Chemical Aspects of Thermal Instability in Jet Fuels From Saudi-Arabian Crude Oils

by

Alam Nizami

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMISTRY

May, 1993

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Nizami, Alam, M.S.

King Fahd University of Petroleum and Minerals (Saudi Arabia), 1993

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COLLEGE OF GRADUATE STUDIES

This thesis written by

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under the direction of his Thesis Advisor and approved by his Thesis Committee, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE IN CHEMISTRY

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26-6-93

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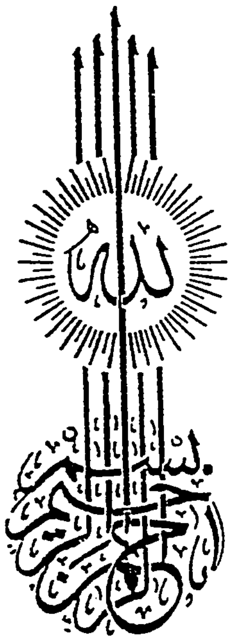
الله
بسم الله الرحمن الرحيم

Dedicated

to

my Parents, Brothers, Sisters
and Wife.

Acknowledgment

> In the name of Allah, Most Gracious, Most Merciful. Read in the name of thy Lord and Cherisher, Who created. Created man from a {leech-like} clot. Read and thy Lord is Most Bountiful. He Who taught {the use of} the pen. Taught man that which he knew not. Nay, but man doth transgress all bounds. In that he looketh upon himself as self-sufficient. verily, to thy Lord is the return {of all}.
>
> (The Holy Quran, surah 96)

First and foremost, all praise to Allah, the Almighty, Who gave me the courage and patience to carry out this work. I am happy to have had a chance to glorify His name in the sincerest way through this small accomplishment and ask Him to accept my efforts. May He guide us and the whole community to the right path (Aameen).

Acknowledgment is due to King Fahd University of Petroleum and Minerals for providing support to this work.

I wish to express my sense of indebtedness and gratitude to my thesis advisor Prof. Mohammed Farhat Ali for his scholarly supervision, invaluable guidance and the countless hours of attention throughout the course of this work. His priceless suggestions made this work interesting and learning for me. He was always kind, understanding and sympathetic to me. Working with him was indeed a wonderful and learning experience which I thoroughly enjoyed.

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All my thanks go to my parents who have always been a consistent source of inspiration and light for me and most particularly in my present venture. Also to my brother, sisters and wife for their deep and affectionate interest in my work.

Finally, I would like to place on record my heart felt thanks to all of my friends and colleagues who were a constant source of encouragement and help.

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خلاصة الألروضة

اسم الطالب : عالم نظامي
عنوان المدراسة : السمات الكيميائية للاثبات الحراري للوقود
النفاث من الخام السعودي
حقلة التخصص : الكيمياء
تاريخ الدرجة : مايو ١٩٩٣ م

أجريت تجارب الثبات المعجلة والعادية للمخزون باستعمال نماذج مركبات نيتروجينية لمشتقات بترولية من الوقود النفاث والديكان العادي تشير إلى أن معدل تكون الثفل يعتمد على معالم وطبيعة المحلول المستخدم ، ظروف التخزين ، الهواء ، ارتفاع الحرارة ، الأكسجين المذاب والضوء وكلها تعجل معدل تكون الثفل . ولكن بازالة الأكسجين المذاب من قاع الوقود النفاث والديكان العادي دل على تقليل المعدل . تؤثر الأحماض الكربواوكسيليكيه على التعجيل بينما مضادات الفينول توحي بتكون الثفل مع نيتروجين يحتوي على مركبات وقوة نشاط التفاعل ظاهرة وتبين تأكسد واضح لتكثف مركبات نيتروجينية ذاتياً . تم تصنيف الثفل بتحليل العناصر وبالأشعة تحت الحمراء ومطياف الكتلة ومعدل انخفاض أو/سى يثبت أن التاكسد هو سمة اللاثبات الحراري للوقود النفاث . تم تعريف حوالي ٢٥ نوعاً من أنواع مختلف المركبات من متوسط خصائص ثفل ٥ر٢ ثنائي ميثيل البيرول . كما استخدم جهاز الرنين النووي المغناطيسي لتصنيف متوسط سمك تركيبة جزيئات عينات تحوي كميات متباينة من وحدات برافينية وأرومية وذلك بمساعدة برمجة الكمبيوتر .

ماجستير في العلوم
جامعة الملك فهد للبترول والمعادن
الظهران ٣١٢٦١
مايو ١٩٩٣ م

THESIS ABSTRACT

NAME OF STUDENT	*: ALAM NIZAMI*
TITLE OF STUDY	*: CHEMICAL ASPECTS OF THERMAL INSTABILITY IN JET FUELS FROM SAUDI ARABIAN CRUDE OILS*
MAJOR FIELD	*: CHEMISTRY*
DATE OF DEGREE	*: MAY, 1993*

Accelerated and ambient storage stability tests were conducted using model nitrogen compounds in petroleum derived jet-A fuel and n-decane, indicating that the rate of sediment formation was dependent on the structural features of nitrogen compounds, the nature of diluent employed and storage conditions. Air, increased temperature, dissolved oxygen and light all strongly accelerate the sediment formation rate but the removal of dissolved oxygen from the base fuel (jet A fuel and n-decane) significantly reduced the rate. Carboxylic acids act as an accelerator while phenols inhibitor toward sediment formation with nitrogen containing compounds. The reaction has a low apparent activation energy and appears to involve a free radical oxidative self condensation of nitrogen compounds. Characterization of sediment was made by elemental analysis, infrared and mass spectroscopy. The lower O/C ratios of sediment proved that the oxidation is a key aspect of jet fuel thermal instability. Approximately 25 different types of possible compounds were identified from average properties of 2,5-dimethylpyrrole sediments. Nuclear magnetic resonance spectroscopies were applied to the characterization of average molecular structural parameters of various fuel samples containing varying amounts of parrafinic and aromatic constituents with the help of computer programming.

MASTER OF SCIENCE DEGREE

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DHAHRAN, SAUDI ARABIA

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CHAPTER 1

INTRODUCTION

1.1. GENERAL INTRODUCTION

Petroleum is a natural, yellow-to-black, thick, flammable liquid hydrocarbon mixture found principally beneath the earth's surface and processed for fractions including natural gas, gasoline, naphtha, kerosene, fuel and lubricating oils, paraffin wax and a wide variety of derived products. It is also called crude oil. It is a non-homogenous mixture of substances of which the main constituents are hydrocarbons along with various quantities of sulfur, oxygen and nitrogen containing compounds and also small amounts of metallic compounds such as sodium, potassium, copper, and zinc. Other compounds exist in very minute quantities, measured as ppm are metallo-organic substances such as iron, vanadium, arsenic, and nickel. Petroleum differs widely among themselves in their physical properties due to variations in the ratios of hydrocarbon types present.

Aviation turbine fuels (jet fuel) are manufactured predominately from straight run kerosene, or kerosene/naphtha blends in the case of wide cut fuel, from the atmospheric distillation of crude oil. Straight run kerosene from some sweet crudes will meet all the requirements of the jet fuel specification without further refinery processing, but for the majority of crudes, the kerosene fraction will contain trace constituents such as nitrogen, oxygen and sulfur containing compounds, which have to be removed before using the kerosene as jet fuel. This is normally effected by hydrotreating (hydrofining) or by a chemical sweetening process (e.g. Merox). Hydrocracking processes have been introduced recently; they produce high quality kerosene fractions ideal for jet fuel blending.

Commercial jet fuels are considered as more than ninety-eight percent of hydrocarbon mixtures of paraffins, naphthenes, aromatics (where paraffinic and naphthenic molecules predominate) and traces of nitrogen, oxygen and sulfur containing organic compounds, which amount to only a few tenths of one percent. However, these trace impurities together with paraffins, naphthenes and aromatics exert a significant deleterious effect on the stability of the fuel.

Fuel stability, or more appropriately fuel instability, is a measure of the general chemical reactivity of a fuel; it is specifically the sediment or deposit forming tendency associated with exposure of fuel to long term storage at ambient temperature (commonly referred to as storage instability) or to short term stress at higher temperature (commonly referred to as thermal instability). Both storage instability and thermal instability are responsible for the deterioration of fuel.

One of the most difficult substance to remove from crude oil is nitrogen. The nitrogen compounds can affect the storage stability of hydrocarbon fuels in a variety of ways depending upon the type and concentration of nitrogen compounds, the chemical make up of basic fuel systems, the presence of other trace materials and condition of the storage. The higher the nitrogen contents of fuel, the poorer its stability. The problem is becoming more serious because of the increased use of lower grade petroleum which is higher in nitrogen content. It was found that the compounds giving the highest amount of sediment are of the pyrrole types, while some amine also afforded measurable sediments [1]. When the nitrogen compounds, both basic and non basic, are present in trace quantities they can act as catalysts toward sediment formation [2-3]. This study also proves that nitrogen compounds are deleterious to the storage stability of the fuels.

One of the most significant and continuing problems with liquid fuel is the formation of solids, now termed filterable sediments which can plug nozzles, filters, and coat heat exchanger surfaces and otherwise degrade engine performance. Deposit formation in the fuels can be triggered by a free radical autoxidation reaction. The rate of reactions proposed in autoxidation schemes are dependent on hydrocarbon structure, heteroatom concentration, oxygen concentration and temperature. Catalysts and free radical inhibitors can materially alter both the rate of oxidation and reaction pathways. The detailed mechanism of hydroperoxide decomposition is complicated since free radicals are sensitive to solvent, structural and stereo electronic effects.

A variety of spectroscopic techniques such as proton and carbon-13 nuclear magnetic resonance spectroscopy, infra-red spectroscopy, and x-ray photoelectron spectroscopy (ESCA) have been applied to the analysis of 2,5-dimethylpyrrole (DMP) promoted sediments [4]. The use of HPLC, GC and GC-MS has also been reported for the analysis of sediment and compound types present in liquid fuels [5]. The elemental analysis, infra-red spectroscopy, solid state ^{13}C spectroscopy and mass spectroscopy were employed for the characterization of sediment obtained from model nitrogen compounds [6]. Electron spin resonance spectroscopy was used to characterize organic radicals such as dimethylpyrrole radical and the concentration of unpaired electrons in the fuel [7]. Generally three different types of technique, such as elemental analysis, fourier transform infrared and mass spectrometry have been applied for the characterization of sediments.

Fuels are complex mixture of hydrocarbon with some N, O, and S containing compounds. However, it is not possible to perform complete identification and quantitative determination of all components of fuels. Several analytical schemes have been devised for characterization of fuel in terms of average molecular structural parameters. In the previous studies of hydrocarbon mixture, the fuels were separated into four fractions, namely, saturates, monoaromatics, diaromatics and polyaromatics by chromatographic techniques. After that each fraction was analyzed by ^{1}H and ^{13}C NMR spectroscopy.

1.2. NEED FOR THE STUDY

Nitrogen compounds are one of the important constituents of petroleum and desired materials. When these compounds are present in petroleum stocks, even in trace amounts, they cause serious problems through formation of sediment or gum. This indicates that the presence of nitrogen compounds in petroleum is undesirable. Therefore removal of these compounds from petroleum derived fuel is of prime importance.

The general area of fuel instability is complex and the reactions that contribute to instability are not fully understood. It is generally recognized that the presence of reactive compounds such as pyrrole, indole and carboxylic acid in liquid fuels are also a major cause of instability and ease of degradation which usually results in the formation of insoluble sediments. Thus, instability is attributed to the formation of auto-oxidation products of hydrocarbon components with nitrogen and oxygen compounds.

Nitrogen containing aromatics have long been associated with storage instability in a variety of fuels [8-9], yet present knowledge regarding the chemistry of their autoxidation is very limited, particularly in complex fuel media. One approach to studying this problem involves the examination of model nitrogen compounds as dopant in stable base fuel. Fuel dopant studies are useful in screening nitrogen compound classes for potential activity.

The chemistry involved in sediment formation in fuel is not simple and presently there is only a limited understanding of the mechanism involved. A chain mechanism involving free radical initiated oxidation of the reactive fuel components by molecular oxygen has been accepted as a fundamental mechanism in sediment formation. More recently, a second oxidation mechanism, electron transfer initiated oxidation (ETIO), has been suggested for autoxidation of pyrroles [10]. Although considerable progress has been made toward uncovering various mechanisms and reactions involved in sediment formation, further elucidation of mechanisms, reactions and determination of their relative importance in fuels of varied composition are necessary for a better understanding of fuel degradation processes and for devising more effective means of preventing fuel degradation.

Consequently, the determination of the route of auto-oxidation of nitrogen compounds is an important one. It is needed because nitrogen compounds are present in very low amounts in petroleum derived fuel. It is also needed because all classes of nitrogen compounds are not deleterious, for example, some amines have been observed to be deleterious while others are not. The challenge is further highlighted by our restricted knowledge of fuel containing nitrogen and oxygen type compounds.

1.3. OBJECTIVE OF THIS STUDY

Jet fuel is a complex mixture of hydrocarbons having small amounts of nitrogen, oxygen and sulfur containing compounds. During storage these compounds react with oxygen or with one another to produce higher molecular weight solid materials commonly called sediment. These sediments are deleterious to fuel quality and tend to foul fuel lines, filters, valves and injection nozzles. For decades, studies have been conducted in an effort to define the reactive compounds, the composition of the sediments produced and mechanisms involved. A systematic research effort investigated the effects of nitrogen compounds and nitrogen compounds in combination with oxygen compounds in jet fuels on sediment formation. It was found that oxygen was required to produce deposit in fuels. The process proceeds through mainly monomer oxidation and coupling of these oxidation products to form polymers. Nitrogen compounds concentrate in sediment because they are more reactive in oxidation and condensation reactions and probably less soluble in fuel.

The elucidation of chemical structure of nitrogen compounds present in sediment is of great importance. It is also a challenge to the analysts because these compounds are present in low quantity in most of the crude oils and occur in complex mixture. The research project will consists of the following steps.

a. A literature survey to determine the state of prior knowledge with respect to the influence of nitrogen compounds on fuel instability.

b. A determination of the magnitude of the sedimentation problem, especially with respect to the nitrogen compound types which promote it in the locally produced jet and kerosene fuels.

c. A study of the effect of light, storage conditions and the presence of compounds containing heteroatoms such as nitrogen and oxygen on the jet fuels.

d. Investigation of the composition, structure and mechanism of the formation of sediments (deposits).

e. A computer program was developed for the calculation of average molecular structural parameters of various types of fuel samples by using elemental analysis, proton NMR and carbon - 13 NMR spectroscopy.

The work will be started using a simplified model system with n-decane as the representative liquid fuel. Nitrogen compounds will be added alone or together with organic acids and phenols at a concentration level within the limits expected to be present in liquid fuels produced in local refineries. The individual effects of the addition of these compounds on sedimentation will be studied by C, H, N and O elemental analyses and by FTIR and mass spectral methods.

CHAPTER 2

LITERATURE REVIEW

2.1. NITROGEN CONTENT OF PETROLEUM

The total nitrogen content of petroleum is low and generally falls in the range of 0.1 - 0.9 percent. Early work indicates that some crudes may contain upto 2.0 percent nitrogen. However, crude oils with trace amounts of nitrogen are not uncommon.

In the comparison of liquid fuels, shale liquids will be higher in oxygen, nitrogen, aromatic and olefinic contents than petroleum based fuels. Coal liquids will be higher in oxygen content but lower in nitrogen content than shale liquids, and extremely high in aromatics with somewhat lower olefinic content [11]. Both coal and shale liquids are much higher in nitrogen content than crude oil [11-13]. The finished synfuels after catalytic denitrogenation can be expected to contain significantly higher levels of nitrogen contents than their petroleum derived counterparts [14-15].

There is an approximate relationship between carbon residue and nitrogen contents of most crude oils. The higher the carbon residue, the higher will be the nitrogen content of that oil.

2.2. ROLE OF NITROGEN COMPOUNDS ON SEDIMENT FORMATION

Nitrogen is one of the most difficult substances to remove from the crude oils. Several fundamental studies have shown that the formation of sediments, gums and color bodies in several liquid fuel are due to the presence of heteroatoamic (N, O and S) compounds. Instability is commonly associated with the formation of insoluble sediments (precipitate that can be isolated by filtration from an aged fuel), gum (precipitate that adheres to the side of the flask after the aged fuel has been removed), color bodies and by the accumulation of hydroperoxides. Heteroatomic reactive compounds lead to the degradation of fuel which usually results in the formation of surface deposits (both fuel system varnishes and particulate matter), gums and insoluble sediments [6, 16-18]. These degradation products can plug fuel storage and transfer filters, foul engine components and heat exchangers and thus reduce the efficiency of engine and fuel systems. The most reactive and hence most deleterious among the heterocyclic compounds were found to be alkylated heterocyclic nitrogen compounds. Other nitrogen compounds and most of those containing oxygen and sulfur generally do not possess any sediment forming properties, but some times, these compounds promote either positive or negative synergistic effects with the sediment forming compounds. A highly deleterious compound which has been studied extensively is 2,5-dimethylpyrrole [6, 16-17].

Several earlier preliminary studies have clearly established the importance of nitrogen compounds in sediment formation. These preliminary studies suggest that the mode of sediment formation depends on the nature of crude petroleum, method of processing and the storage condition.

Frankenfeld and Taylor [1] have shown that nitrogen compounds, especially of pyrrole types (pyrrole and indole derivatives), promoted sediment and sludge formation in JP - 5 jet fuel stored under ambient conditions, but other nitrogen compounds such as anilines, pyridines, alkylamines, quinoline and isoquinoline did not produce any appreciable sediment. The sediment formation is strongly influenced by light, acids and by weather oxygen is present in the fuel.

Li and Li [7] studied the storage stability of jet fuels, where fuel degradation was monitored in the presence of specific nitrogen containing compounds such as 2,5-dimethyl pyrrole(DMP) & N-methylpyrrole (NMP), various sulfur containing compounds, metal phthalocyanines (Fe(II)Pc & Cu(II)Pc) and mixtures of these at various temperatures. The degradation products obtained in the presence of FePc and CuPc indicate that CuPc interacts with petroleum JP - 5 with added DMP more strongly than does FePc.

Taylor [19] studied the effects of various nitrogen compounds such as indole, 2-ethyl pyridine and 2,5-dimethylpyrrole on deposition in a wing tank simulator. He found that the rate of deposit formation increases four to ten fold when added at 1000 ppm nitrogen level. This effect was tested in the range of 93 to 149°C, and it was found that the rate of sedimentation was more pronounced at higher temperatures.

Worstell et al., [20] have shown that the accelerated storage tests (a cover slip gravimetric test) at 120°C of Jet - A, a commercial aviation fuel, with small amounts (1 - 10 ppm N) of substituted pyridines, quinolines, indoles and pyrroles, resulted in significant sediment formation. Worstell et al., [2] have reported that the deposit formation in diesel fuel Texaco D 454 was similarly accelerated by the addition of the same compounds (same test condition). These investigators have reported a very interesting correlation between the basicity of nitrogen compounds (within a given compound class) and the amount of sediment formation, i.e. the more basic the dopant, the more sediment that formed. Worstell et al., [2] also reported that the absolute deposit rates was significantly higher in the diesel fuel than in the jet - A fuel. This conclusion was also supported by Mushrush et al., [21] through the interactive effects of fuel component with nitrogen heterocycles which are responsible for promoting sediment formation.

Mushrush et al., [21] conducted gravimetric stability tests at 43°C and 80°C respectively using DMP and 3-methylindole (MI) as model nitrogen heterocyclic dopant in shale derived diesel fuel. Potential interactive effects have been found for these two model nitrogen heterocycles in the presence of second model dopant tert-butylhydroperoxide (TBHP). Both nitrogen dopants formed large amounts of insoluble sediments and exhibited positive interactive effects. Mushrush et al. [22] performed the same test with same nitrogen dopant (DMP and 3-MI) at 80°C but co-dopants were hexanoic acid, acetic acid, dodecylbenzene sulfonic acid and p-toluene sulfonic acid. Both nitrogen dopant produced large amounts of insoluble sediment and exhibited positive interactive effects with dodecylbenzene sulfonic acids being the most active sediment promoter co-dopant.

Nowack et al. [23] used the jet fuel thermal oxidation tester (JFTOT) to examine the nitrogen content, particularly in relationship to the production of jet fuels from shale oil. Using a tube deposit rating (TDR), the heater tube breakpoint was improved only 10°C by reducing the total nitrogen contents from 954 to 123 ppm, but the filter breakpoint was raised from 232 to 279°C. Addition of 50 ppm of 5-ethyl-2-methyl pyridine to a nitrogen free shale jet fuel did not cause failure on the JFTOT test at 260°C (TDR 4). Doping with 50 ppm of 2,5-dimethylpyrrole gave a TDR of 25 and severe filter plugging at the same temperature.

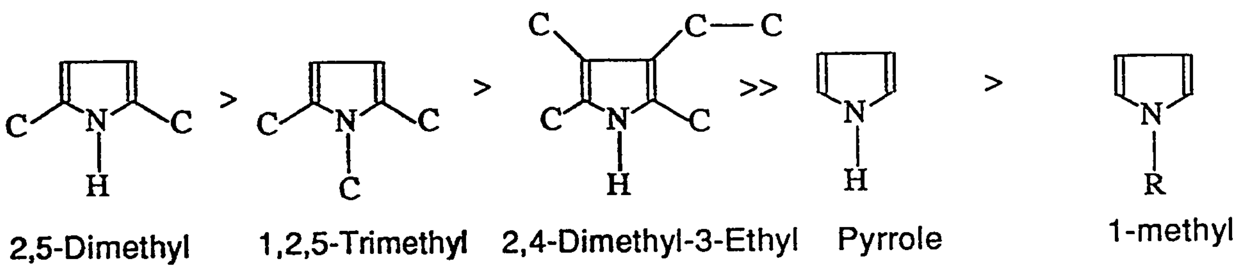
Antoine [24] determined the JFTOT breakpoint for a jet A fuel with and without added nitrogen compounds. At doping levels of 0.01 to 0.1 %, pyrrole dropped the breakpoint about 40°C and indole 20°C. A general trend is that breakpoint decreases as nitrogen concentration increases, and almost all samples with more than 0.01% N failed the specification limit of 260°C.

Frankenfeld et al., [6, 25] shown that the structure of nitrogen compounds has a large effect on the sediment formation under accelerated storage conditions. Some compounds react nearly quantitatively in 4 - 6 months while others show little or no tendency to form sediment even after prolonged storage at elevated temperatures. These observations are consistent with earlier reports [3, 26-27], all of which showed that certain nitrogen heterocycles such as some pyrroles and indoles were especially prone to form sediment while other compounds were much less reactive. However, no concerted attempt has been made to correlate the chemical structure and reactivity toward sediment formation under fuel storage conditions. Both Frankenfeld et al. [6] and Cooney et al. [28] have suggested that the rate of sediment formation was dependent on the structural features of nitrogen compounds, the nature of diluent employed and the storage condition. Scheme 1 clearly explains the correlation between the chemical structure of nitrogen compounds and sediment formation tendencies on the basis of reactivities of the compounds. The reactivity decreases from left to right and from top to bottom (i.e. from series A > B > C).

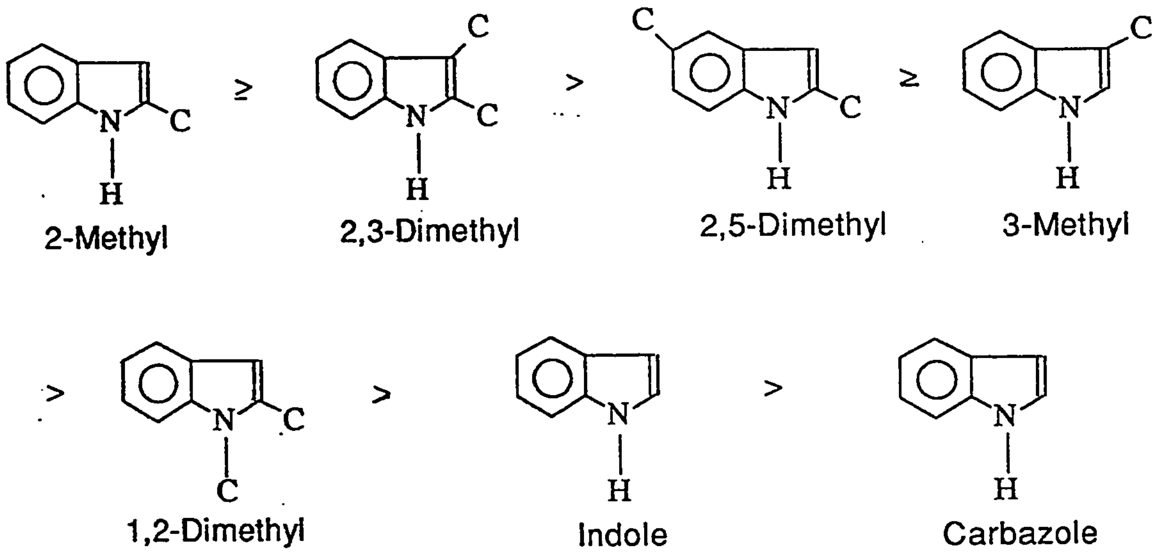
Cooney et al., (28) have suggested that the cover slip test does not have real predictive significance for ambient fuel storage, for various reasons. This most likely accounts for the differences between heterocycle structure/reactivity

SCHEME 1

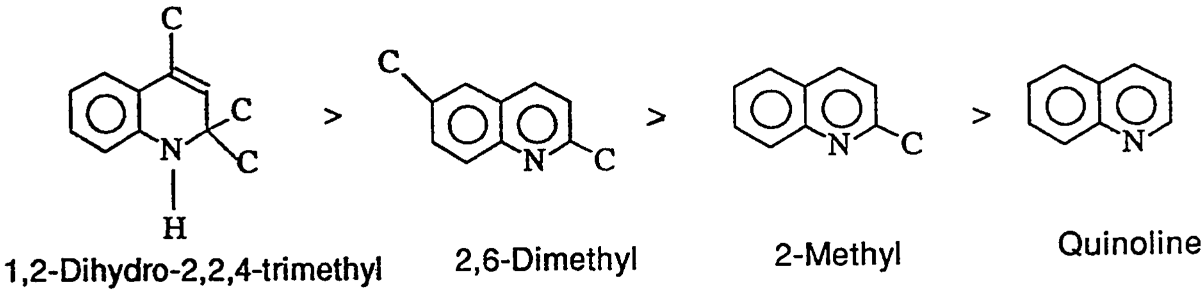
A. PYRROLES



B. INDOLES



C. QUINOLINES



Influence of structure on reactivity of various nitrogen heterocycles toward sediment formation. Rectivity decreases from top to bottom (group A>B>C) and from left to right.

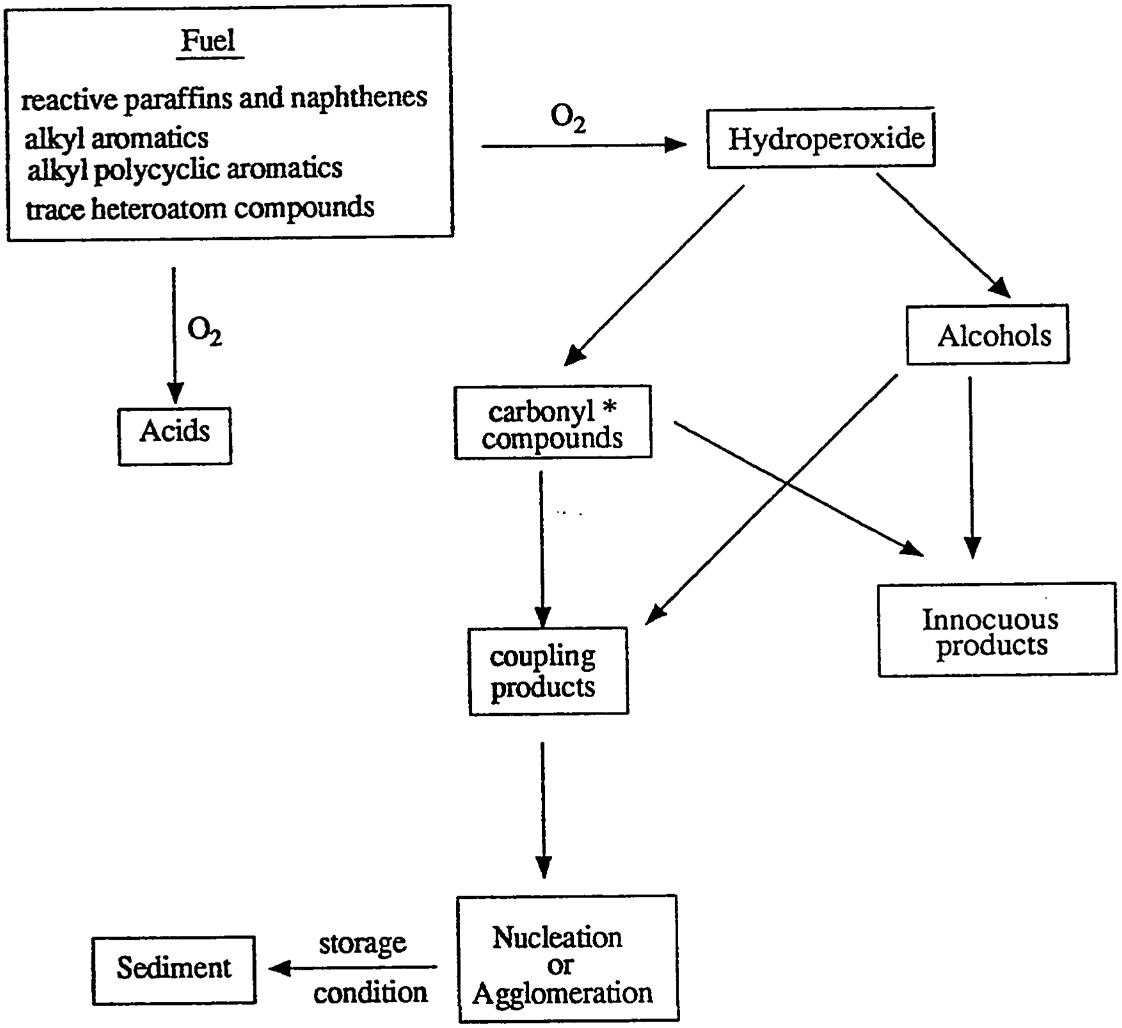
reported by [6, 28] versus [2, 20].

Loeffer and Li [29] studied the extent of deposit formation by adding specific nitrogen and sulfur containing compounds to upgrade coal derived liquids, petroleum derived JP - 5 jet and diesel fuels. Of the nitrogen compound tested, the ability to promote sediment formation is much greater for 2,5-dimethylpyrrole (DMP) than 2,6-dimethylquinoline (DMQ). Of the sulfur containing compounds tested, the decreasing order is thiophenol, tetrathiophene and thiophene. Synergistic effects between DMP and thiophene were observed.

Taylor and Frankenfeld [30] proposed an excellent fuel sediment / gum formation process, shown in Scheme 2. It will be assumed that the hypothesis depicted in Scheme 2 is correct since it agrees with the conclusions of an other investigator [31]. Beaver & Gilmore [32] used the Scheme 2 hypothesis and conceptualized oxidative degradation of fuels, to explain (i) reactive molecules intimately involved in the oxidative storage instability of middle distillates, (ii) types of chemical reaction mechanisms involved in oxidative phase of sediment and gum formation and (iii) postulate the chemical mechanism of stabilizers (additives) operation.

Cooney et al., [33] examined the autoxidation of two model nitrogen compounds i.e. 2,5-dimethylpyrrole and 3-methylindole, in shale derived diesel fuel in the presence of tert-butylhydroperoxide; they showed that the hydroperoxide interacted in a strong synergistic fashion with their nitrogen heterocyclic to lead to the formation of significant amounts of sediment and gum.

SCHEME 2



* Molecules whose molecular weight has increased due to chemical reactions such as esterification or electrophilic aromatic substitution.

Working hypothesis for the oxidative degradation of a diesel fuel during ambient storage

Pedley et al., [34] have reported that alkylindoles are among the main components of the sediment produced by two petroleum derived catalytically cracked diesel fuels after 16 months of ambient storage condition (-5 to 25°C). Two stability improving additives (containing antioxidant, dispersant and metal deactivators) were found to have little effect on the ambient storage stability and also to have a deleterious effect on fuel filterability characteristics. Pedley et al., [35] have identified two classes of compounds instead of one in sediment produced during ambient storage of above mentioned catalytically cracked diesel fuels. These compounds were indolylphenalenes and bis indolyl phenalenes which consist of indole ring systems linked to the phenalene ring system. These indole-phenalene derivatives react with acids to form polar and highly colored insoluble sediments.

Pedley et al., [36] reported that the chemical structures observed in the sediment precursors consisted of indole linked to phenalene ring systems. Oxidation products, i.e. various phenalenones were observed to increase in concentration as the catalytically cracked unstable diesel fuels were aged under ambient storage condition. Pedley et al., [35] have detected both indoles and phenalenes together with autoxidation products of phenalenes, and phenalenones in catalytically cracked unstable diesel fuel, suggesting that the sediment is formed by condensation of phenalenones with indoles. Beranek et al., [37] have presented evidence for the formation of indolylphenalene and bis indolylphenalene, through the direct coupling of phenalenes at the 3-position of indoles without involvement of phenalenones.

Clark and Smith [38] studied the performance of petroleum derived fuel, at 350°C by carbon burnoff, when the fuel was doped with several nitrogen compounds at 40 ppm N level. Quinoline and substituted pyridines produced similar and modest increases in deposition. Indole and 2,5-dimethylpyrrole gave substantially more deposit, but the indole produced four time more sediment than any of the pyridines.

Bhan et al., [39] investigated the reason for poor filterability in several jet fuel by studying the chemical and physical nature of the fuel unfiltrables and interaction of various fuel additives with various filtering media. The presence of insoluble organic sediments and gums are the principal cause of filtration problems. Metals and inorganic contaminants also contributed to the filtration problems by adhering to the filter medium, but their significance is minor. Sediment collected from the problematic jet - A and JP - 5 fuels, revealed that the jet - A fuel sediment was primarily composed of nitrogen containing compounds, where as the sediment from JP - 5 fuel contained hydrocarbon with some oxygen and sulfur compounds.

Dorban and Bernasconi [40] have confirmed the involvement of alkylindoles in sediment formation by examining the nitrogen compounds distribution (before and after aging) in four different light cycle oils (LCO's). All of the nitrogen compounds contained in four LCO's were classified as basic and non-basic. The basic nitrogen compounds were found in the form of various alkyl substituted anilines, while non-basic nitrogen compounds were alkyl substituted indoles and carbazoles. In all four LCOs the distribution of nitrogen compounds was very similar and no other nitrogen compounds were found.

Beaver et al. [41] in their study found that the alkylindoles are responsible for insoluble sediment formation and color during ambient storage of diesel fuels containing LCOs. They also found that the formation of sediment was suppressed by addition of hindered phenol antioxidant.

Lacy et al., [42] provided information about stability in real fuel system, where nitrogen rich extracts have been isolated from a stable shale derived middle distillate fuel and added as a dopant to a stable base fuel in order to induce instability. Alkyl substituted pyridines, tetrahydroquinolenes, quinolines and indoles were the prevalent classes of compounds present in the extract. The effect of this added extract was examined in terms of sediment formation and peroxide number under accelerated storage stability tests. The activity of the extract in inducing fuel instability was correlated with its nitrogen heterocyclic composition.

2.3. ANALYTICAL METHODS OF CHARACTERIZATION

Nitrogen compounds are present in petroleum in various chemical functionalities. It is important to know the type and amount of these compounds in order to choose the appropriate catalysts and condition for their removal during refining.

Characterization of nitrogen compounds and the sediment formed by doping of various nitrogen compounds in fuel is reported in the literature using various analytical techniques which include elemental analysis, vapor pressure osmometry (VPO), fourier transform infrared spectroscopy (FTIR), ultraviolet spectroscopy (UV), gas chromatography (GC), gas chromatography-mass spectroscopy (GC-MS), high resolution mass- spectroscopy (HRMS), X - ray photoelectron spectroscopy (XPS) [4, 29], solid state carbon - 13 nuclear magnetic resonance spectroscopy (^{13}CNMR) [6, 29], light scattering measurement [7, 43]. Each of these methods provide specific structural and compositional information. The information from these various sources when combined can lead to a detailed picture of nitrogen compounds and sediment structures present in petroleum derived fuel.

2.3.1. ELEMENTAL ANALYSIS

The elemental composition of a petroleum sample can be used to derive its empirical formula which is very helpful in the characterization of the materials. Several methods have been employed for determining the elemental composition of petroleum samples and related materials. Dinnen and Coworkers [44] employed the Kjeldahl method for the determination of total nitrogen contents in the distillates of crude oil. McKay et al. [45] employed the micro - Dumas method for the determination of total nitrogen contents of base fractions of different petroleum distillates and residues. McKay et al., [46] also employed macro Kjeldahl and micro columetric (Dohrmann) methods for nitrogen content determination. Holmes and Thompson [47] employed chemiluminescence methods for nitrogen content determination in shale oils.

2.3.2. MOLECULAR WEIGHT DETERMINATION

Molecular weight determination is very important for analyzing complex mixtures in order to find the average weight of the molecules present in the sample. This information together with elemental composition can lead to the characterization of the samples. Various techniques have been used to determine molecular weights of the distillates and residues.

Bhan et al. [38] employed different types of techniques for the determination of molecular weight fraction of Jet - A, JP - 4 and JP - 5 fuel sample sediment. One of them was size exclusion chromatography (SEC), where the columns were packed with 1000, 500 and 100 A^o microstyragel packing, mobile phase was tetrahydrofuran and molecular weights were calculated from polystyrene standards. SEC fraction of fuel jet - A and sediment samples of JP - 4 and JP - 5 were analyzed by low electron voltage, high resolution and electron impact mass spectrometry.

Synder and Buell [48] employed vapor pressure osmometry and mass spectrometry for average molecular weight determination of several petroleum fractions of a California crude oil.

McKay et al. [45] employed four different techniques for average molecular weight determination of high boiling distillates and residues. These techniques were vapor pressure osmometry, electron ionization mass spectrometry, field ionization mass spectrometry and quantitative infrared spectroscopy. The molecular weight used for the characterization of the samples was the average of molecular weights determined by all four methods. Khan et al., [49-50] employed low voltage mass spectrometry for average molecular weight determination.

Serio et al., [51] used field ionization mass spectrometry for the determination of the average molecular weight of fresh and stressed JP - 5 fuel.

Zerlia et al., [52] used vapor pressure osmometry to determine the molecular weight of aromatics, resins and asphaltenes, which were separated from petroleum products.

2.3.3. INFRA-RED SPECTROSCOPY (IR)

Infrared spectroscopy has been widely used for identifying and estimating the various type of heteroatomic funtionalities in the fuel and its sediments formed by aging of doping agents containing various nitrogen compounds.

Frankenfeld et al., [1] employed IR spectroscopy for the identification of DMP sediment, showing that the pyrrole ring is intact in the sediment and that oxygen has been introduced in the form of carbonyl group. The strong $-CH_3$ absorption relative to $-CH_2$ indicates the methyl groups remain intact and that no long chain $-CH_2-$ units from other components of the media have been introduced. N-H absorption was also observed.

Frankenfeld et al. [6] recorded the infrared spectra of sediments from crude or partially refined shale liquids. They showed many similarities to those of nitrogenous sediments obtained in model compound studies. The complicated absorption in the C=O stretching region (1600 - 1750 cm^{-1}) indicated the presence of several different types of carbonyl groups. There also appears good evidence for N-H absorption and a relative lack of methylene units or aromatic bands. This suggests that nitrogenous sediment formation in this type of actual shale middle distillate, as in the case of pure nitrogen compounds, involves oxidative self condensation of nitrogen containing species in the fuel without the participation of reactive hydrocarbons.

Coony et al., [28] recorded the infrared spectra of several samples of filterable sediment obtained from DMP. Spectra exhibit broad peak shapes with prominent carbonyl region absorption. The heterogeneity of the sediment is reflected in the complexity of the fine structure in the carbonyl region. These spectra are representative of those obtained with many samples produced over a range of stress conditions.

Loeffler and Li [29] recorded IR spectra of sediment formed by stressing of petroleum JP-5 with DMP and thiophenol; the results show that OH absorption at 3360 cm^{-1}, the incorporation of oxygen in the sediment as carbonyl (1640 - 1800 cm^{-1}), as well as N-H, CH_2 and CH_3 absorption.

Pedey et al., [33] recorded the IR spectra of sediment produced by the ambient storage of diesel fuel. There are many overlapping absorption bands, making detailed structure assignment difficult. However, the highly aromatic nature of the sediment is obvious from the characteristic absorption at 3075, 1625 and 900 - 750 cm^{-1}. Hydroxyl funtionalities probably contribute to the broad absorption centered at 3275 cm^{-1}, which overlaps with another peak at 3400 cm^{-1}. The absence of strong absorption in the 1870 -1650 cm^{-1} region indicates that carbonyl groups account for very little of the oxygen present in sediment. This contradicts the suggestion made by Sauer et al., [53] that sediments of this type are composed of aromatic nuclei bonded together by ester linkages.

Serio et al., [51] employed FTIR spectroscopy for the structure determination of deposits and insoluble gums of JP - 5 fuel produced in a heated capillary tube at 450°C. The portion of solid product soluble in acetone appeared to be mostly aliphatic in character. Some carbon - oxygen single and double bonds were also detected in this spectra.

Power [54] who has reported the IR data of soluble and insoluble gums which formed in the fuels during accelerated and ambient aging, suggested that the gums derived from accelerated aging are not the same as those which form during ambient storage.

Hazelett and Power [55] recorded the IR spectra of catalytically cracked light cycle oil of bass straight origin, provided the evidence that oxidative coupling of phenols were the most probable mechanism responsible for the increased instability of fuel.

Hassan et al., [56] reported the IR spectrum of each fraction of Panero crude oil, i.e. naphtha, kerosene, diesel oil and residue from Badin block of Sind province. The infrared spectroscopy has provided inportant insight into the functional groups present in each fraction.

2.3.4. ULTRA-VIOLET SPECTROSCOPY (UV)

Ultraviolet spectroscopy has also been used for identification of nitrogen compound types present in the fuel. Many polycyclic nitrogen compounds absorb in the ultraviolet region and, therefore, can be subjected to ultraviolet spectroscopic analysis. These compounds have their maximum absorption at characteristic wavelengths and therefore can be identified. Several investigators have reported the use of ultraviolet spectroscopy for the characterization of nitrogen compound types in crude oils and related materials.

Synder and Buell [48] employed ultraviolet spectroscopy to characterize compounds of nitrogen and oxygen in the distillates of California crude oil. The ultraviolet spectra of separated sub fractions were compared with spectra of model nitrogen compounds. This comparison led to identification of many nitrogen compounds including alkyl homologs and benzologs of pyridine and pyrrole.

Zerlia et al., [52] employed UV spectroscopy for the determination of aromatics, resins and asphaltenes from the petroleum products. UV spectra of petroleum and its products are very similar, showing a small number (one or two) of broad and superimposed bands at almost the same absorption wavelength. However, Zerlia et al., [57-58] suggested that in the processing of UV spectra, some parameters can be derived which appear to depend on certain characteristics of the product examined. Some actual petroleum products (ranging from gasoline to some residues and crude oils) were also examined, and it is shown that the quoted UV parameters are different for different products and linked to some characteristic of product.

Chang et al. [59] reported a sensitive and reliable UV spectrometric method for the analysis of gum content of commercial jet fuel of ASTM type - 1 (JA- 1) produced by Chinese Petroleum Company of Taipie, at temperatures of 105°C, 115°C, 120°C and 135°C. Aromatics, olefins, nitrogen, oxygen and sulfur containing compounds were identified in gum content.

2.3.5. GAS CHROMATOGRAPHY (GC)

Gas chromatography with a selective nitrogen detector is a sensitive, rapid and accurate analytical approach to the analyses of nitrogen compounds in petroleum. The introduction of the thermionic detector (Nitrogen Phosphorus Detector (NPD)) by Kolb and Bischoff [60] using a rubidium silicate bead as the alkali source, has greatly increased the capability for detection of nitrogen compounds in complex mixtures which may be composed of hydrocarbons predominantly. The use of NPD for the detection of nitrogen compounds in a matrix of hydrocarbons, maximizing the nitrogen response and minimizing the hydrocarbon response. It is possible to reduce the hydrocarbon response to zero and to have detectable response of nitrogen compounds.

Dorban and Bernasconi [39] used gas chromatography with nitrogen selective detector to identify the basic and non-basic nitrogen compounds from different light cycle oils (LCOs). The identified basic compound were anilines, alkyl derivatives from C1- to C4- anilines. The identified non basic compounds were indole, C1- to C4- alkylindoles, carbazoles and C1- to C3-alkylcarbazoles.

Baker [61] has reported that response is not necessarily correlated with the number of nitrogen atoms in a molecule. Response also varies with type of nitrogen containing compounds. It was observed that those nitrogen compounds whose structures are favorable for the formation of cyano radicals, offer greater response than those which do not favor cyano radical formation.

Albert [62] used NPD along with flame ionization detection for the determination of nitrogen compounds in light catalytic cycle oil and light vacuum gas oil. The dominant nitrogen compound types (pyridines, quinolines, indoles, and carbazoles) were characterized by boiling points and carbon numbers. Synthetic mixtures of nitrogen compounds were also chromatrographed to determine the relative response of each type of compound. Effect of alkyl substituents on the detector response was also determined. This study offers a fast and reproducible method for the characterization of nitrogen compounds in petroleum and related materials.

Dorban et al. [63] employed gas chromatography with selective nitrogen detection for the identification of nitrogen compounds from the mixtures of light cycle oils and its sediment formed by the aging of LCO's. Alkylindoles and carbazoles were found as the main components.

2.3.6. GAS CHROMATOGRAPHY-MASS SPECTROSCOPY

The group type analysis of nitrogen polycyclic compounds in complex mixtures has provided a great amount of information concerning their general composition. However, the exact identification and quantification of individual constituents is most desirable. The only method that can even approach this task today is combined gas chromatography-mass spectrometry. The use of high-resolution capillary gas chromatographic columns has greatly increased during the last several years. The maximum resolution of mixture components before mass spectral analysis is of utmost importance in providing unambiguous identification of individual compounds. The mass spectrometer is unable to provide the correct composition of a mixture by itself and, therefore, prior separation by high resolution capillary columns is essential. The power of the gas chromatography-mass spectrometry system for the analyses of complex mixtures is demonstrated by various applications found in the literature.

Ho et al., [64] reported gas chromatographic-mass spectrometric characterization of neutral nitrogen compounds separated from synthetic crude oils. Several nitrogen compounds were identified belonging to different classes. The result indicated that shale oil contains mostly alkyl substituted indoles, carbazoles and benzcarbazoles while coal derived liquid contains alkylindoles, phenyl substituted pyrroles and indoles, alkylcarbazoles and alkylbenzcarbazoles.

Yen et al., [65] used GC-MS for the identification of nitrogen containing compounds from shale oil. It was found that pyridine was the basic nucleus of most of the nitrogen compounds present in different fractions. The compounds characterized were mostly alkyl homologs and benzologs of pyridines.

Grigsby et al., [66] used GC-MS to examine the JFTOT tube deposits and filter insoluble. The tube deposits and filter sediments appear to have approximately similar composition such as aromatic hydrocarbon, naphthalenes, phenols, aromatics with one nitrogen, trace of aromatics with two oxygens, trace of aromatics with nitrogen plus oxygen bezothiophenes, dibenzothiophenes, pyridines and indoles etc. The most abundant compound types on the heater tube were naphthalenes and phenols. Naphthalenes appeared at temperatures below 150°C and again at temperature above 300°C showing that naphthalenes were released by two mechanisms. Indoles were the most abundant components found on the filter at probe temperatures above 300°C.

2.3.7. MASS SPECTROSCOPY (MS)

Mass spectrometric methods have been successfully applied to the analyses of complex mixtures like petroleum and shale oils. The mass spectrometric analysis is based on the fact that the organic molecules are transformed into organic ions in the mass spectrometer using different techniques which include electron ionization, chemical ionization, field ionization and field desorption. These ions are sorted out by the instrument according to their mass to charge (m/e) ratios, which are the characteristics of the compounds or compound. In literature, both low resolution and high resolution mass spectrometry have been used for the identification of nitrogen containing compounds.

Frankenfeld et al., [6] employed the mass spectra to record the major mass spectral peaks and their possible structural assignments. The sediment appears to be of fairly low molecular weight, little more than 400 mass units.

Bhan et al., [39] employed high resolution mass spectrometry to characterize the sediment formed from the aging of jet - A, JP - 4 and JP - 5 fuel. Only in jet - A sediment approximately fifteen different types of nitrogen , oxygen and sulfur compounds were identified, among which three types were present in most volatile form. The compounds identified were alkylindoles, alkylcarbazoles, alkylbenzenes, tetralin, alkyldinaphthenobenzine, alkyl naphthalenes, anthracene, alkylbenzothiophene, alkyldibenzothiophene, alkyl phenols, alkylhydroxyfluorenes and alkylfluorenones. Sediment from JP - 5 fuel contained mostly hydrocarbons and some oxygen and sulfur containing compounds.

Dorban et al., [63] employed mass spectrometry for the identification of nitrogen compounds from mixtures of light cycle oils and sediments formed by the aging of LCO's. Alkylindoles and carbazoles were found as the main component.

Grigsby et al., [66] used HR-MS coupled to a temperature programmed inlet probe to examine the JFTOT tube deposits and filter insoluble. On the average, the tube deposits and filter sediments appear to have approximately similar composition. The most abundant compound types on the heater tube were naphthalenes and phenols. Indoles were the most abundant components found on the filter at probe temperatures above 300°C.

Peters and Bendoraitis [67] employed high resolution mass spectroscopic method for analysis of nitrogen containing compounds. The method was applied to petroleum samples and shale oils and a number of nitrogen compounds were characterized.

Goncharov et al., [68] employed low resolution electron impact mass spectrometry for the analysis of nitrogen bases isolated from crude oils of various deposits in the Soviet Union. The compounds identified belong to quinoline and acridine series. It was observed that the amount and types of nitrogen bases differ in oils of various deposits.

Malhotra and John [69] have used pyrolysis / field ionization mass spectrometry (FIMS) to examine fuel deposits from various sources and have concluded that the nature of deposit is not changed drastically by increasing the temperature of aging from ambient to $120^{o}C$.

2.4. REACTION OF OXYGEN WITH ORGANIC MOLECULES

The fundamental chemical reactions involved in sediment formation in fuels are generally believed to involve the reaction of ground state triplet oxygen with various reactive organic molecules, which are component of fuel. There are generally two different types of reaction that can occur between triplet oxygen and organic molecules.

The most common type of reaction between organic molecules and triplet oxygen is peroxyl radical chain oxidation. The accepted chain mechanism of this reaction is summarized as the following

$$R{-}R \xrightarrow{K_1} R^{\cdot} \qquad (1)\ \text{Initiation}$$

$$R^{\cdot} + O_2 \xrightarrow{K_2} RO_2^{\cdot} \qquad (2)\ \text{Propagation}$$

$$RO_2 + R{-}H \xrightarrow{K_3} RO_2H + R^{\cdot} \qquad (3)\ \text{Propagation}$$

$$2RO_2^{\cdot} \xrightarrow{K_4} \text{Inert product} \qquad (4)\ \text{Termination}$$

Where $R{-}R$ is the initiator and $R^{\cdot}$ and $RO_2{}^{\cdot}$ represent the alkyl radical and the chain carrying peroxyl radical respectively [70-71]. The overall rate law for this reaction has been derived by using the standard steady state assumption, i.e. the rate of chain initiation is equal to the rate of chain termination [72].

$$\frac{-d[O_2]}{dt} = \frac{-d[RH]}{dt} = \frac{d[ROOH]}{dt} = \frac{K_3\,[RH]\,K_1^{1/2}}{(2K_4)^{1/2}}$$

Where K_1 is the rate of chain initiation, K_3 and K_4 are the rate constants for chain propagation and chain termination respectively. At low oxygen concentration (1 to 20 ppm) reaction (2) might be the rate controlling step. At high oxygen concentration the rate of reaction (2) is quite high and reaction (3) is the rate controlling step. The rate at which particular substrate oxidizes depends mainly on the rate of chain initiation and absolute value of K_3 and $2K_4$. The rate $K_3 / (2K_4)^{1/2}$ is a measure of the oxidizability of R-H. Termination reaction rate also depends on the oxygen concentration, at high oxygen concentration alcohols and ketones are the major product and at low concentration alkyl radicals undergo polymerization.

Many of the fuel antioxidants follow this type of mechanism. For instance, the effectiveness of both phenolic and amine (primary and secondary) antioxidants can be attributed to their breaking of radical chain.

$$RO_2^{\cdot} + A - H \underset{K_{-5}}{\overset{K_5}{\rightleftharpoons}} RO_2H$$

$$A^{\cdot} \longrightarrow \text{non chain product}$$

Where A— H represents the antioxidant [73]. If K_5 is larger than K_3, the oxidation is inhibited until the antioxidant is consumed.

For the peroxyl radical mechanism of oxidation it is generally observed that the initial rates of oxygen absorption are found to be (i) independent of oxygen when the partial pressure of oxygen above the solution exceeds 100 torr (zero order in O_2), (ii) one half order with respect to the concentration of initiator, and (iii) first order with respect to the concentration of R-H.

The second type of fundamental reaction that can occur between molecular oxygen and electron rich organic molecules as being important in the oxidative degradation of various fuel components, has been designated as Electron Transfer Initiated Oxidation (ETIO) [10]. Any oxidation reaction in which the rate limiting step involves a single electron transfer from the oxidation substrate to molecular oxygen is defined as electron transfer initiated oxidation.

Beaver et al., [32] thought the concept of ETIO represented an entire family of oxidation mechanism in which the common feature was the electron transfer as an integral part of the mechanism. Currently some of the petroleum antioxidants and stabilizers are designated to express the classical peroxyl chain mechanism of oxidation. ETIO represents an alternative oxidation pathway to explain the oxidative degradation of fuel products in the presence of oxidation stabilizers [33, 74].

Both ETIO and peroxyl radical chain oxidation contribute to the oxidative degradation of various petroleum products. Beaver et al., [32] compared the ETIO mechanism with the classical peroxyl radical chain mechanism using tetrahydrocarbazole (THC) as a model substrate, where the rate law of ETIO is second order overall (first order in both $[O_2]$ and [THC]). The rate law through peroxyl radical chain mechanism is first order overall (first order in [RH] and zero order in $[O_2]$). However, both mechanisms incorporate the same initial oxidation product (ROOH) through the same intermediate (an organic hydroperoxide).

Electron transfer initiated oxidation in fuel is very complex mechanistically due to a plethora of potential interactive effects that can occur with fuel components. For instance, Frankenfeld et al., [6] have shown that when certain fuels are doped with 2,5-dimethylpyrrole (DMP) and certain co-dopants (pyrrole or trimethylamine or certain sulfur compounds) less sediment is produced then expected during simulated storage stability tests.

From the perspective of oxidative storage stability, Beaver et al. [10] divided ETIO into two distinct classes of reactions. The first type of reaction classified as Uncontrollable Electron Transfer Initiated Oxidation (UETIO), involves the degradation of a reactive redox intermediate which cannot be sequestered by available antioxidants. The second type of reaction is classified as Controllable Electron Transfer Initiated Oxidation (CETIO), in which the rate of oxidation can be controlled by available antioxidants.

ETIO definition and classification system of Beaver et al. [10] has been supported by several representative examples. Akaba et al. [75] provided an example of controllable electron transfer initiated oxidation (CETIO), by oxidation of adamantylideneadamatane in trifluoracetic acid; this involves an electron transfer from an olefinic system to molecular oxygen and produced radical cations, which minimizes deprotonation and dimerization. When adamantylideneadamatane is oxidized in the presence of an equimolar amount of antioxidant 2,6-di-tert-butylphenol, the oxidation is completely inhibited, suggesting that the antioxidant regenerates adamantyl ideneadamatane by reduction of adamantylideneadamatane cation, and also donates phenolic hydrogen to the hydroperoxy radical. Bruice [76] studied the mechanism of biological oxidation with flavoenzyme mixed function oxidizes; he has shown that the initial step to the formation of biological active flavoenzyme mixed function oxides involves triplet oxygen to yield the radical ion pair. The intermediate is formed upon collapse of the ion pair, which can capture a proton to yield the product. This sequence of events does not allow any antioxidant to interfere with these oxidative steps. Thus the rate of collapse of ion pair is equal to and greater than the rate of diffusion, and therefore this establishes an example of uncontrollable electron transfer initiated oxidation (UETIO).

2.5. HYDROPEROXIDE REACTIONS

Active oxygen species such as peroxides can exert deleterious influences on liquid fuels, because the oxidation of fuel is a complex process involving time, temperature, heteroatoms, hydroperoxides and various other reactive species. Alkyl hydroperoxides are stronger acids and can easily undergo homolytic, heterolytic, and oxidative cleavage of the peroxide bond

[77-78]. In basic medium alkylhydroperoxides give carbonyl compounds while under acidic conditions some of the hydroperoxides have been observed to undergo rearrangement [79].

Hydroperoxide is the main component in the autoxidation of hydrocarbons below 200°C which leads to extensive hydroperoxide formation. The O-O bond is the weakest bond in alkyl and aryl hydroperoxide. The bond energy of RO-OH bond is approximately 175 KJ/mole. Alkoxy and hydroxyl radicals are generated by homolytic cleavage of peroxide bond [80]. Hydroperoxide stability is complex but generally depends on the chemical environment as well as its concentration in the system [81].

Induced decomposition of hydroperoxide is catalyzed by small amounts of metals ions. Trace amount of metal ions are always present in fuel liquids. The reactions of hydroperoxides with metal ions have been well studied [82-84].

Several investigators [3, 70, 85-88] reported the formation of hydroperoxides under mild conditions in fuels. The first systematic investigation of aliphatic hydrocarbon mixture was studied by Bernard et. al., [89]. Now it is accepted as a chain reaction process under mild operating conditions. If the propagation steps are greater than those of termination, then alkyl radicals will react with dissolved oxygen in the system. In the reaction sequence, the peroxy radical is the least reactive of all the radicals generated during reaction [90-92]. Thus a significant concentration of the alkyl peroxy radical must be available for further reaction.

The peroxide hydrogen bond of an alkyl hydroperoxide is weak and the reaction with other radicals in the system is exothermic [93-94]. Hiatt and

McCarrick [95] proposed that at low oxygen concentration of hydroperoxide, the reaction was first order in hydroperoxide, but at higher concentrations, the reaction was second order.

Several mechanisms based on radical involvement have been proposed to explain the formation of both gum and insoluble deposits. Deposit formation in fuels can be triggered by autoxidation and/or hydroperoxide concentration. It starts forming during the early stage of oxidation, but most of the deposit forms during regime of peroxide decomposition [96]. This finding is indicative of free radical involvement. Mayo and Lan [97] proposed that gum formation begins with the dimerization of two alkyl peroxy radicals and that oligomer formation depends on converting the peroxide dimer by chain propagation. In 1987 Mayo and Lan [98] reported that chain termination only involved monomeric peroxy radicals.

Several investigation on the formation / decomposition pathways have been found that concentration of hydroperoxide species is a factor in fuel instability. In jet fuels, hydroperoxide attacks elastomer in aircraft fuel systems with consequent leaks or inoperation of fuel controls. Jet - A, JP - 4 and JP - 5 jet fuels have been associated with such type of problems. The first incident occurred in 1962 with jet A fuel in Japan when fuel hoses of neoprene or nitrile rubber cracked and leaked [99]. The US navy experienced hydroperoxide attack on neoprene fuel pump diaphragms in jets operating in the Philippines in 1976 [100]. In 1983 Fetlke [101] reported the problems with JP - 4 when Buna N-O-rings cracked and leaked from fuel pumps in Thailand. All incidents involved fuel which have been hydrotreated and had peroxide levels from 1 to 8 milliequivalents of active oxygen per kilogram of fuel (peroxide number or P.N.).

Hazlett et al. [17] compared the peroxidation rates in two fuels, one with and one without antioxidants, and showed that a fuel without antioxidant produced peroxides at a linear rate while a fuel containing antioxidants produced peroxides in an exponential fashion, indicating a depletion with time of the antioxidant and its ability to control peroxidation.

2.6. DEPOSIT FORMATION IN DEOXYGENATED MEDIA

Several studies have shown that nitrogen compounds can be highly deleterious to air-saturated fuels both under storage [3] and empty wing tank conditions [19]. However, in deoxygenated fuel, nitrogen compounds have little effect on deposit formation under high temperature conditions. None of the nitrogen compounds caused a significant increase in total deposits over the entire temperature range. In the low temperature regimes, however, the heterocyclic amines, DMP, indole and carbazole promoted sediment formation to a small extent when compared to the base fuel. The primary amines had no observable influence on deposit formation throughout the temperature range.

The formation of deposits in jet fuels is known to involve both chemical and physical changes [102-103]. Furthermore, the deoxygenated fuels doped with various peroxides show an intermediate increase in deposit formation, while the air saturated base fuel, with no added peroxides, exhibits a gradual increase in deposit formation. This suggest a steady generation of peroxidic compounds due to autoxidation of the base fuel by dissolved oxygen. This result strongly suggests that peroxides are a major cause of deposit formation in air saturated fuel systems.

Taylor [102] described the effects of deoxygenation on deposit formation in jet fuel. With most fuels, removal of molecular oxygen markedly lowered the rate of deposit formation. However, certain poor quality fuels showed less improvement.

Taylor [104] has shown that the presence of certain sulfur compounds can markedly increase deposit formation in deoxygenated jet fuels. In oxygen saturated system deposits forms as a result of free radical chain reaction (autoxidation). However in deoxygenated fuels, the process appears different and even more complex.

Taylor and Frankenfeld [105] investigated the effect of deposit formation rate in the presence of trace amounts of nitrogen and oxygen containing compounds in deoxygenated JP - 5 fuel. The change in deposit formation rate was determined over a temperature range of 140 - 450^{o}C in fuels with molecular oxygen contents reduced to less than 1 ppm. The addition of nitrogen compounds did not increase deposit formation over the temperature range studied. However, certain nitrogen compounds led to sludge formation at temperature in the range of 20 - 25^{o}C. Of the oxygen compounds studied, peroxides as a class were found to be highly deleterious to fuel stability. Some acids, esters and ketones were moderately deleterious while others had no significant effect on deposit formation. In general, cycloalkyl compounds were less harmful than their aliphatic or aromatic counterparts. Several interactions between trace impurities were also discovered and they affect deposit formation rates.

2.7. AVERAGE STRUCTURAL PARAMETERS

It is important to analyze the molecular structure of aliphatic and aromatic hydrocarbons and their mixtures, such as petroleum and coal derived liquid fractions, for their application to fuel chemistry and carbon industry. Several analytical schemes have been devised in terms of average molecular parameters (AMPs). Among them the nuclear magnetic resonance (NMR) spectroscopy (both proton and carbon - 13) has been widely used for the structural study of these complex mixtures. In this respect, the principal method consists of using fingerprint regions for the assignment of proton and carbon-13 resonance signals, which are characteristic of the structures of hydrocarbons. All elements other than carbon and hydrogen are being ignored in this approximation. Several investigators have reported the use of proton and carbon - 13 NMR for the determination of average molecular parameters.

Hassan et al., [56] used ^{1}H nmr for the determination of average structural parameters of four fractions, i.e. naphtha, kerosene, diesel oil and residue of Panero crude oil from Badin block of Sind Province in Pakistan.

Takegami [106] employed both proton and carbon-13 NMR to investigate average molecular parameters of various vacuum residues and their fractionated samples. The structural parameters derived from carbon-13 NMR agreed with those derived from proton nmr within experimental error, indicating the accuracy of assignment for carbon distribution under the proton decoupled condition of carbon-13 NMR. The information about the aliphatic region of carbon-13 NMR spectra suggested the existence of long paraffin chains.

Dickinson [107] employed ^1H and ^{13}C NMR spectroscopy for the structural characterization of petroleum derived samples in terms of these hypothetical average molecules. ^{13}C NMR data were obtained which include the relaxation agent chromium acetonylacetonate, pulse delay of 2 seconds and running the spectra in gated proton decoupled mode. Average molecular parameters were calculated from proton and carbon-13 NMR, average molecular weight and elemental analysis. The structures of petroleum residue were compared by constructing hypothetical average molecules based on the average molecular parameters. Some significant structural differences were observed.

Gillet et al., [108-109] developed NMR methodology for obtaining a set of structural parameters to characterize crude oils and petroleum products. Conclusions were drawn regarding the possibility of using characteristic shift ranges to recognize structural features of chemical importance in these products. In this respect the aromatic carbons are divided into four categories: protonated, methyl-substituted, alkyl-substituted and condensed carbons. The latter class includes both bridgehead carbons standing at the junction of two or three aromatic rings, and benzonaphthanic carbons at the junction of an aromatic and a fused naphthenic ring. The evaluation of the carbons pertaining to each of these two subclasses individually is, however, an important point in structural determinations. This method can also be extended to coal liquids without any modification.

Hassan et al., [110] employed both ^1H and ^{13}C NMR spectroscopy for the determination of distillate fractions of Saudi Arabian heavy crude oil. The combined information gained from these analyses provided reliable average molecular parameters. These include estimation of aliphatic and aromatic content, average paraffinic chain length, estimation of hydrogen, methyl and alkyl bearing aromatic carbons for each fractions. The extent of branching in paraffinic chains and amount of aromatic bridgehead carbons were also calculated.

Young and Galya [111] used carbon-13 NMR spectroscopy for the determination of paraffinic, naphthenic and aromatic carbon from natural petroleum derived, shale oil and tar sands fraction with a sufficiently high initial boiling point and the results match well with those from ASTM D-2140. The paraffinic, naphthenic and aromatic carbon results can be integrated into any one of the number of standard and developed carbon-13 NMR analyses schemes in order to take full advantage of the power of NMR characterization.

Netzel and Hunter [112] employed a computer program for the determination of average molecular parameters of jet fuels and various fuel blends containing varying amounts of paraffinic and aromatic constituents.

Delpuech et al., [113] presented a methodology to estimate benzonaphthenic carbons apart from bridgehead carbons using the assumption of William's model. These values yield in turn an estimate of the number of donatable hydrogens of hydroaromatic rings and of bridging alkyl chains. The propagation of numerical errors arising from integrated signal areas is estimated in each case. Two typical applications are given to illustrate the method using three petroleum asphalts and a coal liquid as representative samples.

Gupta et al., [114] examined the spectra of two samples of crude oil (natural petroleum crude oil and coal derived liquid) by using proton and carbon - 13 NMR. From the resulting spectra, a series of average structural parameters has been derived; they were considered as approximate, since they present an over simplified picture of very complex rings containing a wide range of components.

Rongbao et al., [115] employed both proton and carbon - 13 NMR for the estimation of average molecular parameters of polycyclic aromatic compounds. The aromatic quaternary carbons are classified as four types, each of which can be calculated. The equation of Dickinsions for calculation of pericondensed aromatic carbons and of Knight for naphthenic rings were modified. The modified procedure determined the bi-aryl linkages, number of aromatic nuclei and also has been applied to the characterization of pyrolytic pitch fractions.

Cookson et al., [116] employed ^{13}C NMR to characterize the branched plus cyclic saturates fraction from the coal derived and petroleum derived diesel fuels and their major structural features were also compared. The selected multiplet ^{13}C NMR methods provided a unique view of the structural characterization of all the samples. The coal derived samples were composed predominantly of naphthenes consisting of 2 - 3 rings with approximately 1 side chain per molecule. Petroleum samples contain a high proportion of branched alkanes with, on average, 2 branches per molecule. The naphthene content of petroleum samples was predominantly monocyclic with approximately 3 side chains per molecule.

Ali et al., [117] recorded the proton and carbon-13 NMR spectra of asphaltenes separated from heavy crude oil using n-pentane at different temperatures. Average molecular parameters and hypothetical structural models for these asphaltenes were proposed by using NMR measurements, average molecular weight and elemental analysis.

CHAPTER 3

EXPERIMENTAL

3.1. TEST FUELS

All of the fuels used in this experiment were petroleum derived. Samples of test fuel were received from different refining stations. Kerosene (PLT - 71 KD), low straight run naphtha (TK-258 LSRN) and hydro cracked naphtha (TK-242 HCN) were received from 'ARAMCO' Rastanura refinery. Kerosene (RF - 1) and heavy naphtha (RF - 2) were received from isomax unit # 2 of Riyadh refinery. Kerosene (U-1300) and stable naphtha (U-1100) were received from Petromin Shell. These are the commercial fuels and were free of additives.

3.2. CHEMICALS

The chemicals such as 2,5-dimethylpyrrole, 2-methylindole, 2,4,6-trimethylphenol, and 2,6-di-tert-butylphenol were obtained from Aldrich Chemical Company, USA. Decane, decanoic acid, cyclohexanecarboxylic acid, n-hexylamine, n-methylcyclohexylamine and 2,6-dimethylaniline were obtained from Janssen Chemica, Belgium. Pyrrole and indole were obtained from Fluka, Switzerland. Iso-octane and n-hexane were obtained from BDH, England.

3.3. CHARACTERIZATION OF FUEL SAMPLES

The test methods used for the characterization of fuel samples were all standard methods as per American Society of Testing & Materials (ASTM). These methods are briefly summarized as follows:

3.3.1. DISTILLATION OF PETROLEUM PRODUCTS (ASTM D-86)

This method covers the distillation of kerosene, motor gasolines, aviation gasolines, aviation turbine fuels, special boiling point spirits, naphthas, white sprit, gas oils, distillate fuel oils and similar petroleum products.

The distillation procedures measure the amount of liquid vaporized and subsequently condensed as the temperature of the fuel in the distillation flask is raised at a prescribed rate. A record is made of the volume of distillate collected at specified temperatures or, conversely, the temperature at each increment of volume distilled (usually 10 % increments). The temperature at which the first drop of condensate is collected is called the "initial boiling point". The "end point" usually is the highest temperature recorded as the bottom of the flask becomes dry. The test is usually stopped when the final boiling point is reached.

The distillation (volatility) characteristics of petroleum products (generally include distillation limits to assure products of suitable volatility) are indicative of performance in their intended application. The empirical results obtained by this distillation method correlated with automotive equipment performance factors and with other characteristics of petroleum products related to volatility.

3.3.2. DETECTION OF COPPER CORROSION FROM PETROLEUM PRODUCTS BY COPPER STRIP TARNISH TEST (ASTM D-130)

Copper strip corrosion tests are used to detect the relative amounts of sulfur compound present in different types of petroleum products such as kerosene, diesel fuel, distillate fuel oils and lubricating oil, etc. It is a quantitative type test and made to ascertain whether fuels are free of a tendency to corrode copper fuel lines and brass and bronze parts used in the burner assemblies.

The copper strip corrosion test is conducted by immersing a polished copper strip in a sample of fuel contained in a chemically clean test tube. The tube is then placed in a bath maintained at a selected temperature such as 122°F or 210°F for 2 or 3 hours depending upon the test fuel. After washing the strip is examined for evidence of corrosion and judged by comparisons with the corrosion scale as reflected in the ASTM copper strip corrosion standards which are lithographed reproductions of copper strips subjected to degrees of corrosion.

3.3.3. EXISTENT GUM IN FUELS BY JET EVAPORATION (ASTM D-381)

This test method covers determination of the existent gum in motor gasoline, and aircraft fuels. The existent gum value is the amount of gum actually present in the fuel at the time of test.

In an existent gum process, a measured quantity of fuel is evaporated under controlled conditions of temperature and flow of air or steam. For aviation gasoline and aircraft turbine fuel, the resulting residue is weighed and reported as milligrams per 100 ml fuel.

The true significance of this method for determining gum in motor gasoline is not firmly established. So the primary purpose of this test, as concern to motor gasoline, is the measurement of the oxidation products in a sample prior to or during the comparatively mild conditions of test procedure. Since many motor gasolines are purposely blended with non-volatile oils or additives, the heptane extraction step is necessary to remove these from the evaporation residue, so that the deleterious material, gum, may be determined. With respect to aviation turbine fuels, large quantities of gum are indicative of contamination of fuel by higher boiling oils or particulate matter and generally reflect poor handling practices.

3.3.4. KINEMATIC VISCOSITY OF TRANSPARENT AND OPAQUE LIQUIDS (ASTM D-445)

This method covers the determination of the kinematic viscosity of liquid petroleum products, both transparent and opaque, by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. The dynamic viscosity can be obtained by multiplying the measured kinematic viscosity by the density of the liquid.

The time is measured in seconds for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled temperature. The kinematic viscosity is the product of the measured flow time and the calibration constant of the viscometer. Generally centistokes (cSt) has been used as the unit of kinematic viscosity.

The significance of this method depends on behavior of the samples and the coefficient of viscosity should be independent of the rate of shear called Newtonian flow behavior. If the coefficient of viscosity varies significantly with the rate of shear, different results may be obtained from viscometers of different capillary diameter.

3.3.5. NEUTRALIZATION NUMBER BY COLOR INDICATOR (ASTM D-974)

This method covers the determination of acidic or basic constituents in petroleum products and lubricants soluble or nearly soluble in mixtures of toluene. The relative amount of these materials can be determined by titrating with acids or bases. The neutralization number, whether expressed as "acid number" or "base number" is a measure of this amount of acidic or basic substance respectively in the oil, under the conditions of the test.

To determine the total acid number (the quantity of base, expressed in milligrams of potassium hydroxide (KOH), that is required to titrate acidic constituents present in 1 gram of sample) or strong base number (the quantity of acid, expressed in terms of the equivalent number of milligrams of potassium hydroxide (KOH), that is required to titrate base constituents present in 1 gram of sample), the sample is dissolved in a mixture of toluene and isopropyl alcohol containing a small amount of water, and the resulting single phase solution is titrated at room temperature with standard alcoholic base or alcoholic acid solution respectively. The end point is indicated by the color change (orange in acid and green-brown in base) of the added p-naphtholbenzein solution . To determine the strong acid number, a separate portion of the sample is extracted with hot water and the aqueous extract is titrated with potassium hydroxide solution, using methyl orange as an indicator.

3.3.6. DENSITY, RELATIVE DENSITY (SPECIFIC GRAVITY) OR API GRAVITY OF CRUDE PETROLEUM AND LIQUID PETROLEUM PRODUCT BY HYDROMETER METHOD (ASTM D-1298)

The hydrometer method is most suitable for determining the density, relative density or American Petroleum Institute (API) gravity of mobile transparent liquids. It can be used for viscous oil by allowing sufficient time for hydrometer to reach equilibrium, or for opaque oils by employing a suitable meniscus correction. These terms are defined as follows :

Specific Gravity - The ratio of the mass of a given volume of liquid at $60^{o}F$ to the mass of an equal volume of pure water at the same temperature.

Density - The mass of liquid per unit volume at $15^{o}C$ as stated for specified hydrometer.

API gravity - This is a special function of specific gravity that was arbitrarily established to permit gravity calculations in whole numbers. It is related to specific gravity by following formula :

$$\text{API gravity, deg} = \frac{141.5}{\text{sp gr at } 60/60^{0}\text{F}} - 131.5$$

Density, specific gravity and API gravity values permit conversion of volumes at the measured temperature to volumes at the standard petroleum temperatures of $15^{o}C$ or $60^{o}F$. Calculation of weight is possible where compositions are formulated on a weight basis.

In this procedure the sample is brought to the prescribed temperature and transferred to a cylinder at approximately the same temperature. The appropriate hydrometer is lowered into the sample and allowed to settle. After temperature equilibrium has been reached, the hydrometer scale is read. If necessary the cylinder and its contents may be placed in a constant temperature bath to avoid excessive temperature variation during the test.

3.3.7. FLASH POINT OF LIQUIDS BY TAG-OPEN CUP APPARATUS (ASTM D-1310)

This method covers determination of flash points by tag open-cup apparatus of liquids having flash points between 0 and 325°F (-18 and 163°C). The flash point of a fuel is a measure of the temperature to which the fuel must be heated to produce an ignitable vapor air mixture above the liquid fuel when exposed to an open flame.

The flash point test gives an indication of the presence of volatile components in an oil, and it is the temperature to which the oil must be heated under specified test conditions to give off sufficient vapor to form a mixture with air which will ignite in the presence of an open flame.

3.3.8. OXIDATION STABILITY OF DISTILLATE FUEL OIL (ACCELERATED METHOD, ASTM D-2274)

This method measures the stability of distillate fuel oils under accelerated oxidizing conditions. It should be recognized that any correlation between this test and field storage may vary significantly under different field conditions or with distillate from different sources.

A measured volume of filtered oil is aged at a high temperature of 95°C while oxygen is bubbled continuously through the sample. After aging and cooling, the total amount of insoluble matter formed is determined.

3.3.9. THERMAL OXIDATION STABILITY OF AVIATION TURBINE FUEL (JFTOT PROCEDURE) (ASTM D-3241)

This test method covers the procedure for rating the tendencies of aviation turbine fuels or similar to gas turbine fuel oils to deposit decomposition products within the fuel system. The test results are indicative of fuel performance during gas turbine operation and can be used to access the level of deposits formed when liquid fuel contacts a heated surface that is at a specified temperature.

This test method requires 600 ml of test fuel for measuring the high temperature stability of aviation turbine fuel using the Jet Fuel Thermal Oxidation Tester (JFTOT). The tester subjects the test fuel to temperature and conditions similar to those occurring in aviation turbine engine fuel systems. The fuel is pumped at a fixed volumetric flow rate through a heater after that it enters a precision stainless steel filter where fuel degradation products may become trapped. The essential data derived during experiments are the amount of deposits on an aluminum heater tube, and the rate of plugging of a 17 µm nominal porosity precision filter located just downstream of the heater tube.

3.4. FILTRATION AND GLASSWARE PREPARATION

The test fuels were filtered through 0.8 µm nominal pore size, cellulose acetate / nitrate filters (Millipore Corp. Cat. No. AAWP 20500) under vacuum before storage. The storage bottle used in this study were 500 ml clear Pyrex glass. Before use the bottles were washed with gum solvent (an equal volume solution of toluene, methanol and acetone) and then rinsed with acetone prior to scrabbling with a laboratory cleaner. The bottle was well rinsed with tap water and finally flushed with distilled water and placed in an oven at 120°C to dry overday.

3.5. FUEL AGING WITHOUT ADDITIVES

All three different types of fuel such as kerosene (jet A fuel), low straight run naphtha (LSRN) and hydro cracked naphtha (HCN) were taken into 500 ml Pyrex glass bottles. Samples were placed in sunlight for specified periods of time, i.e. from 1 to 4 weeks. During aging for that period, fuel samples were tested periodically and also final colors were recorded. The kerosene sample had been left in sunlight for the study of long term storage instability.

3.6. FUEL AGING WITH ADDITIVES

Solutions were prepared by making 500 ml fuel samples 200 ppm in N level of model nitrogen compounds such as pyrrole, 2,5-dimethylpyrrole, indole, 2-methylindole, n-hexylamine, n-methylcyclohexylamine and 2,6-di methyl aniline. Oxygen compounds were added in amounts equivalent to 50 ppm O level. Three sets of sample were setup for pyrrole, 2,5-dimethylpyrrole, indole, 2-methylindole, n-hexylamine, n-methylcyclohexylamine and 2,6-di methyl aniline. One set was stored in darkness at ambient temperature (24°C). The second set was placed in sunlight and a third set was irradiated with long wave (365 nm) UV light with an intensity of 7000 $\mu\omega/cm^2$. Two sets of samples were setup with a combination of nitrogen (pyrrole and 2,5-dimethylpyrrole) and oxygen (n-decanoinc acid, cyclohexanecarboxylic acid, 2,4,6-trimethyl phenol and 2,6-di-tert-butylphenol) compounds. One set was placed in sunlight and the other was irradiated with uv (365 nm) light with an intensity of 7000 $\mu\omega/cm^2$. Samples were aged for a time period of 1, 5, 10 and 15 days.

After aging for a specified period, fuel samples were filtered through weighed 0.8 mm pore size membrane filters under vacuum. The filter was rinsed with reagent grade iso-octane (to remove traces of high boiling hydrocarbons which are present in most commercial middle distillate fuels) and dried for thirty minutes at 75°C - 80°C (an exception was made in the experiments with pyrrole, here the drying oven temperature was 45°C to prevent spattering and charring of the precipitate). The filter was allowed to cool to room temperature and weighed to quantitate the sediment. The final color of aged fuels was also determined.

3.7. FUEL AGING WITH ADDITIVES IN DEOXYGENATED MEDIA

The sample was prepared by mixing 500 ml of fuel with 200 ppm N level of DMP in a 500 ml Pyrex glass bottle. The sample was irradiated with uv (365 nm, 7000 $\mu\omega/cm^2$) light and was continuously blown with argon gas at the rate of 4 - 6 bubbles per second throughout the reaction period. The samples were withdrawn after 1, 5, 10 and 15 days. After the specified period, each sample was filtered and the residue washed with iso-octane, dried in an oven at 75 - 80°C for approximately half an hour and allowed to cool for weighing. The final color of aged fuel was recorded.

3.8. DECANE AGING WITH ADDITIVE

Two sets of decane solutions were prepared by mixing 200 ml of decane with 1000 ppm N level of DMP in 250 ml borosilicate Erlenmeyer flask. One set was purged with nitrogen gas for approximately 10 - 15 minutes to remove the dissolved oxygen from base fuel (decane). Both sets were irradiated with long uv (365 nm, 7000 $\mu\omega/cm^2$) wave, for the time period of 1 - 20 days. Decane samples were filtered after a period of 1, 5, 10, 15 and 20 days to remove sediments. The filter was dried in an oven at 75 - 80°C before weighing. The final color of the solution was also recorded.

3.9. ACCELERATED STORAGE STABILITY TEST

In accelerated storage stability test, two different types of experiments were performed. In one experiment, a constant amount of DMP concentration at different temperatures was employed, while in the other test, different amounts of DMP concentration at the same temperatures were employed.

DMP solutions were prepared by dissolving 0.280 gm of DMP in 200 ml of additive free jet-A fuel in weighed borosilicate Erlenmeyer flasks. This produced a 0.02M solution. The prepared solutions were stoppered and stored in an oven at 43°C, 67°C and 80°C for period of 2, 4, 6, 8, 10 and 12 days. The sample flasks were removed after a specified period from the oven, allowed to cool in the dark and filtered through weighed 0.8 µm pore size membrane filters under vacuum. The filter was rinsed with reagent grade n-heptane; heptane was also used to wash down the sides of the flasks. The insoluble sediment generally settled to the bottom of the flask and could be dislodged from the flask by rinsing with heptane and collected by filtration through the same funnel. Both flasks and filter papers were dried in an oven at 110°C for one and a half hours, allowed to cool and weighed. The adherent sediment coated the inside of the flask and did not loosen when rinsed with heptane. The sediment weights were collected as follows :

$$\text{Insoluble Sediment} = \frac{\text{increased weight of filter}}{2} \quad (\text{mg / 100 ml fuel})$$

$$\text{Adherent Sediment} = \frac{\text{increased weight of flask}}{2} \quad (\text{mg / 100 ml fuel})$$

Blank corrections, were performed through the same experiment on fuel without 2,5-dimethylpyrrole, and subtracted from sediment weight for 12 days only during the determination of apparent activation energy (Ea.) of sediment. The sum of the insoluble and adherent sediment gives the total sediment weight (W).

In the accelerated storage stability test of different DMP Concentrations, the solutions were prepared by mixing 200 ml of additive free jet - A fuel with 2,5-dimethyl pyrrole in the concentrations range of 375, 500 and 625 ppm N level. The blends were stored in borosilicate Erlenmeyer flasks in an oven at 43°C for a time period ranging from 6 days to 14 days. At the end of each storage period, insoluble and adherent sediments were determined by filtering and weighing as described in the previous experiment.

3.10. ANALYTICAL METHODS OF THE CHARACTERIZATION OF SEDIMENTS

The sediments obtained from model nitrogen compound studies were characterized by elemental analyses, Fourier transform infra-red spectroscopy and mass spectroscopy. The sediments obtained from 2,5-dimethylpyrrole were insoluble in all polar and non polar common organic solvents, so this precludes the measurement of solution spectra.

3.11. ELEMENTAL ANALYSIS

The sediment obtained from DMP under a variety of storage conditions were analyzed for their carbon, hydrogen, nitrogen and oxygen contents using elemental analyzer Carlo Erba Strumentazione model 1106.

3.12. FOURIER TRANSFORM INFRA-RED SPECTROSCOPY

Infrared spectra of all different type of sediments were recorded from Nicolet Perkin Elmer Model 5DXB FTIR Instrument, and are reported in wave numbers (cm^{-1}). Samples of liquid or solid were prepared as films deposited on KBr windows or transferred direct to KBr discs.

3.13. MASS SPECTROSCOPY

The sediment samples obtained under different experimental conditions were analyzed using the JEOL HX 100 mass spectrometer. The sample was introduced into the mass spectrometer via a direct insertion probe (DIP). Operating conditions for mass spectroscopy measurements were as follows.

Ion source temperature	:	250°C
Emission	:	100 mA
Electron energy	:	70 eV
Acc. voltage	:	5 kV
DIP temp. Program	:	50°C to 250°C at 16°/min. (initial time : 1 min., final time : 5 min.)

3.14. AVERAGE MOLECULAR WEIGHT

Average molecular weights of all samples were determined using a Knauer Vapor Pressure Osmometer model 11.00. The thermistor head temperature was 60°C. Benzil was used as a calibration standard for molecular weight determination. Four standard solutions of benzil were prepared in HPLC grade toluene at 0.002, 0.005, 0.008 and 0.01 molal concentrations. Solutions of each fuel were prepared at four different concentrations in the range of 15-25 g/kg of toluene. The solution was introduced into the osmometer and the response was recorded. Four or five readings were taken from each sample and the average value was used. For both fuel and calibration standard, the response / concentration values were plotted against the concentration separately and were extrapolated to zero concentration to obtain the value of $K_{measured}$ and $K_{calibrated}$ respectively. The ratio of $K_{cal.} / K_{meas.}$ yielded the average molecular weight of fuels. Operating conditions of vapor pressure osmometry measurements are as follows:

Instrument used : Vapor Pressure Osmometer
Temperature of thermistor : 60°C
Sensitivity of instrument : 16.00
Response time : 3.0 min.
Concentrations of benzil solutions
(Calibration standards) : 0.002, 0.005, 0.008 and 0.01 molal
Concentrations of fuel solutions : 15 - 25 g / Kg

3.15. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

3.15.1. PROTON NMR

The NMR spectra of all fuel samples were recorded on a JEOL JNM-GX-270 NMR spectrophotometer. The samples were dissolved in $CDCl_3$ in a volume concentration of 50 %. One scan was accumulated with a pulse of 90° and a 1-second relaxation period between consecutive pulses. All chemical shifts were measured relative to external tetramethylsilane (TMS).

3.15.2. CARBON - 13 NMR

The carbon-13 NMR was obtained on a 50 : 50 solution of the fuel in $CDCl_3$ using a 10 mm internal diameter multinuclear probe at 67.8 MHz. The acquisition time was 1.091 s; the pulse delay, 1s; the pulse width, 8.5 µs (equivalent to a 90^o pulse). The spectra were recorded using an average of 2000 scans. Chromium acetylacetonate ($Cr(acac)_3$) was added as a relaxation agent. The carbon signals of the solvent was used as the internal references.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. GENERAL CHARACTERISTIC OF FUELS

The fuels were obtained from different refineries in a non-corrosive container. Tables (1), (2), (3) and (4) summarize some of the pertinent physical and chemical properties of these fuels. The data shown in the tables was obtained by using the standard ASTM methods. From all of the fuels, kerosene (PLT-71 KD) was studied in the greatest detail. The fuel samples, which are representative of various process streams, were collected from the lines before going to the storage tanks. None of the samples used contained any additive.

Kerosene samples from three refineries (PLT-71 KD, RF-1 and U-1300) were found to meet all the ASTM specified requirements for jet - A fuel.

Samples tested (ASTM D1500) were bright (B) and clear (C) in their appearance indicating their clarity.

The specific gravity by ASTM D1298, a simple hydrometric method, ranged from 0.6914 - 0.8188 in all kerosene samples.

Total acid number (ASTM D 974) of all kerosene samples were below 0.01 against a specification limit of 0.1. This test is a measure of the inorganic and total acidity of fuel and indicates its tendency to corrode metals with which it comes into contact.

The copper strip tarnish (ASTM D130) test gave result 1a in all samples measure the fuel sulfur potential corrosivity. The limitation of sulfur content is

TABLE 1

PHYSICAL AND CHEMICAL PROPERTIES OF JET A FUEL (RASTANURA REFINERY)

Test Discription	Method	Units	Kerosene (Jet A fuel)	Specification Limit
API Gravity	ASTM D-1298	kg/l	47.3	51 (max)
				37 (min)
Specific Gravity	ASTM D-1298	kg/l	.6914	0.755 (min)
				0.840 (max)
Total Acid No.	ASTM D-974	mgKOH/g	0.001	0.015 (max)
Appearance	ASTM D-1500	Visual	C & B	
Flash Point	ASTM D-1310	°F	114	100 (min)
Smoke Point	ASTM D-1322	mm	27	25 (min)
JFTOT	ASTM D-3241	TDR	1	3 (max)
JFTOT	ASTM D-3241	Pressure Drop	0.0	25 (max)
Cu Strip	ASTM D-130	212°F	1 A	1 (max)
Gum Existent	ASTM D-381	mg/100 ml	0.8	7 (max)
Silver Corrosion		122°F	o-no-tarn	
Sulfur	ASTM D-1266	wt%	0.14	0.3
Kinematic Viscosity	ASTM D-445		3.78	
Mercaptan Sulfur,	ASTM D-1323	wt%	0.0003	0.003
Paraffin	UOP-870-86	Vol %	74.95	
Olefines,	UOP-870-86	Vol%	0.0	
Naphthene	UOP-870-86	Vol %	5.35	
Aromatics,	ASTM D-1319	Vol%	19.0	20-25 (max)
Distillation	ASTM D86	IBP °F	322	
		10% °F	358	400 (max)
		20% °F	368	
		50% °F	395	
		90% °F	443	
		FBP °F	488	572 (max)
		Total Recovery	98.8	

TABLE 2

PHYSICAL AND CHEMICAL PROPERTIES OF NAPHTHA (RASTANURA REFINERY)

Test Discription	Method		Units	LSRN	HCN
Gravity	ASTM D1298		kg/l	82.1	60.0
Specific Gravity	ASTM D1298		Kg/l	.6625	.7369
Appearance	ASTM D1500		Visual	C & B	C & B
Doctor Test	ASTM D235			Neg	Neg
Color Saybolt	ASTM D-156			+30	+30
Paraffins	UOP-870-86		Vol %	91.41	68.71
Olefines,	UOP-870-86		Vol %	0.0	0.12
Naphthene	UOP-870-86		Vol %	6.33	15.86
Aromatics,	UOP-870-86		Vol %	2.26	15.31
Iso-paraffines			Vol %	39.5	38.7
Cu Strip	ASTM D130		oF	1A	1A
Sulfur, x-ray	ASTM D-1266		wt%	0.008	0.022
Mercaptan Sulfur,	ASTM D-1313		ppm	3	7
Sulfur, Raney Nickel			ppm		0.36
Distillation	ASTM D86	IBP	oF	100	190
		10%	oF	119	222
		20%	oF	122	230
		50%	oF	134	256
		90%	oF	160	303
		FBP	oF	190	330
		Total Recovery		98.9	99.3

TABLE 3

PHYSICAL AND CHEMICAL PROPERTIES OF FUEL SAMPLES (PETROMIN SHELL)

Test Discription	Method	Units	U-1300	U-1100
API Gravity	ASTM D1298	Kg/l	48.39	75.22
Specific Gravity	ASTM D1298	Kg/l	0.7866	0.6845
Appearance	ASTM D1500	Visual	B & C	B & C
Lead	ASTM D2788	mg/l	----	< 10
Existent gum	ASTM D381	mg/100ml	1.0	< 1
Paraffin	UOP-870-86	vol%	57.94	80.95
Naphthenes	UOP-870-86	vol%	23.46	12.74
Aromatics	UOP-870-86	vol%	18.60	6.30
Olefin	UOP-870-86	vol%	0.0	0.0
RSH	ASTM D3227	ppm	< 3	< 3
Doctor test (H_2S)	ASTM D235		-ve	-ve
Sulfur	ASTM D1266	ppm	58	2
Cu strip	ASTM D130	212°F	1a	1b
JFTOT (TDR)	ASTM D2341		< 1	nil
Distillation IBP	ASTM D86	°F	308	101
5%		°F	331	141
10%		°F	337	152
30%		°F	355	175
40%		°F	365	188
50%		°F	375	201
70%		°F	402	230
80%		°F	419	243
90%		°F	441	261
95%		°F	456	271
FBP		°F	479	298

TABLE 4

PHYSICAL AND CHEMICAL PROPERTIES OF FUEL SAMPLES (RIYADH REFINERY)

Test Discription	Method	Units	RF - 1	RF - 2
API Gravity	ASTM D1298	kg/l	53.45	41.32
Specific Gravity	ASTM D1298	Kg/l	0.7651	0.8184
Appearance	ASTM D1500	Visual	C & B	C & B
Flash point	ASTM D1310	°F	122	----
Paraffins	UOP-870-86	Vol %	60.92	48.36
Olefines,	UOP-870-86	Vol %	0.0	0.05
Naphthene	UOP-870-86	Vol %	20.18	34.51
Aromatics,	UOP-870-86	Vol %	18.90	6.30
Cu Strip	ASTM D130	212°F	1A	1A
Distillation	ASTM D86	IBP °F	330	198
		5% °F	353	219
		10% °F	359	226
		20% °F	366	234
		30% °F	370	243
		40% °F	373	253
		50% °F	377	259
		60% °F	381	274
		70% °F	384	285
		80% °F	389	296
		90% °F	396	318
		95% °F	402	326
		FBP °F	415	334
		Total Recovery	98.5	97.5

significant for jet fuels because the sulfur oxides formed during combustion may be corrosive to turbine metal parts.

Mercaptan sulfur content test (ASTM D-235) of jet fuel is limited to a maximum in the range of 0.001 to 0.005 percent by mass because of objectionable odor, adverse effect on certain fuel system elastomers and corrosiveness towards fuel system metals. A negative test indicates the fuel is below a specified limit of mercaptan sulfur.

A low flash point (ASTM D1310) fuel may indicate contamination by more volatile and explosive fuels which will cause fuel to be a fire hazard, with possible continued ignition and explosion. The flash point varies from 113 to 122°F in kerosene samples, which is higher than the specification limit (100°F) of aviation turbine fuels.

The gum existent test (ASTM D-381) provides the amount of gum present and is an indication of the condition of the fuel at the time of test only. Gum is a non-volatile residue left by evaporation of fuel. The gum existent value of the kerosene samples are in the range of 0.8 - 1 mg/100 ml fuel, which are in negligible amounts compared with the specified limit (8 max) of aviation turbine fuels.

The chemical composition of a kerosene fuel is extremely complex because of the presence of an enormous number of compounds. So it is neither practicable nor profitable to perform individual compound analyses. However, it is sometimes helpful to determine the percentage of broad classes of compounds such as aromatics, paraffins, naphthenes and olefins. The olefins are completely absent in these kerosene samples.

Jet fuels are continuously burned in a combustion chamber by injection of liquid fuel into the rapidly flowing stream of hot air. The paraffin hydrocarbons offer the most desirable combustion cleanliness characteristics for jet fuel. Naphthenes are the next most desirable hydrocarbons for this use. Aromatics generally have the least desirable combustion characteristics for aircraft turbine fuel. They tend to burn with a smoky flame and release a greater proportion of their chemical energy as undesirable thermal radiation than the other hydrocarbons. Generally, the greater the content of aromatics in jet fuel, the more smoky the flame. A high smoke point indicates a fuel of low smoke producing tendency. The smoke points of fuel are higher (27 vol %) than the specified limit (25 vol % min). The combustion of highly aromatic jet fuels generally results in smoke and carbon or soot deposition, and it is therefore desirable to limit the total aromatic contents. The aromatic contents in all kerosene samples are lower, ranges from 7.99 - 19 vol % than specification limit i.e. 20 % aromatic for jet A-1 and 25% for Jet A fuel.

The ASTM D-86 distillation test provides a measure, in terms of volatility, of relative proportions of all the hydrocarbon components of aviation turbine fuel. A low volatility fuel results in poor ignition and combustion characteristics. The distillation ranges are very high i.e. in the range of 479 - 488°F in all kerosene samples.

The most important properties of fuel are thermal stability, which are related to the amount of deposit formation in the engine fuel system on heating the fuel in a jet aircraft. The Jet Fuel Thermal Oxidation Tester (JFTOT) (ASTM D-3241) is one of the important tests used to determine whether an aviation turbine fuel meets specification requirement for thermal stability. A schematic representation of apparatus is shown in Figure (1). An aluminum tube,

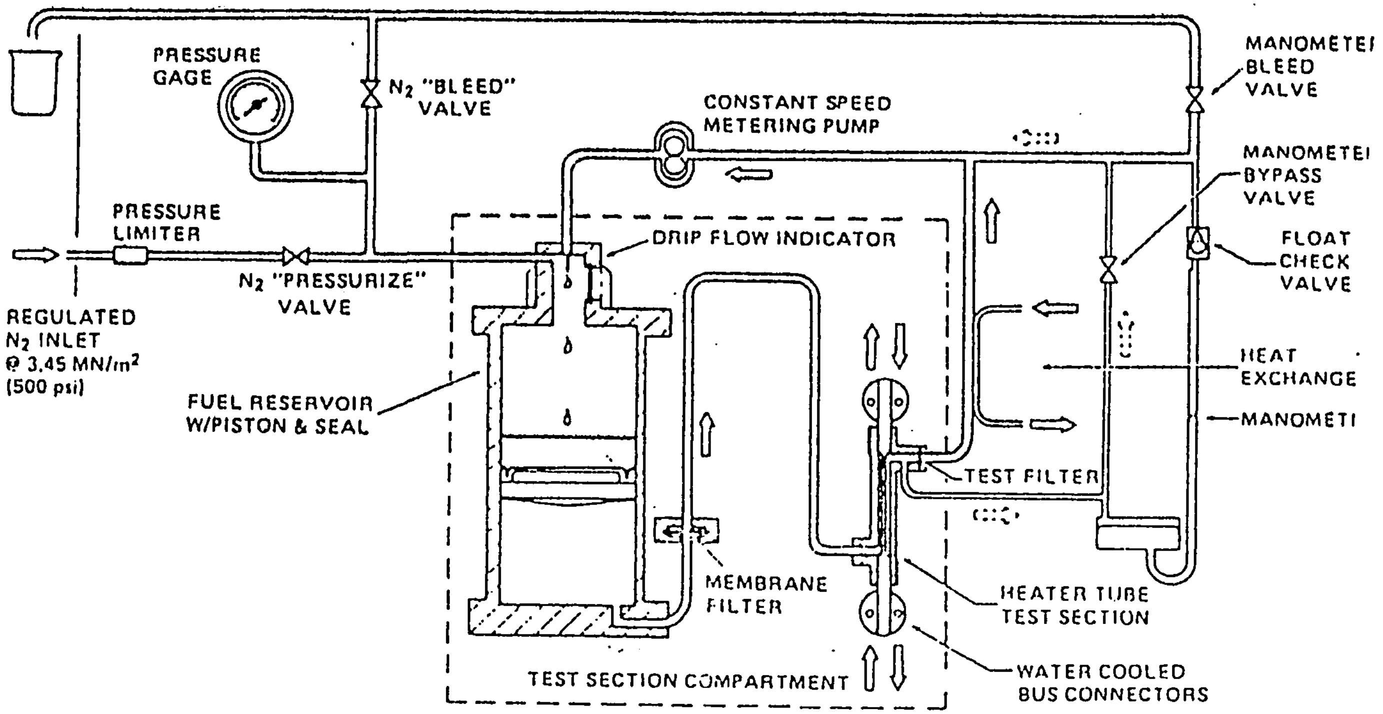


Figure 1. Schematic flow diagram of the JFTOT.

electrically heated to the desired test temperature, is exposed to a continuous flow of fuel, pumped from reservoir through the annulus surrounding the tube, and out through a test filter. The entire system is pressurized to 500 psig with nitrogen to supress fuel vaporization in the heated test section. The stability of fuel was determined from the pressure drop across the filter and by visual assessment of the deposit on the aluminum tube at the end of the test. The specification for aviation turbine fuels requires the tube deposit rating (TDR) be less than 3 compared to ASTM standard color codes, ranging from light tan to brown, and the pressure drop across the filter be no more than 25 mm mercury. A rating of 3 or greater is classified in specification as a "fail". The JFTOT tube deposit rating of 1 or less than 1 and zero pressure drop in all kerosene samples indicate the high thermal stability of jet fuel.

The test fuel used in this investigation in detail was a jet A fuel (kerosene) supplied by Rastanura refinery. This fuel exceeds all the ASTM aviation turbine fuels specifications including most important thermal oxidation specification test (JFTOT, ASTM D-3241) by a wide margin, indicating that the fuel possessed very high thermal stability.

Naphtha samples as supplied by the three refineries consisted chiefly of four grades such as TK-258 LSRN, TK-242 HCN, RF-2 and U-1100. These naphthas are used for the manufacture of a wide range of jet fuels (e.g. JP-4). The color of all naphthas is found to be under the B & C specifications. The specific gravity value was in the range of 66.25 - 76.73 in all naphtha samples. The copper corrosion tarnish test varies from 1a -1b indicating negligible corrosivity properties of naphthas. The aromatic values vary in the range of 6.30 - 16.0 in all naphtha samples, which are lower than specification value.

The olefins are completely absent in all naphtha samples. The distillation ranges of naphthas are 298 - 330°F.

4.2. SEDIMENT FORMATION

Three fuels, kerosene (jet-A fuel), low straight run naphtha (LSRN) and hydro cracked naphtha (HCN), were employed for preliminary study of storage condition in sunlight. Table (5) gives the result on sediment formation of the three (kerosene, LSRN and HCN) fuels. The copper strip test at 212°F of all fuels appeared as 1a after two weeks of storage in sunlight, indicating that fuels are free from corrosivity properties. In third week trace amounts of sediment were formed in kerosene only. The copper strip corrosion test of kerosene provided the strip as 1b, which indicates the presence of insignificant quantities of corrosive compounds. In fourth week both kerosene and low straight run naphtha formed trace amount of sediments and appeared as 1b copper strip in corrosion test. There was no significant change with hydro cracked naphtha throughout the course of storage condition. One month duration experiment of all three fuels also exhibited its stability during storage. The copper strip corrosion test of kerosene and low straight run naphtha resulted in No. 1 strip indicating that amount of sulfur present in fuels does not have any deleterious effects and potential corrosivity.

The appreciable amount of sediments obtained from the kerosene sample after six weeks storage in sunlight as compared to HCN suggests that hydrocracked naphtha is more stable fuel and kerosene is less stable. The infra-red spectra of neat kerosene and the sediment from the aged kerosene are shown in Figures (2) and (3) respectively. The major absorptions were found to be present in both spectra. Two distinct strong bands at 2970 cm^{-1}

TABLE 5

EFFECTS OF SUNLIGHT ON RASTANURA REFINERY FUEL SAMPLES

Tests	Kerosene	LSRN	HCN
<u>1 week</u>			
Color	Colorless	Colorless	Colorless
Sediment	Nil	Nil	Nil
Cu-test, 2 hr. 212 ^{o}F	1a	1a	1a
<u>2 weeks</u>			
Color	Colorless	Colorless	Colorless
Sediment	Nil	Nil	Nil
Cu-test, 2 hr. 212 ^{o}F	1a	1a	1a
<u>3 weeks</u>			
Color	Light Yellow	Colorless	Colorless
Sediment	Trace	Nil	Nil
Cu-test, 2 hr. 212 ^{o}F	1b	1a	1a
<u>4 weeks</u>			
Color	Light Yellow	Light Yellow	Colorless
Sediment	Trace	Trace	Nil
Cu-test, 2 hr. 212 ^{o}F	1b	1b	1a

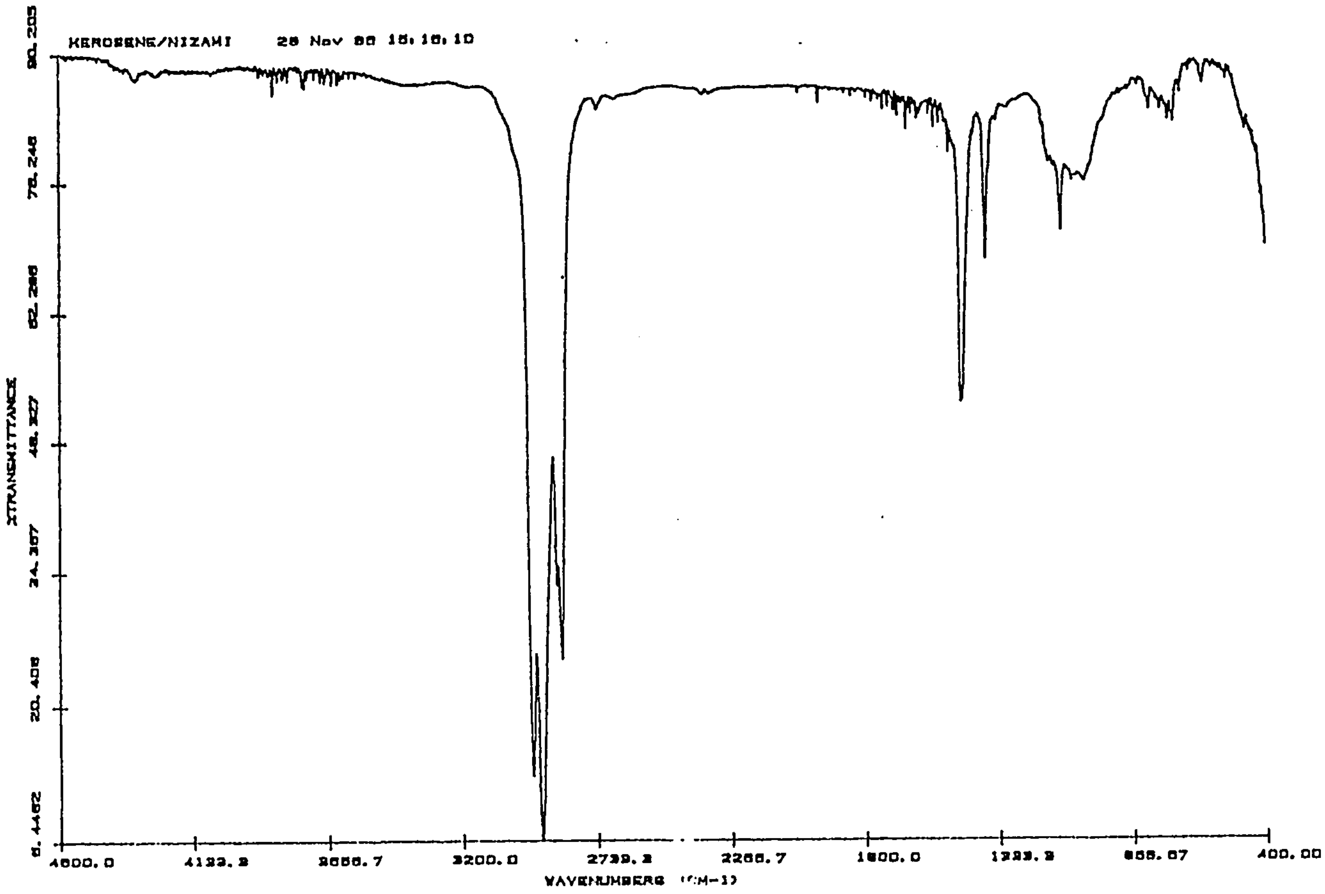


Figure 2. Infrared spectra of neat kerosene sample.

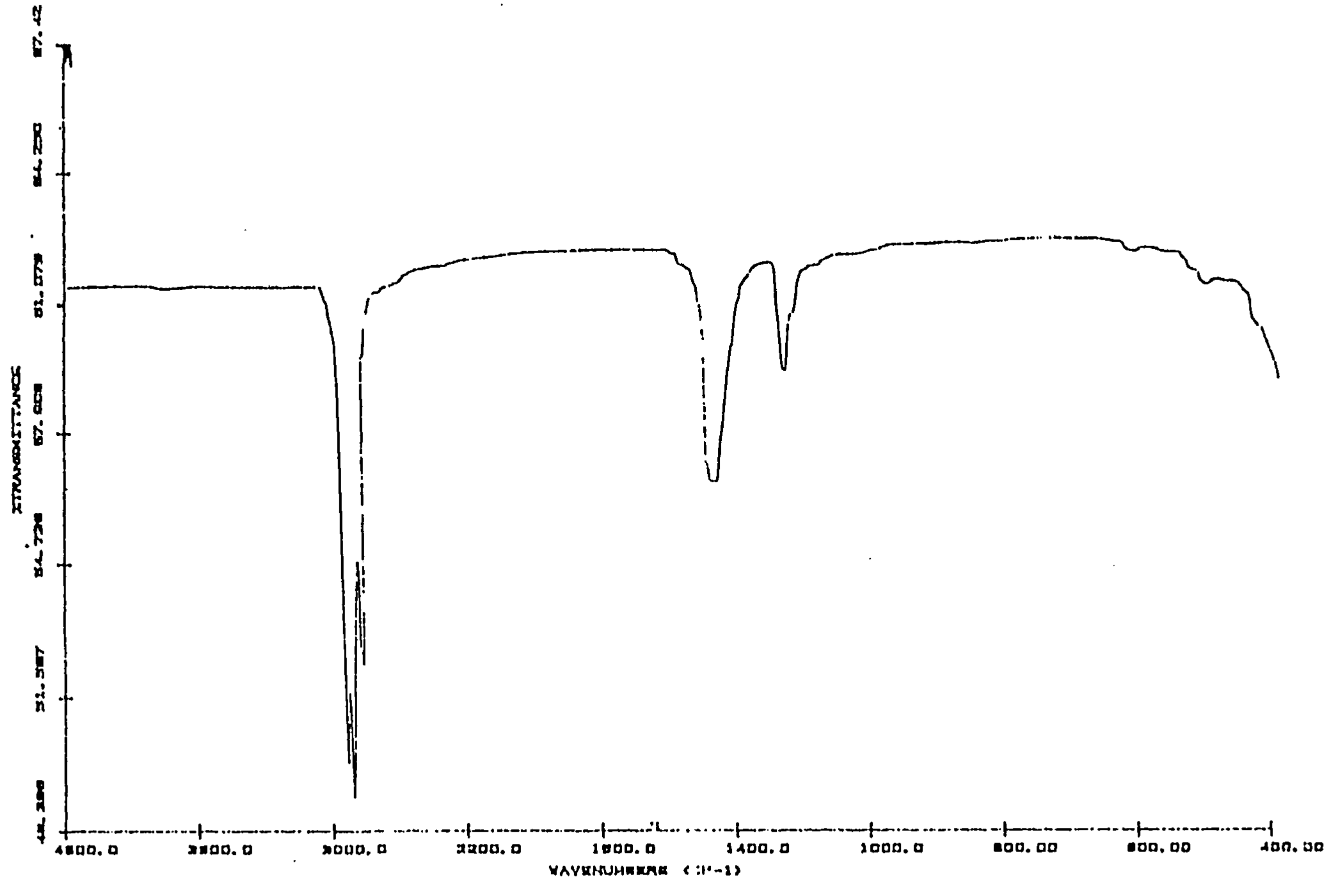


Figure 3. Infrared spectra of kerosene sediment.

and at 2890 cm^{-1} due to asymmetrical stretching vibration ($\nu_{as}CH_3$) and symmetrical stretching vibration (ν_sCH_3) of C-H methyl groups present in both spectra. Similarly the strong bands occurred at 2950 cm^{-1}and 2875 cm^{-1} corresponding to asymmetrical stretching vibration ($\nu_{as}CH_2$) and symmetrical stretching vibration (ν_sCH_2) of C-H methylene groups. Also the broad bands at 1375 cm^{-1} and 1460 cm^{-1} due to symmetrical bending vibration (δ_sCH_3) and asymmetrical bending vibration ($\delta_{as}CH_3$) of C-H in CH_3 group were obtained. The similarity of IR spectra for the kerosene sample and the sediment from the aged samples indicates that the sediment are largely made up of hydrocarbon polymers. The sediment formed in nitrogen-poor petroleum type fuels contain little or no nitrogen and apparently consist of hydrocarbon polymer. Nitrogen compounds in such instances may act only as catalysts [2-3].

4.3. EFFECTS OF ADDING NITROGEN COMPOUNDS ON THE NEAT JET-A FUEL

Nitrogen compounds are known to be deleterious to the stability of fuels by promoting the formation of highly interactable sediment or sludge under storage conditions, due to this it is suspected as a major cause of the instability. However, this problem does not appear to be serious in Saudi Arabian crude oil because of very low nitrogen contents of jet fuel. As a result, the effects of nitrogen compounds on the stability of jet fuels and other distillate fuels has not been studied extensively. In order to investigate this problem in Saudi Arabian petroleum derived jet fuel, the current study was undertaken to investigate the effects of selected nitrogen compounds such as pyrroles, indoles and amines derivatives and their correlation between chemical structure and reactivity toward sediment formation under fuel storage conditions. The above nitrogen compounds selected for this study are representative of compound types known or likely to be present in the petroleum derived jet fuels.

To study the effects of selected nitrogen compounds on the storage stability of jet A fuel, the nitrogen compounds had been divided into two groups, basic groups (amines types) and non-basic or very weakly basic groups (pyrrolic types). Non-basic group was further divided into two classes of compound such as pyrrole types and indole types class. The pyrrole types include : pyrrole, 2,5-dimethylpyrrole compounds and indole types include : indole and 2-methylindole compound. Amine types include : n-hexylamine, n-methyl cyclohexylamine and 2,6-dimethylaniline. These chosen compounds represent a wide range of basicity given in Table (6). The larger the value of pKa (for conjugate acid), the stronger the base.

Base strengths of usual organic compounds depend upon the availability of the unshared pair of electrons on the nitrogen atom and electron donating groups or inductive effects of alkyl groups.

Amine derivatives are strongly basic nitrogen compounds because of the presence of unshared pairs of electrons on the nitrogen atom. Basicity decreases from aliphatic to aromatic compounds primarily due to its stabilization which can be ascribed to the delocalization of the unshared pair of electrons on nitrogen atom over the aromatic ring. Among amine compounds, the basicities are as follows:

n-hexylamine > n-methylcyclohexylamine > 2,6-dimethylaniline

The pyrrole and indole derivatives are non-basic or very weakly basic nitrogen compounds. These non-basic nitrogen compounds provide a

TABLE 6

PROPERTIES OF SELECTED NITROGEN COMPOUNDS (1)

Compounds	pKa (2)
Non basic or very weakly basic nitrogen compounds	
Pyrrole types	
pyrrole	-3.8
2,5-dimethylpyrrole	-0.71
Indole types	
Indole	-2.4
2-methylindole	-0.10
Basic Nitrogen Compounds	
n-Hexylamine	10.64
n-Methylcyclohexylamine	10.49
2,6-dimethylaniline	3.95

(1) D. D. Perrin, Dissociation constant of organic bases in aqueous solution, London, Butterworth, 1965.

(2) pKa = Values for conjugate acids of nitrogen base.

significant range of electronic and structural environments at the nitrogen atom. Pyrrole are five membered ring compounds containing one heteroatom. They derive their aromaticity from delocalization of a loan pair of electrons from the heteroatom. Consequently the loan pair of electrons is not available for protonation and the heterocyclic compounds are not basic or are very weakly basic. Fusion of a benzene ring onto the C2/C3 positions of pyrrole formally produces the corresponding bezopyrrole, known as indole, which is a ten-p electron aromatic system. As with pyrrole, delocalization of the loan pair of electrons from the nitrogen atom is necessary for aromaticity. A consequence of this delocalization is that the loan pair is not available for protonation, like pyrrole, so indole is another weakly basic heterocycle.

Among pyrrole and indole types compounds, electron releasing groups, such as alkyl substituents increase the basicity of nitrogen compounds. Thus, the basicities within the given class compounds are as follow :

2,5-dimethylpyrrole > pyrrole ....(pyrrole type)
2-methylindole > indole ....(indole type)

Three sets of solutions were prepared by dissolving 200 ppm N level of all selected nitrogen compounds. One set was stored in darkness at ambient temperature. The second set was placed in sunlight and the third one was irradiated with long uv light for 1-15 days. The resulting sediment formation of these representative nitrogen containing compounds at the time periods of 1, 5, 10 and 15 days are given in Table (7). The pyrrole type compounds i.e. dimethylpyrrole, indole and methylindole produced the highest amount of sediment. Among amine type compounds, only 2,6-dimethylpyrrole generated measurable sediment; n-hexylamine and n-methylcyclohexylamine produced

TABLE 7

EFFECTS OF MODEL NITROGEN COMPOUNDS ON SEDIMENT FORMATION IN JET A FUEL

Compound Added(1)	Storage Condition(2)	Cumulative Sediment (g/500 ml Fuel)				
		1 Day	5 Days	10 Days	15 Days	Comments
None	Sun light	nil	nil	nil	nil	Clear, Colorless
2,5-Dimethylpyrrole	Sun light	0.052	0.277	0.422	0.501	Dark Tan
Pyrrole	Sun light	0.046	0.221	0.378	0.439	Yellow
2-Methylindole	Sun light	0.034	0.199	0.323	0.365	Dark Red
Indole	Sun light	0.024	0.174	0.289	0.328	Dark Yellow
Hexylamine	Sun light	nil	0.012	0.030	0.042	Very Light Yellow
n-methylcyclohexylamine	Sun light	nil	0.019	0.042	0.071	Very Light Yellow
2,6-dimethylaniline	Sun light	nil	0.038	0.080	0.101	Yellow
None	UV light	nil	nil	nil	nil	Clear, Colorles
2,5-Dimethylpyrrole	UV light	0.050	0.262	0.376	0.425	Dark Tan
Pyrrole	UV light	0.022	0.152	0.264	0.326	Yellow
2-Methylindole	UV light	0.021	0.108	0.176	0.218	Dark Red
Indole	UV light	0.011	0.087	0.145	0.178	Dark Yellow
Hexylamine	UV light	nil	nil	nil	trace	Colorless
n-methylcyclohexylamine	UV light	nil	nil	trace	trace	Colourless
2,6-dimethylaniline	UV light	nil	trace	trace	0.021	Colorless
None	Dark	nil	nil	nil	nil	Clear, Colorles
2,5-Dimethylpyrrole	Dark	0.003	0.007	0.012	0.017	Yellow
Pyrrole	Dark	nil	nil	nil	nil	Clear, Colorless
2-Methylindole	Dark	nil	nil	nil	nil	Red
Indole	Dark	nil	nil	nil	nil	Clear, Colorless
Hexylamine	Dark	nil	nil	nil	nil	Clear, Colorless
n-methylcyclohexylamine	Dark	nil	nil	nil	nil	Clear, Colorless
2,6-dimethylaniline	Dark	nil	nil	nil	nil	Clear,Colorless

(1) Each compounds added to Jet - A fuel at 200 ppm N level

(2) UV light = UV radiation (365nm : 7000 μω/cm^2) : Dark = Stored in dark

colorless solutions which colored with time and with relatively very little sediment formation. In dark storage of all nitrogen compounds only DMP produced a small amount of sediment.

Light, either as sunlight or ultraviolet radiation (365 nm) greatly accelerates the rate of sediment formation. This is illustrated by the plots of sediment formation versus storage time of 1, 5, 10 and 15 days for 2,5-dimethylpyrrole (DMP), pyrrole, 2-methylindole and indole as shown in Figures (4), (5), (6), and (7) respectively. These figures indicate the samples stored in sunlight formed more sediment than UV irradiated stored samples. In sunlight, the samples are not only irradiated by uv long wave radiation but also different types of radiation which have deleterious effect on fuel stability, but still unknown. In uv radiation, the samples are only irradiated at a selected wavelength. This provides the reason why sunlight produced more sediment than uv light.

The pyrrole and indole derivatives such as pyrrole, 2,5-dimethylpyrrole and indole, 2-methylindole showed large differences in the tendencies towards sediment formation as shown in Figures (8) and (9). The rate of sediment formation depends upon the basicity (within given class compounds) of these nitrogen (pyrrole, 2,5-dimethylpyrrole, indole and 3-methylindole) containing compounds. Basicity of these nitrogen compounds decreases within a given class of compound in the order of

2,5-dimethylpyrrole > pyrrole and 2-methylindole > indole

The more basic the compound (within a given class of compound) the more sediment is formed. Worstell et al., [20] also conducted an accelerated storage test of jet A fuel at 120°C with four classes of compounds namely

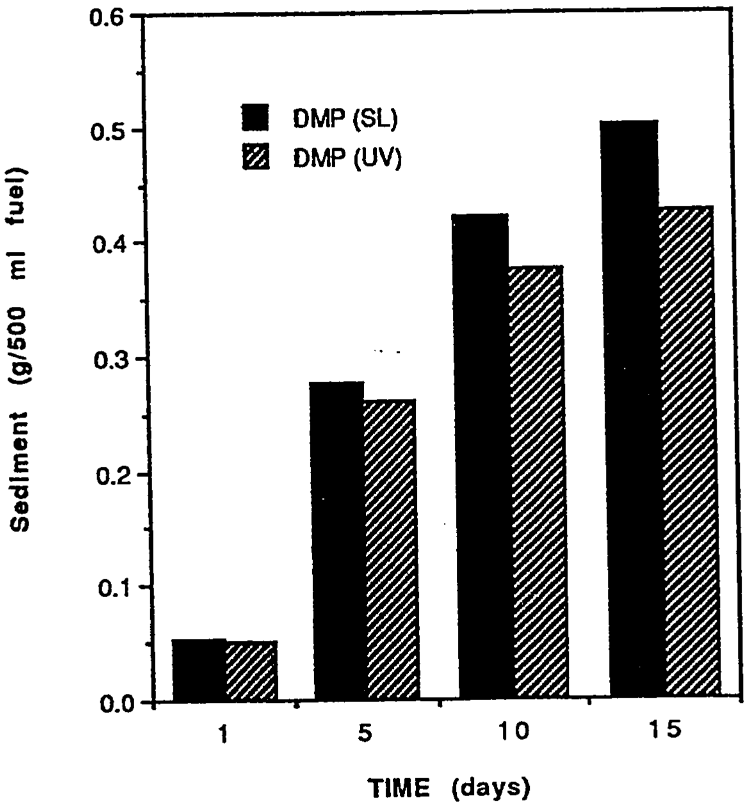


Figure 4. Effects of sunlight and UV radiation on sediment formation with 2,5-DMP in Jet A fuel

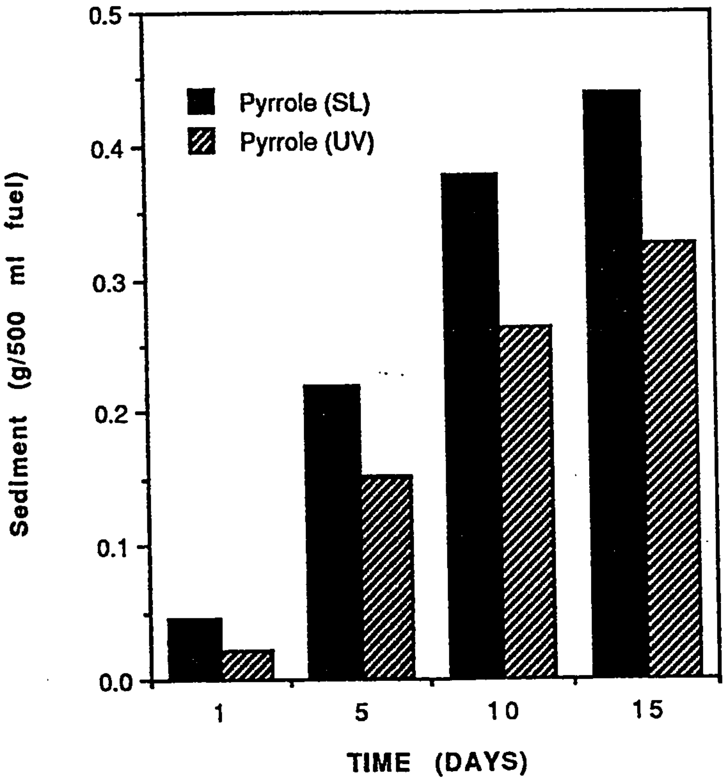


Figure 5. Effects of sunlight and UV radiation on sediment formation with pyrrole in Jet A fuel

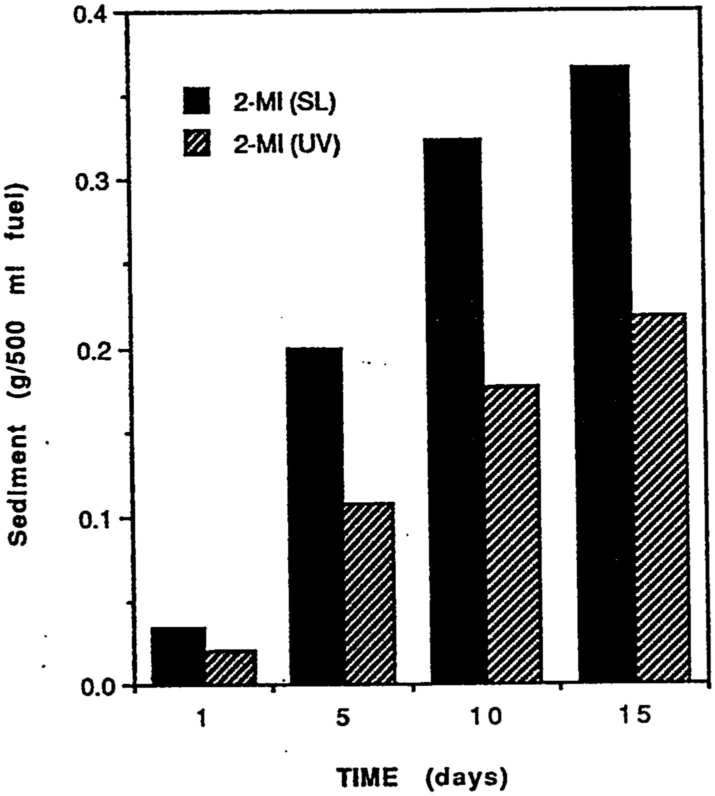


Figure 6. Effects of sunlight and UV radiation on sediment formation with 2-methylindole in Jet A fuel

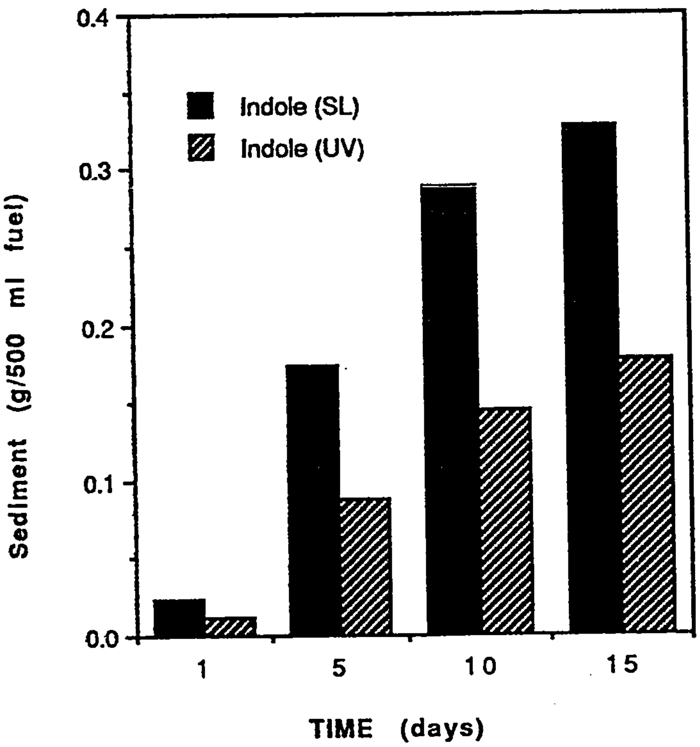


Figure 7. Effects of sunligh and UV radiation on sediment formation with indole in jet A fuel

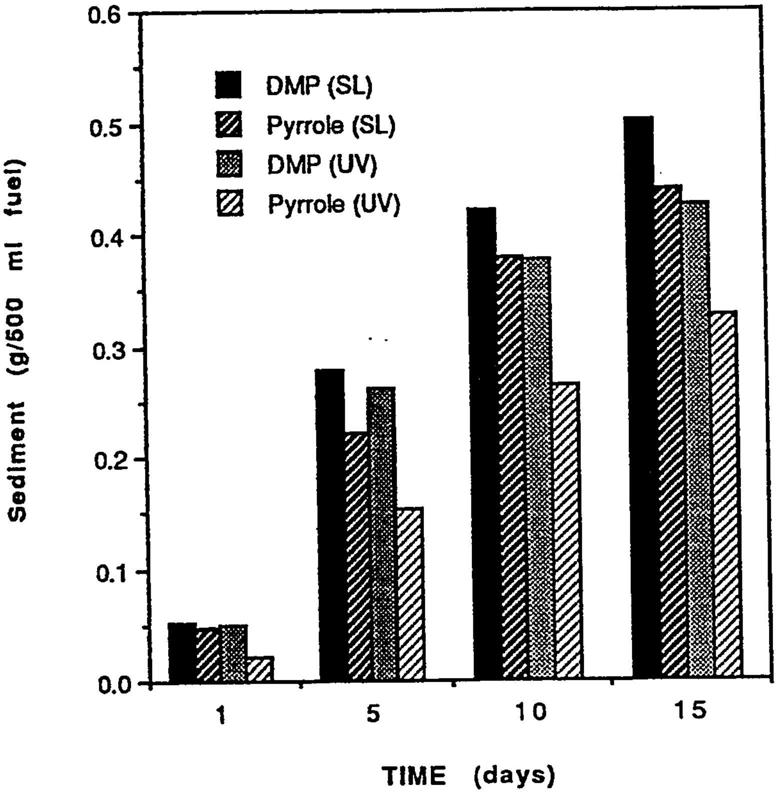


Figure 8. Effects of basicity of pyrrole derivatives on sediment formation in Jet A fuel

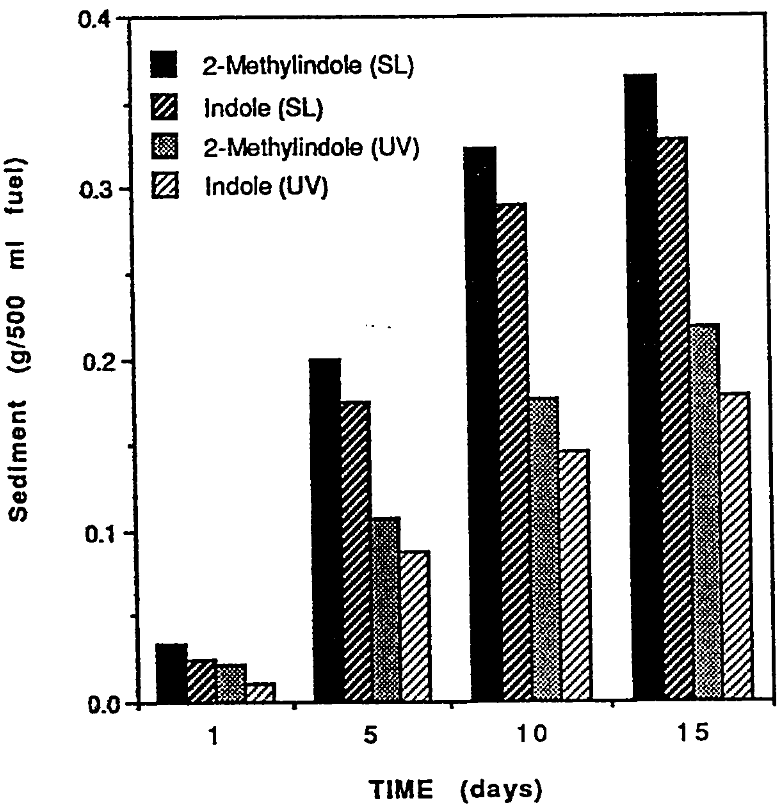


Figure 9. Effects of basicity of indole derivatives on sediment formation in Jet A fuel

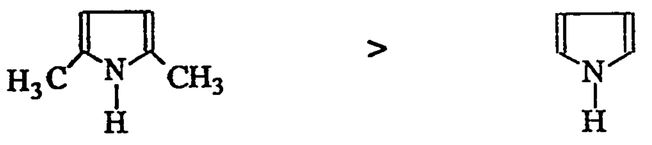
pyrroles, indoles, pyridines and quinolines, reported that the amount of sediment formation was related to the basicity of nitrogen compounds (within the given compound class). The presented work is also in good agreement with Worstell et al. [20].

The amine containing compounds such as n-hexylamine, n-methyl cyclohexyl amine and 2,6-dimethyl aniline also have a tendency to produce some color under storage conditions but gave no measurable sediment except 2,6-dimethylaniline. Several of the investigators [1, 6, 26-27] reported similar results during the aging of fuels with amine derivatives.

In the comparison of pyrrole and amine type compounds, amine type compounds are much more basic than pyrrole and indole type compounds, even though the amine type produced an insignificant quantity of sediment compared to pyrrole type. In response to sediment formation, the basic properties will not apply with amine type compounds such as pyrrole and indole type compounds. It is known that the sediment formation reactions proceed through the free radical mechanism [3]. In pyrrole and indole type compounds, the formation of pyrrole radical during reaction is stabilized by resonance, where as in amine types compounds (except 2,6-dimethyl aniline) radicals do not stabilize due to the molecular structure. Owing to the resonance property, the 2,6-dimethyl aniline generated measurable amount of sediment compared to methylcyclohexylamine and hexylamine.

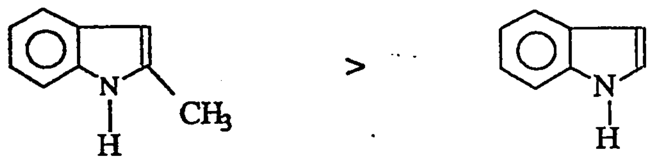
Scheme 3 correlates the sediment formation of model aromatic nitrogen heterocycles (pyrrole, 2,5-dimethylpyrrole, indole and 3-methylindole) with their structure. By far the most active compounds were the alkylated pyrroles. The position of the alkyl group on the heterocyclic ring is important. Alkyl

SCHEME 3



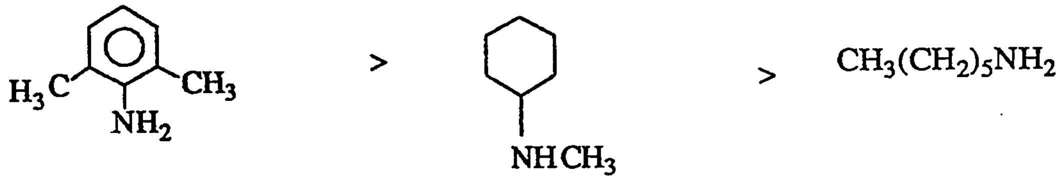
2,5-Dimethylpyrrole   Pyrrole

B. Indoles



2-Methylindole   Indole

C. Amines



2,6-Dimethylaniline   n-Methylcyclohexyl amine   Hexylamine

Influence of structure on reactivity of nitrogen heterocycles towards sediment formation. Reactivity decreases from top to bottom (group A > B > C) and from left to right.

groups on carbon atoms adjacent to nitrogen atoms activate the compounds towards sediment formation. Fusing of aromatic ring to the hetero ring (indoles vs pyrroles) also tends to reduce reactivity. Compounds without alkyl side chains produced measurable sediment under the condition of test. According to the basis of structural effects on nitrogen compounds, the amount of sediment formation decreases from pyrrole to indole derivatives as follows:

2,5-dimethylpyrrole > pyrrole > 2-metyl indole > indole

as also shown in Figures (10) and (11) respectively. These results can be extended to the other types of nitrogen compounds.

Frankenfeld et al., [6] and Cooney et al., [28] investigated the effects of nitrogen (pyrrole, indole and quinoline derivatives) compounds on sediment formation and suggested that the rate of sediment formation was dependent on the structural features, not on the basic properties of nitrogen compounds. The above results also agree with the work reported by them [6, 28].

4.4. INFLUENCE OF ORGANIC ACIDS AND PHENOL ON SEDIMENT FORMATION

Oxygen containing compounds are one of the undesirable substances in liquid fuels. Several studies have shown that the oxygen containing compounds are responsible for the degradation of fuels, which lead to the formation of sediment, gum and color bodies in liquid fuels [6]. The oxygen compounds identified in jet fuel range fractions are carboxylic acids, phenols, furans, ketones, alcohols, esters, amides, hydroperoxide and peroxide [118]. The interaction of these oxygen containing compounds with nitrogen containing compounds influence their sediment forming tendencies in base fuel. Such types of interaction may be "positive" (i.e., accelerating) or "negative"

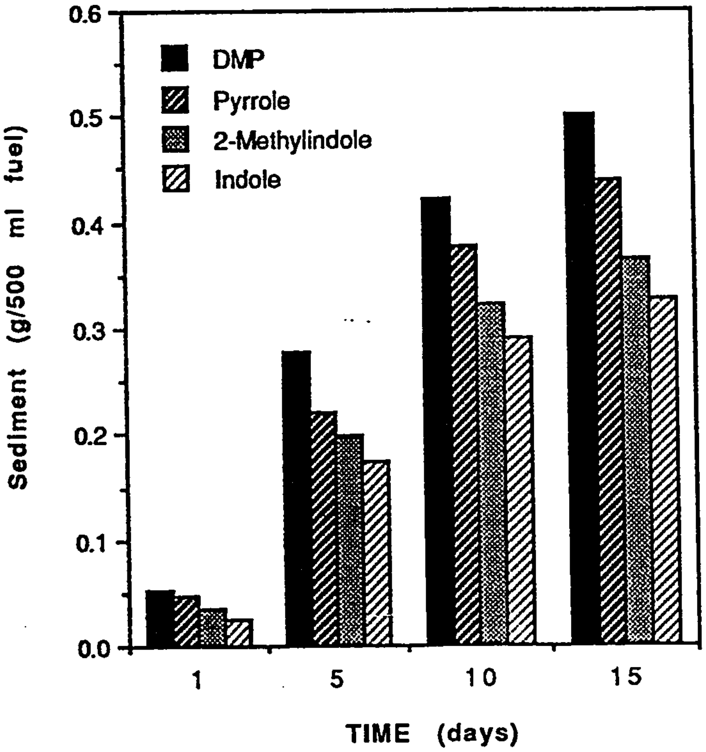


Figure 10. Structural effects of model nitrogen compounds on sediment formation in Jet A fuel under sunlight storage

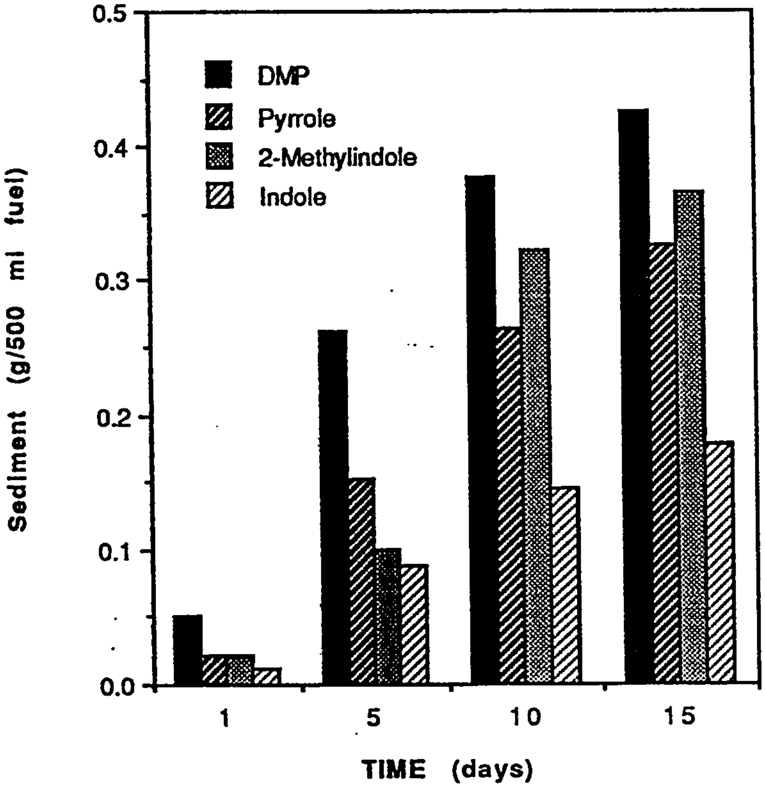


Figure 11. **Structural effects of model nitrogen compounds on sediment formation in Jet A fuel under UV radiation**

(i.e. inhibiting) in nature. Thus, in a "positive" interaction, a mixture of nitrogen and oxygen compounds will generate more sediment than the sum of the two interactants acting independently. "Negative" interactions have the opposite effect.

Frankenfeld and Taylor [1] studied the effects of acids (decanoic acid, cyclohexanecarboxylic acid and benzoic acid) with DMP in decane on the rate of sediment formation. The decanoic acid and cyclohexanecarboxylic acids significantly increased the rate of sedimentation in the dark as well as when exposed to sunlight, while benzoic acid showed no effect under light storage, but did tend to increase deposit formation in dark. A number of phenols (2,4,6-trimethylphenol, 2,6-di-tert-butylphenol, 2,4-dimethylphenol, 2,6-di-tert-butyl-4-methylphenol and 2-hydroxy-3-isopropylphenol) were also investigated by [1]. All had inhibitory effects, although considerable variation was observed.

In order to investigate the effects of oxygen containing compounds in Saudi Arabian petroleum derived jet A fuel, two different types of acids and phenol were examined. These compounds varied considerably in their influence on fuel instability. In order to study the interactive effects of acid/nitrogen compounds and phenol/nitrogen compounds, the following blends were prepared.

1. 50 ppm O level of decanoic acid and 200 ppm N level of DMP.
2. 50 ppm O level of decanoic acid and 200 ppm N level of pyrrole.
3. 50 ppm O level of cylohexanecarboxylic acid and 200 ppm N level of DMP.
4. 50 ppm O level of cylohexanecarboxylic acid and 200 ppm N level of pyrrole.

5. 50 ppm O level of 2,6-di-tert-butyl phenol and 200 ppm N level of DMP.
6. 50 ppm O level of 2,6-di-tert-butyl phenol and 200 ppm N level of pyrrole.
7. 50 ppm O level of 2,4,6-trimethyl phenol and 200 ppm N level of pyrrole.

This investigation is also extended to determine whether the oxidation of nitrogen compound such as 2,5-dimethylpyrrole, is subject to acid catalysis (e.g. decanoic acid or cyclohexanecarboxylic acid), or if the condensation products could form in lieu of true catalysts.

Two sets of each blend were prepared by dissolving 200 ppm N level of DMP and pyrrole and 50 ppm of O level of decanoic acid, cyclohexane carboxylic acis, 2,4,6-trimethylphenol and 2,6-di-tert-butylphenol in 500 ml fuel. These levels were chosen as representative of probable maximum for jet fuels derived from petroleum. One set was placed in sunlight and other was irradiated with uv light for the time period of 1, 5, 10 and 15 days respectively.

Table (8) lists the amount of sediment formation by n-decanoic acid (DA) and cyclohexanecarboxylic acid (CCA) with DMP and pyrrole at the intervals of 1, 5, 10 and 15 days. A strong "positive" interaction was encountered between pyrrole derivatives and acids. With DMP, the carboxylic acids (n-decanoic acid and cyclohexanecarboxylic acid) all interacted in a synergistic fashion to increase the amount of sediment generation. The DMP-cyclohexanecarboxylic acid blends produced slightly more sediment than the DMP - decanoic acid blend. In the comparison of DMP and DMP - acid blend, the sediment formation is enhanced in the presence of acid, thus the DMP - acid blend accounted for more sediment than DMP alone in sunlight as well as uv light as shown in Figure (12). Similar types of results were obtained in the case of

TABLE 8

EFFECTS OF ORGANIC ACIDS ON SEDIMENT FORMATION WITH 2,5-DMP & PYRROLE IN JET A FUEL

Compound Added(1)	Storage Condition(2)	Cumulative Sediment (g/500 ml Fuel)				
		1 Day	5 Days	10 Days	15 Days	Comments
2,5-Dimethylpyrrole	Sun light	0.052	0.277	0.422	0.501	Dark Tan
DMP + Decanoic Acid	Sun light	0.084	0.343	0.463	0.531	Dark Tan
DMP + Cyclohexanecarboxylic Acid	Sun light	0.088	0.356	0.468	0.535	Dark Tan
Pyrrole	Sun light	0.046	0.221	0.378	0.439	Yellow
Pyrrole + Decanoic Acid	Sun light	0.054	0.282	0.438	0.489	Dark Yellow
Pyrrole+Cyclohexanecarboxylic Acid	Sun light	0.063	0.307	0.451	0.495	Dark Yellow
2,5-Dimethylpyrrole	UV light	0.050	0.262	0.376	0.425	Dark Tan
DMP + Decanoic Acid	UV light	0.076	0.314	0.415	0.465	Dark Tan
DMP+Cyclohexanecarboxylic Acid	UV light	0.078	0.326	0.420	0.471	Dark Tan
Pyrrole	UV light	0.022	0.152	0.264	0.326	Yellow
Pyrrole + Decanoic Acid	UV light	0.049	0.192	0.305	0.360	Dark Yellow
Pyrrole+Cyclohexanecarboxylic Acid	UV light	0.059	0.204	0.316	0.367	Dark Yellow

(1) Nitrogen compounds added at 200 ppm N level, acids at 50 ppm O level.

(2) UV light = UV radiation (365nm : 7000 $\mu\omega/\mathrm{cm}^2$) : Dark = Stored in dark.

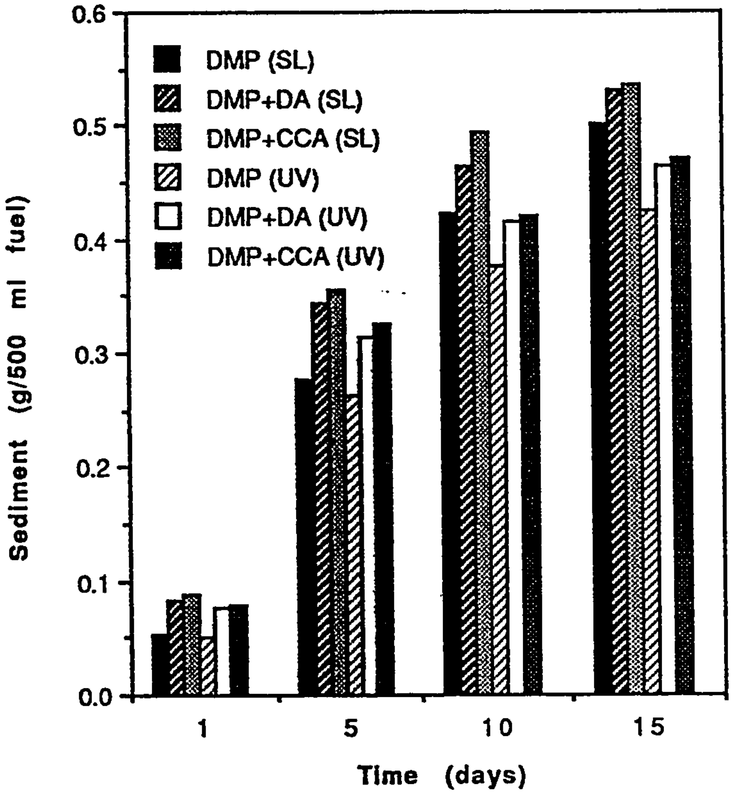


Figure 12. Effects of acids on sediment formation in sunlight and UV with DMP in Jet A fuel

pyrrole and acids (n-decanoic acid and cyclohexanecarboxylic acid) blend as shown in Figure (13).

The samples of DMP induced sediment were analyzed for their elements and the results are shown in Table (14). The analysis of DMP sediment produced from interaction of carboxylic acids (decanoic acid and cyclohexane carboxylic acid) in sunlight as well as uv light have 61.99% C, 6.28% H, 10.46% N and 17.94% O respectively. These are almost identical in the elemental composition of DMP sediments i.e. 60.95% C, 6.15% H, 10.44% N and 18.88% O respectively, which were obtained from without carboxylic acids. This data indicate that the DMP derived sediments produced in interactive experiments of carboxylic acids proved to be remarkably similar to the insoluble materials generated by DMP without co-dopant. Thus, it would appear that the carboxylic acids are serving as true catalysts of DMP oxidation.

The results on sediment formation are summarized in Table (9) by 2,4,6-trimethylphenol and 2,6-di-tert-butylphenol with DMP and pyrrole. The phenols have an inhibitory effect i.e. "negative" interaction and significantly decrease the rate of sediment formation with DMP and pyrrole. One of the most effective inhibitors was 2,6-di-tert-butylphenol (DtBP). The DMP - 2,6-di-tert-butylphenol blend accounted less sediment than DMP alone. Plots of sediment formation with DMP, both with and without added 2,6-di-tert-butylphenol are shown in Figure (14).

In case of pyrrole and pyrrole - phenol blend, similar type of results were obtained. The pyrrole - 2,4,6-trimethylphenol (TMP) blend contributed more sediment than pyrrole - 2,6-di-tert-butylphenol blend both in sunlight as well as in uv light as shown in Figure (15).

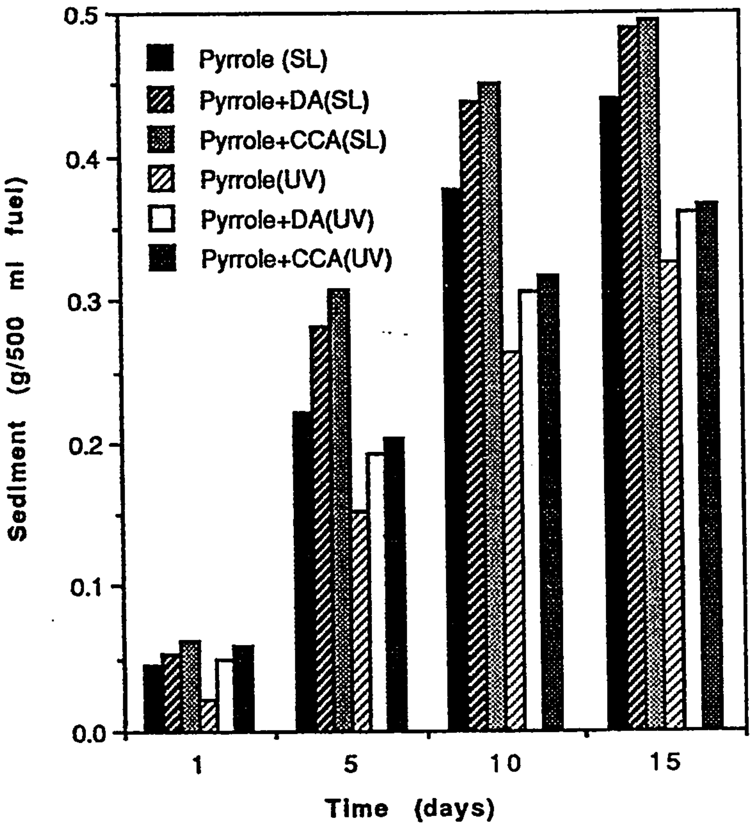


Figure 13. Effects of acids on sediment formation in sunlight and UV with pyrrole in Jet A fuel

TABLE 9

EFFECTS OF PHENOL ON SEDIMENT FORMATION WITH DMP AND PYRROLE IN JET A FUEL

Compound Added(1)	Storage Condition(2)	Cummulatilve Sediment (g/500 ml fuel)				Comments
		1 Day	5 Days	10 Days	15 Days	
Pyrrole	Sun light	0.046	0.221	0.378	0.439	Yellow
Pyrrole + 2,4,6-trimethylphenol	Sun light	0.020	0.132	0.235	0.294	Dark Yellow
Pyrrole + 2,6-di-tert-butylphenol	Sun light	0.013	0.105	0.198	0.257	Yellow
2,5-Dimethylpyrrole	Sun light	0.052	0.277	0.422	0.501	Dark Tan
DMP + 2,6-di-tert-butylphenol	Sun light	0.026	0.134	0.201	0.243	Dark Tan
Pyrrole	UV light	0.022	0.152	0.264	0.326	Yellow
Pyrrole + 2,4,6-trimethylphenol	UV light	0.011	0.059	0.118	0.145	Dark Yellow
Pyrrole + 2,6-di-tert-butylphenol	UV light	nil	0.045	0.096	0.123	Yellow
2,5-Dimethylpyrrole	UV light	0.050	0.262	0.376	0.425	Dark Tan
DMP +2,6-di-tert-butylphenol	UV light	0.022	0.113	0.167	0.202	Dark Tan

(1) Nitrogen compounds added at 200 ppm N level, phenol at 50 ppm O level

(2) UV light = UV radiation (365nm : 7000 µω/cm^2) : Dark = Stored in dark

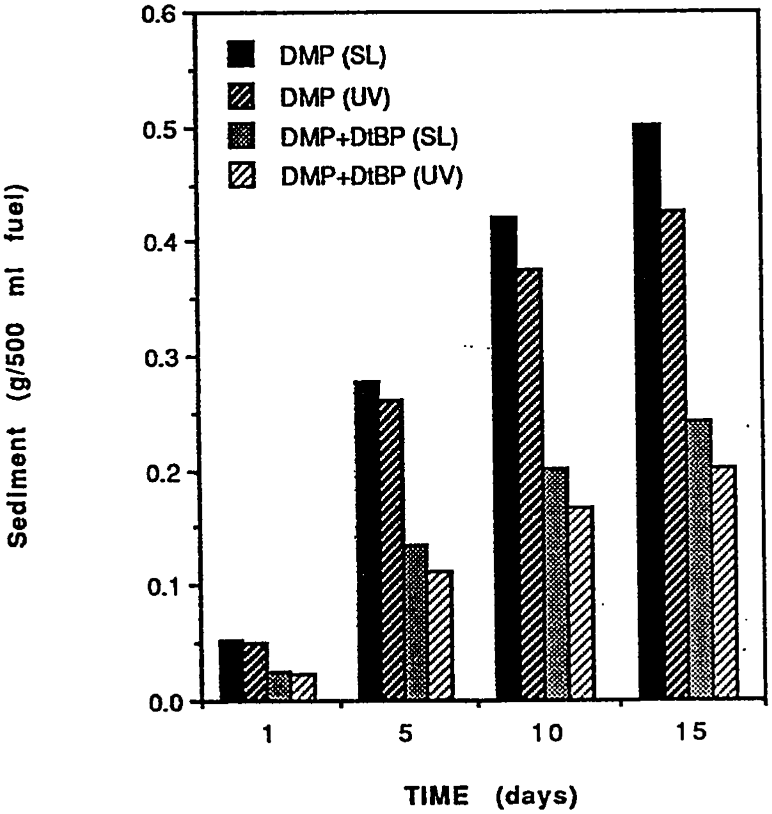


Figure 14. Effects of phenol on sediment formation in sunlight and UV with DMP in Jet A fuel

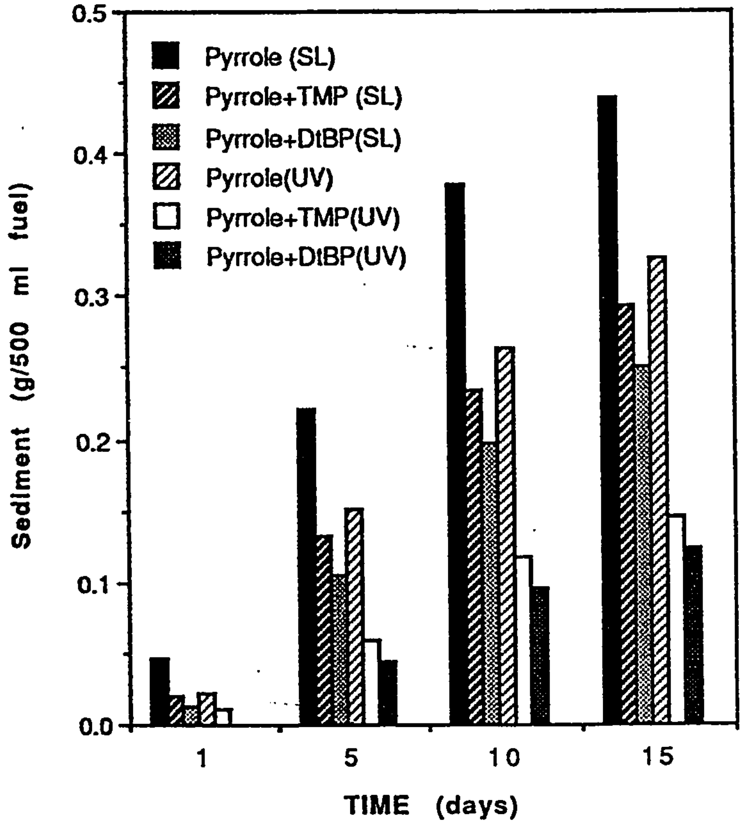


Figure 15. Effects of phenols on sediment formation in sunlight and UV with pyrrole in Jet A fuel

The 2,6-di-tert-butylphenol produced less sediment (i.e. less reactive) than 2,4,6-trimethylphenol due to two probable reasons. The tert-butyl groups and methyl groups are most effective in retarding sedimentation, while the tert-butyl groups tended to reduce effectiveness more, although this effect is not large. The sediment formation reaction proceeds through the peroxyl radical formation and the presence of two ortho-tert-butyl groups hinder the approach of peroxyl radical.

In the comparison of nitrogen containing compounds, acid blend, and phenol blend, Figure (16) indicated that DMP - cyclohexanecarboxylic acid blends are major promoters of sedimentation while DMP - 2,6-di-tert-butylphenol blend is an inhibitor towards sedimentation. The rate of sedimentation decreases in the order of

DMP-CCA > DMP-DA > DMP > DMP-DtBP

As shown in Figure (17) similar type of results were obtained in the case of pyrrole. The rate of sediment formation decreases in the order of

pyrrole-CCA > pyrrole-DA > pyrrole > pyrrole-TMP > pyrrole-DtBP

These studies resulted that the acids are promoter and phenols are inhibitors toward the generation of sediment.

4.5. SEDIMENT FORMATION IN DEOXYGENATED MEDIA

Previous studies have shown that the presence of nitrogen compounds can be highly deleterious to air-saturated fuels under normal storage conditions [3]. Where as in a study using deoxygenated JP-5 fuel, the addition of nitrogen compounds as pure materials did not increase deposit formation over the temperature range of 140 - 450°C [105]. However, certain nitrogen

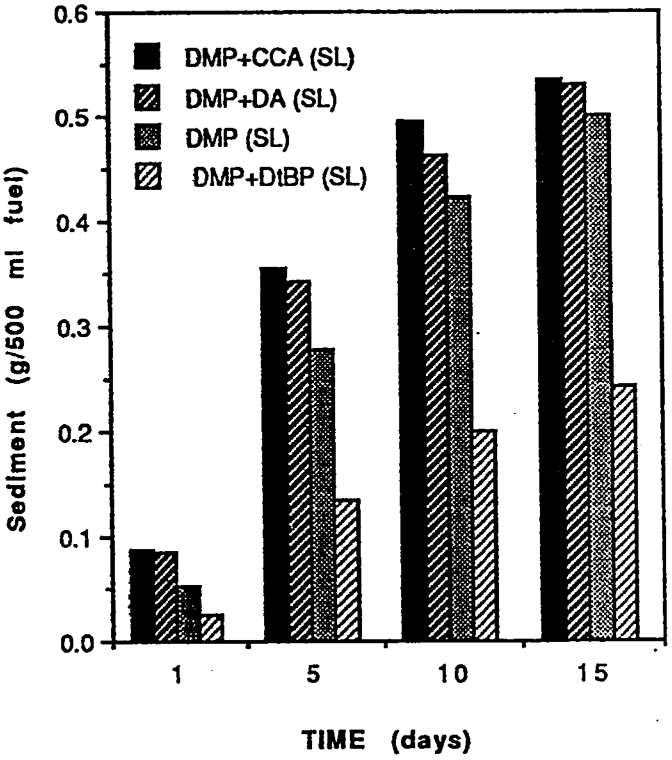


Figure 16. Effects of acids & phenol on sediment formation in sunlight with DMP in Jet A fuel

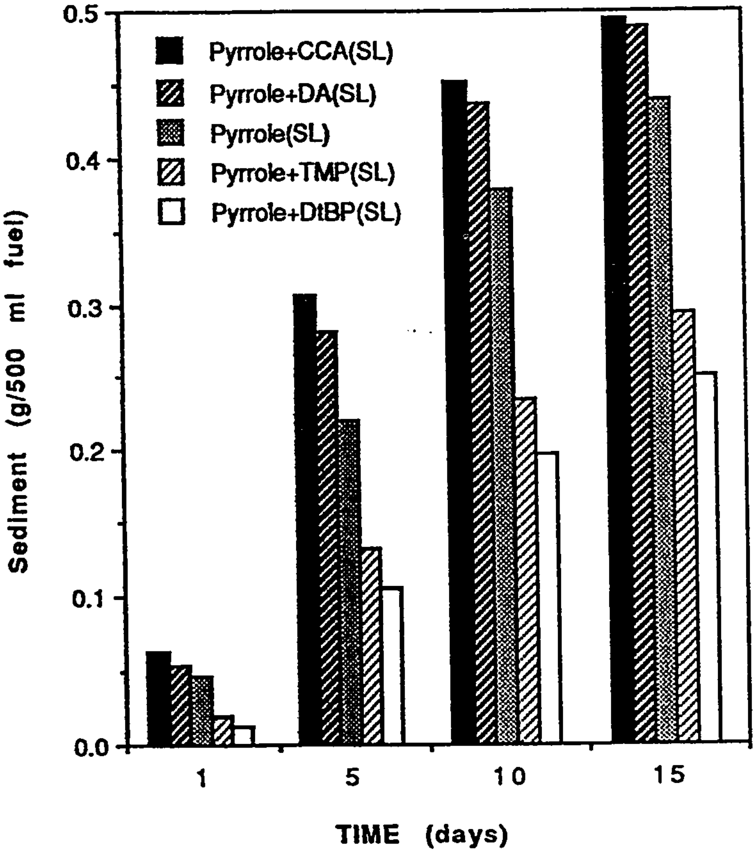


Figure 17. Effects of acids & phenols on sediment formation in sunlight with pyrrole in Jet A fuel

compounds such as heterocyclic amines, DMP, indole and carbazole were found to produce sludge even at low temperature ranges of 20 - 25°C.

In the present study the initial work was carried out on the jet A fuel samples as received without any deaeration at ambient temperature. The samples were exposed to sunlight or uv light in order to investigate the storage stability characteristics. The study was further extended to include deoxygenated fuel in order to study the effects of oxygen on deposit formation rate, where the oxygen content rate was continuously reduced.

The solution was prepared by dissolving 200 ppm N level of DMP in jet A fuel sample. Argon gas was blown in this solution throughout the reaction period, i.e. 1 - 15 days. The amount of sediment formed in deoxygenated media are shown in Table (10) for the time period of 1, 5, 10 and 15 days respectively. The deposit formation under deoxygenated fuel conditions are compared with air saturated fuel in Figure (18). The air saturated fuel generated more sediment than the corresponding deoxygenated fuel. The deposit formation in jet fuel is known to involve both chemical and physical changes. In air saturated fuel system the sediment are formed as a result of free radical chain reaction (autoxidation) at ambient temperature [101, 103]. However, in deoxygenated fuels, the process appears to be different and even more complex [104].

Furthermore, the deoxygenated fuels show an intermediate increase in deposit formation at ambient temperature, while the air saturated fuel system exhibit a gradual increase in deposit formation. This suggests a steady generation of peroxide compounds due to autoxidation of the base fuel by

TABLE 10

EFFECTS OF DMP ON SEDIMENT FORMATION IN DEOXYGENATED JET A FUEL

Compound Added(1)	Storage Condition(3)	Cumulative Sediment (g/500 ml Fuel)				
		1 Day	5 Days	10 Days	15 Days	Comments
2,5-Dimethylpyrrole	UV light	0.012	0.030	0.037	0.041	Yellow
2,5-Dimethylpyrrole(2)	UV light	0.050	0.262	0.507	0.710	Dark Tan

(1) Dimethylpyrrole added to deoxygenated Jet - A fuel at 200 ppm N level

(2) Dimethylpyrrole added to air saturated Jet - A fuel at 200 ppm N level

(3) UV light = UV radiation (365nm : 7000 $\mu\omega/cm^2$)

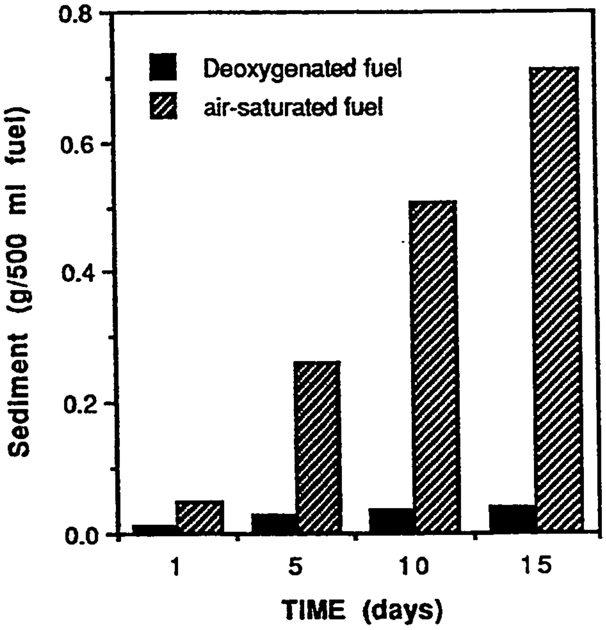


Figure 18. Plots of sediment formation with DMP in deoxygenated versus air-saturated jet A fuel.

dissolved oxygen. These results strongly suggest that peroxides, which are formed as intermediates during the reaction period, are a major cause of deposit formation in air saturated fuel systems.

The above experiment was extended for a period of 30 days, and the argon gas was continuously purged through the test sample. Figure (19) shows a plot of sediment formation versus storage time. This shows that the rate of sediment formation was initially high but gradually very slow and after a period of 15 days there was approximately no further increment. This indicates that the dissolved oxygen is directly proportional to the sediment produced.

4.6. SEDIMENT FORMATION IN n-DECANE

Frankenfeld et al. [1] used n-decane, as a model fuel system, and investigated the effects of nitrogen compounds (pyrrole, indole and amines derivatives) on sediment formation. Pyrrole and indole derivatives increased the rate of sediment formation rate but amine derivatives did not produce any appreciable amount of sediment.

A study was also conducted on the effect of oxygen on sediment formation in a simple hydrocarbon media like n-decane. It was thought that such study will enable us to compare the results with the result reported earlier using air saturated and deoxygenated jet A fuel. The experiments were performed under air saturated n-decane and deoxygenated decane. Two sets of blends were prepared by dissolving 1000 ppm N level of DMP in 200 ml of decane. One set was purged with nitrogen to remove the dissolved oxygen from decane and the other was used without removing any dissolved oxygen. Table (11) gives the results on sediment formation by both deoxygenated and air saturated decane at the intervals of 1, 5, 10, 15 and 20 days respectively.

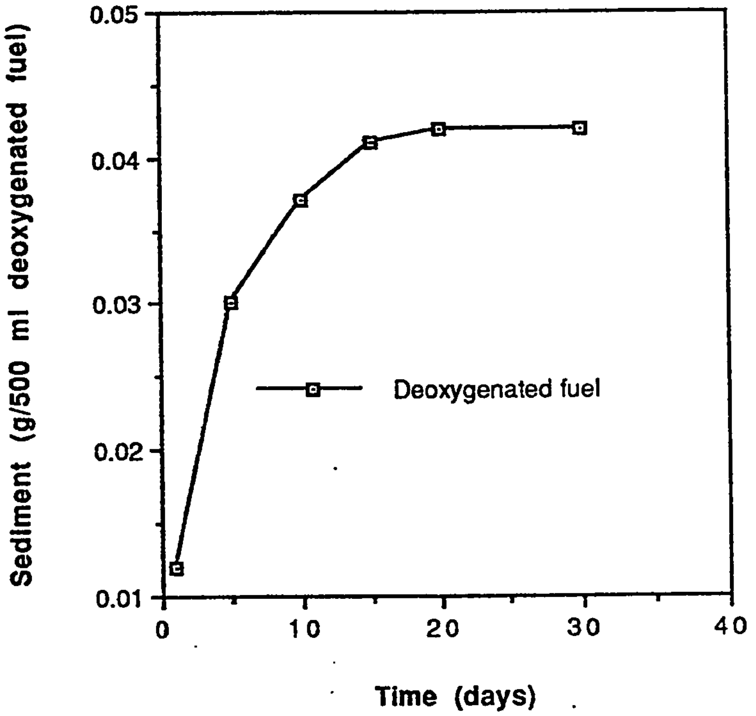


Figure 19. Plots of sediment formation versus storage period in deoxygenated jet A fuel

TABLE 11

EFFECTS OF DMP ON SEDIMENT FORMATION IN N-DECANE

Compound Added(1)	Storage Condition(2)	Cumulative Sediment (g/200 ml Fuel)					
		1 Day	5 Days	10 Days	15 Days	20 Days	Comments
2,5-Dimethylpyrrole*	UV light	0.008	0.012	0.013	0.013	0.013	Colorless
2,5-Dimethylpyrrole	UV light	0.072	0.093	0.125	0.148	0.162	Yellow

* Purged decane + 2,5-dimethylpyrrole

(1) Dimethylpyrrole added to decane at 1000 ppm N level

(2) UV light = UV radiation (365nm : 7000 $\mu\omega/\text{cm}^2$)

The result shows that the purged decane afforded only trace amounts of sediment, and unpurged samples generated appreciable amounts of sediment as indicated in Figure (20). The sediment formation in deoxygenated n-decane was initially high but leveled off after 10 days. However, in air saturated n-decane, the rate of sediment formation was found to increase gradually with storage time. This experiment also supports the further statement that oxygen is responsible for sediment formation and the reaction proceeds through the free radical mechanism. From our investigation of deoxygenated n-decane the rate of sediment formation become constant i.e. no further increment after 10 days may be due to the incomplete removal of oxygen from n-decane by 10 - 15 minutes purging, which resulted in the sediment formation. Sediment formation stopped after the consumption of all of the oxygen, which can be seen from plots in Figure (21).

The dissolved oxygen appears to play a significant role in sediment formation rate for both jet-A fuel and n-decane. However, the effect is much more pronounced in jet fuel than in pure n-decane. The chemical characteristics of base fuels exert a significant influence on the amount of nitrogenous sediment formation. Jet A fuel is a complex mixture of different types of hydrocarbons, traces of heteroatoms and some metals. Therefore it is more prone to autoxidation as compared to a pure hydrocarbon fuel. As a result, the fuel becomes more complex and the sediment formation rate increases (i.e. n-decane < jet A fuel).

All these experiments have suggested that the rate of sediment formation was dependent upon the structural features of nitrogen compounds, dissolved oxygen, the nature of diluent employed and storage conditions.

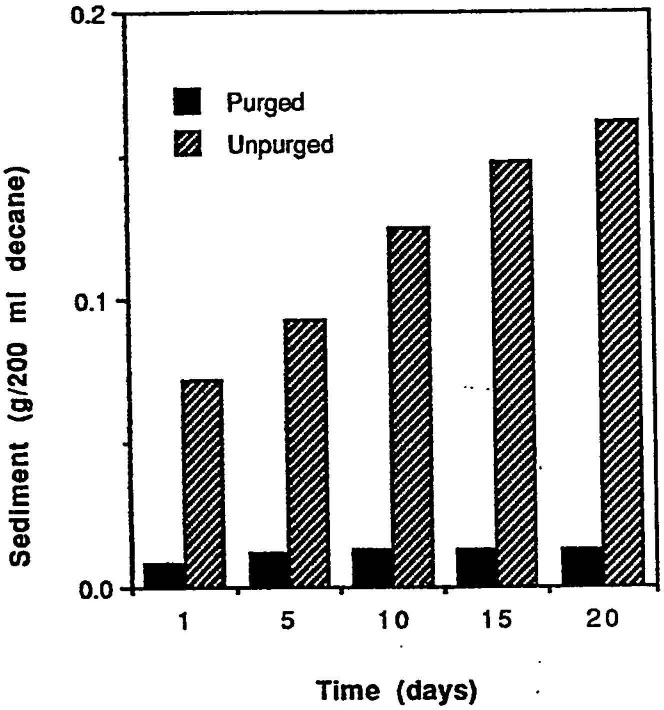


Figure 20. Plots of sediment formation with DMP in purged versus unpurged decane

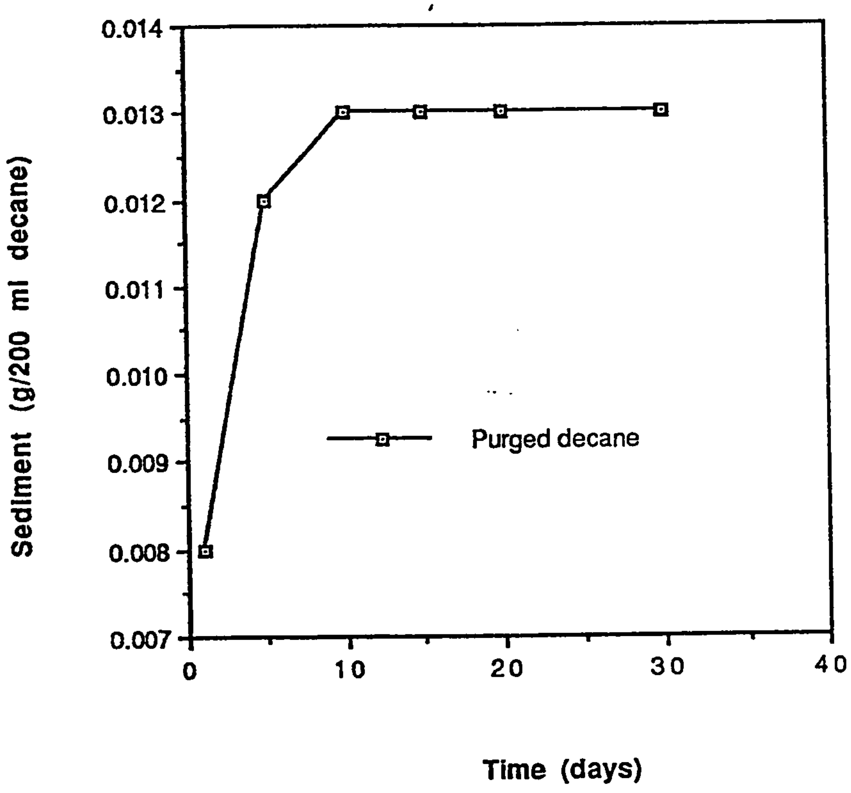


Figure 21. Plots of sediment weight versus storage period in purged decane

4.7. DEPOSIT FORMATION BY ACCELERATED STABILITY TEST

The effects of temperature on reaction was investigated with DMP in jet A fuel. The experiments were carried out over a temperature range of 43 - 80°C. Table (12) lists the insoluble sediment, adherent sediment, total sediment (W) and blanks (no DMP added to the fuel) from a 0.02M DMP solution in 200 ml jet - A fuel. Figure (22) gives the plots of W versus time for each of the three temperatures (43, 67 and 80°C) for each stress period of 2, 4, 6, 8, 10 and 12 days. A plot of ln W versus 1/T is linear as shown in Figure (23). The total sediment obtained from a 0.02 M DMP solution in jet A fuel after storage for 12 days, corrected for the blanks, then the temperature variation data can be used to calculate the apparent activation energy (Ea) for total sediment as Ea = 12.65 K Cal mol^{-1}. This apparent activation energy is approximately same (i.e. Ea = 12.7 $KCalmol^{-1}$) as that reported by Frankenfeld et al. [6] for a 0.107 M DMP solution in a petroleum derived jet fuel from Bayway, NJ, refinery from a linear plot when the jet fuel was stored for 14 days at the temperature range of 23 - 68°C. Li & Li [7] also obtained apparent activation energy Ea = 12.7 K Cal mol^{-1} for a 0.0286 M DMP solution in petroleum derived Jet A fuel from Gulf Research and Development Co. from a linear plot for 12 days storage of jet A fuel at the temperature range of 43-80°C.

The experiment was repeated using different DMP concentrations such as 375, 500, 625 ppm N level DMP in jet - A fuel and samples were stressed at 43°C for 6 -14 days. Table (13) lists the total sediment, g / 100 ml fuel. Figure (24) shows the sediment formation for different DMP concentration at 43°C in dark storage conditions. Linear plots for the periods of 6, 8, 10, 12 and 14 days were obtained as shown in Figure (25). Linear curve were also obtained by Frankenfeld et al. [6] when the experiment was carried out in jet fuel for 14 - 56

TABLE 12

SEDIMENTATION RESULTS, G/100 ML, WITH CONSTANT DMP CONCENTRATIONS IN JET A FUEL

Storage for days	Storage temperature (^{o}C)	Insoluble sediment	Adherent sediment	Total sediment (W)
2	43	0.0014	0.0005	0.0019
2	67	0.0045	0.0007	0.0052
2	80	0.0073	0.0008	0.0081
4	43	0.0017	0.0007	0.0024
4	67	0.0061	0.0010	0.0071
4	80	0.0116	0.0012	0.0128
6	43	0.0021	0.0008	0.0029
6	67	0.0093	0.0011	0.0104
6	80	0.0184	0.0014	0.0198
8	43	0.0026	0.0009	0.0035
8	67	0.0107	0.0015	0.0122
8	80	0.0229	0.0020	0.0249
10	43	0.0029	0.0009	0.0038
10	67	0.0121	0.0022	0.0143
10	80	0.0257	0.0027	0.0284
12	43	0.0032	0.0011	0.0043
12	67	0.0131	0.0024	0.0155
12	80	0.0271	0.0031	0.0302
12[a]	43	0.0005	0.0003	0.0008
12[a]	67	0.0006	0.0004	0.0010
12[a]	80	0.0009	0.0006	0.0015

a = No DMP added to jet A (blanks)

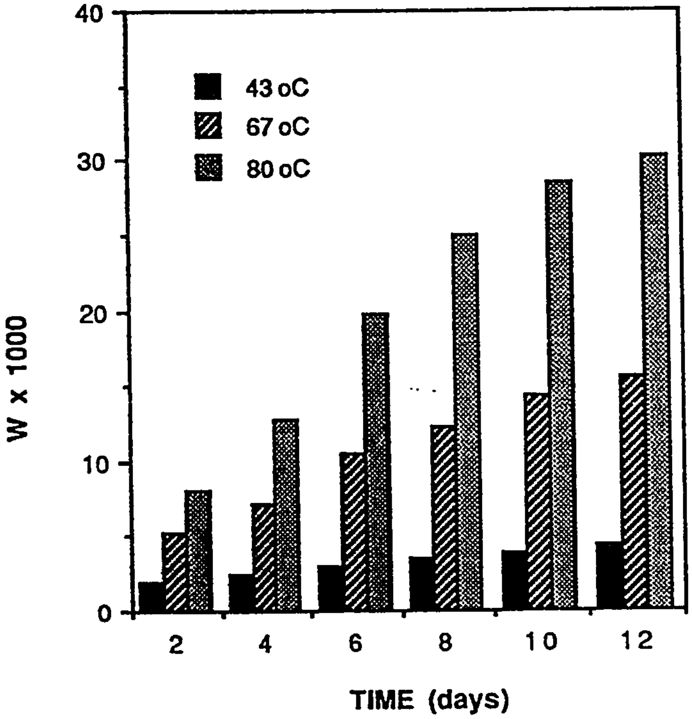


Figure 22. Plots of total sediment weight (W) versus time at 43°, 67° and 80° C

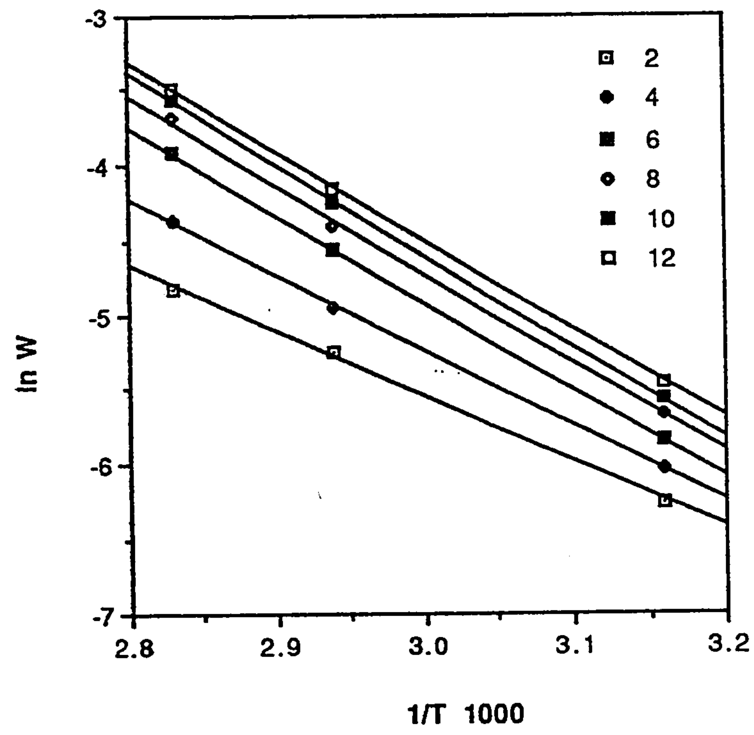


Figure 23. Plots of ln W versus 1/T for systesm of figure 22

TABLE 13

SEDIMENTATION RESUTLS, G/100 ML FUEL, WITH DIFFERENT DMP CONCENTRATIONS IN JET A FUEL

Conc. DMP	6 days	8 days	10 days	12 days	14 days
375 ppm N	0.014	0.018	0.023	0.027	0.030
500 ppm N	0.021	0.025	0.029	0.033	0.035
625 ppm N	0.026	0.031	0.034	0.038	0.041

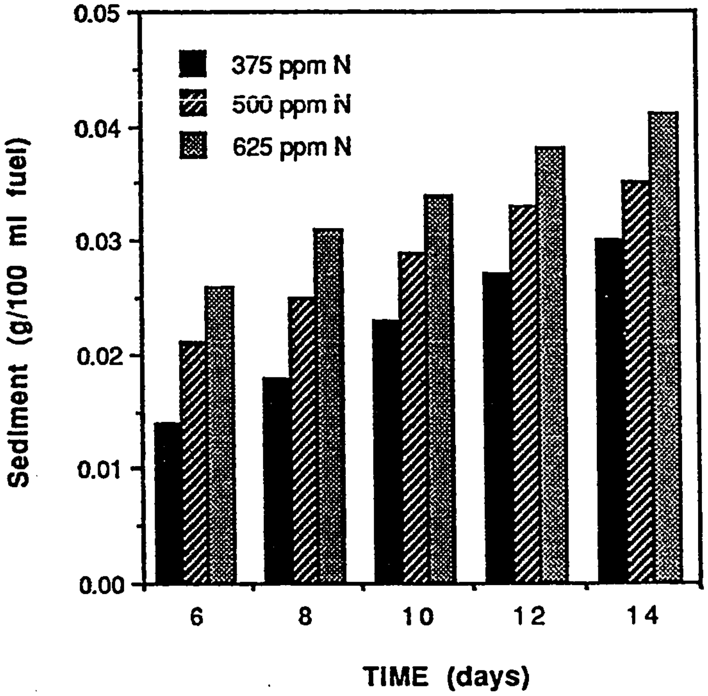


Figure 24. Effects of different DMP concentrations on sediment formation at 43°C in dark storage

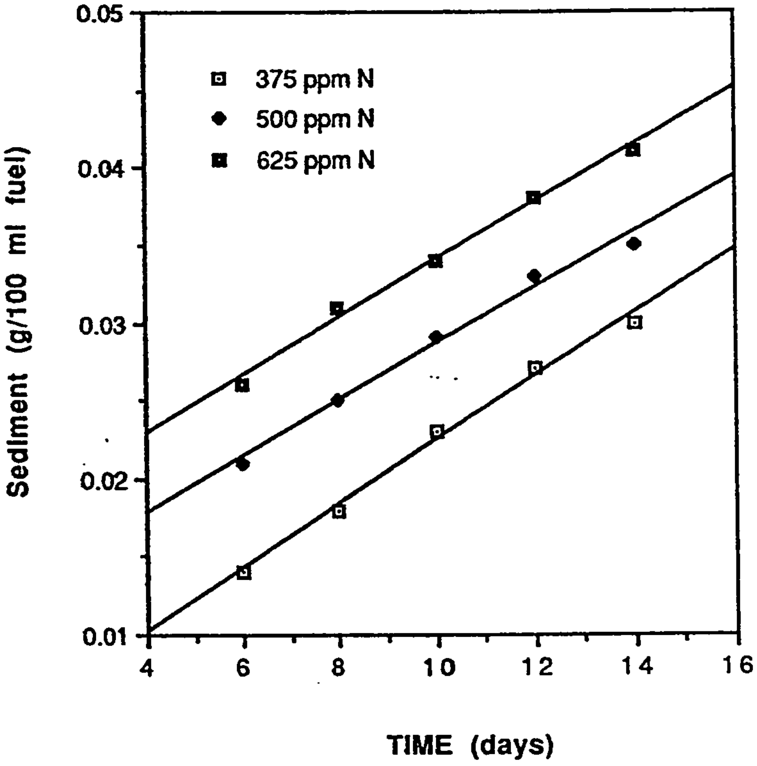


Figure 25. Plots of total sediment weight versus time of figure 24.

days in dark storage at 43.3°C. Li and Li [7] also obtained approximately linear curves for a JP - 5 fuel containing 0, 0.286, 0.429 and 0.572 M DMP when stressed at 80°C for 6 - 14 days.

These experiments show that sediment formation increases with increase in either DMP concentration or temperature and storage times, and the relations are linear as shown in Figures (23) and (25).

4.8. ELEMENTAL COMPOSITION OF SEDIMENTS

The elemental analyses of sediments obtained from DMP doped jet A fuel, under different experimental conditions are repeated in Table (14). The elemental ratio and empirical formula of all sediment samples are given in Tables (15) and (16) respectively. The storage conditions, oxidation at different temperatures and presence of acids may effect the rate of formation and quantity of sediment, but they do not seem to alter the characteristics of sediment. Elemental analysis of sediments suggest that the deposits are largely made up of repeating units of DMP. The composition of DMP is C_6H_9N. This is clear from table (14) i.e. average (of all 10 experiments) C/N ratio of DMP (6.5/1) is very close to C/N ratio of DMP (6/1). Thus, no other carbon containing species have been introduced into the polymer. On the other hand, considerable oxygen (average 1.5 atoms per N) has been incorporated, mostly at the expense of hydrogen atoms while preserving the C/N ratio at six. The empirical formula of all sediment samples are shown in table (14).

The elemental ratios for all the sediments shown in Table (15) indicate that carbon was the major element, but high concentration of oxygens and low concentrations of nitrogen were also present in these deposits. The H/C ratio

TABLE 14

ELEMENTAL COMPOSITONS OF THE SEDIMENTS

Sediment	Storage condition	Storage time	% C	% H	% N	%O	% S	Total
DMP	Sunlight	1 day	62.95	6.28	10.67	16.79	ND	96.69
DMP	UV light	15 days	58.95	6.02	10.22	20.98	ND	96.17
DMP + DA	Sunlight	1 day	60.32	6.26	10.19	19.10	ND	95.87
DMP + DA	UV light	15 days	64.20	6.34	10.23	16.08	ND	96.85
DMP + CCA	Sunlight	1 day	60.63	6.19	9.98	19.21	ND	96.01
DMP + CCA	UV light	1 day	60.86	6.24	10.72	19.29	ND	97.11
DMP + CCA	UV light	15 days	63.95	6.38	10.92	16.01	ND	97.26
DMP	Dark (43^{o}C)	15 days	62.60	5.70	11.80	16.60	ND	96.70
DMP	Oxidation (80^{o}C)	10 hours	61.70	6.00	11.40	17.50	ND	96.60
DMP	Oxidation (95^{o}C)	10 hours	61.61	5.94	11.53	17.51	ND	96.59

ND = Not detected < 0.3 %.

TABLE 15

ATOMIC RATIO OF DIFFERENT ELEMENTS PRESENT IN SEDIMENTS

Additives	Storage condition	Storage time	C/N	H/C	O/C
DMP	Sunlight	1 day	4.50	1.82	0.31
DMP	UV light	15 days	6.7	1.22	0.27
DMP + DA	Sunlight	1 day	7.0	1.23	0.23
DMP + DA	UV light	15 days	7.3	1.19	0.19
DMP + CCA	Sunlight	1 day	7.0	1.24	0.24
DMP + CCA	UV light	1 day	6.6	1.23	0.24
DMP + CCA	UV light	15 days	6.8	1.20	0.19
DMP	Dark (43°C)	15 days	6.2	1.10	0.19
DMP	Oxidation (80°C)	10 hours	6.3	1.16	0.21
DMP	Oxidation (95°C)	10 hours	6.2	1.16	0.21

TABLE 16

EMPIRICAL FORMULA OF SEDIMENTS

Sediment	Storage condition	Storage time	Empirical formula
DMP	Sunlight	1 day	$C_{6.8} H_{8.2} N O_{1.4}$
DMP	UV light	15 days	$C_{6.7} H_{8.2} N O_{1.8}$
DMP + DA	Sunlight	1 day	$C_{7.0} H_{8.6} N O_{1.6}$
DMP + DA	UV light	15 days	$C_{7.3} H_{8.7} N O_{1.7}$
DMP + CCA	Sunlight	1 day	$C_{7.0} H_{8.7} N O_{1.7}$
DMP + CCA	UV light	1 day	$C_{6.6} H_{8.1} N O_{1.6}$
DMP + CCA	UV light	15 days	$C_{6.8} H_{8.2} N O_{1.3}$
DMP	Dark (43°C)	15 days	$C_{6.2} H_{6.8} N O_{1.2}$
DMP	Oxidation (80°C)	10 hours	$C_{6.3} H_{7.3} N O_{1.3}$
DMP	Oxidation (95°C)	10 hours	$C_{6.2} H_{8.8} N O_{1.3}$

for all samples were ranging from 1.10 to 1.82, indicating that aromatic or heteroatomic compounds were significantly involved in the deposit formation. The O/C ratios, between 0.16 to 0.31, supported the view point that oxidation is a key aspect of jet fuel thermal instability.

4.9. INFRA-RED SPECTROSCOPY

The sediments obtained from a variety of storage conditions were analysed by infrared spectroscopy. Sediment analyses indicate the sediment is derived from oxidation of DMP with no incorporation of fuel constituents. No changes were observed in the IR spectra of stressed fuel samples with increasing length of stress shown in figures (2) (i.e. pure fuel sample), (26) (i.e. fuel and DMP solution irradiated with UV radiation upto 15 days) and (27) (i.e. fuel and DMP solution stressed at 95^{o}C about 10 hours). Thus, the soluble primary oxidation products derived from DMP are highly reactive and are rapidly converted to insoluble sediments.

Figures (28a, 28b), (29a, 29b), (30a, 30b), (31a, 31b), (32a, 32b) and (33a, 33b) show infra-red spectra of 1 day and 15 days sunlight exposed sediment, 15 days UV radiated exposed sediments, uv irradiated decane sediment, uv irradiated deoxygenated fuel and uv irradiated purged decane sediment. The infrared spectra of sediments obtained from accelerated oxidation testing of kerosene with 200 ppm N level of DMP at 80^{o}C and 95^{o}C are shown in Figures (34) and (35).

The broad strong intensity band at 3361 - 3263 cm^{-1} in infrared spectra of all sediments suggests the presence of a hydroxyl (O-H) or amino (N-H) group. To confirm the functional group corresponding to the peak, 15 days uv and sunlight exposed samples were dried in a vacuum to remove the moisture.

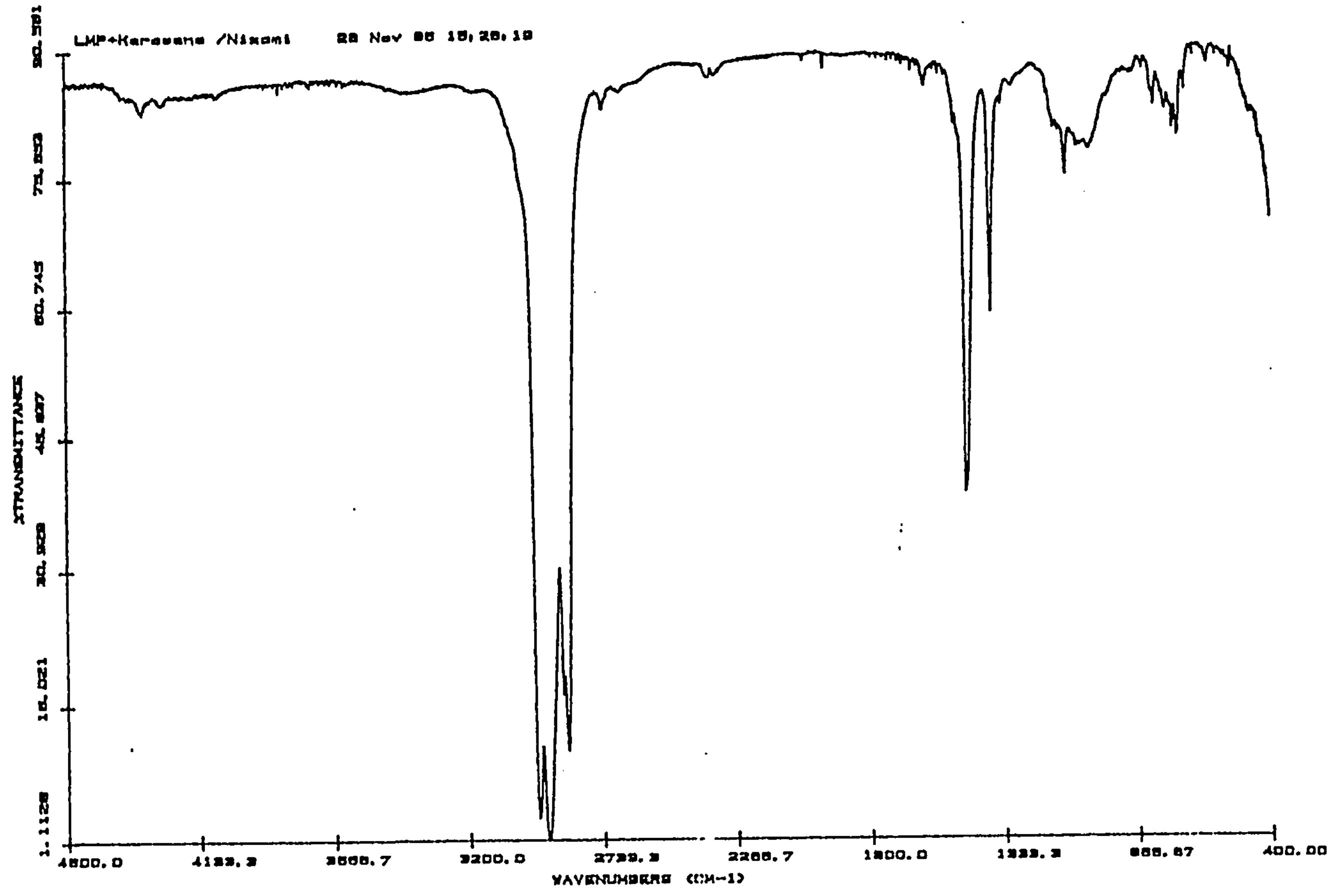


Figure 26. Infrared spectra of kerosene with DMP.

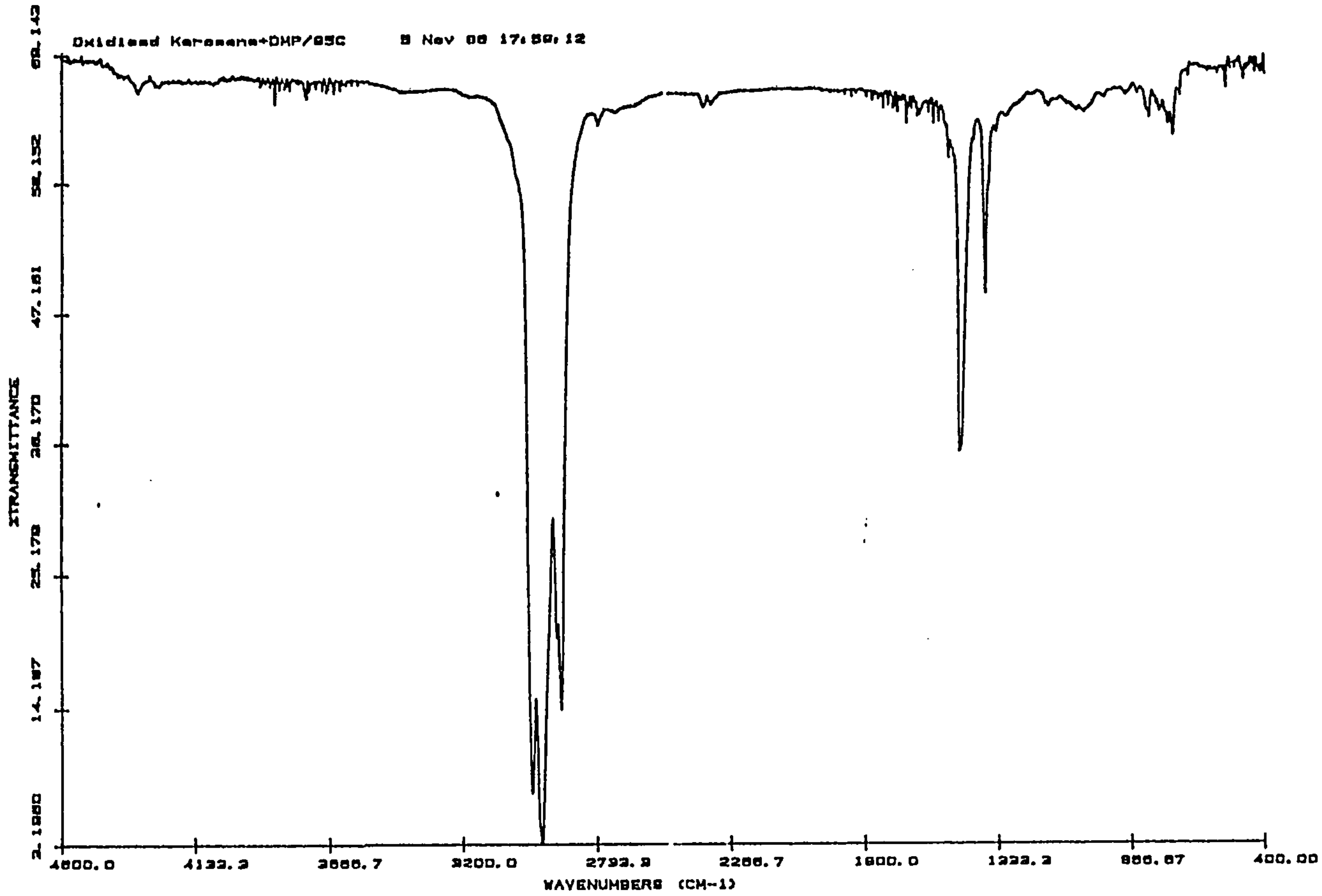


Figure 27. Infrared spectra of kerosene with DMP accelerated at 95°C.

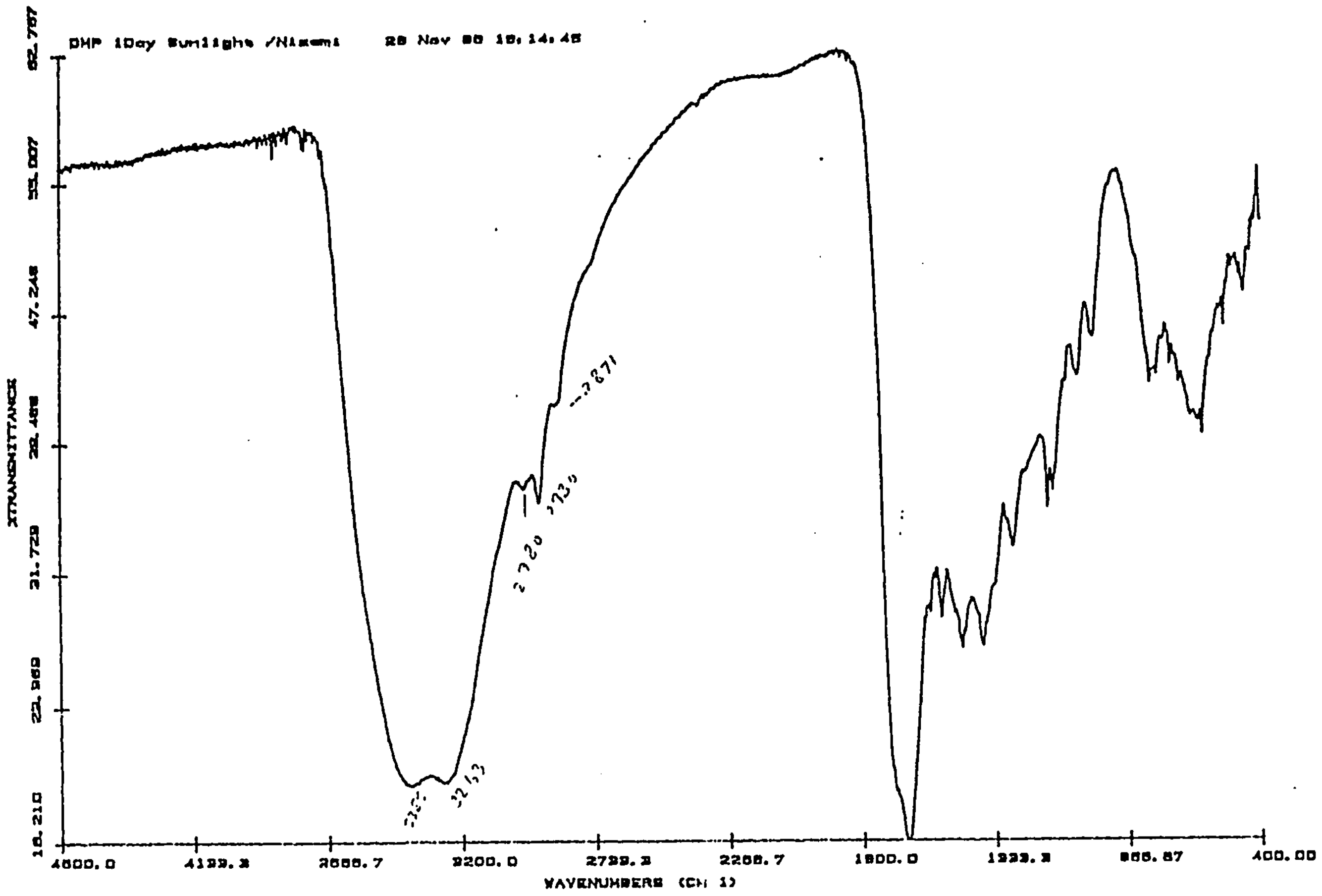


Figure 28a. Infrared spectra of 1 day sunlight exposed DMP sediment.

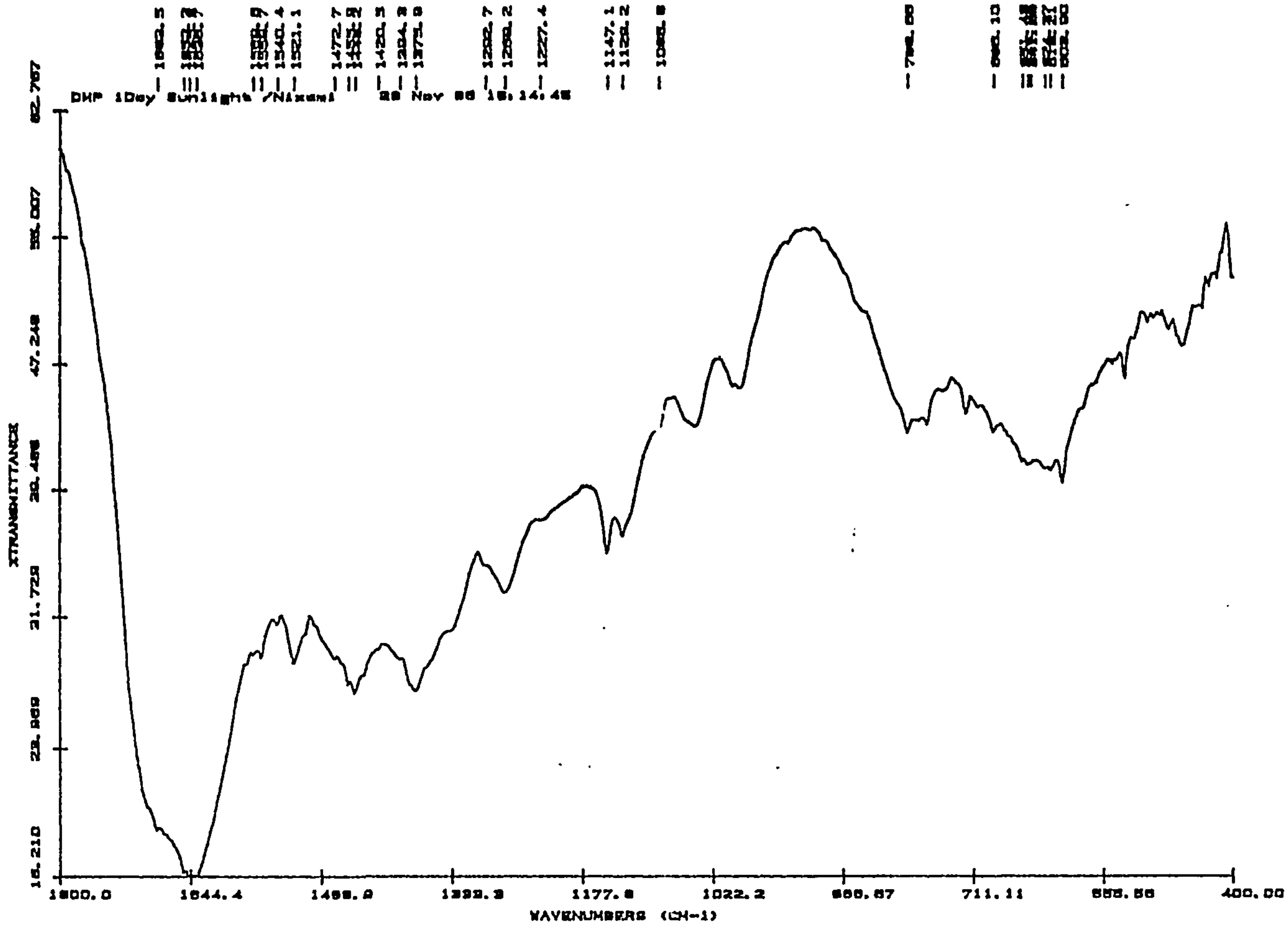


Figure 28b. Infrared spectra of 1 day sunlight exposed DMP sediment.

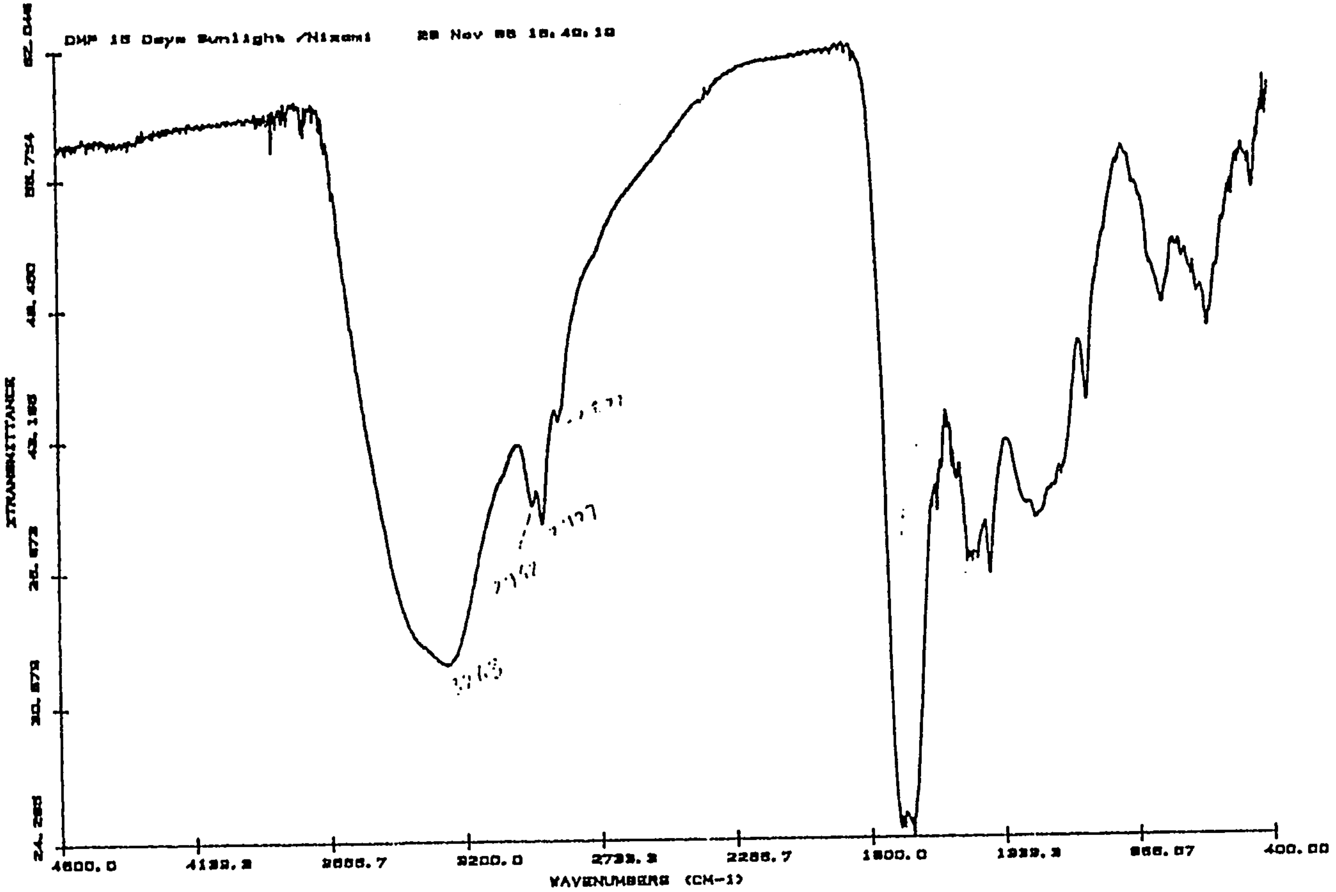


Figure 29a. Infrared spectra of 15 days sunlight exposed DMP sediment.

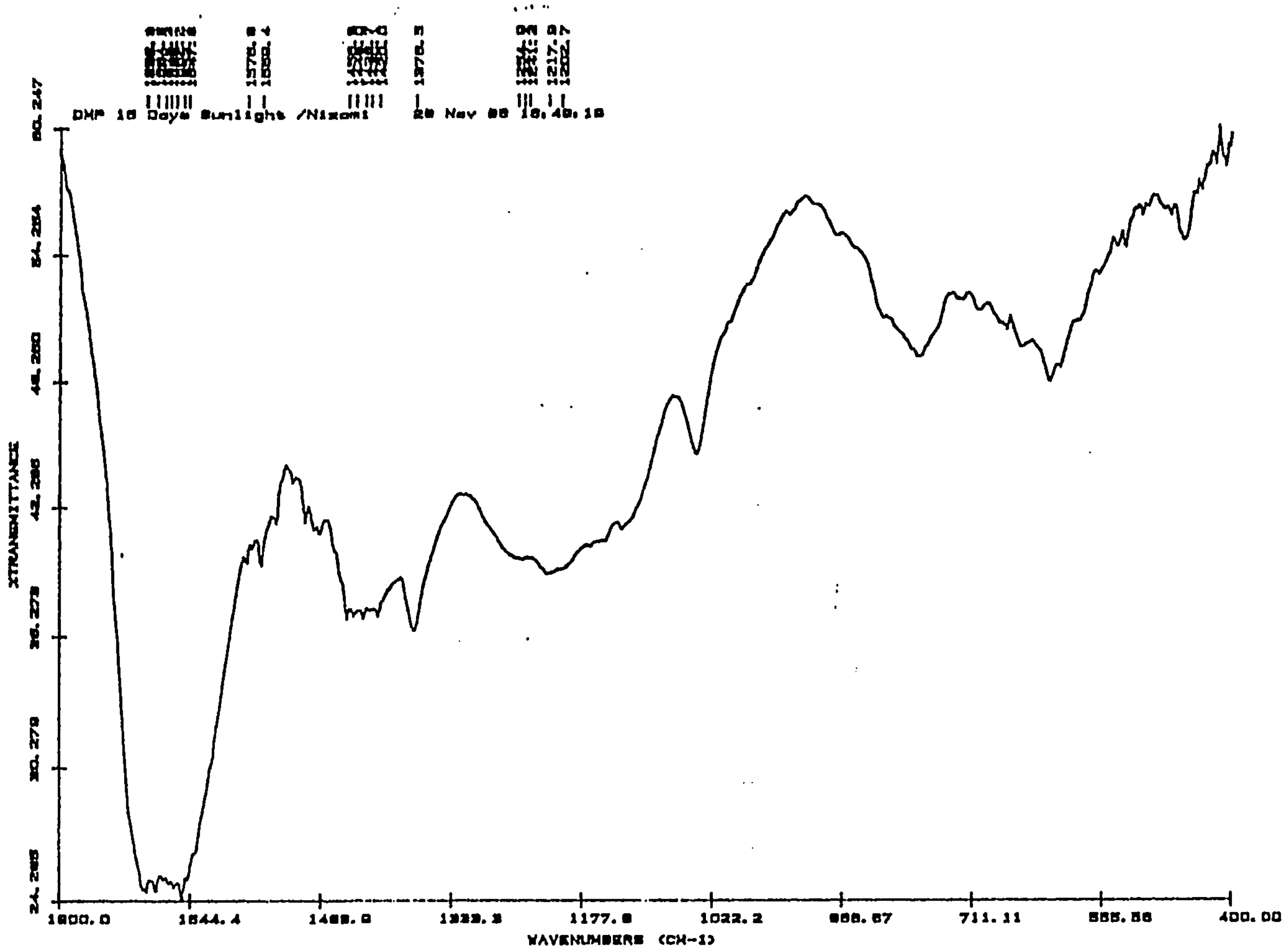


Figure 29b. Infrared spectra of 15 days sunlight exposed DMP sediment.

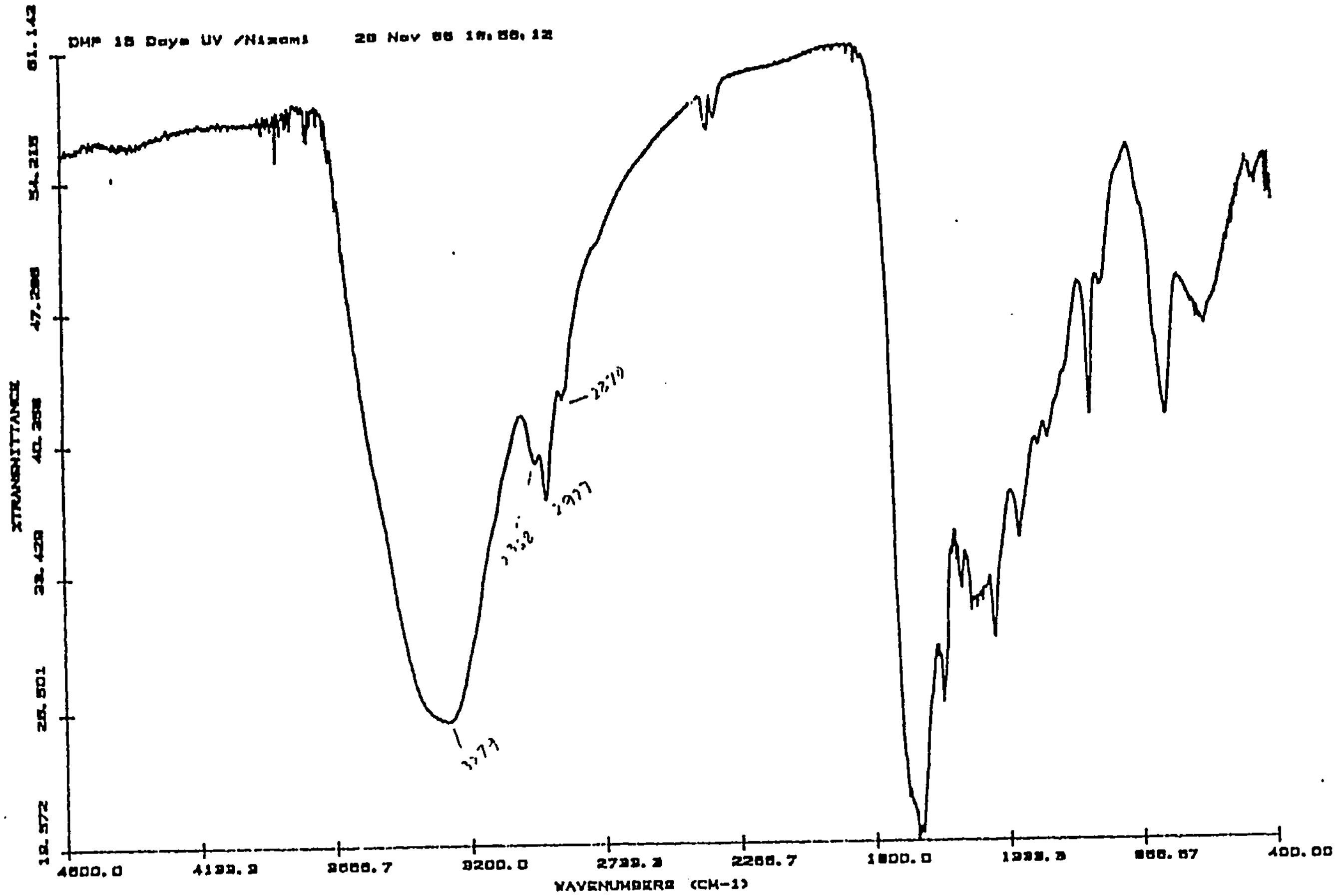


Figure 30a. Infrared spectra of 15 days UV exposed DMP sediment.

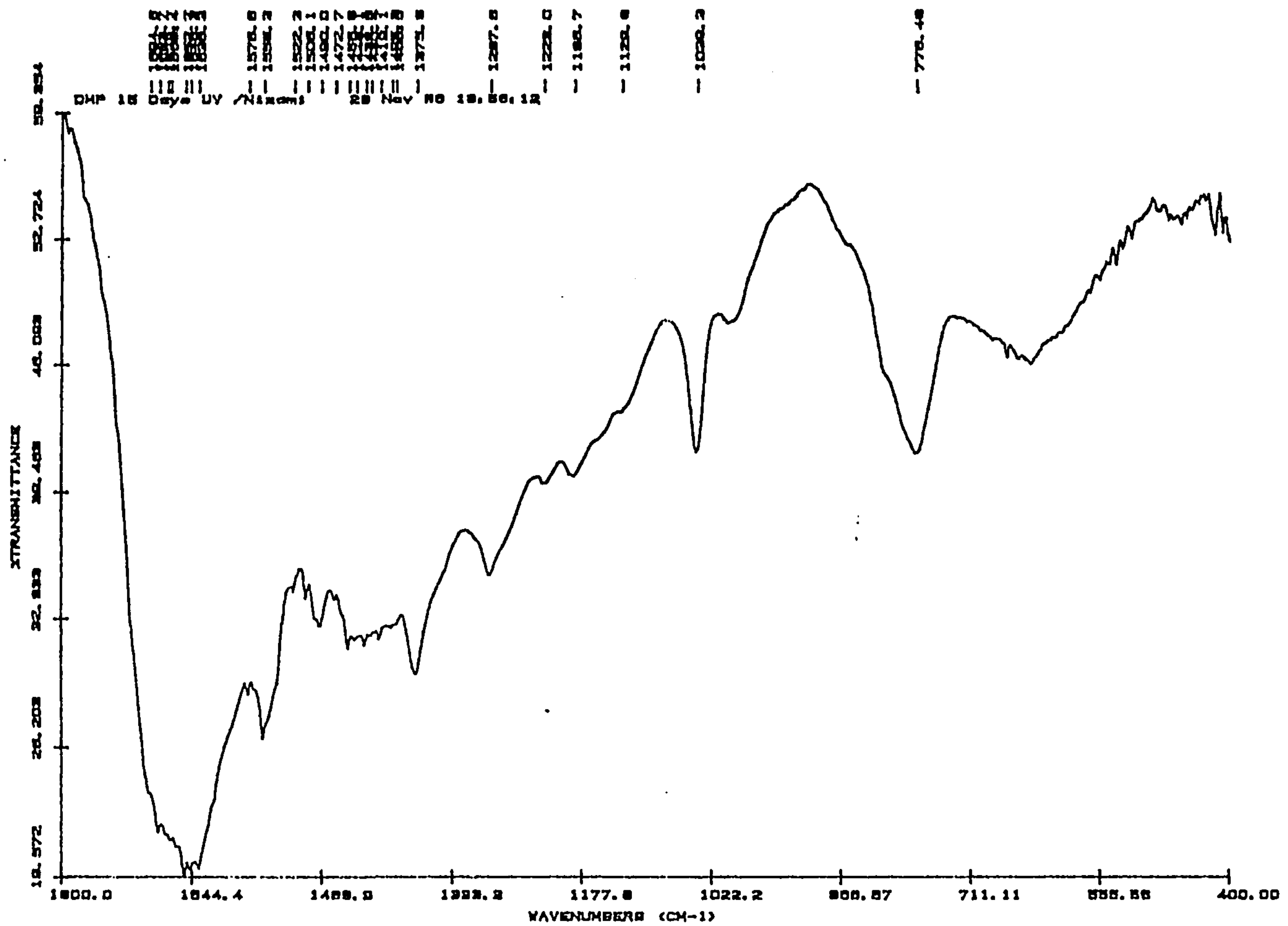


Figure 30b. Infrared spectra of 15 days UV exposed DMP sediment.

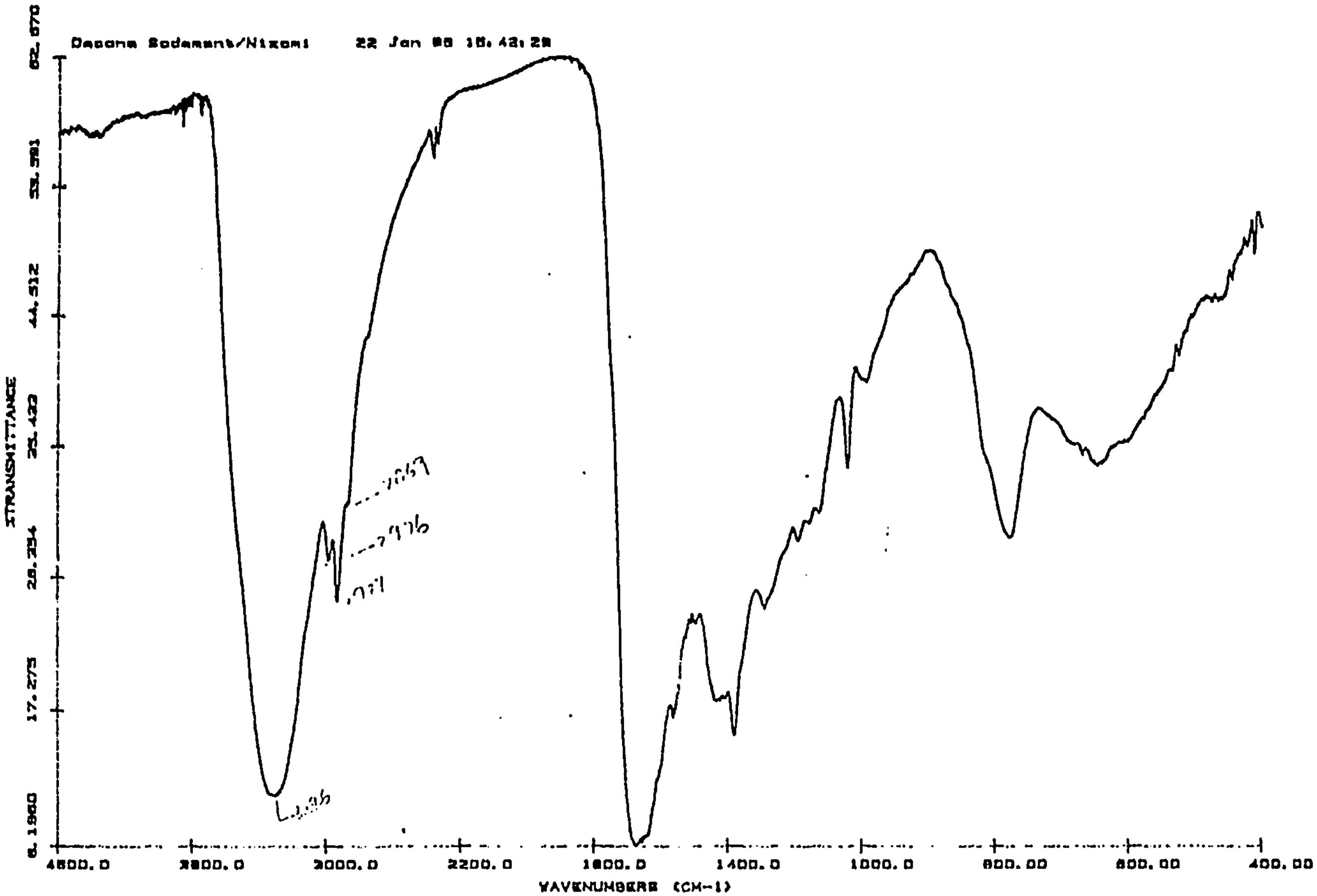


Figure 31a. Infrared spectra of UV exposed n-decane sediment.

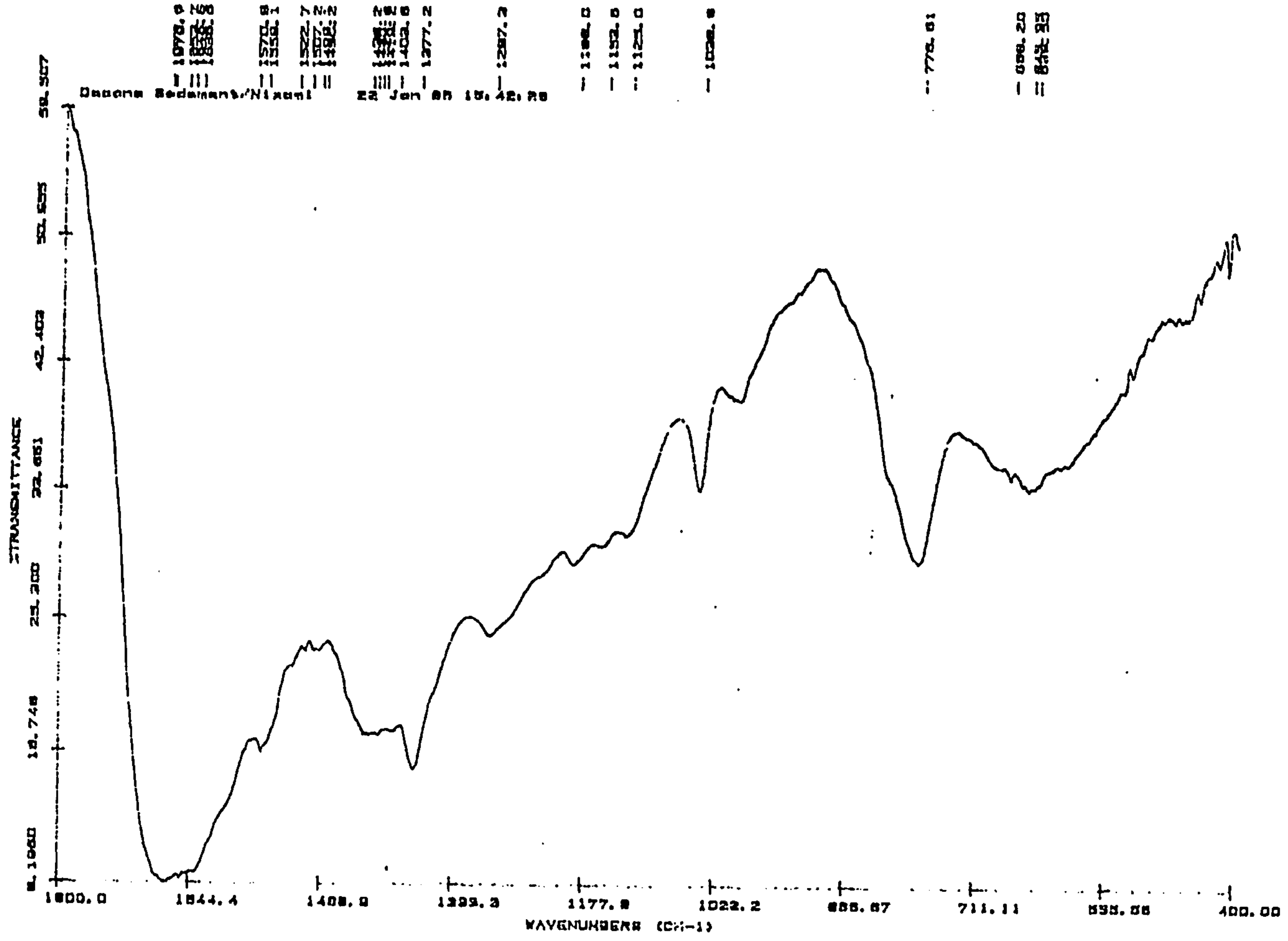


Figure 31b. Infrared spectra of UV exposed n-decane sediment.

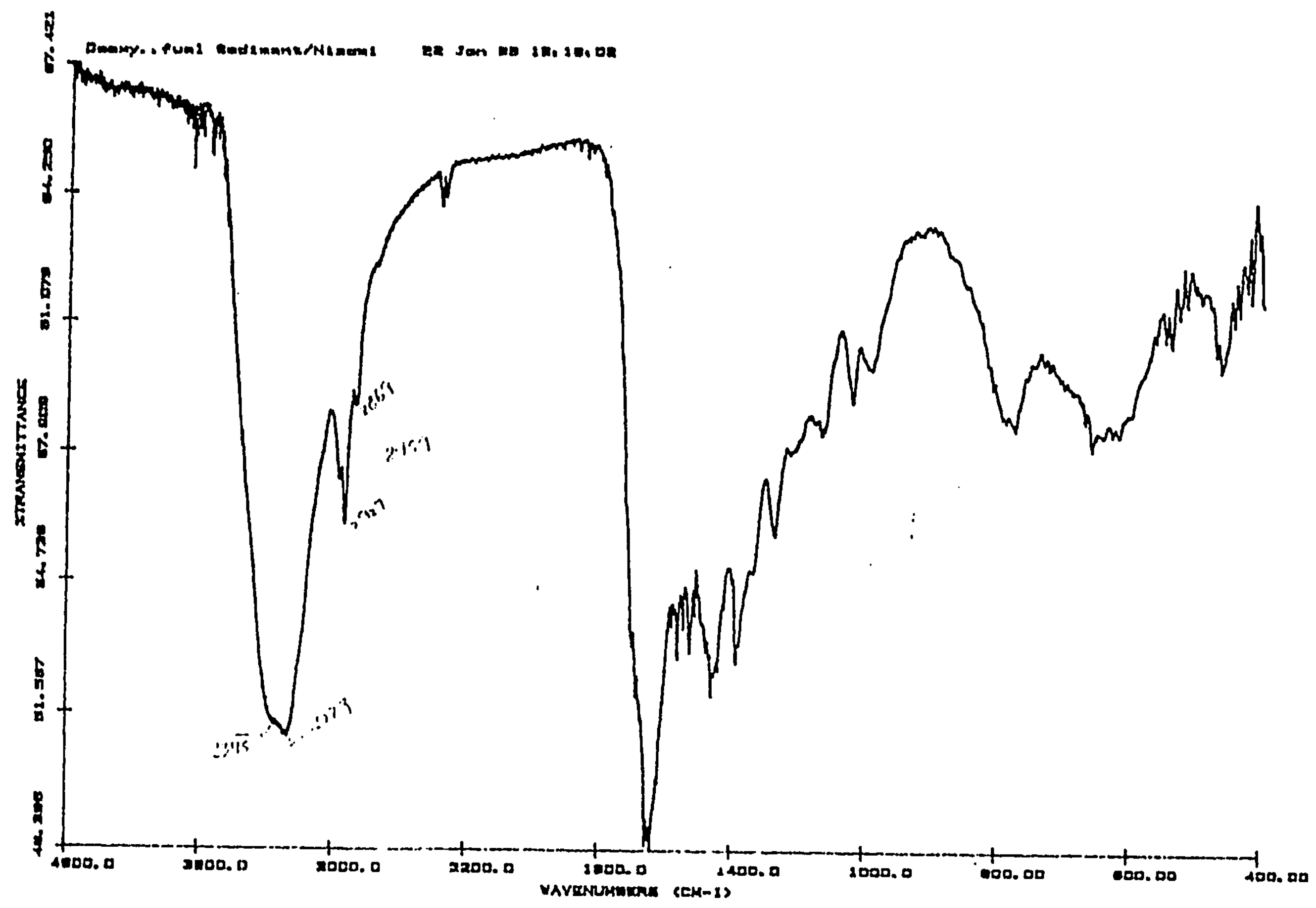


Figure 32a. Infrared spectra of deoxygenated kerosene sediment.

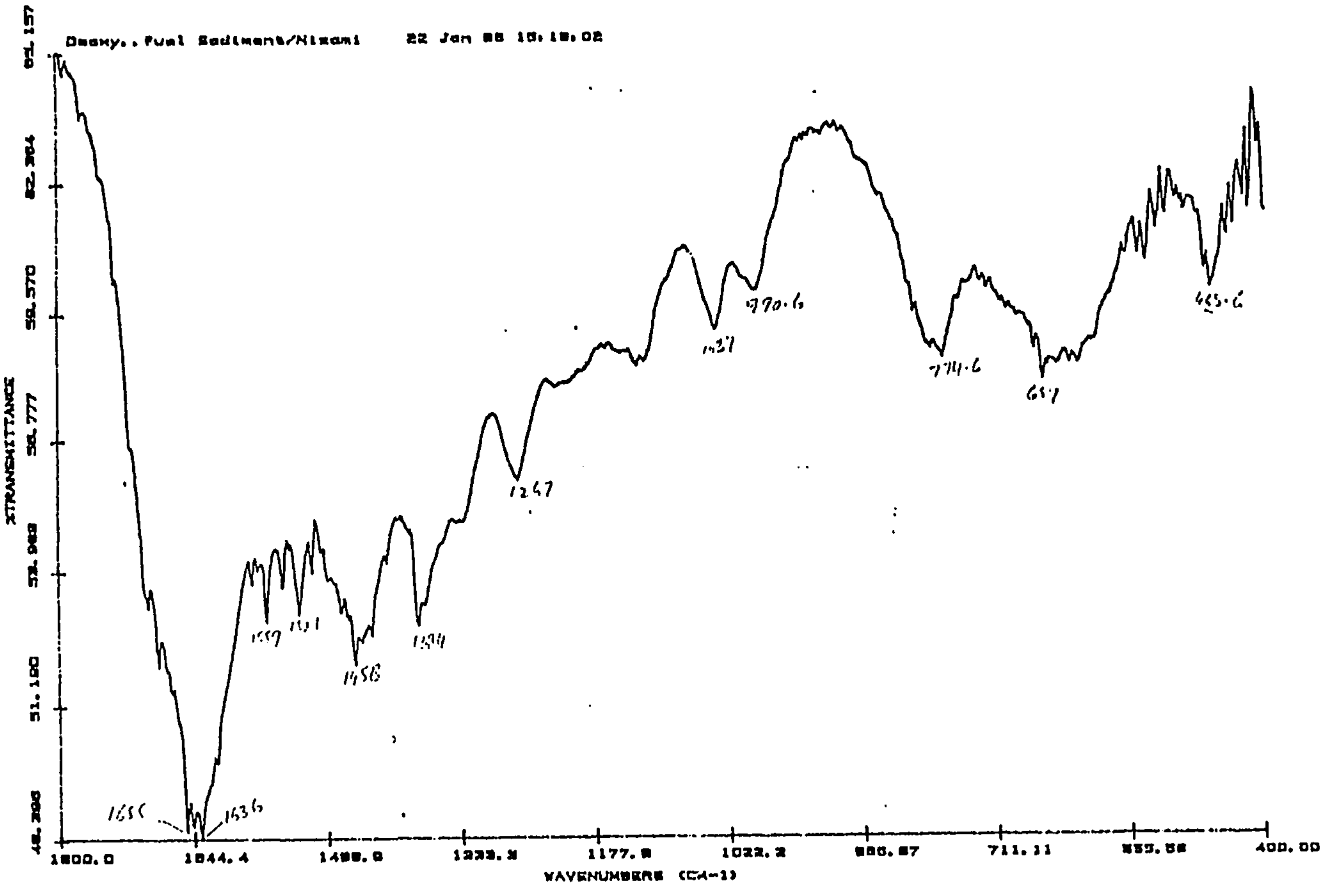


Figure 32b. Infrared spectra of deoxygenated kerosene sediment.

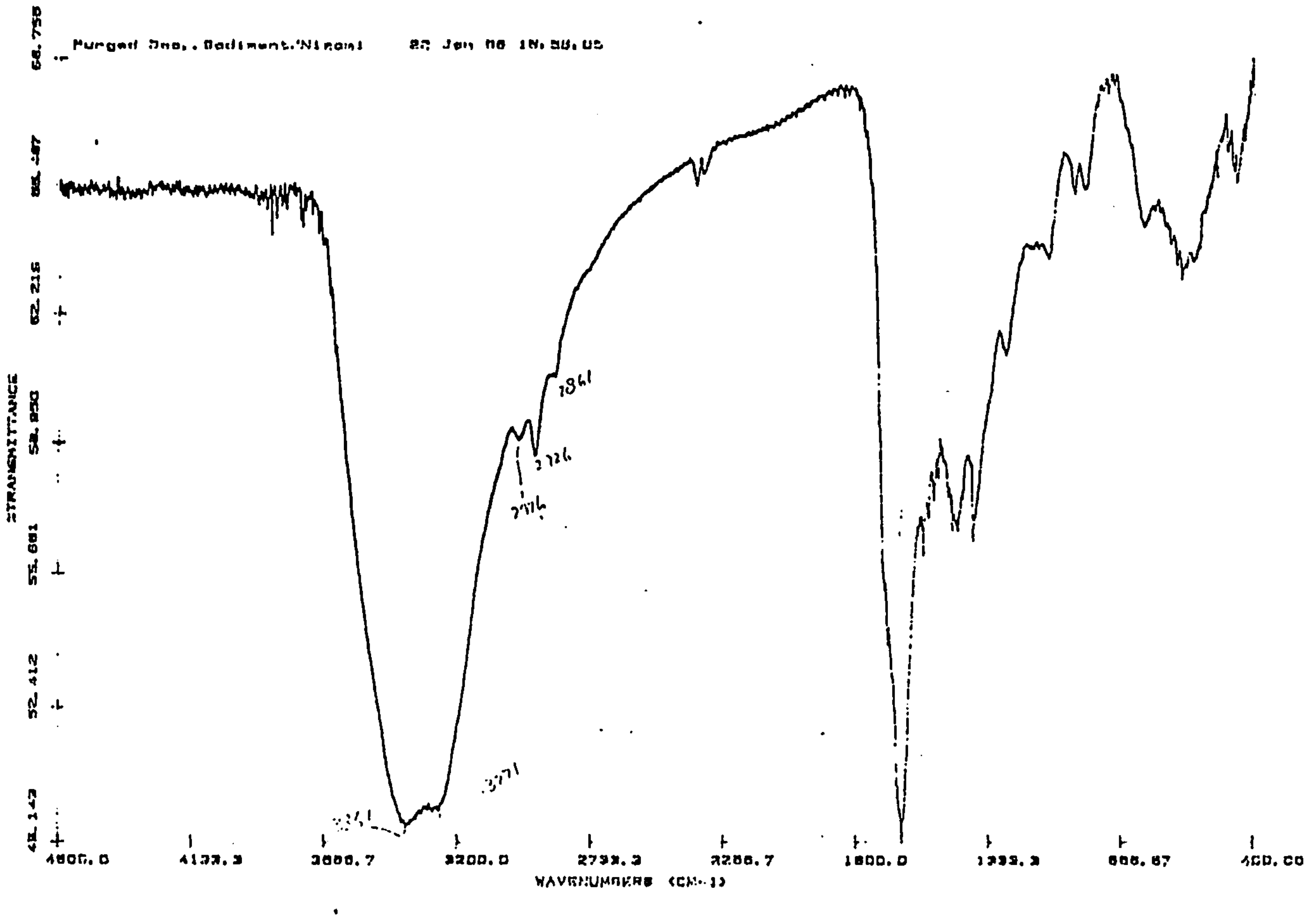


Figure 33a. Infrared spectra of purged n-decane sediment.

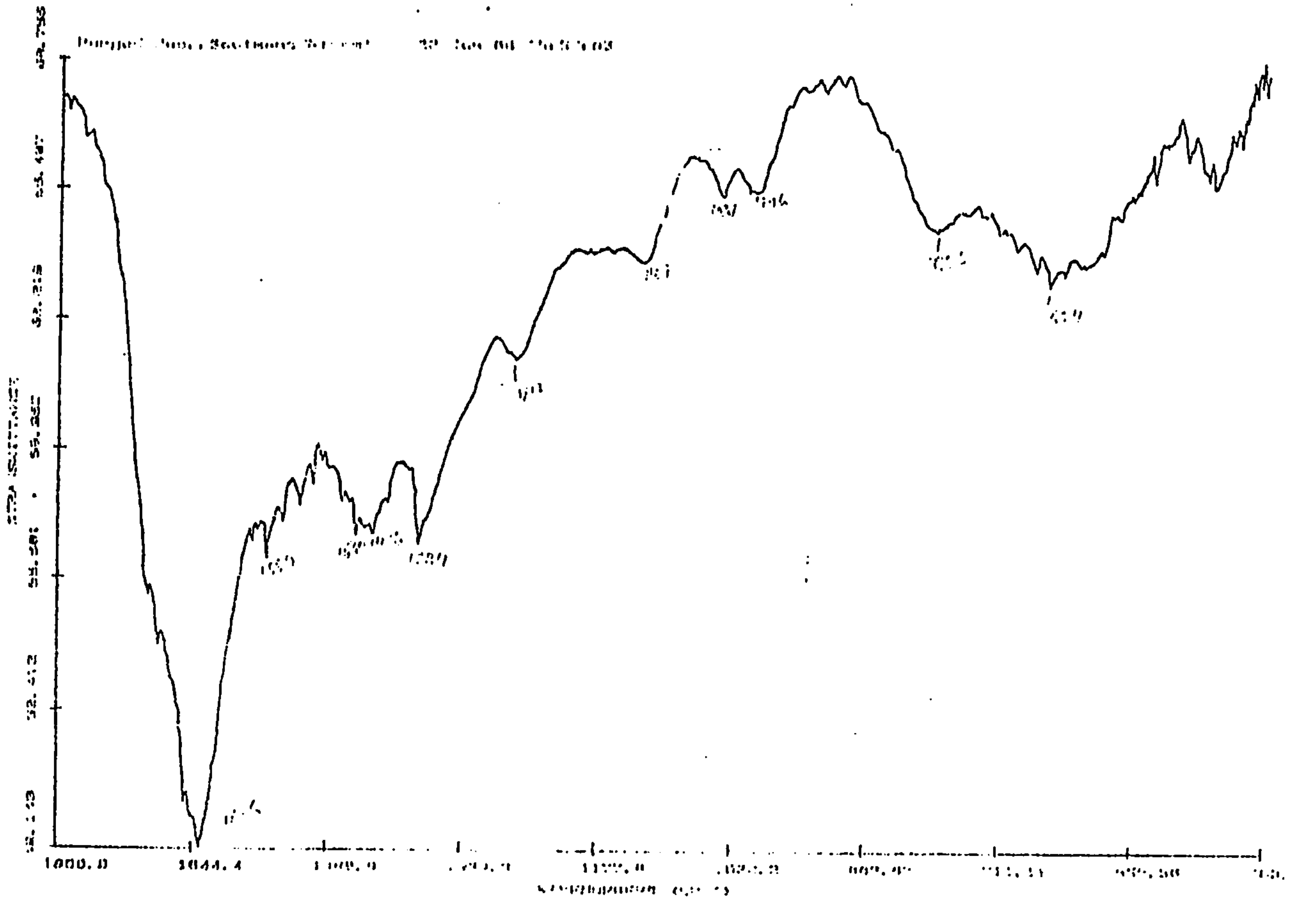


Figure 33b. Infrared spectra of purged n-decane sediment.

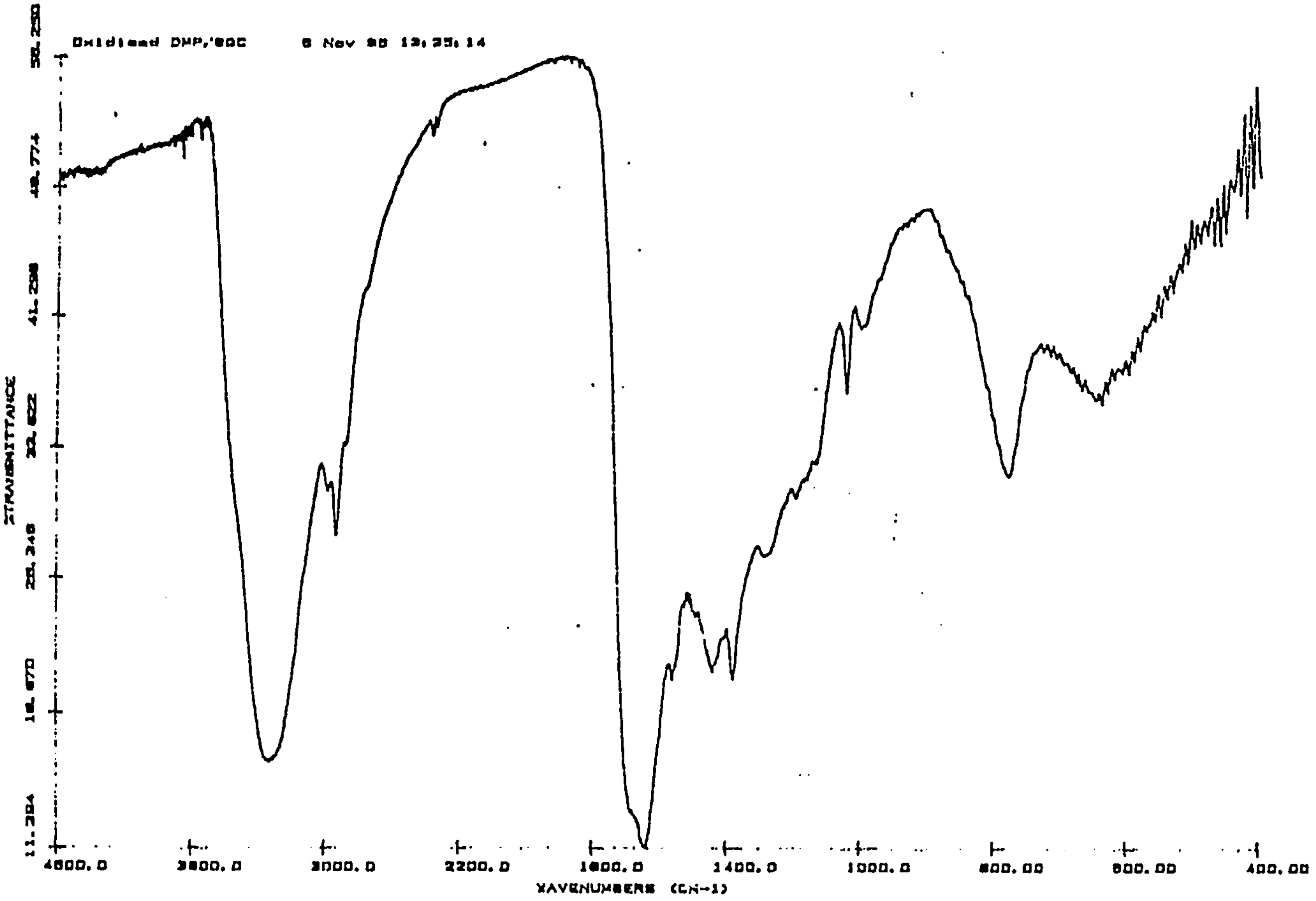


Figure 34. Infrared spectra of DMP sediment oxidized at 80°C.

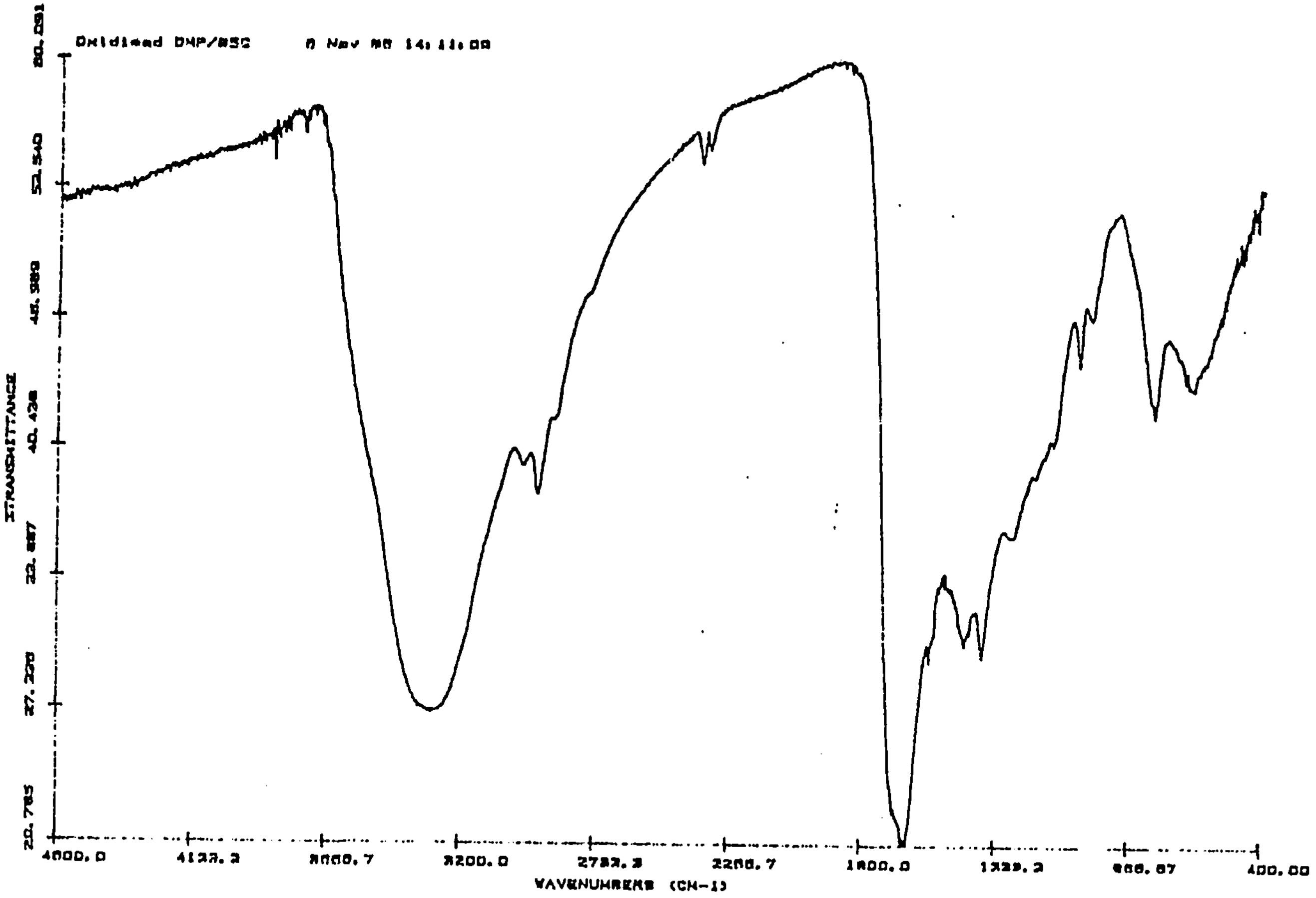


Figure 35. Infrared spectra of DMP sediment oxidized at 95oC.

Similar spectra were obtained even after the removal of moisture, which confirms the presence of amino group only.

The most noteworthy features and very strong absorption band of all sediments are in the range of 1700-1630 cm^{-1}, which indicate the presence of several different types of C=O group as shown in Figures (28b), (29b), (30b), (31b), (32b) and (33b) respectively. The carbonyl stretching vibrations are shifted to lower frequencies in all of these spectra primarily by conjugation with double bonds and by substitution with electron donating group. The weak absorption band at 1150 - 1085 cm^{-1} are very likely to be due to symmetrical C-O-C stretching vibration. Many of the investigators recorded the presence of carbonyl groups in the nitrogenous sediments obtained from different experimental conditions [6, 28].

The ketone type moderate absorption bands appear in the region of 1300 - 1100 cm^{-1} as a result of C-C-C stretching vibration and C-(CO)-C bending vibration. This type of absorption may consist of multiple bands. The weak band appears at 786 - 774 cm^{-1} due to peroxide (-O-O-) bond.

The C-H stretching vibration frequencies between 3100 cm^{-1} and 3000 cm^{-1} are generally observed only for hydrogen atoms which are bonded to sp^2 hybridized carbon atoms, and less than 3000 cm^{-1} for hydrogen atoms which are bonded with sp^3 hybridized carbon. Two distinct bands occurred between 2980-2959 cm^{-1} and 2871-2861 cm^{-1} corresponding to asymmetrical ($\nu_{as}CH_3$) (in which 2 C-H bonds of the methyl group are extending while the third one is contracting) and symmetrical (ν_sCH_3) (in which 3 of the C-H bonds extended and contracted in phase) stretching vibration of C-H in CH_3 group. These two main frequencies are not altered in position within the range even in the presence of a double bond adjacent to the methyl group, but in some case the lower CH_3 frequency (2872 cm^{-1}) was split into two by a resonance effect. The mean value of these pairs, however, remained within a few wavenumbers of 2871 cm^{-1}. Two characteristic bands between 2930 - 2927 cm^{-1} and at between 2870 - 2845 cm^{-1} arise corresponding to in-phase (asymmetrical stretching ($\nu_{as}CH_2$)) and out-of-phase (symmetrical stretching (ν_sCH_2)) vibration of hydrogen atom in the CH_2 group, but sediment spectra show only in-phase vibration at 2927 cm^{-1} with the out-of-phase vibration overlapped by the symmetrical stretching vibration of the CH_3 group.

The CH_2 and CH_3 groups give rise to absorption near 1460 - 725 cm^{-1} due to hydrogen bending vibrations. In the case of the CH_3 group two frequencies arise from the bending of the hydrogen atom about a carbon atom; the asymmetrical bending vibration ($\delta_{as}CH_3$) occurs between 1458-1452 cm^{-1} whilst the symmetrical bending vibration (δ_sCH_3) occurred between 1384 - 1375 cm^{-1}. The absorption band at 1375 cm^{-1} arising from the symmetrical bending of methyl C-H bonds, is very constant in position when the methyl group is attached to another carbon atom. The intensity of this band is greater for each methyl group in the compound than the asymmetrical methyl bending vibration or the methyl scissoring vibration.

The bending vibration of C-H bonds in methylene groups is generally of four modes referred to as scissoring, rocking, wagging and twisting. All four modes occurred in every sediment spectrum. The scissoring band (δ_sCH_2) in the spectra of sediment occurs at nearly constant position near 1472 cm^{-1}. The band resulting from the methylene rocking vibration (ρCH_2), when all methyl groups rock in phase, appears near 725 cm^{-1}. The weak bands observed in the region of 1350 - 1150 cm^{-1} are due to methylene twisting and a wagging vibration.

A band appears at 1600 cm^{-1} resulting from the C=C stretching vibration. The olefinic type of C-H bonds can undergo bending vibration in-phase or out-of-phase with respect to each other. The C-H bond in-plane bending vibration occurred at 1420 cm^{-1} and this is one of the means of identification of the presence of double bonds. Deformation frequency of methylene group adjacent to carbonyl group occurred also at 1420 cm^{-1}. The bands appearing in the region of 1000 - 650 cm^{-1} are due to the out-of-plane C-H bending vibration of olefinic types or aromatic ring type materials.

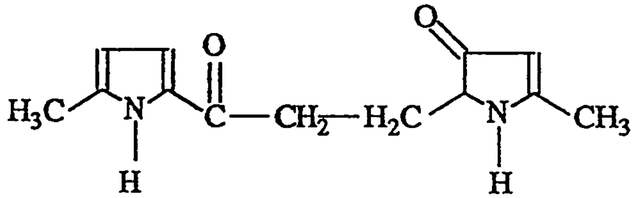
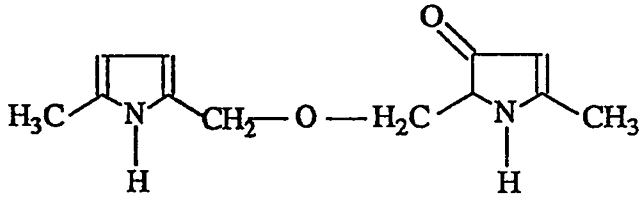
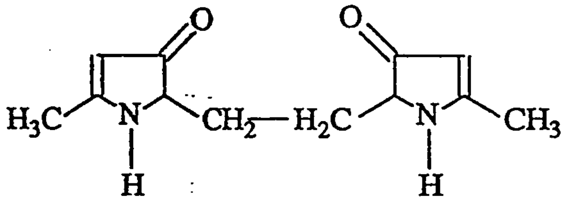
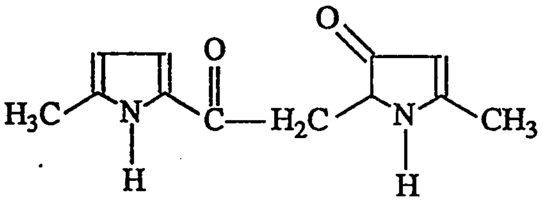
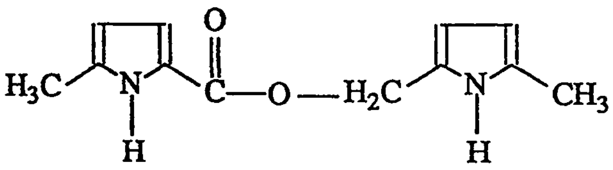
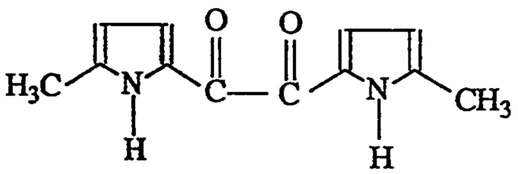
All of the sediment obtained from a variety of storage conditions exhibit similar types of infra-red spectra, which result exclusively from auto-oxidative self condensation of nitrogen compounds. These analysis prove that similar types of compound would be present in all sediment samples.

4.10. MASS SPECTROSCOPY

The major mass spectral peaks and their possible structural assignments are shown in Schemes 4, 5, 6 and 7. The sediments appear to be of fairly low molecular weight and rarely more than 400 mass units.

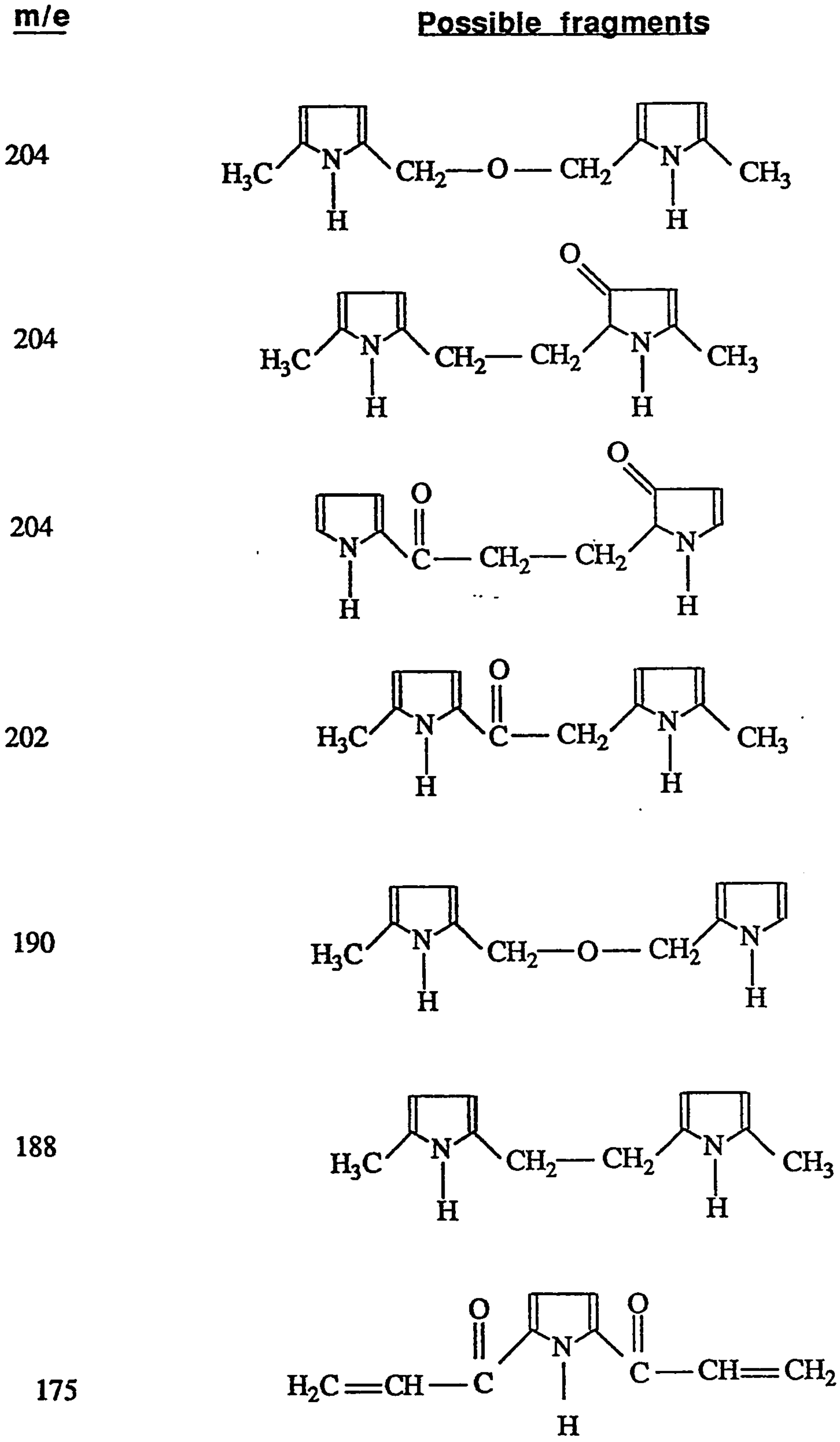
The mass spectrum of pure 2,5-dimethylpyrrrole is shown in Figure (36). The spectrum shows a series of ions at m/e 42, 67, 81 and 94 corresponding to $C_2H_4N^+$, $C_4H_5N^+$, $C_5H_7N^+$ and $C_6H_8N^+$ fragments of DMP respectively. The base peak at m/e 94 (i.e. M-1) and the molecular ion peak appeared at m/e 95 ($C_6H_9N^+$).

SCHEME 4

m/e	Possible Fragments
232	
220	
220	
218	
218	
216	

Principal Mass Fragments of DMP Sediment

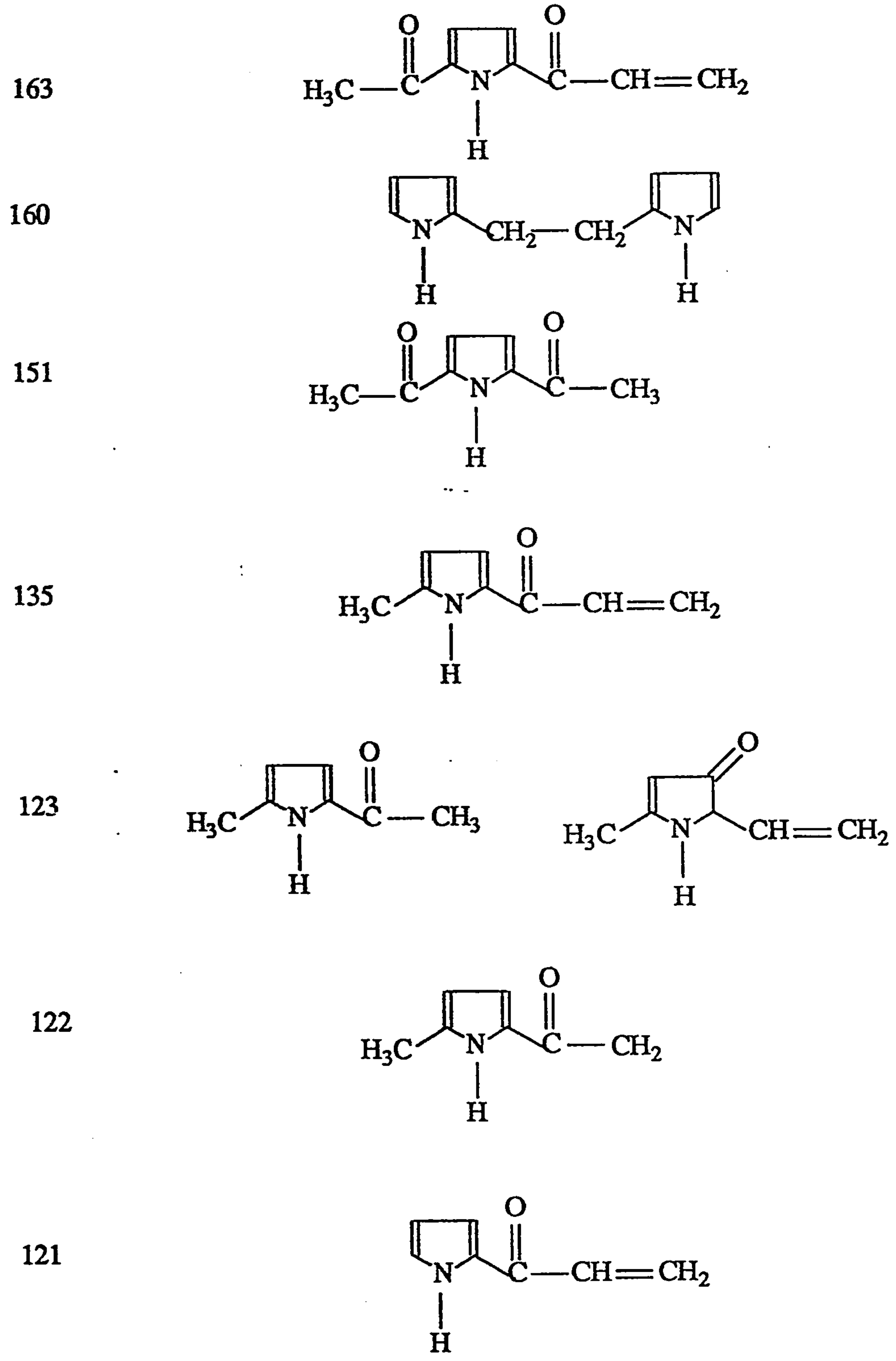
SCHEME 5



Principal mass fragments of DMP sediments

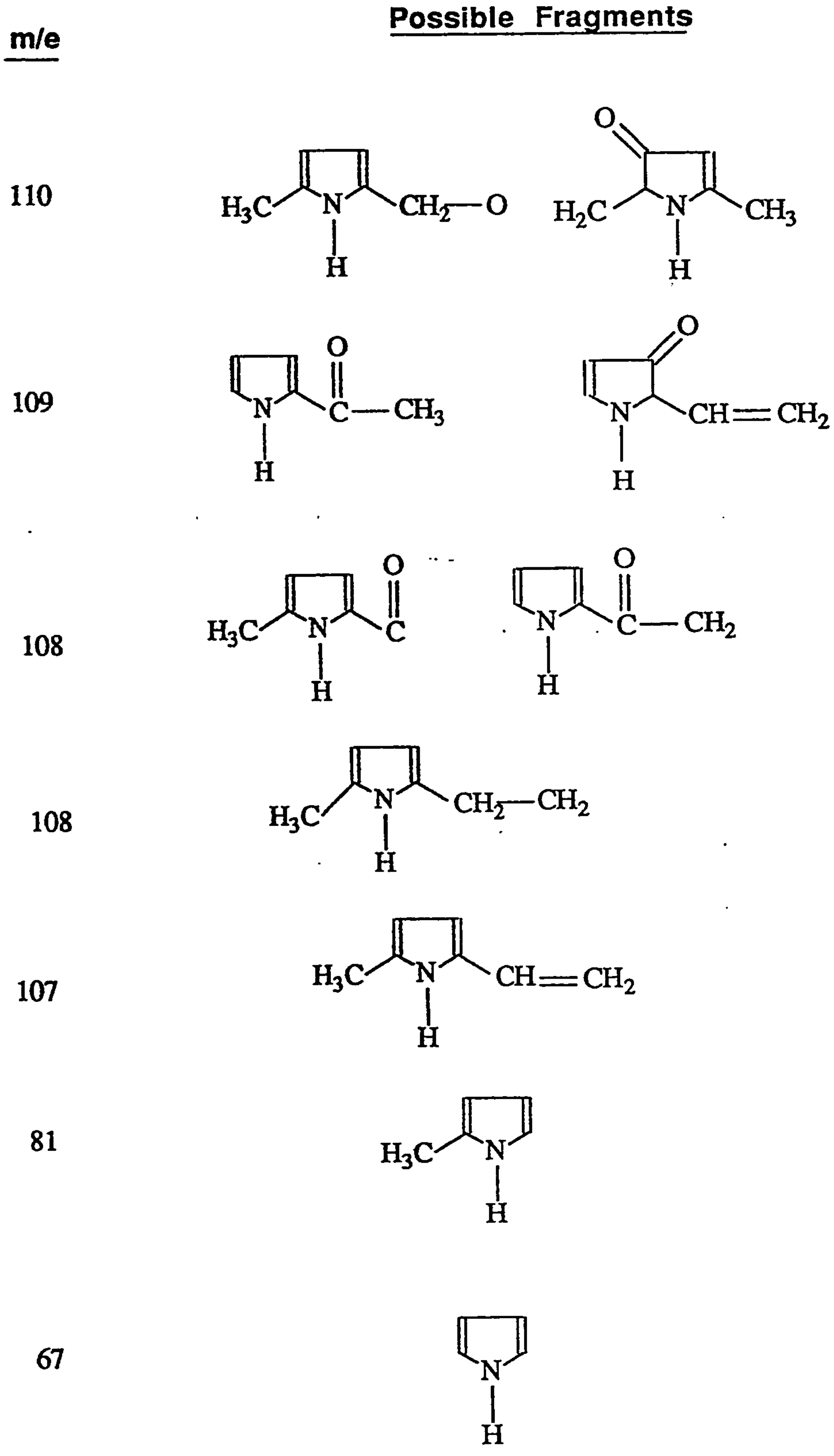
SCHEME 6

m/e **Possible Fragments**

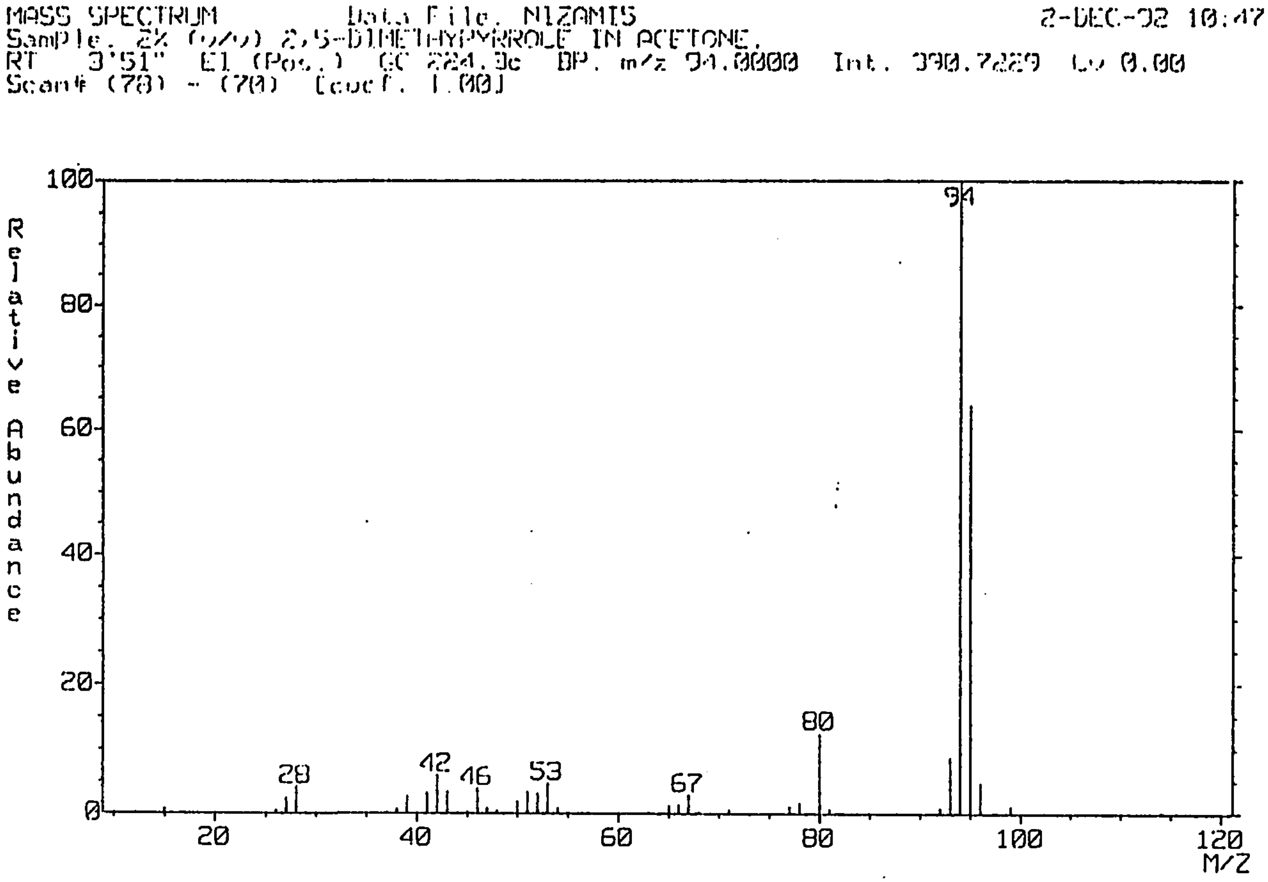


Principal mass fragments of DMP sediments

SCHEME 7



Possible mass fragments of DMP sediments



```
MASS SPECTRUM          Data File. NIZAMIS                              2-DEC-92 10:47
Sample. 2% (v/v) 2,5-DIMETHYPYRROLE IN ACETONE.
RT   3'51"  EI (Pos.)  GC 224.3c  BP. m/z 94.0000  Int. 390.7229  Lo 0.00
Scan# (70) - (70)  [coef. 1.00]
```

Figure 36. Mass spectra of neat 2,5-dimethylpyrrole.

The mass spectra of sediment samples are complicated because of the polymeric nature of sediments; however, some generalizations are possible. The mass spectra of samples suggest that the sediment may consist of several compound types. The mass spectra of 1 day sunlight exposed sediment and 15 days UV exposed sediment are shown in the figures (37) and (38a, 38b). The mass spectra of DMP sediment at 43^{o}C dark storage, oxidized DMP sediment at 80^{o}C and 95^{o}C are shown in the figures (39), (40) and (41) respectively. The mass spectra obtained in all of these cases appear to be similar. It is very difficult to emphasize the importance of locating the molecular ion peak in polymeric nature of sediment samples. Even in the case where the molecular ion peak is very small, only a little extra information can often lead to the identification. This information can be available from the source and history of samples, from the fragmentation pattern and from other spectra.

The spectra of DMP sediments obtained from variety of storage conditions have many prominent peak. The peaks at m/e 220 and 110 are corresponding to $C_{12}H_{16}N_2O_2^+$ and $C_6H_8NO^+$ molecular ions respectively. Two possible structures of m/e 220 are given in Scheme 4. One of the possible structures of m/e 220 undergoes McLafferty rearrangement (i.e. abstractable hydrogen γ to C=O system) to produce a fragment of m/e 123 Scheme 8. Such rearrangements often account for a prominent characteristic peak and are consequently very useful for our purpose to propose the mechanism of some possible fragment formations. Rearrangements result in the elimination of common stable neutral molecules (e.g. the olefinic product) and will be encountered in the discussion of mass spectra of chemical class. Rearrangement peaks can be recognized by considering the mass (m/e) number of fragmentation and the corresponding molecular ion. A simple (no

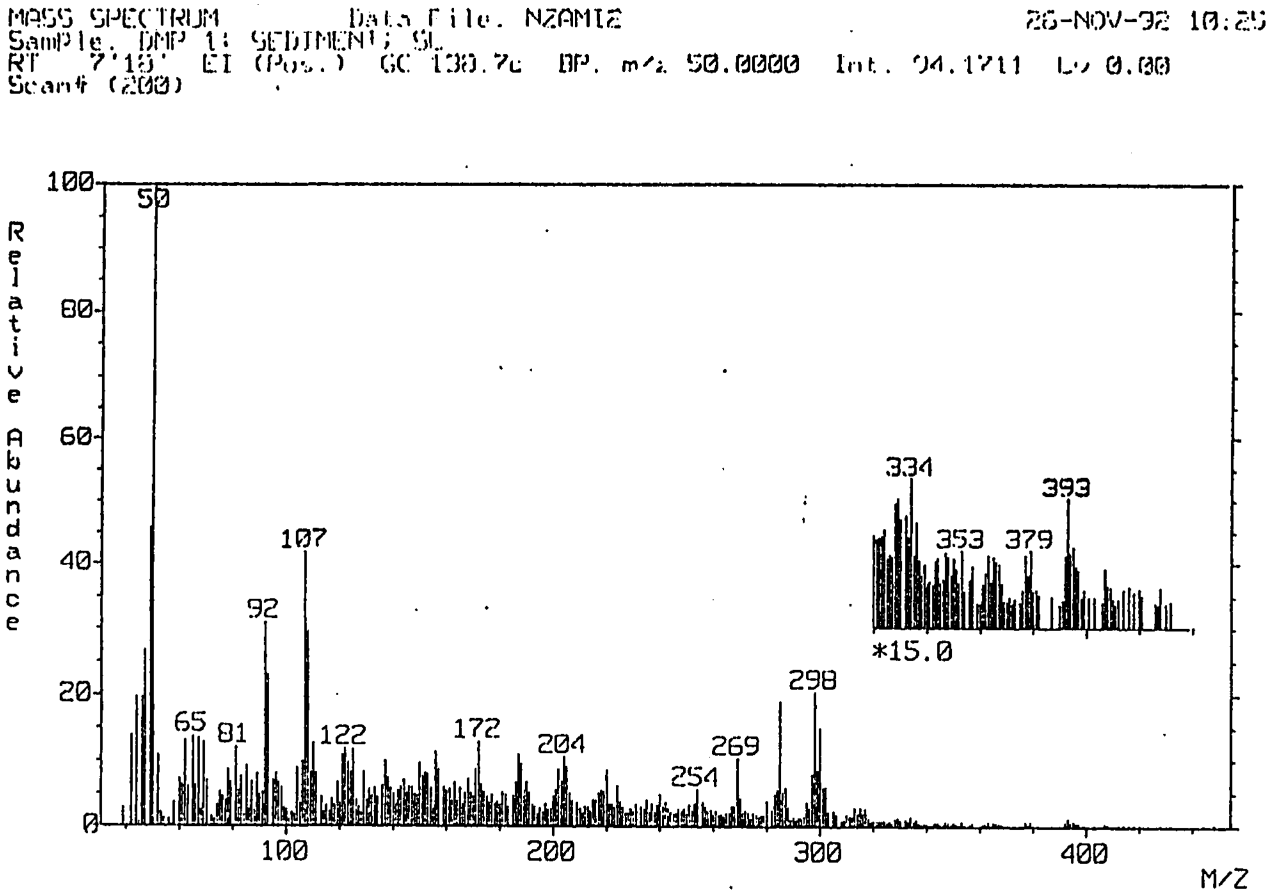


Figure 37. Mass spectra of 1 day sunlight exposed DMP sediment.

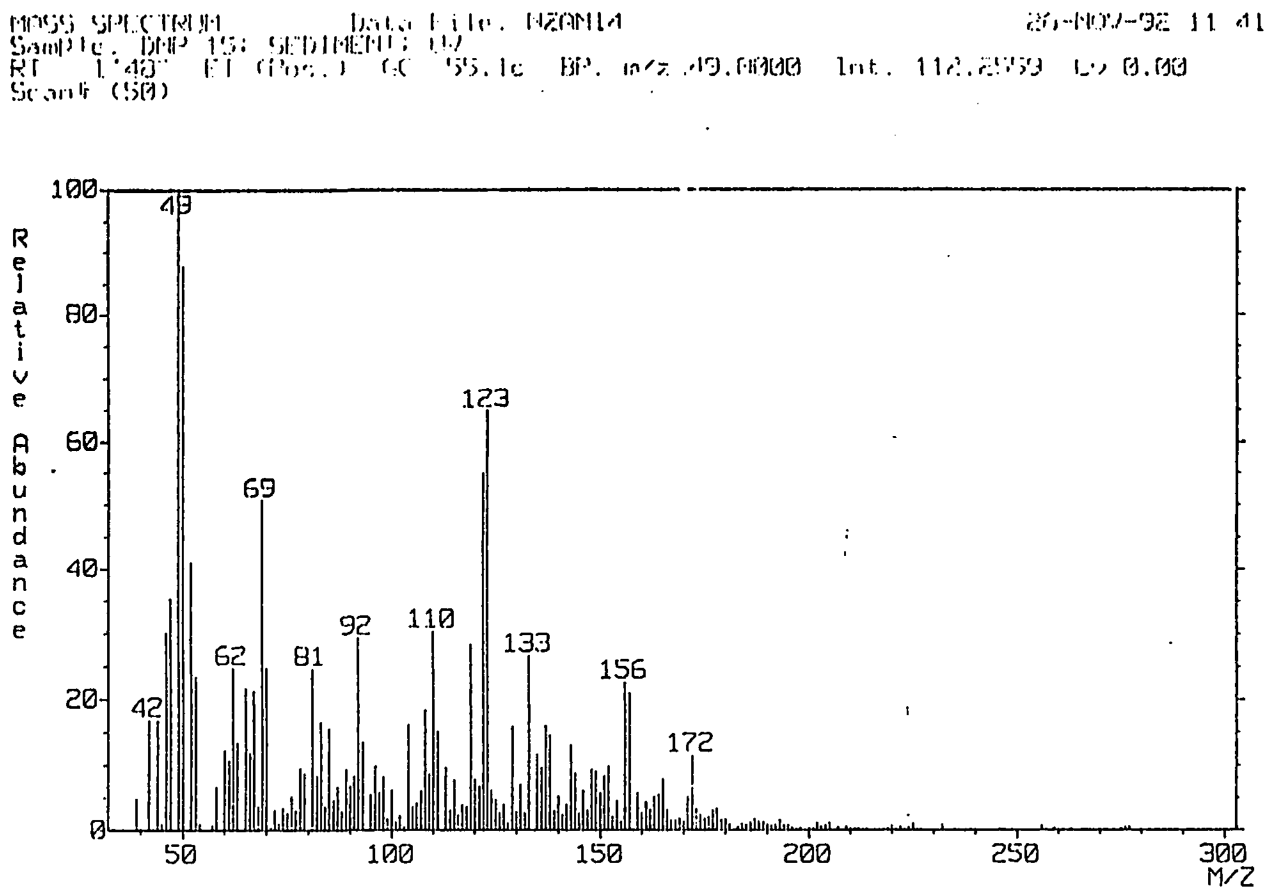


Figure 38a. Mass spectra of 15 days UV exposed DMP sediment.

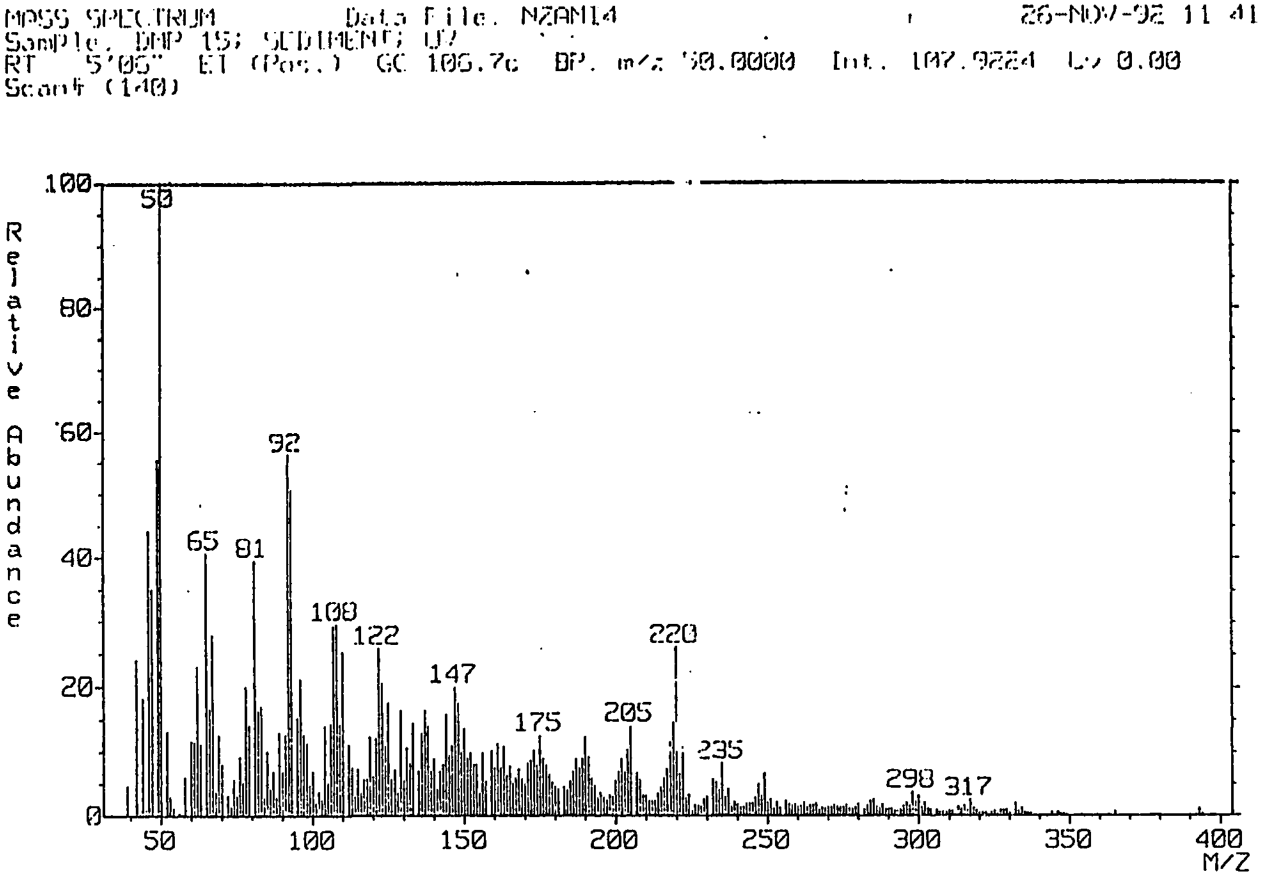


Figure 38b. Mass spectra of 15 days UV exposed DMP sediment.

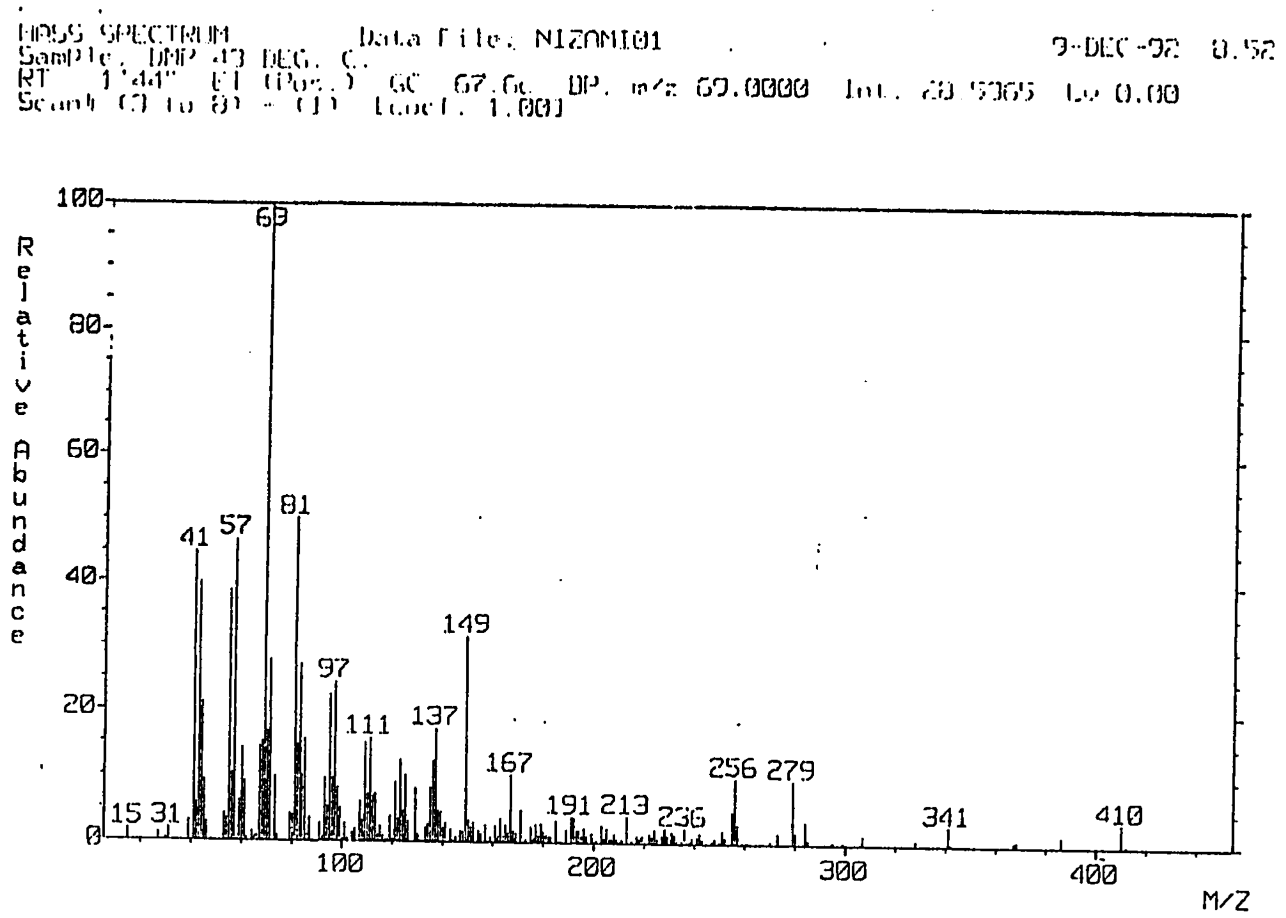


Figure 39. Mass spectra of DMP sediment at 43^{o}C in dark storage.

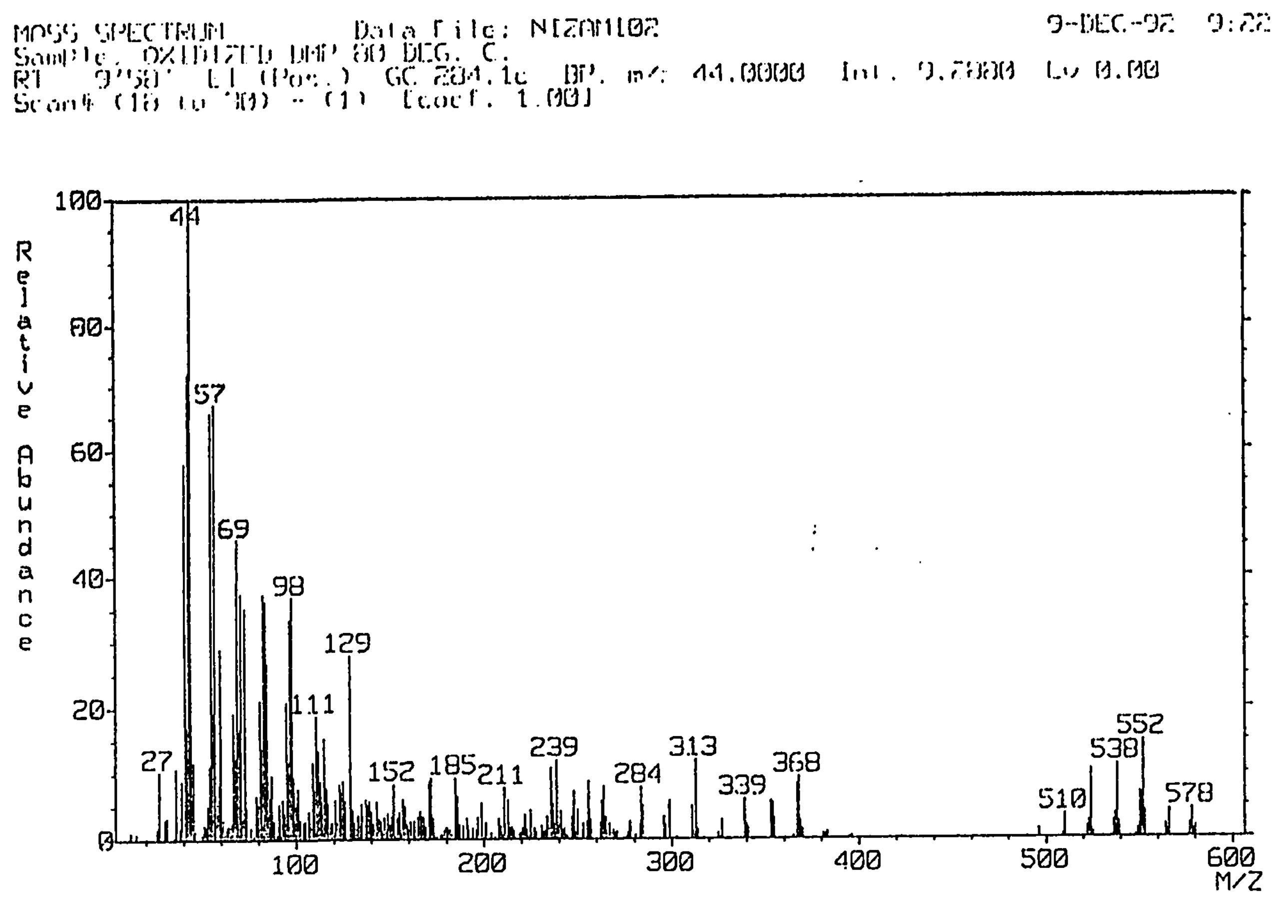


Figure 40. Mass spectra of DMP sediment at 80°C in dark storage.

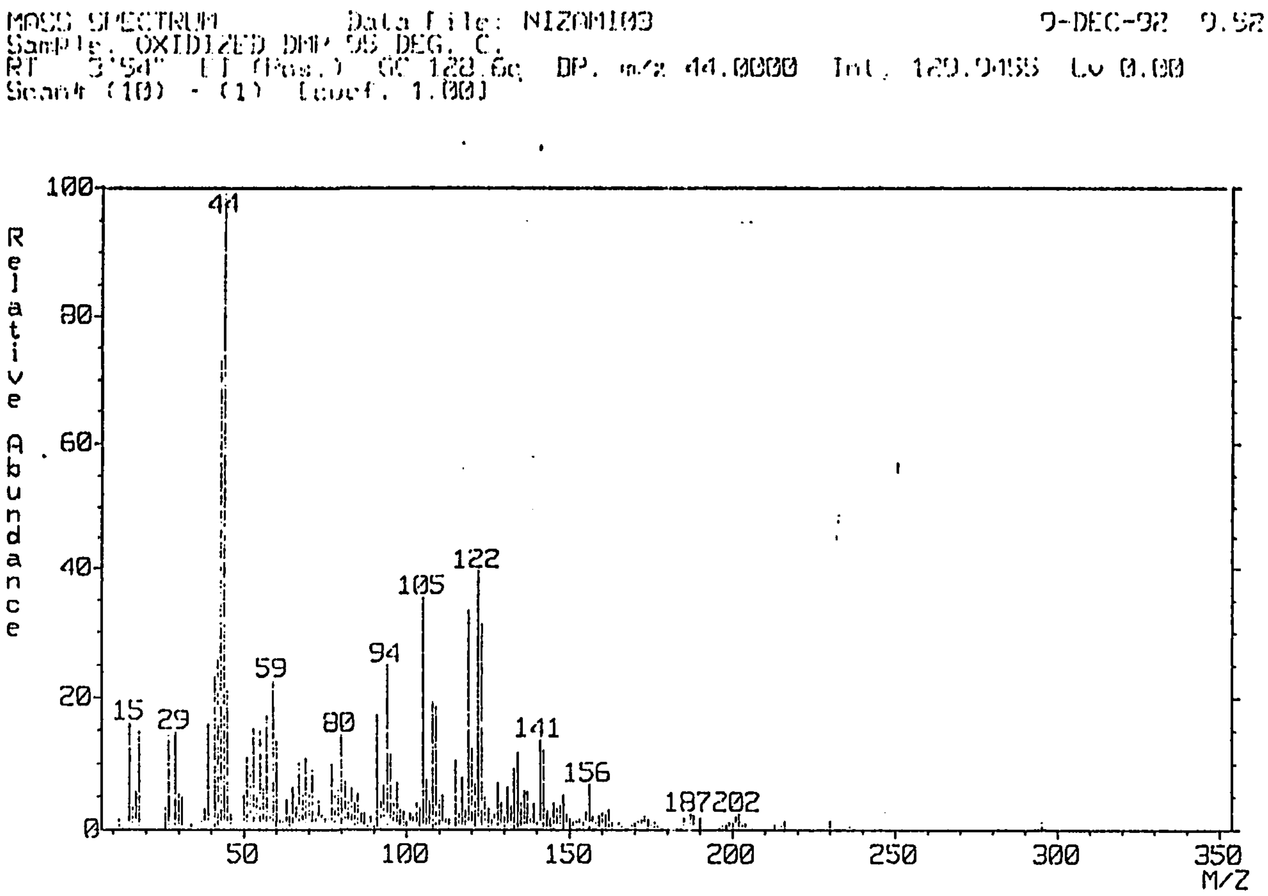
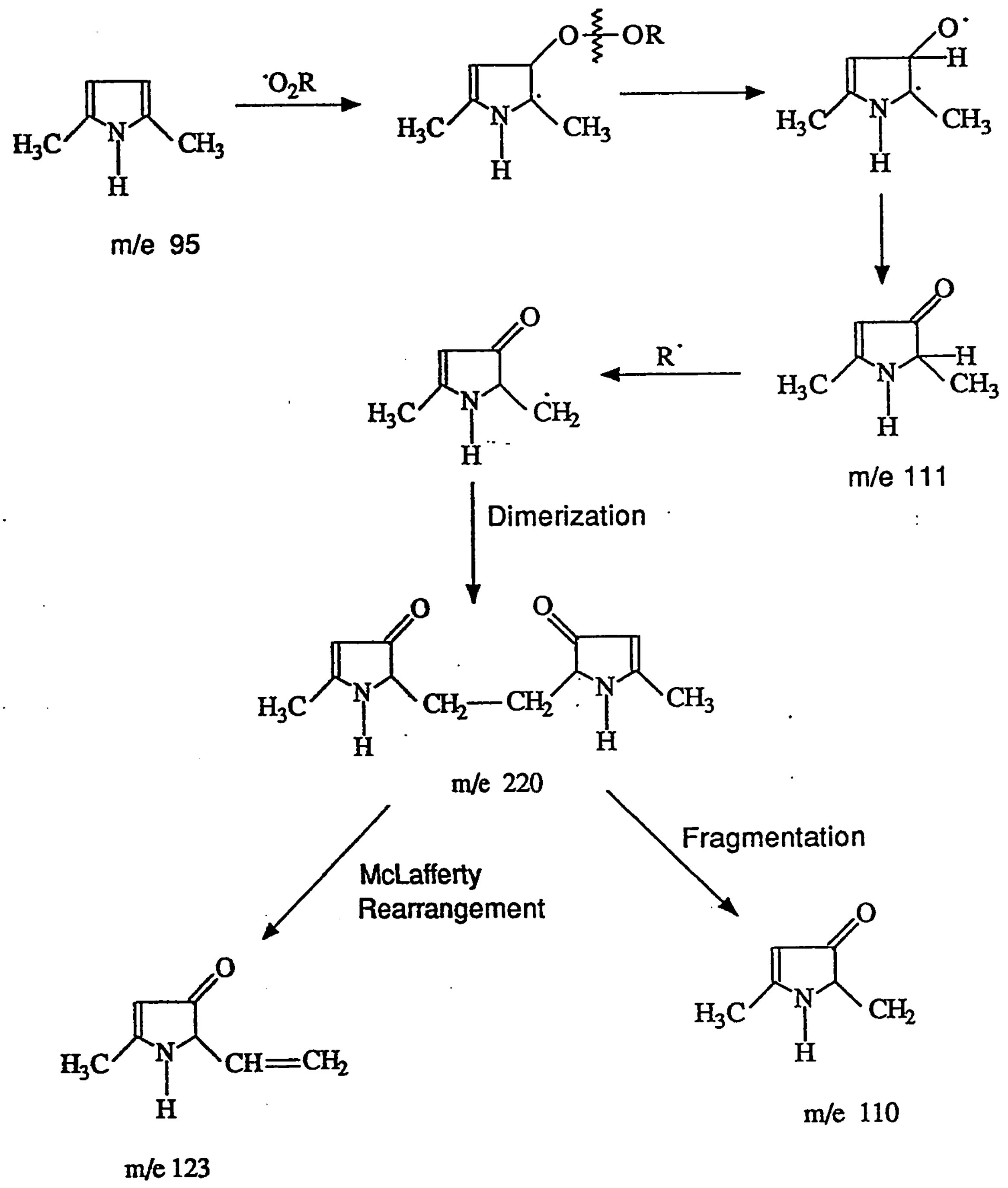


Figure 41. Mass spectra of DMP sediment at 95°C in dark storage.

SCHEME 8

Mechanism of Possible Fragments Formation



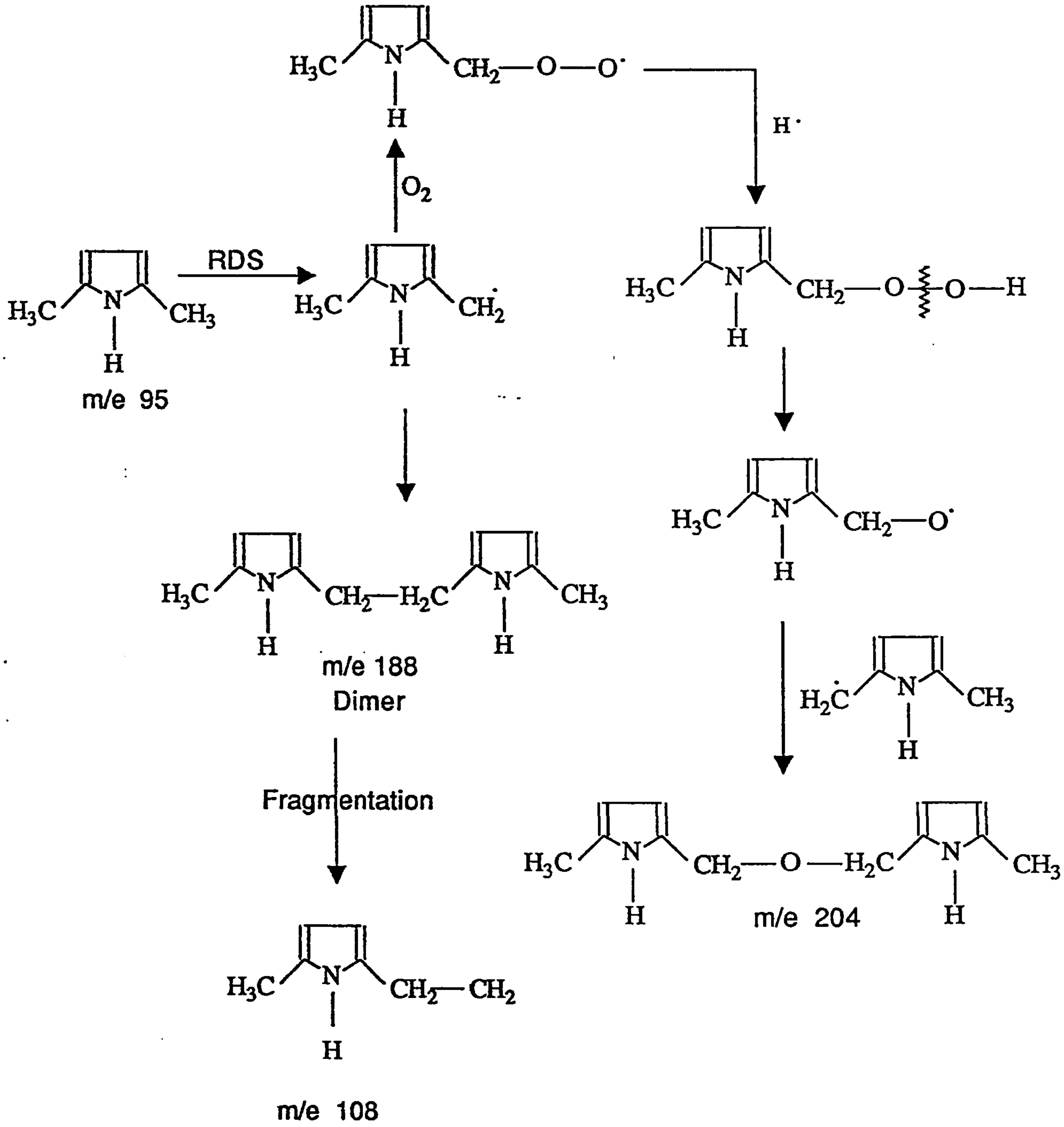
rearrangement) cleavage of an even-numbered molecular ion gives an odd numbered fragmentation and an odd-numbered molecular ion gives an even numbered fragment. One of the possible structures of m/e 220 undergoing cleavage to produce the smaller fragment at m/e 110, is shown in Scheme 8.

The m/e 232 has $C_{13}H_{16}N_2O_2^+$ molecular ions with two abstractable hydrogen γ to carbonyl group, which also undergoes McLafferty rearrangement and produced the fragments at m/e 135 and 123. These molecular ion peaks further undergo cleavage and produced the smaller fragment at m/e 121, 109 and 108 respectively as shown in Scheme 10. The m/e value at 218 and at 202 represent the $C_{12}H_{14}N_2O_2^+$ and $C_{12}H_{14}N_2O^+$ ions respectively. The peaks at 204 m/e value represents the $C_{12}H_{16}N_2O^+$ and $C_{11}H_{12}N_2O_2^+$ types of ions respectively. The possible structures of these compounds are shown in Schemes 5. At m/e 188 ($C_{12}H_{16}N_2^+$) the diamer of dimethylpyrrole is formed, which undergoes further cleavage to form the fragment at m/e 108 Scheme 11.

Approximately 25 different types of possible structures were identified from average properties of sediments, as analyzed by elemental analyses, infrared and mass spectrometric methods. A list of possible structures of compounds from DMP sediment obtained from different experimental conditions have been reported [6]. Beaver et al., [10] detected the presence of peroxide intermediate by reaction between 1-alkylpyrrole and oxygen; also they did isolation and characterization of oxidation products. The proposed possible compound fragments are shown in Schemes 4, 5, 6, 7 and the mechanism of some possible fragment formations in Schemes 8, 9, 10 and 11 respectively. Most of the smaller m/e value compounds are formed by

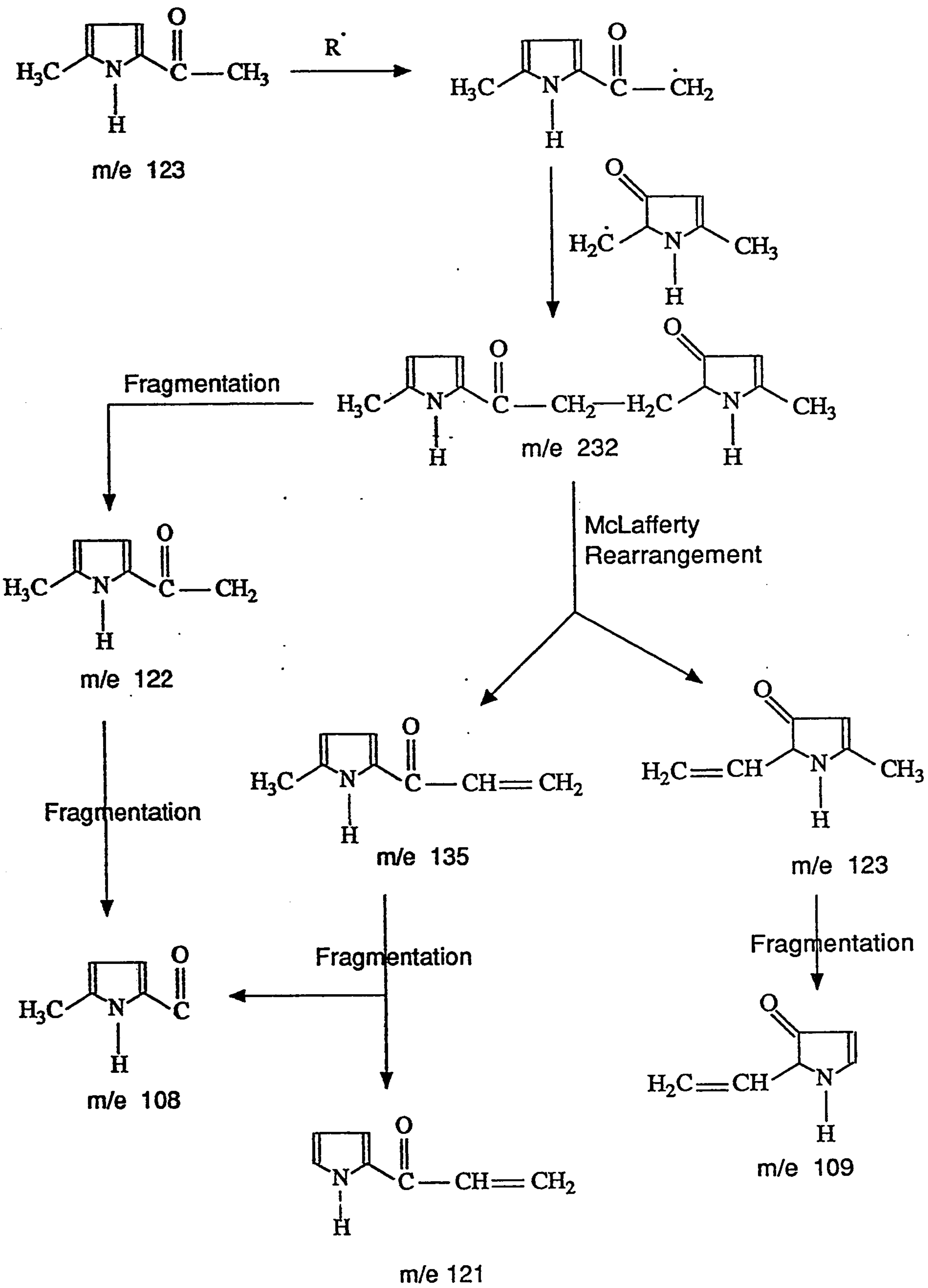
SCHEME 9

Mechanism of some possible fragments formation



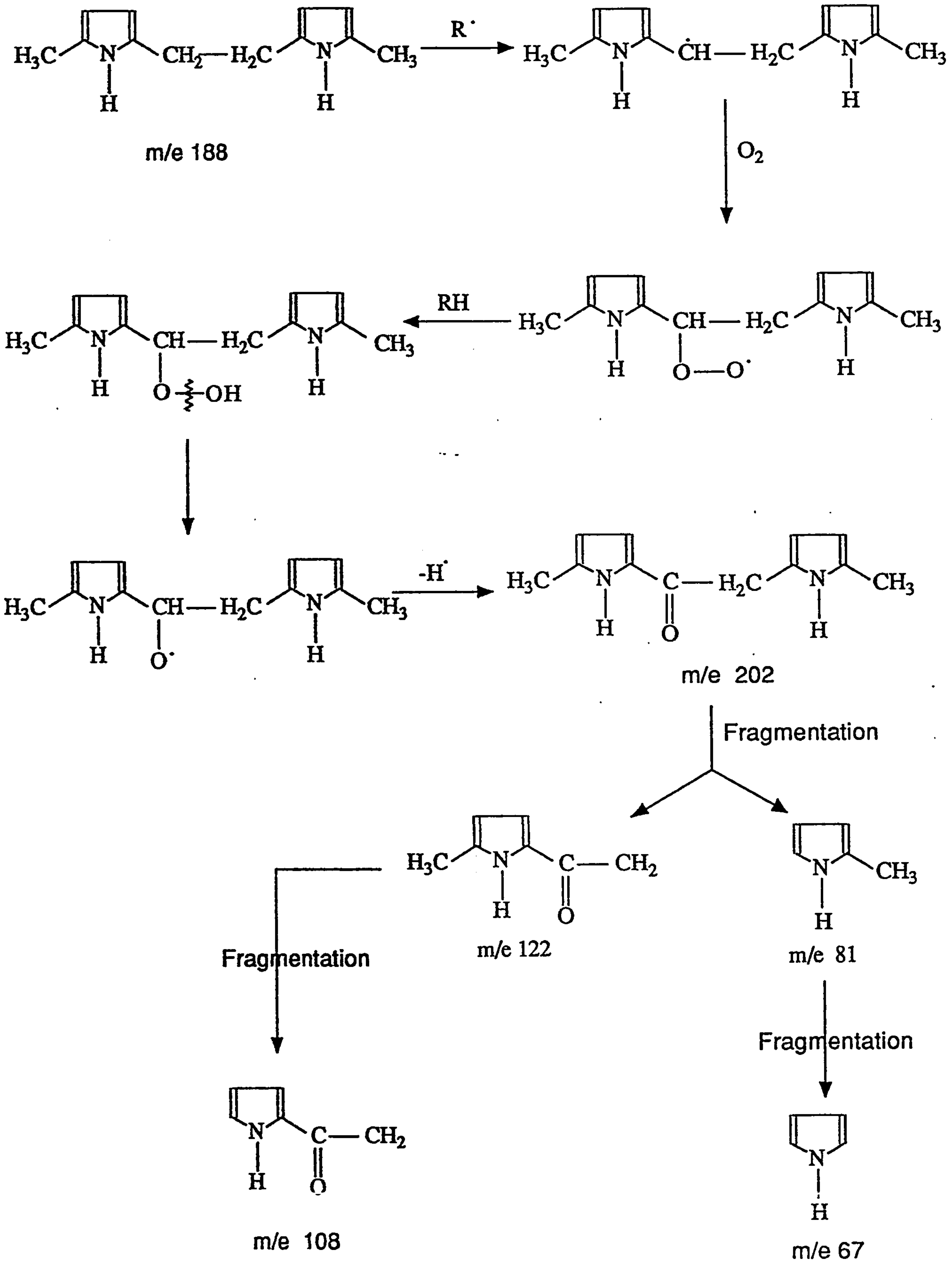
SCHEME 10

Mechanism of Some Possible Fragments Formation



SCHEME 11

Mechanism of Some Possible Fragments formation



fragmentation of larger m/e value compounds. The smaller fragments have been shown in Schemes 8, 9, 10 and 11 wherever it was possible during the proposed reaction mechanism.

4.11. SUGGESTED MECHANISM OF SEDIMENTATION

Any mechanism proposed for deposit formation must address two key observations: (a). dissolved oxygen reacts with fuel components and sets up a sequence of reactions which leads to deposit formation and (b). compounds containing oxygen, nitrogen and sulfur are intimately involved in deposit formation.

Compounds containing heteroatoms are more easily oxidized than most hydrocarbons found in jet fuels. Reactions between such compounds and dissolved oxygen represent the first step towards sediment formation. Jet fuels exhibit degradation in the presence of oxygen but it becomes more severe at lower temperatures if the fuel is saturated with air. Degradation also occurs even in the absence of oxygen but leads to a very small amount of deposit formation. The fuel / oxygen reactions, which involve free radical reactions, are termed autoxidation processes. They involve three sequential reaction steps, namely initiation, propagation and termination, which are shown in Scheme (12). They provide a very useful conceptual framework to rationalize fuel autoxidation.

The reactions have been drastically altered by the presence of molecular oxygen. The photo-oxygenation reaction frequently depends on the electronic state of oxygen molecule involved. In the ground state molecular oxygen is triplet. The highest occupied molecular orbitals (HOMOs) are the degenerate Π^* orbitals, each containing a single electron termed as $^3\Sigma$ state.

SCHEME 12

SUGGESTED FREE RADICAL MECHANISM

INITIATION

$$R{-}H + {}^{\cdot}O{-}O^{\cdot} \longrightarrow R^{\cdot} + HOO^{\cdot} \qquad (1)$$

PROPAGATION

$$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot} \qquad (2)$$

$$ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot} \qquad (3)$$

$$ROOH \longrightarrow RO^{\cdot} + {}^{\cdot}OH \qquad (4)$$

$$RO^{\cdot} + RH \longrightarrow ROH + R^{\cdot} \qquad (5)$$

$$HO^{\cdot} + RH \longrightarrow H_2O + R^{\cdot} \qquad (6)$$

TERMINATION

$$R^{\cdot} + {}^{\cdot}OH \longrightarrow ROH \qquad (7)$$

$$R^{\cdot} + R^{\cdot} \longrightarrow R{-}R \qquad (8)$$

$$ROO^{\cdot} + R^{\cdot} \longrightarrow ROOR \qquad (9)$$

$$ROH \xrightarrow[\text{Excess}]{O} \text{Acids, Esters and Ketones}$$

The reaction (1) i.e. initiation step, forms an alkyl free radical or pyrrole free radical between ground $^3\Sigma$ oxygen state (i.e. molecular oxygen) and substrate molecule. The ESR evidence of pyrrole radical during autoxidation of DMP was reported earlier [7]. The propagation steps (2), (3), (5) & (6) carry the chain to stable products, a hydroperoxide, alcohol and water. Some of the propagation steps form free radicals which proceed to further reaction. A single initiation reaction can afford many hydroperoxide molecules, depending on the chain length of propagation steps. Reaction (2) is relatively fast but may be rate controlling at low oxygen concentration. Reaction (3) is normally rate controlling. If the oxygen supply is limited and temperature is raised, or sufficient oxygen is present, the hydroperoxide concentration will reach a limiting concentration. Where hydroperoxide decomposition occurs (step (4)) it ensures additional free radical reaction, which leads to the formation of alcohol, ketone and small hydrocarbons. Termination reaction rates also depend on oxygen concentration. At low oxygen concentration reaction (8) is predominant and polymers are formed. At high oxygen concentration reaction, acids, esters and ketones are formed as major products. Termination reactions also occurs between free radicals steps (7) and (9).

Thus the rate of reactions in autoxidation are dependent upon temperature, hydrocarbon structures and oxygen concentration. Catalyst and free radical initiators can also materially alter rates, particularly for the step (1).

4.12. ELEMENTAL ANALYSIS OF FUEL SAMPLES

The elemental analysis of all fuel samples were determined in terms of weight fraction of carbon and hydrogen. These values are shown in Table (17).

TABLE 17

ELEMENTAL ANALYSIS DATA OF FUEL SAMPLES

	Weight Percent	
Sample	Carbon	Hydrogen
Rastanura Refinery		
PLT - 71 KD	84.6	14.3
TK - 258 LSRN	83.5	16.4
TK - 242 HCN	86.2	14.8
Riyadh Refinery		
RF - 1	85.3	13.7
RF - 2	84.4	14.4
Petromin Shell		
U - 1300	85.2	14.8
U - 1100	83.2	15.0

4.13. MOLECULAR WEIGHT OF FUEL SAMPLES

The average molecular weights of the fuel samples were determined by vapor pressure osmometry. The molecular weights are given in the Table (18).

4.14. ANALYSIS OF NMR

Nuclear magnetic resonance spectroscopy has been used extensively to characterize different types of fuels in terms of average molecular structural parameters. Previously the fuels were separated into four fractions such as saturates, monoaromatics, diaromatics and polyaromatics by chromatographic techniques. After that each fraction was analysed by ^{1}H and ^{13}C NMR spectroscopy. The computer program eliminates the chromatographic separation of fuels which were directly analysed by ^{1}H and ^{13}C NMR spectroscopy.

4.14.1. PROTON NMR

^{1}H nmr spectroscopy has been widely used as a powerful tool for investigating the composition of petroleum derived products but still severely limited by narrow range of chemical shift during quantitative analysis. Intensities of signals in 0.5 - 4 ppm are considered as aliphatic protons and in 6.6 - 8.3 ppm are ascribed to aromatic protons as heteroatomas are neglected. Intensities of olefinic hydrogen absorption in the region of 4.0 - 6.0 ppm are generally very low for petroleum fractions, however, in the fuel samples studied this part is completely absent. Several of the investigators [106, 108-109, 119] divided the aliphatic region into three parts, while in computer programming, it was divided into five parts: $H\alpha$-1 (2.3 - 4.0 ppm); are the methylene hydrogen attached to a saturated carbon in a position a to aromatic ring; $H\alpha$-2 (1.9 - 2.3

TABLE 18

AVERAGE MOLECULAR WEIGHT OF SAMPLES

Sample	Average molecular weight
PLT - 71 KD	209.6
RF - 1	209.2
U - 1300	210.2

ppm); are the methyl hydrogen attached to a saturated carbon in a position α to aromatic ring; Hβ (1.0 - 1.6 ppm) are the protons attached to paraffinic methylenes and methyls or methylene protons β, or further removed from an aromatic ring; Hβ-N (1.6 - 1.9 ppm) are the naphthene hydrogen attached to carbon β to aromatic ring. Hγ (0.5 - 1.0 ppm) are the protons of paraffinic methyls and methyls γ, or further, removed from an aromatic ring. Table (19) represents the classification and definitions with symbol for each type of hydrogens used in this program.

4.14.2. CARBON - 13 NMR

The application of ^{13}C NMR spectroscopy to the characterization of crude petroleum. and petroleum fractions has grown enormously in recent years. New techniques which eliminate the effects of long spin-latice relaxation times (T1) by using reagents (chromium acetylacetonate) help in relaxing the carbon nuclei, so that the relaxation times are reduced and pulses can be repeated at short interval of times. These are associated with certain types of carbon and Nuclear Overhauser Enhancement (NOE) (by setting the spectrometer in a gated decoupling mode where by the decoupler is on during data acquisition and off during the pulse delay time) of ^{13}C NMR spectroscopy have greatly improved the quantitative aspects of fossil fuel analysis. Carbon-13 NMR spectroscopy provides much more detailed information about the carbon functional groups present in the molecule. Parameters such as aliphatic chain structure, methylene, methyl and methine carbons and aromatic ring size and substitution are some of the additional information that can be obtained from ^{13}C NMR spectroscopy.

TABLE 19

^1H AND ^{13}C NMR NORMALIZED AREA INPUT PARAMETERS

Symbol		Definitions	Chemical Shift Range (ppm from TMS)
H_{Mo}	=	Monoaromatic hydrogens	6.6 - 7.2
H_{Di}	=	Diaromatic hydrogens	7.2 - 7.8
H_{Tri}	=	Triaromatic hydrogens	7.8 - 8.3
H_{Ol}	=	Olefinic hydrogens	4.0 - 6.0
$H_{\alpha\text{-}1}$	=	Methylene hydrogens α to aromatic ring	2.3 - 4.0
$H_{\alpha\text{-}2}$	=	Methyl hydrogens α to aromatic ring	1.9 - 2.3
$H_{\beta\text{-}N}$	=	Naphthene hydrogens β to aromatic ring	1.6 - 1.9
H_{β}	=	β-CH_2- and β-CH_3 to aromatic ring and normal alkane -CH_2- hydrogens	1.0 - 1.6
H_{γ}	=	γ-CH_3 to aromatic ring and normal or branched alkane -CH_3 hydrogens	0.5 - 1.0
C_{Ar}	=	Total aromatic carbons	100 -150
C_{Al}	=	Total aliphatic carbons	5.0 - 50
C_1	=	Methyl carbons of n-alkane	13.8-14.2
C_2	=	C_2-Methylene carbons of n-alkanes	22.7-23.0
C_3	=	C_3 -methylene carbons to n-alkanes	31.8-32.0
$C_{4,5,n}$	=	$C_{4,5,n}$ -Methylene carbons of n-alkanes	29.0-30.0

The integration intensities in the range of 0 - 50 ppm and 100 - 150 ppm are due to the saturated carbon and aromatic carbon respectively. The saturated carbon (0 - 50 ppm) can be devided into straight chain aliphatic and naphthenic carbons, both of which could be evaluated according to the methods of [108-109, 120]. Pulse sequence could be helpful to distinguish between primary (CH_3), secondary (CH_2), tertiary (CH) and quaternary (C) carbons in carbon - 13 spectra of hydrocarbon. In the computer programming, the aliphatic regions are divided into C1 (13.8 - 14.2 ppm) are the methyl carbon of n-alkane; C2 (22.7 - 23.0 ppm) are the methylene C-2 carbon of n-alkane; C3 (31.8 - 32.0 ppm) are the methylene C-3 carbon of n- alkane; and C4,5,n (29 - 30 ppm) are the methylene C-4, 5,----, n carbons of n-alkane. Table (19) represents the classification and definitions with symbol for each type of carbons used in this program.

4.15. ANALYSIS OF FUEL SAMPLES

The combination of ^1H NMR spectroscopy with ^{13}C NMR spectroscopy has proven useful in assessing the average molecular composition of petroleum fractions. The spectra of fuel samples are reported in Figure 42 - 55 in spectral index. It can be seen from the broad envelop of low intensity signal in the aromatic region of the ^1H (6.6 - 8.3 ppm) and ^{13}C (110 - 160 ppm) spectra indicate that the fuel samples have a small amount of aromatic material. The aromatic proton band was observed entirely in the region up field, i.e. from 6.6 - 7.2 ppm, indicating the presence of an alkyl substituted monoaromatic species. The percentage of aliphatic and aromatic constituents of fuels are given in Table (20). The kerosene samples examined in this experiment, show that the Rastanura refinery kerosene sample (PLT-71 KD) had the lowest amount and the Riyadh refinery kerosene had the highest

Table 20

PERCENTAGE OF ALIPHATIC AND AROMATIC HYDROGEN AND CARBON IN FUEL SAMPLES

Sample name	NMR	Aliphatic %	Aromatic %
PLT - 71 KD	^{1}H	96.2	3.8
PLT - 71 KD	^{13}C	92.2	7.8
TK - 258 LSRN	^{1}H	98.0	2.0
TK - 258 LSRN	^{13}C	97.5	2.5
TK - 242 HCN	^{1}H	95.1	4.9
TK - 242 HCN	^{13}C	86.5	13.5
RF - 1	^{1}H	93.2	6.8
RF - 1	^{13}C	87.1	12.9
RF - 2	^{1}H	94.6	5.4
RF - 2	^{13}C	87.3	12.7
U - 1300	^{1}H	96.1	3.9
U - 1300	^{13}C	85.7	14.3
U - 1100	^{1}H	96.6	3.4
U - 1100	^{13}C	92.0	8.0

amount of aromatic content. Among naphtha samples, Low straight run naphtha (TK - 258 LSRN) has lowest amount and hydrocracked naphtha (TK - 242 HCN) has highest amount of aromatic content. The value for the apparent side chain length calculated from the ^1H spectra assuming : (1) that all aliphatic material was joined to an aromatic ring and (2) that the carbon to hydrogen ratio of carbon in or attached to aromatic rings equaled that of all other aliphatic carbons.

From the ^1H spectra, it is seen that the aromatic proton signal pattern extended down field from 7.2 - 7.8 ppm, indicating the presence of diaromatic-condensed ring compounds. This was also reflected in the values obtained for the aromatic proton (Ar-H) and carbon (Ar-C) content for each fuels. Tri-aromatic condensed rings are completely absent from all fuel samples.

The ^{13}C NMR spectra of fuels displayed signals at 14.2, 23, 31.9, 29.7 and 30 ppm corresponding to C1,C2, C3, C4 and C5 ----n respectively strongly suggested the predominance of long aliphatic side chain from alkyl substituted, monoaromatic species in the fuel.

All of the information provided from fuel samples studied in these experiments led to the conclusion that they are composed of a mixture of paraffinic chains, naphthenic-saturated rings and long aliphatic side chain, aliphatic-substituted aromatics.

For the computation of various average molecular parameters derived from NMR data, all area measurements have been normalized. The normalized proton and carbon - 13 data for all samples studied in this investigation are given in Tables (21) and (22) respectively. Elemental

TABLE 21

NORMALIZED PROTON NMR INTEGRATION DATA

Sample	H_{Mo}	H_{Di}	H_{Tri}	H_{Ol}	$H_{\alpha\text{-}1}$	$H_{\alpha\text{-}2}$	$H_{\beta\text{-}N}$	H_{β}	H_{γ}
Rastanura Refinery									
PLT - 71 KD	3.2895	4.6053	0.0000	0.0000	0.6237	0.1559	0.4158	6.3150	0.233
TK - 258 LSRN	0.0000	10.000	0.0000	0.0000	0.0000	0.1020	0.2555	5.2041	4.438
TK - 242 HCN	6.1224	8.1633	0.0000	0.0000	0.5258	0.1840	0.8412	11.409	1.209
Riyadh Refinery									
RF - 1	3.3088	8.4559	0.0000	0.0000	0.9120	0.5901	1.3948	8.3154	0.536
RF - 2	5.5555	10.185	0.0000	0.0000	0.5814	0.6871	1.5328	11.258	1.532
Petromin Shell									
U - 1300	7.6923	5.1282	0.0000	0.0000	0.9365	0.2081	0.8845	11.811	0.416
U - 1100	1.4706	5.8824	0.0000	0.0000	0.1035	0.1035	0.3105	5.7971	1.294

TABLE 22

NORMALIZED CARBON - 13 NMR INTEGRATION DATA

Sample	C_{Ar}	C_{Al}	C_1	C_2	C_3	C_4	$C_{5,n}$
Rastanura Refinery							
PLT - 71 KD	5.1282	5.0976	0.1084	0.3254	0.0542	0.4067	0.000
TK - 258 LSRN	6.0000	5.8974	0.8205	0.1026	0.3077	0.2051	0.000
TK - 242 HCN	7.0370	7.0520	0.6589	0.6936	0.4046	0.7746	0.000
Riyadh Refinery							
RF - 1	16.275	16.418	0.1148	0.0574	0.1148	1.3203	0.000
RF - 2	12.594	12.600	0.4009	0.9164	0.1145	0.2291	0.000
Petromin Shell							
U - 1300	12.337	12.252	0.0583	0.2334	0.4084	1.8670	0.000
U - 1100	10.000	10.000	0.8695	0.0924	0.4348	0.7609	0.000

analysis data and average molecular weight are given in Tables (17) and (18) respectively.

The average molecular structural parameters of all fuel samples obtained from the computer program are shown in tables (23) & (24). A listing of the computer program for calculating the average molecular parameters of hydrocarbon mixtures is given in the appendix.

TABLE 23

KING FAHAD UNIVERSITY OF PETROLEUM & MINERALS
OIL TESTING CENTRE
SPECTROSCOPY SECTION

AVERAGE MOLECULAR STRUCTURE PARAMETERS OBTAINED FROM NUCLEAR MAGNETIC RESONANCE TO CHARACTERIZE HYDROCARBON MIXTURE

SERIES NAME : FUEL SAMPLE NUMBER OF SAMPLES: 5

RECEIVED BY : RAS & RDH REFIN
SERIES DISCRIPTION : HYD.MIXTUR
DATE OF COMPUTATION : 93/01/15

SPECTROSCOPIST :NIZAMI

****

REPORT OF ANALYSIS

****

MEASURED PARAMETERS

PARAMETER\			SAMPLE NAME		
**********	PLT-71KD	TK-257LSRN	TK-242HCN	RF - 1	RF - 1
HMO	3.2895	0.0000	6.1224	3.3088	5.5555
HDI	4.6053	10.0000	8.1633	8.4559	10.1850
HTRI	0.0000	0.0000	0.0000	0.0000	0.0000
HOL	0.0000	0.0000	0.0000	0.0000	0.0000
HALP1	0.6237	0.0000	0.5258	0.9120	0.5814
HALP2	0.1559	0.1020	0.1840	0.5901	0.6871
HBETAN	0.4158	0.2555	0.8412	1.3948	1.5328
HBETA	6.3150	5.2041	11.4090	8.3154	11.2580
HGAMA	0.2339	4.4388	1.2092	0.5365	1.5328
HAR	7.8948	10.0000	14.2857	11.7647	15.7405
HOL	0.0000	0.0000	0.0000	0.0000	0.0000
HAL-T	0.7796	0.1020	0.7098	1.5021	1.2685
HBET-GAM	6.9647	9.8984	13.4594	10.2467	14.3236
C13 ENTER	1.0000	1.0000	1.0000	1.0000	1.0000
CS	0.0000	0.0000	0.0000	0.0000	0.0000
CB	0.0000	0.0000	0.0000	0.0000	0.0000
CU	0.0000	0.0000	0.0000	0.0000	0.0000
CAR	5.1282	6.0000	7.0370	16.2750	12.5940
CAL	5.0976	5.9874	7.0520	16.4180	12.6000
C1	0.1084	0.8205	0.6589	0.1148	0.4009
C2	0.3254	0.1026	0.6936	0.0574	0.9164
C3	0.0542	0.3077	0.4046	0.1148	0.1145
C4	0.4067	0.2051	0.7746	1.3203	0.2291

C5	0.0000	0.0000	0.0000	0.0000	0.0000
CHEM ENTER	1.0000	1.0000	1.0000	1.0000	1.0000
CARBON	84.8000	83.5000	86.2000	85.3000	84.4000
HYDROGEN	14.3000	16.4000	14.8000	13.7000	14.4000
MW	0.0000	0.0000	0.0000	0.0000	0.0000

PARAMETERS CALCULATED FROM PROTON NMR

FA SUP H	7.8948	10.0000	14.2857	11.7647	15.7405
FMO	0.4912	0.0000	0.5017	0.3467	0.4235
FDI	0.5088	1.0000	0.4983	0.6533	0.5765
RS	0.3091	0.0271	0.1553	0.3841	0.2286
% AR	70.3526	64.1292	67.1331	70.0969	67.8246
% MOAR	34.5557	0.0000	33.6775	24.3018	28.7210
% DIAR	35.7969	64.1292	33.4556	45.7950	39.1035
% OL	0.0000	0.0000	0.0000	0.0000	0.0000
% PAR	29.6474	35.8708	32.8669	29.9031	32.1754
R SUPER H	34.4984	1.7586	13.1744	19.4242	10.1637

PARAMETERS CALCULATED FROM H,C NMR AND ELEMENTALANALYSIS

(H/C)T	2.0092	2.3401	2.0457	1.9136	2.0328
(H/C)AR	7.9548	11.7129	14.5964	11.2073	15.9951
(H/C)PAR	-27.7892	-42.1666	-54.2986	-41.0195	-59.9158
F S+B SUPC	-15.3607	-22.9007	-28.7244	-22.0152	-31.4980
F U SUP C	15.8622	23.4013	29.2239	22.5131	31.9978
F A SUP C	0.5015	0.5005	0.4995	0.4978	0.4999
CL	13.5037	6.4999	8.3512	29.0017	7.1429
F N SUP C	0.1755	0.2398	0.3590	0.0979	0.1318
F B SUP C	0.8245	0.7602	0.6410	0.9021	0.8682

TABLE 24

KING FAHAD UNIVERSITY OF PETROLEUM & MINERALS
OIL TESTING CENTRE
SPECTROSCOPY SECTION

AVERAGE MOLECULAR STRUCTURE PARAMETERS OBTAINED
FROM NUCLEAR MAGNETIC RESONANCE TO
CHARACTERIZE HYDROCARBON MIXTURE

SERIES NAME : FUEL SAMPLE NUMBER OF SAMPLES: 2

RECEIVED BY : PETROMIN SHELL
SERIES DISCRIPTION : HYD.MIXTUR
DATE OF COMPUTATION : 93/01/15

SPECTROSCOPIST :NIZAMI

****

REPORT OF ANALYSIS

****

MEASURED PARAMETERS

PARAMETER\			SAMPLE NAME		
**********	U - 1300	U - 1100			
HMO	7.6923	1.4706	0.0000	0.0000	0.0000
HDI	5.1282	5.8824	0.0000	0.0000	0.0000
HTRI	0.0000	0.0000	0.0000	0.0000	0.0000
HOL	0.0000	0.0000	0.0000	0.0000	0.0000
HALP1	0.9365	0.1035	0.0000	0.0000	0.0000
HALP2	0.2081	0.1035	0.0000	0.0000	0.0000
HBETAN	0.8845	0.3105	0.0000	0.0000	0.0000
HBETA	11.8106	5.7971	0.0000	0.0000	0.0000
HGAMA	0.4162	1.2940	0.0000	0.0000	0.0000
HAR	12.8205	7.3530	0.0000	0.0000	0.0000
HOL	0.0000	0.0000	0.0000	0.0000	0.0000
HAL-T	1.1446	0.2070	0.0000	0.0000	0.0000
HBET-GAM	13.1113	7.4016	0.0000	********	0.0000
C13 ENTER	1.0000	1.0000	0.0000	0.0000	0.0000
CS	0.0000	0.0000	0.0000	0.0000	0.0000
CB	0.0000	0.0000	0.0000	0.0000	0.0000
CU	0.0000	0.0000	0.0000	0.0000	0.0000
CAR	12.3370	10.0000	0.0000	0.0000	0.0000
CAL	12.2520	10.0000	0.0000	0.0000	0.0000
C1	0.0583	0.8695	0.0000	0.0000	0.0000
C2	0.2334	0.0924	0.0000	0.0000	0.0000
C3	0.4084	0.4348	0.0000	0.0000	0.0000
C4	1.8670	0.7609	0.0000	0.0000	0.0000

```
C5                0.0000       0.0000       0.0000       0.0000       0.0000
CHEM ENTER        1.0000       1.0000       0.0000       0.0000       0.0000
CARBON           85.2000      83.2000       0.0000       0.0000       0.0000
HYDROGEN         14.8000      15.7000       0.0000       0.0000       0.0000
MW                0.0000       0.0000       0.0000       0.0000       0.0000

               PARAMETERS CALCULATED FROM PROTON NMR

FA SUP H         12.8205       7.3530       0.0000       0.0000       0.0000
FMO               0.6692       0.2507       0.0000       0.0000       0.0000
FDI               0.3308       0.7493       0.0000       0.0000       0.0000
RS                0.2681       0.0869       0.0000       0.0000       0.0000
% AR             67.5345      63.5950       0.0000       0.0000       0.0000
% MOAR           45.1973      15.9425       0.0000       0.0000       0.0000
% DIAR           22.3372      47.6524       0.0000       0.0000       0.0000
% OL              0.0000       0.0000       0.0000       0.0000       0.0000
% PAR            32.4655      36.4050       0.0000       0.0000       0.0000
R SUPER H        37.5031       6.5400       0.0000       0.0000       0.0000

        PARAMETERS CALCULATED FROM H,C NMR AND ELEMENTALANALYSIS

(H/C)T            2.0697       2.2483       0.0000       0.0000       0.0000
(H/C)AR          13.3131       8.2660       0.0000       0.0000       0.0000
(H/C)PAR        -49.0992     -28.5672       0.0000       0.0000       0.0000
F S+B SUPC      -26.0327     -16.0319       0.0000       0.0000       0.0000
F U SUP C        26.5344      16.5319       0.0000       0.0000       0.0000
F A SUP C         0.5017       0.5000       0.0000       0.0000       0.0000
CL               70.0480       7.7502     ********       0.0000       0.0000
F N SUP C         0.2095       0.2158       0.0000       0.0000       0.0000
F B SUP C         0.7905       0.7842       0.0000       0.0000       0.0000
```

CHAPTER 5

CONCLUSIONS

The test fuel used in this investigation was a petroleum derived jet A fuel from Rastanura refinery. The physical and chemical tests of fuel exceed all the aviation turbine fuel specifications including the most important, thermal oxidation stability test, by a wide margin. This indicates that the fuel possessed very high thermal stability. The one month sunlight storage experiment also exhibited the stability of fuel.

The effects of nitrogen compounds on thermal stability (storage point of view) of petroleum derived jet fuel were investigated in sunlight, ultra-violet radiation as well as in dark storage conditions. Nitrogen compound types found in petroleum caused formation of significant quantities of sediment in a relatively short time. Seven different types of nitrogen compounds and four oxygen compounds were surveyed as fuel dopant. Each nitrogen compound was added to 500 ml fuel at a concentration equivalent to 200 ppm nitrogen and 50 ppm oxygen level (in case of blends). It was found that the quantity of sediment formation was greater in samples stored under sunlight than in samples stored under ultra-violet light, while in dark storage, among all nitrogen compounds, only 2,5-dimethylpyrrole (DMP) generated a small amount of sediment. The pyrrole and indole derivatives produced the highest amount of sediment but other nitrogen compounds such as amine derivatives did not produce any appreciable sediment except 2,6-dimethylaniline.

The rate of sediment formation depends upon the basicity (within a given class of compounds) of pyrrole and indole derivatives. The more basic the compounds the more sediment is formed (within a given class of compounds). In the comparison of pyrrole and indole derivatives, structural effects play an important role towards sediment formation. The position of substituents adjacent to the nitrogen atom on the pyrrole and indole derivatives greatly influenced sediment formation rates. Compounds with alkyl groups in the 2 & 5 position were the most active and produced more sediment.

The interaction of nitrogen containing compounds with acids and phenols, exerts a strong but complex effect on the rate of sediment formation. A positive interaction was encountered with acid-nitrogen blends and negative with phenol-nitrogen blends. So that addition of carboxylic acids significantly increased and phenols reduced sediment formation rates, with both DMP and pyrrole.

Accelerated storage stability tests were performed to determine the apparent activation energy (Ea) for total sediment weight. The apparent activation energy (Ea) was 12.65 K Cal mole^{-1} and the relation was approximately linear. The rate of sediment formation increases with increasing DMP concentration or temperature and storage time.

To determine the role of oxygen on sediment formation, experiments were performed in deoxygenated base fuel e.g. jet A fuel and n-decane. The dissolved oxygen of jet fuel and n-decane interacted in strong synergistic fashion with 2,5-dimethylpyrrole leading to the formation of significant amounts of sediments with storage times. Removal of dissolved oxygen from the jet fuel and decane significantly reduced the amount of sediment formation. The results indicated that the oxygen is responsible for the sediment formation and the reaction proceeds through the free radical mechanism. Initially the rate of sediment formation was very high in deoxygenated conditions, but gradually this rate decreased or leveled off after few days of storage. This indicate that the sediment formation stopped after the consumption of all the oxygen content. The amount of sediment formation was more in jet fuel than n-decane because of the complex nature of fuel.

The sediment formation with DMP under different experimental conditions was studied by elemental analyses, FTIR as well as mass spectroscopy.

Elemental analysis of the sediment revealed that the sediment had nearly identical nitrogen to carbon ratios as 2,5-dimethylpyrrole indicating that most of the sediment was derived directly from the neat DMP. The H/C ratio of sediments indicates that the aromatic or heteroatomic compounds were significantly involved in the deposit formation. The low O/C ratios supported the view point that oxidation is a key aspect of jet fuel thermal instability.

Elemental analysis of the DMP derived sediment and DMP induced sediment from carboxylic acid under different storage condition indicated that the composition of DMP sediment are remarkably similar in every case. Thus, it appears that the carboxylic acids are serving as true catalysts during the oxidation of DMP.

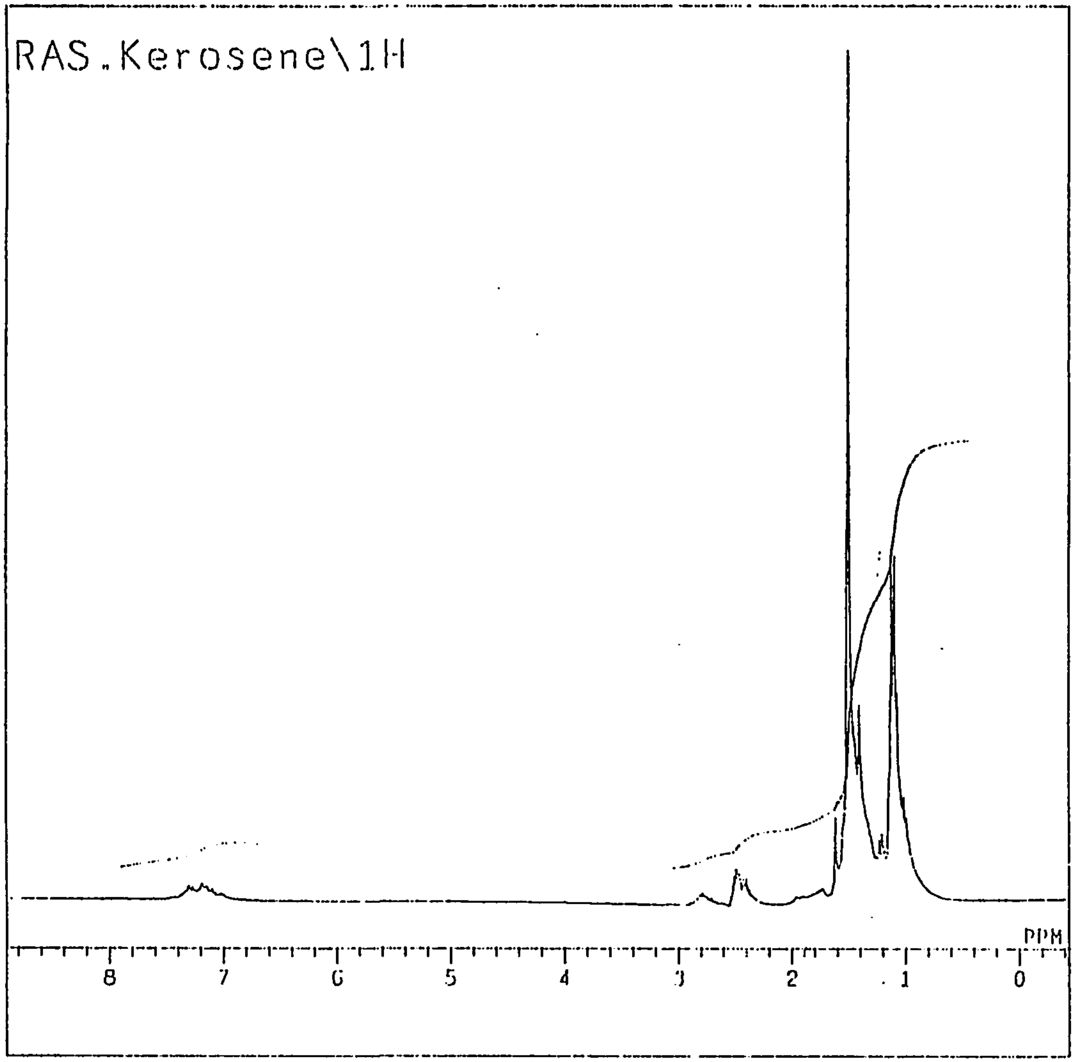
Infrared spectroscopic study of sediments show that the sediments obtained from accelerated aging are the same as those obtained from ambient storage. Sediment analysis data indicate that sediment is derived from the oxidation of DMP with no incorporation of fuel constituents as confirmed by the IR spectra of neat fuel samples and DMP doped fuel samples. The strong absorption band in the IR spectra of sediments at 1700 - 1630 cm^{-1} revealed the presence of different types of carbonyl groups.

The mass spectra of sediment samples are complicated because of the polymeric nature of sediments. The mass spectra suggests that the sediment may consist of several compound types. The major mass spectral peak of mass spectroscopy indicates that the sediments appear to be of fairly low molecular weight, little more than 400 mass unit.

Approximately 25 different types of possible structures were identified from average properties of sediments, as analyzed by elemental analyses, infrared and mass spectrometric methods.

The average molecular parameters of various fuel samples were determined with the help of computer programming by using elemental analysis, proton and carbon-13 NMR spectroscopy. From proton and carbon-13 NMR spectra, normalized area parameters were calculated. This investigation indicate that the fuel samples are primarily composed of a mixture of paraffin chains, naphthenic saturated rings, large aliphatic side chains and aliphatic substituted aromatics.

SPECTRAL INDEX



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ACQTM        1.638 sec
PD           1.000 sec
PW1           13.5 us
ADBIT     16
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IRSET       112.00 kHz
IRFIN       5400.0 Hz
IRATN          120
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Figure 42. Proton NMR spectra of PLT-71 KD.

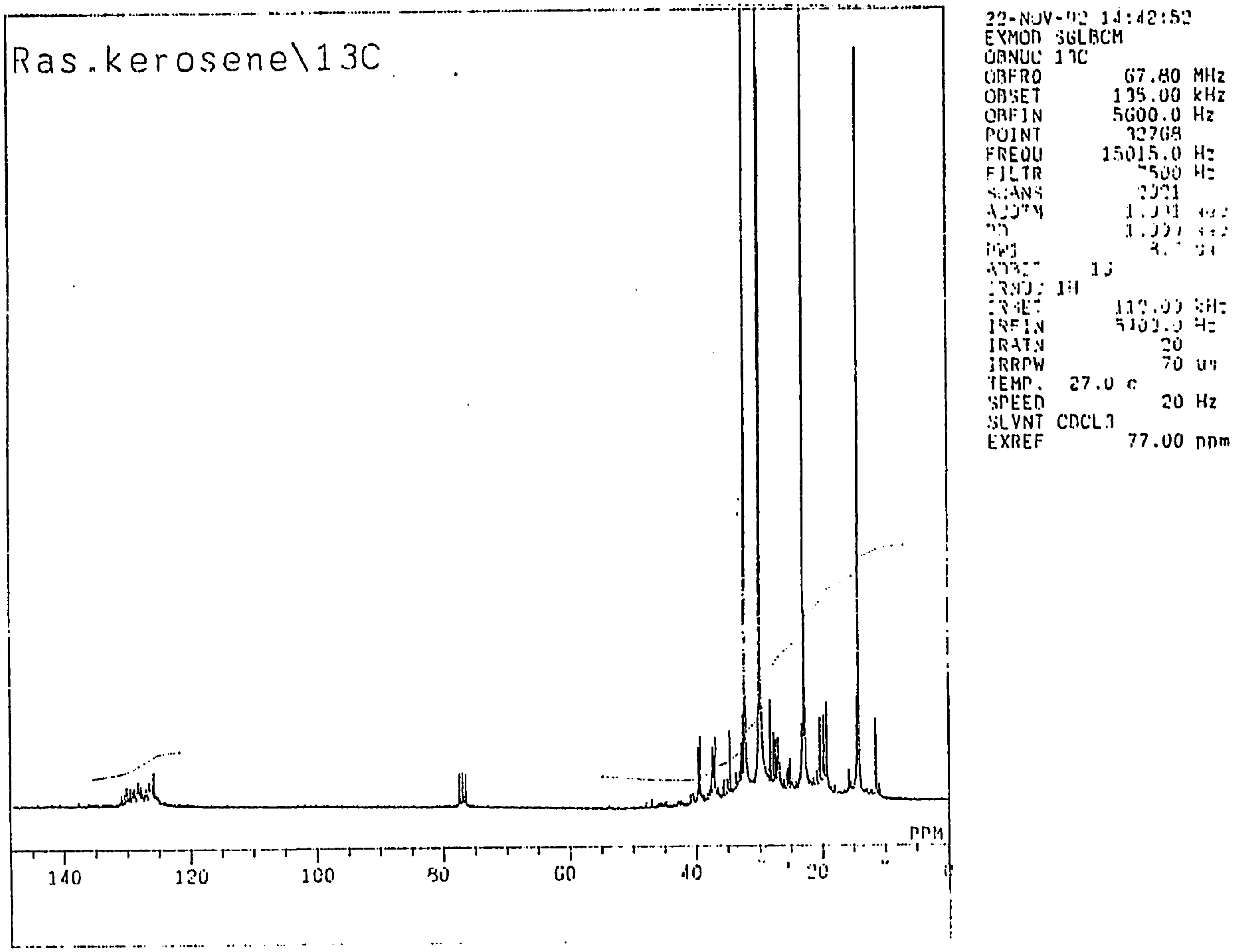
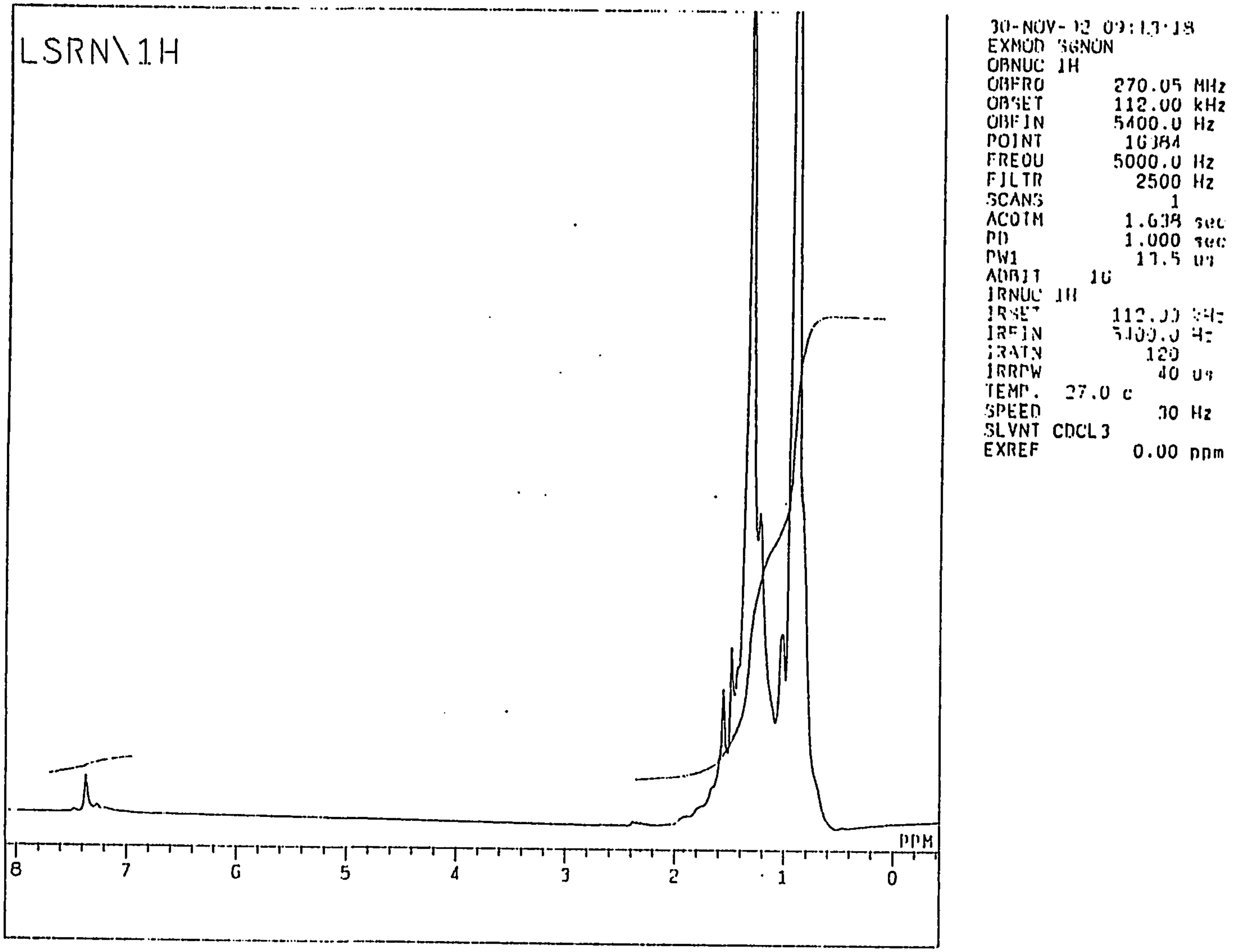


Figure 43. Carbon-13 NMR spectra of PLT-71 KD.



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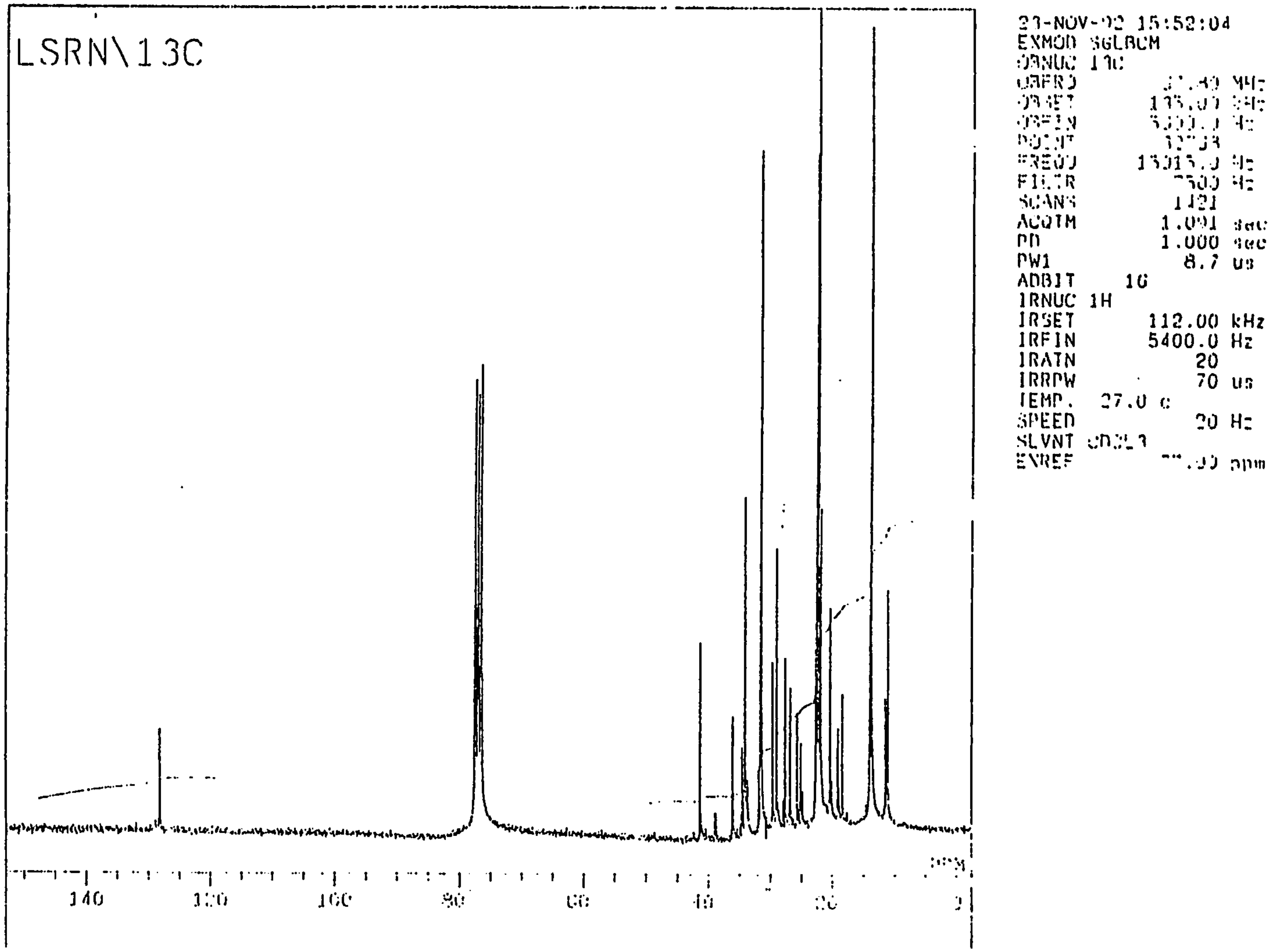
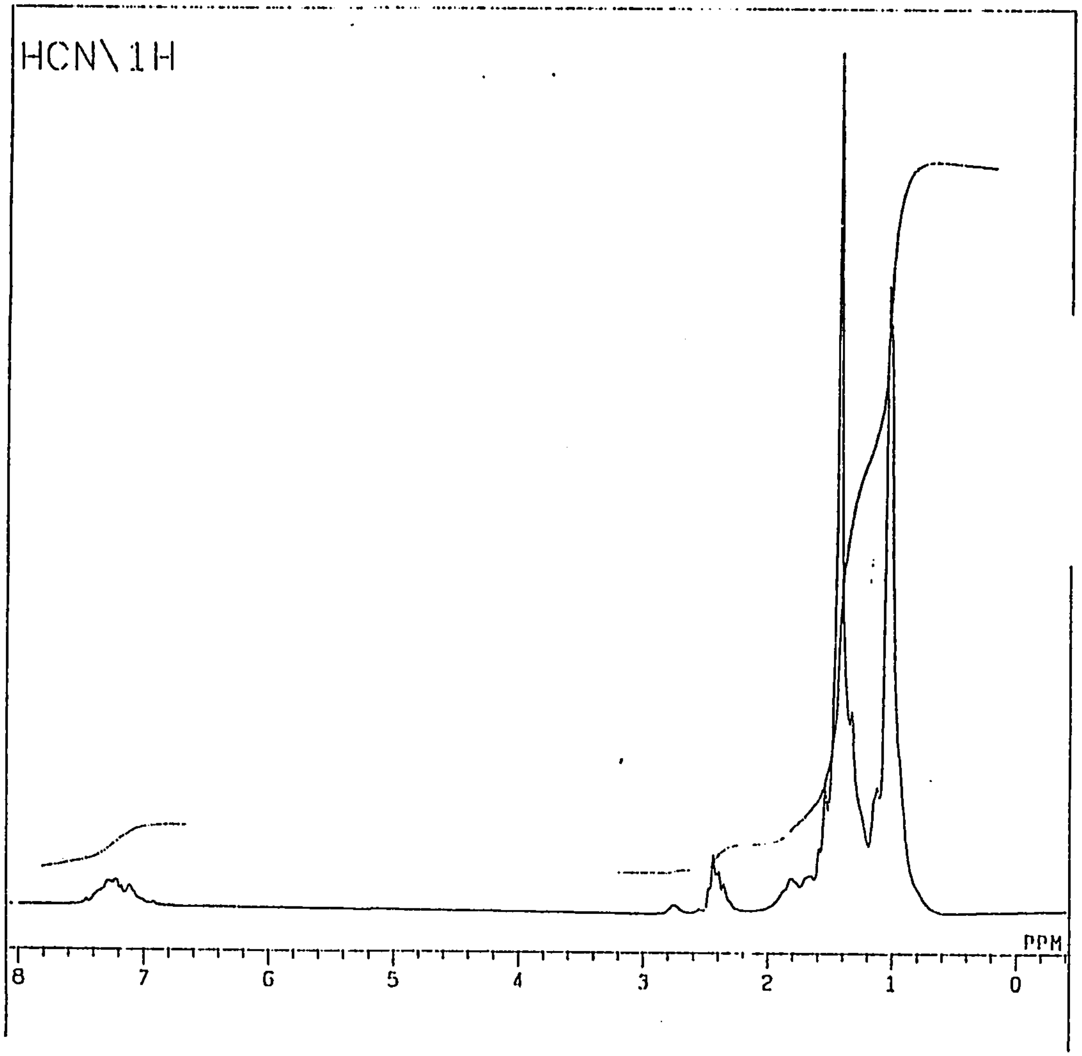
OBNUC 1H
OBFRQ        270.05 MHz
OBSET        112.00 kHz
OBFIN        5400.0 Hz
POINT         16384
FREQU        5000.0 Hz
FILTR          2500 Hz
SCANS             1
ACQTM         1.638 sec
PD            1.000 sec
PW1            17.5 us
ADBIT      16
IRNUC 1H
IRSET        112.00 kHz
IRFIN        5400.0 Hz
IRATN           120
IRRPW            40 us
TEMP.   27.0 c
SPEED            30 Hz
SLVNT CDCL3
EXREF          0.00 ppm
```

Figure 44. Proton NMR spectra of TK-258 LSRN.



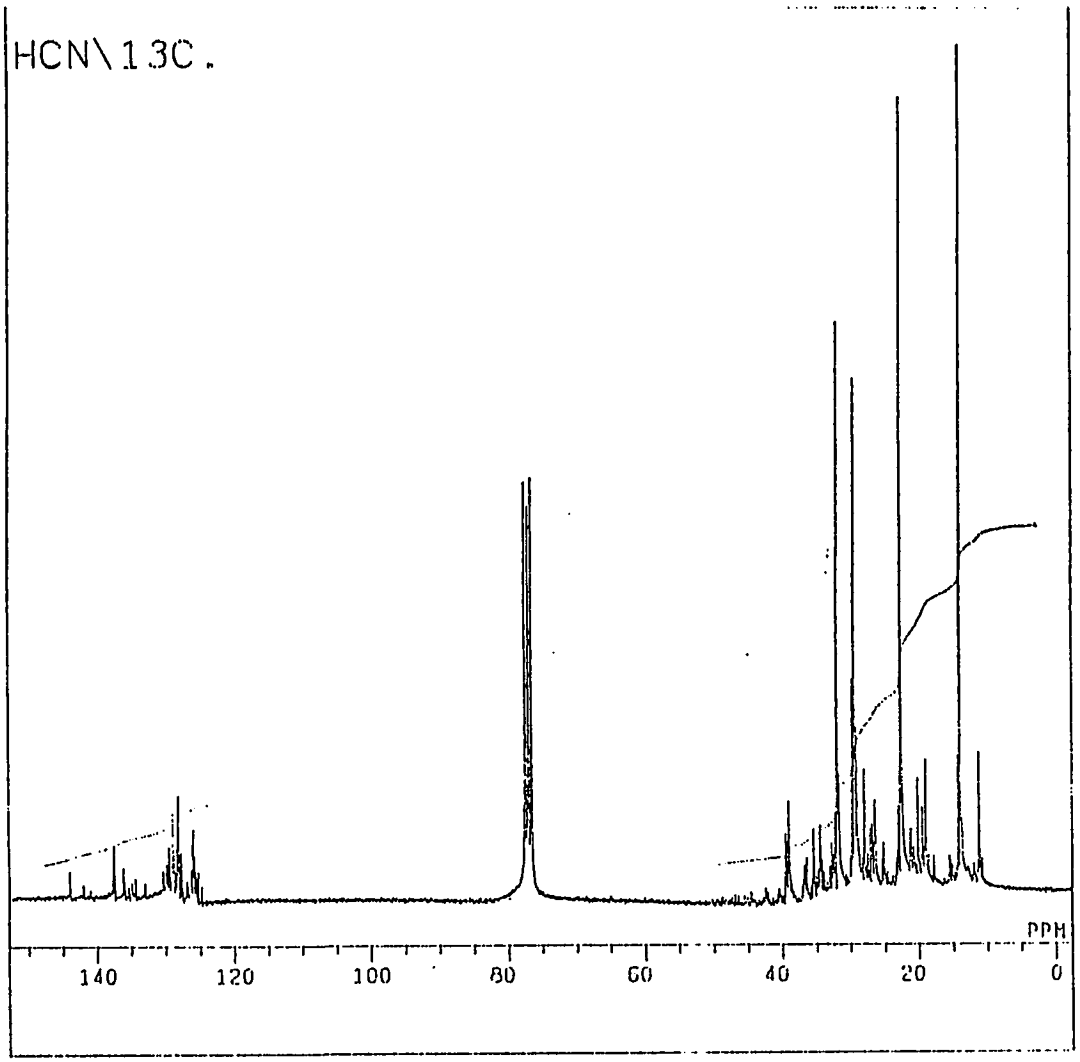
```
23-NOV-92 15:52:04
EXMOD SGLBCM
OBNUC 13C
OBFRQ          22.49 MHz
OBSET         135.00 KHz
OBFIN         5000.0 Hz
POINT          32768
FREQU        15015.0 Hz
FILTR           7500 Hz
SCANS           1121
ACQTM          1.091 sec
PD             1.000 sec
PW1              8.7 us
ADBIT     16
IRNUC 1H
IRSET         112.00 kHz
IRFIN         5400.0 Hz
IRATN             20
IRRPW             70 us
TEMP.   27.0 c
SPEED             20 Hz
SLVNT CDCL3
EXREF          77.00 ppm
```

Figure 45. Carbon-13 NMR spectra of TK-258 LSRN.



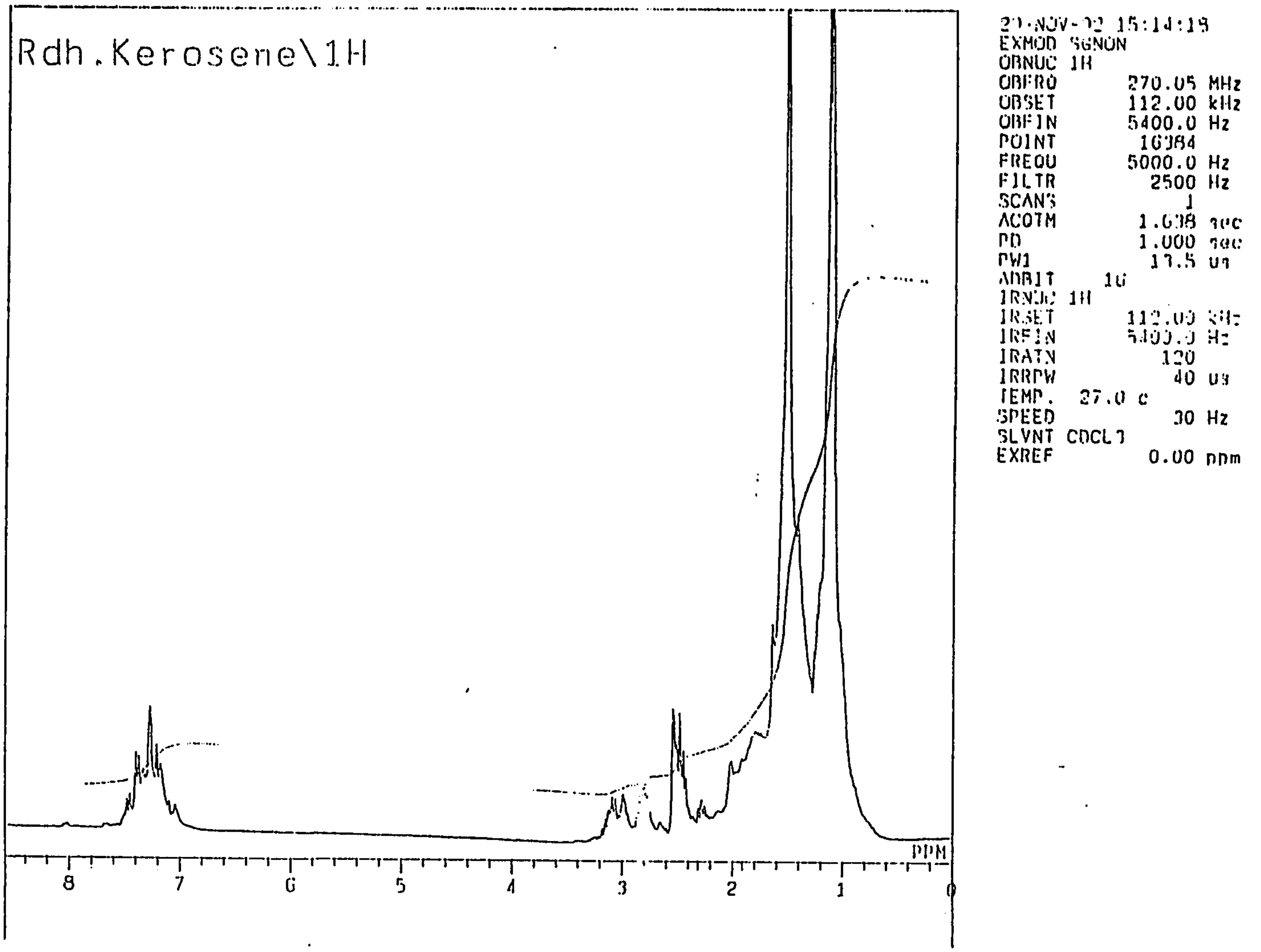
```
30-NOV-92 08:52:18
EXMOD SGNON
OBNUC 1H
OBFRQ       270.05 MHz
OBSET       112.00 kHz
OBFIN       5400.0 Hz
POINT        16384
FREQU       5000.0 Hz
FILTR         2500 Hz
SCANS            1
ACQTM        1.638 sec
PD           1.000 sec
PW1           13.5 us
ADBIT    16
IRNUC 1H
IRSET       112.00 kHz
IRFIN       5400.0 Hz
IRATN          120
IRRPW           40 us
TEMP.   27.0 c
SPEED           30 Hz
SLVNT CDCL3
EXREF         0.00 ppm
```

Figure 46. Proton NMR spectra of TK-242 HCN.



```
21-NOV-92 14:41:01
EXMOD SGLBCM
OBNUC 13C
OBFRQ       67.80 MHz
OBSET      135.00 kHz
OBFIN      5000.0 Hz
POINT       32768
FREQU     15015.0 Hz
FILTR        7500 Hz
SCANS        2175
ACQTM       1.091 sec
PD          1.000 sec
PW1           8.7 us
ADBIT    16
IRNUC 1H
IRSET      112.00 kHz
IRFIN      5200.0 Hz
IRATN          20
IRRPW          70 us
TEMP.   27.0 c
SPEED          20 Hz
SLVNT CDCL3
EXREF       77.00 ppm
```

Figure 47.   Carbon-13 NMR spectra of TK-242 HCN.



```
20-NOV-92 15:14:19
EXMOD SGNON
OBNUC 1H
OBFRQ       270.05 MHz
OBSET       112.00 kHz
OBFIN       5400.0 Hz
POINT        16384
FREQU       5000.0 Hz
FILTR         2500 Hz
SCANS            1
ACQTM        1.638 sec
PD           1.000 sec
PW1           13.5 us
ADBIT    16
IRNUC 1H
IRSET       112.00 kHz
IRFIN       5400.0 Hz
IRATN          120
IRRPW           40 us
TEMP.   27.0 c
SPEED           30 Hz
SLVNT CDCL3
EXREF         0.00 ppm
```

Figure 48. Proton NMR spectra of RF-1.

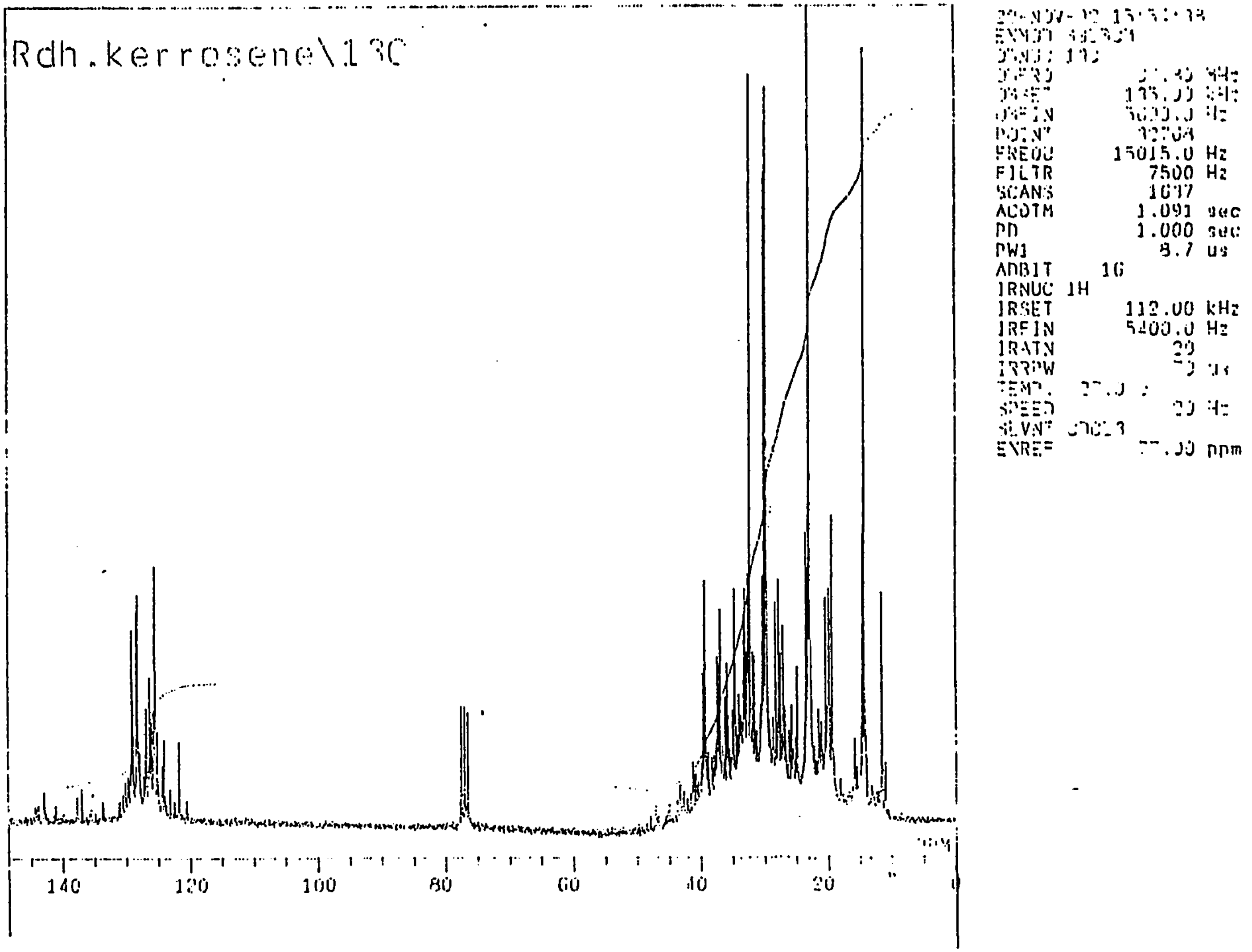
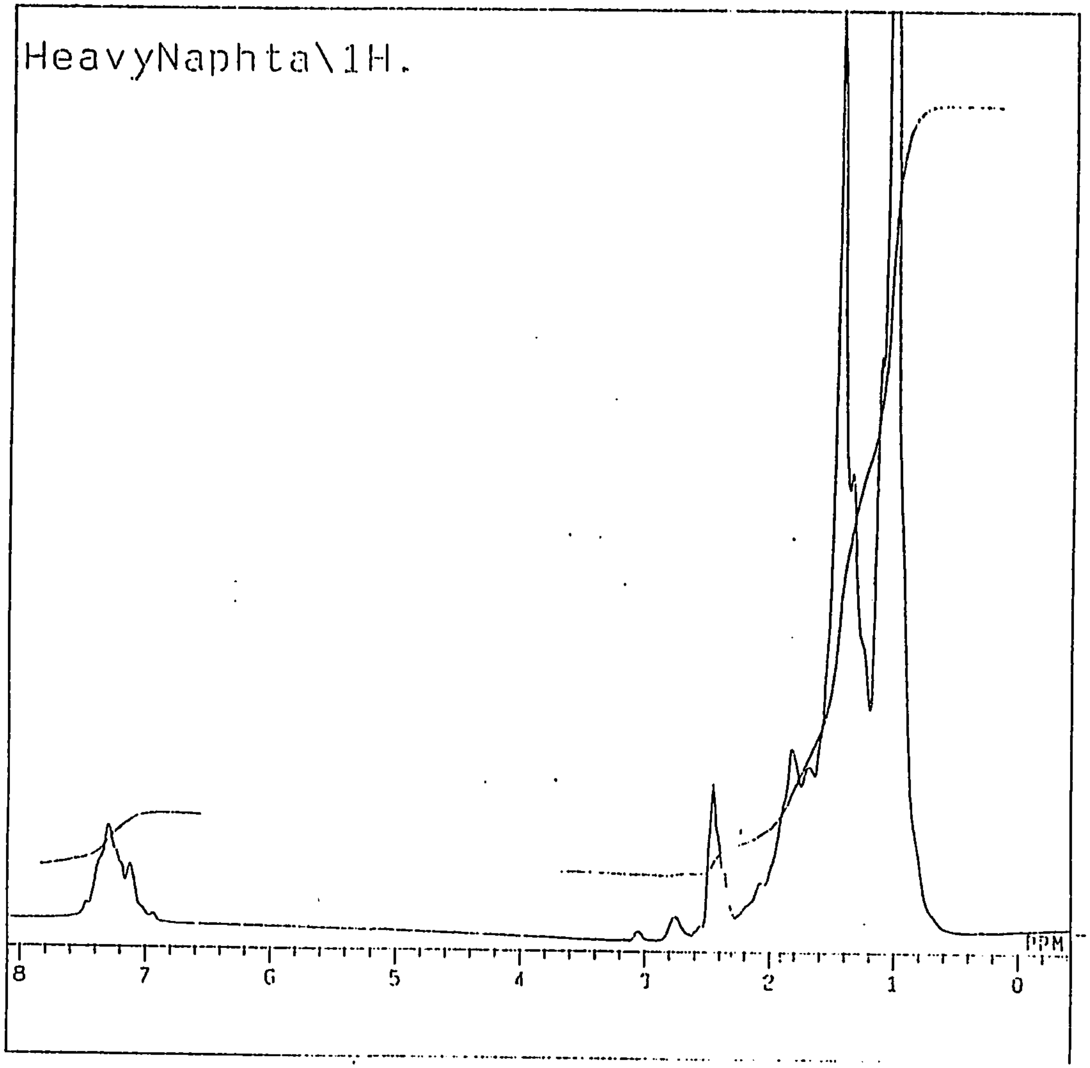
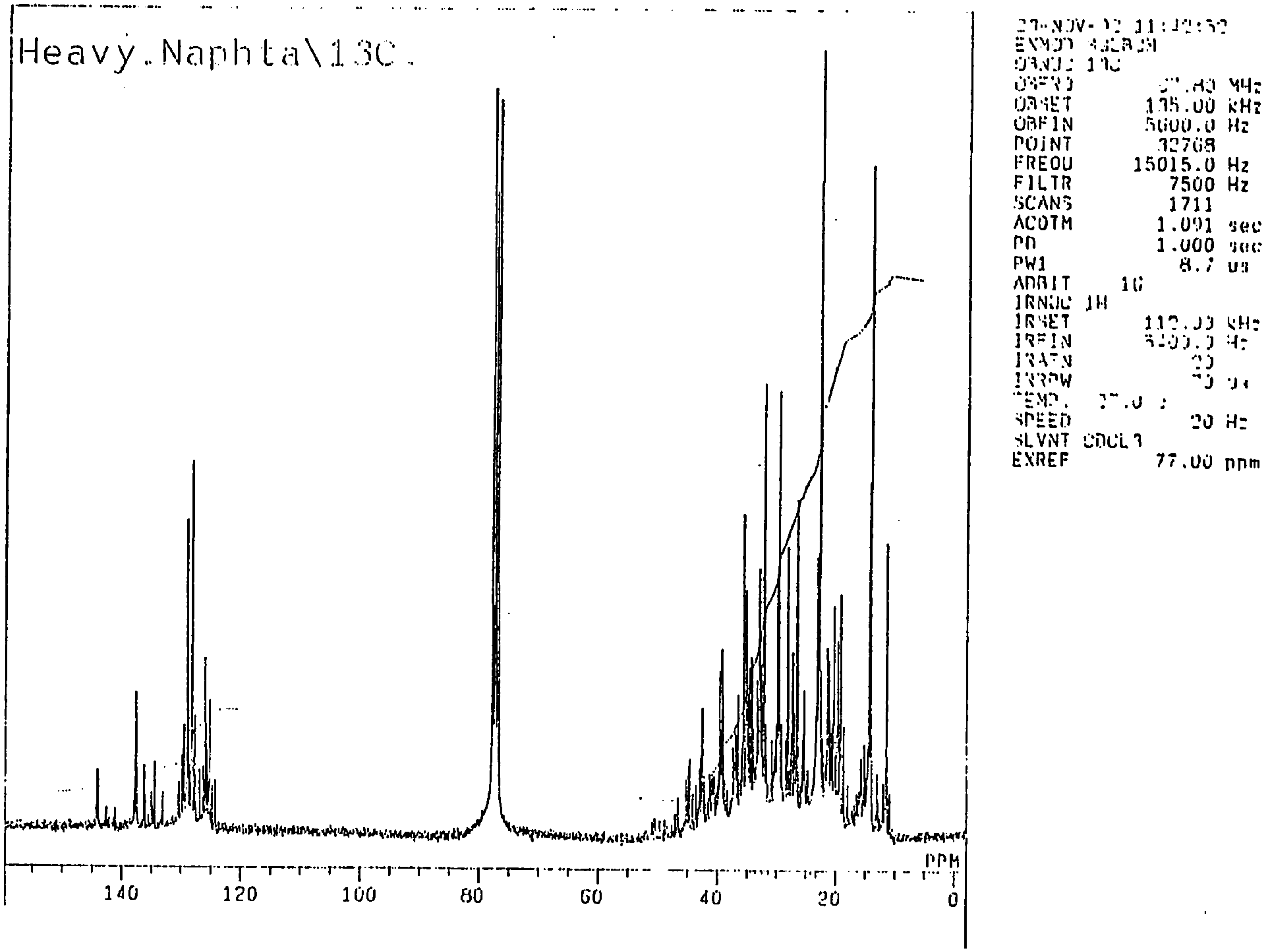


Figure 49. Carbon-13 NMR spectra of RF-1.



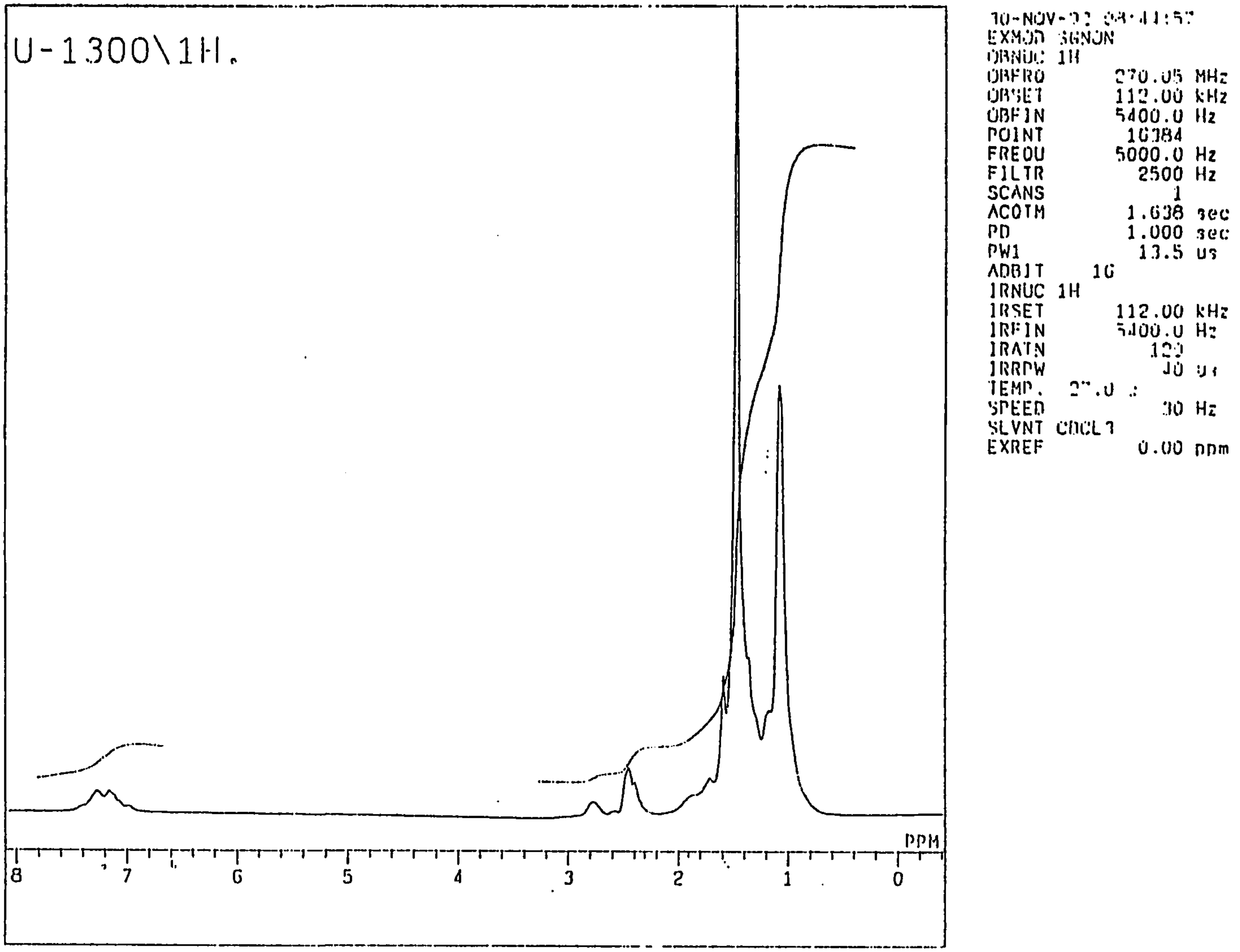
```
29-NOV-92 15:47:25
EXMOD SGNON
OBNUC 1H
OBFRQ       270.05 MHz
OBSET       112.00 kHz
OBFIN       5400.0 Hz
POINT        16384
FREQU       5000.0 Hz
FILTR         2500 Hz
SCANS            1
ACQTM        1.638 sec
PD           1.000 sec
PW1           13.5 us
ADBIT     16
IRNUC 1H
IRSET       112.00 kHz
IRFIN       5400.0 Hz
IRATN          120
IRRPW           40 us
TEMP.   27.0 c
SPEED           10 Hz
SLVNT CDCL3
EXREF         0.00 ppm
```

Figure 50. Proton NMR spectra of RF-2.



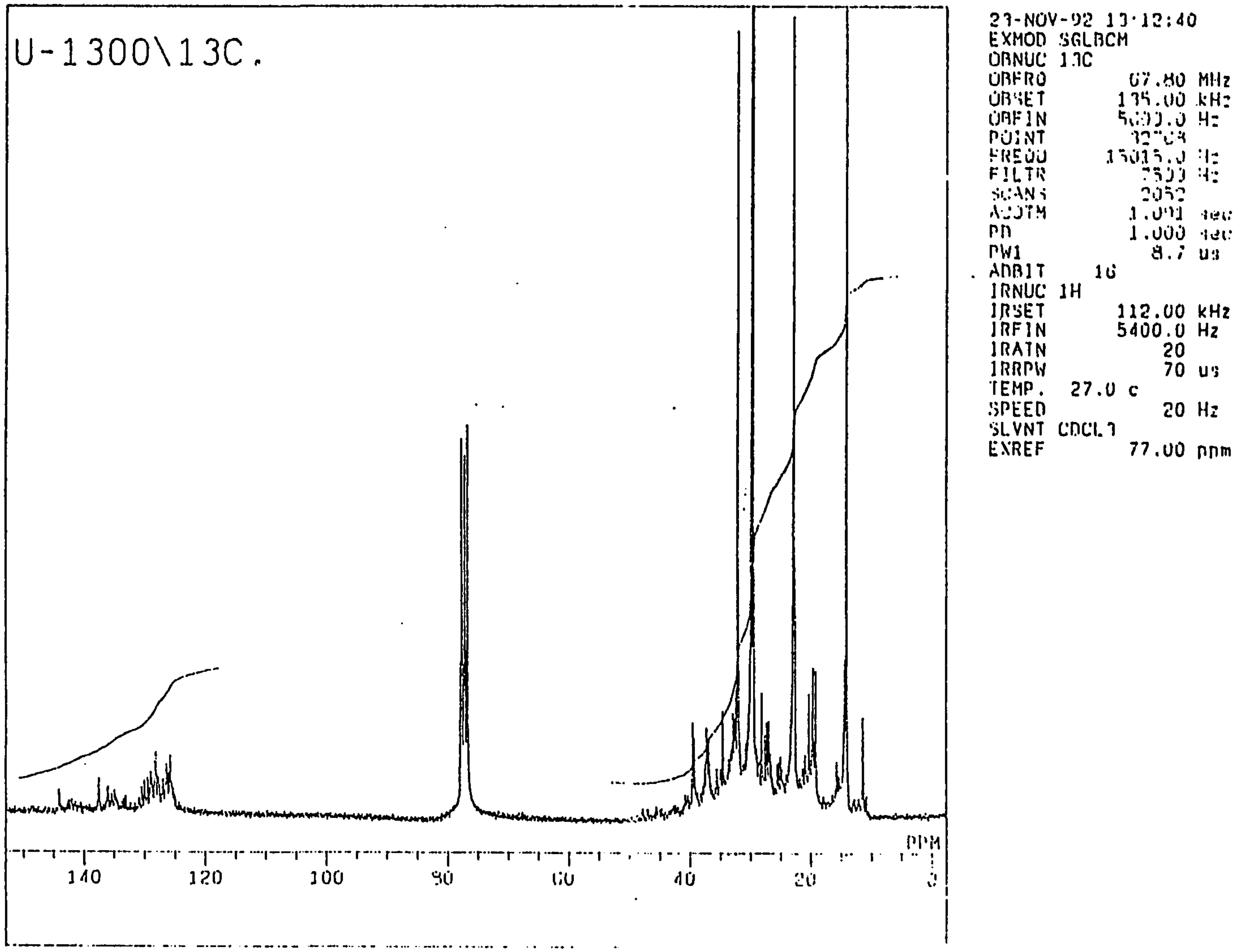
```
27-NOV-92 11:42:52
EXMOD [illegible]
OBNUC 13C
OBFRQ        67.80 MHz
OBSET       135.00 kHz
OBFIN       5600.0 Hz
POINT        32768
FREQU      15015.0 Hz
FILTR         7500 Hz
SCANS         1711
ACQTM        1.091 sec
PD           1.000 sec
PW1            8.7 us
ADBIT    16
IRNUC 1H
IRSET       112.00 kHz
IRFIN       5400.0 Hz
IRATN           20
IRRPW           40 us
TEMP.   27.0 c
SPEED           20 Hz
SLVNT CDCL3
EXREF        77.00 ppm
```

Figure 51. Carbon-13 NMR spectra of RF-2.



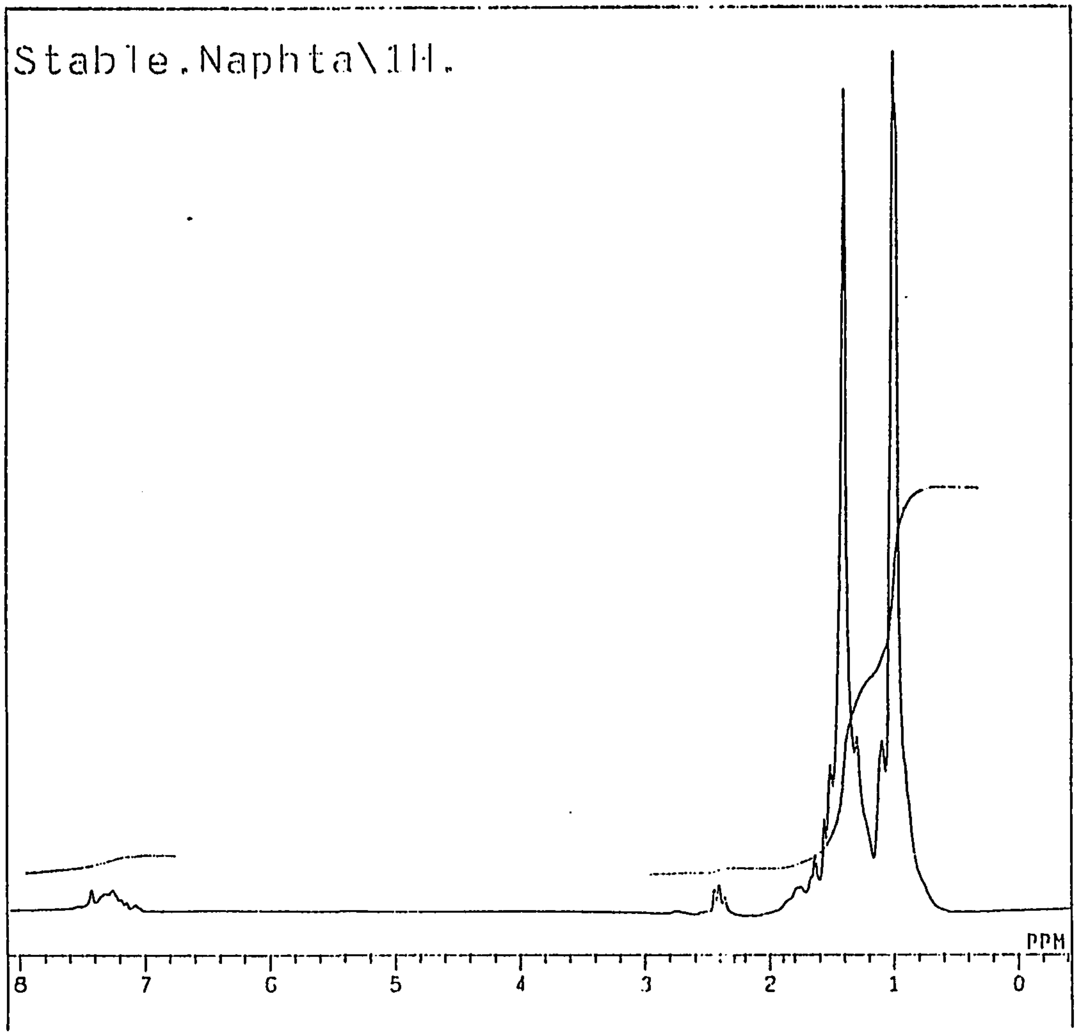
```
10-NOV-92 08:41:57
EXMOD SGNON
OBNUC 1H
OBFRQ        270.05 MHz
OBSET        112.00 kHz
OBFIN        5400.0 Hz
POINT         16384
FREQU        5000.0 Hz
FILTR          2500 Hz
SCANS             1
ACQTM         1.638 sec
PD            1.000 sec
PW1            13.5 us
ADBIT     16
IRNUC 1H
IRSET        112.00 kHz
IRFIN        5400.0 Hz
IRATN           120
IRRPW            40 us
TEMP.   27.0 c
SPEED            30 Hz
SLVNT CDCL3
EXREF          0.00 ppm
```

Figure 52. Proton NMR spectra of U-1300.



```
23-NOV-92 13:12:40
EXMOD SGLBCM
OBNUC 13C
OBFRQ       67.80 MHz
OBSET      135.00 kHz
OBFIN      5000.0 Hz
POINT       32768
FREQU     15015.0 Hz
FILTR        7500 Hz
SCANS        2052
ACQTM       1.091 sec
PD          1.000 sec
PW1           8.7 us
ADBIT     16
IRNUC 1H
IRSET      112.00 kHz
IRFIN      5400.0 Hz
IRATN          20
IRRPW          70 us
TEMP.   27.0 c
SPEED          20 Hz
SLVNT CDCL3
EXREF       77.00 ppm
```

Figure 53. Carbon-13 NMR spectra of U-1300.



```
30-NOV-92 08:21:11
EXMOD SGNON
OBNUC 1H
OBFRQ       270.05 MHz
OBSET       112.00 kHz
OBFIN       5400.0 Hz
POINT        16384
FREQU       5000.0 Hz
FILTR         2500 Hz
SCANS            1
ACQTM        1.638 sec
PD           1.000 sec
PW1           13.5 us
ADBIT    16
IRNUC 1H
IRSET       112.00 kHz
IRFIN       5400.0 Hz
IRATN          120
IRRPW           40 us
TEMP.  27.0 c
SPEED           10 Hz
SLVNT CDCL3
EXREF         0.00 ppm
```

Figure 54. Proton NMR spectra of U-1100.

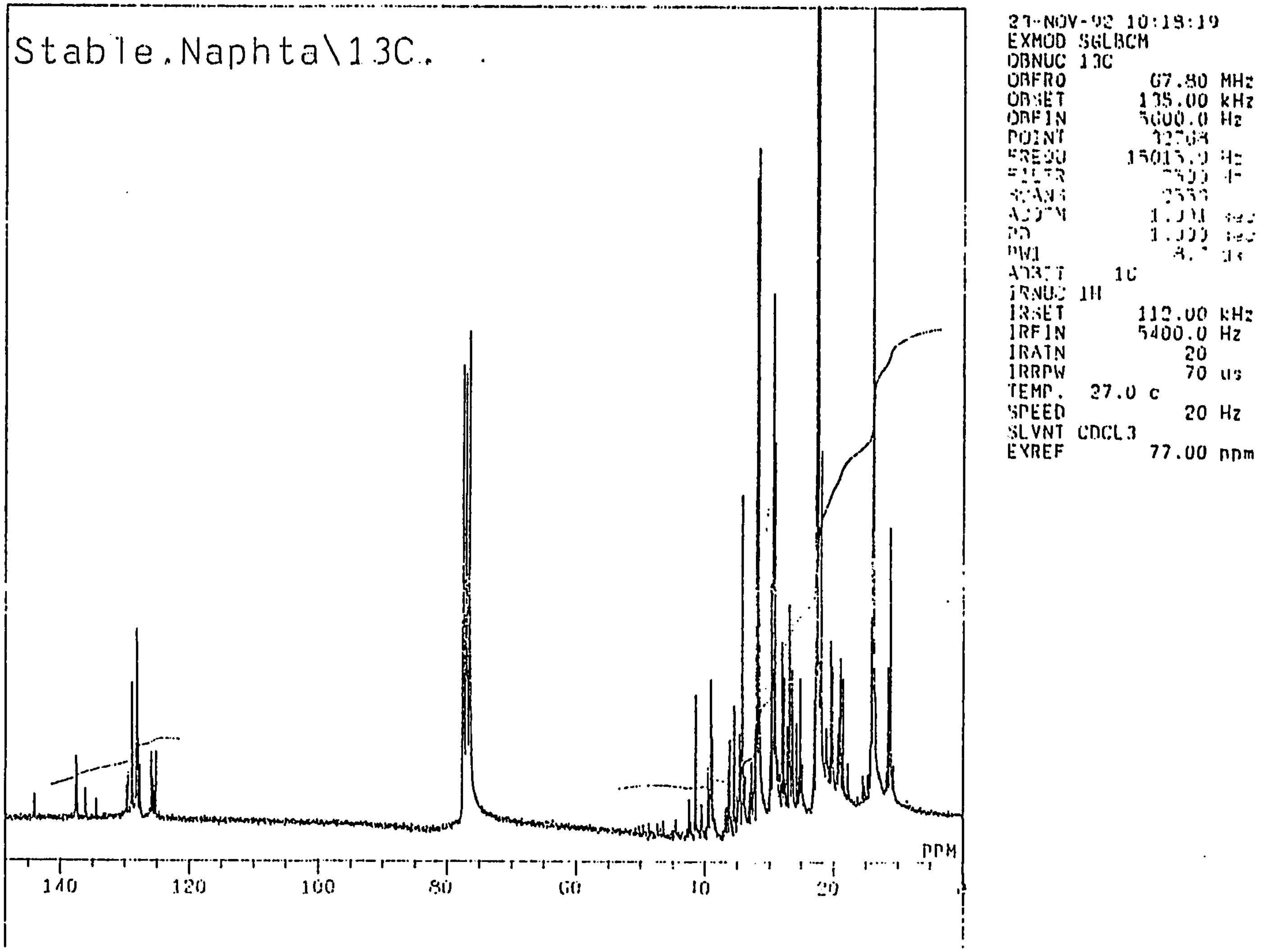


Figure 55. Carbon-13 NMR spectra of U-1100.

APPENDIX

COMPUTER PROGRAM TO DETERMINE AVERAGE MOLECULAR STRUCTURE PARAMETERS FOR HYDROCARBON MIXTURES

```
C***********************************************************           HNM00010
C    PROGRAM TO DETERMINE AVERAGE MOLECULAR PARAMETERS USING   *        HNM00020
C    JUST PROTON NMR DATA, CARBON 13 DATA AND CHEMICAL         *        HNM00030
C    ANALYSIS OF CARBON AND HYDROGEN WEIGHT FRACTIONS.         *        HNM00040
C***********************************************************           HNM00050
C                                                              *        HNM00060
C    SUBROUTINES, FILES AND FUNCTION USED                      *        HNM00070
C                                                              *        HNM00080
C***********************************************************           HNM00090
C                                                              *        HNM00100
C    * FUNCTION DVZERO                                         *        HNM00110
C           THIS FUNCTION CHECKS FOR ZERO VALUES WHICH WILL    *        HNM00120
C           RESULT IN DIVISION BY ZERO THUS TERMINATING THE    *        HNM00130
C           PROGRAM RUN.                                       *        HNM00140
C                                                              *        HNM00150
C    * THE DATA ENTERED IN THE FOLLOWING ORDERS                *        HNM00160
C          A. PERSON OR GROUP WHO SUBMITTED THE WORK           *        HNM00170
C          B. COMPUTATION DATE                                 *        HNM00180
C          C. SERIES NAME                                      *        HNM00190
C          D. SERIES DISCRIPTION                               *        HNM00200
C          E. SPECTROSCOPIST                                   *        HNM00210
C          F. NUMBER OF SAMPLES                                *        HNM00220
C          G. DATA FOR SAMPLES IN FOLLOWING ORDER              *        HNM00230
C             1. SAMPLE NAME                                   *        HNM00240
C             2. H MONOAROMATIC                                *        HNM00250
C             3. H DIAROMATIC                                  *        HNM00260
C             4. H TRIAROMATIC                                 *        HNM00270
C             5. H OLEFINIC                                    *        HNM00280
C             6. H ALPHA 1                                     *        HNM00290
C             7. H ALPHA 2                                     *        HNM00300
C             8. H BETA N                                      *        HNM00310
C             9. H BETA                                        *        HNM00320
C            10. H GAMMA                                       *        HNM00330
C            11. 1.0 SINCE CARBON DATA IN TO BE ENTERED        *        HNM00340
C                ENTER C-13 DATA AS FOLLOWES                   *        HNM00350
C            12. CARBON SUBSTITUTED (0 IF UNKNOWN)             *        HNM00360
C            13. CARBON BRIDGED (0 IF UNKNOWN)                 *        HNM00370
C            13. CARBON UNSUBSTITUTED (0 IF UNKNOWN)           *        HNM00380
C            14. AROMATIC CARBON                               *        HNM00390
C            15. ALIPHATIC CARBON                              *        HNM00400
C            16. C1-METHYL CARBON PEAK(0 IF UNKNOWN)           *        HNM00410
C            17. C2-METHYLENE PEAK (0 IF UNKNOWN)              *        HNM00420
C            18. C3-METHYLENE PEAK (0 IF UNKNOWN)              *        HNM00430
C            19. C4-METHYLENE PEAK (0 IF UNKNOWN)              *        HNM00440
C            20. C5-METHYLENE PEAK (0 IF UNKNOWN OR CANNOT     *        HNM00450
C                      DISTINGUISH FROM C4-METHYLENE PEAK)     *        HNM00460
C            21. 1.0 SINCE CHEM. ANALYSIS DATA IS TO BE ENTERED*        HNM00470
C                ENTER CHEMICAL DATA AS FOLLOWES               *        HNM00480
C            22. CARBON WEIGHT FRACTION                        *        HNM00490
C            23. HYDROGEN WEIGHT FRACTION                      *        HNM00500
C            24. AVERAGE MOLECULAR WEIGHT                      *        HNM00510
C                                                              *        HNM00520
C***********************************************************           HNM00530
C    LIST OF MOLECULAR PARAMETERS USED IN THIS PROGRAM         *        HNM00540
C                                                              *        HNM00550
```

```
C          PARAMETER NAME                           SYMBOL          *          HNM00560
C                                                                   *          HNM00570
C       1. H MONOAROMATIC                           HMO             *          HNM00580
C       2. H DIAROMATIC                             HDI             *          HNM00590
C       3. H TRIAROMATIC                            HTRI            *          HNM00600
C       4. H OLEFINIC                               HOL             *          HNM00610
C       5. H ALIPHATIC 1                            HALP1           *          HNM00620
C       6. H ALIPHATIC 2                            HALP2           *          HNM00630
C       7. H BETA                                   HBETA           *          HNM00640
C       8. H BETA NAPHTHENE                         HBETN           *          HNM00650
C       9. H GAMMA                                  HGAMA           *          HNM00660
C      10. H AROMATIC                               HAR             *          HNM00670
C      11. H OLEFINIC                               HOL             *          HNM00680
C      12. H ALIPHATIC TOTAL                        HAL-T           *          HNM00690
C      13. H BETA-GAMMA                             HBET-GAM        *          HNM00700
C      14. ENTRY C-13 DATA                                          *          HNM00710
C              (1.0 = YES, 0.0 = NO)                C13 ENTER       *          HNM00720
C      15. CARBON SUBSTITUTED                       CS              *          HNM00730
C      16. CARBON BRIDGED                           CB              *          HNM00740
C      17. CARBON UNSUBSTITUTED                     CU              *          HNM00750
C      18. C AROMATIC                               CAR             *          HNM00760
C      19. C ALIPHATIC                              CAL             *          HNM00770
C      20. C ALKANE 1                               C1              *          HNM00780
C      21. C ALKANE 2                               C2              *          HNM00790
C      22. C ALKANE 3                               C3              *          HNM00800
C      23. C ALKANE 4                               C4              *          HNM00810
C      24. C ALKANE 5                               C5              *          HNM00820
C      25. ENTRY OF CHEMICAL ANALYSIS                               *          HNM00830
C            DATA (1.0 = YES, 0.0 = NO)             CHEM ENTER      *          HNM00840
C      26. HYDROGEN WEIGHT FRACTION                 HYDROGEN        *          HNM00850
C      27. CARBON WEIGHT FRACTION                   CARBON          *          HNM00860
C      28. AVERAGE MOLECULAR WEIGHT                 MW              *          HNM00870
C      29. FRACTION OF AROMATIC HYDROGEN            FA SUP H        *          HNM00880
C      30. FRACTION OF AROMATIC                                     *          HNM00890
C                  THAT IS MONOAROMATIC             FMO             *          HNM00900
C      31. FRACTION OF AROMATIC                                     *          HNM00910
C                  THAT IS DIAROMATIC               FDI             *          HNM00920
C      32. NUMBER OF ALKYL SUBSTITUENT                              *          HNM00930
C                  PER MOLECULE                     RS              *          HNM00940
C      33. PERCENT OF AROMATIC IN MIXTURE           % AR            *          HNM00950
C      34. PERCENT OF MONOAROMATIC IN MIXTURE       % MOAR          *          HNM00960
C      35. PERCENT OF DIAROMATIC IN MIXTURE         % DIAR          *          HNM00970
C      36. PERCENT OF OLEFINIC IN THE MIXTURE       % OL            *          HNM00980
C      37. PERCENT OF PARAFFINIC MATERIAL                           *          HNM00990
C                  IN THE MIXTURE                   % PAR           *          HNM01000
C      38. NUMBER OF METYLENE TO                                    *          HNM01010
C                 NUMBER OF METHYL                  R SUPER H       *          HNM01020
C      39. TOTAL HYDROGEN TO CARBON IN MIXTURE      (H/C)T          *          HNM01030
C      40. AROMATIC HYDROGEN CARBON RATIO           (H/C)AR         *          HNM01040
C      41. PARAFFINIC HYDROGEN CARBON RATIO         (H/C)PAR        *          HNM01050
C      42. FRACTION OF SUBSTITUTED AROMATIC         F S+B SUPC      *          HNM01060
C      43. FRACTION OF UNSUBSTITUTED AROMATIC       F U SUP C       *          HNM01070
C      44. FRACTION OF AROMATIC CARBONS             F A SUP C       *          HNM01080
C      45. CARBON CHAIN LENGTH                      CL              *          HNM01090
C      46. FRACTION OF NORMAL ALKANE                F N SUP C       *          HNM01100
```

```
C      47. FRACTION OF BRANCHED ALKANE          F B SUP C        *
C                                                                *
C*****************************************************************
      DIMENSION P(35,100),Q(47,100),
     1     HOL(100),CS(100),CU(100),CB(100),PEROL(100),MW(100),
     2     CARB(100),CHEM(100),DA(16)
      REAL HAR,HAL,HB,TS,RS,FMONO,AINT,TEST,COR,T,B,WRC,TOTL,
     1 IDUM,PEROL, P, Q,HOL,CS,CB,CU,MW,CHEM,CARB
      INTEGER J,N,I,DVZERO,I1,K
      CHARACTER*25 A,F
      CHARACTER*15 C,D,E*40
      CHARACTER*10 ID(100),LBL(47),LBLA(47),LBLB(47)
C*****************************************************************
C              INPUT OF SAMPLE INFORMATION                       *
C*****************************************************************
      DO 47 I=1,47
 47   READ(15,*)LBL(I)
 1000 READ(15,*) A
      READ(15,*) C
      READ(15,*) D
      READ(15,*) E
      READ(15,*) F
      READ(15,*) N
      DO 1040 J=1,N
 1015 READ(15,*) ID(J)
C*****************************************************************
C            INPUT OF PROTON NMR DATA                            *
C*****************************************************************
 1001 READ(15,*) P(1,J)
 1002 READ(15,*) P(2,J)
 1003 READ(15,*) P(3,J)
      TOTL=P(1,J)+P(2,J)+P(3,J)
      READ(15,*) HOL(J)
 1004 READ(15,*) P(4,J)
      TOTL=TOTL+P(4,J)
 1005 READ(15,*) P(5,J)
      TOTL=TOTL+P(5,J)
 1007 READ(15,*) P(7,J)
      TOTL=TOTL+P(7,J)
 1006 READ(15,*) P(6,J)
 1008 READ(15,*) P(8,J)
      IF (DVZERO(P(8,J),ID(J),6) .EQ. 0) GOTO 1090
C*****************************************************************
C          INPUT OF CARBON 13 NMR DATA                           *
C*****************************************************************
      TOTL=0
      READ(15,*) CARB(J)
      READ(15,*) CS(J)
      READ(15,*) CB(J)
      READ(15,*) CU(J)
 1011 READ(15,*) P(9,J)
      TOTL=P(9,J)
 1012 READ(15,*) P(10,J)
      IF (DVZERO(P(10,J),ID(J),6) .EQ. 0) GOTO 1090
 1016 READ(15,*) P(11,J)
```

```
      IF (DVZERO(P(11,J),ID(J),6) .EQ. 0) GOTO 1090
      READ(15,*) P(12,J)
      READ(15,*) P(13,J)
      READ(15,*) P(14,J)
      READ(15,*) P(15,J)
C***************************************************************
C        INPUT CHEMICAL ANALYSIS DATA                          *
C***************************************************************
      READ(15,*) CHEM(J)
      TOTL=P(11,J)+P(12,J)+P(13,J)+P(14,J)+P(15,J)
 1017 READ(15,*) P(17,J)
 1018 READ(15,*) P(16,J)
      READ(15,*) MW(J)
      IF (DVZERO(P(17,J),ID(J),6) .EQ. 0) GOTO 1090
C***************************************************************
C       CALCULATION OF PARAMETERS                              *
C***************************************************************
 1019 HAR=P(1,J)+P(2,J)+P(3,J)
      IF (DVZERO(HAR,ID(J),6) .EQ. 0) GOTO 1001
      HAL=P(4,J)+P(5,J)
      IF (DVZERO(HAL,ID(J),6) .EQ. 0) GOTO 1001
      HB=P(6,J)+P(7,J)+P(8,J)
C***************************************************************
C       CALCULATION OF % MONO AND DIAROMATIC MOLECULES         *
C***************************************************************
      TS=0
      RS=0
      DO 1025 IN=1,10
      FMONO=P(1,J)/(P(1,J)+P(2,J)*(6.0-RS)/(8.0-RS))
      AINT=(8.0-2.0*FMONO)/(P(1,J)+P(2,J)+P(4,J)/2.0+P(5,J)/3.0)
      RS=AINT*(P(4,J)/2.0+P(5,J)/3.0)
      TEST= ABS(RS-TS)
      IF (TEST-0.005) 1030,1020,1020
 1020 TS=RS
 1025 CONTINUE
      WRITE (10,260)
      GOTO 1015
 1030 CONTINUE
C***************************************************************
C                  CALCULATION OF ALL PARAMETERS               *
C***************************************************************
      P(19,J)=FMONO
      P(20,J)=1.0-FMONO
      P(18,J)= HAR
      P(21,J)= RS
      COR=(6.0-RS)/(8.0-RS)
      T=COR*P(2,J)+P(1,J)+1.0/2.0*P(4,J)+1.0/3.0*P(5,J)
      TEMP=1.0/3.0*P(8,J)+HOL(J)
      B=T+1.0/2.0*(P(6,J)-1.5*P(4,J))+1.0/2.0*P(7,J)+TEMP
      P(22,J)=(T/B)*100.0
      P(23,J)=P(22,J)*P(19,J)
      P(24,J)=P(22,J)*P(20,J)
      PEROL(J)=100.0*(HOL(J)/B)
      P(25,J)= 100.0-P(22,J)-PEROL(J)
      P(26,J)=3.0*(P(6,J)-1.5*P(4,J))/(2.0*P(8,J))
```

```
      WRC= 12.01/1.008                                                  HNM02210
      P(27,J)=WRC*(P(16,J)/P(17,J))                                     HNM02220
      P(32,J)=P(9,J)/(P(9,J)+P(10,J))                                   HNM02230
      P(33,J)=2.0*(P(14,J)+P(15,J))/P(11,J)+6.0                         HNM02240
      P(34,J)=(P(11,J)+P(12,J)+P(13,J)+P(14,J)+P(15,J))/P(10,J)         HNM02250
      P(35,J)=1.0-P(34,J)                                               HNM02260
      P(28,J)=WRC*(P(16,J)*P(18,J))/P(17,J)*P(32,J)                     HNM02270
      P(29,J)=WRC*(P(16,J)*(1.0-P(18,J)))/(P(17,J)*(1.0-P(32,J)))       HNM02280
      P(31,J)=WRC*P(16,J)*P(18,J)/P(17,J)                               HNM02290
 1040 P(30,J)=P(32,J)-P(31,J)                                           HNM02300
C***********************************************************************HNM02310
C                     PRINT ROUTINE FOR OUTPUT                         *HNM02320
C***********************************************************************HNM02330
      DO 1050 J=1,N                                                     HNM02340
      Q(1,J)=P(1,J)                                                     HNM02350
      Q(2,J)=P(2,J)                                                     HNM02360
      Q(3,J)=P(3,J)                                                     HNM02370
      Q(4,J)=HOL(J)                                                     HNM02380
      Q(5,J)=P(4,J)                                                     HNM02390
      Q(6,J)=P(5,J)                                                     HNM02400
      Q(6,J)=P(5,J)                                                     HNM02410
      Q(8,J)=P(6,J)                                                     HNM02420
      Q(7,J)=P(7,J)                                                     HNM02430
      Q(9,J)=P(8,J)                                                     HNM02440
      Q(10,J)=Q(1,J)+Q(2,J)+Q(3,J)                                      HNM02450
      Q(11,J)=Q(4,J)                                                    HNM02460
      Q(12,J)=Q(5,J)+Q(6,J)                                             HNM02470
      Q(13,J)=Q(7,J)+Q(8,J)+Q(9,J)                                      HNM02480
      Q(14,J)=CARB(J)                                                   HNM02490
      Q(15,J)=CS(J)                                                     HNM02500
      Q(16,J)=CB(J)                                                     HNM02510
      Q(17,J)=CU(J)                                                     HNM02520
      DO 1041 I=18,24                                                   HNM02530
      I1=I-9                                                            HNM02540
      Q(I,J)=P(I1,J)                                                    HNM02550
 1041 CONTINUE                                                          HNM02560
      Q(25,J)=CHEM(J)                                                   HNM02570
      Q(26,J)=P(17,J)                                                   HNM02580
      Q(27,J)=P(16,J)                                                   HNM02590
      Q(28,J)=MW(J)                                                     HNM02600
      DO 1042 I=29,35                                                   HNM02610
      I1=I-11                                                           HNM02620
      Q(I,J)=P(I1,J)                                                    HNM02630
 1042 CONTINUE                                                          HNM02640
      Q(36,J)=PEROL(J)                                                  HNM02650
      DO 1043 I=37,47                                                   HNM02660
      I1=I-12                                                           HNM02670
      Q(I,J)=P(I1,J)                                                    HNM02680
 1043 CONTINUE                                                          HNM02690
 1050 CONTINUE                                                          HNM02700
      CALL MYLABEL (LBL,LBLA,LBLB,47)                                   HNM02710
      WRITE (10,180)                                                    HNM02720
      WRITE (10,190) D,N                                                HNM02730
      WRITE (10,200) A                                                  HNM02740
      WRITE (10,210) E                                                  HNM02750
```

```
      WRITE (10,220) C                                                  HNM02760
      WRITE (10,230) F                                                  HNM02770
      WRITE (10,240)                                                    HNM02780
      DO 1089 I1=1,N,5                                                  HNM02790
      K=I1+4                                                            HNM02800
      WRITE (10,245)                                                    HNM02810
      WRITE (10,110) (ID(J),J=I1,K)                                     HNM02820
      DO 1060 I=1,28                                                    HNM02830
      WRITE (10,120)LBL(I),(Q(I,J),J=I1,K)                              HNM02840
 1060 CONTINUE                                                          HNM02850
      WRITE (10,130)                                                    HNM02860
      DO 1070 I= 29,38                                                  HNM02870
      WRITE (10,120)LBL(I),(Q(I,J),J=I1,K)                              HNM02880
 1070 CONTINUE                                                          HNM02890
      WRITE (10,250)                                                    HNM02900
      DO 1080 I=39,47                                                   HNM02910
      WRITE (10,120)LBL(I),(Q(I,J),J=I1,K)                              HNM02920
 1080 CONTINUE                                                          HNM02930
 1089 CONTINUE                                                          HNM02940
C*****************************************************************      HNM02950
C                         FORMATS                                *      HNM02960
C*****************************************************************      HNM02970
  260 FORMAT('ITERATION FOR FRACTION OF HMONO DID NOT CONVERGE          HNM02980
     1IN',/,'TEN PASSES','ENTER DATA AGAIN')                            HNM02990
  110 FORMAT (1X,'**********',5(2X,A10),/)                              HNM03000
  120 FORMAT (1X,A10,2X,F8.4,4(4X,F8.4))                                HNM03010
  130 FORMAT (/,17X,'PARAMETERS CALCULATED FROM PROTON NMR',/)          HNM03020
  180 FORMAT (///,12X,'KING FAHAD UNIVERSITY OF PETROLEUM & MINERALS    HNM03030
     1',/,26X,'OIL TESTING CENTRE',                                     HNM03040
     2/,25X,'SPECTROSCOPY SECTION',/,                                   HNM03050
     3/,13X,'AVERAGE MOLECULAR STRUCTURE PARAMETERS OBTAINED',/,        HNM03060
     418X,'FROM NUCLEAR MAGNETIC RESONANCE TO',/,18X,                   HNM03070
     5'CHARACTERIZE HYDROCARBON MIXTURE',//)                            HNM03080
  190 FORMAT (5X,'SERIES NAME :',A20,5X,'NUMBER OF SAMPLES',            HNM03090
     1':',I3,/)                                                         HNM03100
  200 FORMAT (5X,'RECEIVED BY : ',2A15,/)                               HNM03110
  210 FORMAT (5X,'SERIES DISCRIPTION : ',5A10,/)                        HNM03120
  220 FORMAT (5X,'DATE OF COMPUTATION : ',A10,/)                        HNM03130
  230 FORMAT (5X,'SPECTROSCOPIST :',2A10,/)                             HNM03140
  240 FORMAT (/,72('*'),/,25X,'REPORT OF ANALYSIS',/,72('*'))           HNM03150
  245 FORMAT (//,26X,'MEASURED PARAMETERS',///,1X,'PARAMETER\',25X,     HNM03160
     1'SAMPLE NAME')                                                    HNM03170
  250 FORMAT (/,9X,'PARAMETERS CALCULATED FROM H,C NMR AND ELEMENTAL',  HNM03180
     1'ANALYSIS',/)                                                     HNM03190
 1090 STOP                                                              HNM03200
      END                                                               HNM03210
C ****************************************************************      HNM03220
C           SUBROUTINE TO PROVIDE DATA LABELS                    *      HNM03230
C ****************************************************************      HNM03240
      SUBROUTINE MYLABEL (LBL1,LBL2,LBL3,N)                             HNM03250
      INTEGER N                                                         HNM03260
      CHARACTER*15 LBL1(N),LBL2(N),LBL3(N)                              HNM03270
      DO 20 I=1,N                                                       HNM03280
 20   CONTINUE                                                          HNM03290
      RETURN                                                            HNM03300
```

```
      END                                                               HNM03310
C *****************************************************************     HNM03320
              FUNCTION DVZERO(VAL,NAME,O)                               HNM03330
C *****************************************************************     HNM03340
      REAL VAL                                                          HNM03350
      INTEGER O                                                         HNM03360
      DVZERO=1                                                          HNM03370
      IF (VAL.NE.O) RETURN                                              HNM03380
      WRITE (10,10) NAME                                                HNM03390
 10   FORMAT ('THE PARAMETERS ENTERED FOR SAMPLE',A10,'WILL',           HNM03400
     1 'ABORT',/,'THE PROGRAM SINCE IT RESULTS IN DIVISION',            HNM03410
     2 'BY ZERO!!!',/,'CHECK DATA IN NMR!!!!')                          HNM03420
       DVZERO=0                                                         HNM03430
       RETURN                                                           HNM03440
       END                                                              HNM03450
```

DATA LABELS

'HMO'
'HDI'
'HTRI'
'HOL'
'HALP1'
'HALP2'
'HBETN'
'HBETA'
'HGAMA'
'HAR'
'HOL'
'HAL-T'
'HBET-GAM'
'C 13 ENTER'
'CS'
'CB'
'CU'
'CAR'
'CAL'
'C1'
'C2'
'C3'
'C4'
'C5'
'CHEM ENTER'
'CARBON'
'HYDROGEN'
'MW'
'FA SUP H'
'FMO'
'FDI'
'RS'
'% AR'
'% MOAR'
'% DIAR'
'% OL'
'% PAR'
'R SUPER H'
'(H/C)T'
'(H/C)AR'
'(H/C)PAR'
'F S+B SUPC'
'F U SUP C'
'F A SUP C'
'CL'
'F N SUP C'
'F B SUP C'

'RAS & RDH REFIN'

'93/01/15'

'FUEL SAMPLES'

'HYD. MIXTURE'

'NIZAMI'

5

'PLT-71 KD'	'TK-258LSRN'	'TK-242HCN'	'RF - 1'	'RF - 2'
3.2895	0.0	6.1224	3.3088	5.5555
4.6053	10.0	8.1633	8.4559	10.185
0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0
0.6237	0.0	0.5258	0.9120	0.5814
0.1559	0.1020	0.1840	0.5901	0.6871
0.4158	0.2555	0.8412	1.3948	1.5328
6.3150	5.2041	11.409	8.3154	11.258
0.2339	4.4388	1.2092	0.5365	1.5328
1.0	1.0	1.0	1.0	1.0
0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0
5.1282	6.0	7.0370	16.275	10.0
5.0976	5.9874	7.0520	16.418	10.0
0.1084	0.8205	0.6589	0.1148	0.8695
0.3254	0.1026	0.6936	0.0574	0.0924
0.0542	0.3077	0.4046	0.1148	0.4348
0.4067	0.2051	0.7746	1.3203	0.7609
0.0	0.0	0.0	0.0	0.0
1.0	1.0	1.0	1.0	1.0
84.6	83.5	86.2	85.3	84.4
14.3	16.4	14.8	13.7	14.4
209.6	0.0	0.0	209.2	0.0

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