DETERMINATION OF HYDROCARBON-TYPE COMPOSITION OF SOME NIGERIAN PETROLEUM PRODUCTS - A COMPARATIVE STUDY OF NUCLEAR MAGNETIC RESONANCE AND CHROMATO-GRAPHIC METHODS.

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CONTENTS

Declaration i

Thesis recommendation ii

Dedication iii

Acknowledgement iv

Objectives of the project vii

CHAPTER ONE - INTRODUCTION

1.01 Origin of petroleum 1

1.02 Chemical composition of petroleum .. 4

1.03 Petroleum products 1. 18

1.04 Fuel additives 27

1.05 Physical properties of turbo-fuel .. 28

1.06 Storage and handling problems 37

1.07 Typical aviation kerosene specification 34

1.08 Reformate 35

1.09 Analytical Methods 38

1.10 Nuclear mognetic Resonance spectroscopy 40

1.11 Average parameters that can be calculated for petroleum products 55

1.12 Chromoatography 57

CHAPTER TWO: MATERIALS AND METHODS

2.1 Nuclear magnetic resonance spectroscopy 61

2.2 Fluorescent indicator adsorption (FIA) method 65

CHAPTER THREE: RESULTS AND DISCUSSIONS.

3.1 Results 81

3.2 Summary of resultsfor aviation turbine kerosine 83

R e f e r e n c e s 88

D E C L A R A T I O N

I declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any other University or Institution. Information derived from the published or unpublished work of others has been acknowledged in the text.

OLANIYI GBENGA OLUSEGUN

Date:.....

THESIS RECOMMENDATION

We hereby recommend that the thesis prepared by O. G. Olaniyi entitled "Determination of Hydrocarbon-Type compositon of Some Nigerian petroleum products - A comparative study of Nuclear magnetic resonance and chromatographic methods" be accepted in partial fulfilment of the requirement for the degree of M.Sc Analytical Chemistry.

Internal Examiner

Date:.....

External Examiner

Date:.....

DEDICATION

This project is being humbly dedicated to the improverished peoples of the "Third-World" who seem doomed to their erstwhile role of mere pawns in the chess-board of international ideological chicanery, and particularly, to the memories of Major Kaduna Chukwuma Nzeogwu; Dr. Walter Rodney; Dr. Kwame Nkrumah; the people who have enlivened my hopes about the inevitability of a better tomorrow in the "Third-World." I intend to maintain a dialectical relationship with these down-trodden human species after my academic pursuits.

A C K N O W L E D G E M E N T

It would be inviduous to attempt to name everybody that contributed in any measure to the successful completion of this work. However, I would like to acknowledge the intellectual resourcefulness of my supervisor Dr. H. T. Bozimo, who incidentally is the acting Head of the Department of Chemistry. He designed the project and piloted it to completion through advice, suggestions and technical assistance. Really in a milieu like ours where there is manifest apathy towards academics, it amounts to a blessing to have a scholar like Dr. Bozimo as supervisor. I had it in abundance. The ever-ready assistance of the Chief - technologist, Mr. Smith, when materials and reagents are needed is commendable. Perhaps if his forerunners has been committed to the progressive development of this country's intellects as he is, the whole decolonisation exercise might have been an unnecessary Venture.

I am in indebted to my parents late Mr. Francis Akinbolade Olaniyi and Mrs. Funmilola Olaniyi who have been painstakingly bearing the financial burden of my education. I wish to thank my colleagues and the technical staff of the M.Sc laboratory for providing a conducive atmosphere for the pursuits of scholarship.

most especially Mr. Femi Ladeji my co-worker whose quiet disposition saw us through trying periods. Finally, the cooperative attitude of the staff members of the chemical laboratory's of Kaduna refinery whenever we went there for sampel collection is immensely appreciated.

OLANIYI GBENGA OLUSEGUN

OBJECTIVES OF THE PROJECT

Different techniques have been used traditionally to determine the hydrocarbon-type content of petroleum fractions, but often with poor agreement among the results for a given sample. The most common of these techniques is the chromatographic method. It is the objective of this work to appraise three of these techniques - proton muclear magnetic resonance (PNMR), Gas liquid Chromatography (GLC) and Fluorescent Indicator adsorption (FIA) by using them to analyse for the hydrocarbon - type composition of two petroleum fractions (Reformate and Aviation Kerosine). The results obtained are to be compared and inferences drawn as to the relative advantages and disadvantages of the techniques based on (a) The cost of the method

(b) Time required for the analysis.

(c) The amount of sample required

(d) The tediousness of the method.

(e) The degree of precision of the results obtained

(f) The sensitivity of the technique.

It is considered desirable to determine the hydrocarbon - type composition of petroleum fractions because the results can be used as criteria in quality assessment. It has been observed that the performance characteristics and other properties depend on their chemical compositions. The factors responsible for this quality characterisation are the content of aromatic, olefinic and saturated hydrocarbons. For example, the amounts of aromatic and saturated hydrocarbons affect the combustion properties of fuels while olefins have a marked effect on fuel's stability. There is suggestive evidence to show that a close correlation exists between the amount of structural branching in a Fuel's paraffinic hydrocarbons and its octane-number. Information obtained from the hydrocarbon-type composition of petroleum fractions can be used to determine their octane numbers. It is easier and more economical to determine hydrocarbon - type than octane number.

Petroleum fractions are subjected to various refining treatments to meet final product specifications.

Most often, these treatments lead to a change in the constituent hydrocarbons. A rapid method of determining the proportions of the hydrocarbons would be a valueable tool for controlling technological parameters during production.

It is hoped that useful public health information can be obtained from the determination of the aromatic contents of petroleum products. This is because, it has been shown that many aromatic compounds of petroleum products are carcinogenic. Benzo (α) pyrene has been isolated from coal tar and is now recognised as a powerful agent for the production of malignant tumors in laboratory animals. By screening for aromatics an estimate of the total load of potential carcinogens would be obtained as a prerequisite to planning an effective reduction to carcinogens during the handling of petroleum products. It is known that carcinogenicity is a function mainly of substituted polynuclear aromatic hydrocarbons whose methyl substituents show resonance signals in the 2.0 - 3.0 ppm region. Therefore the observation of signals here and calculation of their relative intensities would at least, furnish some estimate of polynuclear methyl aromatic hydrocarbons.

Attempts will be made to determine Hydrogen/carbon ratios with a view to providing information on the average empirical molecular weights of hydrocarbons in the petroleum samples and their degrees of unsaturation.

ABSTRACT

Although several methods exist for the analysis of petroleum products for hydrocarbon - type composition there is often poor agreement among the results. In this project two of these methods - Nuclear magnetic resonance and chromatography (GLC & FIA) were used to analyse sample of reformate and aviation turbine kerosene (ATIC) obtained from the refinery of the Nigerian National Petroleum Corporation (N.N.P.C), Kaduna, for their hydrocarbon - type composites "PONA." The equations derived for the calculation of "PONA" were extended and used to calculate the hydrogen-carbon ratio with a view to estimating the empirical molecular weights of the samples. Attempts were also made to calculate the average molecular weights of the samples by adopting the N.M.R method of Sandor and Barcza with ethylene glycol as standard. Comparatively the results obtained from the two methods indicate that the aromatic contents of reformates is higher than that of aviation turbine kerosene while the paraffinc content of aviation turbine kerosene is much higher than that of reformate. Olefi's are present to a much lesser extent in the two samples

1.21 ± 2.46 in reformate and 1.67 - 2.59 in aviation turbine kerosene. The standard deviation for the values of olefins are higher than what could be accounted for by random statistical errors. A correlation of the set of data obtained from N.M.R method with those obtained from chromatographic method was affected using the statistical package for social sciences (SPSS) programme of the computer. Numerically the correlation coefficients indicate a not-too-good relationship. The hydrogen-carbon ratio showed that there are approximately two hydrogen atoms to one atom of carbon in the molecule. The results obtained for the actual molecular weights were inconsistent. The N.M.R technique is less tedious than the chromatographic methods.

I N T R O D U C T I O N

CHAPTER ONE

ORIGIN OF PETROLEUM

The term "peteroleum" literally means rock oil or mineral oil, but in modern technical usage, it has a wider meaning which includes natural gas, mineral wax and bitumen in addition to crude oil [1]. In some contexts the terms oil and petroleum are used interchangeably.

There have been many theories on the origin of petroleum, some emphasizing a vegetable or animal background and others a close relationship to coal [2]. Certain of these theories emphasize that any organic matter of either background can be transfomed into petroleum products. However there seems to be general agreement that petroleum was formed from organic matter in near shore marine deposits in an environment deficient in oxygen, and asociated with the sediments that later solidified into rocks, limestones, dolomites, shales and sandstones. This agreement is based on the general similarities of the composition and nature of petroleum constituents to the basic structural elements of compounds

occurring in living organisms. Of the more than 500 identified compounds found in petroleum, most belong to the paraffin, naphthene, or aromatic groups of organic compounds, and all could be derived through living Organisms. Moreover a great number of the minor constituents of petroleum are compounds with sulphur, phosphorus, nickel, vanadium and other elements. The common and ubiquitous occurence of these elements, even in small quantities, both in organisms and in the organic material buried in sediments and sedimentary rocks is an important reason for accepting organisms as a source of petroleum. Among the compounds that could contribute these elements are porphyrins, like those from chlorophylls, and the hemins of plants and animals. These compounds are easily destroyed at temperatures higher than 300°C. Thus, the survival of these compounds suggests that the making of petroleum has not been under higher temperature conditions. The idea has been put forward that the process of transforming organic matter into petroleum hydrocarbons must include an array of complex chemical and biochemical reactions such as fragmentation of organic polymers, decarboxylation of organic acids;

decarboxylation and deamination of amino acids and reduction of alcohols, sulfides, ethers, aldehydes and Ketones. Anaerobic bacteria may play a role in the transformation of organic material to petroleum. Catalysts in the form of host-sediment minerals such as hydrated aluminium oxides, hydrated aluminium silicates and complex hydrated iron compounds may aid in performing the chemical changes. As chemical alterations progress, the fluid components may move slowly through capillary and larger openings, always toward more stable temperature and pressure conditions. There exists a continuous opportunity for selective movement of organic compounds as well as selective chemical transformations. The chemical transformations proceed in agreement with the laws of chemical thermodynamics so that the resulting compounds have greater thermodynamic stability.

Crude oil, as the unrefined petroleum is called, is a viscous liquid ranging from almost water white through amber brown-green to black in colour with specific gravity ranging from about 0.80 to 0.99.

CHEMICAL COMPOSITION OF PETROLEUM

The mechanism by which petroleum was formed has not been established definitely save the fact that the presence of molecules which have structures reminiscent of those of plant and animal materials suggests formation from those materials over geologic periods of time. The local distributions of plants and animal life are quite varied at the present time and, presumably were similarly varied in the period in which the petroleum precursors were formed. Thus, the composition of the products derived from these precursors is not fixed with respect to either the molecular structures present or the proportions in which they occur, and the composition of petroleum may differ from region to region, pool to pool, and even from well to well within a pool. Application of separation and identification techniques available has resulted in the isolation and characterization of several hundred individual hydrocarbons which represent about 50 - 95% of the material present in crude oil. The greater portion of the compounds isolated consists of lower-boiling hydrocarbon; but progress is reportedly being made in the identification of the higher-boiling components.

HYDROCARBONS IN PETROLEUM: It is conventional to classify hydrocarbons as either saturated hydrocarbons or unsaturated hydrocarbons.

SATURATED HYDROCARBONS:

Each of the three classes of saturated hydrocarbons (normal paraffins, branched paraffins and cycloparaffins) has been found in petroleum. The saturated molecules are characterized chiefly by their inert nature. It is this property of inertness which promotes their use in solvents, food preservation and other non-fuel applications.

NORMAL PARAFFINS:

They have been found throughout the boiling range of petroleum. The number of carbon atoms contained in normal paraffins varies from one in methane, the simplest member of the series, to as many as seventy-eight. The abundance of normal paraffins in petroleum products varies considerably. In spite of their inert nature, the normal paraffins in petroleum have been isolated or identified rather readily. A combination of favourable properties and circumstances has been responsible for this.

These factors include the following:

(i) There is only one normal paraffin at each carbon number.

(ii) The melting (freezing) point of the normal paraffin of a given carbon number is higher than that of any of the isomeric branched paraffins.

(iii) Normal paraffins above C_6 form stable solid complexes with urea whereas branched paraffins generally do not.

(iv) The presence of only primary and secondary carbon atoms with the associated bonds joining them in the normal paraffin molecule imparts a high stability to its molecular ion and, therefore, high sensitivity of detection by mass spectrometry.

BRANCHED CHAIN SATURATES: Comparatively, branched paraffins are more difficult to isolate or identify as individual compounds than normal paraffins. The simplest member of the series is Isobutane. At each carbon number above four the number of possible branched isomers increases - two at C_5, four at C_6

and so on until, at C_{20}, there are more than 366,000 possible structures. The branched paraffins lack those properties of mormal paraffins which assist in their isolation and identification. They do not, in general, form stable complexes with urea. The tertiary and quarternary carbon-atoms in the molecules are joined by bonds which break readily upon ionization in the mass spectrometer, and the mass spectrum consists largely of fragment ions which cannot be related specifically to the original molecules unless they have been separated beforehand. In spite of the difficulties inherent in the task, a number of branched paraffins have been separated and identified. The physical properties of the branched alkane fractions separated indicate that they are composed largely of monomethyl, dimethyl, and trimethyl substituted paraffins.

CYCLIC SATURATES:

Both the normal paraffins and the branched paraffins have the molecular formula C_nH_{2n+2}. The cycloparaffins, by virtue of the bonds expended in completing the ring or rings, contain a lower proportion of hydrogen at a given carbon-number. Their

molecular formul r are C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4} etc, each additional ring in the molecule being evidenced by two less hydrogen atoms. The cycloparaffins (naphthenes) which have been isolated from petroleum all contain rings having five, six, or seven carbon atoms. Bicyclo paraffins such as cis- and trans - decahydronaphthalene with six-membered rings, cis-bicyclo 3.3.0 octane with five membered rings, and trans-bicyclo [4.3.0]nonane with one six - and one five-membered ring have been isolated. Cyclo- paraffins containing up to seven rings have been observed in petroleum with the aid of mass spectrometry. It has also been shown that in petroleum samples the concentration of polycycloparaffins increases with increasing molecular weight.

UNSATURATED HYDROCARBONS:

There are two principal types of unsaturated hydrocarbons in petroleum: olefins and aromatics. The extent of their occurrance in crude oil varies considerably. Olefins have been reported only in a few instances. On the other hand, aromatic compounds of almost every known type have been found in petroleum.

A combination of these hydrocarbon types may be present in a single molecule. The compounds in the

high boiling range are the most complex and the presence of molecules containing one or more naphthenic and one or more aromatic rings has been confirmed. Generally, the paraffinic content becomes less and the naphthenic and aromatic contents become greater as the boiling range increases.

NON-HYDROCABON COMPONENTS:

Crude oils contain appreciable amounts of organic non-hydrocarbon constituents, mainly sulphur-, nitrogen and oxygen containing compounds and, in smaller amounts, organometallic compounds in solution and Inorganic salts in colloidal suspension [5] . Although their concentration in distillute fractions may be quite small, their influence is important. In refinery operations the deposition of inorganic salts suspended in the crude can cause serious breakdowns, the thermal decomposition of deposited inorganic chlorides with evolution of free hydrochloric acid can give rise to serious corrosion problems in the distillation equipment. The presence of organic acidic components i.e. mercaptans and acids, can also promote metallic corrosion. In finished products, the presence of traces of non-hydrocarbons may impart objectionable characteristics;

discoloration or lack of stability on storage (formation of gums) in distillate fuels, caused by the presence of nitrogen compounds; the adverse effect on additives or improvers, as in motor gasolines, where the presence of traces of sulphur reduces the effectiveness of organic lead antiknock additives [3] .

SULPHUR COMPOUNDS:

Organic sulphur compounds are present in all known crude oils, although their concentration can vary between wide limits. Generally the higher the density of thecrude oil the greater is the sulphur content. The distribution of sulphur in a given crude oil is not uniform, but increases with increase in the molecular weight of the fractions, concentrating in the distillation residues. Sulphur-containing compounds also increase in number and complexity with increase in the molecular weight of the fraction.

In the low boiling fractions of a crude (below 200^{o}C) the main sulphur bearing compounds present are the mercaptans or thiols.

C - C - C - C - SH. Butane thiol

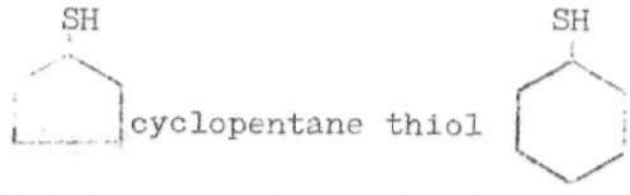
They are highly objectionable in commercial products on account of their unpleasant smell, and their

acidic properties. Oil fractions contain'ng them are said to be "sour". By the rise of suitable oxidants they are often converted into non-corrosive disulphid: in

C - C - S - S - C - C

the so- called "Sweetening processes".

Alkyl mercaptans with the thiol group attached to a primary carbon-atom are predominant in the boiling range up to 100°C (from C_1 to C_5). In the higher boiling ranges, compounds with the SH group attached to a secondary carbon atom of an alkyl or iso-alkyl chain become the most abundant, accompanied by a progressive decrease in concentration. In the kerosi: range, cyclic mercaptans with cyclopentane or cyclohexane rings are often present.

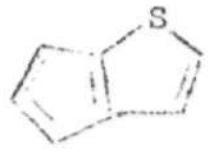


cyclopentane thiol cyclohexane thio

Thiophen and monomethyl thiophens have been isolated from gasolines; alkylthiophens and benzothiophens hav: been isolated from kerosines.



Thiophen



Although sulphur compounds concentrate preferentially in the heavy distillates, residual. Oils and bitumens, very little is known of the actual identity of these compounds.

NITROGEN COMPOUNDS:

The majority of crudes contain only small amounts of total nitrogen, of the order of 0.1 per cent by wt or less. In the lighter fractions up to the kerosine range, nitrogen compounds are present only in traces. With increasing boiling point the nitrogen content increases, and reaches a maximum in asphaltic distillation residues.

Nitrogen compounds, unlike the sulphur derivatives, are relatively stable to heat and do not decompose in the normal refinery processes.

A distinction is made between basic and non-basic compounds, based initially on extraction with diluted mineral acids, with subsequent regeneration of the bases with strong alkalis. The majority of nitrogen

compounds isolated from crude oil fractions belong to the basic group, and they are more amenable to separation. The knowledge obtained so far about the components of the non-basic group is mainly based on the identification of chemical classes by mass spectroscopy.

Several basic nitrogen compounds have been isolated, mainly from gas oils. These are Quinoline and pyridine and their alkyl-substituted analogues.

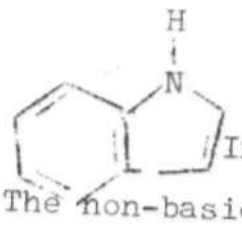


Quinoline

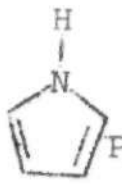


Pyridine

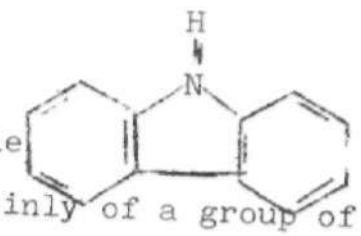
The non-basic nitrogen compounds identified consist mainly of derivatives of indoles, pyrroles and carbazoles.



Indole



Pyrrole



Carbazole

The non-basic components consist mainly of a group of compounds known as porphyrins. The basic structure, which consists of four pyrrole rings joined by methyne groups, forms very stable complexes with metals, mainly

vanadium and nickel. The porphyrins are associated with highly asphaltic crudes and are active poisons for the catalysts used in cracking processes. They are also powerful interfacially active agents promoting the formation of stable emulsions of petroleum with water, and as such they play a very important role in the displacement of crude oil from reservoir surfaces. Their structure is closely connected with chlorophylls and haemoglobin.

OXYGEN COMPOUNDS:

The total amount of combined oxygen in crude oils is relatively low, varying from traces to a maximum of 2 per cent by wt. The oxygen content increases with the boiling point of the fraction, the greater portion of oxygen containing constituents being concentrated in the residual oils where oxygen contents as high as 8 per cent have been recorded.

In the low- and medium - boiling range distillate fractions, oxygen is mainly present in the form of acidic compounds, such as organic acids, and, to a limited extent, phenols. For this reason the determination of total oxygen content is customarily replaced by a determination of acidity of the fraction.

For a given crude, the acidity is usually a maximum in the kerosine-gas oil range, while straight-run gasolines, heavy fractions and residues contain only traces of acidic compounds.

The main acidic constituents of the lower boiling fractions are aliphatic carboxylic acids. Straight-chain acids with from C_1 to C_{20} carbon atoms in the chain have been isolated and identified. A few branched-chain carboxylic acids have also been identified, but these occur in relatively small amounts. As the caron number of the acids increases from C_6 to C_{20} the relative amount of aliphatic carboxylic acids decreases. Monocyclic and bicyclic carboxylic acids form the bulk of the acidic compounds in the kerosine and light gas-oil fractions. They are collectively referred to as "naphthenic acids".

Only a few non-acidic oxygen - containing compounds have been identified in crude oils. Esters of aliphatic acids occur in some petroleum fractions, whilst ketones, from acetone to methyl butyl ketone, have been separated from gas-well condensates.

METALS IN PETROLEUM:

Aside from "clean" hydrocarbons and nonhydrocabons which are heterocyclics containing suifur, nitrogen and oxygen, petroleum contains the following additional components [1].

(a) Minerals such as silica and metals

(b) high molecular weights large asphaltic molecul.

The concentrations of these contaminants may be minor, but they are the source of environmental pollutants and the cause of corrosion of equipment and poisoning of processing catalysts. The refining process serves to elimi ate these contaminants by chemical conversion and upgrading. Metal components are removed by slurry processes using asphathenes. Asphaltic molecules are usually converted through depolymerisation by means of dehydrode sulfurizatio n. Therefore, to ensure a clean end fuel from nature petroleum disu lurization, denitri fication and demetallization are necessary. The removal of metals is a more complex problem on account of the following factors:

(i) Metals are chelated or complexed by ligands that are completely miscible with petroleum. thus making separation difficult.

(ii) The amounts of metals is very small, usually ranging from 1 - 10,000 ppm.

(iii) Metals are generally associated with the asphaltic fraction.

(iv) Metals can exhibit catalytic effects during conversion.

(v) Refining and upgrading must involve the use of catalysts, which can be poisoned by metals [12] .

OCCURRENCE

Spectrographic analyses have shown that crude oil contain about 28 elements. These metals are, U, Zn, Zr, V, Sr, Sn, pb, Ni, Nd, Mo, La, Ga, Cu, Cr, Co, Ca, Ba, B. As, Ag, K, Na, mg, Mn, Tl, fe, Al. The more abundant metals are V and Ni. It has been revealed that both increase with the asphaltic content of the crude oil. The lighter oils contain less metal. The metallic components in petroleum can be classified into the following categories.

(a) Metalloporphyrin chelates

(i) Vanadyl and nickel porphyrins. .

(ii) Chlorophyll a and other hydroporphins

(iii) highly aromatic porphin chelate.

(iv) porphyrin decomposition liqands.

(b) Transition metal complexes of tatradentate mixed ligands such as V, Ni, fe, Cu, Co and Cr.

(i) simple complexes from resin molecules.

(ii) chelates from asphaltene sheets.

(c) Organometallic compounds derived from Hg, Sb and As.

(d) Carboxylic and salts of the polar functional groups of resins, such as Mo and Ge salts.

(e) Colloidal minerals, such as silica and Nacl.

PETROLEUM PRODUCTS

A diverse range of products has been obtained by fragmenting crude oil. Approximately 2500 are currently produced wholly or in part from petroleum, in addition to 3000 petrochemicals. Many of the petroleum products of mommerce are blended, compounded, or otherwise modified materials, not the primary stocks as they come from petroleum - refining plants. Owing, to the diverse nature of petroleum products, their classification poses problems. However using volatility as the sole criterion. Petroleum products and related materials have been grouped into following seven broad categories [4].

(1) LIGHT PETROLEUM PRODUCTS P.Pt (29.44 - 210°C)

These include degreasing fluids, Gasolines caviation, marine, motor) and natural gas. Insecticide, base oils, Naphthas - light and heavy solvents - aliphatic and aromatic and tractor fuels.

(2) INTERMEDIATE PETROLEUM PRODUCTS: (B.pt 37.7-287.7°C)

Included in this category are:

(a) Aviation turbine and Jet fuels (type A, A_{-1} and B)

(b) Diesel fuel (grade 1D and 2D).

(c) Heating oils and gas oils (grades 1 & 2)

(d) Kerosene.

(e) Mineral seal oil.

(3) LUBRICATING OILS (B.pt 210°C - 315.5°C)

The following among others are classified as lubricating oils;

(a) Grease

(b) Hydraulic fluids

(c) Lubricants - Automotive, aviation, industrial, marine and Railroad.

(d) Oils:- Electrical insulating and metal processing.

(4) CRUDE OIL AND HEAVY (RESIDUAL) PETROLEUM PRODUCTS

This category includes Asphalt; Cokes, Diesel fuel (grade 4D) and Heating fuel grades 4, 5 and 6)

(5) PETROLEUM WAXES:

These are mainly microcrystalline waxes, paraffin waxes, petroleum wax distillate and wax emulsions.

(6) LIQUEFIED PETROLEUM GASES:

These gases are Butadiene, Butane and Butene mixtures, Butylene, ethylene, Isobutane, propane and propylene.

(7) MATERIALS USED IN PROCESSING AND REFINING CRUDE PETROLEUM AND FRACTIONS:

This sub-group includes absorbert catalysts;

(a) Alkylating

(b) Cracking

(c) Polymerising

(d) Reforming chemical treating agents and sol-

GASOLINE

In relation to the other petroleum products, gasoline is most widely marketed and therefore ranked highest in the scale of utility values and popularity. Motor gasoline is essentially a complex mixture of

hydrocarbons distilling between about 30°C and 210°C and consisting of compounds generally in the range C_4 to C_{12}. It is possible for gasolines produced from different refineries to vary widely in composition. This is because of different operational techniques being used by refineries. It is the prerogative of each refiner to adopt the processes that will enable him to meet the required quality and volume of all of his products at minimum cost. The production of gasolines can be from any of the fefining techniques - distillation, polymerisation, Isomerisation, alkylation, catalytic reforming and cracking. Each provides excellent blending components. The principal proper' affecting the performance of a gasoline in an engine are volatility and combustion chracteristics. These properties are adjusted to some extent according to the topography and climate of the country in which the gasoline is to be used.

There are many ways by which the volatility of a motor gasoline affect the performance of the engine, the chief of which are ease of starting, rate of warming up, vapour lock, carburettor icing. The fuel must be sufficiently volatile to give easy starting, rapid,

warm-up and adequate vapourisation for proper distribution between the cylinders.

Knock or detonation occurs when the unburnt gases ahead of the flame front spontaneously ignite, giving rise to an excessive rate of pressure rise. The knock rating of a gasoline is expressed as octane number (ON), this being the percentage by volume of Iso-octane (octane number 100 by definition) in admixture with normal heptane (octane number zero by definition) which has the same knock characteristics as the fuel being assessed. In order to achieve the required octane levels in commercial gasolines, anti - knock additives are used. The most common of these are the lead alkyls such as tetraethyl lead (TEL) and tetramethyl lead (TML). [11].

Other additives used in modern motor gasolines include anti-oxidants and metal deactivators for inhibiting gum formation, surface-active agents and freezing point depressants for preventing carburettor icing. An additional incentive to reduce sulphur in gasoline stems from the fact that all forms of organic sulphur compounds seriously impair anti-knock affectiveness of the lead alkyl compounds that are added to

5. PETROLEUM REFINERY PROCESSES

The flow diagram below gives a simplified overview of Petroleum refinery operations.

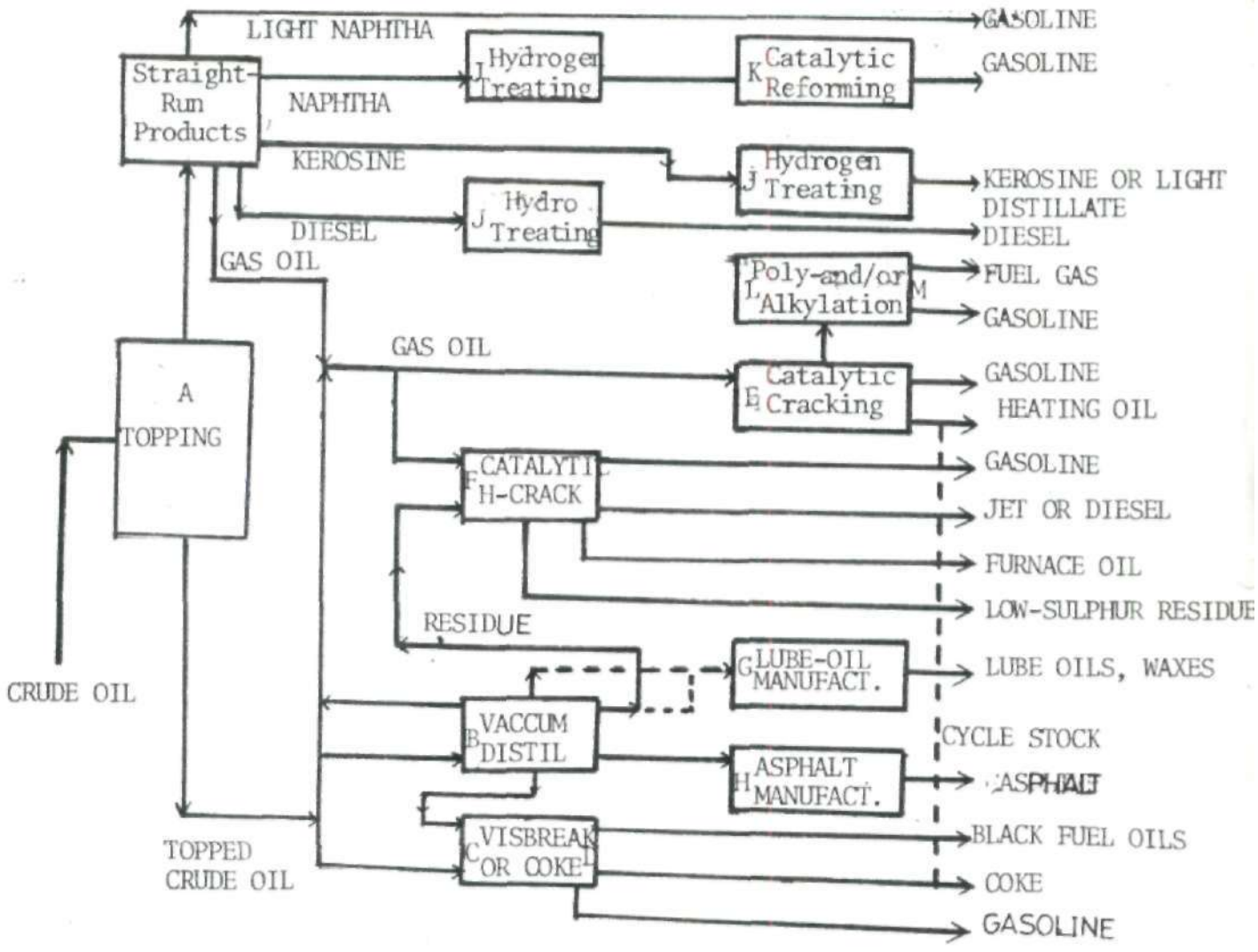


Fig.1 BASIC REFINERY OPERATIONS

motor gasolines. Hydrogen sulphid and mercaptan sulfur are most undesirable contaminants because, apart from their corrosive nature, they possess an extremely unpleasant odour.

AVIATION KEROSINE

Aviation gasolines for use in aircraft spark-ignitum piston engines have been in use for more than 50 years. The incentive for more power from less weight with a low fuel consumption and for considerable operational flexibility, spurred on considerably by two World wars, supported continuous research and development on aviation gasolines [5] .

The original development of the jet engine was carried out using illuminating kerosine as the fuel. This was one to reduce the fire hazard in high pressure fuel systems, and because of the ready availability. Other gasolines are equally suitable for use in jet engine operations with respect to combination, ignition characteristics and engine life but the environmental requirements such as pumpability at low temperatures and ease of relighting at high altitudes were the important quality factors that led to the choice of kerosine type of fuel as the principal fuel for gas turbine engines.

A prime characteristic of a turbo-fuel is that it shall be stable, clean burning and non-corrosive to the materials of construction of the aircraft engine. Turbo-fuels are distillate fractions derived from crude petroleum, and consist predominatly of hydrocarbons. The minor non-hydrocarbon components consist of surphur, nitrogen and oxygen compounds in the fuel, and traces of particulate matter and water (moisture) as contaminants. The hydrocarbons may be split into four types, paraffins, olefins, naphthenes (cycloparaffins) and aromatics. The distribution of these hydrocarbon types will vary with the crude source. An approximate distribution is as follows:

Paraffin	33-61 per cent vol.
Olefins	0.5-5 per cent vol.
Naphthenes	10.45 per cent vol.
Total anomatics	12-25 per cent vol.

It is obvious from the above that paraffins and naphthenes are the major components in Jet fuels, their ratio varying with crude source.

Paraffins have a high heat of combustion on a weight basis, with naphthenes slightly less and

aromatics the lowest. However, when heat of combustion is considered on a volume basis, the order is changed, with monocyclic aromatics having higher values than paraffins which in turn are marginally higher than naphthenes.

Aromatics are present in turbo-fuels principally as monocyclic hydrocarbons although polynuclear aromatics, essentially two- and sometimes three- ring compounds, do occur in small quantities. These polynuclear aromatics contribute to highly luminous flames, giving high radiant heat in the combustion chamber. It is customary in modern refinery processes to remove polynuclear aromatics by hydrotreating. This is desirable from the point of view of combustion because aromatics cause smokiness and carbon deposition.

Olefins are limited, usually to 5 per cent by vol, on account of their instability (chemical reactivity and the ease with which they will form gums). They have good burning qualities and are intermediate between paraffins and naphthones in terms of heat of combustion.

Alcohols are excluded from turbo-fuels for two reasons: their affinity for water and their low calorific value.

The non-hydrocarbons present in turbo-fuels are compounds containing sulphur, nitrogen and oxygen. The amount of sulphur and nitrogen present in dependent on the crude source composition and on the method of processing. The total sulphur content is usually small, the limit varies with specifications and is generally 0.2 percent by wt, and never greater than 0.4 percent by wt. Mercaptan sulphur is controlled specifically for its corrosiveness to copper and cadmiums, and for the disagreeable odour. Most specifications restrict the marcaptain sulphur of a furbo-fuel to less than 0.001 percent by wt. Mercaptan sulphur and/or other complex corrosive compounds are also limited by a copper strip corrossion test, which defines the maximum stain that the strip may have after being heated in the fuel at a specified temperature for a specified time. Nitrogen compounds occur mainly in the heavy end of the fuel and are detected in gums and sediments. The amount of nitrogen present is not

limited by specifications.

Oxygen, also, is not limited except when present in naphthenic acids or phenols which are controlled by an acidity test [5] .

FUEL ADDITIVES:

Oxidation inhibitors are used in turbo-fuels to prevent gum formation. Additionally they are added to retard peroxide formation in certain hydrotreated fuels for peroxides, if present in the fuel, will attack nitrile rubber hoses used on the fuel system of fome aircraft engines. A metal deactivator is permitted in Jet fuel specifications. This has the effect of removing, by chelation, any dissolved copper that may be present in the fuel as a result of refinery processing. Copper is undesirable in the fuel as it will catalyse oxidation reactions and so help to form gums.

An anti-icing additive is sometimes required to be added to a fuel and is obligatory in certain specifications. It purpose is to ensure that dissolved water in the fuel, which will tend to come out of solution as the fuel temperature drops, does not freeze

in the fuel system. The use of this additive is necessary if the engine fuel system is not equpped with fuel heaters.

Anti-smoke additives are avilable to reduce the amount of smoke emitted from Jet engines on take-off.

Fuel-solube biocides may be put into fuels to inhibit microbial and fungicidal growth in aircraft fuel systems. There are two approaches to the use of these additives. If one, shock treatment is used, that is the system is treated on a periodic basis with a powerful biocide. In the other a biocide is added to the whole fuel.

PHYSICAL PROPERTIES OF TURBO-FUELS

Physical properties are of considerable importance with regard to engines because they affect storage and handling facilities and constitute a relatively simple and effective means of controlling quality.

(a) Viscosity:

This property is specified to ensure that:

(i) fuel line pressure losses are maintained at acceptable levels when operating at low temperature.

(ii) fuel injection nozzles and fuel system controls will be operating at or near to design specifications.

The viscosity of the fuel can affect the life of the fuel pump, as it relies on the fuel to lubricate its moving parts, where this lubrication is hydrolymanic. However, under certain conditions of operation boundary layer lubrication occurs and in this situation fuel viscasity has little or no effect.

VOLATILITY:

The most important reason for controlling the volatility of turbo-fuels is the loss of fuel from unpressurized aircraft fuel tanks due to boiling-off at high altitudes. For this reason, amongst others, the low-volatility kerosine type fuel is attractive.

Differences in volatility have varying effects on a turbo-fuel so that the final blend is a compromise to achieve as many desirable properties as possible. A high front-end volatility facilitates easy engine staring and aids re-lighting at high altitude. On the other hand it promotes fuel losses due to boil-off at high artitude and causes unsteady flow in fuel system lines in the high-temperature zones of the engine.

A low front-end volatility used to cause coid-start difficuilties but these have now been overvome by the use of high-energy, low-tension ignition systems.

The problem of fuel boiling-off at high altitude is at present minimized by the corresponding low temperatures encountered at high altitudes and enhance low fuel temperatures in the aircraft fuel system. On a subsonic transatlantic of light, for example, air temperatures down to -65°C are likely to be encountered resulting in fuel temperatures of -30 to -35°C. At these low temperatures there is negligible fuel boil-off in spite of the low pressure. With the advort of the supersonic transport, however, the situation could change for it will fly higher and much faster and in these conditions air will heat the skin of the aircraft and hence the fuel.

WATER SOLUBILITY: Dissolved water is always present in turbo-fuel, the amount varying with the relative humidity of the atmosphere above it and the temperature. Water is only slightly soluble in turbo-fuels (42 ppm in the kerosine type at 15°C) but exhibits a considerable decrease in solubility with decrease in temperature. With the large volumes of fuel now being

carried in aircraft, significant amounts of water can be thrown out of solution in the aircraft fuel tank as the outside temperature decreases.

STORAGE AND HANDLING PROBLEMS:

Procedures for storage, handling and Into-plane refuelling of aviation turbo-fuel are handled by professionalbodies that lay down the regulations to be followed. Particulate matter and free water have always been undesirable contaminants in aviation turbo-fuels. Although the volume of fuel used by gas turbine engines is steadily increasing, the total amount of contaminant in the fuel is steadily decreasing, on a unit volume basis. A quality requirement for a fuel ex-refinery is that it be clear and bright and free from suspended matter, but on its journey to the aircraft the fuel may travel by sea-going tanker, rail-car or pipeline and is liable to pick up dirt, finely divided rust and/or free water. To ensure that the fuel is cleaned up at the time of delivery into aircraft, filter separators are used in the distribution system. Filter separators remove solid particulate matter by filtration and separate out the free water by a coalescing action.

Most aviation turbo-fuel specifications stipulate the maximum dirt content allowed into plane and this is of the order of 1mg/litre of fuel. As a control on the dirt content of the fuel, samples are taken from the loading line during refuelling. A bypass system is set up and a measured portion of the fuel is passed through a fine cellulose membrane filter which has been accurately weighed. The filter, treated to remove all liquid fuel, is dried and accurately re-weighed to give the dirt content of the fuel on a weight basis.

The fuel velocities involved in modern transport systems, large tankers and pipelines, tend to promote the dislodging of fine scale from the system, and hence a practice has developed of allowing the fuel to settle for a given time in product tankage to allow the scale to settle to the bottom of the tank.

SPECIFIC GRAVITY:

This is a very important parameter in the design of fuel tanks in aircraft. Fuels varying over a very considerable specific gravity range can readily satisfy the essential quality requirements of a turbo-fuel. However, it is necessary, in order to get a satisfactory

engine control, to limit the specific gravity of a particular type of fuel. The particular specific grav... limits laid down in current specifications are, in fa... a compromise between ideal engine design requirement, product availability and cost [6] .

TYPICAL AVIATION KEROSINE SPECIFICATIONS

Specific gravity at 60/60°F	0.775 - 0.845
Flash point, °F	100 min
Smoke Point, mm	20 min
Total Sulphur, % wt	0.2 max
Corrosion Copper strip	1 max
Corrosion silver strip	1 max
Approximate boiling point	288 max
Freeze point, °C	-50 max
Aromatics, % vol	20 max
Olefins, % vol	5 max
Existent gum, mg/100ml	7 max
Calorific value	18400 min
Preheater tube deposit	< 3 max
Viscosity at 30°F fcst	15 max
Interface rating	Sharp, no emulsion
Separation	no precipitate
Electrical conductivity, ps/m	50 - 300

ADDITIVES;

Anti-oxidant, mg/l	8.5 - 24*
Metal deactivator, mg/l	5.7 max**
Corrosion inhibitor, mg/l	12.9 max

* Obligatory only if hydrogen treated

** On request

Source of Data; Reference [5] Pages 546 - 547

REFORMATE

Like aviation turbine kerosine, reformate is one of the intermediate products obtained during the 'cracking' of crude petroleum. The term cracking is applied to the phenomenon of decomposition of hydrocarbons or of petroleum fractions, by the action of heat (thermal cracking) or by heat in the presence of suitable catalysts (catalytic cracking). The products resulting from the decomposition are of a lower molecular weight than the feedstocks, and mainly olefinic in character.

The name reformate is derived from the process involved in the production of the samples - Reforming. The process involves hydrotreating the original products of cracking. In this case Naphtha is desirable if only to fulfil the demand for better knock - resisting gasolines. There are two main methods of reforming petroleum products. (a) Thermal reforming and (b) Catalytic reforming.

Thermal reforming is a pyrolytic process, in which the paraffins and naphthenes present in the virgin gasoline are dehydrogenated, converting them into olefins. In the mild thermal cracking conditions of the process, the boiling range of the gasoline is lowered, effecting

an additional improvement in the octane number, but the losses due to gases and polymer far formation are considerable. Advances in catalytic techniques rendered this obsolete.

The development of catalytic reforming processes stems from the demand for high purity aromatic hydrocarbons and high-octane gasoline. In the case of the samples under consideration in this project, Virgin naphthas are treated over molybdena-alumina catalysts in an atmosphere of hydrogen, in order to minimize the formation and deposition of carbon on the catalyst. Under the conditions of temperature and pressure used, aromatic hydrocarbons are formed by the dehydrogenation of cyclohexanes and by isomerization and dehydrogenation of cyclopentanes and paraffins.

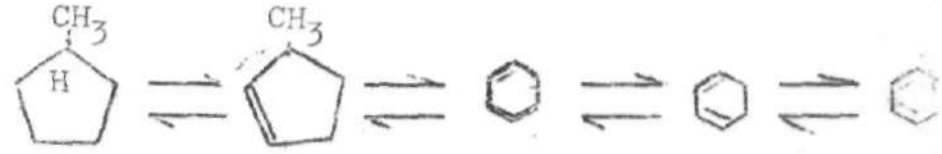
The catalysts that are being used are passivated by traces of olefins, sulphur and nitrogen compounds; they are permanently poisoned by small amounts of lead or arsenic. Because of this, the feedstocks are pretreated either by a mild sulphuric acid treatment or by a mild hydrogenation treatment over more rugged catalysts.

The fundamental reactions occuring in catalytic reforming are as follows;

(1) Dehydrogenation of six-membered ring naphthenes by the action of the platinum catalyst.



(2) Isomerization of alkylcyclopentanes to cyclohexanes. The first step of the reaction is the partial dehydrogenation of cyclopentane rings by the action of the platimum catalyst, forming a cyclic mono-olefin intermediate, followed by an isomerization step promoted by the acidic sites on the catalysts, with the formation of a mono-olezinic six-membered ring. This is further dehydrogenated to yield the corresponding benzenic compound.



(3) Conversion of paraffins into aromatic hydrocarbons. Paraffins with six carbon atoms in the chain, as a minimum configuration, are isomerized into a cyclopentane ring by the

action of the acidic catalyst (6) .

Secondary reactions also occur, depending on the severity of the conditions of operation, consisting mainly of catalytic cracking, with subsequent hydrogenation of the products formed. These secondary reactions account for the presence of low molecular weight paraffins in the reaction products.

In the even of a ban being imposed, by anti-pollution regulations, on the use of lead alkyls as octane number improvers, the process may well become the major source of high-octane components for motor gasolines.

ANALYTICAL METHODS

The most obvious way of studying the composition of various products of petroleum is to separate them by various methods of separation without altering the constituents. Some of these methods are distillation, crystallisation, thermal diffusion and chromatography. Many of these methods are capable of separating the hydrocarbons according to their type. The solubility and adsorbability, for instance, are largely influenced by the aromaticity of the hydrocarbon. In principle, both extraction and chromatography may be used for more or less sharp separation of petroleum fractions into non-aromatic, mono-aromatic, di-aromatic and Polyaromatic

fractions. In an analogous way, thermal diffusion separates, roughly, according to the compactness of the molecule; application of this method to a saturate fraction may lead to paraffinic, mono-naphthenic, di-naphthenic fractions.

By applying a deliberate sequence of methods of separation one suceeds, in favourable cases, in splitting up the oil into type concentrates which are fractions containing essentially molecles of the same type. From the type of the fractions and their magnitude, adequate unformation is obtained about the composition of the sample under investigation. Depending on the ultimate objective, type separation procedures may vary, from a simple chromatographic saturate-aromatic separation to vary elaborate combinations of different methods of separation [7] .

For the analysis of the heavier fractions, there is often a need for rapid and simple methods of a routine character, which do not give broad information but supply only limited data on the composition of the oil. To be more precise, it is often necessary to employ methods for estimating the chemical composition of hydrocarbon mixtures without separating them into type concentrates, and preferably, without any chemical or pre-treatment.

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance spectroscopy arises from the interaction between the nuclei of matter and electromagnetic forces when a sampel is subjected simultaneously to two magnetic fields, one stationary and the other varying at some radiofrequency H .

On the basis of quantum theory, nuclei are characterized by a spin quantum number I (which can have positive values $^{n}/2$, n can be, 0, 1, 2) and magnetic moment (μ). The spinning nucleus is electrically charged, and generates a magnetic field as it spins when a nucleus with I = $\frac{1}{2}$, such as a proton is placed in an applied magnetic field Ho, one orientation is aligned parallel to the direction of the field and is considered to be of low energy, and the other orientation is aligned against the direction of the field (anti-parallel) and is considered to be of high energy. Since these orientations correspond to two energy states, transitions can be induced between them. The absorption of energy is governed by the relationship.

$$h\nu = \Delta E$$

Where h is Planck's constant and v and E are the frequency and the energy, respectively. For nuclear

absorption, the frequency v which will effect the transition is given by $hv = \frac{\mu Ho}{I}$ or $v = \frac{\gamma Ho}{2\pi}$

Where γ is the gyromagnetic ratio for the nucleus. The absorption or emissium of the quantum of energy hv causes the nuclear magnet to turn over or "flip" from one orientation to the other [5] .

A precessing proton will only absorb energy from the radio frequency source if its precessional frequency is the same as the frequency of the radiofrequency beam; when this occurs, the nucleus and the radiofrequency beam are said to be in resonance, hence the term nuclear magnetic resonance. The only nuclei that exhibit the n.m.r. phenomenon are those for which the spin quantum number I is greater than 0; the spin quantum number I is associated with the mass number and atomic number of the nuclei as follows:

Mass number	Atomic number	Spin quantum
odd	odd or even	$\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$
even	even	0
even	odd	1, 2, 3.

As said earlier on, under the influence of an external magnetic field, a magnetic nucleus can take up different orientations with respect to that field; the number of possible orientations is given by (2I + 1).

The precessional frequency of all protons in the same external applied field is not the same and the precise value for any one proton depends on the chemical environment. Because the shift in frequency depended on chemical environment, the relative resonance frequency is referred to as the chemical shift. This forms the basis of n.m.r. as a tool in chemical analysis. The chemical shift is a ratio of the necessary change in field to the applied field hence is a dimensionless constant, usually designated by d, and specified in parts per million (ppm). To measure chemical shift an arbitrary comparison standard is adopted. For protons the universally accepted reference is tetramethyl silane, TMS. TMS is chosen because (i) it gives an intense sharp signal even at low concentrations. (ii) The signal arises on the n.m.r. spectrum well clear of most common organic protons.

(iii) The substance is chemically inert and has a low boiling point os that it is easily removed from a recoverable sample of a valuable organic compound;

(iv) It is soluble in most organic solvents, and can be added to the sample solution ($\simeq$ 1%) as an internal standard.

Another unit of chemical shift is Y (tau). it is defined as 10 - δ. Some of the factors that affect the values of chemical shift are (i) Electronegativity - shielding and deshielding.

(ii) Vander waals deshielding; in a rigid molecule it is possible for a proton to occupy a sterically h hindered position, and in consequence the election cloud of the hindering group will tend to repel, by electrostatic repulsion, the electron cloud surrounding the porton. The proton will be deshielded and appear at higher values than would be predicted in the absence of the effect.

(iii) Anisotropic effects; This effect is due to the manner in which π - electrons circulate under the influence of the applied field. The effect can lead to downfield shifts known as paramagnetic shifts or upfield shifts known as diamagnetic shifts.

Another feature that is often observed in NMR spetra is due to the interaction of the spin of a proton with that of another proton. (Vicinal protons). These protons having different chemical and magnetic environments, come to resonance at different positions in the n.m.r. spectrum; they do not give rise to single peaks (singlet)

but doublets. The separation between the lines of each doublet is equal; this spacing is called the couplying constant J. If a non-first-order spectrum is obtained at 60 mHz, a number of techiques can be applied to simplify the complexity and enable more accurate analyses of chemical shift and coupling constant data to be made. Such techniques include:

( ) Increased field strength; If a compound gives a complex n.m.r spectrum at 60 MHZ, it will normally be improved by recording at 100MHZ or 220MHZ, although the degree of improvement depends on the particular chemical shift differences and coupling constants involved.

(ii) Use of chemical-shift reagents.

(iii) Double Resonance [8] .

THEORY OF NMR SPECTROMETRY AS APPLIED TO THE ANALYSIS OF PETROLEUM PRODUCTS

NMR spectrometry as an instrument of chemical analysis is a relatively new development, the literature information on the use of the technique in petroleum analysis is comparatively scanty. However the few available publications on the use of the technique have shown how valuable it is in petroleum analysis. It has

also revealed the subtle deficiencies of the conventional analytical methods.

The application of nuclear magnetic resonance spectrometry to hydrocarbon - type determinations in petroleum products is based on the calculation of the relative number of carbon atoms classified as aromatic, olefinic, paraffinic and naphthenic. For example the 6, 7, 8 and 9 carbon atoms of benzene, toluene, xylene and ethyl benzene respectively are classified as aromatic. Isopentane, n-heptane and iso-octane have 5, 7 and 8 carbon atoms respectively and are classified as paraffinic. 2-methyl 2-butene has five carbon atoms classified as olefinic. This classification notwithstanding some carbon atoms can be erroneously counted as belonging to other categories because their peaks resonate in regions where other hydrocarbon types normally appear.

To a first order approximation, the hydrocarbon type composition is given by:

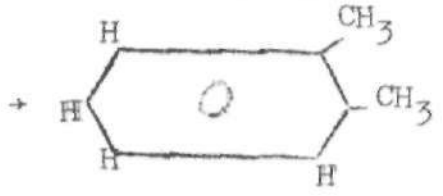
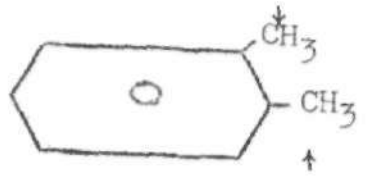
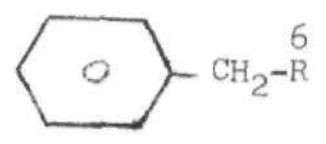
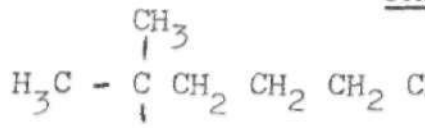
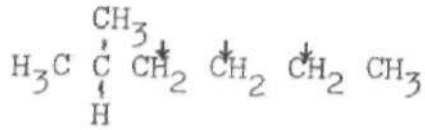
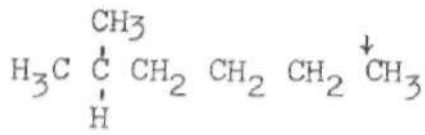
$$\% \text{ paraffinic} = \frac{Cp \times 100}{Ca + Cp + Co} \quad \ldots\ldots\ldots \quad (1)$$

$$\% \text{ olefin} = \frac{Co \times 100}{Ca + Cp + Co} \quad \ldots\ldots\ldots \quad (2)$$

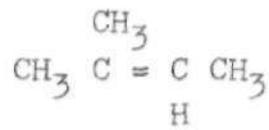
$$\% \text{ Aromatic} = \frac{Ca \times 100}{Ca = Cp + Co} \quad \ldots\ldots\ldots \quad (3)$$

(Ca, Cp and Co are carbon atoms for aromatic, paraffinic and olefinic hydrocarbons respectively).

The various organic functional groups encountered in NMR spectroscopy of petroleum products, as well as the spectral regions where these protons resonate, are shown in the table below.

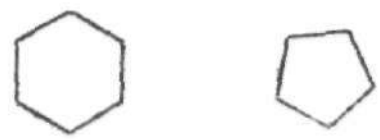
Proton Type	SPECTRAL REGION (ppm from TMS)	Integnal Designation
	6.5 - 80	A
 	6 2.0-3.0	C
PARAFFINS		
	1.5 - 2.0	D
	1.0 - 1.5	E
	0.6 - 1.0	F

OLEFINS



4.5 - 6.0 B

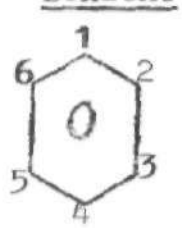
NAPHTHENES

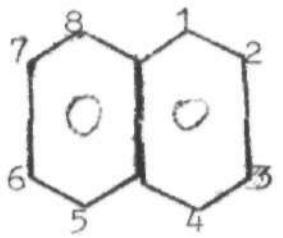


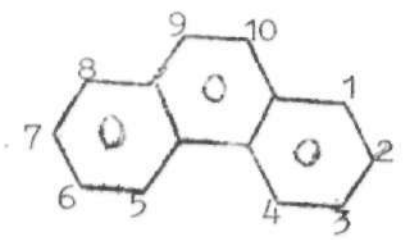
1.65 - 1.90 D

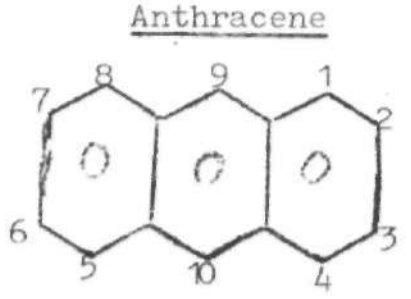
b carbons of the type Θ CH_2 - R are counted as methyl. This is because α - methyl are more numerous than α - methylene groups, the errors introduced are slight.

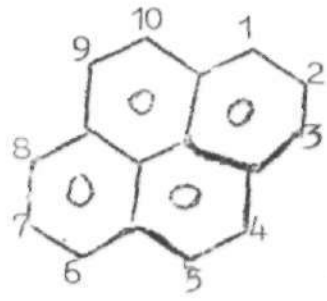
CHEMICAL SHIFTS OF METHYL GROUPS SUBSTITUTED ON AROMATIC RINGS

RING SYSTEM Benzene	Methyl substituent	Spectral Region ppm from TMS
	1	2.37
	1, 2	2.25
	1, 3	2.30
	1, 4	2.28
	1, 3, 5,	2,25
	1, 2, 4, 5.	2.15
	1, 2, 3, 4, 5,	2.13, 2.18
	1, 2, 3, 4, 5, €	2.17

Napthalene	Methyl substituent	Spectral Regi ppm from TMS
	1	2.65
	2	2.50
	1, 2	2.47, 2.57
	1, 5	2.70
	1, 6	2.50, 2.63
	2, 3	2.40
	2, 3, 6	2.38, 2.47

Phenanthrene		
	1	2.73
	2	2.53
	3	2.62
	9	2.72

Anthracene		
	2	2.55
	9	3.05
	9, 10	3.05



1	2.95
2	2.80
4	2.87

Based on the definition of aromatic, paraffinic and olefinic carbons and the chemical shifts associated with the protons of these carbons, equations (1) - (3) can be restructured as follows.

$$\% \text{ Aromatic} = \frac{(A + C/3)}{(A + C/3) + (D + E/2 + F/3) + B} \times 100 \quad \ldots (4)$$

$$\% \text{ Olefin} \quad \frac{B}{(A + C/3) + (D + E/2 + F/3) + B} \times 100 \quad \ldots (5)$$

$$\% \text{ Paraffin} \quad \frac{(D + E/2 + F/3)}{(A + C/3) + (D + E/2 + F/3) + B} \times 100 \quad \ldots (6)$$

Correction Factors

As stated earlier on, the analysis of petroleum products using proton NMR techniques has certain shortcomings. Some carbon atoms go "uncounted" because they are completely substituted and give no NMR signal. Other carbons are erroneously counted as

belonging to a given hydrocarbon class their protons resonate in regions of the NMR spectrum where other hydrocarbon types normally appear. The densities of light paraffins and aromatics are significantly different. Thus correction factors for these three effects will have to be taken into consideration when calculating the relative percentages of the hydrocarbon composites in the samples to make the results more accurate and reliable.

CORRECTIONS FOR DENSITY AND CARBON COUNT CORRECTIONS

A AROMATICS

The densities of aromatic hydrocarbons are significantly greater than those of light paraffins. Thus equation 4 gives a high estimate of the volume percent aromatic content, and the aromatic term $(A + C/3)$ in equations 4 through 6 needs to be multiplied by a constant to correct for the density difference. The weighted average density for each hydrocarbon class, defined as weighted average density.

$$= \frac{\sum_i \{\text{Vol. \% (i)}\} \{\text{density (i)}\}}{\sum_i \{\text{Vol. \% (i)}\}}$$

The weighted average density for the aromatics is 0.8732 g/ml and for the paraffins is 0.6612g/ml. The aromatic term (4 + C/3) must therefore be multiplied by 0.7572 (the ratio of 0.6612/0.8732) to correct for the density difference.

(B)

Not all of the aromatic carbon atoms are counted by NMR spectrometry. The ring carbons to which the methyl groups are attached to toluene and xylene, for example have no remaining hydrogen atome and give no NMR signal. The weighted average ratio is defined as $\frac{\text{carbons counted}}{\text{carbons present}}$.

$$= \frac{\Sigma_i\{\text{vol. \% (i)}\} \quad \frac{\text{no carbons counted i}}{\text{no carbons present}}}{\Sigma_i \{\text{Vol. \% (i)}\}}$$

The weighted ratio for the aromatics is 0.7835, The aromatic term (A + C/3) must be multiplied by 1/0.7835 = 1.2763 to correct for the uncounted carbon atoms. The overall constant to be applied to the aromatic term (A + C/3) is, therefore 0.7572 x 1.2763 = 0.97

Corrections for paraffins

No density corrections are necessary for the paraffins because the aromatic and olefinic components are both normalized to the paraffin density. The weighted average ratio (carbons counted/carbons present) is calculated to be 0.9831. Therefore, the paraffinic term ($D + E/2 + F$) in equations 4 through 6 must be multiplied by $1/0.9831 = 1.02$

Corrections for olefins

The weighted average density for the olefine is 0.6908 g/ml. The weighted ratio (carbons counted/carbons present) is calculated to be 0.2917 for the olefins. The overall constant to be applied to the definit term B is $(0.6612/0.6808) \times 1/0.2917 = 3.33$. from this high correction factor it becomes very important to determine the olefinic integral with high precision because olefins comprise only about 2% to 3% of the total raw integral for gasoline samples.

Another factor which would affect the reliability of the results is cross-resonance. Alkyl parts of olefins, for example, would resonate in the methine/naphthene region of 1.5 to 2.0 ppm methylene region of 1.0 - 1.5 ppm and methyl region of 0.6 to 0.10 ppm. This will result in low olefin volume percentage and high paraffinic percent

The greatest problem would arise in the 1.5 to 2.0 ppm region where methyl and methylene substituents attached to c = c groups resonate. Myers and colleagues corrected for this in gasolines by subtracting twice the integrated intensity of the signal occuring in this 1.5 to 2.0 ppm region. This correction was adopted in this work.

After taking into account all of these correction factors, equations 4 through 6 become:

$$\text{Aromatics, Vol. \%} = \frac{(A + C/3)\ 0.97 \times 10^2}{(A+C/3)0.97 + (D-2B+E/3)1.02 + 3.33} \quad \ldots\ldots (7)$$

$$\text{Paraffins, Vol. \%} = \frac{(D-2B+E/2+F/3)1.02 \times 10^2}{(A+C/3)0.97+(D-2B + E/2+F/3)1.02+3.33} \quad \ldots (8)$$

$$\text{Olefins, Vol. \%} = \frac{3.333 \times 10^2}{(A+C/3)0.97+(D-2B+E/2+F/3)1.02+3.33B} \quad \ldots (9)$$

A further source of error arises in the assignmen of the signal occurring in the 1.5 to 2.0 ppm. Methine groups of paraffins resonate between 1.5 and 2.00 ppm and $-CH_2-$ group of naphthenes resonate between 1.65 and 1.90 ppm. In assigning, the signal in the 1.5 to 2.0 ppm three assumptions could be made.

(1) That all the signals occuring here are due to methine proton resonance. This would result in a zero value for the naphthenes and very high values for the paraffins. This does not seem to be very reasonable.

(2) That all the signals here are due to proton resonance of $-CH_2-$ of naphthenic groups. This will result in two high values for naphthenes and low values for paraffins.

(3) That the signal is due to equal contribution by paraffin -CH- and naphthene $-CH_2-$ protons. This appears to be a more reasonable assumption than the other two extremes.

Based on assumption (3) above the % naphthene is calculated by dividing D by 4 and expressing the quotient as a percentage of total proton number, thus:

$$\% \text{ naphthene} = \frac{D/4 \times 100}{(4+C/3)0.97+(D/4-2B+E/2+F/3)1.02 + 3.3}$$

The hydrogen/carbon ratio can be determined using the equation.

$$\frac{A + B + C + D + E + F}{(A+C/3)1.28 + (D-23+E/2+F/3)1.02 + 3.42B}$$

clutter and his colleagues [13] have reviewed various theories which have been applied to pNMR and C-13 NMR analysis of petroleum fraccions. Using integrated intensities of the various proton signals, the parameters associated with an average molecule can be calculated.

Some of the parameters that can be calculated from pNMR are listed and defined in the table below.

AVERAGE PARAMETERS THAT CAN BE CALCULATED FOR PETROLEUM PRODUCTS

n = average number of carbon atoms per alkyl substituent.

f = average carbon-hydrogen weight ratio of akyl group.

% As = Percentage substitution of alkyl groups on non bridge aromatic ring carbons.

$\#C_A$ = average number of aromatic rings per average molecule.

RA = average number of aromatic rings per average molecule.

R_S = average number of alkyl substituents per average molecule.

R_N = average number of naphthenic rings per average molecule.

Fa = molar ratio of aromatic carbon to total carbon in sample.

BI = branchiness index

MW = Average molecular weight

$\%C_S$ = fraction of Naphthenic carbon.

r = number of naphthenic rings per substituent.

%C = fraction of non-bridge aromatic ring carbon

The use of proton magnetic resonance spectrometry has, among others, two very important features in the analysis of petroleum products:

(1) It provides direct and accurate measures of aromaticity or aromatic carbon as a fraction of the total carbon atoms.

(2) It provides a series of parameters or indices of an average molecule based entirely on the nuclear magnetic resonance spectrum and an excellent characterization of complex multicomponent fractions.

One of the most outstanding advantages of the NMR method is that it focuses on the carbon skeletons of rather complex structures of petroleum products. Thus, since C^{-13} is a quantitative measure of the

types of carbon atoms present in a given samples, it is possible to determine the true aromatic groups in the petroleum products [9] .

CHROMATOGRAPHY

Chromatography is based on the principle of interaction between several, usually two, different phases. In the "classic" column chromatographic adsorption analysis, the stationary phase (for example, activated carbon, alumina, silical gel or other fine-grained, solid porous substance with a large surface area) is distributed, as evenly as possible, inside a glass tube. The solution of the sample mixture (the mobile phase) is introduced at the top of the column, percolates through the stationary phase and Interacts with it, so that the different substances dissolved in the mobile phase are temporarily retained by the stationary phase. If the column is then washed with the solvent or with an appropriate sequence of different solvents, the adsorbed substances can again be collected in succession at the bottom of the column, so that they are often recovered as pure compounds.

The separated components can then be identified by appropriate detectors (e.g. f.i.d) or by other identification techniques [10] .

Chromatographic methods can be broadly classified according to the physical states of the moving and stationary phases; gas, liquid or solid. The mobile phase can be either a liquid or a gas. Thus, combination of a liquid stationary phase with gas or liquid moving phases gives, respectively, gas liquid (GLC) and liquid - liquid (LLC) chromatography. Combination of a solid stationary phase with gas or liquid moving phases gives, respectively, gas-solid, (GSC) and liquid-solid (LSC) chromatography. These chromatographic methods can be further classified according to the forces which hold the sample in the stationary phase. Thus, chromatography with liquid stationary phase generally involves simple dissolution of the sample, and these methods are referred to as partition methods. Chromatography with a solid stationary phase can either involve surface adsorption of unchanged molecules, or ion exchange of ionic molecules. Thus layer chromatography refers to a

stationary film phase in combination with a liquid mobile phase.

The table below lists the most popular absorbent used in column chromatography.

Absorbent	Chemical - Structure	Estimated Usage %	Surface properties	Application
Silica	$(Sio_2)_x$	80	Slightly - acidic	General purpose Adsorbent
Alumina	$(A/_2O_3)_x$	10	Slightly basic[a]	General purpose absorbent
Charcoal			Graphitized n'n-polar	Sample clean up
Florisit	Magnesia silica caprecipitate	2	Strongly acidic	General purpose adsorbent
Polyamides	-	3	Basic	Phenols and aro-natic nitro compounds.
Other (clay, kieselguhr, diatomaceous earth, celite etc).	-	5	Relatively non-polar	very-polar compounds

(a) Depends on method of precipitation.

Table adapted from C.F SIMPSON - practical

High performance liquid chromatography page 90.

CHAPTER TWO

MATERIALS AND METHODS

Nuclear Magnetic Resonance:

Varian T-60 Nuclear magnetic resonance spectrometer operating at 60 MHZ with a T - 6055 Perma - Lock. Time averaging computer made by Nicolet instruments corporation, U.S.A, model 1074 with the following accessories and plug - Ins.

1. Analogue to Digital coverter model SD 71A
2. NMR sweep control SW 74
3. Dio Single Beam 5103N Oscilloscope

Millipore filter Disc (Catalog No SFH - 10 - Stohler Isotope chemicals limited).

Disposable filter Disc (Catalog No SFD - 5 stohler Isotope chemicals limited).

The "Diamond" 5mm Thin wall NMR tubes (Catalog No S - 5).

Materials:

Fourty-four, 44, samples of reformate and twenty-eight, 28, samples of aviation turbine kerosene (later ordinary flammable kerosene) were collected from the Kaduna refinery on different dates between April and November, 1981 and labelled serially according to

dates of collection. The samples of reformate were labelled A_1, A_2, A_3, A_4 ..... A_{44} and those of aviation turbine kerosene B_1, B_2,..... B_{13}. B_{14}, B_{15}..... B_{28} were for those of ordinary flammable kerosene.

The ethylene glycol used as standard was supplied by the departmental store.

METHOD

To different weights of samples in NMR tube were added different weights of ethylene glycol (see table of Data) and 1% $^{v}/_{v}$ tetramethylsilane in carbon tetrachloride to give signal at chemical shift position zero. Thereafter the spectra were run at 250 seconds sweep time in the spectrometer under the best possible adjusted resolution and their respective integrals taken at 50 seconds sweep time. The calculation of molecular weights for the method is based on the principle enunciated by Sandar Barcza [14] . It consists of comparing the integrated intensities of an added standard and a recognizable peak or group of peaks of the unknown (sample) in a solution containing a known weight of

standard and (unknown sample). The molecular weight is then given by the following formula.

$$M = \frac{IsnWMs}{InsWs}$$

M = the molecular weight of the unknown (sample)

Is = the intensity of the standard

I = the intensity of the unknown (sample)

n = the number of protons in the recognizable peak

or a group of peaks of the unknown.

ns = the number of protons of the standard peak

W = the weight of the unknown (sample)

Ws = the weight of standard

Ms = the molecular weight of standard.

Attached over-leaf are specimens of the spectra and the designation of the various chemical shift positions according to Myers et al.

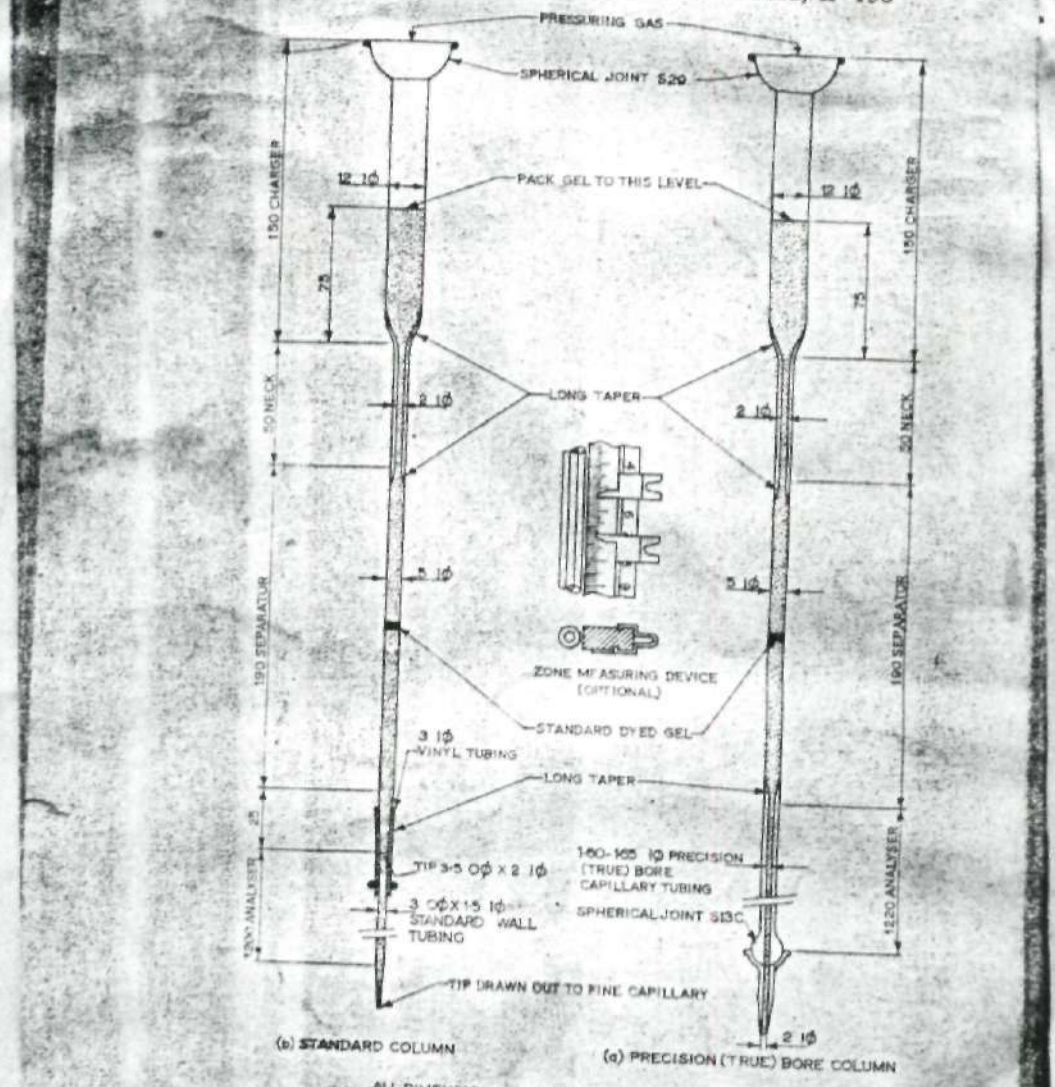


FIG 1

ADSORPTION COLUMNS

NOTE: Columns conforming to IP 156/65T may be used while stocks last.

FLUORESCENT INDICATOR ADSORPTION: (flA)

MATERIALS:

(a) Silica Gel ——— 100 to 200 mesh (150 - 75 m particle size) manufactured to ensure minimum olefin polymerization and to conform to sieve test requirements. Dried at 177°C for 3 hours, then transferred into the dessicator for protection from atmospheric moisture.

(b) Fluorescent indicator Dyed Gel ——— standard dyed gel, consisting of a mixture of recrystallised petrol Red AB4 and parrified portions of the olefin and aromatic dyes obtained by chromatographic adsorption.

(c) Isopropyl Alcohol

(d) Pressuring Gas ——— air (or nitrogen) delivered to the top of the column at pressures controllable over the range 0 to 15 Psig.

(e) Adsorption columns ——— With standard Wall tubing, made of glass and consisting of a danger section with a capillary neck, a separation section, and an analyser section.

(f) Zone - measuring device ——— the zones may be marked with a glass-writing pencil and the distances measured with a meter rule, with the analyser section

lying horizontally. Alternatively, the meter rule may be fastened adjacent to the column. This later technique was adopted.

(g) Ultra-Voilet light source ——— UV lamp was used at 366nm.

(h) Electric Vibrator —— for vibrating individual columns or the frame supporting multiple columns.

(i) Hypodermic syringe to inject the sample.

A photocopy of the set-up is attached.

METHOD:

Approximately 0.75ml of sample was introduced into the glass adsorption column packed with activated silica gel. A small layer of the silica gel contained a mixture of fluorescent dyes. When all the sample had been adsorbed on the gel, alcohol was added to desorb the sample and force it down the column. The hydrocarbons were separated according to their adsorption affinities into aromatics (including some diolefins and aromatics with olefinic side chains plus any sulphur, nitrogen, and oxygen compounds), olefins, and saturates. The fluorescent dyes were also separated selectively, with hydrocarbon types, to make the

boundaries at the aromatic, olefin, and saturate zones visible under ultraviolet light. The volume percentage of each hydrocarbon type was calculated from the length of each zone in the column.

$$\text{Aromatics, \% by vol} = \frac{La}{L} \times 100$$

$$\text{Olefins, \% by vol} = \frac{Lo}{L} \times 100$$

$$\text{Saturates, \% by vol} = \frac{Ls}{L} \times 100$$

where La = length of the aromatic zone in mm

Lo = length of the Olefin zone in mm

Ls = length of the saturate zone in mm and

L = sum of La + Lo + Ls.

Limitation of the Method:

The various percentages may not be the exact values because aromatic olefins, some diolefins, and compounds containing sulphur, nitorgen, or oxygen are determined as aromatics.

Owing to the serious difficulties encountered in removing the silica gel from the glass column, in our own laboratory, the FlA technique became impractical. As a result of this, we had to get the FlA results on aviation turbine kerosene from

the Nigerian National Petroleum Corporation (N.N.P.C) Kaduna. Similarly data on reformates were obtained from the refinery. The Nigerian National Petroleum corporation used the gas-liquid chromatographic technique to determine hydrocarbon-type composition of the reformate samples.

N.M.R. DATA FOR SAMPLES OF REFORMATE
CALCULATED ACCORDING TO EQUATION (7) TO(9)
ON PAGE 53

Sample Label	% Aromatic	% Olefine	% Paraffin
A_1	55.72	0.00	44.28
A_2	56.40	0.93	42.67
A_3	56.28	0.00	43.72
A_4	53.57	0.00	46.43
A_5	57.22	2.15	42.63
A_6	52.05	1.77	46.18
A_7	53.47	1.38	45.16
A_8	56.51	0.00	43.49
A_9	57.12	0.00	42.88
A_{10}	52.09	0.00	47.91
A_{11}	53.95	0.00	46.05
A_{12}	51.88	0.00	48.12
A_{13}	52.98	0.00	47.02
A_{14}	55.96	0.00	44.04
A_{15}	50.38	0.85	48.78
A_{16}	52.52	0.00	47.48
A_{17}	50.53	0.00	49.47
A_{18}	52.95	0.00	47.05
A_{19}	55.62	0.00	44.38
A_{20}	53.24	0.00	46.76

N.M.R. DATA FOR SAMPLES OF ATK

Sample Lable	% Aromatic	% Olefine	% Paraffin
A_{21}	53.35	0.00	46.65
A_{22}	55.13	0.00	44.87
A_{23}	54.85	0.00	45.15
A_{24}	54.45	0.00	45.55
A_{25}	53.44	1.46	45.10
A_{26}	52.28	2.17	45.55
A_{27}	54.31	1.69	44.00
A_{28}	55.22	0.00	44.73
A_{29}	51.79	0.00	48.21
A_{30}	52.24	0.00	47.76
A_{31}	51.67	0.00	48.33
A_{32}	53.36	0.00	46.64
A_{33}	54.58	0.00	45.42
A_{34}	51.60	0.00	48.40
A_{35}	52.74	2.05	45.21
A_{36}	54.07	1.81	44.12
A_{37}	52.19	0.00	47.81
A_{38}	52.19	0.00	47.81
A_{39}	50.46	3.61	45.93
A_{40}	51.50	0.00	48.50
A_{41}	50.71	0.00	49.29
A_{42}	51.57	3.13	45.30
A_{43}	52.68	1.48	45.84
A_{44}	51.64	0.00	48.36

N.N.P.C. DATA FOR SAMPLES OF REFORMATE III

Sample Label	% Aromatic	% Olefine	% Paraffin
A_2	51.80	0.00	48.80
A_4	57.20	0.00	42.80
A_5	58.00	0.00	42.00
A_6	59.20	0.00	40.80
A_7	62.50	0.00	37.50
A_{18}	66.60	0.00	34.40
A_{19}	64.90	0.00	35.10
A_{21}	61.00	0.00	39.00
A_{22}	67.60	0.00	32.40
A_{23}	60.50	0.00	39.50
A_{24}	62.20	0.00	37.80
A_{25}	68.00	0.00	32.00

N.M.R. DATA FOR SAMPLES OF ATK IV

Sample Label	% Aromatic	% Olefin	% Paraffin
B_1	9.70	5.17	85.13
B_2	12.79	0.00	87.21
B_3	11.62	0.80	87.58
B_4	10.08	8.30	81.61
B_5	9.85	0.00	90.15
B_6	10.85	0.00	89.15
B_7	9.25	3.18	87.57
B_8	8.66	4.78	86.56
B_9	8.15	0.52	91.33
B_{10}	12.70	0.00	87.30
B_{11}	14.19	0.00	85,81
B_{12}	12.33	0.00	87.67
B_{13}	16.16	0.00	83.84
B_{14}	11.85	0.00	88.15
B_{15}	13.22	0.00	86.78
B_{16}	11.66	0.00	88.34
B_{17}	12.13	0.00	87.87
B_{18}	12.69	0.00	87.31
B_{19}	13.34	0.00	86.66
B_{20}	10,58	0.00	89.42

N.M.R. DATA FOR SAMPLES OF ATK

Sample Label	% Aromatic	% Olefin	% Paraffin
B_{21}	11.03	3.07	85.90
B_{22}	14.27	0.00	85.73
B_{23}	17.80	4.20	78.00
B_{24}	11.02	4.87	84.11
B_{25}	11.36	3.08	85.50
B_{26}	11.51	0.00	88.49
B_{27}	15.37	6.46	78.17
B_{28}	14.90	0.00	85.10

N.N.P.C DATA FOR SAMPLES OF ATK

Sample Label	% Aromatic	% Olefin	% Paraffin
B_1	17.80	1.20	81.00
B_2	16.90	0.50	82.60
B_5	18.30	1.00	80.70
B_7	19.40	1.00	79.60
B_{13}	15.80	0.80	83.40

REFORMATE VI

Sample Label	H:C	Sample Labels	H:C
A_1	1.60	A_{23}	1.61
A_2	1.59	A_{24}	1.56
A_3	1.44	A_{25}	1.51
A_4	1.61	A_{26}	1.75
A_5	1.58	A_{27}	1.58
A_6	1.36	A_{28}	1.44
A_7	1.63	A_{29}	1.59
A_8	1.60	A_{30}	1.66
A_9	1.57	A_{31}	1.68
A_{10}	1.68	A_{32}	1.57
A_{11}	1.57	A_{33}	1.56
A_{12}	1.56	A_{34}	1.56
A_{13}	1.56	A_{35}	1.44
A_{14}	1.61	A_{36}	1.59
A_{15}	1.65	A_{37}	1.50
A_{16}	1.51	A_{38}	1.50
A_{17}	1.56	A_{39}	1.58
A_{18}	1.61	A_{40}	1.58
A_{19}	1.57	A_{41}	1.57
A_{20}	1.60	A_{42}	1.56
A_{21}	1.61	A_{43}	1.82
A_{22}	1.61	A_{44}	1.57

AVIATION TURBINE KEROSENE VII

Sample Label	H:C	Sample Label	H:C
B_1	2.22	B_{15}	2.15
B_2	2.25	B_{16}	2.22
B_3	2.27	B_{17}	2.20
B_4	2.21	B_{18}	2.11
B_5	2.05	B_{19}	1.95
B_6	2.17	B_{20}	2.25
B_7	2.19	B_{21}	2.21
B_8	2.20	B_{22}	2.11
B_9	2.22	B_{23}	2.04
B_{10}	2.13	B_{24}	2.15
B_{11}	2.13	B_{25}	2.15
B_{12}	2.15	B_{26}	2.15
B_{13}	1.95	B_{27}	2.11
B_{14}	2.13	B_{28}	2.10

Sample Label	WEIGHTS		SAMPLE INTERALS								Standard Integrals		
	Sample	Standard	A	B	C	D	E	F	Total	Paraffin	1	2	Total
A_{21}	0.1895	0.2695	32.50	0.00	36.00	4.00	40.00	39.00	151.50		1.00	2.00	3.00
A_{22}	0:3163	0.3546	28.00	0.00	31.00	2.00	32.00	35.00	128.00		6.00	11.00	17.00
A_{23}	0.2132	0.1167	26.50	0.00	31.00	3.00	29.00	34.00	123.50		5.00	11.00	16.00
A_{24}	0.3038	0.3513	37.00	o.00	36.00	5.00	40.00	42.00	160.00		8.00	15.00	23.00
A_{25}	0.3210	0.3710	30.00	0.33	34.00	2.00	39.00	37.00	132.00		8.00	17.00	25.00
A_{26}	0.2594	0.2345	25.50	3.00	30.00	4.00	28.00	29.00	119.50		25.00	48.00	73.00
A_{27}	0.3632	0.2711	32.00	0.40	36.50	4.00	39.00	34.00	145.90		11.00	21.00	32.00
A_{28}	0.2555	0.1461	30.50	0.00	35.00	3.00	35.00	38.00	126.50		0.80	2.00	2.80
A_{29}	0.3924	0.2332	29.50	0.00	31.00	4.00	41.00	32.50	139.50		1.50	3.00	4.50
A_{30}	0.3041	0.3327	25.50	0.00	27.50	5.00	30.00	39.00	136.50		1.00	2.00	3.00
A_{31}	0.3076	0.1746	25.00	0.00	41.00	6.00	30.50	40;00	142.50		2.00	4.00	6.00
A_{32}	0.3322	0.3618	30.00	0.00	35.00	5.00	40.00	31.00	141.00		1.00	2.00	3.00
A_{33}	0;3756	0.2810	32.00	0.00	36.00	5.00	38.50	32.50	143.50		1.00	2.00	3.00
A_{34}	0.3135	0.3239	28.00	0.00	36.00	6.00	37.00	3.00	133.00		0.50	1.00	1.50
A_{35}	0.3607	0.4309	35.50	0.50	32.00	4.00	40.00	39.00	151.00		4.00	8.00	12.00
A_{36}	0.3939	0.3640	30.00	0.40	35.00	4.50	35.00	34.00	137.00		6.00	12.00	18.00
A_{37}	0.3756	0.2810	32.00	0.00	36.00	5.00	38.00	43.00	143.00		1.00	2.00	3.00
A_{38}	0.2243	0.2050	31.00	0.00	39.00	5.00	38.00	43.00	156.00		2.00	3.50	5.50
A_{39}	0.3710	0.3455	26.00	0.75	30.00	5.00	36.00	29.00	126.75		12.50	25.00	37.50
A_{40}	0.2444	0.2831	28.50	0.00	32.00	6.00	31.00	36.00	133.50		0.93	1.67	2.60
A_{41}	0.3801	0.2947	31.50	0.00	34.00	7.00	39.00	37.00	148.50		1.00	2.00	3.00
A_{42}	0.3593	0.4269	31.50	0.75	33.00	6.00	41.00	33.00	145.25		1.50	4.50	6.00
A_{43}	0.3593	0.4269	31.00	0.35	35.00	5.00	40.00	33.00	144.35		1.50	3.00	4.50
A_{44}	0.3314	0.3854	29.00	0.00	32.00	6.00	38.00	31.00	136.00		1.50	3.00	4.50

REFORMATE VIII

Sample Label	Weights 'Sample	Weights 'Standard	A	B	C	D	E	F	'Total	'Paraffin	Standard Integrals 1	Standard Integrals 2	Standard Integrals Total
A_1	0.1455	0.2818	24.00	1.50	25.50	2.00	20.00	30.00	101.50		10.50	22.00	32.50
A_2	0.1898	0.2368	22.00	0.00	24.00	3.00	26.00	26.00	97.00		8.80	18.00	26.50
A_3	0.1547	0.2595	22.00	0.00	22.00	3.00	20.00	26.00	94.00		8.50	18.00	26.50
A_4	0.1478	0.1689	22.00	0.00	26.00	4.00	23.00	30.00	104.00		4.00	9.00	13.00
A_5	0.2016	0.1519	34.00	0.50	35.00	3.50	30.00	40.00	142.50		6.00	12.50	18.50
A_6	0.2927	0.1517	30.00	0.40	31.00	4.00	39.00	34.00	118.50		5.50	12.00	17.50
A_7	0.2689	0.1588	29.50	0.50	34.00	3.00	35.00	38.00	139.50		5.00	11.00	16.00
A_8	0.2575	0.0900	40.00	0.00	43.00	3.00	46.00	45.00	177.00		9.00	18.00	27.80
A_9	0.2733	0.2148	49.00	0.00	47.00	5.00	45.00	59.00	202.00		34.00	69.00	103.00
A_{10}	0.1819	0.1516	32.50	0.00	46.00	4.00	43.00	49.00	174.50		2.00	4.00	4.00
A_{11}	0.1605	0.2235	33.00	0.00	35.00	5.00	38;50	36.50	147.50		1.25	3.00	4.25
A_{12}	0.2452	0.2164	30.00	0.00	33.00	8.00	33.00	35.00	139.00		1.00	2.00	3.00
A_{13}	0.1389	0.1615	31.00	0.00	32.00	7.00	31.00	38.00	139.00		1.50	3.00	4.50
A_{14}	0.2036	0.1573	35.00	0.00	37.00	5.00	37.00	44.00	158.50		1.67	2.33	4.00
A_{15}	0.2452	0.2020	30.00	0.00	32.50	4.00	36.00	48.00	150.50		1.60	3.20	4.70
A_{16}	0.2537	0.2570	30.00	0.00	31.00	6.00	34.00	35.00	136.00		1.00	2.30	3.30
A_{17}	0.2526	0.2289	26.50	0.00	29.00	9.00	26.00	35.00	125,50		1.00	2.00	3.00
A_{18}	0.2447	0.3167	26.50	0.00	27.00	3.00	30.00	36.00	122.50		1.00	2.00	3.00
A_{19}	0.2597	0.3567	35.00	0.00	36.00	3.00	40.00	38.00	152.00		1.00	2.00	3.00
A_{20}	0.1798	0.2280	32.50	0.00	36.00	4.00	40.00	39.50	152.00		2.00	4.00	6.00

TABLE XI

ATK

SAMPLE LABEL	WEIGHTS		SAMPLE INTEGRALS							STANDARD INTEGRALS		
	SAMPLE	STANDARD	A	B	C	D	E	F	TOTAL	1	2	TOTAL
B_1	0.1576	0.1648	3.00	0.75	5.50	0.00	55.00	43.00	106.00	3.00	7.50	10.50
B_2	0.1507	0.2748	3.50	0.00	8.00	0.00	48.00	48.00	107.50	1.00	3.00	4.00
B_3	0.1957	0.1164	2.0	0.08	6.00	0.00	35.00	34.00	77.00	6.00	13.50	19.50
B_4	0.2450	0.2364	2.50	1.00	5.00	0.00	45.50	34.00	87.00	6.00	14.00	20.00
B_5	0.2911	0.2754	3.00	0.00	6.00	0.00	56.50	66.500	102.50	2.50	6.00	8.50
B_6	0.2773	0.1424	2.50	0.00	6.00	0.00	58.00	42.00	108.50	1.00	2.00	3.00
B_7	0.3446	0.1110	3.00	0.50	6.00	0.00	64.00	42.00	115.00	12.50	24.50	37.00
B_8	0.3223	0.1250	4.00	0.75	2.00	0.00	63.00	43.00	114.00	1.00	2.00	3.00
B_9	0.2333	0.1973	3,00	0.08	4.00	0.00	62.00	46.00	115.00	12.00	24.00	36.00
B_{10}	0.1378	0.1932	3.50	0.00	10.00	0.00	64.00	38.00	115.50	0.75	2.25	3.00
B_{11}	0.2840	0.332	4.75	0.00	10.00	0.00	63.00	45.00	122.75	1.00	2.00	3.00
B_{12}	0.1898	0.1691	3.75	0.00	9.50	0.00	64.50	43.50	121.25	1.00	2.00	3.00
B_{13}	0.2723	0.2564	6.50	0.00	7.00	0.00	65.50	40.00	107.50	0.75	2.00	2.75
B_{14}	0.3028	0.1717	3.50	0.00	10.00	0.00	70.00	40.00	123.50	1.50	3.00	4.50

SAMPLE LABEL	SAMPLE	STANDARD	A	B	C	D	E	F	TOTAL	1	2	TOTAL
B_{15}	0.3005	0.3868	4.50	0.00	9.00	0.00	61.00	69.00	123.50	0.75	2.00	2.75
B_{16}	0.3432	0.1444	3.00	0.00	10.50	0.00	59.00	52.00	124.50	1.00	3.00	4.00
B_{17}	0.3929	0.2144	2.50	0.00	10.00	0.00	53.00	41.00	106.50	1.50	3.50	5.00
B_{18}	0.3654	0.1904	3.75	0.00	9.00	0.00	63.00	38.00	113.75	1.75	4.00	4.75
B_{19}	0.6070	0.4816	3.50	0.00	9.00	0.00	52.00	44.00	108.50	1.00	2.00	3.00
B_{20}	0.4004	0.3087	2.00	0.00	9.00	0.00	50.00	45.00	106.50	1.00	2.00	3.00
B_{21}	0.3940	0.2597	3.00	0.50	9.50	0.00	58.00	53.00	124.00	5.00	11.00	16.00
B_{22}	0.3678	0.4277	5.00	0.00	11.00	0.00	69.00	45.00	130.00	0.50	2.50	3.00
B_{23}	0.2422	0.2193	5.40	0.60	11.00	0.00	52.00	35.00	103.00	0.60	2.20	2.80
B_{24}	0.2060	0.4560	2.50	0.75	10.00	0.00	61.00	40.00	114.25	4.00	8.00	12.00
B_{25}	0.2367	0.2406	3.00	0.50	10.00	0.00	64.00	43.00	120.50	2.50	5.50	8.00
B_{26}	0.3545	0.3242	3.00	0.00	9.50	0.00	63.50	40.00	116.00	1.50	2.50	4.00
B_{27}	0.3587	0.5898	4.50	1.00	11.00	0.00	53.00	45.00	114.50	3.50	7.00	10.50
B_{28}	0.2709	0.2718	4.00	0.00	10.00	0.00	57.00	34.00	105.00	0.75	1.00	1.75

CHAPTER THREE

RESULTS AND DISCUSSION

The results of the chromatographic and nuclear magnetic resonance analyses of the petroleum fractions are shown in the tables of results. A look at the nuclear magnetic resonance results shows that for the refomate samples the mean aromatic percentage volume is 54.54±1.54; Olefin 1.21 ± 2.46; and Paraffin 44.27 ± 3.31. While the chromatographic method gives the values 61.33 ± 4.83; 0.00 ± 0.00 and 38.66 ± 4.71 as percentage volume composition for aromatic, Olefin and paraffin respectively.

Summary of the results for reformate:

Variable	Mean	Standard deviation
% Aromatic^{n}	54.54	1.54
% Olefin^{n}	1.21	2.46
% Paraffin^{n}	44.27	3.31
% Aromatic^{f}	61.23	4.83
% Olefin^{f}	0.00	0.00
% Paraffin	38.66	4.71

The superscripts n and f denote the methods used in the analyses. n stands for nuclear magnetic resonance and f for fluorescent indicator adsorption.

Multiple regression analyses were carried out, using the statistical package for the social sciences (SPSS), version 6.50, April 1, 1976 Computer programme. This gave the following pair-wise correlation coefficients between nuclear magnetic resonance data and the corresponding chromatigrophic data.

% Olefin^{n}	0.3293				
% Paraffin^{n}	-0.7115	-0.8976			
% Aromatic^{f}	0.3628	-0.6021	0.6105		
% Olefin^{f}	99.0000	99.0000	99.0000	99.0000	
% Paraffin^{f}	0.3845	0.6292	-0.6418	-0.9970	99.000
	% Aromatic^{n}	%Olefin^{n}	%Paraffin	%Aromatic^{f}	%Olefi

Aviation Turbine Kerosene:

The average percentage volume of aromatic in the aviation kerosene using the nuclear magnetic resonance method, is 11.55$\pm$ 2.93, Olefin 1.67 $\pm$ 2.39 and paraffin 86.78 $\pm$ 2.43. The chromatographic analysis of aviation turbine kerosene indicate that the Percentage volume of aromatic component is 17.64 $\pm$ 1.37 while percentage volume of the olefinic and paraffinic components are 0.90 $\pm$ 0.26 and 81.46 $\pm$ 1.53 respectively.

SUMMARY OF THE RESULTS FOR AVIATION TURBINE KEROSENE

Variable	Mean	Standard deviation
% Aromatic^{n}	11.55	2.93
% Olefin^{n}	1.57	2.39
% Paraffin^{n}	86.78	2.43
% Aromatic^{f}	17.64	1.37
% Olefin^{f}	0.90	0.26
% Paraffin^{f}	81.46	1.53

As stated earlier on, the superscripts n and f denote the method employed in the analysis, n stands for NMR and f for FIA.

Multiple regression analysis were also carried out, as for the reformate samples. This gave the following pair correlation coefficients between NMR data and the corresponding chromatographic data.

% Olefin^{n}	-0.6014				
% Paraffin	-0.6156	-0.2593			
% Aromatic^{f}	-0.9261	0.4905	0.6358		
% Olefin^{f}	+0.6161	0.7382	0.0168	0.5316	
% Paraffin^{f}	0.9315	-0.5679	-0.5732	-0.9892	-0.6503
	%Aromatic^{n}	%Olefin^{n}	%Paraffin^{n}	%aromatic^{f}	%olefin

Overall the data highlight a remarkable difference in the olefin values obtained by the two methods. In the reformate samples the chromatographic methods indicate that olefins are not present while the nuclear magnetic resonance gives a value of 1.21 ± 2.46. In aviation turbine kerosene nuclear magnetic resonance indicates a value of 0.90 ± 0.26. This is perhaps a suggestive evidence that the nuclear magnetic resonance method is more sensitive than the fluorescent indicator adsorption method. For the determination of olefins. The fact that olefins were detected only in few samples and values obtained for them very disparate might account for the rather high value of standard deviations. This implies that the olefin results are not statistically reliable.

As regard the correlation coefficients, the negative sign which appeared in some of the values indicates the existence of inverse proportionality between the two sets of data. For those coefficients which have the positive sign, it shows that there is a direct relationship between the sets of data. The numerical size of the correlation coefficient is thus a measure of the strength of the relation between both sets of data. So far, the comparative analysis done

is based on an implicit but faulty assumption that both the nuclear magnetic resonance method and chromatographic method operate on the same principle. In the chromatographic technique, there is a molecular separation followed by the detection and analysis of molecules. The NMR method, on the other hand, observes the carbon or hydrogen on an atom-by-atom basis, and is therefore classified as an "atomic" analysis. To compare the results obtained from these two methods one must convert the contents of aromatic, olefinic and saturate carbon and hydrogen atoms for the NMR analyses to a molecular basis.

It is not possible to identify from chemical shift data the derivatives of benzene that are potent carcinogens due to poor resulution of the aromatic region of the spectra obtained.

The results obtained for the actual molecular weights of the samples are inconsistent. It may be because it was not possible to obtain a homogenous solution of the sample and standard as recommended by Sandor and Barcza. Much as it would have been interesting to test this idea, time constraints posed a severe limitation on this work. It would be a worthwhile venture in future to repeat the experiment

with an easily homogenized standard. Hexamethyl-cyclotrisiloxane may serve the purpose. However, the carbon-hydrogen ratio calculated, a measure of the degree of saturation and unsaturation, indicate that for every atom of carbon, there are, on average, two of hydrogen.

In conclusion, because of the specificity of the chemical shifts associated with various functional groups, nuclear magnetic spectranetry has proved to be a very effective tool for the analysis of chemical samples and resolution of mixtures into their components. It has also proved to be more economical than most test techniques in time, manpower and chemicals.

In petroleum analysis, it is a fast technique for the identification of the generic hydrocarbon type into paraffin, clefins and animatics. But the resolution of paraffin into cyclic and non-cyclic classes or into normal and Iso-paraffins is not readily attainable from chemical shift data because of overlap between the $-CH_2-$ signals of cycloparaffins at 1.65 - 1.90 ppm. This makes identification and estimation of the alkane types in petroleum smaples irreproducible and unreliable.

Thus in addition to the traditional chromatographic method of analysing petroleum products for hydrocarbon-type, nuclear magnetic resonance spectrometry with the appropriate correction factors can be used even when non-volatile products —— semi-solids and solids are involved. Here lies the beauty of the NMR method.

REFERENCES CITED

1. Yen, T.F., The role of trace metals in petroleum Second edition, Inc., New York, 1968 pp.1-5.

2. Anthony Standen, Encyclopaedia of Chemical Technology, 2nd edition Interscience publishers Inc. New York, 1963, Vol. 15, pp.150 - 175.

3. Ojanomare, A. Determination of Hydrocarbon-Type Composition of Some Petroleum Products available in Samaru Markets Using NMR and chromatographic methods. Unpublished M.Sc. Thesis: Ahmadu Bello University, December 1980 pp.40-45.

4. Allison, J.P. Criteria for quality of Petroleum products 2nd Edition, West-port, 1967 pp.97 - 103.

5. Forster Snell and Lislie Fhre. Encyclopaedia of Industrial Chemical Analysis, Interscience publishers, New York; 1966, Vol. 14, Pages 207 - 215.

6. Cowper, A.B. Textbook of petroleum technology 2nd edition Inc, New York, 1963, 1964 pp.198 - 206.

7. Meites, L. Handbook of Analytical Chemistry 3rd edition, Willie Interscience publishers, New York, 1969 pp.27-30

8. William Kamp, Organic spectroscopy 2nd edition, Avi. Inc, Westport. Connecticut, 1978 pp. 76; 120

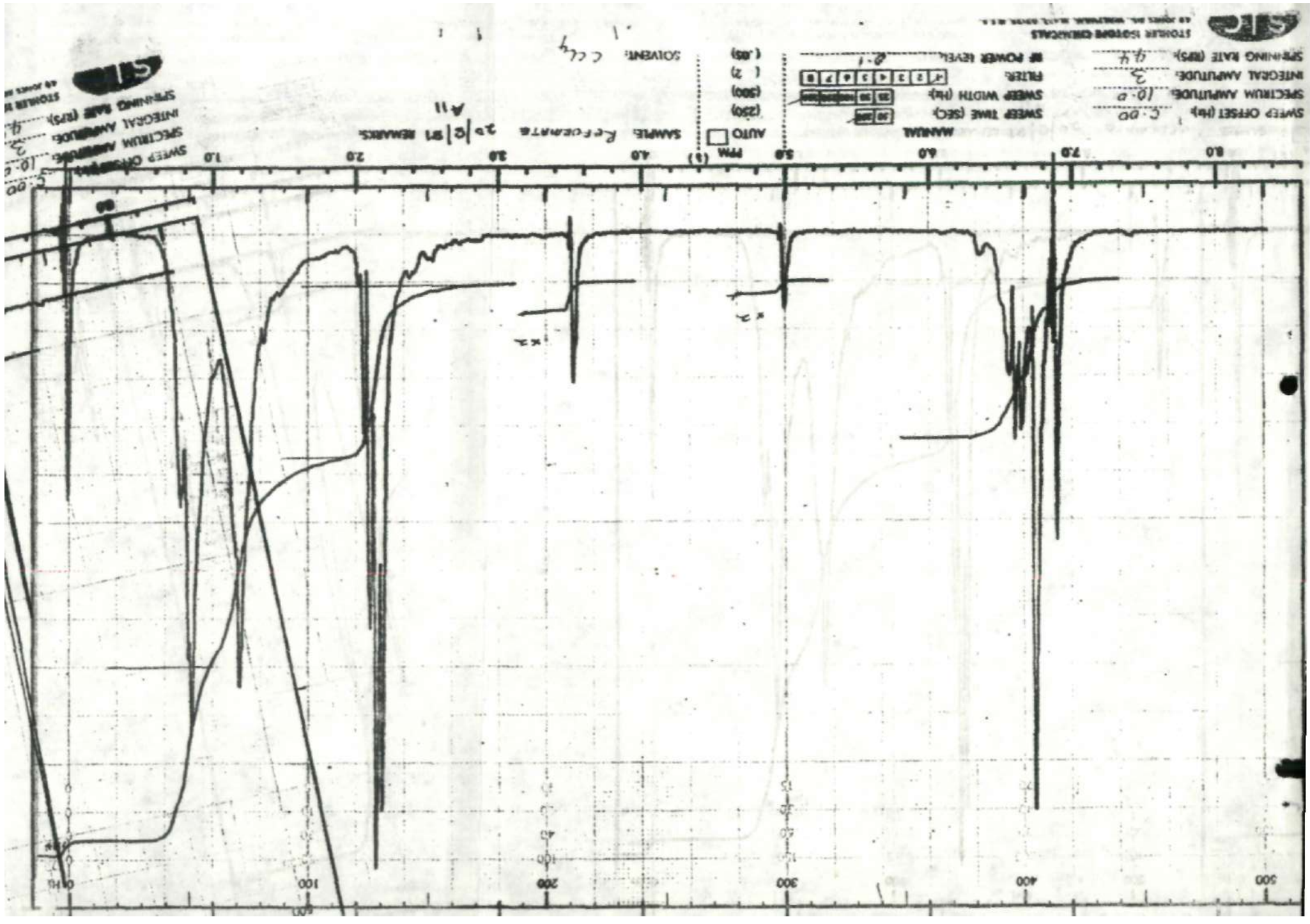
9. Ihionu Peters. NMR analysis of some petroleum products, (Unpublished M.Sc. Thesis. Ahmadu Bello University, Zaria March 1978 pp. 67 - 73

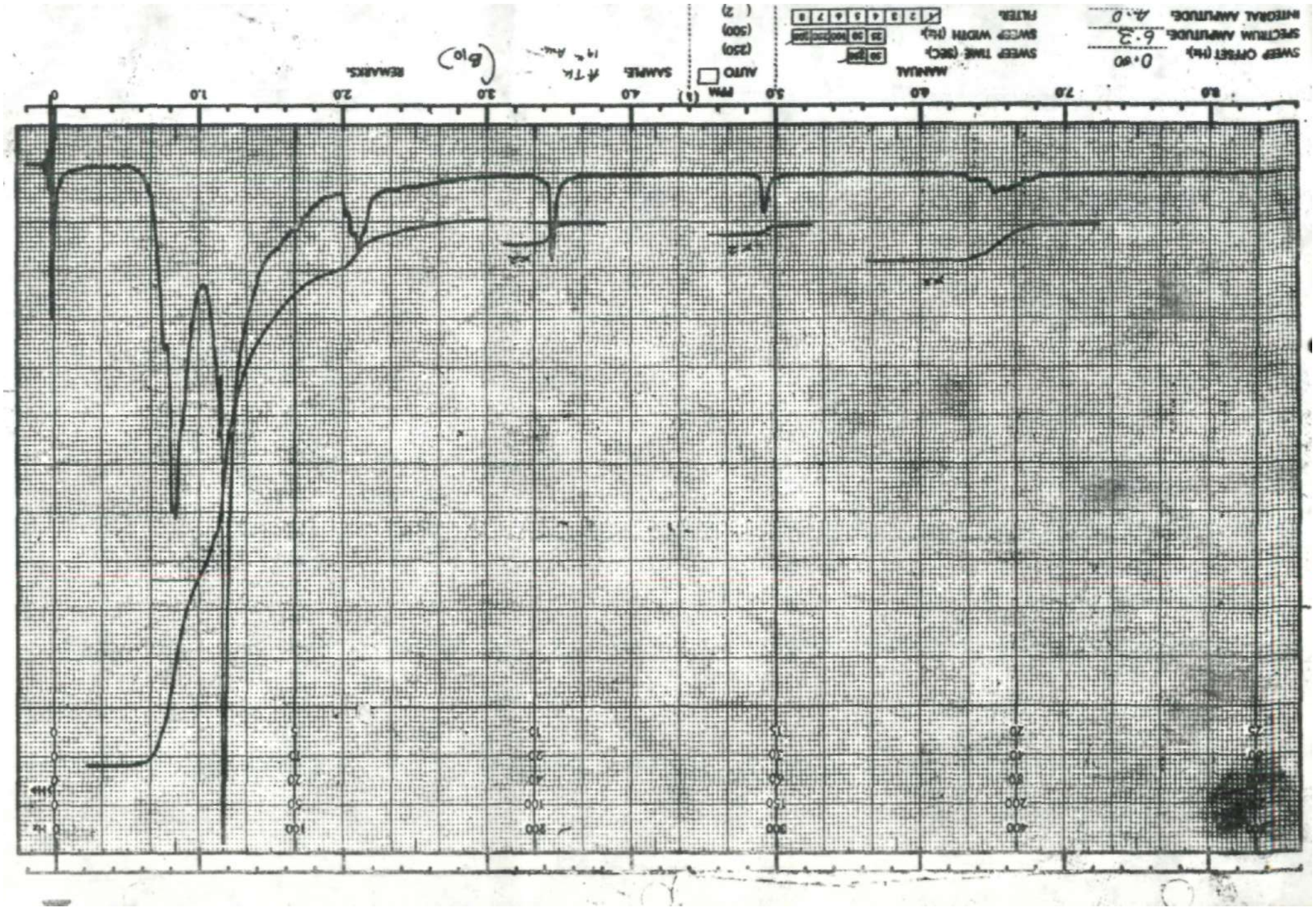
10. Galeng. W. Ewing, Instrumental Methods of Chemical Analysis 3rd edition, Will, New York, 1979 pp 357 - 365

11. Ozubiko, R.S., Ruberto, D.G. and Dovies, E.I., Anal. Chem. 44, pp 170 - 174 (1972)

12. Jewell, D.W, D.M. Clugston and Edward Faurimaky., Anal. Chem., 53 pp 183 - 187 (1981)

13. Barcza, S.J. org. Chem. 28, pp 1914 - 1915 (1963)


SWEEP OFFSET (Hz)
SPECTRUM AMPLITUDE
INTEGRAL AMPLITUDE
SPINNING RATE (RPS)
SWEEP TIME (SEC)
SWEEP WIDTH (Hz)
FILTER
RF POWER LEVEL
MANUAL
AUTO
SAMPLE
SOLVENT
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
100
200
300
400
500


SWEEP OFFSET (Hz) 0.60
SPECTRUM AMPLITUDE 6.3
INTEGRAL AMPLITUDE 4.0
MANUAL
SWEEP TIME (SEC)
SWEEP WIDTH (Hz)
FILTER
AUTO
(250)
(500)
(2)
RPM (1)
SAMPLE
REMARKS
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0 Hz
100
200
300
400
0
5
10
15
20
0
10
20
30
40
0
20
40
60
80
0
50
100
150
200
0
100
200
300
400
0
25
50
75
100