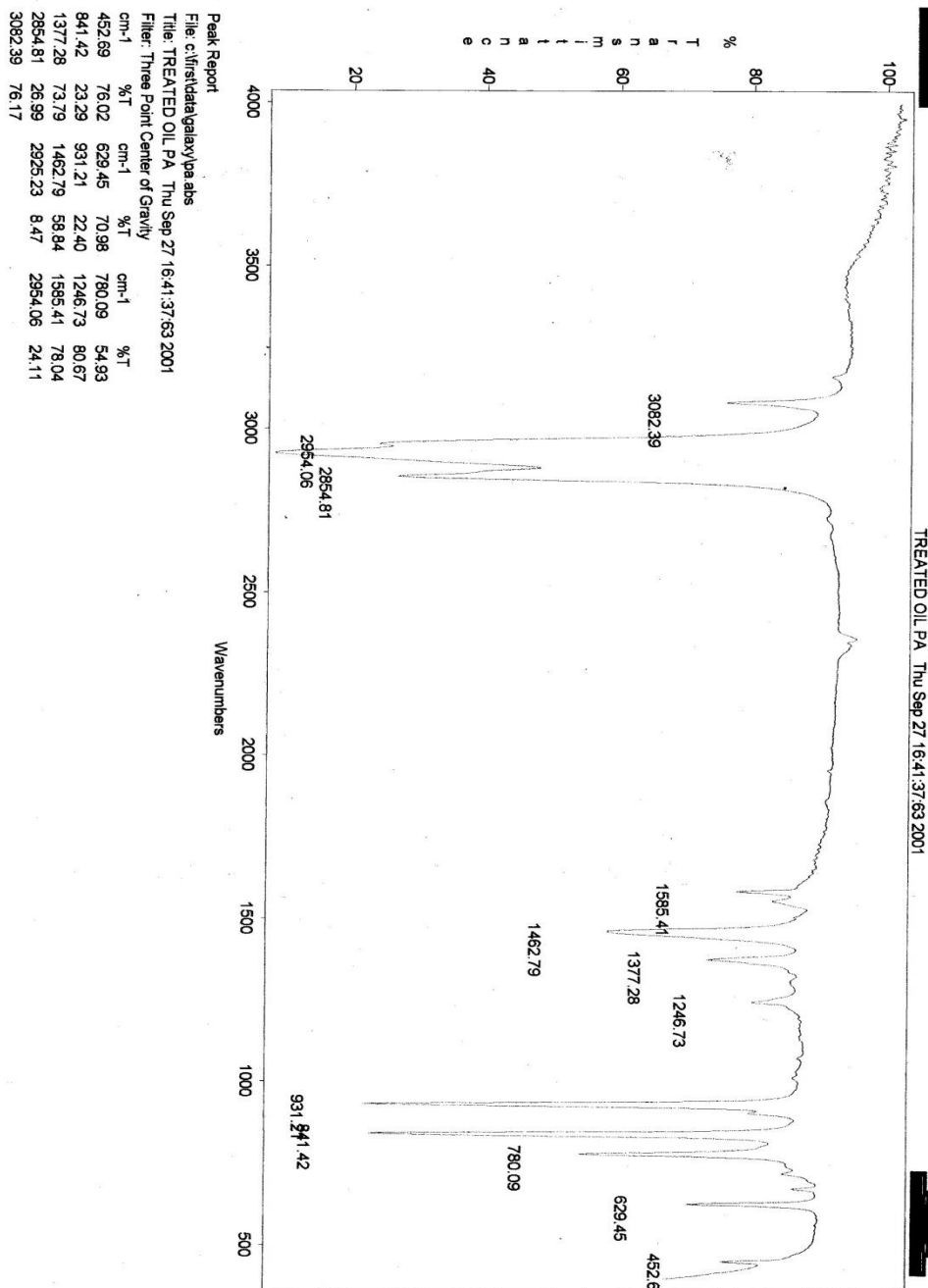


Figure 3. FT-IR Spectrum of Aromatic Hydrocarbons.



The results of the infrared spectroscopic analysis performed on the sample, using a Perkin-Elmer model 1310 and Nicolet 5DXC Fourier transformed infrared spectrometer are shown below.

**Table 1:** The FT-IR data of Trichloroethylene Eluate (Liquid please)

Absorption measured numbers (cm <sup>-1</sup> )	Frequencies in wave	Percentage Transmittance of Absorption	Remarks
3082.39		76.17	Aromatic and olefinic C-H stretching vibrations
2954.06 2854.81		24.11 26.99	C-H stretching vibrations of methyl and or methylene group(s) of saturated H.C or even the above groups attached to phenyl group as is the case of C <sub>8</sub> -aromatics
1585.41		78.04	Ring stretching vibrations of aromatics C=C.
1462.79 1377.28 1246.73		58.84 73.79 80.67	
931.21 841.42 780.09 629.45		22.40 23.29 54.93 70.98	Out-of-plane C-H bending vibrations which indicates the substitution pattern on the aromatic rings.

## DISCUSSION OF RESULTS

Infrared spectroscopy gives information about both the molecular structure and the functional group present in the sample. Detailed infrared analysis of the sample that was collected in the experiment, making use of trichloroethylene (eluant) was performed so as to ascertain the presence or other wise of aromatic hydrocarbons in the sample. In the interpretation of the infrared spectra of this experiment, it has been deemed necessary to bring to light the percentage transmittance of the infrared absorptions because of the direct relationship that exists between the absorption at various frequencies and the transmittance at any point of absorption. This relationship is an index of concentration (Beer-Lambert Law).

In the spectrum of the infrared analysis performed on the sample that was eluted with trichloroethylene (trilene) that is shown in table 1, there is a weak absorption at

3082.39cm<sup>-1</sup> which is indicative of the C-H stretching vibration of aromatics and olefins<sup>26-29</sup>. The absorptions at 1585.41cm<sup>-1</sup>, 1462.79cm<sup>-1</sup> and 1377.28cm<sup>-1</sup> are indicative of the C - -C ring stretching vibrations of aromatics<sup>1,28</sup>.

The absorptions at 931.21 cm<sup>-1</sup>, 841.42 cm<sup>-1</sup>, 780.09 cm<sup>-1</sup> and 629.45 cm<sup>-1</sup> are pointing to the C-H out-of-plane bending vibrations which indicate the substitution patterns on the aromatic rings. In the same spectrum, there are strong absorptions at 2954.06 cm<sup>-1</sup> and 2854.81 cm<sup>-1</sup> respectively, showing the presence of either a relative proportion of aliphatic hydrocarbons demonstrating the C-H stretching vibrations of saturated hydrocarbons, or the absorption arising from the alkyl substituents on the aromatic rings as is the case of C<sub>8</sub> – aromatics<sup>27-29</sup>. Table I of the infrared result makes this explanation simpler.

The absorptions at 3082.39 cm<sup>-1</sup> of the infrared spectrum is of much concern as it demonstrates traces of aromatic



hydrocarbons in the sample. To establish this inference, the chromatographic experiment was repeated with a different organic solvent tetrachloroethylene as the eluant. The infrared analysis of this extract with tetrachloroethylene showed the absorption at  $3082.39\text{ cm}^{-1}$  absent. This disappearance indicates that the absorption was not due to the presence of the single proton in the previous organic solvent (trichloroethylene)<sup>29</sup>. This is the basis of our next research work on this subject matter.

### CONCLUSION

The fourier transform infrared analysis of the sample show the presence of aromatic hydrocarbons in the sample. This has been strongly highlighted in Table 1 and in the discussions of the fourier transform infrared analysis of the sample. The spectrum highlighted various point of absorptions in the work that suggest strongly the presence of aromatic hydrocarbons in the sample.

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