INVESTIGATION AND CHARACTERIZATION OF INTERFERING PYROLYSIS PRODUCTS OF WOOD DEBRIS IN FIRE ARSON ANALYSIS

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DECLARATION

This thesis is my original work and has not been submitted for research leading to award of a degree at any university.

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DEDICATION

This work is dedicated to the Almighty God and my entire family for the support throughout this study. May God bless you.

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ABSTRACT

Laboratory identification of flammable products in fire debris is vital in crime scene investigations. Debris collected from a fire scene is intricate and contains background compounds from the substrate material and pyrolysis products that arise from combustion and pyrolysis of the material produced in the fire. Effective isolation of the target compounds from the pyrolysis products is one of the main problems encountered by forensic scientists in any fire arson analysis. This study focused on interference caused by pyrolysis products of wood debris. The main objective was to investigate and characterize selected pyrolysis products of wood debris in fire arson analysis. Mahogany, Medium Density Fiberboard, chipboard and block board were pyrolyzed using a muffle furnace at a controlled temperature of 350 °C and 450 °C for thirty minutes. The sample analysis was done in triplicates to establish reproducibility. The interfering pyrolysis products obtained ranged from straight chained aliphatic hydrocarbons to highly fused aromatic hydrocarbons. These hydrocarbons were found to elute at retention times similar to certain specific target compounds of gasoline and diesel. However pyrolysis products of chipboard showed very little interference with Ignitable Liquid residues (ILR) of diesel and gasoline. Chromatographic analysis based on retention time of the compounds eluted revealed possible conflicts between some of the pyrolysis compounds and the target ILR compounds of gasoline and diesel. Some of the compounds in diesel, for example 17-pentatriacontene, were found to be present in the pyrolysis compounds. The % abundance of these pyrolysis products in the samples were determined and compared with the % abundance of the target compounds in gasoline and diesel. The % abundance of the pyrolysis products were higher than the target compounds of gasoline and diesel hence possible shielding of the target compounds during analysis. The presence of pyrolysis products makes it difficult to elucidate and analyze the chromatograms effectively hence may lead to false positive interpretations. On the other hand, a false negative conclusion may be reached if the pyrolysis compounds are not known hence disregarding compounds originating from ILR. Therefore Creation of databases of pyrolysis products and ILR are important. Further studies are recommended on clean wood samples to set a database of their pyrolysis and interfering products.

Keywords: Pyrolysis, fire, debris

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LIST OF ABBREVIATIONS

ASTM- American Society for Testing and Materials

CO- Carbon Monoxide

CO_2- Carbon dioxide

DCM- Dichloromethane

FID- Flame Ionization Detector

GC- Gas Chromatography

H_2O-Water

ILR- Ignitable Liquid Residues

MDF- Medium Density Fiberboard

M/z ratio- mass to charge ratio

MS- Mass Spectrometer

MSD- Mass Selective Detector

NIST- National Institute of Standards and Technology

NFPA- National Fire Protection Association

RtS - Retention Time of Standard Accelerant Mixture compounds

RtM - Retention Time of Mahogany Compounds

RtD -Retention Time of Medium Density Fiberboard compounds

RtB-Retention time of Block board Compounds

SAM- Standard Accelerant Mixture

TCC-Target Compound Chromatogram

USA- United States of America

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Arson is the willful and malicious damage to property (De Vos, 2005). The circumstances for arson fires are as varied as the behavior of the fire characteristics, method of ignition and the motivation for the fire setters. Crimes of arson have proved to be of great challenge to law enforcement agencies and insurance companies. A report by United States Fire Administration (Almirall and Furton, 2004), indicates an estimated 15 deaths per million populations caused by fire alone. This is one of the highest in the industrialized world. In Kenya, arson has been one of the common human disasters on the rise in the recent years. In 2004, fire at City Hall Nairobi destroyed an entire floor where valuable documents were kept and property estimated to be worth KShs 70 million was destroyed (Mutugi and Maingi, 2011). Learning institutions have not been spared. During the 2013 academic year, at least thirty four separate cases of arson were reported in secondary schools. In 2012 a comparable amount of cases in high schools were reported by the Kenyan media (Cooper, 2014). The administration block at Milo mixed secondary school in Bungoma East district was burnt by rioting students in collaboration with support staff (Nang'unda, 2013). Disasters at Bombolulu Girls Secondary School in 1998 and, Kyanguli Boys high School in 2001 caused deaths of twenty five and sixty eight students respectively, loss of property and psychological impact on the education sector (Nang'unda, 2013). Institutions of higher learning have also fallen victim to reported cases of arson during student demonstration. Figure 1.1 below shows a student hostel set on fire during recent student unrest after a disputed students' election at the University of Nairobi.

Figure 1.1: Student hostel on fire (Daily Nation, 11th May 2016)

Several works in psychology and clinical psychiatry have attempted to explain the various theories that account for peculiar and illogical acts of arson. Horbey and Bowlby (2011) concluded that there is no general acceptable theory on psychopathological fire setting. However, many arsonists are a product of a broken social environment with criminal and antisocial tendencies (Horbey and Bowlby, 2011). Canter and Fritzon (1998) hypothesized that there is behavioral consistencies in the actions of arsonists when committing a crime that characterize them. Cooper (2014) in her analysis of Kenyan cases of arson in secondary schools considers these actions as related to historical and contemporary trends of protests and rebellion among Kenyan citizens as a way of expression of dissatisfaction and displeasure to authority.

State police divisions that specialize in scientific investigations are mainly founded with a sole purpose of obtaining concrete scientific evidence to deal with crime of arson (Pommier and Donichak, 2004). An investigation process puts into consideration the potential seats of fire which in turn gives more information on the origin points of fire and also the burning dynamics within the burnt structure (Harrison, 2012). Laboratory identification of flammable products in fire debris sampled on crime scene is vital in crime scene investigations. There are various types of fuel accelerants used by arsonists. The most common type of accelerants used is petroleum based since it is readily available. They are summarized in Table 1.1 below:

Table 1.1: Types of Petroleum based accelerants

CLASS NO:	CLASS NAME	PEAK SPREAD	EXAMPLES
1	Light Petroleum distillate	C4-C11	Ethers, rubber cement solvent, Naphtha
2	Gasoline	C4-C12	All brands and grades of Gasoline and gasohol
3	Medium petroleum distillate	C8-C12	Mineral Spirit, paint thinners, dry cleaning solvents, polishes, some lamp oils
4	kerosene	C9-C17	Jet-A fuel, insect sprays
5	heavy petroleum distillate	C9-C23	diesel, Number 2 fuel oils

Most of the accelerants named above are highly volatile and in many cases lead to explosion. A case report by Heath *et al.*, (2011) illustrates a scenario whereby the arsonist becomes a victim of explosion just after fire setting. In 2008, a tanker ferrying gasoline exploded after getting involved in an accident near Sacchangwan area of Rift valley province in Kenya (Mutugi and Maingi, 2011).

Reliable and concrete evidence report is an important requirement for a just prosecution in arson court cases. De Vos (2005) compares the proof of crime of arson to a homicide investigation where the victim’s body has turned to dust and although the proof of crime is still present, methodical analysis that is done with accuracy and precision is required to prove its existence.

The circumstances of arson fires are as varied as are the characteristics of fire behavior, method of ignition as well as the motivation of fire starters as they relate to the detection of arson (De Vos, 2005).

According to Almirall and Furton (2004), prosecution of crime involving arson faces difficulties due to insufficient physical proof that can be associated with the susupect. Moreover, the analysis of accelerants in fire debris samples is a complex process and sometimes problematic. Application of Gas Chromatography has been vital in identification of various accelerants in forensic science. However, Stauffer (2001) emphasizes that Gas Chromatography-Flame Ionization Detector (GC-FID) alone is not sufficient since sample identification is only based on retention time matching, which is not sufficient for confirmation of the presence of specific analytes. It is necessary to confirm identity of the compounds in order to obtain accurate results about the composition of the sample. Tan *et al.*, (2000) supports the use of Gas Chromatography-Mass Spectrometry (GC-MS) in the analysis and identification of accelerant residues in fire debris. Compound recognition depends on two types of pattern matching techniques namely:

1. Extracted ion profile matching whereby the intensity profiles for characteristic ions are visually matched and compared with known profiles of petroleum distillates (Tan *et al*., 2000).

2. Target compound analysis whereby retention time is used in designing the target compound chromatogram (TCC) which in turn is used for visual comparison of the TCC of a known accelerant (Tan *et al*., 2000).

Fire debris analysis is essential for the determination of potential ignitable liquid residues (ILR) in cases of suspected arson and the process is usually a two-step, which involves isolation and concentration followed by chromatographic separation and identification (Borusiewicz, 2002).

The presence of target compounds after characterization of the isolated compounds suggests the presence of ILR. Borusiewicz (2002), while discussing the factors influencing the possible detection of ILR traces, mentions that the type of burnt material influences the recovery of ILR during extraction process.

Schwartz *et al.* (2013) tested the hypothesis that compound specific isotope analysis can be used to predict and identify the accelerant from post-combustion residues. The study concluded that despite the fact that different types of ILR can be differentiated using the specific isotope analysis, this was not possible for the post-combustion residue. Therefore standard pattern recognition and chemometric techniques are considerably more reliable for pre- and post-combustion analysis on weathered ILR (Schwartz *et al.*, 2013).

Proper analysis requires understanding of the fundamental properties of the fuels involved in fire, which basically include density, thermal conductivity, heat capacity, ignitability and flame spread characteristics (Fernandes *et al.*, 2002).

Debris collected from a fire scene is intricate and it contains background and pyrolysis products that arise from the material during the burning process. Effective isolation of the target compounds from the pyrolysis compounds is one of the greatest challenges encountered by forensic chemists in any fire arson analysis (Almirall and Furton, 2004).

Despite the fact the procedures of extraction and chromatographic analysis of ILR are relatively simple; the interpretation of the results requires an advanced skill. According to Stauffer (2003) substrate background products are some of the major sources of interfering pyrolysis products, although there are many other multiple factors that influence formation of pyrolysis products.

Interferences are quite common in both qualitative and quantitative analyses. According to Alaska Scientific Crime Detection Laboratory (2011) fire debris manual, the two main factors that contribute to interference are:

1. Extraneous compounds that arise from the type of pyrolysis and combustion products of the substrate material formed during the fire.
2. Missing components that are as a result of exposure of the sample to heat. Lighter components are lost in the process resulting in enhanced chromatographic patterns at the heavy end. Unexplained missing components from the middle of the pattern are sufficient ground for negative conclusions.

This study focused on investigating the extraneous compounds formed during the pyrolysis of wood debris in an event of arson and comparing them with the target compounds of gasoline and diesel.

1.2 STATEMENT OF THE PROBLEM

An increase in the number of fire cases in the country is of great concern. The prosecution of suspected arsonists in arson cases requires concrete evidence that conclusively pinpoints that indeed the fire was not accidental but rather intentional (Stauffer, 2001). The greatest challenge for forensic scientists is to give an accurate result on a case involving arson. The presence of interfering pyrolysis products and other background interferences in fire debris samples makes it a complex process during analysis of data. Some of these pyrolysis products are present in most accelerants used in arson (Almirall and Furton, 2004). Without proper consideration of these interference compounds may lead to inconclusive data. This study seeks to solve this problem by investigating the presence of pyrolysis products from selected wood samples and identify the pyrolysis products using GC-MS. The common compounds both in the wood debris and the accelerants are identified and isolated. Ability to identify these compounds enables the analyst to differentiate the interfering compounds from the ILR.

1.3 OBJECTIVE

The main objective of this study was to investigate and identify selected pyrolysis products of wood debris in fire arson analysis.

1.3.1 Specific Objectives

1. To investigate and identify the pyrolysis products of selected charred wood samples of mahogany, Medium Density Fiberboard (MDF), chipboard and block board at constant pyrolysis temperatures of 450 ºC and 350 °C.
2. To compare the pyrolysis products from the above selected wood materials.
3. To compare the pyrolysis products of the wood samples and the target compounds in gasoline and diesel.

1.4 JUSTIFICATION AND SIGNIFICANCE OF THE STUDY

Just prosecution of suspected fire setters is important hence forensic analysis aims to conclusively establish the source of fire and hence assist the investigators in determining the intention of the arsonist. Insurance industry is one of the most affected since proper investigation has to be done and conclusively determine whether the cause of fire was either intentional or accidental before compensation. The nature of analysis for fire debris is complex because, in a case of fire, the evidence is destroyed with time (De Vos, 2005). Furthermore, the materials undergo further physical and chemical changes with the progression of fire (Borusiewicz, 2002).

Interference due to pyrolysis of the substrate material is an important factor to be considered in any fire debris analysis. This study was aimed to effectively isolate and identify the pyrolysis products of selected wood debris that would cause interference with the target compounds of gasoline and diesel.

Incorrect conclusion in forensic fire arson tests can lead to prosecution of innocent victims (Almirall and Furton, 2004). Reliable data from analytical tests can be obtained when pyrolysis compounds are identified and assist in giving positive results.

CHAPTER TWO

LITERATURE REVIEW

2.1 PYROLYSIS OF ORGANIC MATTER

Pyrolysis is basically thermal decomposition of organic matter under inert atmospheric conditions or in limited supply of air leading to release of volatile organic compounds and formation of char (Sinha *et al.*, 2006). Stauffer (2003) describes pyrolysis as chemical breakdown of a material into simple compounds using heat in limited supply of air. The rate of pyrolysis is proportional to the amount of heat energy transferred. If an oxidant is introduced then a flaming fire results. In a study conducted by Clodfelter and Hueske (1976) on reproducibility of pyrolysis products when different substrates are burned, a comparison of the resulting chromatograms revealed a similarity in patterns of the ILR and the pyrolysis products.

Li Ying-yu *et al.* (2013) investigated on the background interference products in carpets, using micro Solid Phase extraction technique and GC-MS in extraction and identification processes respectively, concluded that several compounds regularly encountered due to pyrolysis or combustion products, for example toluene and propyl benzene, were detected in fresh gasoline as well. Farnandes *et al.* (2002) while investigating on the effect of volatile residues on burnt household items in detection of fire accelerants, using passive headspace adsorption technique for extraction, concluded that the volatile residues obtained during burning of household items such as flooring finishes and adhesives could easily be mistaken for ILR.

A study by Almirall and Furton (2004) on the identification of background and pyrolysis compounds, after controlled burning of a wide variety of substrates normally found in homes and offices, concluded that many of the compounds frequently encountered as a result of either combustion or pyrolysis products are also target compounds for the ILR mixture.

Pyrolysis of wood usually begins at temperatures of about 200 ºC and lasts until 450 ºC-500 ºC, depending on the species of the wood (Sinha *et al.*, 2006). According to Deitenberger and White (2001) the process of wood pyrolysis can be divided into four temperature regimes, each with its own end products. These include;

1. 100 ºC to 200 ºC whereby the wood is dehydrated and generates mainly water vapor and other incombustible gases and liquids like CO_2 and acetic acid.

2. 200 ºC to 300 ºC whereby wood pyrolysis is significant such that large amounts of CO and tar are given off.

3. 300 ºC to 450 ºC there is significant depolymerization of cellulose, aliphatic side chains split from the aromatic rings in the lignin.
4. Above 450 ºC the remaining wood is char. It undergoes further degradation through oxidation to form H_2O, CO_2 and CO.

According to Sinha *et al.* (2006), pyrolysis of wood undergoes two processes namely;

1. Physical process whereby heat is transferred leading to a rise in temperature of the fuel. This initiates a series of pyrolysis reactions which leads to formation of volatile compounds and char. Condensation of some volatiles on the cooler parts of the fuel results in tar formation.

2. Chemical process which is largely affected by the chemical composition of the fuel. The pyrolysis products formed are as a result of independent reactions of each major constituent of wood namely cellulose, hemicellulose and lignin.

2.1.1 Cellulose

This is a glucon polymer consisting of linear chains of B (1, 4) d-glucopyranose units (Sinha *et al*., 2006). Shafizadeh (1982) studied the pyrolysis of cellulose with increase in temperature. He came to a conclusion that reduced degree of polymerization was observed for temperatures less than 300 °C At higher temperatures, tar, char and gaseous products were formed. Laevoglucosan was the major constituent of tar which vaporized and decomposed further at much higher temperatures.

2.1.2 Hemicellulose

Hemicellulose is polysaccharide made up of glucose, mannose, galactose, xylose, arabinose, 4-0 methylglucuronic acid and galacturonic acid residues. According to Soltes and Elder (1981), thermal stability of hemicellulose leads to decomposition at very low range of 200 °C to 260 °C and happens in two steps namely; breakdown of the polymer into monomer units that further breaks down into volatile products. The decomposition of Hemicellulose leads to formation of more volatiles; less tar and char which comprises of mostly acetic acid, formic acid and a few furfural derivatives (Sinha *et al*., 2006).

2.1.3 Lignin

Lignin is an irregularly arrayed polymer made of highly substituted phenyl propane units that can be processed to yield aromatics. A study by Soltes and Elder (1981) revealed that 55 % of the pyrolized lignin is made up of char while 20 % and 15 % consisted of aqueous portion and tar respectively. The aqueous portion composed of methanol, acetic acid, acetone and water while the homologous phenolic compounds were found in tar.

Schwartz *et al.* (2005) showed in their study of how the substrate porosity, accelerant volatility and temperature of materials during combustion were key factors in determining the volatile organic profiles of fire debris. Further study by William *et al.* (1990) concluded that the rate of pyrolysis process is majorly influenced by cations that are present in wood, such as potassium and calcium. Potassium is dominant in the catalysis of pyrolysis whereas calcium tends to stabilize the wood towards pyrolysis.

Pyrolysis is a complicated process and may lead to formation of complicated chromatographic patterns of different products. This is dependent on the substrate material and the physical conditions present during pyrolysis. These conditions include temperature, pressure, and presence of additional reactants. Furthermore, some substrates have multiple compounds, which undergo pyrolysis simultaneously (Stauffer, 2001). However, the pyrolysis of these composite materials can be considered as independent hence reducing the problem of establishing the pyrolysis products (Stauffer, 2001).

2.2 MODELS OF FIRE PROGRESSION

The core task for any fire investigator is to determine the origin and cause of the fire. For this reason fire pattern analysis is employed in order to establish the path, progression and spread characteristics of the fire from the origin (May, 2010). Harrison (2012) describes two models of fire progression in any archaeological structures. These two models include:

1. Directional fire indicators which encompass the point of lowest burn, ‘V’ pattern analysis and heat shadowing principles (Harrison, 2012). By locating positions of lowest burn in a structure it is possible to comment on the origin of fire or location of concentration of fuel within a compartment. On the other hand, ‘V’ pattern analysis is associated with the upward spread characteristic of convectional heat. Flaming combustion tends to expel smoke products upwards forming a plume. The smoke forms a ‘V’ shaped pattern whereby the base indicates the seat of fire. This pattern can establish locations of concentrations of fuel within a compartment. Heat shadowing which is a concept within this model involves assessment of areas of the structure that are protected from burning. These areas assist to dismiss areas of the compartment as potential seat of fire (Harrison, 2012).
2. Intensity related fire indicators which include, char depth analysis, plaster spall analysis and geomatic alteration (Harrison, 2012). Char depth analysis involves assessment of preserved charring which in turn assists in locating focal points of fire damage. Plaster spall analysis is focused on the degree of spalling and associated discoloration of the wall materials which are potential indicators of temperatures throughout the compartment. Geomatic alterations seek to correlate the heat related discoloration with the physic-chemical alterations to the soil structures (Harrison, 2012).

The models described above are based on protocols contained in National Fire Protection Association (NFPA) guide that were first published in 1992 which provided a scientific approach to forensic scientists in any arson analysis (May, 2010).

A study by Ogle and Schumacher (1998) on fire patterns that result on either smoldering or flaming combustion on upholstery furniture, observed that the smoldering fire patterns tended to have char zones with thickness similar to fuel element. On the other hand the flaming fire patterns had thin char zones with thicknesses smaller than the fuel element. Ogle and Schumacher (1998) concluded that, in order to determine the cause of a fire, the investigator needs to view other considerations like human and environmental factors other than fire pattern observations only.

On vehicles involved in arson, Icove *et al*. (2014) recommended quadrant method of analysis whereby the vehicle was subdivided into four quadrants which assisted the forensic analyst in determining the potential seats of fire and in the sampling process.

2.3 PRINCIPLES OF GC- MS ANALYSIS

Gas Chromatography is a separation technique that has been used since 1952. It has undergone impressive evolution such that it has become one of the most efficient and accurate separation methods used in chemistry (Stauffer, 2001). A study by Smith (1982) to identify the products of pyrolysis from burning carpet concluded that Mass Selective Detector (MSD) was superior to Flame Ionization Detector (FID) due to its ability to differentiate and identify compounds with similar retention times.

To accomplish complete separation in GC, the sample must be converted to gaseous phase. For liquid samples, conversion to vapor phase occurs at the injector port. The eluent is an inert carrier gas that can either be hydrogen, nitrogen or helium. Separation occurs as the vapor constituents equilibrate between the carrier gas and the solid stationary phase (Dass, 2007).

The sample is detected as it emerges from the column producing a gas chromatogram. The retention times and intensities of the detector response are displayed. Quantitative analysis is possible since the peak area is proportional to the concentration of the sample (Dass, 2007).

The MS is interfaced directly from a GC so that analytes can be further analyzed after separation. It basically deals with ions of a substance. The basic steps in MS analysis include:

I. Ionization process which converts the molecules or atoms into gas phase ionic species. This takes place by either addition or removal of an electron or a proton (Dass, 2007). The excess energy generated during this process may break the molecule into unique characteristic fragments (Dass, 2007).
II. Separation and mass analysis of molecular ions and their charged fragments on the basis of their mass-to-charge (m/z) ratios (Dass, 2007).
III. The ion current due to these mass separated ions is measured, amplified and displayed in the form of mass spectrum (Dass, 2007).

The first two steps mentioned above are carried out in a vacuum mainly to reduce collisions between ions and other compounds present which may lead to further fragmentations, producing different species through ion-molecular reactions. This reduces sensitivity and resolution (Dominic and Nico, 2007).

Nichols *et al.* (2013) emphasized the fact that Gas chromatography remains to be the suitable method for fire debris analysis since the nature of the ILR are said to be multicomponent and moderately volatile fluids.

CHAPTER THREE

MATERIALS AND METHODS

The procedure for extractions and interpretation of data in this study followed the Alaska Department of Public Safety Crime Detection Laboratory fire debris analysis manual (2011) which uses the following ASTM standards as reference guides:

1. ASTM E1386 Standard Practice for Separation and Concentration of Ignitable Liquid Residue from Fire Debris Samples by Solvent Extraction
2. ASTM E1618 Standard Test Methods for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry
3. ASTM E1387 Ignitable Liquid Classification System

The method employs a gas chromatograph (GC) which is interfaced to a mass spectrometer (MS) detector and a computer program that is able to handle and store chromatographic and mass spectral data. A muffle furnace was employed in the pyrolysis of the samples so that temperature and time can be controlled hence obtaining reproducible results.

3.1 SAMPLE MATERIALS

Four types of wood materials were used in this analysis namely Medium Density Fiberboard, Mahogany, Chipboard and Block board. Figure 3.1 below shows Medium Density Fiberboard (MDF) sample. Chung *et al.* (2000) describes the composition of this material to be 85-100 % softwood and 1-15 % hardwood, bound together with urea-formaldehyde resin. The smooth, uniform surface and solid edges makes MDF a suitable material for most paintings and decorative overlays in most buildings (Ayrilmis and Winandy, 2009).

Figure 3.1.1: Medium Density Fibreboard sample

Figure 3.1.2 below shows mahogany sample. This is one of the most valuable tropical hardwoods and has the following physical characteristic: hardness, and reddish brown colour which is as a result of phragmalin-type liminoids (Cabral *et al*., 2011).

Figure 3.1.2: Mahogany sample

Figure 3.1.3 below shows chipboard sample. This material is a recycled form of wood whereby wood chips from various woody materials are bound together with special resins under high pressure using the latest technology to make attractive finishes. It is one of the common types of wood that is widely used today for office and household furniture since it is affordable and very convenient to use (Ayrilmis and Winandy, 2009).

Figure 3.1.3: Chipboard sample

Figure 3.1.4 below shows blockboard sample. It is made of strips of softwood material which is sandwitched between two sheets of hardwood material at the top and bottom. They are bound together using resins under high pressure.

Figure 3.1.4: Blockboard sample

3.2 SAMPLE COLLECTION AND PREPARATION

Clean wood samples were obtained from the woodwork workshop department at Chiromo campus. The pyrolysis of these samples was done at a controlled constant temperature of 350 °C and 450 ºC for 30 minutes using Bibby Stuart muffle furnace (SF7/P series Model). The charred samples were collected in sampling bags made of nylon 6-6 since they offer lowest background noise and also they do not need pre-cleaning. The bags were sealed and kept at room temperature and exposure to heat was avoided.

3.3 SAMPLE EXTRACTION

The charred wood samples were crushed into fine powder. 1 g of the sample was weighed and transferred into a clean conical flask. 10 ml of dichloromethane (HPLC grade) was added. The mixture was stirred for 2 hours using an orbital shaker at 150 revolutions/minute and the extracts filtered through 11 µm grade 1 Whatman filter paper. Anhydrous sodium sulphate was used as a drying agent. The extraction process was repeated twice with fresh solvent of (dichloromethane) DCM. 1 ml of Iso-octane was added to the extracts and then concentrated using rotary evaporator. The samples were then quantitatively transferred to the vials and further concentration was done using a stream of pure nitrogen gas, 99.999 % obtained from Gas Labs. The sample extracts were refrigerated at 4 ºC before instrumental analysis.

Standard Accelerant Mixture (SAM) stock solution was prepared by taking equal parts of gasoline and diesel in a ratio of 1:1 and then 0.1 ml of the mixture was diluted with 0.5 ml of DCM. Figure 3.2.1 below shows the extracts of the burnt wood samples pyrolyzed at 350 °C and 450 °C in a muffle furnace for 30 minutes respectively.

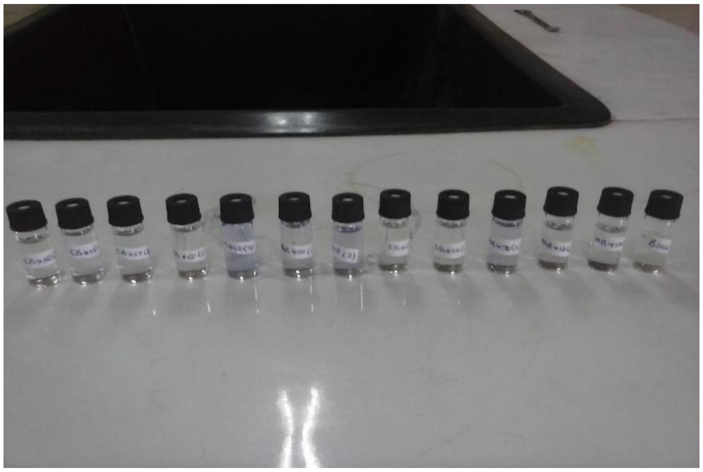

Figure 3.2.1: Burnt wood extracts

Figure 3.2.2 shows the extracts of the unburnt wood samples

Figure 3.2.2: Unburnt wood extracts

3.4 SAMPLE ANALYSIS

The sample analysis was performed on Hewlett-Packard 6890 Series gas chromatograph fitted with an Agilent 6890 series auto-injector and interfaced to a Hewlett-Packard 6890 Series quadruple mass selective detector. The GC was fitted with a DB-5MS 30 m 0.25 μm capillary column and the carrier gas was Helium, 99.999 % purity obtained from Gas Labs.

The initial oven temperature was 40 °C and this was maintained for four minutes. A ramp rate of 10 °C/minute was performed to final temperature of 280 °C and held for two minutes to a total run time of 30 minutes. The mass analyzer scanned from 31-350 m/z with a scan rate of 3-4 scans/second. The mass spectrometer line was maintained at 280 °C.

3.5 QUALITY ASSURANCE

The sample analysis was done in triplicates to ensure precision and accuracy of the results obtained. Sample blanks were also analyzed to cater for contamination during the sample preparation steps during analysis. Storage blanks were also analyzed to ensure no cross-contamination of the volatile compounds occurred during the storage process.

3.6 IDENTIFICATION AND ANALYSIS OF MASS SPECTRAL DATA

NIST 2008 was used in identification of compounds from the ion fragments. The retention times of each identified compound in the sample was compared with the retention times of the target compounds in the Standard Accelerant Mixture. The % abundance of each peak of the identified compound was determined in relation to the sum of the total peak areas of the other compounds in the sample.

% Abundance = $[(corrected\ Peak\ Area)/(\sum corrected\ peak\ areas)]X100\%$

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 GASOLINE-DIESEL STANDARD MIXTURE

The Standard Accelerant Mixture (SAM) containing gasoline and diesel in equal proportionate ratio of 1:1 produced a chromatogram shown in Figure 4.1.1. The lighter components of gasoline were eluted early while the components heavy of diesel were eluted between retention times of thirteen to twenty two minutes. Slight background noise was observed, however the peaks for the identified target compounds were reproducible.

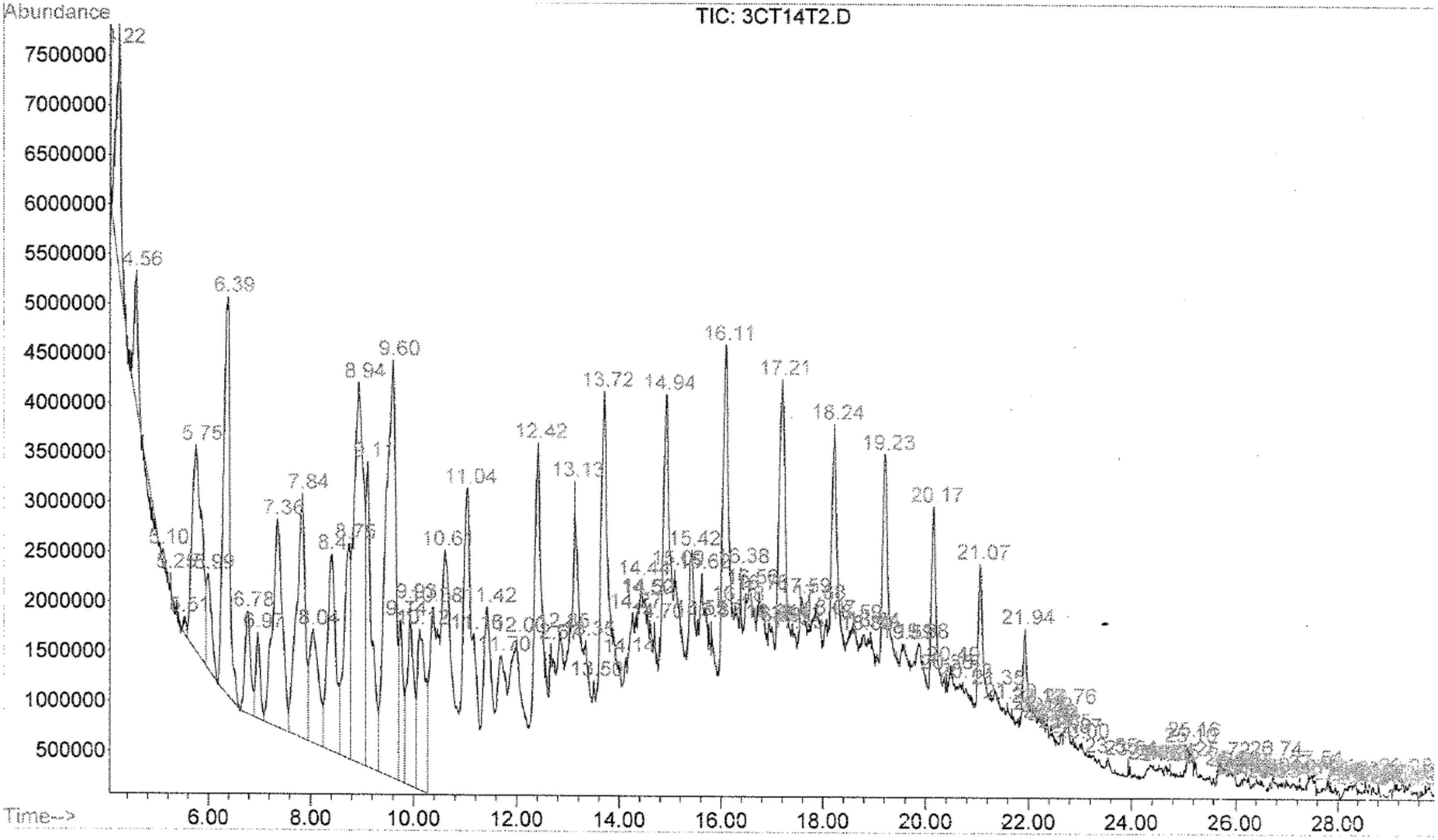

Figure 4.1.1: Chromatogram for Standard Accelerant Mixture (SAM)

The compounds in the SAM were identified and summarized in Table 4.1.1. The % abundance of each compound in the sample mixture was also obtained (Table 4.1.1).

Table 4.1.1: Identified Compounds in Standard Accelerant Mixture (SAM)

RtS (mins)	**SAM Compound**	**% Abundance**
5.75	1-ethyl-4-methylbenzene	2.688
6.39	1,2,4-trimethylbenezene	0.338
7.36	1,2-diethylbenezene	1.165
7.84	1,2,4,5-tetramethylbenzene	0.023
8.41	2,ethyl-1,4-dimethylbenzene	0.972
8.94	1-methyl-4-(1-methyl)-benzene	1.568
9.60	2-benzylidene-1-heptanol	2.947
10.61	Indane	0.215
11.04	1,2,3,4-tetrahydro-6-methylNaphthalene	0.901
12.42	2-methylnaphthalene	0.618
13.13	Decane	0.089
13.72	Naphthalene	0.196
14.94	Indane	0.014
16.11	5,8-diethyl-dodecane	0.215
17.21	Heptadecane	2.282
18.24	Phytane	3.762
19.23	Nanodecane	1.317
20.17	Eicosane	2.146
21.07	17-pentatriacontene	1.337
21.94	Tricosane	4.182

4.2 MAHOGANY

The chromatogram for the unburnt sample of mahogany showed little background interference from the substrate material, with few and clear reproducible peaks obtained at retention times of between eight and twenty five minutes as shown in Figure 4.2.1 below.

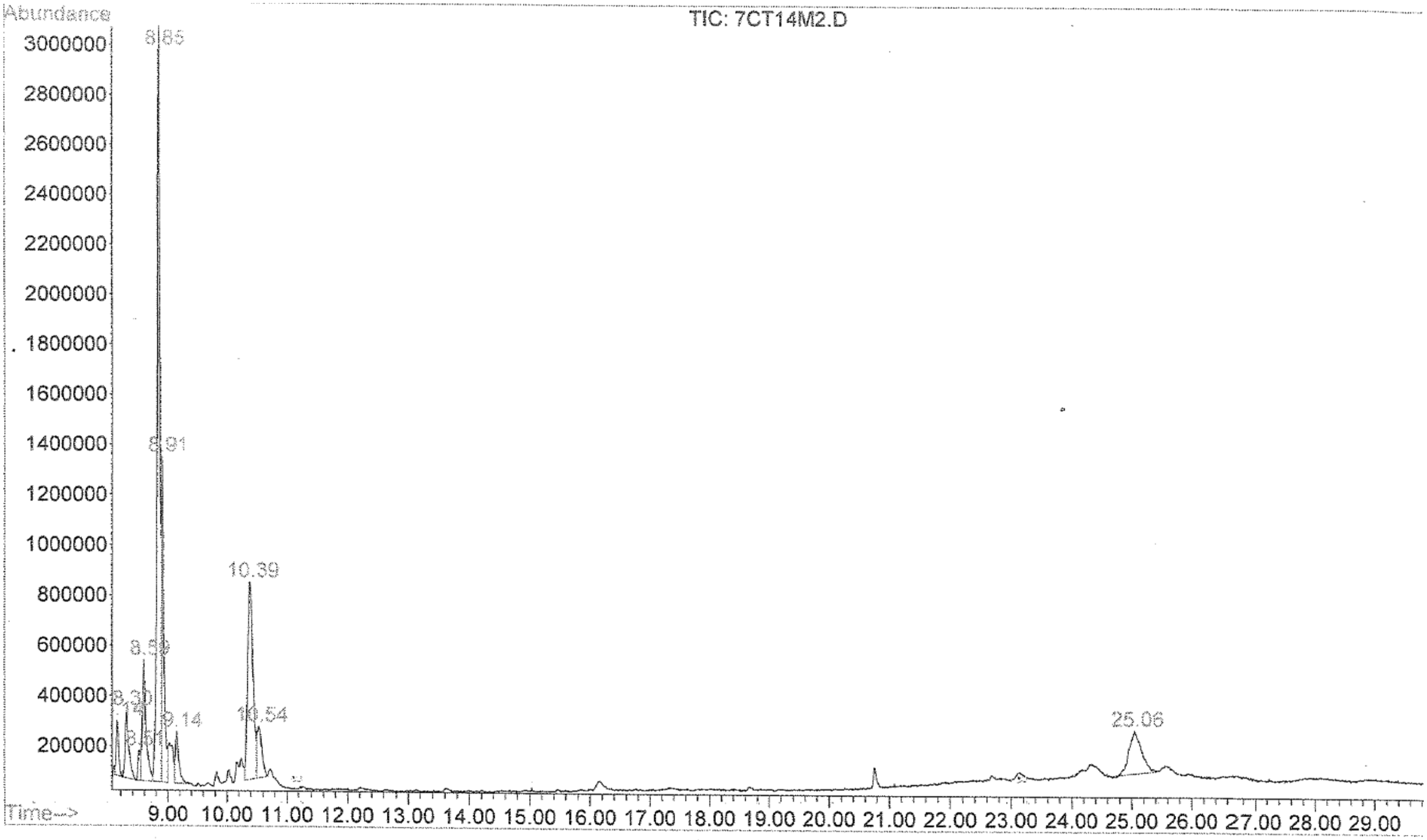

Figure 4.2.1: Chromatogram for unburnt Mahogany

These compounds were identified and summarized in Table 4.2.1. The compounds mostly consisted of a sesquiterpene, and fused aromatic hydrocarbons. None of these compounds were observed in the pyrolyzed mahogany sample.

Table 4.2.1: Identified Compounds in unburnt Mahogany sample

RtM (mins)	**Compounds of Unburnt Mahogany sample**	% Abundance
8.14	Aromadandrene	2.322
8.29	hexahydro-4,7-dimethyl-1(1-methylethyl)-Naphthalene	3.989
8.59	4,7-dimethyl-1(1-methylethyl)-Naphthalene	7.663
8.84	4,7-dimethyl-1(1-methylethyl)-1S-Cis-Naphthalene	30.848
8.89	4,7-dimethyl-1(1-methylethyl)-1S-trans-Naphthalene	14.419
9.15	α-calacorene	3.215
10.36	tau-cardinol	20.460
10.52	Ethyl iso-allocholate	4.839
25.06	γ-Sitosterol	11.085

At pyrolysis temperature of 350 °C, only one reproducible peak was obtained at retention time 18.72 minutes. The chromatogram had a lot of background interference as shown in Figure 4.2.2. The compound in the sample was identified as 3, 8, 8-Trimethoxy-3-piperidyl-2, 2-binaphthalene-1, 1, 4, 4-tetrone (Figure 4.2.3) and it was not obtained in the unburnt substrate material.

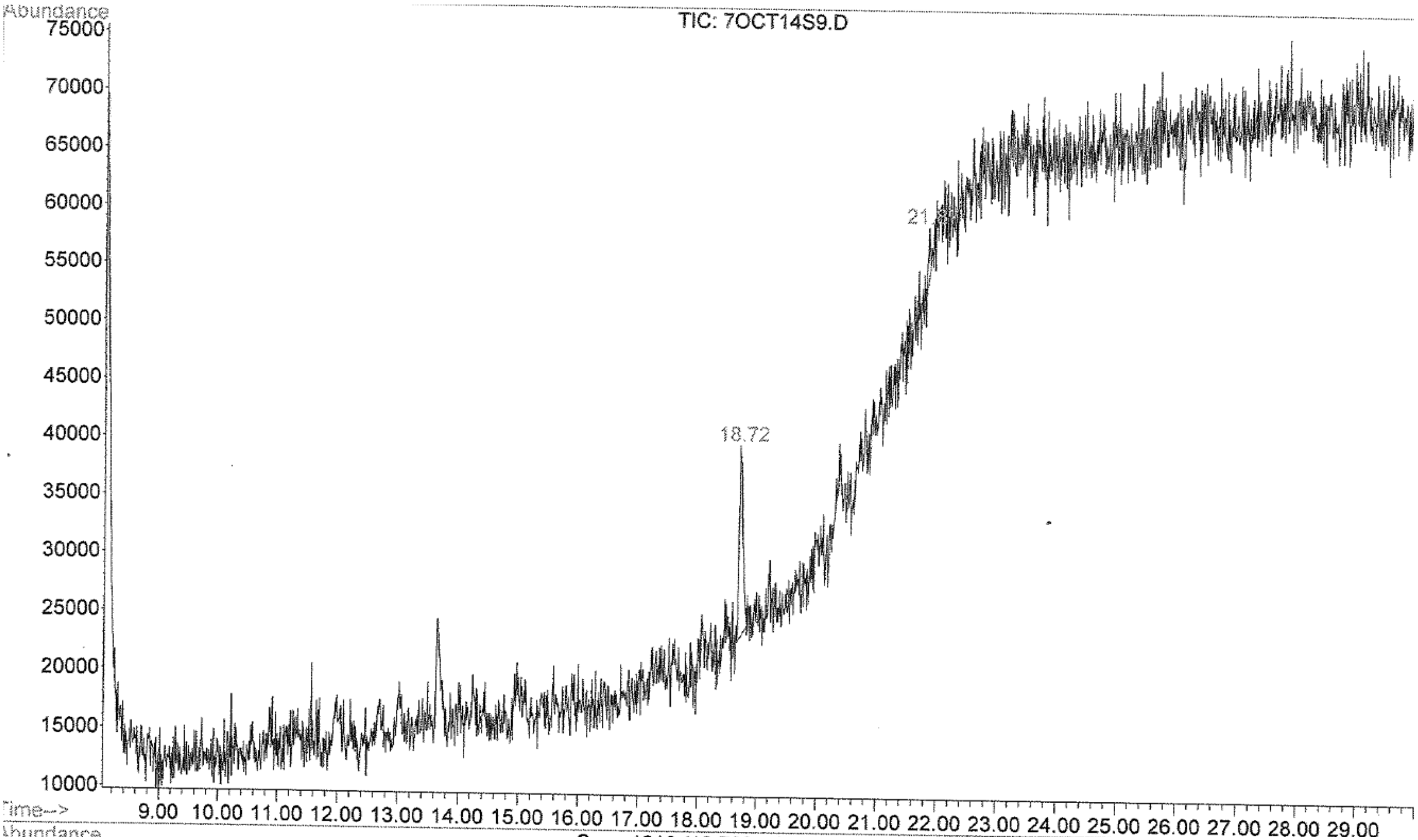

Figure 4.2.2: Chromatogram for mahogany sample pyrolyzed at 350 °C

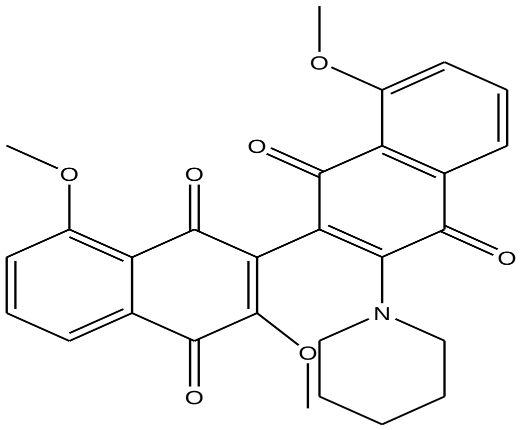

Figure 4.2.3: Chemical Structure of 3, 8, 8-Trimethoxy-3-piperidyl-2, 2-binaphthalene-1, 1, 4, 4-tetrone

Appendix 1 shows the mass spectrum obtained for this compound. From the structure obtained, this compound has highly fused aromatic rings. This compound showed no interference with the target compounds of the SAM.

At pyrolysis temperature of 450 °C several reproducible peaks were obtained at retention times of between 8 minutes and 19 minutes. The chromatogram had very little background interference as shown in Figure 4. 2. 4.

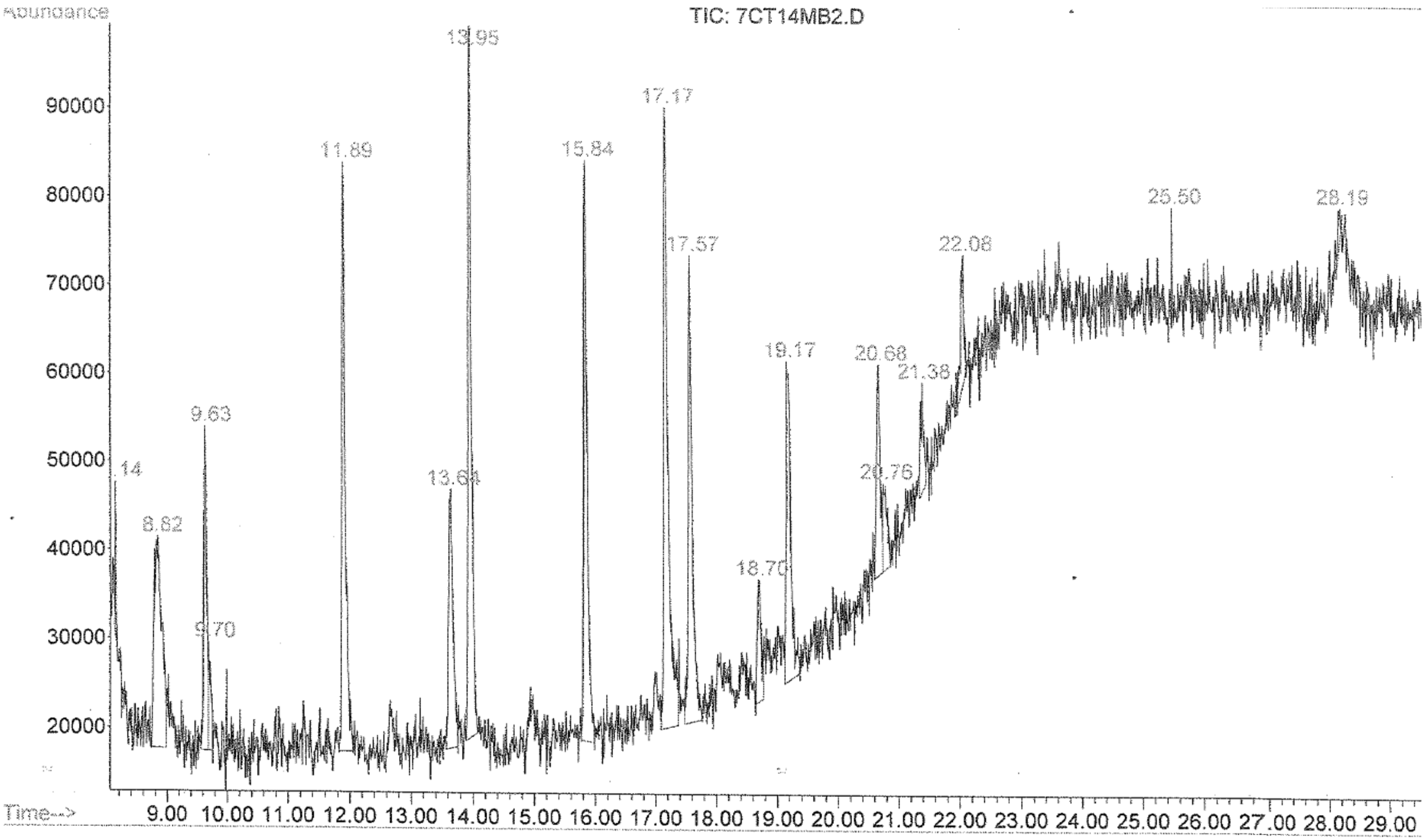

Figure 4.2.4: Chromatogram for mahogany sample pyrolyzed at 450 °C

The compounds were identified and were found to be both aromatic and aliphatic hydrocarbons as summarized in table 4. 2. 2. It was observed that the compounds were absent in the unburnt substrate in Table 4.2.1.

Table 4.2.2: Identified pyrolysis products of mahogany sample at temperature of 450 °C

RtM (mins)	**Compounds of charred Mahogany sample at 450** °C	**% Abundance**
8.82	3,5-bis(1,1-dimethyl)-phenol	4.040
9.63	10-Heneicosene	3.961
11.89	1-Eicosene	9.669
13.64	Pthalic acid,Butyl undecyl ester	4.962
13.95	1-Docosene	10.375
15.84	1,3,5-trimethyl-2-octadecyl,cyclohexane	9.544
17.17	Olean-13(18)-ene	13.501
17.57	1,3,5-trimethyl-2-octadecyl,cyclohexane	6.954
18.69	pyridazine	2.958
19.17	17-pentatriacontene	6.332
20.68	1-hexacosene	3.625
21.38	Docosanoic acid, 1,2,3-propanetriyl ester	1.658
22.08	3,8,8-Trimethoxy-3-piperidyl-2,2-binaphthalene-1,1,4,4-tetrone	3.453

The compounds identified above showed interference with target compounds of the accelerants. A comparison of the retention times of these pyrolysis compounds in the sample and that of Standard Accelerant Mixture show close similarity in elution times. 17-pentatriacontene (Figure 4.2.5) was observed in both the Standard Accelerant Mixture and in charred mahogany sample. Appendix 2 shows the Mass spectrum for 17-pentatriacontene.

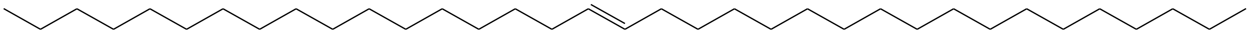

Figure 4.2.5: Chemical structure of 17-pentatriacontene

Furthermore the % abundances of the pyrolysis products in the charred sample (Table 4.2.3) were much higher when compared to the target compounds (Table 4.2.1). This implies that the target compounds of the gasoline and diesel would be shielded by the pyrolysis products as shown in Table 4.2.3.

Table 4.2.3: Comparison of pyrolysis products of mahogany and target compounds of SAM

RtS (Mins)	**SAM Compound**	**% Abundance**	**RtM(mins)**	**Charred Mahogany Compound**	% Abundance
8.94	1-methyl-4-(1-methyl)-benzene	0.972	8.82	3,5-bis(1,1-dimethyl)-phenol	4.040
9.60	2-benzylidene-1-heptanol	1.568	9.63	10-Heneicosene	3.961
11.04	1,2,3,4-tetrahydro-6-methylNaphthalene	2.947	11.89	1-Eicosene	9.669
13.13	decane	0.089	13.64	Pthalic acid,Butyl undecyl ester	4.962
13.72	naphthalene	0.196	13.95	1-Docosene	10.375
14.94	Indane	0.014	15.84	1,3,5-trimethyl-2-octadecyl,cyclohexane	9.544
16.11	5,8-diethyl-dodecane	0.215	17.17	Olean-13(18)-ene	13.501
17.21	heptadecane	2.282	17.57	1,3,5-trimethyl-2-octadecyl,cyclohexane	6.954
18.24	phytane	3.762	18.69	Pyridazine	2.958
19.23	Nanodecane	1.317	19.17	17-pentatriacontene	6.332
20.17	eicosane	2.146	20.68	1-hexacosene	3.625
21.07	17-pentatriacontene	1.337	21.38	Docosanoic acid, 1,2,3-propanetriyl ester	1.658
21.94	tricosane	4.182	22.08	3,8,8-Trimethoxy-3-piperidyl-2,2-binaphthalene-1,1,4,4-tetrone	3.453

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4.3 MEDIUM-DENSITY FIBERBOARD (MDF)

The nature of this sample, as discussed earlier, explains the background interference observed in the chromatogram for the unburnt sample in Figure 4.3.1. This is as result of the resins and other synthetic materials used in its manufacturing process. However, few significant reproducible peaks were obtained (Figure 4.3.1). The compounds were identified and summarized in Table 4.3.1. These compounds were not present in the pyrolyzed sample (Figure 4.3.2). The other peaks could not be identified from the NIST library.

Table 4.3.1: Identified compounds in unburnt Medium- Density Fiber board.

RtD (mins)	**Compounds in unburnt MDF sample**	**% Abundance**
11.10	3-acetoxy-7,8-Epoxylanostan-11-ol	0.275
13.63	2,7-Diphenyl-1,6-dioxypyrdazino[4,5:2' ,3']pyrrolo[4' ,5'-d]pyridazine	1.080
14.67	25-[(trimethylsilyl)oxy]-(3β,5Z,7E)-9,10-Secocholesta-5,7,10-triene1,3-diol	1.083
17.22	Ethyl iso-allocholate	5.971
20.96	Primaric acid	4.276
22.07	pyridazine	6.437

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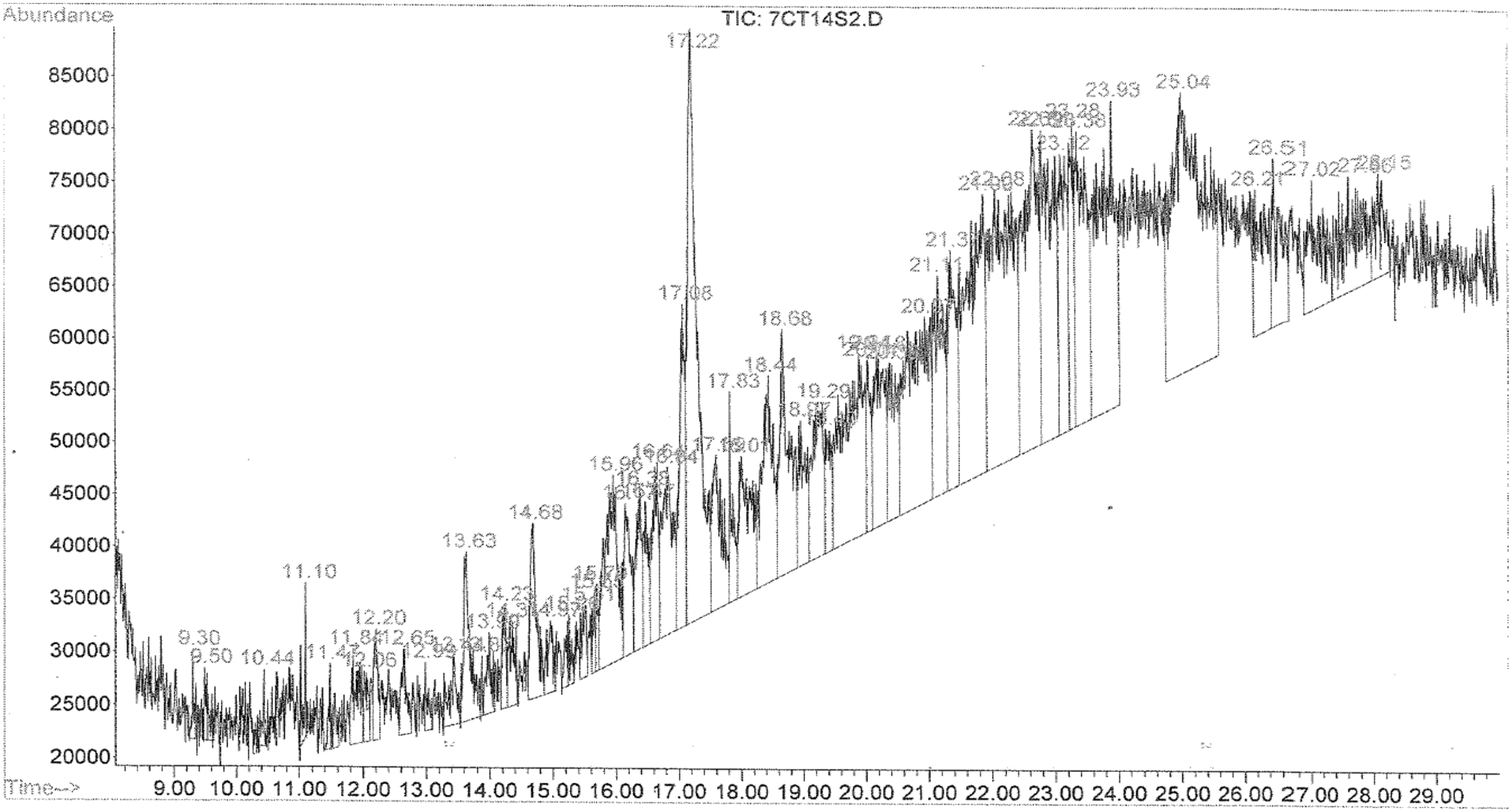

Figure 4.3.1: Chromatogram for unburnt MDF sample

Pyrolysis of MDF at 350 °C produced two compounds namely 1, 2-Benzenedicarboxylic acid, butyl octyl ester (Figure 4.3.2) and 1, 2-Benzenedicarboxylic acid, diisoctyl ester (Figure 4.3.3) at retention times of 13.65 and 18.73 respectively as shown in figure 4.3.4. These pyrolysis products show no interference with the target compounds of Standard Accelerant Mixture of gasoline and diesel (Table 4.1.1).

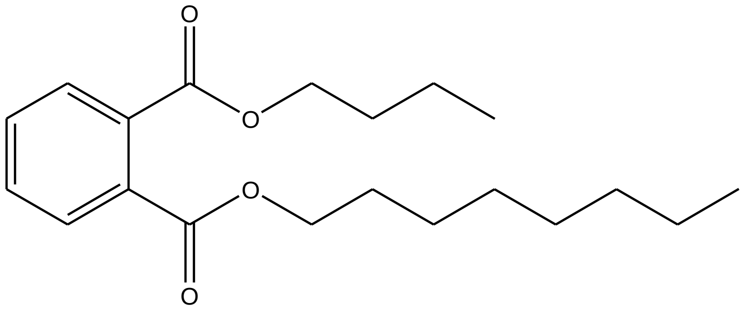

Figure 4.3.2: Chemical structure of 1, 2-Benzenedicarboxylic acid, butyl octyl ester

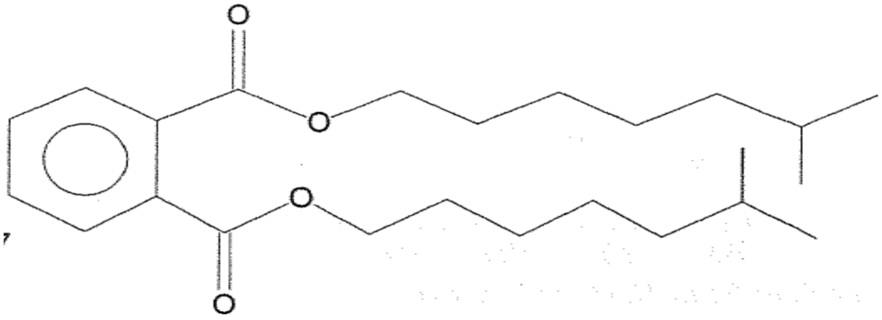

Figure 4.3.3: Chemical Structure of 1, 2-Benzenedicarboxylic acid, diisoctyl ester

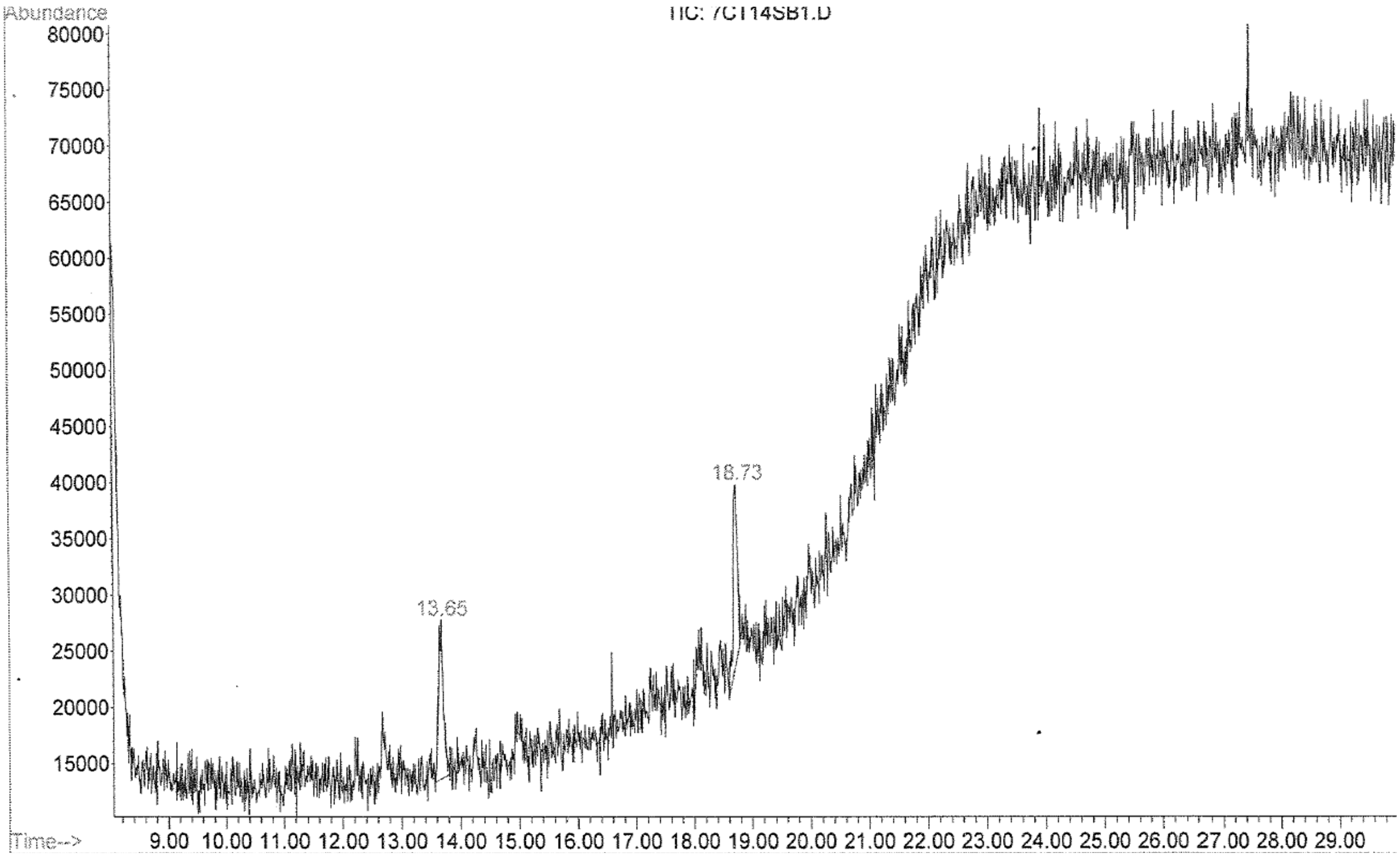

Figure 4.3.4: Chromatogram for MDF at pyrolysis temperature of 350 °C

At pyrolysis temperature of 450 °C more compounds were obtained as shown in Figure 4.3.5 below. The chromatogram had very little background interference and peaks were reproducible. The compounds were identified and summarized in table 4.3.2.

Table 4.3.2: Identified pyrolysis products in charred MDF sample.

RtD (min)	**Compounds of Charred MDF sample at 350** °C	% Abundance
8.79	3,5-bis(1,1-dimethyl)-phenol	7.293
9.63	1,3,5-trimethyl-2-octadecyl-cyclohexane	6.280
11.89	10-Heneicosene	10.419
13.64	1,2-Benzenedicarboxylic acid,butyl octyl ester	6.264
13.95	1-Docosene	11.653
15.84	10-Heneicosene	9.396
17.17	8-ethoxy-4,5-dihydro-1-Quinoline	14.565
17.57	1-hexacosene	8.573
19.17	17-pentatriacontene	6.331
20.65	Oleic acid eicosyl ester	3.656
20.77	1-heptatriacotanol	3.274
22.06	Docosanoic acid, 1,2,3-propanetriyl ester	3.465
28.20	Ethyl iso-allocholate	0.868

The pyrolysis products of MDF at 450°C show interference with specific target compounds of the Standard Accelerant Mixture based on retention times. Furthermore 17-pentatriacontene was also found to be present in both standard accelerant mixture (Table 4.1.1) and Pyrolysis products of medium density fiberboard (Table 4.3.2).

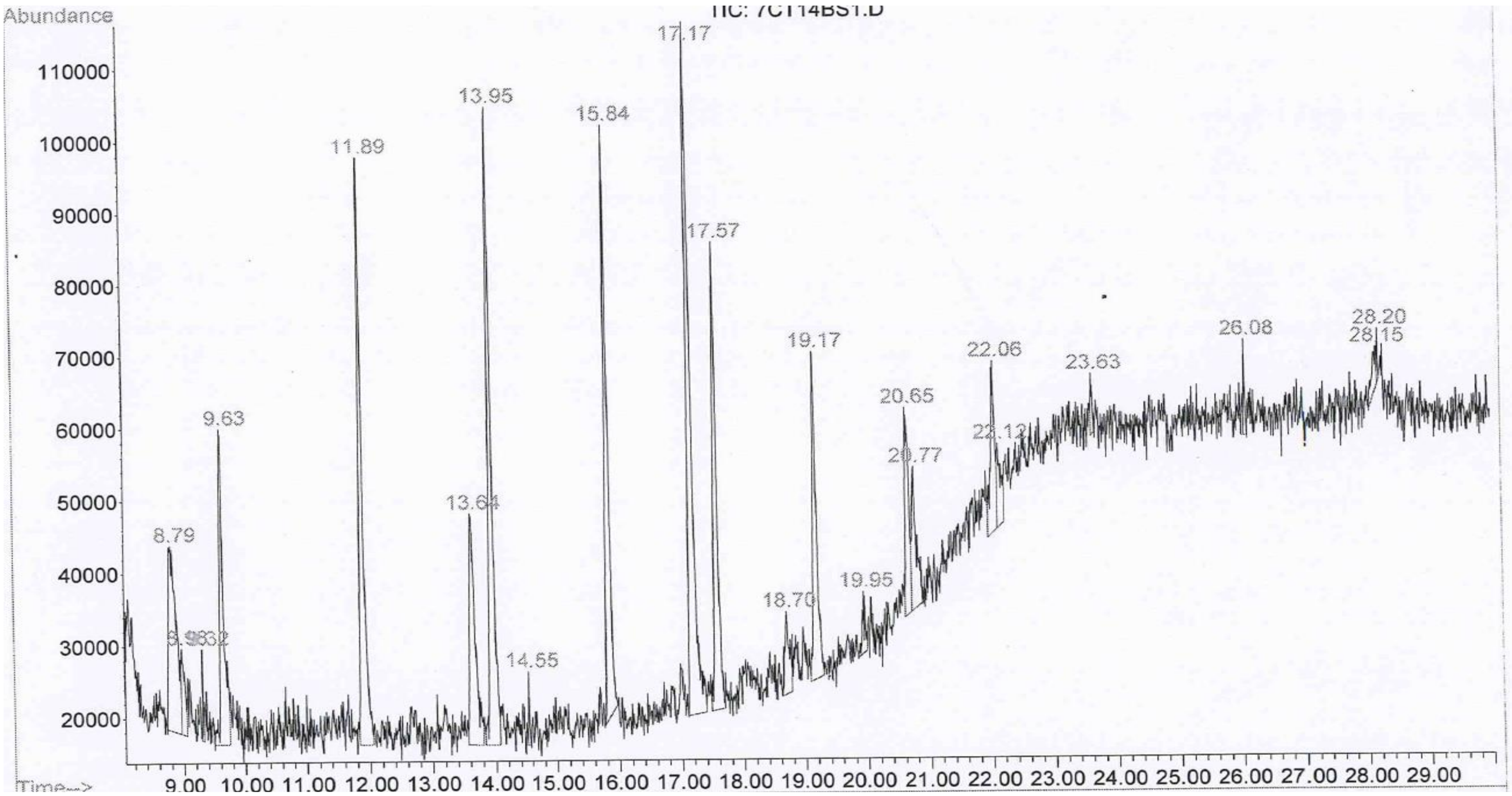

Figure 4.3.5: Chromatogram for MDF sample pyrolyzed at 450 ° C

The % abundances of the pyrolysis compounds in the sample (Table 4.3.3) was observed to be much higher than the target compounds in the accelerant mixture (Table 4.1.1), hence possible shielding of the target compounds of the accelerants by the pyrolysis products during analysis. Table 4.3.3 gives a summary of how the pyrolysis products compared to the target compounds in SAM.

Table 4.3.3: Comparison of pyrolysis products of MDF and target compounds of Standard Accelerant Mixture (SAM)

RtS (min)	**SAM Compounds**	% Abundance	**RtD (min)**	**Compounds of Charred MDF**	% Abundance
8.94	1-methyl-4-(1-methyl)-benzene	0.972	8.79	3,5-bis(1,1-dimethyl)-phenol	7.293
9.60	2-benzylidene-1-heptanol	1.568	9.63	1,3,5-trimethyl-2-octadecyl-cyclohexane	6.280
12.42	2-methylnaphthalene	2.947	11.89	10-Heneicosene	10.419
13.13	Decane	0.089	13.64	1,2-Benzenedicarboxylic acid,butyl octyl ester	6.264
13.72	Naphthalene	0.196	13.95	1-Docosene	11.653
14.94	Indane	0.014	15.84	10-Heneicosene	9.396
16.11	5,8-diethyl-dodecane	0.215	17.17	8-ethoxy-4,5-dihydro-1-Quinoline	14.565
17.21	Heptadecane	2.282	17.57	1-hexacosene	8.573
18.24	Phytane	3.762	19.17	17-pentatriacontene	6.331
19.23	Nanodecane	1.317	20.65	Oleic acid eicosyl ester	3.656
20.17	Eicosane	2.146	20.77	1-heptatriacotanol	3.274
21.07	17-pentatriacontene	1.337	22.06	Docosanoic acid, 1,2,3-propanetriyl ester	3.465
21.94	Tricosane	4.182	28.20	Ethyl iso-allocholate	0.868

4.4 CHIPBOARD

The compounds extracted from the unburnt substrate material of chipboard sample were observed to be mainly consisting of highly fused aromatic rings of ketones, aldehydes and carboxylic acid. The chromatogram had a lot of background interference however few reproducible peaks were obtained as shown in Figure 4.4.1. The identified compounds in the unburnt material (Table 4.4.1) were not obtained in the pyrolyzed samples.

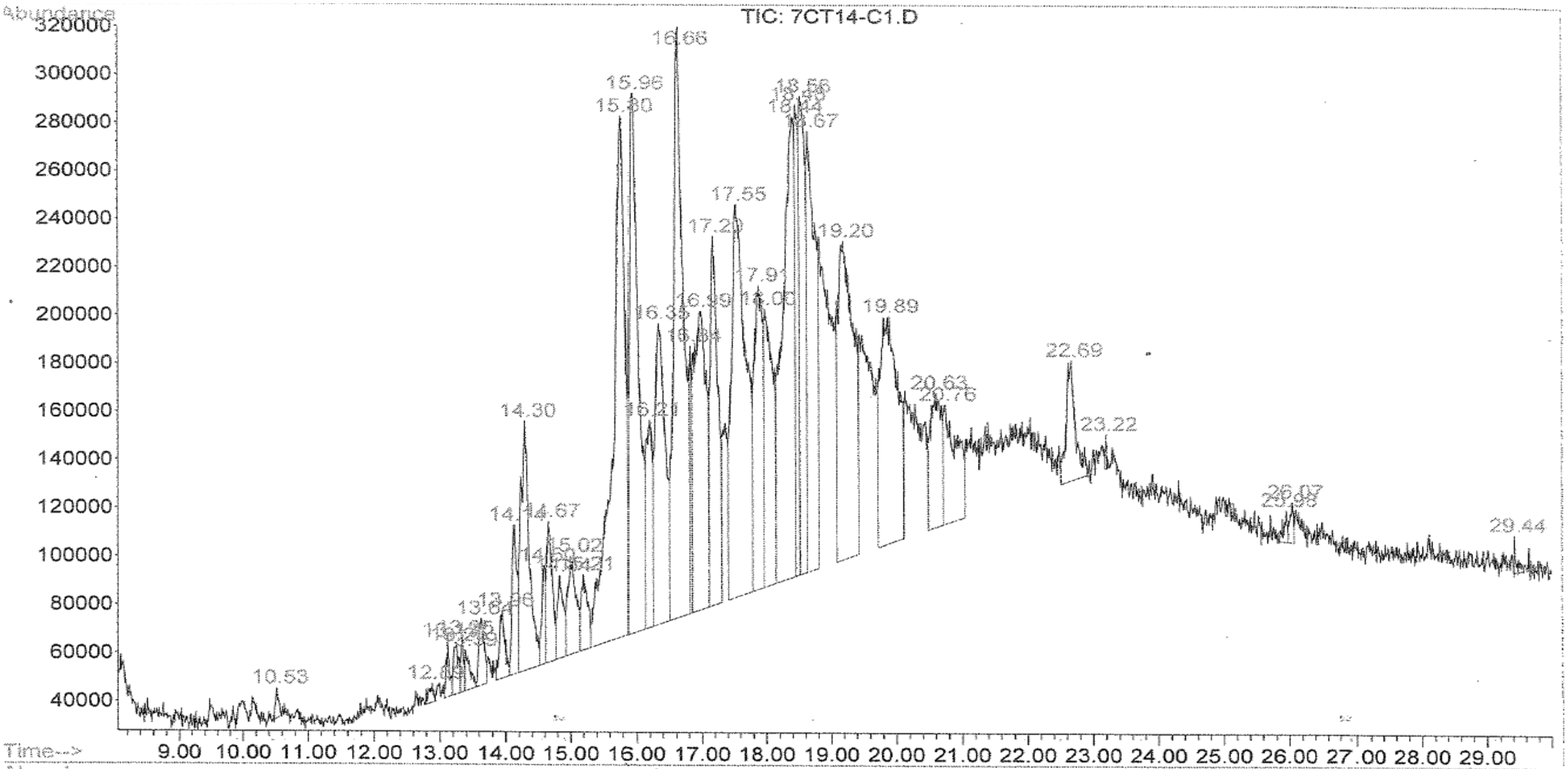

Figure 4.4.1: Chromatogram for Unburnt Chipboard

Table 4.4.1: Identified compounds in unburnt Chipboard sample in Figure 4.4.1

RtC (mins)	**Compounds in unburnt Chipboard**	**% Abundance**
13.64	Primaric Acid	0.427
14.30	2-[4-methyl-6-(2,6,6-trimethylcyclohex-1-enyl)hexa-1,3,5-trienyl]cyclohex-1-en-1-carboxyaldehyde	2.521
15.80	Androst-5,7-diene-3-ol-`17-one	6.132
16.65	Retinol	6.156
17.20	9-cis-Retinal	3.782
19.89	Primaric Acid	3.404
22.69	Pyridazine	6.346

The chromatogram for chipboard sample pyrolyzed at temperature of 350 °C showed two reproducible peaks at retention times of 13.62 and 18.70 as illustrated in Figure 4.4.2. The compounds were identified to be phthalic acid- hexyl tridec-2-yn-1-yl ester (Appendix 5) and 3, 8, 8-Trimethoxy-3-piperidyl-2, 2-binaphthalene-1, 1, 4, 4-tetrone (Figure 4.2.3) respectively. These compounds show no interference with the target compounds of gasoline and diesel.

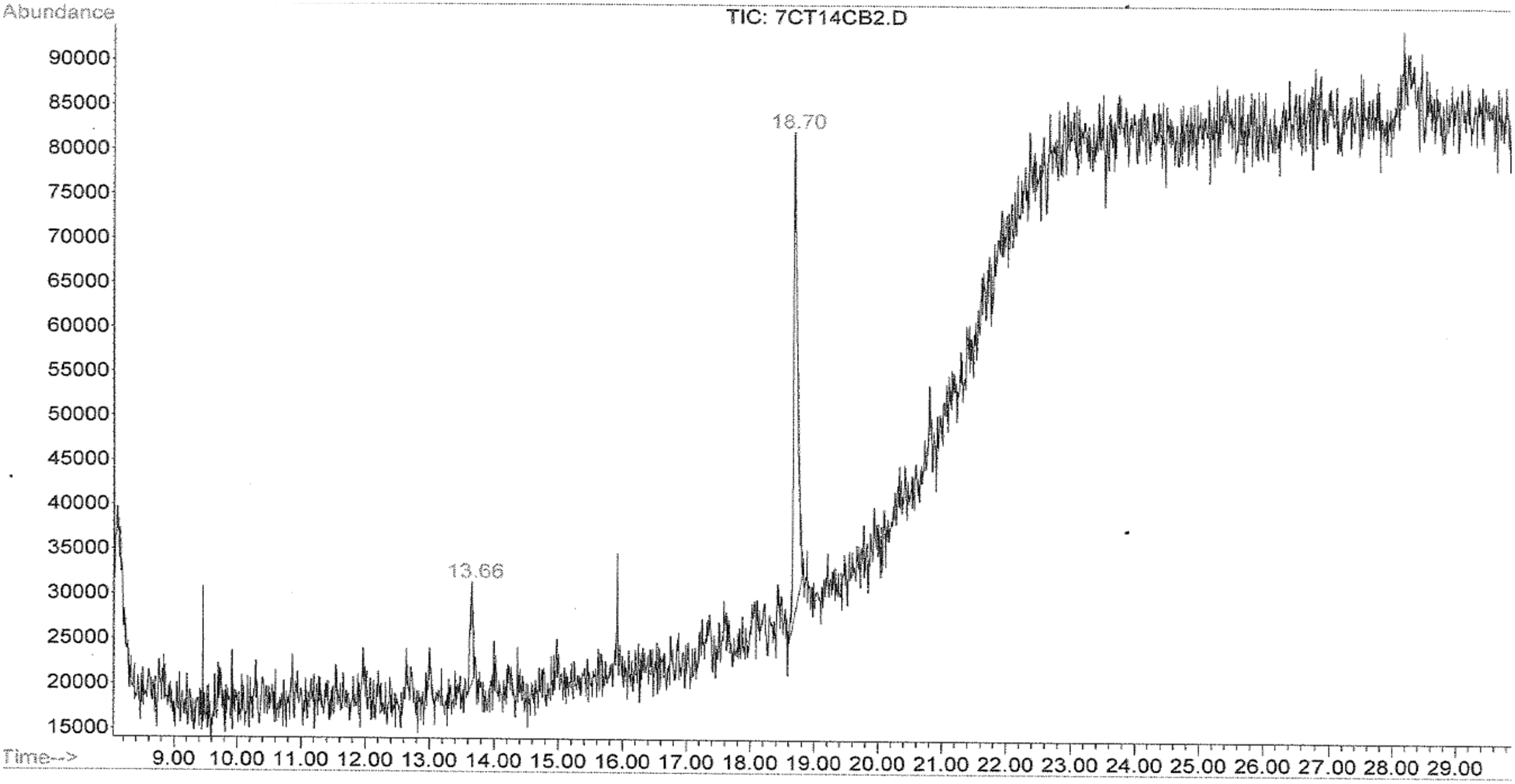

Figure 4.4.2: Chromatogram for Chipboard sample pyrolyzed at 350 °C

At pyrolysis temperature of 450 °C the chipboard material produced three compounds as illustrated by the chromatogram in Figure 4.4.5. The observed peaks were reproducible despite the background interference that was observed in the sample. The compounds were identified to be Ethyl iso-allocholate (Figure 4.4.3)**,** 1, 2-Benzenedicarboxylic acid, butyl octyl ester (Figure 4.3.2) and 1, 3, 5-trimethyl-2-octadecyl-cyclohexane (Figure 4.4.4) respectively. These compounds do not cause interference with gasoline or diesel compounds.

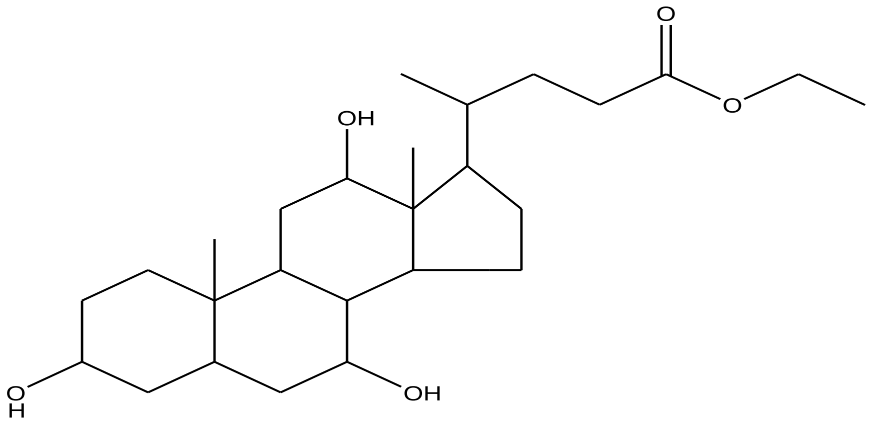

Figure 4.4.3: Chemical structure of Ethyl iso-allocholate

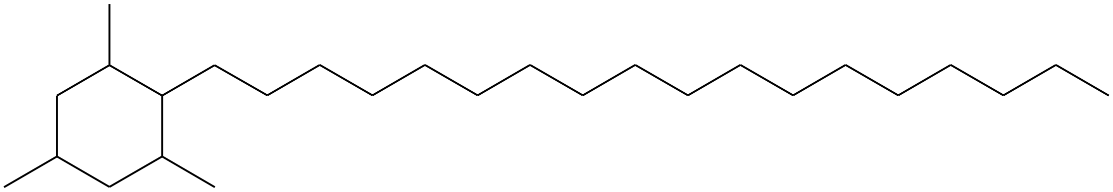

Figure 4.4.4: Chemical structure of 1, 3, 5-trimethyl-2-octadecyl-cyclohexane

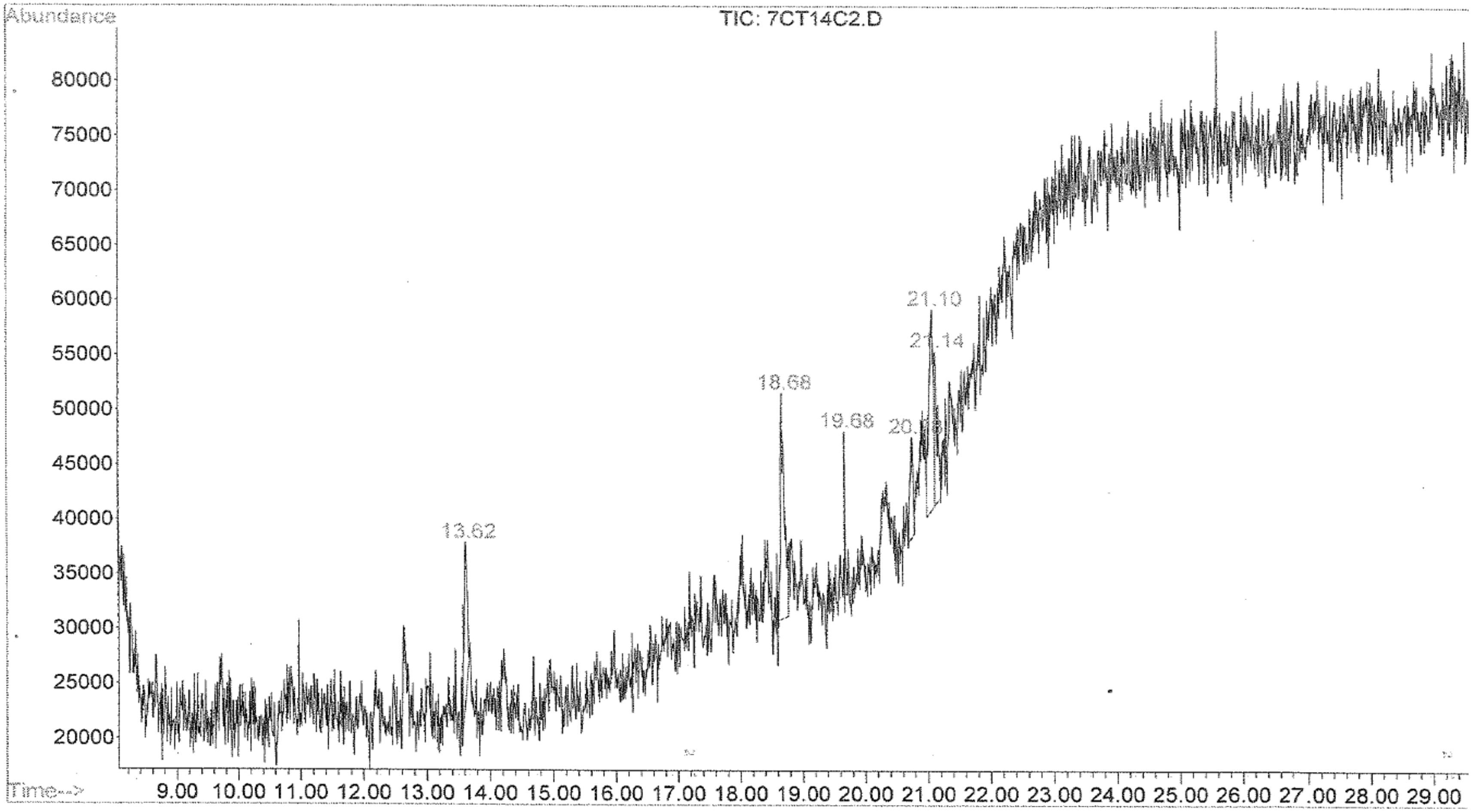

Figure 4.4.5: Chromatogram for Chipboard Pyrolyzed at 450 °C

The pyrolysis products of the chipboard sample pyrolyzed at temperatures 350 °C and 450 °C respectively showed no interference with the standard accelerant mixture. The compounds identified were different and none eluted at retention time close to the target compounds in gasoline and diesel.

4.5 BLOCK BOARD

The chromatogram for the unburnt block board sample in Figure 4.5.1 shows a lot of background interference however few reproducible peaks were identified and summarized in Table 4.5.1. These compounds were absent in the burnt samples although some were common in other wood samples discussed above.

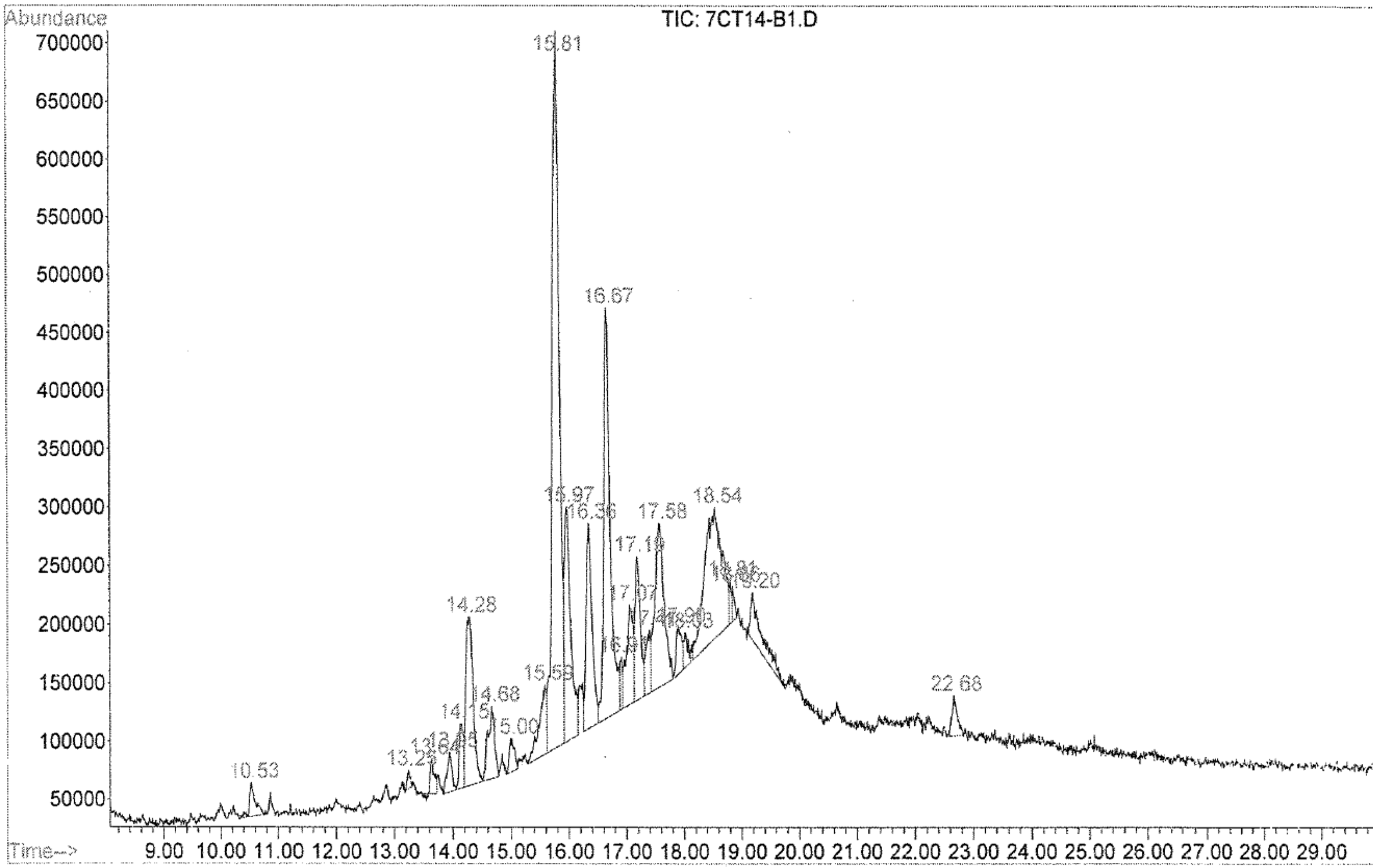

Figure 4.5.1 Chromatogram for unburnt block board

Table 4.5.1: Identified compounds in unburnt block board

RtB (mins)	**Compounds In unburnt block board**	**% Abundance**
10.53	(*E*)-methyl heptadec-10-en-8-ynoate	0.979
13.67	11α-Hydroxyresbufogenin	0.626
13.94	Primaric Acid	0.942
14.28	Retinol	6.104
15.81	2-[-4-methyl-6-(2,6,6-triethylcyclohex-1-enyl)hexa-1,3,5-trienyl]cyclohex-1-en-1-carboxyaldehyde	24.416
15.97	Pyridazine	7.321
16.36	Retinol	5.952
16.67	9-cis-Retinal	12.980
17.19	Retinoic acid, methyl ester	3.137
17.58	Androst-5,7-diene-3-ol-17-one	7.342
18.54	Primaric Acid	11.176

At pyrolysis temperature of 350 °C the identified compounds in Figure 4.5.2 shows interferences with some of the target compounds of gasoline and diesel in the Standard Accelerant Mixture. The pyrolysis compounds elute at retention times similar to these target compounds. Furthermore the % abundance of these pyrolysis compounds in the sample is much higher compared to the target compounds of the Standard Accelerant Mixture hence this would result in possible shielding of the target compounds during analysis.

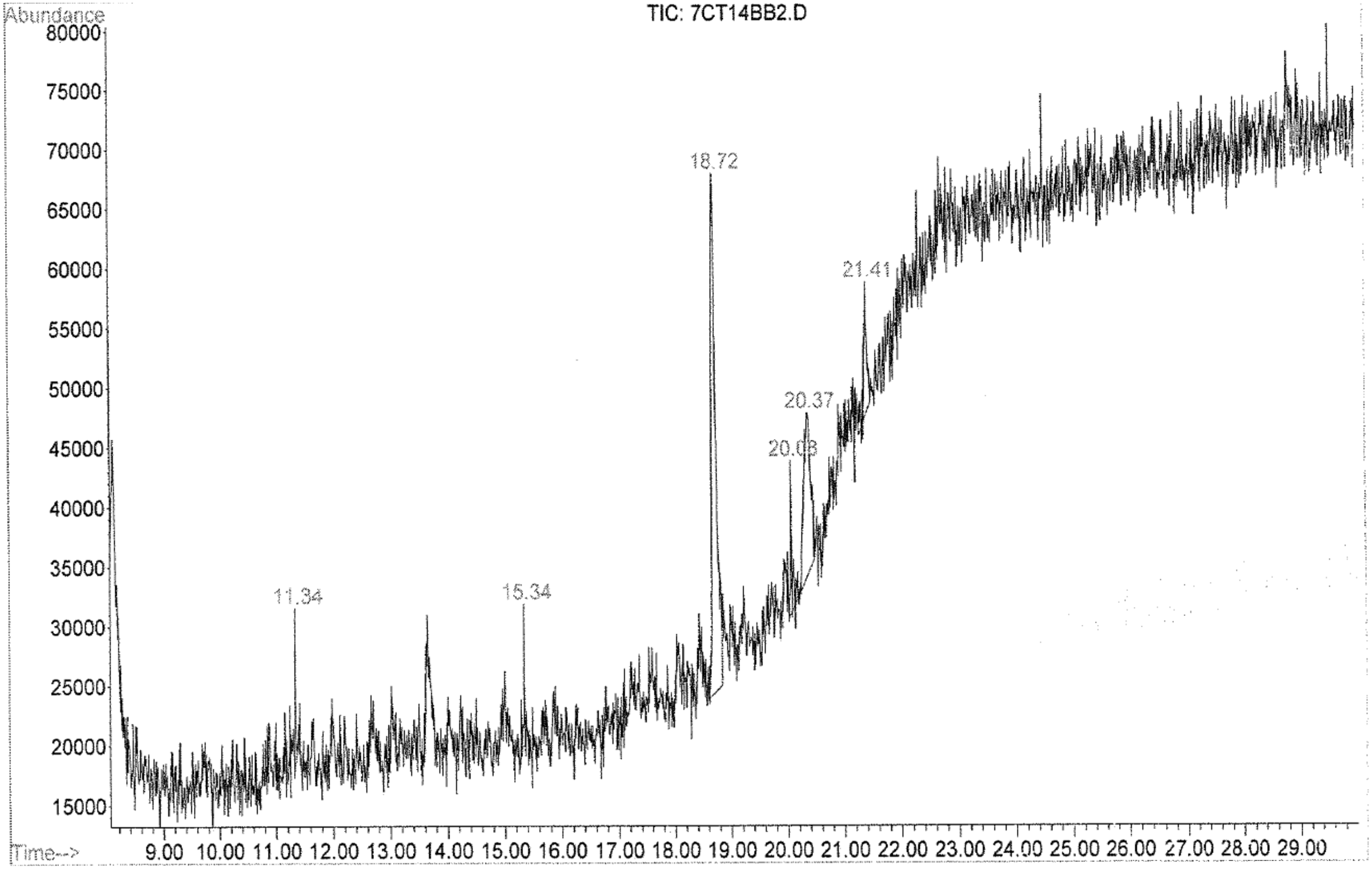

Figure 4.5.2: Chromatogram for Block board pyrolyzed at 350 °C

Table 4.5.2: Comparison of the target compounds and the pyrolysis products

RtS (mins)	**SAM Compounds**	% Abundance	**RtB (mins)**	**Charred Block board Compounds at 350 °C**	% Abundance
11.04	1,2,3,4-tetrahydro-6-methylNaphthalene	0.901	11.34	9-hexyl-heptadecane	2.633
14.94	Indane	0.014	15.34	Strogogenin	2.421
18.24	phytane	3.762	18.72	1,2-Benzenedicarboxylic acid,butyl octyl ester	54.311
20.17	eicosane	2.146	20.08	Docosanoic acid, 1,2,3-propanetriyl ester	4.528
21.07	17-pentatriacontene	1.337	20.37	2-(1,3-dihyro-1-methyl-3oxo-2H-indol-2-ylinedene)-1,3-dihydro-1-methyl-2H-Indol-3-one	26.872
21.94	tricosane	4.182	21.41	3,8,8-Trimethoxy-3-piperidyl-2,2-binaphthalene-1,1,4,4-tetrone	9.236

The chromatogram for the sample at pyrolysis temperature of 450 °C in Figure 4.5.3 showed a lot of background interference. However, reproducible peaks were present and these compounds were identified. A comparison of these pyrolysis products and the target compounds of gasoline and diesel in the Standard accelerant mixture showed interference based on the retention times. The % abundances of these pyrolysis compounds in the sample were also much more than these target compounds of the accelerants. This is summarized in Table 4.5.3.

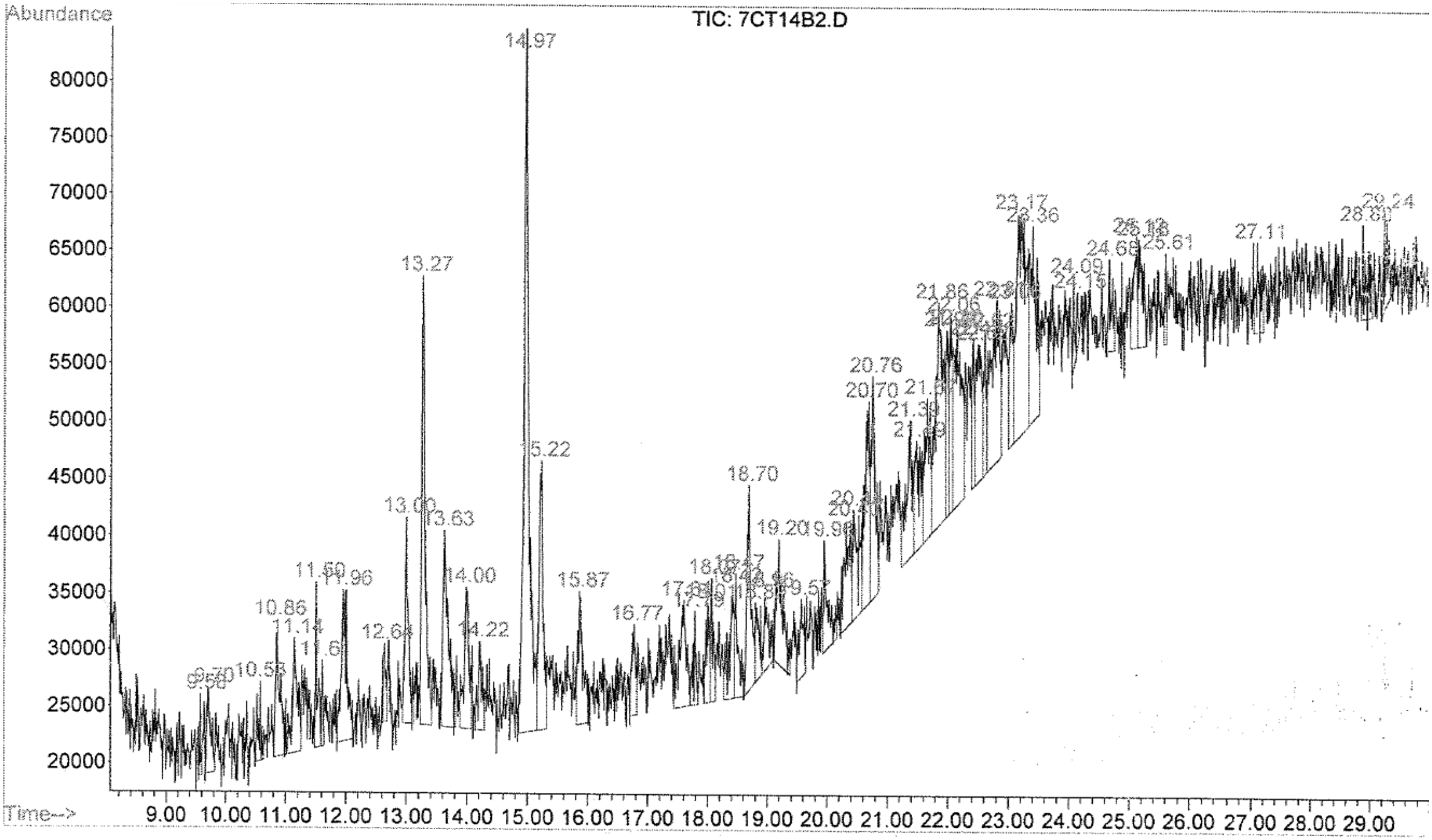

Figure 4.5.3: Chromatogram for Block board pyrolyzed at 450 °C

Table 4.5.3: Comparison of the Pyrolysis products of block board sample and target compounds of SAM

RtS (mins)	**SAM Compounds**	% Abundance	**RtB(mins)**	**Charred Block board Compounds at 450 °C**	% Abundance
10.61	propylene-benzene	0.215	10.86	9-hexyl-heptadecane	1.619
11.04	1,2,3,4-tetrahydro-6-methylNaphthalene	0.901	11.14	methyl 12-(2-octylcyclopropyl)dodecanoate	1.592
12.42	2-methylnaphthalene	0.618	12.64	9-hexyl-heptadecane	2.263
13.13	decane	0.089	13.27	3-ethyl-5-(2-ethylbutyl)-octadecane	4.318
13.72	naphthalene	0.196	13.63	1,2-Benzenedicarboxylic acid,butyl octyl ester	2.817
14.94	Indane	0.014	14.97	Methyl 13-octadecenoate	9.099
16.11	5,8-diethyl-dodecane	0.215	15.22	3-[[N-hydroxymethyl]aminocarbonyloxy]-Nor-diazepam	2.832
17.21	heptadecane	2.282	15.87	9-hexyl-heptadecane	1.896
18.24	phytane	3.762	18.70	Docosanoic acid, 1,2,3-propanetriyl ester	2.189

4.6 COMPARISON OF PYROLYSIS PRODUCTS BETWEEN THE WOOD SAMPLES

In this study, four types of wood materials were used namely; mahogany, Medium density Fiberboard (MDF), chipboard and block board. These wood materials were pyrolyzed at temperatures of 350 °C and 450 °C and the pyrolysis products identified.

At pyrolysis temperature of 350 °C few compounds were identified for all the four wood samples. 3, 8, 8-Trimethoxy-3-piperidyl-2, 2-binaphthalene-1, 1, 4, 4-tetrone (Appendix 1) was observed in mahogany and chipboard, while 1, 2-Benzenedicarboxylic acid, butyl octyl ester (Appendix 3) was common in MDF and Block board. This compound was also obtained in Chipboard at pyrolysis temperature of 450 °C.

More compounds were formed at pyrolysis temperature of 450 °C. At this pyrolysis temperature, Docosanoic acid, 1, 2, 3-propanetriyl ester (Appendix 4) was observed in mahogany, MDF and block board. Moreover 17-Pentatriacontene (Appendix 2), 10-Heneicosene (Appendix 6), and 1-Docosene (Appendix 7) were only present in MDF and mahogany. However, the % abundance for these compounds varied in the different types of samples.

The compounds extracted in the unburnt substrate of the wood samples in this study, consisted of mainly terpenes for example Aromadendrene in MDF (Appendix 8), ketones and carboxylic acid compounds. These compounds were however not observed in the burnt samples. The analysis of the unburnt substrate was mainly done to isolate the compounds that would arise from the substrate material yet do not undergo pyrolysis.

The pyrolysis products identified in MDF, Mahogany and block board eluted at retention times similar to target compounds of Standard accelerant. However these compounds were identified and found to be different from the target compounds used in identification of ignitable liquid residues. Some of the compounds on the other hand were found identical to the target compounds of diesel.

Almirall and Furton (2004) observed a difference in chromatographic patterns for ILR and the patterns for the background, combustion and pyrolysis products. This was also observed in this study. The chromatogram for extracts of Mahogany, MDF and Chipboard and their pyrolysis products were totally different from the chromatographic pattern for gasoline and diesel.

Ettling and Adams (1968) first described the formation of some hydrocarbons during pyrolysis of wood, although they did not identify the compounds. The pyrolysis products of wood identified consisted of highly fused aromatic compounds, straight chained aliphatic and cyclic hydrocarbons. Howard and Mckague, (1984) reported the results of an actual case where compounds benzene, alkyl benzenes and cyclic alkenes were identified as pyrolysis products.

The materials and resins used in the manufacture of chipboard would probably have contributed to the high background interference observed in the chromatogram for the pyrolysis sample. Only two compounds were effectively isolated in this case. These compounds do not show interference with gasoline or diesel.

The compounds identified to elute at same retention times as the target compounds for ILR could give a false positive during analysis that involve only pattern recognition of the ILR. On the other hand, a false negative may be concluded when the ILR compounds are in lower concentration hence lower % abundance, as observed in the results above. Stauffer (2001) emphasizes sample identification based on matching of retention time only is not sufficient in fire debris analysis.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The pyrolysis products of mahogany, medium density fiberboard, chip board and block board, at pyrolysis temperatures of 350 °C and 450 °C, were identified. Chromatographic analysis based on retention time and the % abundance of the compounds eluted revealed possible conflicts between some of the pyrolysis compounds and the target ignitable liquid residues (ILR) compounds of gasoline and diesel. These compounds range from straight chain aliphatic hydrocarbons, cyclic hydrocarbons to highly fused aromatic compounds. The % abundance of the pyrolysis products were higher than the target compounds of gasoline and diesel hence possible shielding of the target compounds during analysis.

However it was observed that chipboard pyrolyzed at controlled temperature of 350 °C and 450 °C produced very few significant and reproducible peaks. The compounds were identified and showed no interference with the target compounds of gasoline or diesel.

A comparison of the pyrolysis products between the sample materials showed similarity in compounds produced at pyrolysis temperatures of 350 °C and 450 °C.

5.2 RECOMMENDATIONS

The presence of pyrolysis products makes it difficult to elucidate and analyze the chromatograms effectively hence may lead to false positive interpretation of the forensic data. On the other hand a false negative conclusion may be reached if the pyrolysis compounds are not known hence disregarding compounds originating from ignitable liquid residues.

a. Therefore Creation of databases of pyrolysis products and ILR are important.

b. Further studies can be done on wood samples through preparation of clean samples and compare their pyrolysis and interfering products to real world situations.

c. The concentrations of the compounds can be studied further since this study mainly focused on the qualitative analysis of the compounds.

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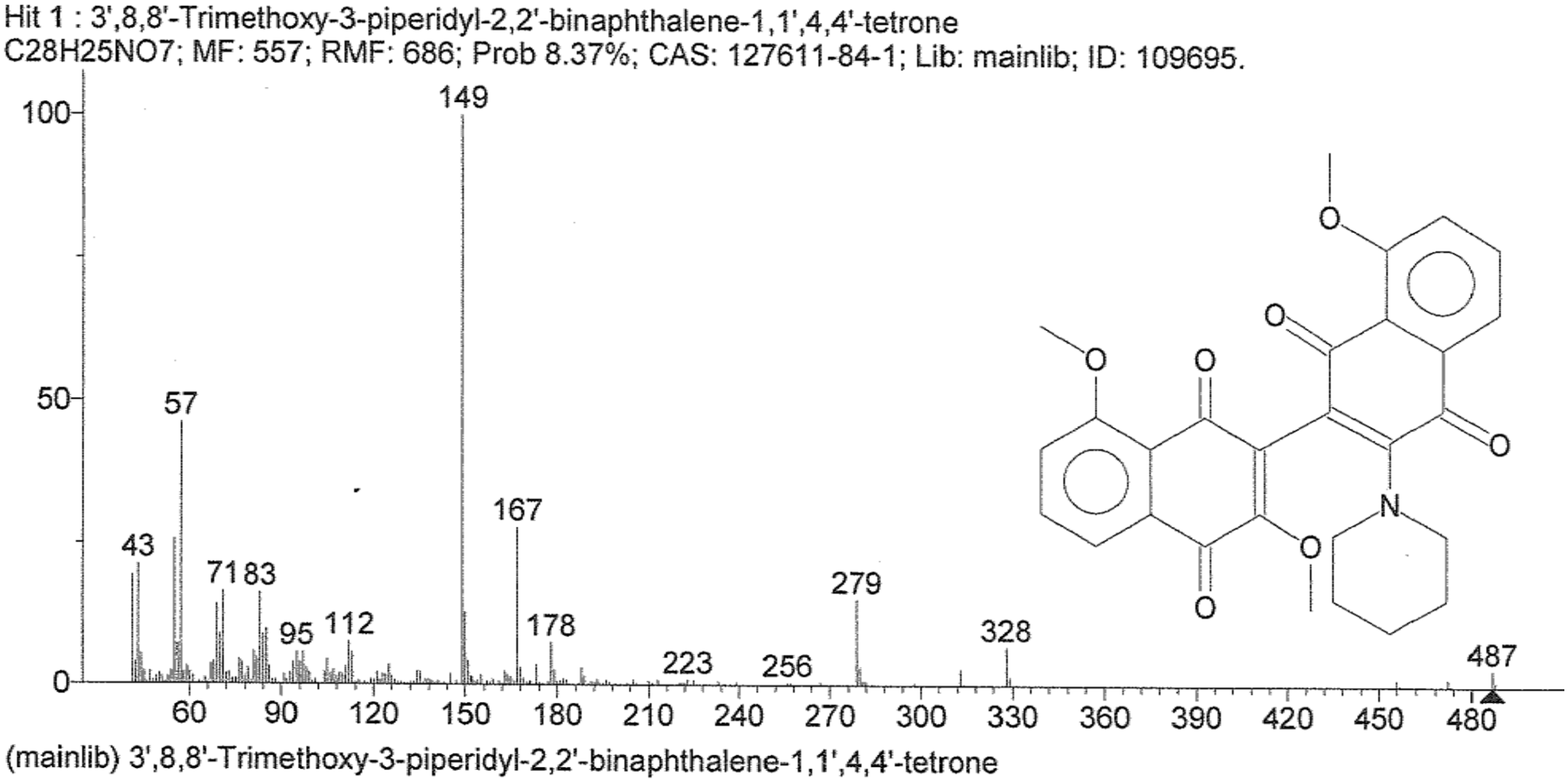
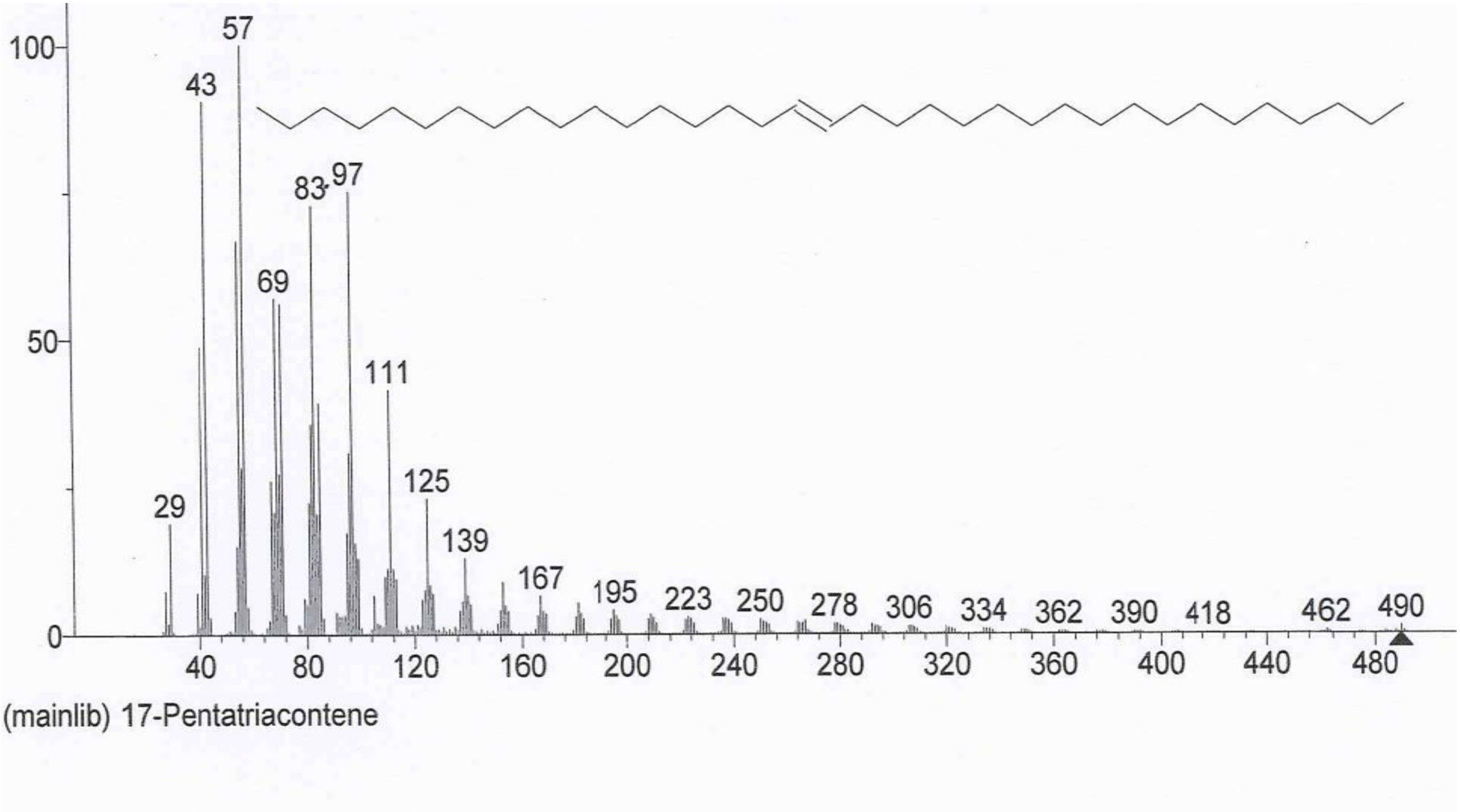
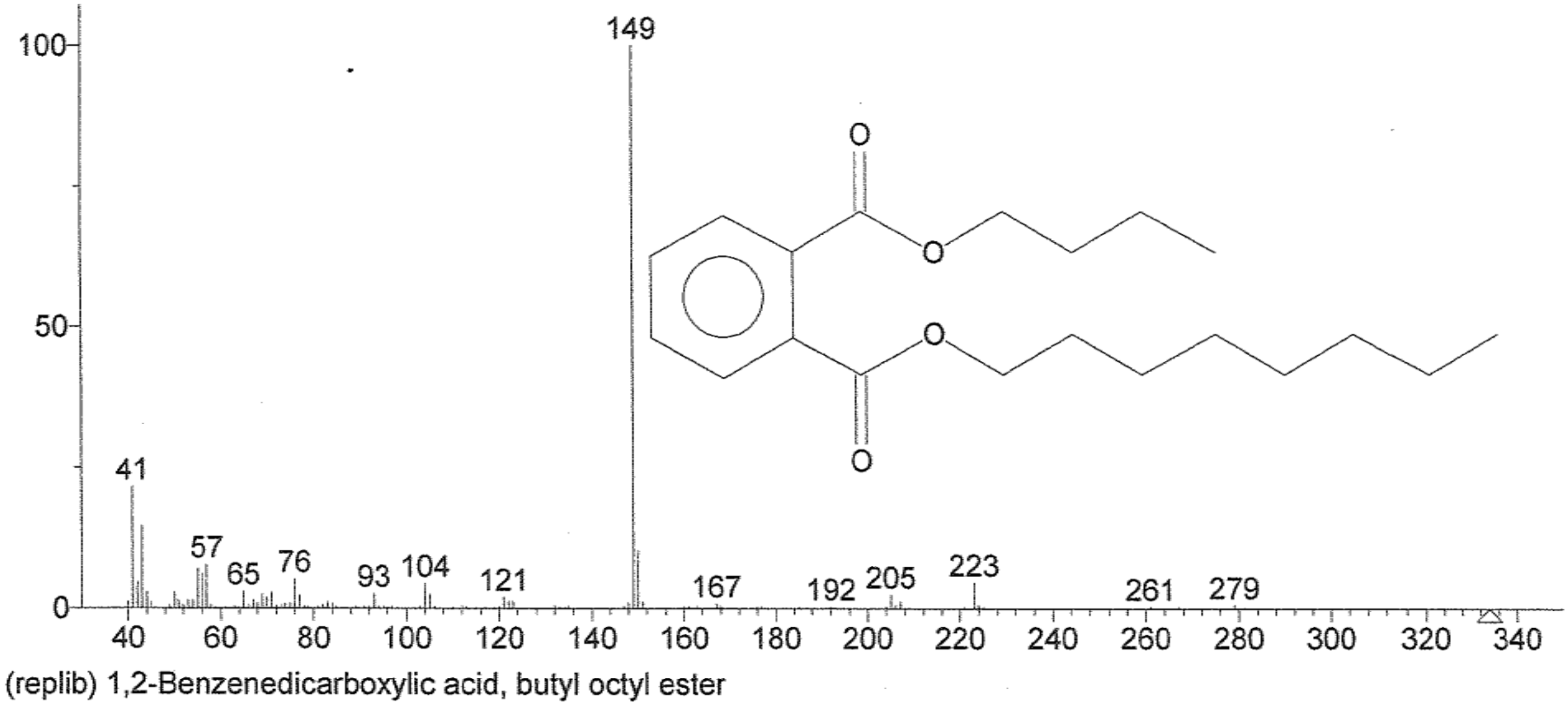
APPENDICES



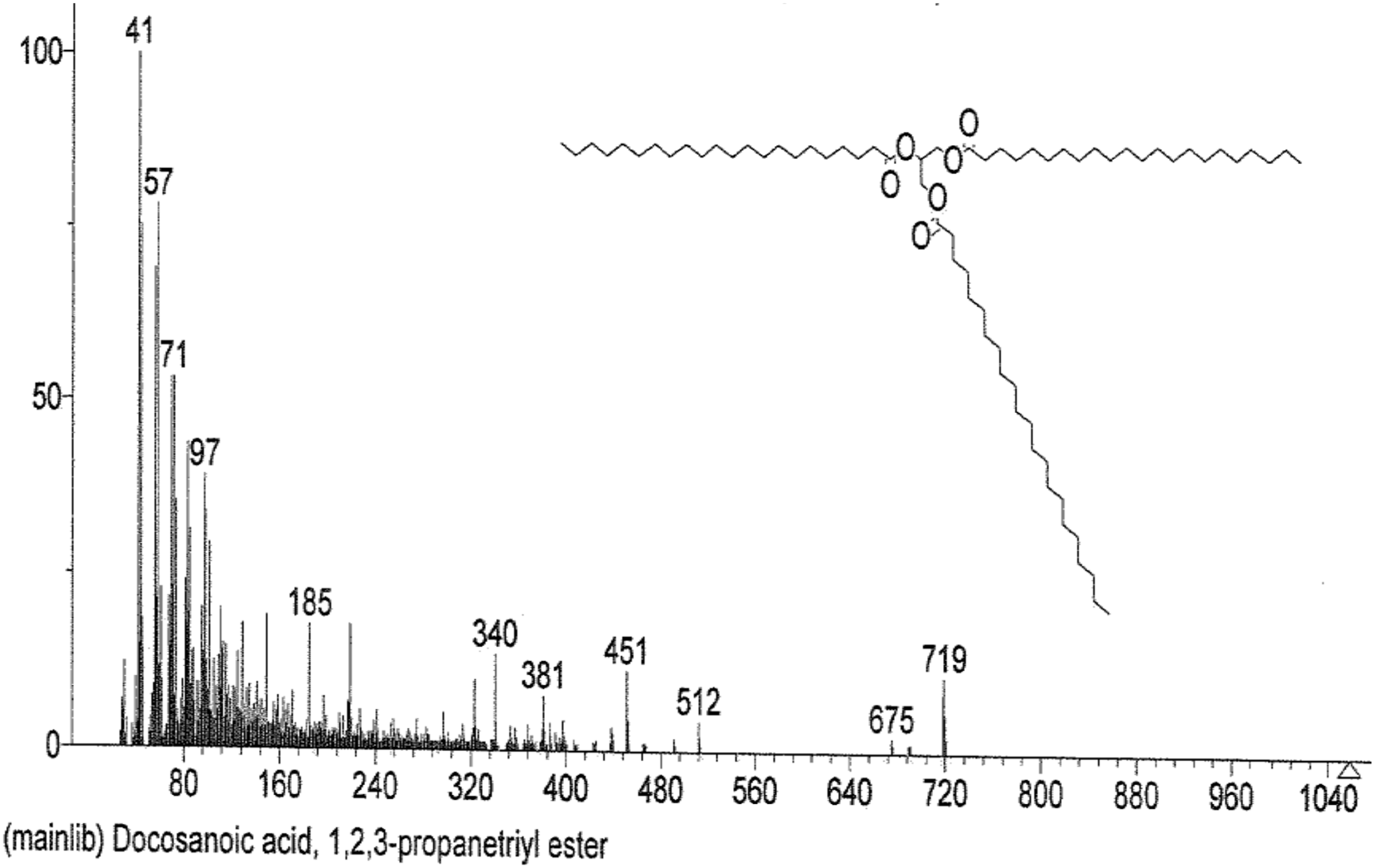
Appendix 1: Mass spectrum for 3, 8, 8-Trimethoxy-3-piperidyl-2, 2-binaphthalene-1, 1, 4, 4-tetrone



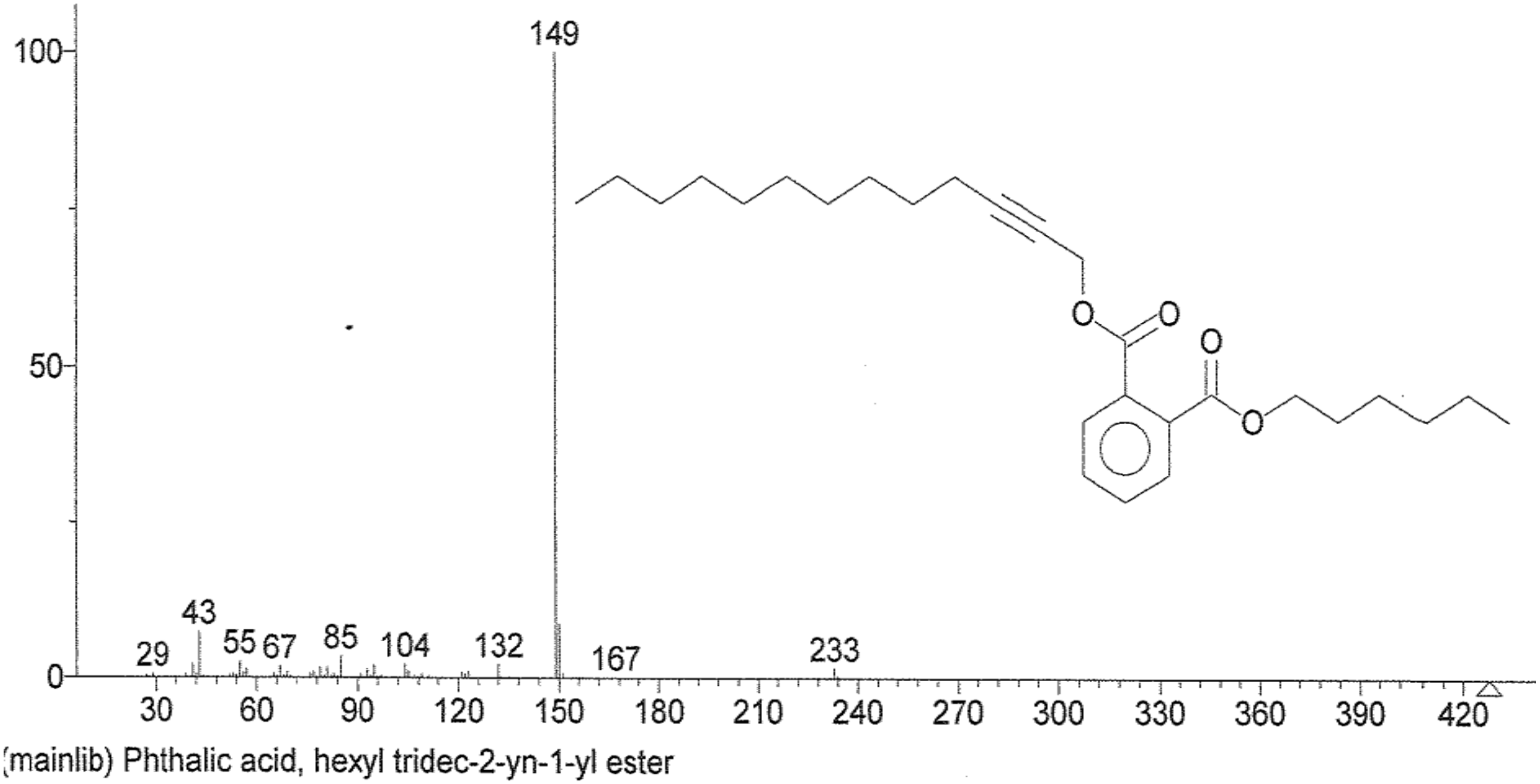
Appendix 2: Mass spectrum for 17-pentatriacontene



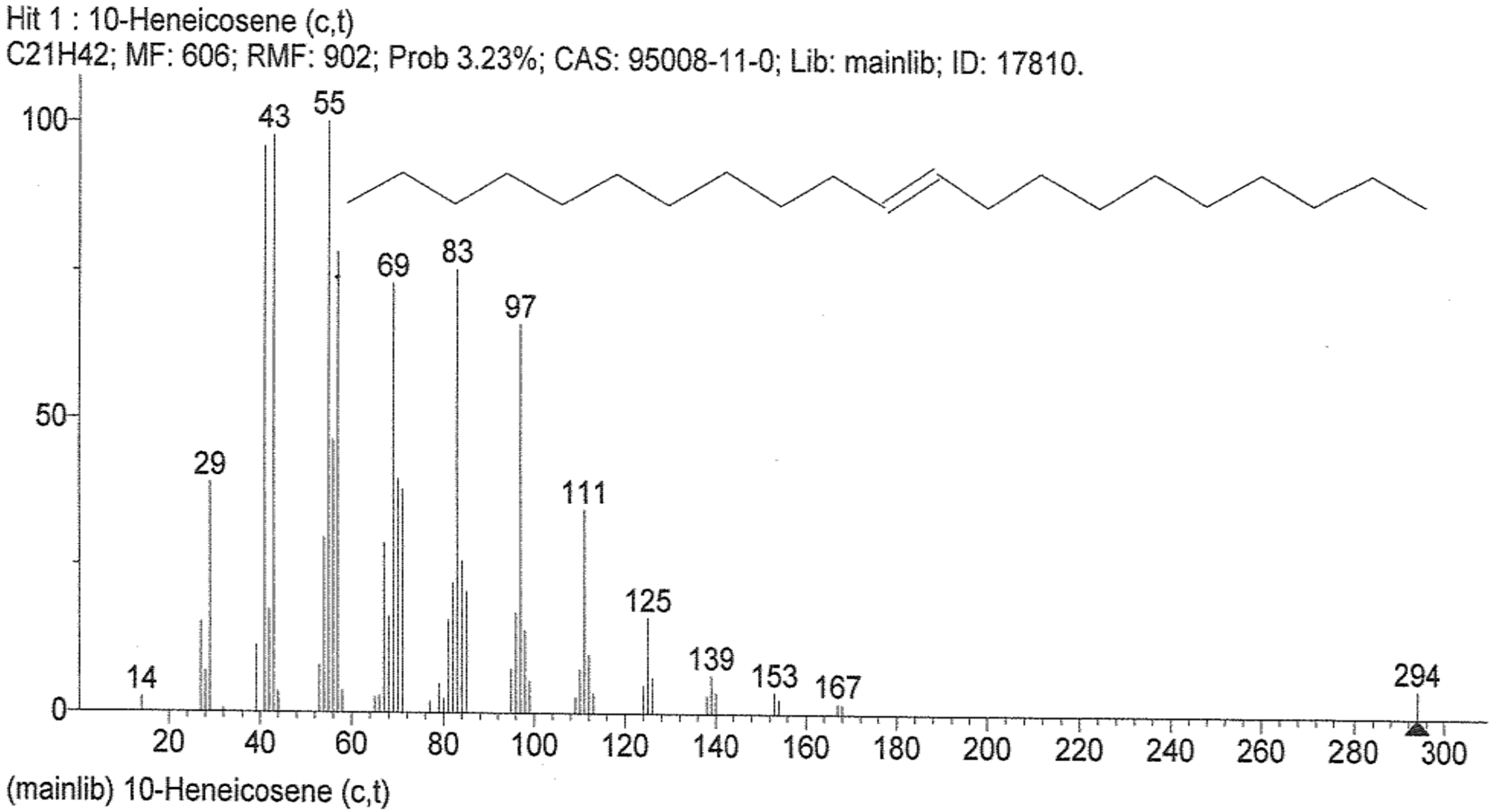
Appendix 3: Mass Spectrum for 1, 2-Benzenedicarboxylic acid, butyl octyl ester



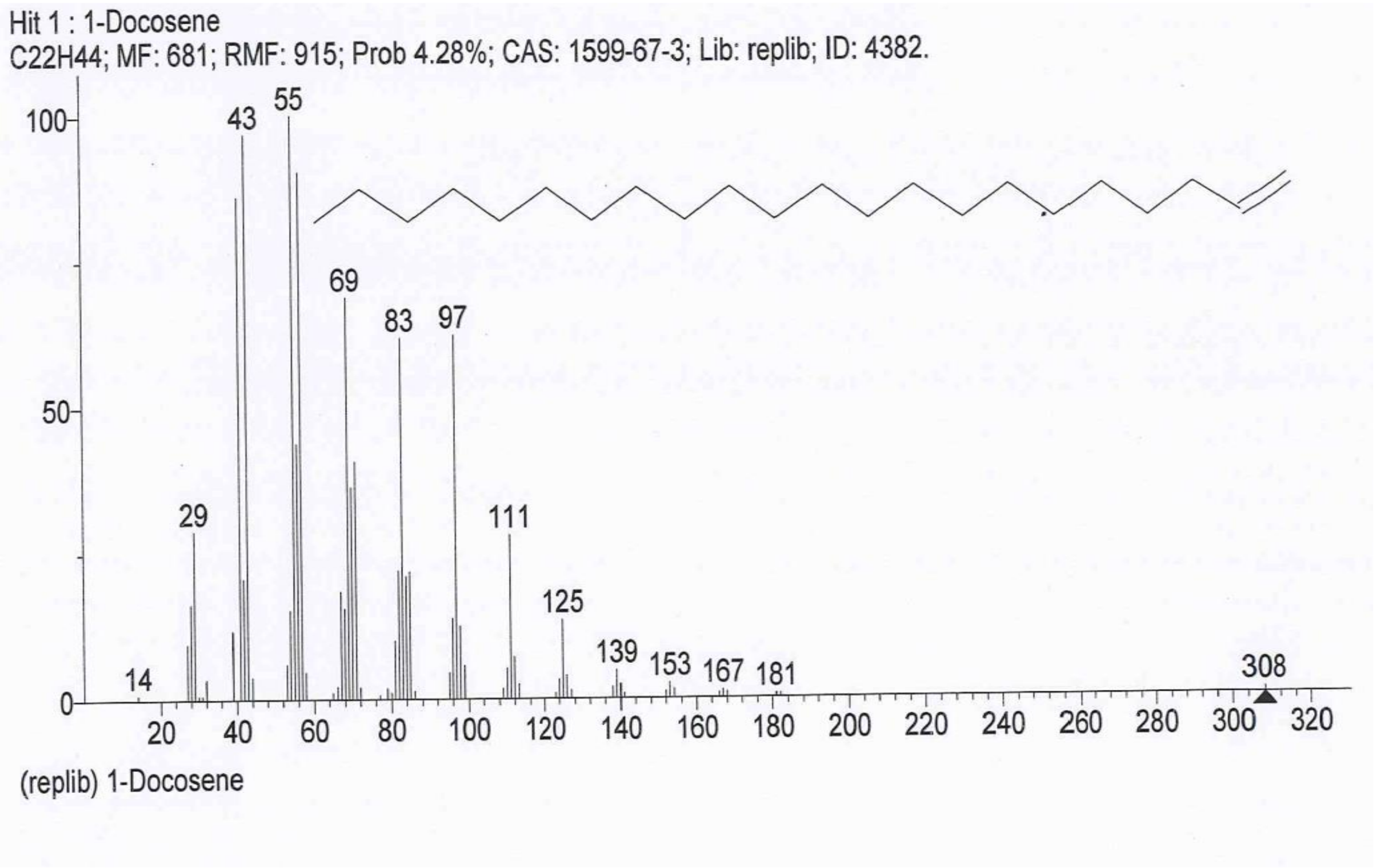
Appendix 4: Mass spectrum for Docosanoic acid, 1, 2, 3-propanetriyl ester



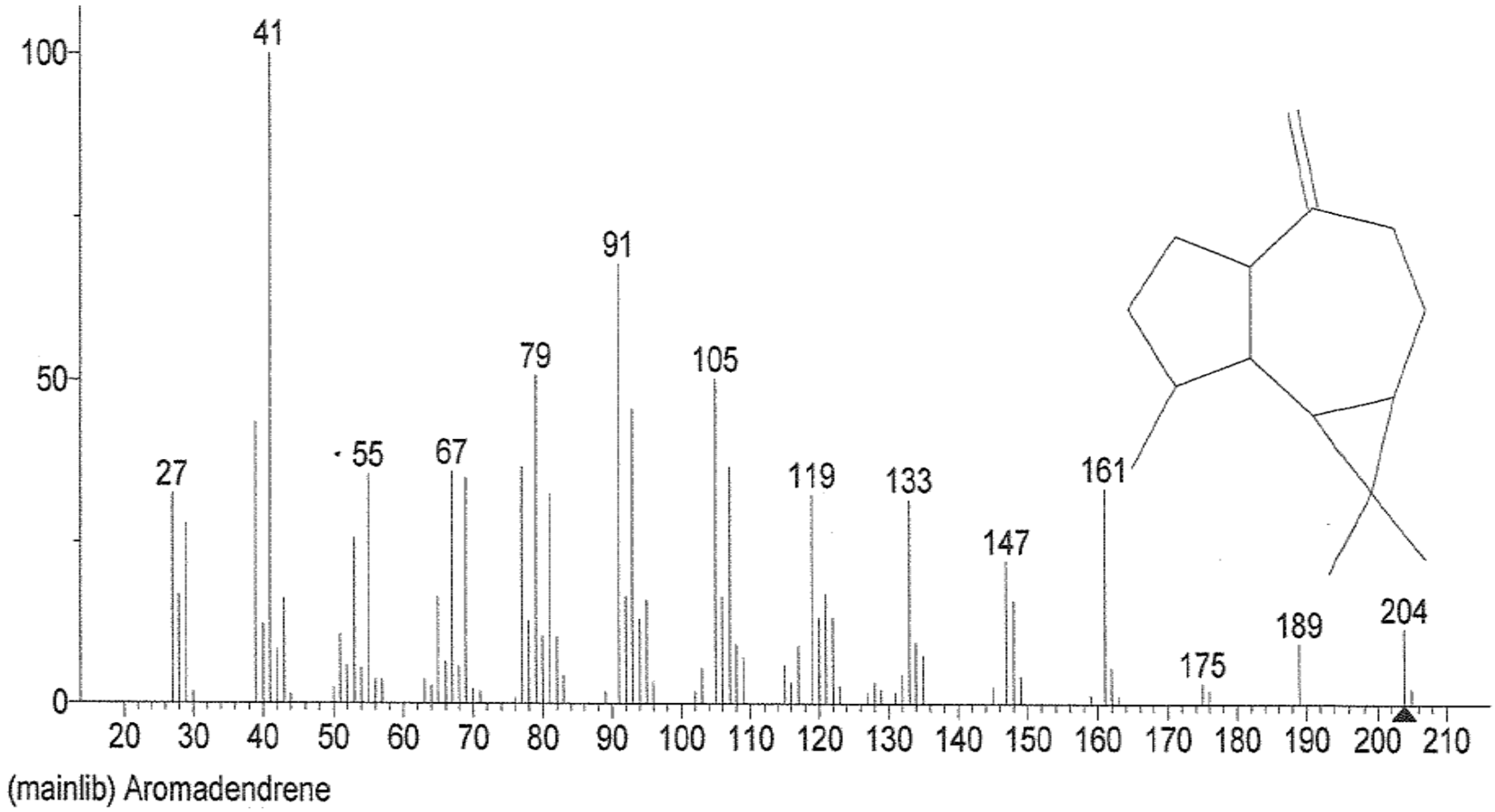
Appendix 5: Mass spectrum for Phthalic acid, hexyl tridec-2-yn-1-yl ester



Appendix 6: Mass spectrum profile for 10-Heneicosene



Appendix 7: Mass spectrum profile for 1-Docosene



Appendix 8: Mass spectrum for Aromadendrene