

**STUDIES ON THE COMPOSITION OF THERMALLY OXIDISED  
FISCHER-TROPSCH WAXES**

A thesis submitted to the  
**UNIVERSITY OF CAPE TOWN**  
in fulfilment of the requirements for the degree of  
**MASTER OF SCIENCE**

by

**DERICK RAYMOND JOHANNES**  
B.Sc. (Hons Polymer Science) *Stellenbosch*

Department of Chemistry  
University of Cape Town  
Rondebosch  
7701  
South Africa

September 1998

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## **ABBREVIATIONS**

AED: Atomic Emission Detector

ASTM : American Standard Test Methods

DSC: Differential Scanning Calorimetry

DMF : Dimethyl formamide

GLC : Gas liquid chromatography

GC-MS: Gas Chromatograph coupled with a Mass Spectrometry

HTGC: High temperature Gas Chromatography

IR: Infrared Spectrometry

FFAP: Crosslinked Polyethylene Glycol-column

PONA: Crosslinked Polydimethylsiloxane column

HO· : hydroperoxide

RO· : alkoxy radical

R· : alkyl radical

RO<sub>2</sub>·: peroxy radical

ROOH : hydroperoxide

FID-GC : Flame Ionisation Detector coupled to the Gas Chromatograph

AED-GC : Atomic Emission Detector coupled to the Gas Chromatograph

### **Explanation of terms used in the dissertation**

'Initial oxidation products': Those oxidation products forming during the early stages of the oxidation which does not involve any chain scission. They have the same carbon chain length as the parent hydrocarbon

'Scission products': Those compounds normally forming later during the oxidation involving rupture of the carbon chain, thus having molecular masses less than those of the parent hydrocarbon. They are formed by the further oxidation of the 'initial oxidation products'.

## ABSTRACT

A composition of thermally oxidised Fischer-Tropsch hard wax was proposed based on a study of the oxidation products of model compounds, n-C16, n-C24 and n-C32. The model compound oxidation yielded isomers of alcohols and ketones with carbon numbers ranging from 2 to the same carbon number as that of the parent hydrocarbon, lactones ranging from carbon 6 to two less than the carbon number equal to that of the highest parent hydrocarbon, acids having carbon numbers ranging from two up to two less than the parent hydrocarbon and straight chain esters in low concentration having molecular mass similar to or higher than the parent hydrocarbon. Only methyl, ethyl and propyl esters of acids with carbon number similar to the parent hydrocarbon, were identified.

Oxidised Fischer-Tropsch hard wax was distilled and the distillate was found to contain similar products to those of the model compounds. No 'new' products were detected which indicated that the same mechanism is occurred in the Fischer-Tropsch oxidation with the production of similar oxidation products as for the model compound oxidation.

Fractionation of oxidised Fischer-Tropsch wax and the analyses of the fractions using IR, DSC and HTGC techniques verified the proposed composition of thermally oxidised Fischer-Tropsch hard wax.

The most important conclusion that can be drawn from the research done for this dissertation, is that none of the analytical results refuted the proposed composition of thermally oxidised Fischer-Tropsch hard wax.

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# 1 INTRODUCTION

## 1.1 Background and Aims of Project

### 1.1.1 Definition of A 'Wax'<sup>(1)</sup>

The term 'wax' has evolved from the Anglo-Saxon 'weax', a name given to the substance obtained from the honeycomb of the bee. It is nowadays difficult to provide a simple definition of the word 'wax' because many compounds of different chemical composition are termed 'waxes'. The name, in various languages, refers to beeswax and it appears that the properties of this material have established a generally accepted notion of the characteristics of a 'wax'. The characteristic properties of a 'wax', when one considers beeswax, leads one to expect that such a material would generally be:

- solid at normal ambient temperatures,
- of appearance and feel similar to beeswax
- very fluid when molten (i.e. melt has low viscosity just above its melting point),
- able to resolidify after melting and cooling,
- insoluble in water (water-proof)
- combustible
- capable of providing a glossy finish to surfaces after polishing by rubbing lightly.

These are the properties that most naturally occurring waxes possess. However, with developments in technology, more and more substances, of different chemical compositions but displaying the properties given above, have become commercially available and have been given the name 'wax'. They comprise waxes of plant, insect and animal origin as well as from mineral sources (e.g. petroleum) and from chemical synthesis. These waxes all display, to a greater or

lesser degree, the same general waxy characteristics, in appearance, feel, consistency and in their melting and solidification behaviour. Therefore, the term 'wax' has no chemical significance unless it is further defined, e.g. paraffin wax, natural ester wax, Fischer-Tropsch wax, etc.

The older chemical definition distinguishes waxes from fats and oils. Fats and oils were defined as consisting of various esters of glycerol and fatty acids with the acids having chain lengths of  $C_{16}$ - $C_{20}$ , while the plant and animal waxes consist mainly of mixed esters of higher molecular mass acids and higher molecular mass alcohols. This definition, however, excludes the hydrocarbon waxes, synthetic waxes and certain natural ester waxes.

The more modern definition of a 'wax' includes substances conforming to the characteristic properties as listed above. However, the list represents a broad generalisation of properties, and individual waxes which vary widely within these properties are also termed 'waxes'. Included in this definition are waxes which are chemically modified (e.g. by oxidation, which entails the reaction of oxygen with the hydrocarbon molecules of the wax) to produce new materials, and waxes which are blended to produce a range of physical properties very different to the original waxes. Such techniques can tailor waxes to suit particular applications.

### 1.1.2 Fischer-Tropsch Waxes

Fischer-Tropsch waxes are produced in a process which reacts carbon monoxide and hydrogen over an iron or cobalt catalyst to give the hydrocarbon and water.<sup>(2)</sup> Fischer-Tropsch waxes comprise mainly long straight-chain saturated hydrocarbons with only a very small proportion of branched molecules. They are of a higher average molecular weight than the petroleum paraffin waxes<sup>(1)</sup>. Table 1 lists the major differences between Fischer-Tropsch wax and

paraffin wax.

**Table 1 : Comparison of characteristics of Fischer-Tropsch wax and paraffin wax**

<b>Fischer-Tropsch wax</b>	<b>Paraffin wax</b>
synthetic wax	natural wax
mostly normal paraffins	fair amount of branched paraffins
no cyclic compounds	contains cyclic compounds
low viscosity	medium viscosity
high melting point	intermediate melting point
relatively hard wax	medium to soft wax

### 1.1.3 Fischer-Tropsch Process

In the initial stages of the process, coal or other carbon-containing material is gasified to produce synthesis gas, composed primarily of carbon monoxide and hydrogen. The Fischer-Tropsch process converts the synthesis gas components to a wide range of hydrocarbons, spanning methane to the hard waxes of carbon numbers up to approximately 100.

The distribution of Fischer-Tropsch products is governed by the Anderson-Shulz-Flory polymerisation law<sup>(3)</sup>. The law states that the stepwise chain growth is independent of the length of the carbon chain. The stepwise chain growth probability is dependent on the operating conditions (temperature and pressure), gas composition and the composition of the catalyst. These factors are responsible for the spread of products formed during the synthesis.

In the Fischer-Tropsch process, it would be desirable to tailor the reaction to form a single type of product by the careful selection of catalyst and choice of operating conditions. However, the consequence of the law is that a wide range of products is formed. It is generally desired to form a particular product for which there is a demand in the market, such as transportation fuels.

However, due to the Anderson-Shulz-Flory law, the theoretical yield of the transportation fuels is low in relation to the by-products. To obtain the necessary yield of the desired product, a surplus of the by-products is produced.

Fischer-Tropsch hard wax can be considered to be a by-product in the production of the medium waxes for which there is a demand, especially for the candle industry. Ways to modify the Fischer-Tropsch hard wax and increase the number of possible applications, are continuously being investigated. Oxidation of the Fischer-Tropsch wax is one of the ways of functionalising the wax. The oxidised Fischer-Tropsch wax has different properties when compared to the unfunctionalised Fischer-Tropsch waxes. For instance, it can be saponified with various cations, it is easier to emulsify and has better solvent retention than the unfunctionalised Fischer-Tropsch waxes. It can therefore be used in applications which are different to those of the unfunctionalised Fischer-Tropsch waxes. For example some of the applications of oxidised Fischer-Tropsch waxes are in solvent paste furniture formulations, in floor and automotive polish formulations, as anti-corrosion coatings for metals and as industrial emulsions in textile processing. On the other hand, unfunctionalised Fischer-Tropsch hard waxes are used as hardening and finishing agents in the manufacture of candles, as additives which improve and control setting characteristics in the manufacture of hot melt adhesives and also as a component in chewing gum base.<sup>(2)</sup>

#### 1.1.4 Bubble Reactor

Fischer-Tropsch hard wax is oxidised in a bubble reactor at Sasol. A diagram of a typical laboratory bubble reactor is given in Figure 1.

The wax to be oxidised is put in the reactor and is heated to the temperature required for the oxidation. Air or oxygen is then passed through a porous frit to form bubbles with the oxygen inside the bubble contacting the liquid at the liquid/gas interface. The oxidation reaction occurs either at this bubble interface or if the transfer of oxygen from the bubble is efficient, in the bulk of the liquid. The rate of oxidation is determined by a number of factors, namely, air or oxygen flow rate, temperature of the reaction, and porosity of the frit, which determines the size of the bubbles and the surface area for the oxidation reaction.

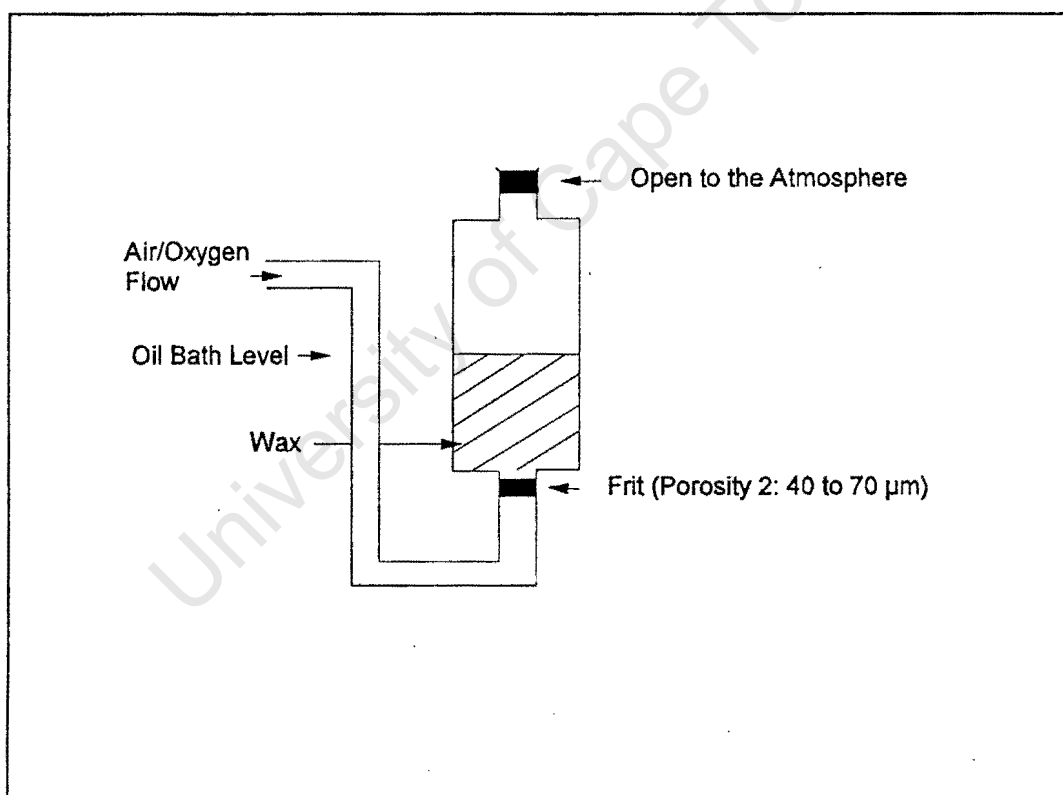


Figure 1: DIAGRAM OF A TYPICAL LABORATORY BUBBLE REACTOR

### 1.1.5 Mass Transfer in Liquid Phase Oxidations

In the liquid-phase oxidation of hydrocarbons oxygen must diffuse through the gas-liquid interface before reaction can occur in the liquid bulk. This rate of diffusion is often the rate-limiting step in the overall process. Therefore, the rate of diffusion of oxygen is an important

parameter in determining the products of the autoxidation reactions. In the oxidation reaction, the rate of the reaction is limited by mass transfer and the reaction takes place at the surface of the air bubbles, i.e. the reaction takes place at the gas-liquid interface. This localisation of the reaction to a small surface area can lead to higher temperatures at the surface of the bubble relative to the bulk liquid because the small surface area has to absorb the heat of the oxidation reaction. Therefore, the temperature in the liquid bulk is expected to be considerably lower than that of the film. Higher temperatures could cause degradation to unwanted products due to over-oxidation. Also, as the reactive intermediates accumulate in the film, they have a higher probability of reacting with each other rather than with oxygen. Certain reactions in the autoxidation scheme, as given in Section 1.1.7, need a high concentration of oxygen while others proceed without oxygen. Because the oxygen is consumed within a short distance of the bubble-liquid interface, the concentration of oxygen in the bulk liquid is essentially zero. There will be a large build up of product and reactive intermediates in the film relative to the bulk liquid. The reactions occurring in the film will therefore be different to the reactions occurring in the bulk liquid because of the relative availability of oxygen and the difference in temperature.<sup>(4)</sup>

### 1.1.6 Autoxidations

*Hawley's Condensed Chemical Dictionary*<sup>(5)</sup> defines autoxidation as:

' A spontaneous, self-catalyzed oxidation occurring in the presence of air, it usually involves a free-radical mechanism. It is initiated by heat, light, metallic catalysts or free-radical generators. Industrial processes, such as production of phenol and acetone from cumene are based on autoxidation. Other instances are the drying of vegetable oils, the

spoilage of fats, gum formation in lubricating oils and the degradation of high polymers exposed to sunlight for long periods.'

Reaction of an organic substance with molecular oxygen under mild conditions is termed autoxidation. It is an everyday phenomenon, examples of which include the atmospheric deterioration of food, rubber, paintwork and lubricating oils.<sup>(6)</sup>

These autoxidations have been studied in the past<sup>(7)</sup> in an effort to find methods to prevent or inhibit its occurrence. For instance, antioxidants have been developed to improve the thermal oxidative stability of mineral oils. A study of the action of antioxidants<sup>(7)</sup> was made to find the most effective method of increasing the stability of the hydrocarbons in mineral oil towards oxidation. The relation between the structure of substituted phenols and their ability to react or interact with the intermediate products of the oxidation was studied.<sup>(7)</sup>

Useful applications of autoxidation include the atmospheric drying of linseed oil paints<sup>(6)</sup> and the oxidation of petroleum hydrocarbons under controlled conditions to produce starting materials for the production of detergents, organic solvents, man-made fibres, etc.<sup>(8)</sup>

More recent active interest in autoxidation is in the mechanism, property changes and kinetics of the photo degradation and photo-oxidation of polymers. All unstabilised organic polymers undergo degradation or oxidation when exposed to UV solar or artificial radiation. With an increase in the harshness of the conditions to which these materials are exposed, especially in outdoor applications, there is ever increasing pressure on manufacturers to provide more rigorous stabilisation methodologies to overcome the various environmental problems.<sup>(9)</sup>

The basic means of propagation of these autoxidation reactions was at first not clear. It was apparent that many autoxidations were chain reactions but the nature of the chain carriers were not known. Excited molecules and transient cyclic peroxides were amongst the species

proposed. The peroxide theory of autoxidation was first formulated by Bach<sup>(10)</sup> and Engler<sup>(11)</sup> in the 1890's. Farmer *et al.*<sup>(12)</sup> and Baseman and Gee<sup>(13)</sup> also conducted studies to elucidate the process of autoxidation. Eventually, with the identification of hydroperoxides, Bolland<sup>(14)</sup> and Bateman<sup>(15)</sup> proposed the modern theory that autoxidations proceeded by a free radical mechanism. Emanuel<sup>(16)</sup> conducted detailed chemical research on the chain oxidation process while working independently in the USSR.

### 1.1.7 Mechanism of Autoxidation

In order to explain the low-temperature liquid-phase oxidation of hydrocarbons, Emanuel<sup>(17)</sup> proposed the following mechanism:

- (1)  $\text{RH} \rightarrow \text{R}\cdot + \cdot\text{H}$
- (2)  $\text{R}\cdot + \text{O}_2 \rightarrow \text{RO}_2\cdot$
- (3)  $\text{RO}_2\cdot + \text{RH} \rightarrow \text{ROOH} + \text{R}\cdot$
- (4)  $\text{RO}_2\cdot + \text{RO}_2\cdot \rightarrow \text{ROOR} + \text{O}_2$
- (5)  $\text{ROOH} \rightarrow \text{RO}\cdot + \cdot\text{OH}$
- (6)  $\text{RO}\cdot + \text{RH} \rightarrow \text{ROH} + \text{R}\cdot$
- (7)  $\text{HO}\cdot + \text{RH} \rightarrow \text{H}_2\text{O} + \text{R}\cdot$
- (8)  $\text{ROOH} + \text{RH} \rightarrow 2\text{ROH}$
- (9)  $\text{ROOH} \rightarrow \text{R}_1\text{COR}_2 + \text{H}_2\text{O}$
- (10)  $\text{ROH} \rightarrow \text{R}_1\text{COR}_2$  (oxidation)
- (11)  $\text{R}_1\text{COR}_2 \rightarrow \text{acids}$

( $\text{R}_1$  and  $\text{R}_2$  indicate breakdown products of peroxides and the alcohols.)

The mechanism of the autoxidation consists of a number of elementary steps. Oxidation proceeds with the participation of a number of short-lived active centres ( $R\cdot$ ,  $RO\cdot$ ,  $RO_2\cdot$ , and  $HO\cdot$  radicals), as well as long living intermediates ( $ROOH$ ). The active centres,  $RO\cdot$  and  $HO\cdot$  radicals, react very rapidly with the substrate, for example



i.e., they will be transformed to  $R\cdot$  type radicals.

Thus, the chain-carrying radicals of the autoxidation are  $R\cdot$  and  $RO_2\cdot$ .

The initiation of the autoxidation process usually occurs by thermal initiation, by UV solar radiation or by artificial radiation, i.e. by a process capable of providing sufficient energy for reaction (1) to proceed.

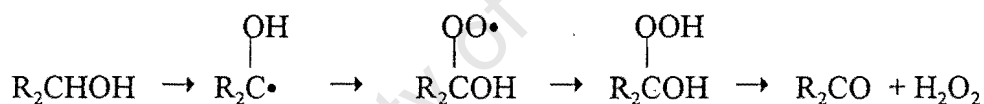
The chain propagation cycle of the autoxidation is represented by reactions (2) and (3).<sup>(18)</sup> The reaction between the alkyl radical and oxygen takes place at a very fast rate, with the rate constant of the order of  $10^7$  to  $10^8 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ . This is due to the high reactivity of both the molecular oxygen and the alkyl radicals. It is an exothermic reaction, liberating  $117 \text{ kJ mol}^{-1}$ .<sup>(19)</sup>

The abstraction of hydrogen in reaction (3) occurs more readily if  $R\cdot$  is stabilised by resonance. The composition of the hydrocarbon plays an important role in the rate of autoxidation. Hydrocarbons containing a hydrogen atom 'activated' by a neighbouring carbonyl, olefinic or aromatic system autoxidise readily, whereas saturated hydrocarbons are more stable and require higher temperatures for the autoxidation.<sup>(6)</sup> The energy of activation of the reaction between the peroxy radical and the hydrocarbon (reaction 3) varies from 12,5-20,9  $\text{kJ mol}^{-1}$  for the very active compounds, such as certain dienes and allyl ethers, through 20,9-41,84  $\text{kJ mol}^{-1}$  for alkenes and the alkyl aromatic compounds to 41,84-62,76  $\text{kJ mol}^{-1}$  for the alkanes.<sup>(15)</sup>

The breakdown of hydroperoxides according to reactions (8) and (9) leads to the production of

alcohols and ketones. The rate of decomposition of the hydroperoxides depends on the medium in which the reaction occurs. Substances such as water and alcohols<sup>(20)</sup> or carboxylic acids,<sup>(21)</sup> which are capable of forming hydrogen bonds with the hydroperoxide, accelerate the decomposition. The bond energy of the hydroperoxide (ROO-H) amounts to 368 kJ mol<sup>-1</sup> and is larger than the bond energy for the carbonyl (H-CH<sub>2</sub>COR) which is 360 kJ mol<sup>-1</sup> but less than the C-H bonds in saturated hydrocarbons. The reactivity of the C-H bond increases from primary to tertiary. The bond energies are 385 kJ mol<sup>-1</sup>, 410 kJ mol<sup>-1</sup> and 439 kJ mol<sup>-1</sup> for the tertiary, secondary and primary hydrocarbons, respectively.<sup>(18)</sup>

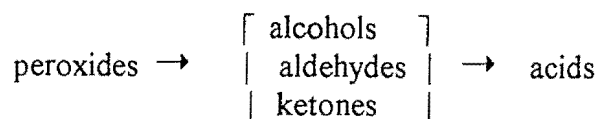
Ketones are also formed by the oxidation of secondary alcohols according to reaction (10) and by the following mechanism:<sup>(23)</sup>



Acids are produced from ketones according to reaction (11), which involves the rupture of the carbon skeleton. The carboxylic acids are much more resistant to the conditions of liquid oxidation. The acids are thus easier to isolate than the alcohols and the ketones. However, the acids do react, but at a much slower rate than the alcohols and ketones. The  $\beta$ -carbon is easiest to attack to form hydroxy acids and, to a larger extent, the keto acids. The authors<sup>(23)</sup> claim that under normally used process conditions, esterification reactions are also taking place. These reactions are non-radical reactions and large portions of acids and alcohols react to form esters which are as stable as the acids. They claim that the esters are, after the hydroperoxides, alcohols, aldehydes, ketones and acids, the most important products of the autoxidation. This dissertation will show that the esters present among the reaction products are mostly cyclic esters formed by

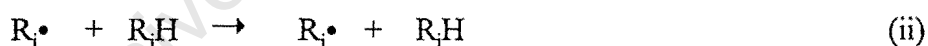
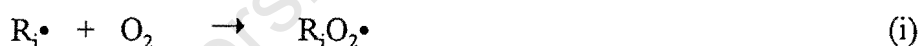


represented by the following scheme:



All the stages occur by chain mechanisms, although simple molecular conversions cannot be excluded.<sup>(18)</sup> A variety of products result from the autoxidation of hydrocarbons. However, the concentration of hydroperoxides passes through a maximum and then diminishes, while the concentration of alcohols and ketones establishes itself at a certain level, and the concentration of acids increases continuously. Up to the present time peroxy radicals have been considered to play a major role in liquid phase oxidation and the alkyl radicals were thought to play no practical part in the oxidation.<sup>(23)</sup>

Recently it has been established<sup>(27)</sup> that in multi-component systems (typical of Fischer-Tropsch wax oxidations) the following competing reactions may also be important:



The second reaction (ii) leads to a complete stop in the consumption of component  $R_jH$ . The probability of this reaction occurring depends on the difference in activation energy of the two reactions and also on the oxygen concentration. For instance, the formation of oxidation products with relatively weak C-H bonds or the lack of oxygen may cause alkyl radicals to play a significant role in the autoxidation reactions via reaction (ii).

### 1.1.8 Aims of the Project

Various methods of functionalising hard wax to increase its applicability in the industry have been successfully employed at Sasol. Fischer-Tropsch waxes are straight-chain

hydrocarbons with a normal carbon-number distribution spanning approximately 28 to 100 and with an average carbon number of approximately 50.

The oxidation of the waxes yields a complex array of oxygenates, as indicated by the mechanism of the autoxidation discussed in Section 1.1.7. The oxidation process entails bubbling oxygen or air through molten wax at temperatures above 130°C. The oxidation is terminated when a specific desired acid value\* is reached. The resulting oxidised waxes have complex compositions with high molecular masses, making analysis by the conventional analytical techniques presently available, almost impossible.

Fischer-Tropsch hard waxes are oxidised to various acid values, depending on their area of application. Although the technology to produce oxidised waxes has been established and practised for a number of years, very little is known or has been published on the structure and composition of these waxes. However, it is becoming increasingly important to know the composition of these oxidised waxes in order to understand the role that the different components in these waxes play in their various applications. Information on the structure and composition of the oxidised wax is also necessary for both the further modification of the oxidised wax and the manipulation of the oxidation process to produce waxes with specific functionalities.

This dissertation will provide an insight into the composition of the thermally oxidised Fischer-Tropsch hard wax.

To accomplish this the research was focused on the following:

\* **Acid value** : Quantity of base expressed in milligrams of KOH per gram of sample that is required to titrate a sample to a specified endpoint.

- *Oxidation and analysis of model compounds, namely hexadecane (n-C16), tetracosane (n-C24) and dotriacontane (n-C32).* Results from these oxidations will give an indication of the typical oxidation products of long-chain hydrocarbons and indicate whether different products are formed when the chain length of the hydrocarbon changes.
  
- *Vacuum distillation of the Fischer-Tropsch oxidised wax and analysis of the distillate.* These results will show that the lighter fraction of Fischer-Tropsch wax, which can be analysed using available analytical techniques, has the same composition as the oxidised model compounds.
  
- *Separation of the oxidised wax into fractions using a silica gel column and analysis of these fractions.* These results will show that the Fischer-Tropsch wax has essentially the same distribution of oxidation products as the model compounds, but only of longer chain length.

From the results of the above, a general composition of the oxidised hard wax will be proposed.

## 2 HISTORICAL REVIEW OF AUTOXIDATION

### 2.1 General Review of Oxidation

#### 2.1.1 Fatty Acids From Wax

In Germany, during the 1950's, fatty acids were produced from the oxidation of a paraffin wax which comprised saturated hydrocarbons containing about 20 - 25 carbon atoms.<sup>(28)</sup> It was claimed that fatty acids of various molecular masses were produced, ranging from formic acid to the acid with the same number of carbon atoms as the highest hydrocarbon present. However, this is contrary to the results obtained in the present work on the model compound oxidations (Section 3.3), where only acids with carbon numbers up to two less than the parent hydrocarbon could be detected. After distillation of these fatty acids to remove them from the other oxygenates, synthetic soaps, which were equivalent in detergent action to the soaps from vegetable or animal fats and oils, were made from them.

#### 2.1.2 Some Factors Affecting the Rate of Oxidation

In the oxidation of higher molecular mass hydrocarbons, the oxidation occurs via the hydroperoxide intermediate, and the production of fatty acids takes place statistically.<sup>(29)</sup> Initially, equimolar amounts of all the theoretically possible fatty acids are formed. It has been observed that the concentration of lower fatty acids is larger than that expected from the theoretical considerations.<sup>(29)</sup> This implies that the lower fatty acids originate from the further oxidation of higher fatty acids. This assumption is supported by the work of Zerner,<sup>(30)</sup> who further oxidised natural fatty acids. He found that stearic acid (18 carbon atoms) was readily attacked by atmospheric oxygen with the formation of lower fatty acids, hydroxy acids, dicarboxylic acids and

carbon dioxide. Lauric acid (12 carbon atoms) is attacked substantially less and caprylic acid (8 carbon atoms) is scarcely attacked at all.

Oxidation of higher hydrocarbons takes place at different rates, depending on the purity of the starting material. Oxidation-inhibiting materials present in the reaction mixture, such as sulfur containing compounds, increase the induction period and will continue to inhibit the oxidation until they are destroyed by the oxidation process. The reaction then progresses in the same way as for pure waxes. If the wax contains no reaction-inhibiting materials but substantial amounts of cyclic or unsaturated material, the reaction will start at a reasonable rate but the rate will decrease or even stop completely due to the formation of oxidation inhibiting materials.<sup>(29)</sup>

### 2.1.3 Role of Peroxides in the Oxidation of Hydrocarbons.

Peroxides play an important role in the liquid-phase oxidation of hydrocarbons. Evidence that they are the primary intermediate products of the oxidation process is given in the work on the liquid-phase oxidation of alkyl aromatics and alicyclic hydrocarbons by Robertson,<sup>(31)</sup> Farmer,<sup>(32)</sup> and Bolland.<sup>(33)</sup> They found that during the initial stages of the oxidation the amount of peroxides formed corresponded directly to the amount of oxygen consumed. As the reaction proceeded this was no longer so and the amount of oxygen consumed exceeded the amount of hydroperoxides formed. They concluded that for these products, during the initial stages of the oxidation, hydroperoxides were virtually the only oxidation products. At later stages, processes leading to the production of oxygenated products other than peroxides start to play a role. In the oxidation of saturated hydrocarbons and cycloparaffins, a significant amount of peroxides which are more stable to oxidation is formed.<sup>(34,35)</sup> In these cases, because of the higher temperatures needed for the further decomposition of peroxides to reach significant proportions, stable

oxidation products are detected, together with peroxides, at the beginning of the reaction.

The rate of decomposition of the hydroperoxide and the subsequent formation of stable oxidation products was studied by Maizius.<sup>(36)</sup> The reaction was stopped at various stages during the oxidation and purged with nitrogen. This allowed the study of the oxidation products at the temperature of their formation. It was found that the formation of the stable oxidation products, namely ketones, alcohols, esters and acids, was proportional to the rate of decomposition of the hydroperoxide. Hydroperoxides of the type ROOH are the major intermediate products of the oxidation of all classes of hydrocarbons, namely, paraffins, olefins, aromatics, etc. The unimolecular decomposition of these hydroperoxides ( $\text{ROOH} \rightarrow \text{RO}\cdot + \cdot\text{OH}$ ) generates new radicals which are responsible for the autocatalytic nature of the process. Maizius concluded that the hydroperoxides were the primary products of the oxidation and that the alcohols and ketones formed as a result of the decomposition of the hydroperoxides. The esters were formed from other processes not involving hydroperoxides but rather involving alcohols and acids while the acids were formed by the decomposition of ketones.

#### 2.1.4 Position of Primary Oxidation Products on the Hydrocarbon Chain

Attempts have been made to determine the position of the primary oxidation products on the hydrocarbon chain by studying the autoxidation of n-hexadecane.<sup>(37)</sup> The oxidation was stopped at the alcohol stage by oxidising in the presence of boric acid. The boric acid reacts with the alcohols which form, thus preventing the alcohols from reacting further to form secondary oxidation products. The boric acid esters were then hydrolysed and the alcohols analysed by chemical methods. It was found that during the initial stages of the oxidation of hydrocarbons, i.e. up to the formation of alcohols, no degradation of the hydrocarbon chain occurs. Oxidation

of hydrocarbons leads to the formation of all the possible isomers of the secondary alcohols with the same number of atoms as the original hydrocarbon chain. The secondary alcohols are found in practically equal amounts. The authors<sup>(37)</sup> therefore concluded that the longer chain hydrocarbons will behave similarly and have the same structure of secondary alcohols as in the hexadecane oxidation. Primary alcohols having the same number of hydrocarbons as the parent molecule were absent.

### 2.1.5 Oxidation of Olefins

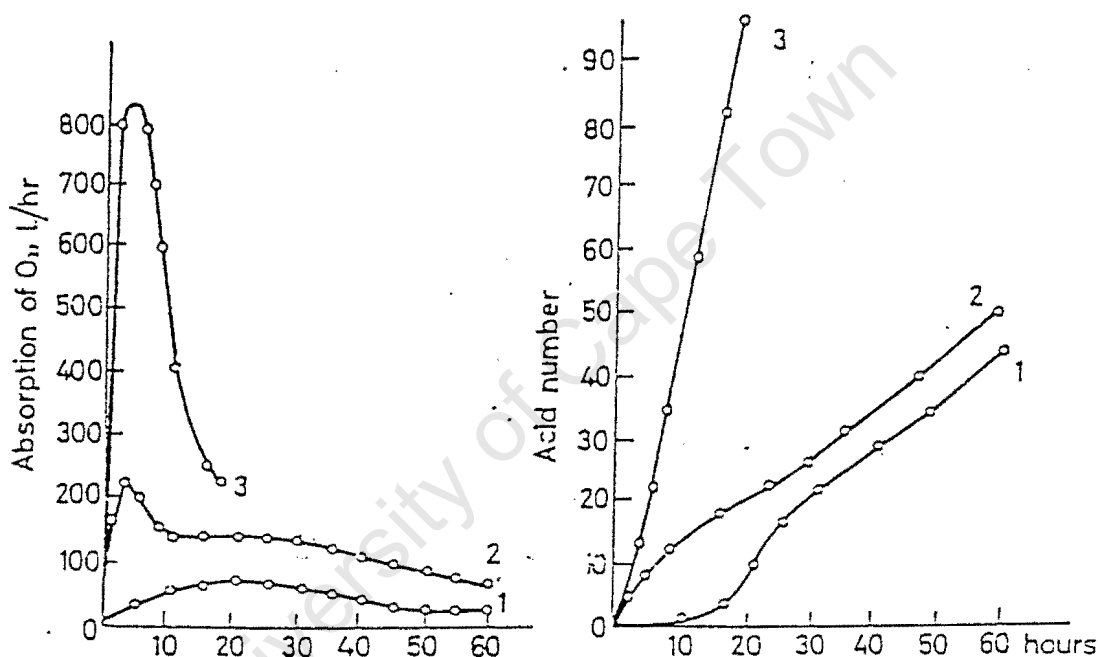
The oxidation of olefins in the liquid phase also proceeds by a chain mechanism through the formation of hydroperoxides. It has been established experimentally by Mitchell and Shelton<sup>(38)</sup> that under these conditions, oxygen adds mainly to the primary, secondary or tertiary carbons adjacent ( $\alpha$ -position) to the double bond. The hydrogen atoms at these positions are more labile due to the interaction of the  $\sigma$  and  $\pi$  bonds (hyperconjugation). In addition to the 'normal' oxidation products such as esters, ketones, aldehydes, alcohols, acids etc.,<sup>(39)</sup> epoxides, glycols and glycol esters have also been isolated in the autoxidation of unsaturated compounds.<sup>(40)</sup> In some cases, they form the major products of the oxidation of olefins. The oxidation of the olefins, therefore, in some instances progresses to the formation of final oxidation products which are not necessarily acids. If the rate of oxidation is monitored by the rate of formation of acids, the rate would appear to be very slow.

### 2.1.6 Oxidation of High Molecular Mass Hydrocarbons

Pope, Dykstra and Edgar<sup>(41)</sup> put forward a theory almost seventy years ago that oxidation of a hydrocarbon begins at the end of the molecule. This found wide acceptance and support.

fresh and recycled paraffins. This is illustrated in Figure 2.

When fresh paraffin wax was used, the absorption of oxygen occurred before the first acidic products were produced and rose to a maximum corresponding to the greatest rate of production of acids. In the oxidation of a mixture of fresh and recycled paraffin wax (1:2) which contained a certain amount of non-acid containing products, the absorption of oxygen began quite briskly with the immediate formation of acidic products.

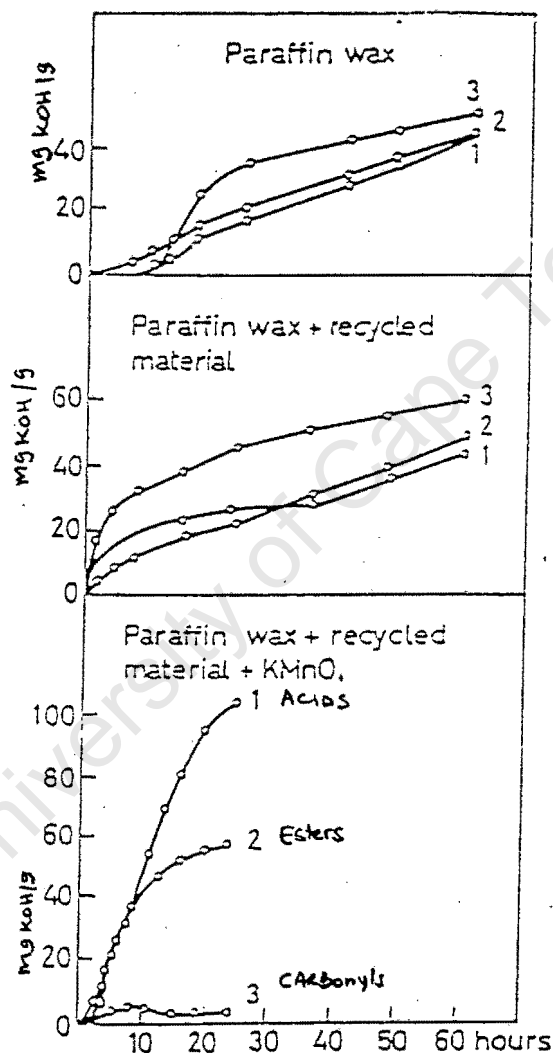


**Figure 2:** Rate of absorption of oxygen and the kinetic curves for the accumulation of acids in the oxidation of paraffin wax. (1)-the initial paraffin wax; (2)-fresh paraffin wax + recycled paraffin wax; (3)- fresh paraffin wax + recycled paraffin wax +  $\text{KMnO}_4$  (reproduced from ref. 45).

When this mixture of fresh and recycled paraffin wax was oxidised after the addition of 0.2 percent of potassium permanganate the consumption of oxygen began immediately and increased steadily to a sharp maximum, and then fell rapidly. The amount of oxygen consumed was considerably more than in the oxidation of the mixture without using a catalyst. The acids also increased at a constant rate which was greater than in the case where no catalyst was added (see Fig.2).

The formation of oxidised products also differed when oxidising under the above sets of

conditions. In the oxidation of fresh paraffins, the esters began to accumulate before the formation of free acids or carbonyl compounds (Figure 3).



(Methods for the determination of acids, esters and carbonyls are recorded in ASTM D1386-83, D1387-89 and D4423-91 respectively)

**Figure 3 :** Kinetic curves for the accumulation of acids (1), esters (2) and carbonyl compounds (3) in the oxidation of paraffin wax (reproduced from ref. 45).

## 2.2. Review of Model Compound Oxidation

### 2.2.1 Bifunctional Compounds in the Oxidation of n-Alkanes

It was originally reported by Rust<sup>(46)</sup> in 1957 that in the oxidation of certain branched alkanes, intramolecular transfer of a hydrogen atom to form bifunctional products is a major reaction path. He found that good yields of 2,4-dihydroperoxy-2,4-dimethylpentane could be obtained from the oxidation of 2,4-dimethylpentane and that the oxidation of 2,5-dimethylhexane gave a lower yield of the bifunctional product. Mill and Montorsi<sup>(47)</sup> subsequently showed that the ratio of mono- to bifunctional products in the oxidation of 2,4-dimethylpentane was 1:7. The generality of intramolecular propagation in the oxidation of alkanes with alternating tertiary hydrogens was confirmed by Van Sickle.<sup>(48)</sup> He found that the major product in the oxidation of 2,4,6-trimethylheptane was 2,4,6-trihydroxyperoxy-2,4,6-trimethylheptane, which was obtained by intramolecular abstraction of hydrogen atoms at the tertiary carbon atoms prior to the formation of the hydroperoxide.

The question as to the amount of bifunctional product formed in the oxidation of n-alkanes has been investigated by Sickle et al.<sup>(49)</sup> They investigated the oxidation products of n-pentane at 100°C and n-octane at 125°C and searched specifically for bifunctional products. The yields of bifunctional products from the oxidation of n-pentane and n-octane were small, in marked contrast to the oxidation products of 2,4-dimethylpentane and 2,4,6-trimethylheptane, where bi- or polyfunctional products predominated.

The authors concluded<sup>(49)</sup> that the oxidation of linear hydrocarbon substrates hardly ever occurs with the participation of intramolecular abstraction of hydrogen atoms to form bifunctional compounds. The case of alternately branched alkanes, where bifunctional products predominate, must be considered exceptional and an explanation should be sought for this phenomenon rather

than for the fact that bi- or polyfunctional compounds do not readily form in n-alkane autoxidations. The authors<sup>(49)</sup> speculated that unusual steric effects, such as orientation-restricted chain rotation mechanisms or partial screening from external attack of the reactive hydrogens of the substrate by the cluster of methyl groups, must be factors which have to be considered.

### 2.2.2 Products in n-Nonane and n-Decane Oxidations

Recently, Goosen and Morgan<sup>(50)</sup> studied the products of the oxidation of n-nonane and n-decane. They studied the formation of products from the first stage, the second stage, and the final stage of the autoxidation.

During the first stage of oxidation, isomeric nonane and decane hydroperoxides were formed and showed a steady build-up for the first hour; then they slowly decreased for the next 2 hours and thereafter remained constant. During this period, negligible amounts of the isomeric ketones and alcohols were produced. The concentration of the nonyl hydroperoxides was greater than the concentration of the decyl hydroperoxides in the respective oxidations. After this initial stage in which the hydroperoxides are produced and reach a maximum concentration, the isomeric ketones and alcohols are produced. This is in accord with the finding<sup>(18)</sup> that the hydroperoxides are the precursors of the ketones and the alcohols, as discussed in Section 1.1.7. Bateman and Hughes<sup>(51)</sup> attributed the change in the reaction of hydroperoxide decomposition to a bimolecular process at higher concentrations of hydroperoxide. However, Hait et al.<sup>(52)</sup> held a view that the alkyl hydroperoxides do not significantly decompose below 150°C and that they are susceptible to radical-induced chain decomposition. Hajdu and coworkers<sup>(53)</sup> have established, while studying the oxidation of ethyl benzene, that peroxy radicals induce the decomposition of alkyl hydroperoxides. Therefore, the initial slow decomposition of hydroperoxides, which later

Very recently, Goosen and Kindermans<sup>(54)</sup> found that the yields of disubstituted products found in the autoxidation reaction of n-decane decreased in the order of 2,5- > 3,6- > 4,7-disubstitution, which suggests a more facile oxidation of the alkane towards the terminal position of the alkane chain. However, the terminal methyl, even though statistically favoured for the reaction, is less susceptible to oxidation. Since most of the significant minor products are  $\alpha,\delta$ -bifunctionalised, it is concluded that the bifunctionalised process does not occur by either random abstraction or by intramolecular hydrogen abstraction by peroxy radicals, since this would require a less favourable seven-membered-ring transition state. Intramolecular hydrogen abstraction reactions by alkoxy radicals, which involve a more favourable six-membered-ring transition state, could best account for these reactions.

In order to investigate the formation of secondary products, the authors<sup>(54)</sup> added oxidation products from the first stage of the oxidation to the autoxidation reaction of decane. The presence of 3-decanone in the autoxidation of decane led to an increase in the formation of octanal and octanoic acid and heptanal and heptanoic acid. These products probably form by the  $\alpha$ -fragmentation of the  $\alpha$ -keto-alkoxy radicals and the aldehydes are formed by the alkylcarbonyl radical abstracting hydrogen from a suitable substrate. This result indicates that the  $\alpha$ -methylene hydrogens of ketones are particularly reactive towards free radical abstraction, as also reported by Cooper and Melville.<sup>(55)</sup>

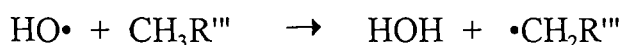
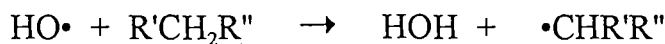
The addition of 3-decanol to the autoxidation of decane first led to an increase in the induction period and thereafter the concentration of 3-decanone increased significantly and its rate of production was relatively greater than that of the other decanones. These results indicate that the alcohol is a precursor of ketone formation. The increased production of 3-decanone supports the fact that alcohols are more readily oxidised than alkanes in the autoxidation reactions.<sup>(56)</sup>

in the reaction. They thus concluded that approximately half the carboxylic acids had to be converted to esters during the reaction.

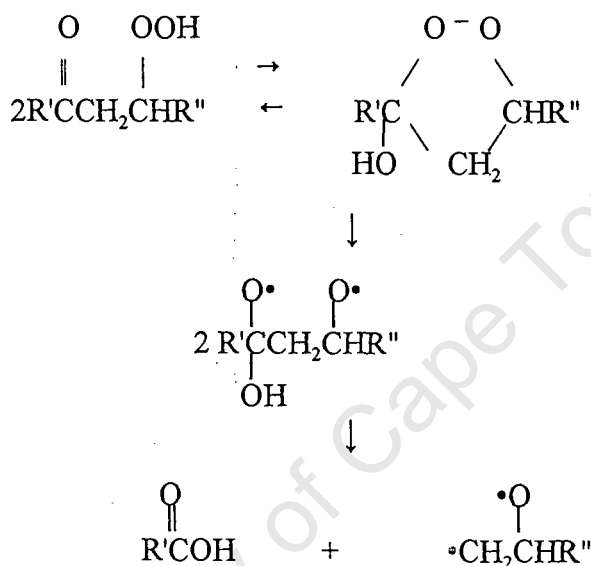
This statement implies that the acids are converted to esters during the reaction and that the esters are formed solely by the intermolecular reaction of acids and alcohols present during the oxidation. However, the research for this dissertation has shown that cyclic esters ( $\gamma$ -lactones) were detected in substantial amounts in both the model compound oxidation (Chapter 3) and in the analysis of the distillate from the vacuum distillation of oxidised hard waxes (Chapter 4). These cyclic esters are not formed by the reaction of an alcohol and an acid but rather via the hydroperoxide and the intramolecular abstraction of a hydrogen atom to form a dihydroxy alkyl radical which was shown to be the precursor of the  $\gamma$ -lactones in the previous section.<sup>(54)</sup> A different mechanism, such as possibly the  $\alpha$ -fragmentation of the  $\alpha$ -keto-alkylperoxy radical, must account for the equal concentrations of acids and 'esters' in the oxidation products. Zeinakov and Leikakh<sup>(58)</sup> also found that oxidations at higher temperatures have the effect of increasing the functionalisation of n-hexadecane, i.e. less unreacted hexadecane is present when oxidising at higher temperatures than at lower temperatures.

During the oxidation of n-hexadecane (n-C16) at 150°C and an air flow-rate of 840 dm<sup>3</sup>h<sup>-1</sup>, a series of saturated acids of normal structure, ranging from caprylic acid (C8) to myristic acid (C14) were detected.<sup>(57)</sup> This is in agreement with the findings of this dissertation (Chapter 3). The only difference is that acids ranging from as low as acetic acid to the acid containing two carbon numbers lower than the parent hydrocarbon were detected in the present work. The acid containing the same number of atoms as the parent compound was not detected. This is to be expected if the acids are scission products of the oxidation.

Jensen et al.<sup>(59)</sup> proposed a reaction scheme for the formation of products during the n-C16



Jensen et al.<sup>(60)</sup> later proposed a process for the formation of alkanolic acids and methyl ketones. This proceeds by the decomposition of  $\alpha,\gamma$ -hydroperoxy ketones, as depicted below:



The latter diradical isomerises to form the methyl ketone.

The additional acids, which are present in larger quantities than the methyl ketones, also observed in the present dissertation (Chapter 3), can be formed by  $\beta$ -scission of alkoxy radicals:



followed by free radical oxidation of aldehydes to acids:



The reactions proposed by the various authors in this chapter, accounts for the formation of most of the products identified in the oxidation of both the model compounds and Fischer-Tropsch hard wax. The identity of these oxidation products will be dealt with in Chapters 3, 4, and 5. Research results from the literature reviewed in this chapter which are of particular interest to the industrial process of thermally oxidising hard wax, are the following:

## 3. MODEL COMPOUND OXIDATIONS

### 3.1 Introduction

The oxidation products of Fischer-Tropsch hard wax oxidation range from compounds having two carbon atoms to as many as 100 carbon atoms and cannot be analysed meaningfully using standard analytical techniques. To help towards elucidating the composition of the oxidised Fischer-Tropsch hard wax, n-hexadecane (n-C16), n-tetracosane (n-C24) and n-dotriacontane (n-C32) were used as model compounds to study the oxidation products formed during bubble oxidations, with the purpose of relating these results to the Fischer-Tropsch hard wax oxidations. Fischer-Tropsch hard wax can be seen as being composed of a number of such straight-chain 'model compounds', with carbon numbers ranging from C30 to C100. Samples from the reaction mixture of each of the model compounds were drawn at regular intervals and were analysed by GC-MS, HTGC and AED-GC. The information obtained from these experiments gave an indication of the products formed during the oxidation of Fischer-Tropsch hard wax.

In this dissertation it is proposed that each of these straight-chain molecules is oxidised in the same way as the model compounds, with the formation of similar oxidation products. The oxidation products from hard wax can therefore be predicted by considering the oxidation products of the model compounds.

A set of experiments was designed, using model compounds, with two main aims. The first was to identify the oxidation products completely for the model compounds.

The second was to attempt to relate the results of model compound oxidations to the oxidation products of the Fischer-Tropsch hard wax.

The Fischer-Tropsch hard wax is a blend of hydrocarbons of different chain lengths and the commercial oxidation of these waxes is done at various temperatures.

of the n-C32 caused the undiluted hydrocarbon to solidify in the syringe, thus complicating the injection of the sample into the injector port of the GC. Only qualitative analysis of the reaction mixtures was carried out by visually comparing peak heights to get an indication of relative concentrations of the oxidation products. For a reliable quantitative study 'pure' compounds had to be purchased to calibrate the GC and this could not be justified economically because the focus of the project was to identify the products formed during the oxidation of hydrocarbons

A Hewlett-Packard GC-MSD system ( 5890 series 2 GC coupled to a model 5972 MSD ) was used to analyse the samples. The oxidised material is separated into its individual components in the analytical column housed in the GC. These separated components then pass into the MS detector where fragmentation and ionisation occurs. A unique and characteristic mass spectrum is obtained and is used to fingerprint the compound. The identity of the individual components is facilitated by a complex algorithm known as Probability Based Matching (PBM) which is the basis of Wiley 138 database..

### 3.2.2 Raw Materials

n-Hexadecane was obtained from Sarchem (GLC assay 99%), n-tetracosane and n-dotriacontane were obtained from The Humphrey Chemical Company in Connecticut USA (GLC assay 99%).

### 3.2.3 Instrumental Analysis Parameters

GC-MS operating conditions:

*Mass Spectrometric Conditions:*

Mass window: 20-400 amu

Ionisation mode: Electron Ionisation

Interface temperature: 280°C

Ion source temperature: 170°C

Ion source pressure:  $1 \times 10^{-5}$  kPa

Threshold: 50

Type of mass analyser: Quadrupole

#### *GC Conditions*

Injector temperature: 220°C

Initial oven temperature: 35°C

Initial hold time: 0 min

Ramp rate: 5°C min<sup>-1</sup>

Final oven temperature: 230°C

Final hold time: 30 min

Split ratio: 1:100

Injector volume: 1.0 µl

#### *HTGC Chromatography conditions*

The samples were analysed on a HTGC equipped with an aluminium clad column (length 12 m, ID 0.53 mm) and using a Flame Ionisation Detector.

Initial column temperature: 60°C for 5 minutes

Final column temperature: 440°C for 5 minutes

Injector temperature : 40°C for 0 minutes

Ramp rate for the column : 10°C min<sup>-1</sup>

Ramp rate for the injector : 70°C min<sup>-1</sup>

Detector temperature : 450°C

Carrier gas : Hydrogen

Flow rate : 5 cm<sup>3</sup> min<sup>-1</sup>

Injector volume: 1.0 µl

*AED-GC Conditions*

Injector temperature: 300°C

Initial Oven temperature: 30°C

Initial Hold Time: 0 min

Ramp rate: 4°C min<sup>-1</sup>

Final oven temperature: 30°C

Final hold time: 5 min

Split ratio: 1:100

Column head pressure: 214 kPa

### 3.3 Results and Discussion

#### 3.3.1 Identification of the Products Formed During the Oxidation of n-Hexadecane and n-Tetracontane.

The chromatogram of the n-C24 oxidation products, with the peaks numbered and the corresponding table identifying the numbered compounds, is given in Appendix 1(a). All the peaks appearing in the chromatogram were identified. Only the major products of the n-C16 oxidation were labelled (Appendix 1(b)) because the oxidation products of the n-C16 and n-C24 hydrocarbons are practically identical.

Sections of the chromatograms of n-C24 and n-C16 oxidation products are given in Figures 4 and 5 respectively for easier referencing. The complete chromatograms are given in Appendices 1(a) and 1(b). The chromatograms of the oxidation products from the n-C16 and n-C24 oxidations are remarkably similar. The non-polar PONA column separates the oxidation products into two distinct bands as seen in Figures 4 and 5, namely, the products with carbon numbers lower than the parent molecule, termed the 'scission products' in this dissertation, and

those with carbon numbers equal to, or greater than the parent molecule, termed the 'initial oxidation products' in this dissertation. The 'scission products' of the oxidation are mostly alkanes,  $\gamma$ -lactones, ketones, aldehydes and acids.

The PONA column separates the 'scission oxidation products' into definite groups. For instance, hexanoic acid (C6 acid), 2-octanone (C8 ketone), octanal (C8 aldehyde), decane (C10 alkane) and dihydro-5-ethyl-2-(3H)-furanone (C6 lactone) form one such group. This pattern, i.e.  $C_x$  acid, a  $C_{x+2}$  ketone, a  $C_{x+2}$  aldehyde, a  $C_{x+4}$  alkane and a  $C_x$   $\gamma$ -lactone appears regularly throughout the range of 'scission oxidation products' as can be seen in Figures 4 and 5 and in the complete chromatograms displayed in Appendices 1(a) and 1(b).

A substantial amount of the parent alkane remains unaffected by the oxidation process (also refer to Figure 9 on p 46). This is in agreement with the findings of Hendry et al.<sup>(56)</sup> that the functionalised molecules are more readily oxidised than the alkanes.

The scale of the n-C16 chromatogram shown in Appendix 1(b) was expanded, enabling the identity of the some of the 'initial oxidation' products to be determined. This was not possible in the chromatograms appearing in Appendix 1(b). Sections of the chromatogram with the scale expanded from 20 min for full scale (as used for the chromatograms in Appendices 1(a) and 1(b), to 10 min and 5 min for full scale (see chromatograms in Appendix 1(c)), appear in Figure 6. From these chromatograms the hexadecanones (time 51 to 52 min), hexadecanol (52.7 min), tetradecanoic acid (50.5 min) and the C14 lactone (52.7 min) were detected. Some straight chain esters such as butyl nonanoic ester, propyl decanoic ester and possibly butyl undecanoic ester (~49 min) could also be detected which was not possible when using the 20 min full scale range. However, even with this expansion of the time scale, not all the peaks could be identified because of co-elution in the 'initial oxidation product' peak area.

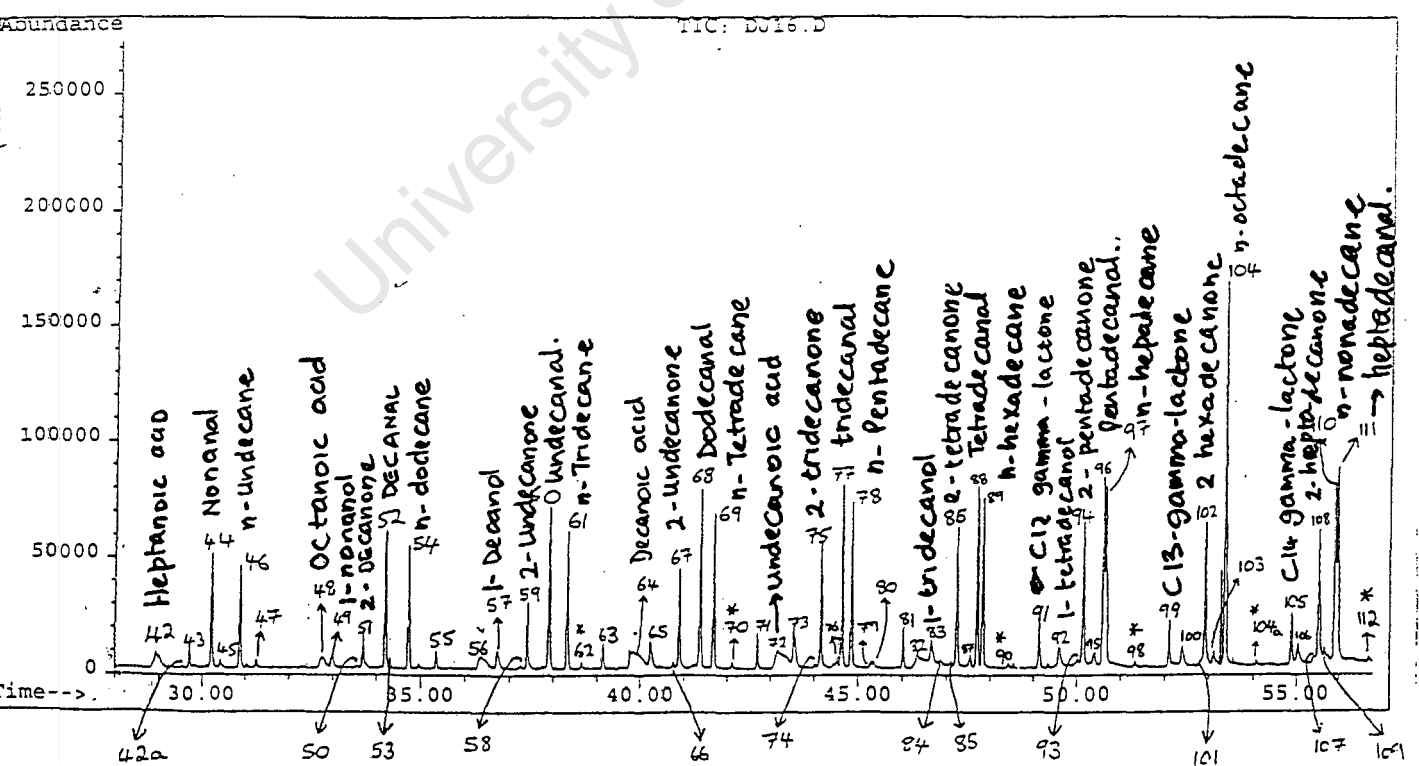
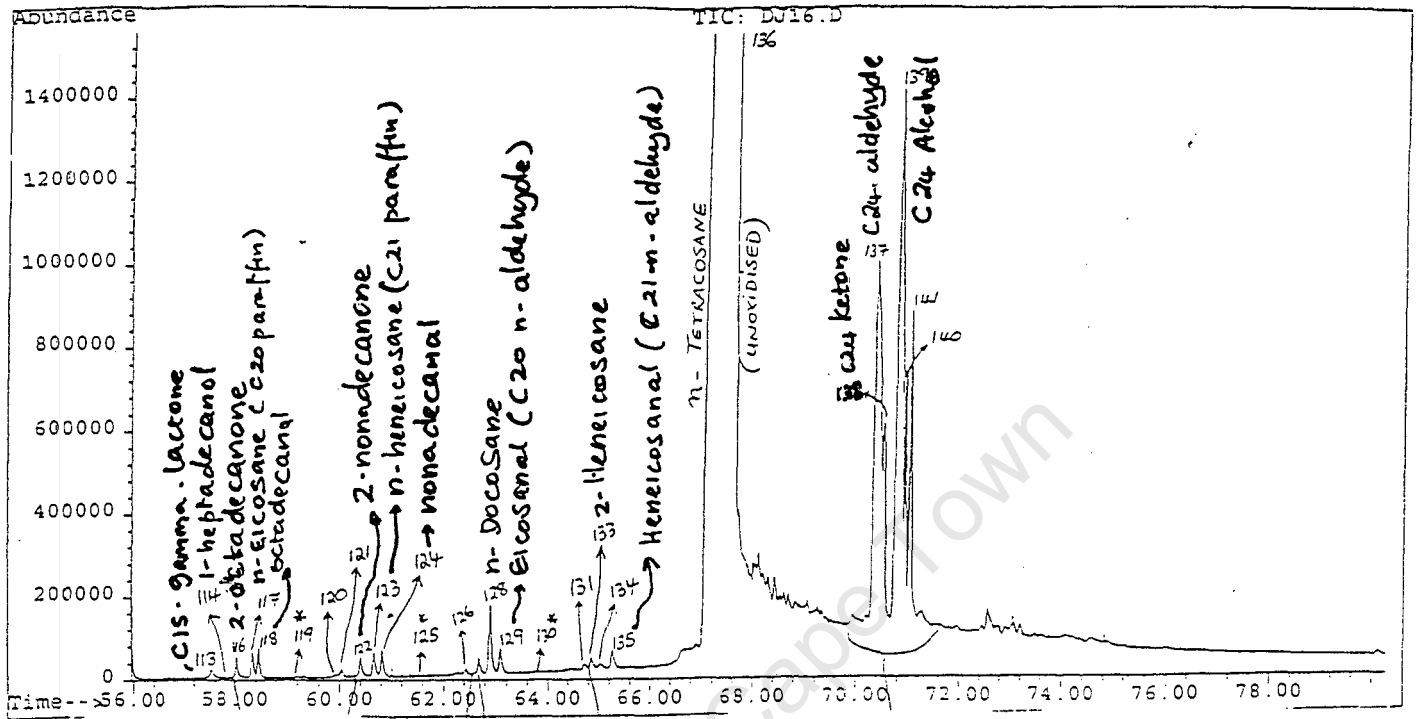


FIGURE 4: GC-MS chromatograms of the reaction mixture from the n-C24 oxidation after 3 hours at 150°C

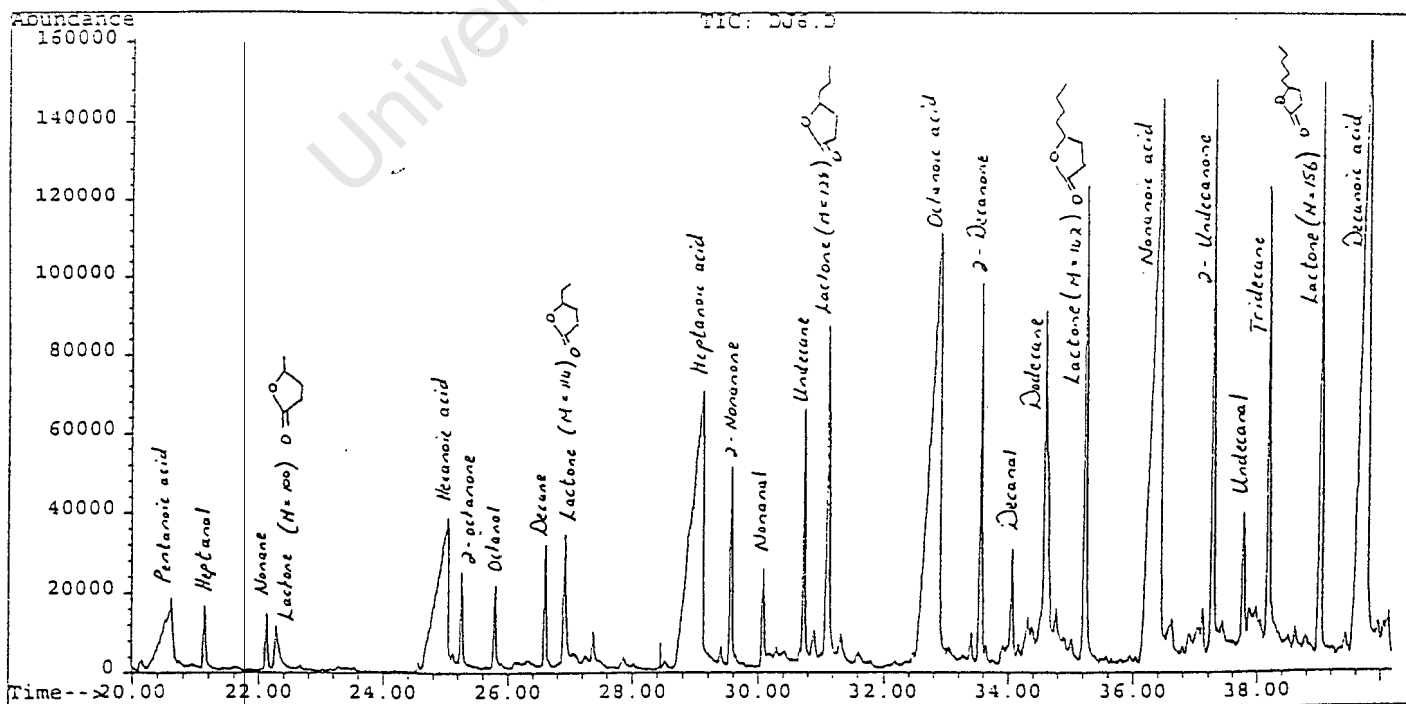
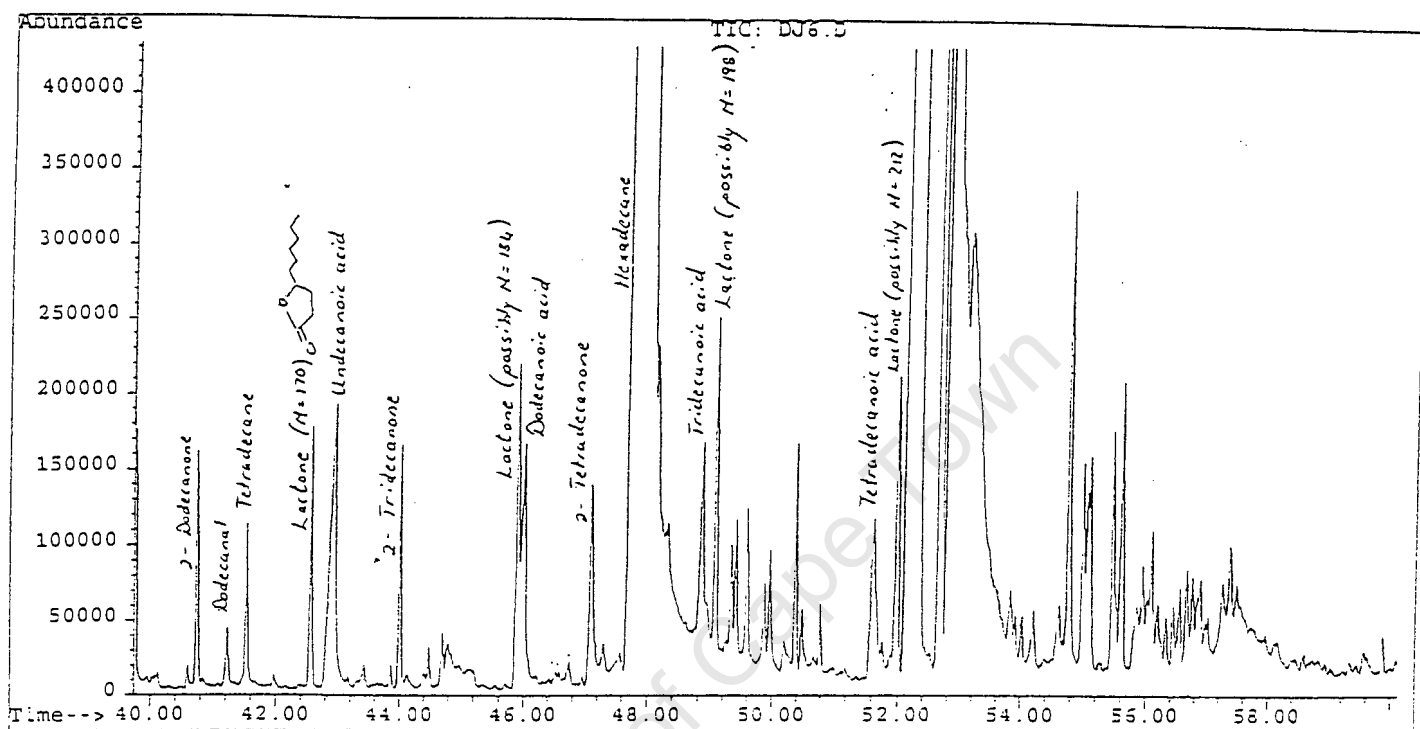


FIGURE 5: GC-MS chromatograms of the reaction mixture from the n-C16 oxidation after 3 hours at 150°C

The polar FFAP column separates the oxidised components into polar and non-polar fractions and was used to examine the products of the C16 oxidation. The complete chromatograms are given in Appendix 1(d). The non-polar fractions are eluted first, but their detection is not satisfactory when compared to the PONA column because the alkanes can be seen only to range from nonane to tetradecane. To analyse the non-polar fractions the PONA column gave better results with alkanes as low as ethane being detected (chromatogram in Appendix 1 (b)). The FFAP column separated the polar fractions more efficiently than the PONA column. A section of the chromatogram is depicted in Figure 7. Acids ranging from acetic acid (~17 min) to tetradecanoic acid (43 min) were detected. Pentadecanoic and hexadecanoic acids were not detected

The following characteristics of the oxidation products of the model compounds were observed:

- The alkanes have carbon numbers starting at C2 up to one less than the parent hydrocarbon. n-Tricosane (C23) was detected in the n-C24 oxidation products (number 134 of the table appearing in Appendix 1(a)).
- The aldehydes and ketones range from C2 to the oxygenate with the same number of carbon atoms as the parent molecule (chromatogram in Appendix 1(d) clearly indicates the presence of hexadecanones and number 137 in the table in Appendix 1(a) indicates a possible C24 aldehyde). The methyl ketones are predominantly formed during the oxidation. Small amounts of di-ketone were detected.
- The  $\gamma$ -lactones range from C6 to two carbon atoms less than the parent hydrocarbon (chromatogram in Appendix 1(c) indicates the presence of a C14 lactone in the oxidation products of n-hexadecane).
- The acids range from C2 (acetic acid) up to two less than the parent hydrocarbon. The higher carbon number acids and lactones could not be detected in the n-C24 chromatogram

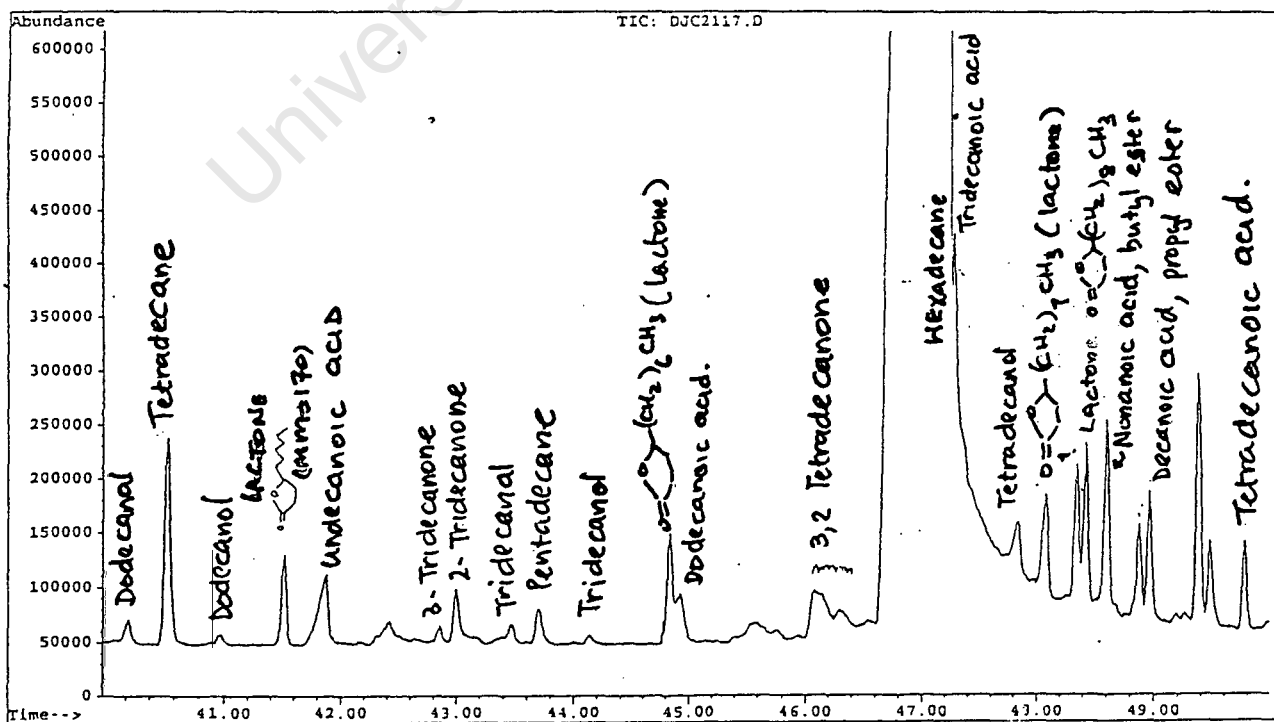
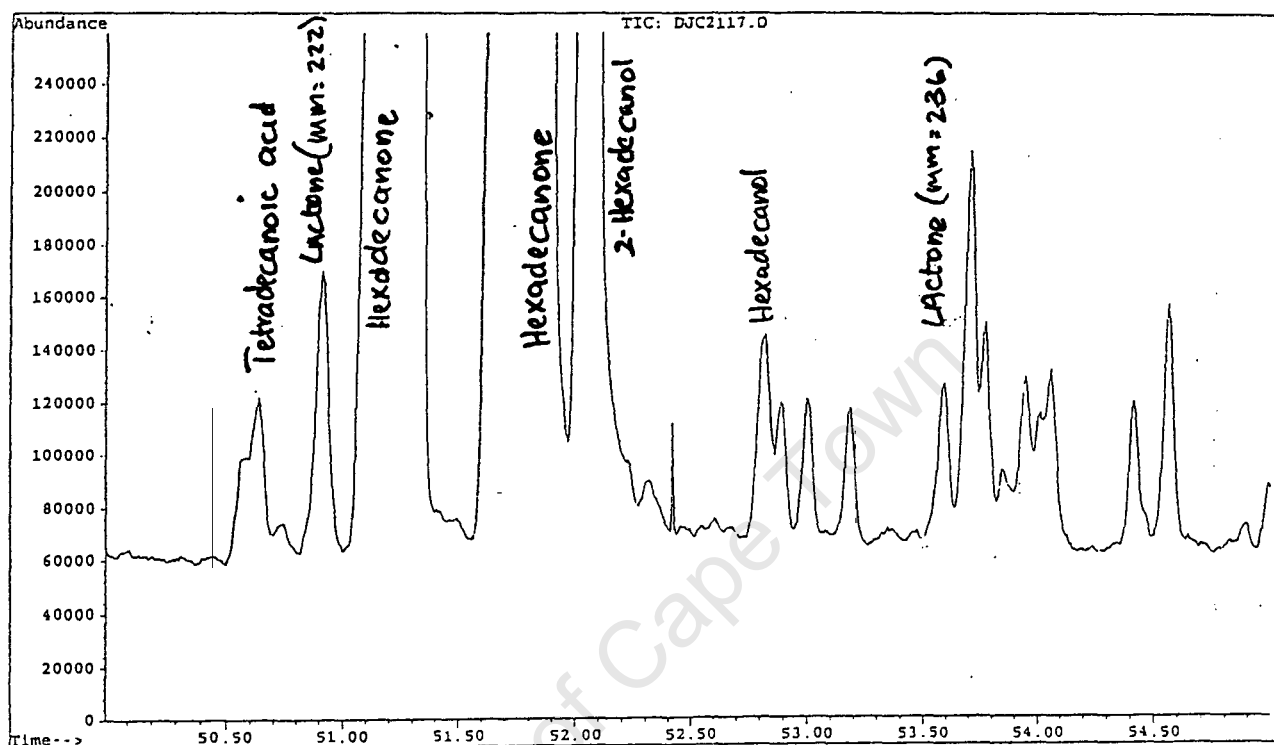


FIGURE 6: GC-MS chromatograms of the reaction mixture from the n-C16 oxidation using an expanded scale

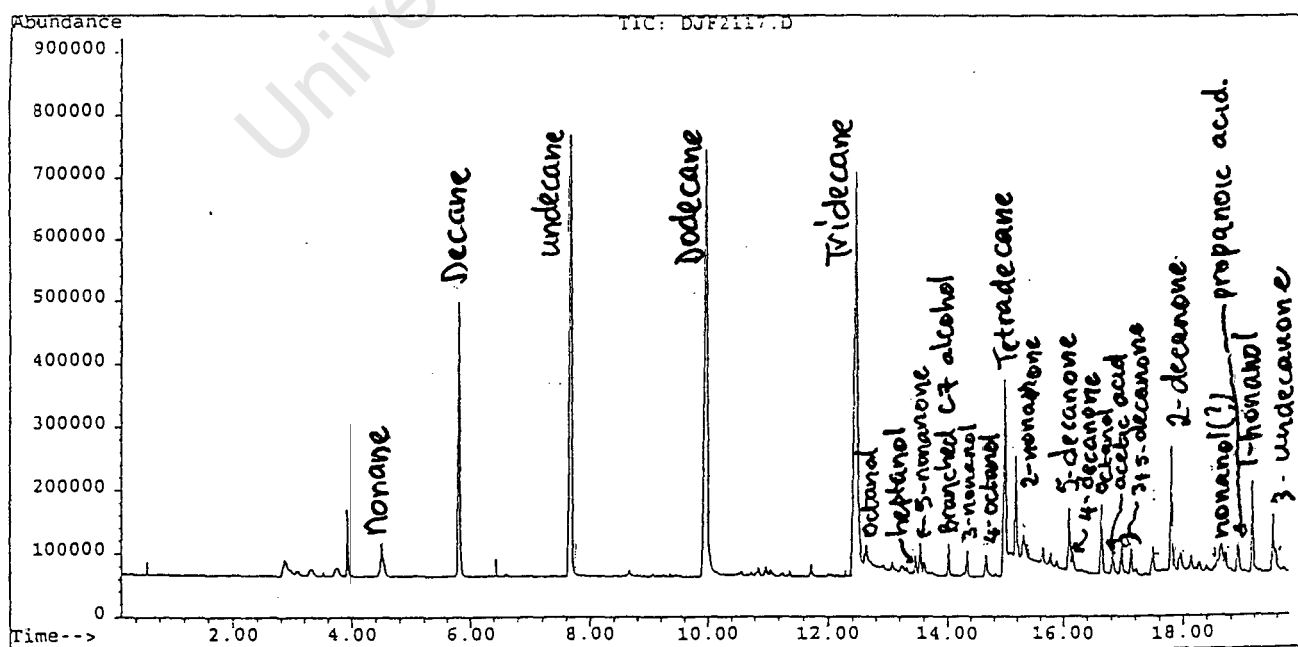
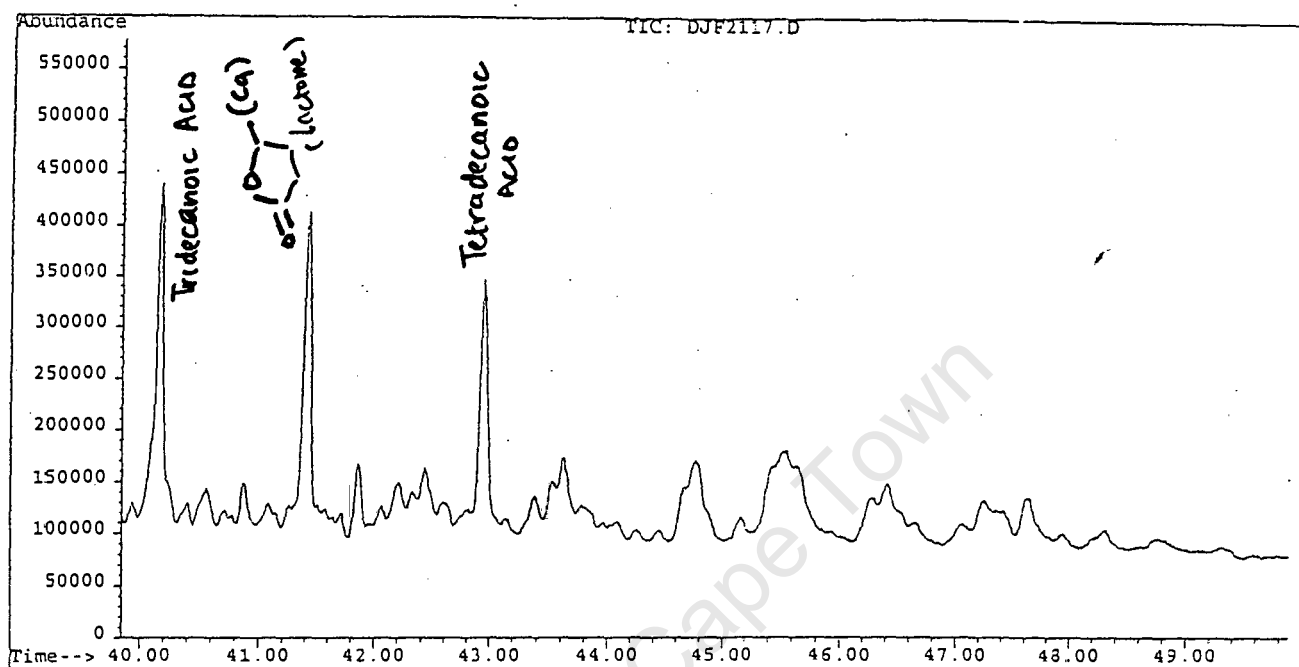


FIGURE 7: GC-MS chromatograms of the reaction products from the n-C16 oxidation using a FFAP column

but were detected in the n-C16 chromatograms given in Appendices 1(b) and 1(c).

- No straight-chain esters were present in the 'scission products section' of the oxidation.

Straight chain esters were detected in the 'initial oxidation product' range, namely, nonanoic acid butyl ester, etc., given in Appendix 1(c). These esters could not be conclusively identified because they elute in the complex 'initial oxidation products' section of the chromatogram where the separation of the peaks is not as effective, resulting in a large degree of co-elution.

- Alcohols were detected only in small amounts in the 'scission section' of the chromatogram.

Larger quantities of alcohols were detected in the 'initial oxidation product' section. 2- and 3-Hexadecanols were detected in the oxidation products of n-hexadecane. These are indicated on the chromatograms in Appendices 1(a) and 1(d). Primary alcohols do not appear to be present in this section.

Fischer-Tropsch wax, which consists of long straight-chain molecules, will display a similar array of oxidised products. The individual hydrocarbon molecules will be oxidised to form scission products, namely acids, alkanes,  $\gamma$ -lactones, aldehydes, alcohols and ketones with chain lengths smaller than the parent molecule. The 'initial oxidation products', with chain lengths equal or greater than the parent hydrocarbon, will also be present.

### 3.3.2 Comparison of Products Forming At Different Time Intervals During n-Hexadecane Oxidation

The oxidation of n-hexadecane was carried out at 150°C in the bubble reactor with an air flow rate of 0.1 cm<sup>3</sup> min<sup>-1</sup> per 50 g of hexadecane. A sample was taken after 2.5 hours from the 5 hour oxidation. The chromatograms of these samples are given in Figure 8 and labelled for the 2.5

hour and 5.0 hour reaction mixtures. They were taken from the same oxidation reaction mixture. In another experiment, two separate oxidations were done and were allowed to run for 4 hours and 9 hours before they were terminated. The chromatograms of these reaction mixtures are given in Figure 9.

From the chromatograms it is clear that the full range of oxidation products are present very early in the oxidation. The products forming in the first stage of the oxidation, the 'initial oxidation products,' and in the second stage of the oxidation, 'the scission products', which are formed by the oxidation or further reaction of the 'initial oxidation products', are present even as early as in the 2.5 hour sample. The products present in the reaction mixtures at different times during the reaction are similar to those that are present early in the reaction. The same peaks for the 'scission products' were detected in the 2.5 hour sample as in the 9 hour sample. This is in agreement with the literature<sup>(34,35)</sup> which proposes that, in the oxidation of saturated hydrocarbons, stable oxidation products were formed at the beginning of the reaction. Thus, it would not be unusual for the scission products of the oxidation of the saturated hydrocarbon chain to occur very early in the oxidation process. It is only the relative peaks heights, which correspond to the concentration of these 'scission products', that increase as the oxidation progresses.

It appears that the concentration of 'initial oxidation products' remains practically constant during the oxidation. No new oxidation products are formed as the oxidation reaction progresses from 2.5 hours to 9 hours at 150°C. The GC-MS peaks of the oxidation products present after 9 hours are similar to those which were present after 2,5 hours. To summarise, the major difference between the samples taken at different time intervals was the relative concentration of the oxidation products as indicated by the peak heights of the products..

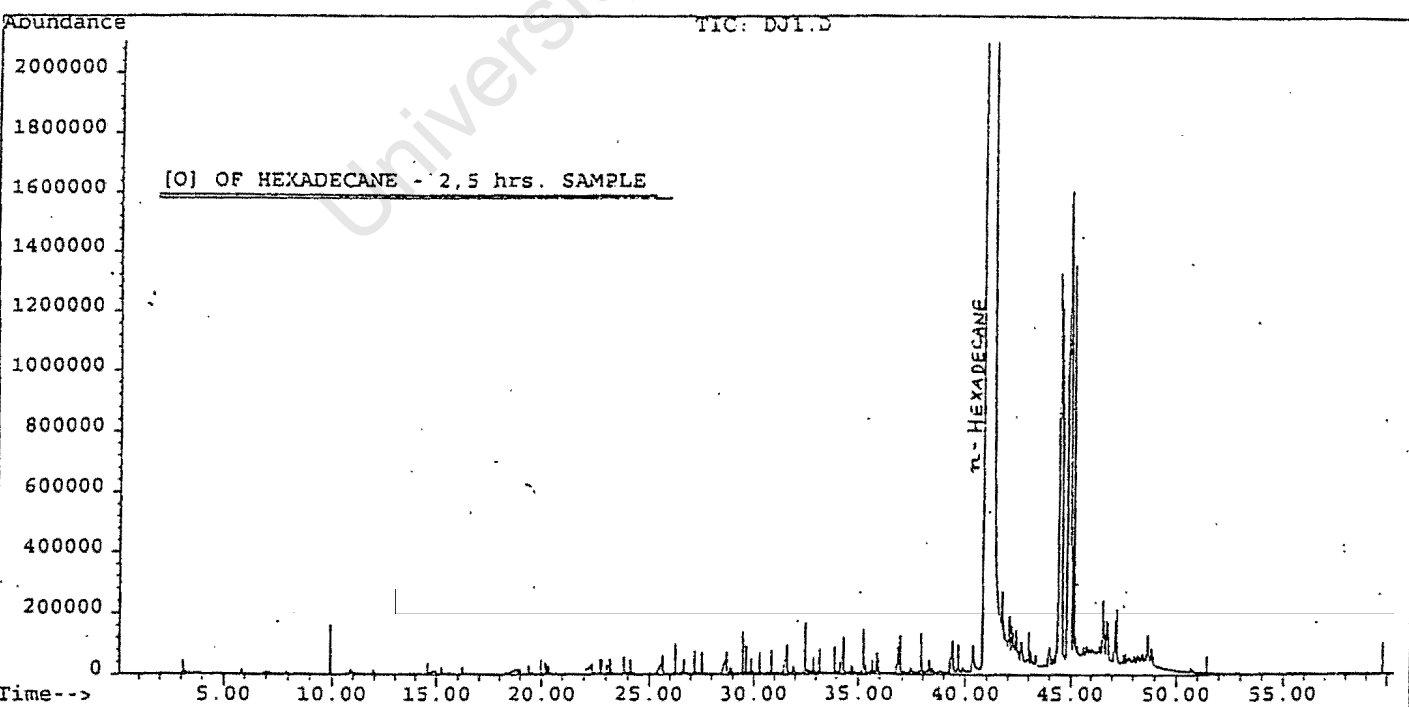
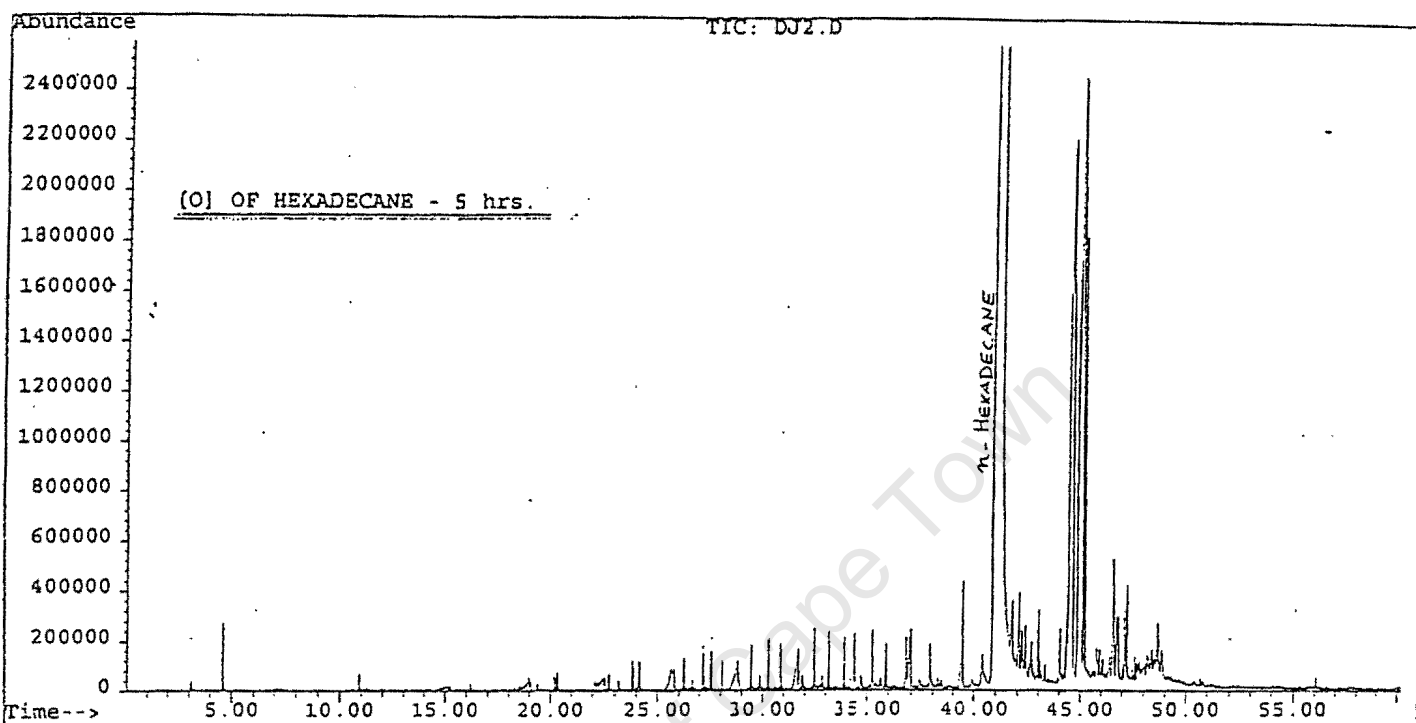


FIGURE 8: GC-MS chromatograms of the n-C16 oxidation reaction mixture sampled after 2.5 hours and at conclusion (5.0 hours)

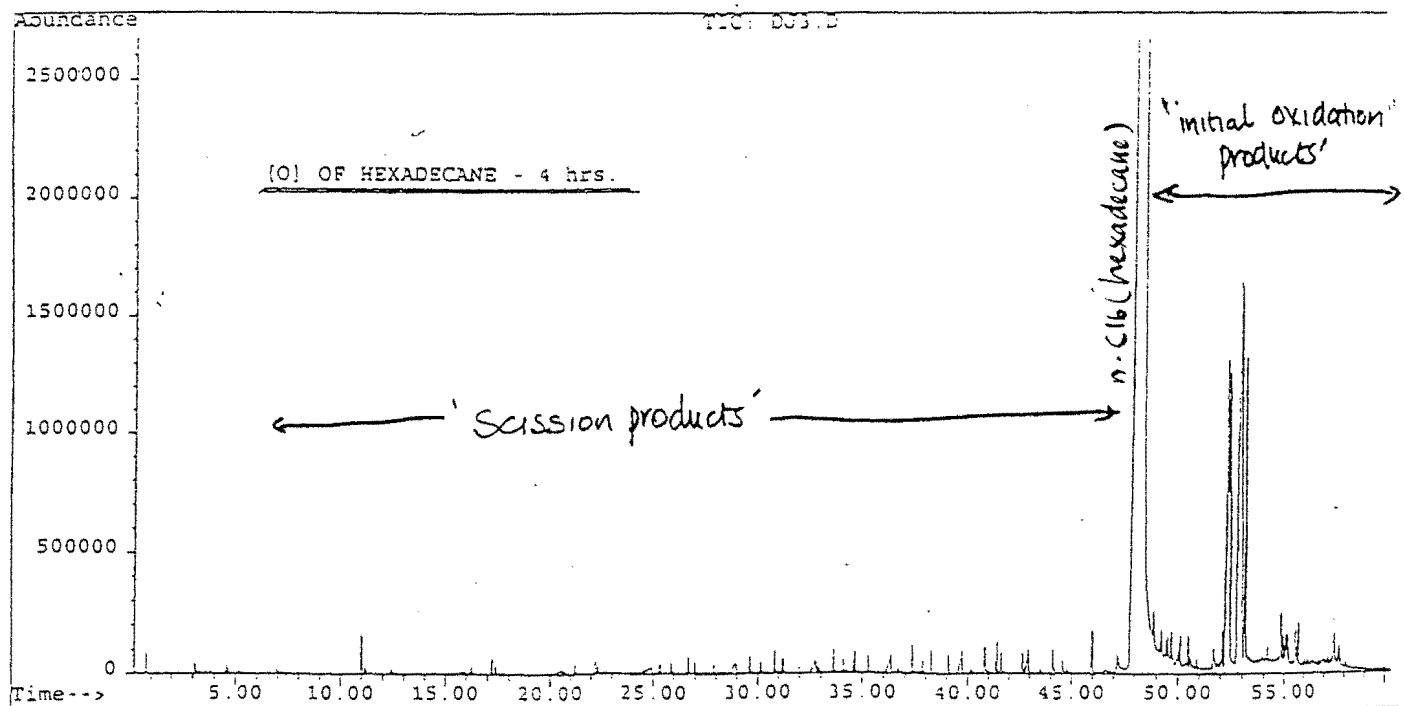
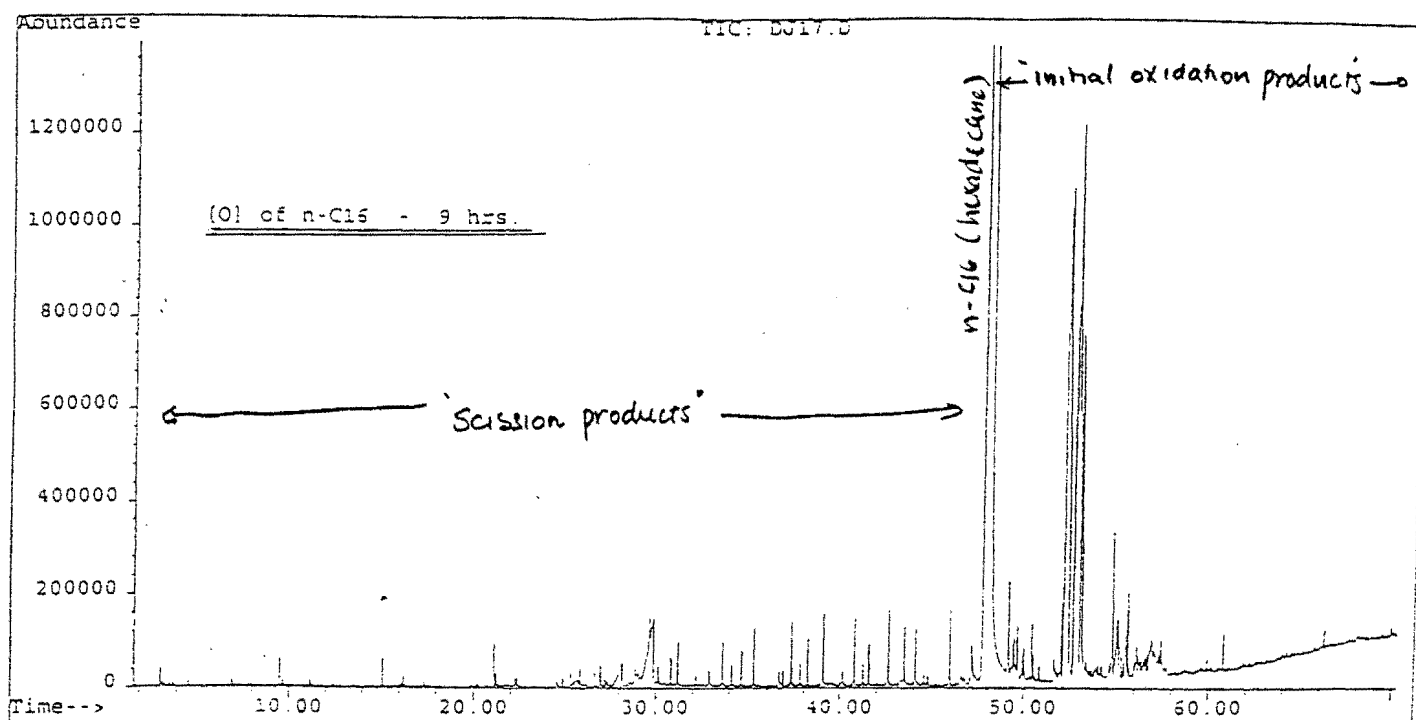


FIGURE 9 : GC-MS chromatograms of the reaction mixtures of n-C16 oxidation terminated after 4 hours and 9 hours

### 3.3.3 Effect of Temperature on the Oxidation Products of n-Hexadecane.

In two separate experiments, n-hexadecane was oxidised in the bubble reactor at constant temperatures of 140°C and 170 °C respectively, for 5 hours at an air flow rate of 0.1 cm<sup>3</sup> min<sup>-1</sup> per 50 g of hydrocarbon. The samples were analysed on a FFAP column using the conditions given in Section 3.2 and products were identified with the aid of the Wiley 138 database. The chromatograms of the oxidation products are given in Figure 10. Only the identities of the major peaks were labelled on the chromatograms. Similar compounds were detected for both the 170°C reaction and for the 140°C reaction. The same peaks were present in the reaction mixtures from both temperatures and as found in the previous section, it was only the intensities of the peaks that differed, i.e., the concentrations of the products.

The FFAP column separates the oxidation compounds into non-polar and polar components, with the non-polar components eluting first. In the 'non-polar region' (0 to ~20 min) the peak heights increased relatively more than the peak heights in the 'polar' region (~25 to 50 min) when the reaction temperature was changed from 140°C to 170°C. This means that more alkanes were formed at the higher temperature.

The concentration of the other oxidation products also increased with the increase in the temperature of the reaction but not by as much as the concentration of the alkanes. These results indicate that the oxidation of straight-chain hydrocarbon molecules at different temperatures results in similar oxidation products, with the concentration of the various oxidation products increasing at higher temperature. Essentially similar oxidation products are formed at the different temperatures.

The final acid values were 12,7 mg KOH per gram and 28,3 mg KOH per gram for the reactions run at 140°C and the 170°C, respectively. The acid values increases at a faster rate at

the higher temperature for the same period of oxidation and indicates an increase in the concentration of the acids. No 'new' acids were formed as the temperature increased.

The appearance of additional acids forming as a result of the oxidation of the existing acids was not observed. The concentrations of the longer-chain acids in the chromatograms in Figure 10 appear to increase when the 140°C to the 170°C oxidation reaction products are compared while the acid value increases, e.g. relative abundance of decanoic acid increases from ~600000 units for the 140°C reaction to ~800000 units for the 170°C reaction. No major concentrations of multifunctional acids were detected. The region from 30 to 34 min was, however, not resolved completely by the FFAP column and the products represented by peaks in this region could not be identified. Octanoic acid and nonanoic acid are expected to be present in this region.

These results are at odds with the theory of Hinselwood,<sup>(43)</sup> who proposed that the oxidation of hydrocarbons yields a whole series of acids, starting with formic acid and ending with the acid containing the same number of carbon atoms as the parent molecule. The acids that contain approximately half the number of carbon atoms of the parent molecule will predominate. The chromatogram in Figure 5 on page 39 indicates that decanoic acid has the greatest relative concentration of the acids.

Also, the acids in Figure 10 have a bell shaped distribution with propanoic acid and tetradecanoic acid having the smallest peaks in the distribution. This bell shaped distribution of the relative concentrations of the acids identified in the reaction mixtures of the model compounds indicate that the theory proposed by Hinselwood<sup>(43)</sup> namely that oxidation takes place most actively when the oxygen attacks a methylene group situated at the maximum possible distance from a methyl group, is at odds with the findings of this dissertation. Furthermore, hexadecanoic acid or pentadecanoic acid could not be detected in any of the chromatograms appearing in Figures 4 to 10. This is to be expected if the acids are scission products of the oxidation.

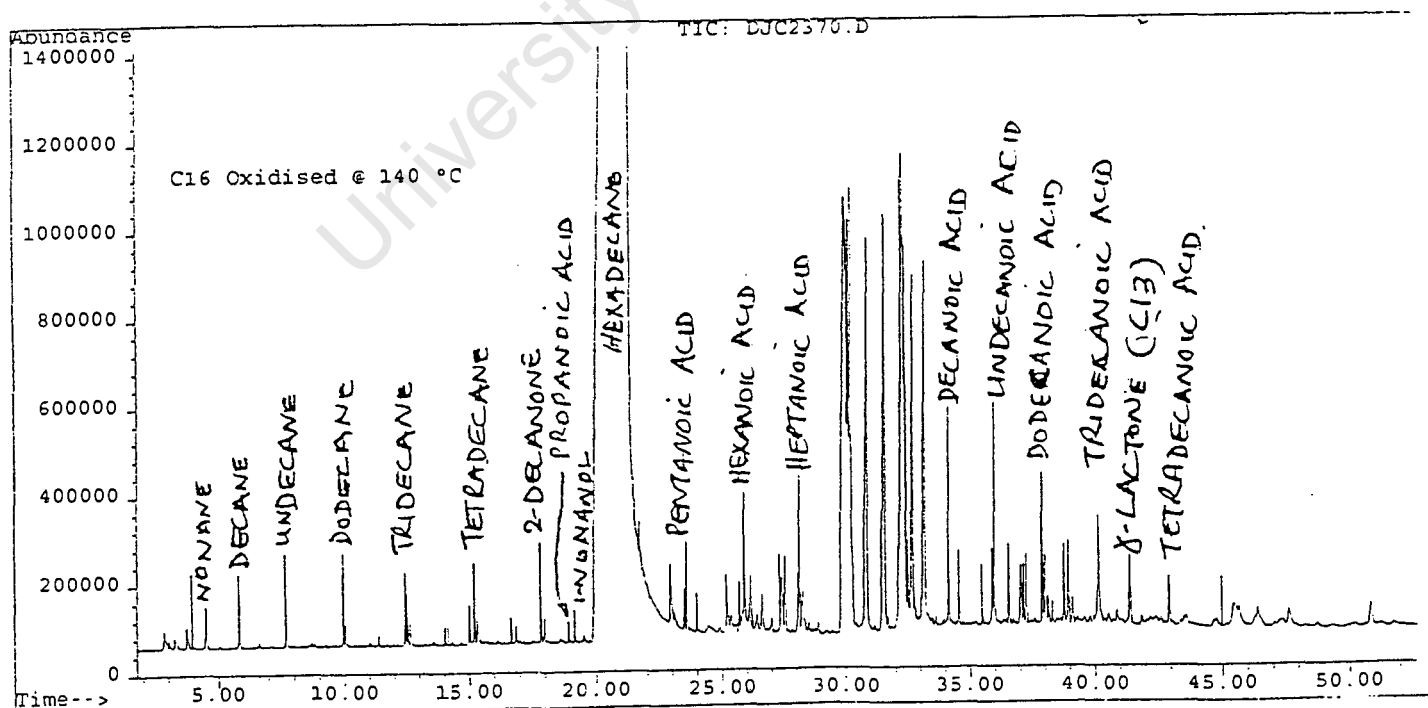
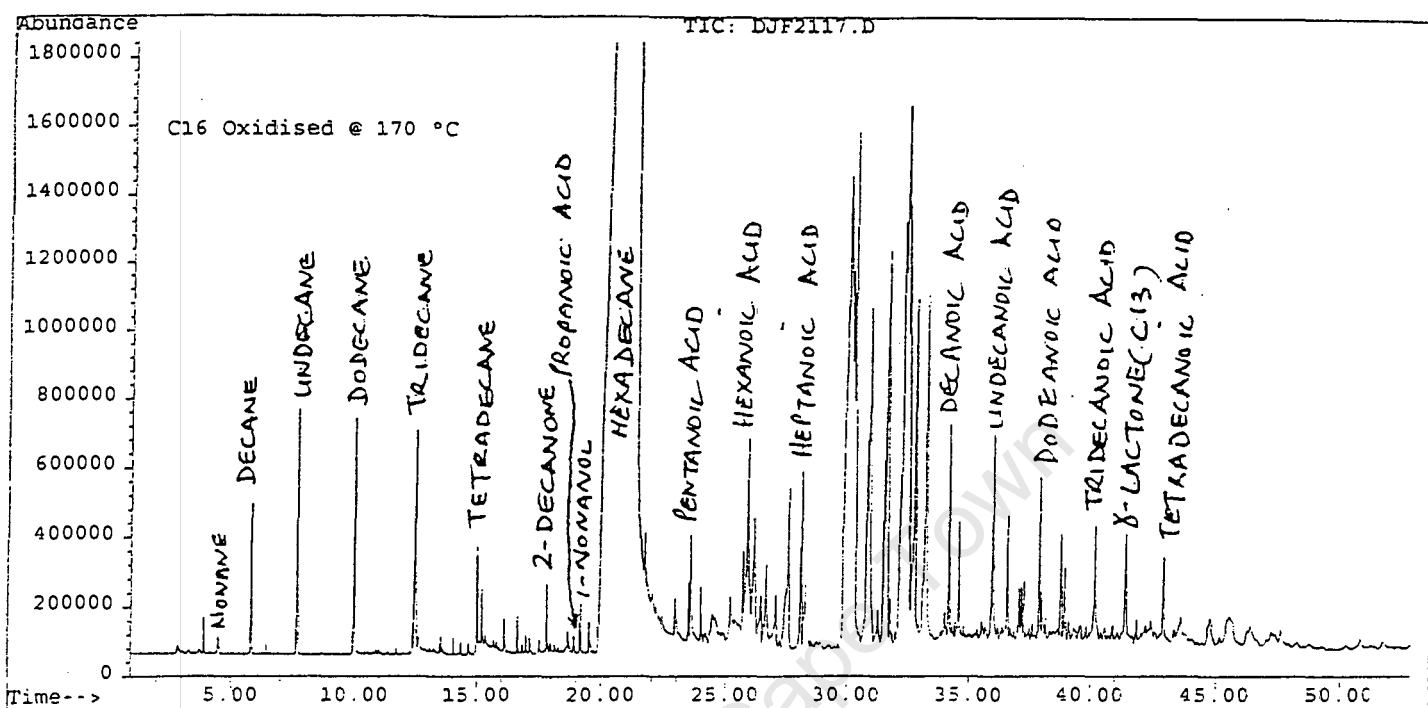


Figure 10: GC-MS chromatograms of the reaction mixture from the n-C16 oxidation for 5 hours at 170 °C and 140 °C

### 3.3.4 Effect of Changes in Carbon Chain Length on the Oxidation Products of the Model Compounds

The model compounds, n-C16, n-C24 and n-C32, were oxidised in a constant temperature bath at 150°C with an air flow equivalent to 0.1 cm<sup>3</sup> min<sup>-1</sup> per 50 g of hydrocarbon. Samples of the reaction mixtures were drawn after 1 hour, 2 hours and 3 hours and analysed by GC-MS to identify the products forming at these time intervals. This was done to determine whether the difference in carbon chain length of the model compounds influences the formation of the oxidation products. Only qualitative analysis of the reaction mixtures was carried out as explained in the Experimental section on page 34.

The oxidation products for the three model compounds are similar but there are marked differences in the concentration of both the 'scission products' and the compounds in the 'initial oxidation product' region. The products of the reaction cannot be compared directly from the peak heights in the chromatograms because the n-C32 sample has a high melting point and had to be dissolved in toluene before it was injected into the GC-MS for analysis. Qualitative comparisons can be made relative to the starting hydrocarbon peak and by comparing the relative abundances of the peak heights.

The GC-MS results are given in Figures 11 to 13. The formation of oxidation products initially increases at a faster rate in the 'initial oxidation product' section of n-C24 and n-C32 when compared visually to the concentrations of n-C16 in the chromatograms for samples taken after 1 hour (Figure 11). The concentrations of n-C24 and n-C32 then appear to remain virtually constant at this concentration for the next two hours (Figures 12 and 13). For the n-C32 oxidation, the concentration of compounds in the 'initial oxidation region' increases marginally

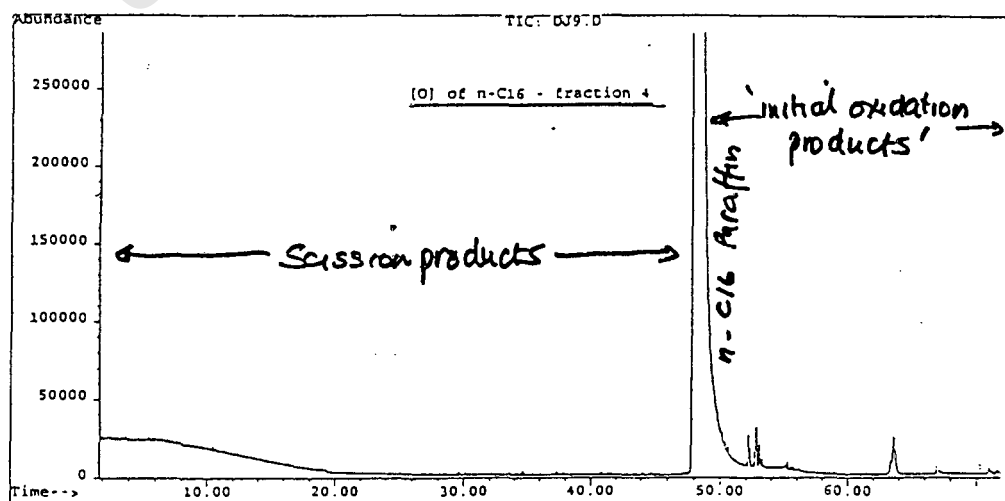
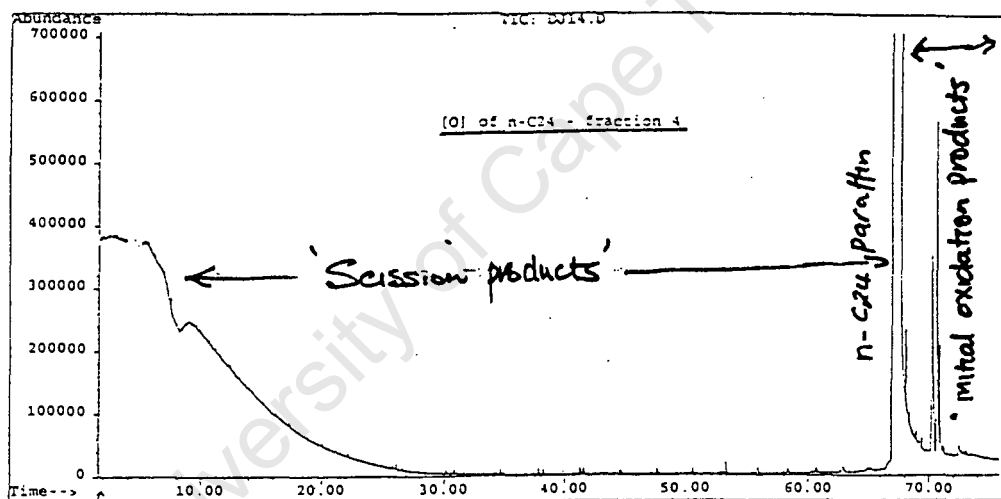
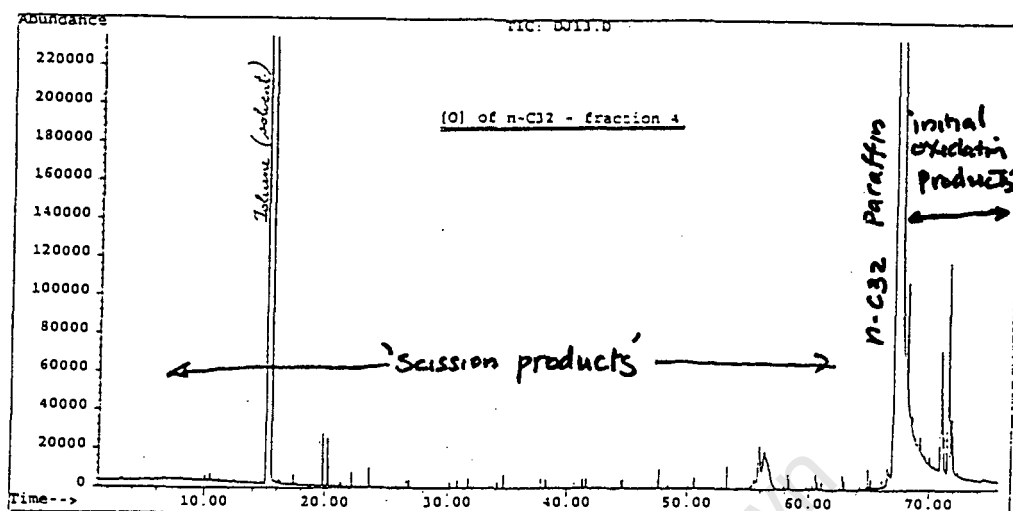


FIGURE 11: GC-MS chromatograms of the reaction mixture of model compounds n-C16, n-C24 and n-C32 after 1 hour

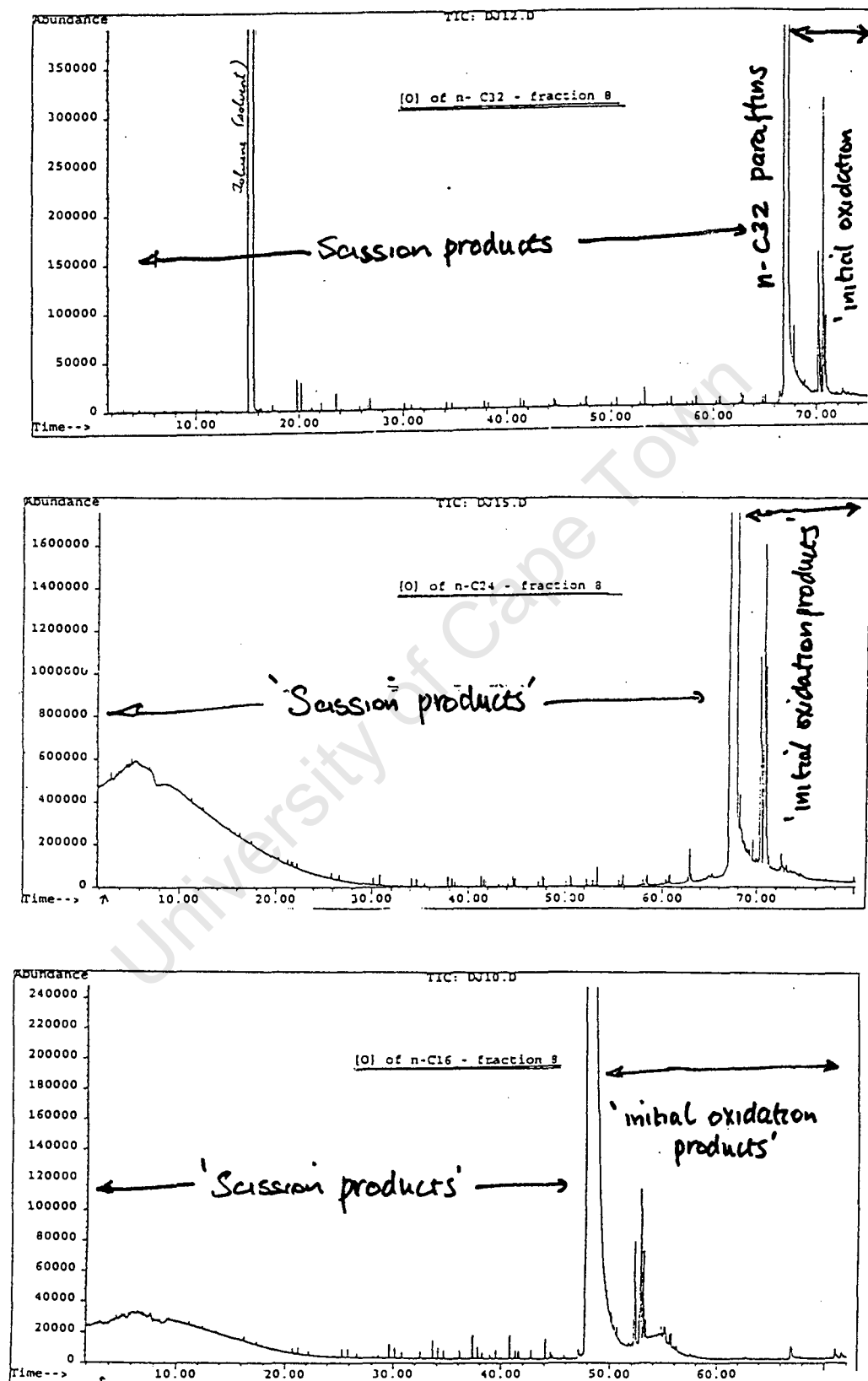


FIGURE 12: GC-MS chromatograms of the reaction mixture of model compounds n-C16, n-C24 and n-C32 after 2 hours

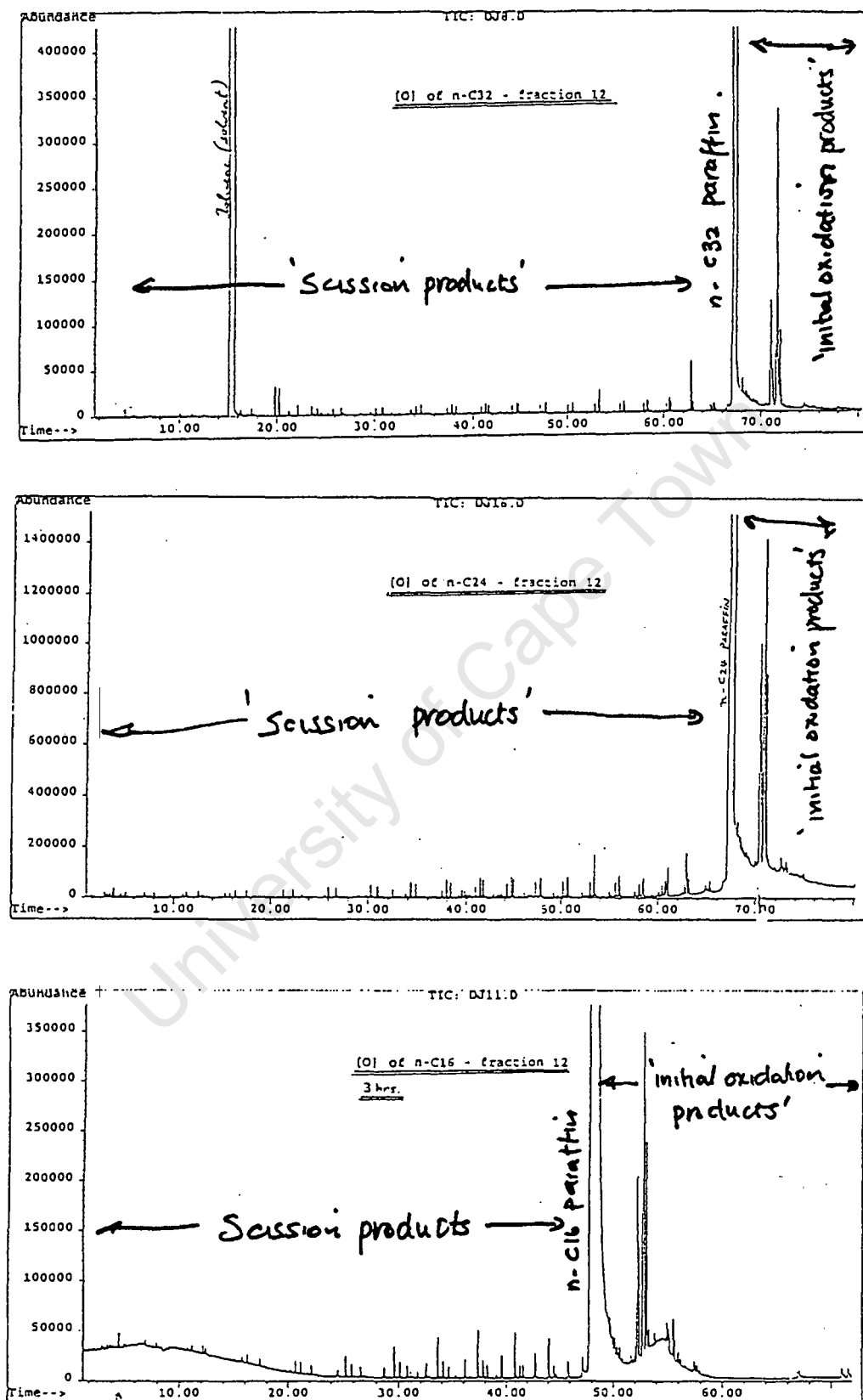


FIGURE 13: GC-MS chromatograms of the reaction mixture of model compounds n-C16, n-C24 and n-C32 after 3 hours

from 1 hour to 2 hours and hardly increases from the 2 hour to the 3 hour sample. On the other hand, the concentration of the n-C16 'initial oxidation products' increases slowly but steadily as the reaction progresses. The oxidation products in the 'initial oxidation product' section of the n-C16 oxidation start at a low concentration and increase in concentration more steadily when compared to the other two model compounds. These results indicate that the formation of the 'initial oxidation products' is initially faster for the n-C24 and n-C32 compared with n-C16.

The concentration of products in the 'scission section' of the chromatogram increases steadily throughout the oxidation for all three model compounds. The peaks are barely perceptible in the 'scission product' region of the n-C16 oxidation after 1 hour and the increase in the peak height (which is proportional to the concentration) in this region, as the reaction progresses, is faster than for the other two model compounds. This indicates that the n-C16 chains break down into smaller chain products at a faster rate than the hydrocarbon chains of the other two model compounds.

An interesting feature of the oxidation is that the 'initial oxidation region' appears to have similar peaks for all the model compounds, namely, n-C16, n-C24 and the n-C32. No extra peaks appear in this region which would be indicative of extra products forming during the oxidation as the molecular mass is increased. According to the literature,<sup>(37)</sup> the oxidation of hydrocarbons leads to the formation of all the possible isomers of secondary alcohols with the same number of atoms as the original hydrocarbon. The authors were studying the position of alcoholic groups on the carbon chains. Therefore, it would be expected that at least more secondary alcohol isomers of n-C32 should appear in the 'initial oxidation products' region of the chromatogram than for n-C16. The n-C32 hydrocarbon has a greater number of carbon atoms resulting in more possible isomers. The similarity of the chromatograms as the chain length increases, however, indicates that not all isomers of the parent hydrocarbon are formed. The results from the

identification of the products formed in the oxidation of model compounds in Figures 4 and 5 indicated that only the 2- and 3-isomers of the ketones and the alcohols of the parent hydrocarbons were formed in significant amounts in the 'initial oxidation product' section. This is in agreement with the theory proposed by Pope et al.<sup>(41)</sup> that the oxidation takes place from the end of the molecule.

Some of the observations that could be made about the effect that changes in the chain length of hydrocarbons have on their oxidation are:

- (i) the longer chain length hydrocarbons are oxidised at a faster rate to what appears to be a kinetic balance of the initial oxidation products and the subsequent scission reactions.
- (ii) the shorter chain hydrocarbons appear to be oxidised at a faster rate to shorter chain oxidation products i.e., the longer chain hydrocarbons have more stable initial oxidation products.
- (iii) The nature of the functional groups present on the oxidised hydrocarbon chains do not appear to change with changes in the chain length of the hydrocarbon.

### 3.3.5 Oxidation of A Blend of Model Compounds

Fischer-Tropsch wax comprises a normal distribution of straight-chain hydrocarbons and information on the oxidation of a blend of straight-chain hydrocarbons would provide information on whether certain chain lengths are preferentially oxidised. This would assist in formulating a proposed composition of the oxidised Fischer-Tropsch hard wax. Model compounds, namely n-C16, n-C24 and n-C32, were blended in equal mass proportions. This blend was oxidised at 170°C for 5 hours, using an air flow of 0.1 cm<sup>3</sup> min<sup>-1</sup> per 50 g of hydrocarbon.

The reaction mixture was first analysed by a Varian model 3410 HTGC to determine the

relative concentrations of the starting material, i.e. the relative concentrations based on peak heights of n-C16, n-C24 and n-C32 in the blend before and after the oxidation. The HTGC chromatograms before and after the oxidation are given in Figure 14.

From the HTGC chromatogram it can be seen that the relative concentrations of the model compounds in the blend decrease faster during oxidation as the hydrocarbon chain length is increased i.e. n-C32 decreases faster than n-C16. Therefore it can be assumed that during the oxidation of Fischer-Tropsch wax, the longer-chain components in the bell-shaped distribution of carbon chain lengths would be oxidised at a faster rate than the shorter-chain components unless other factors such as steric hindrance or chain folding play a more significant role in the rate of oxidation of the longer chain hydrocarbons.

The oxidation products of the blend and of the individual model compounds were studied by AED-GC and the chromatograms are given in Figures 15 to 20. An AED detector was used instead of the usual FID detector in order to detect only the carbon containing molecules.

AED-GC detects only the carbon containing compounds in the sample when run in the carbon mode. This technique was used to determine;

- (i) the change in the relative concentrations of only the carbon containing molecules as the oxidation reaction progressed and
- (ii) whether additional products are formed while oxidising the blend when compared to the oxidation products of the individual model compounds.

Figure 15 depicts the oxidation products of a blend of the model compounds as given by AED-GC. The full chromatogram (0 to 90 minutes) of the oxidised blend is given in this figure. The chromatogram (Figure 15) shows that, as is expected, each hydrocarbon chain is oxidised in a similar manner to the individual model compounds. n-C16, n-C24 and n-C32 i.e., each have their own set of 'initial oxidation products' and 'scission products' similar to when they were

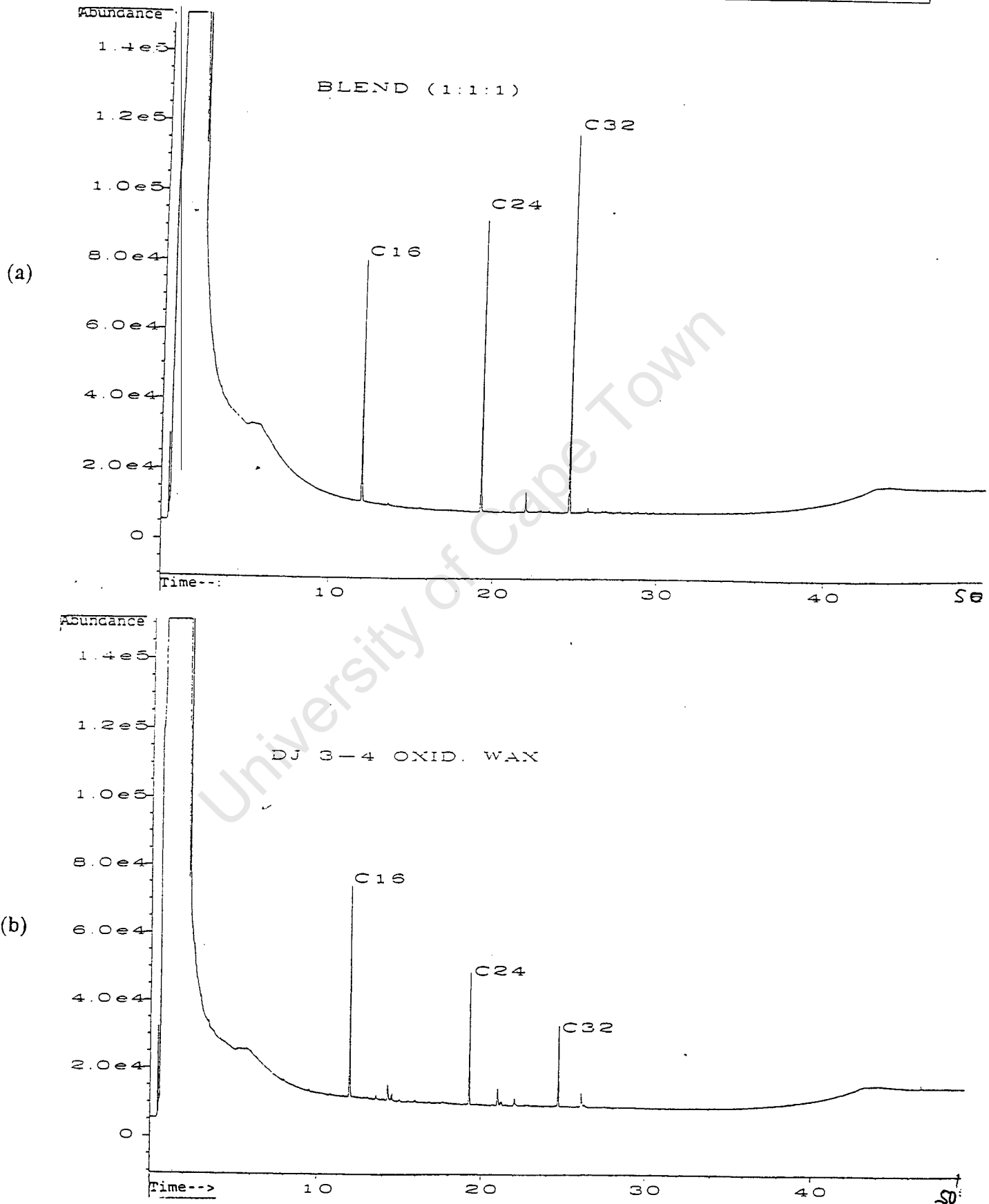


FIGURE 14: HTGC of the oxidation reaction mixture of a blend of model compounds (a) before oxidation and (b) after oxidation

individually oxidised. The 'scission' and the 'initial oxidation products' are formed for each individual model compound within the blend. This chromatogram (Figure 15) shows that the higher carbon number compounds are oxidised faster than the lower carbon number compounds when comparing the relative areas of the n-C16, n-C24 and n-C32 peaks. The concentration of the 'initial oxidation products' is less in the n-C32 model compound of the blend than for the n-C16 and n-C24 model compounds.

The scale of the chromatogram of the oxidation products of the blend (Figure 15) was expanded and compared with the oxidation products from the oxidation of the individual model compounds. Each individual model compound was analysed using the AED detector under the same conditions used for the blend of these model compounds. The different regions in Figure 15 were compared to the corresponding model compound i.e. region 30 to 50 min in Figure 15 was compared to the oxidation products of n-C16, region 50 to 70 min to the oxidation products of n-C24 and the region from 70 to 90 min to the oxidation products of n-C32. These are the retention times of each individual component under the given set of parameters. The oxidation products in these regions of Figure 15 were compared with the corresponding chromatograms of the oxidation products from the individual model compounds.

#### ***Region 0 to 30 minutes of Figure 15***

This region contains the 'scission products' from the oxidation of the blend. The chromatograms in Figures 16 and 17 indicates that the 'scission products' of the blend and of the individual components are almost identical. Oxidation products from the oxidation of the individual components (i.e. n-C16, n-C24 and n-c32) are identical to those from the oxidation of a blend of model compounds. The oxidation products from the oxidation of a blend of model compounds were thus composed of 'scission products' of the oxidation of the individual compounds in the blend superimposed onto each other.

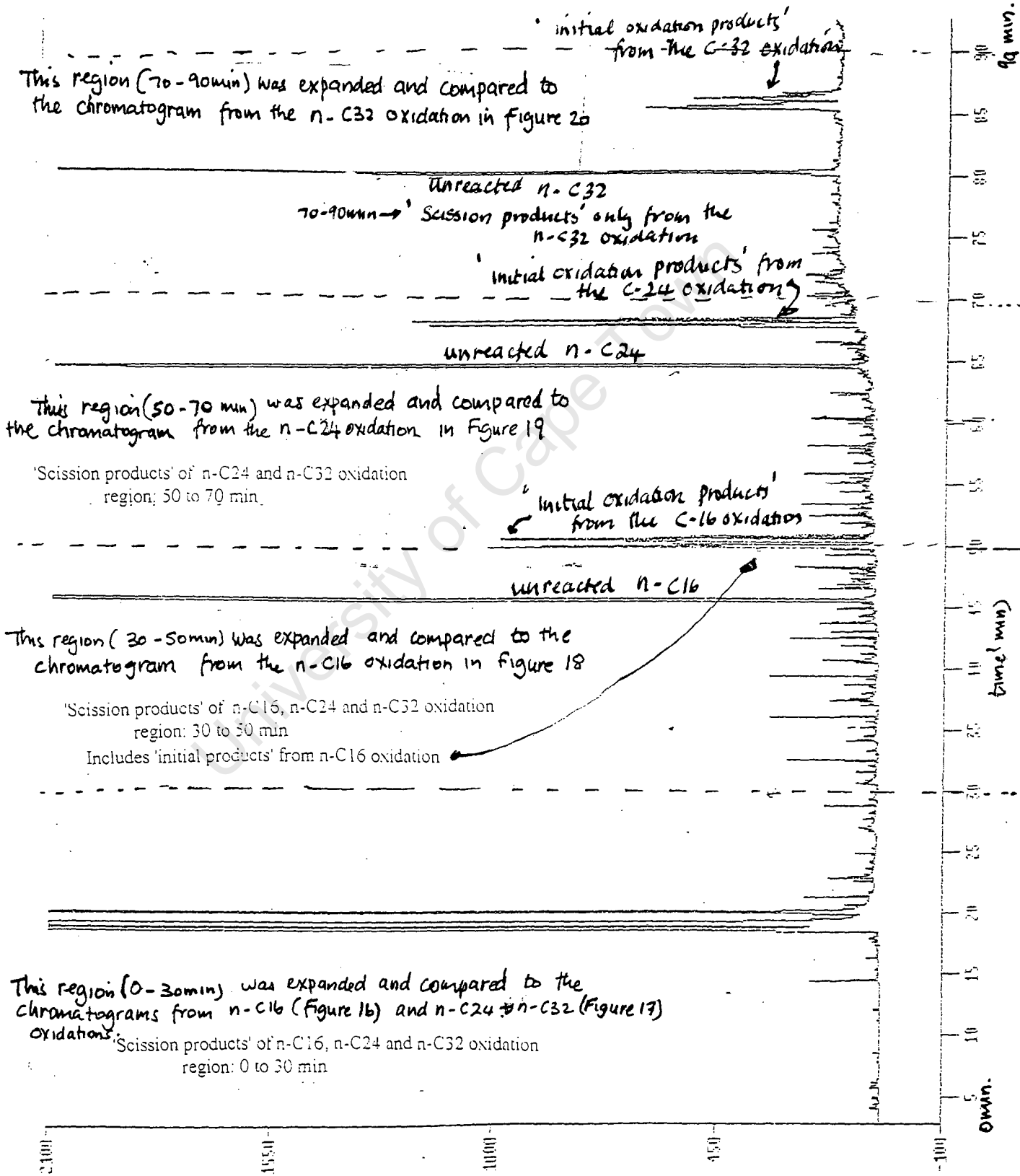


FIGURE 15 : AED-GC of the reaction mixture of the oxidation reaction of a blend of model compounds after 5 hours.

*Region 30 to 50 minutes of Figure 15*

The AED-GC chromatogram in Figure 18 compares the oxidation products from the oxidation of a blend of model compounds with those from oxidised n-C16. This region of the chromatogram of the oxidised blend of model compounds corresponds to the 'scission' and 'initial oxidation product' region (30 to 50 min) of the oxidised n-C16. The oxidation products are similar except for differences in concentration and 'new' peaks in the 36 to 38 minute region of the n-C16 oxidation products which could not be accounted for.

*Region 50 to 70 minutes of Figure 15*

The chromatograms in Figure 19, which compares the 'primary oxidation products' and a section of the 'scission products' from the oxidation of n-C24 with the corresponding oxidation products from the oxidation of blend of model compounds, indicate that the oxidation products are almost identical. The peaks that are different in the blend from 50 to 51 minutes are from the 'initial oxidation products' from the oxidation of n-C16.

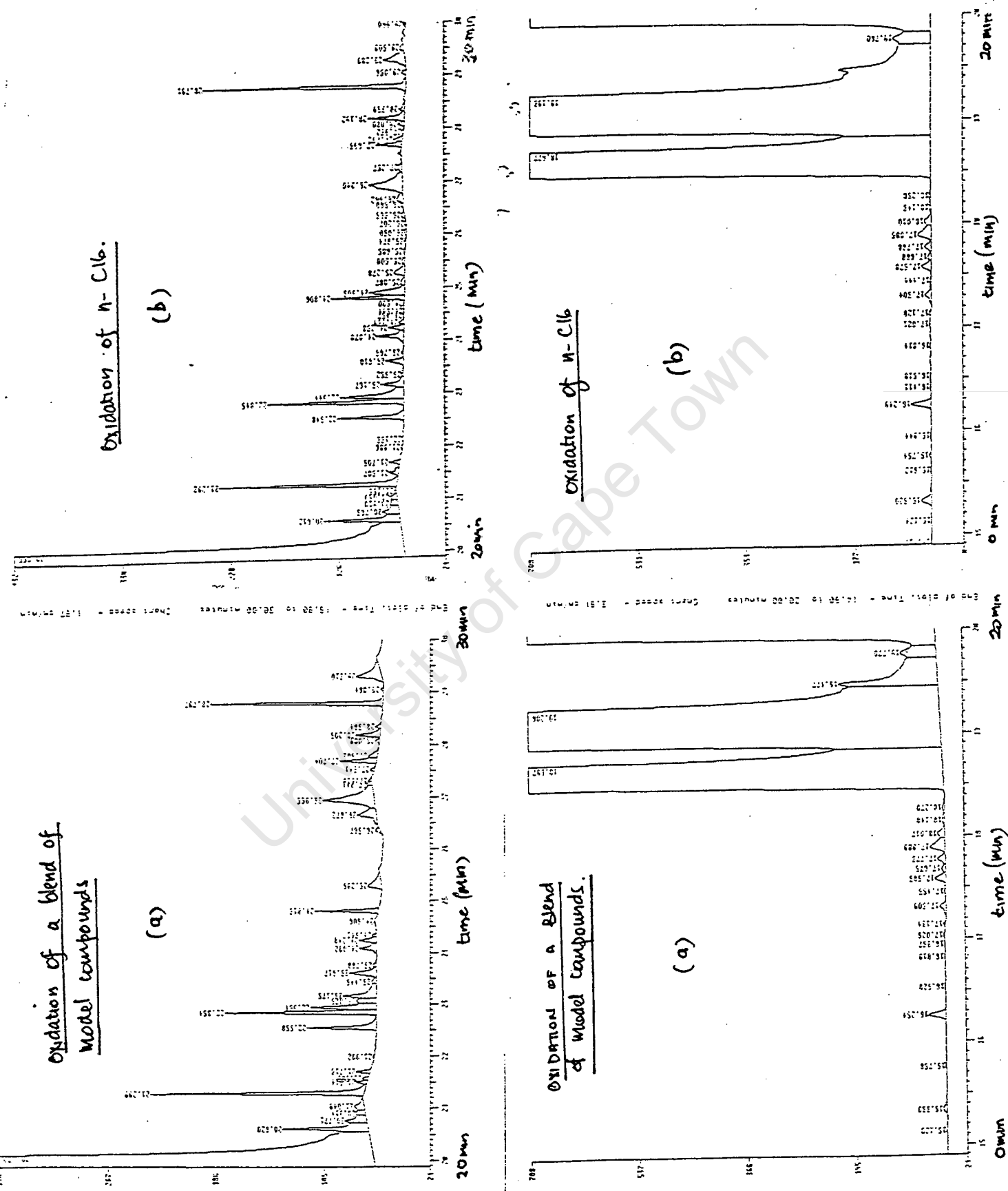


FIGURE 16: AED-GC of the reaction mixture from the oxidation of (a) a blend of model compounds and (b) n-C16 in the 0 to 30 minute region

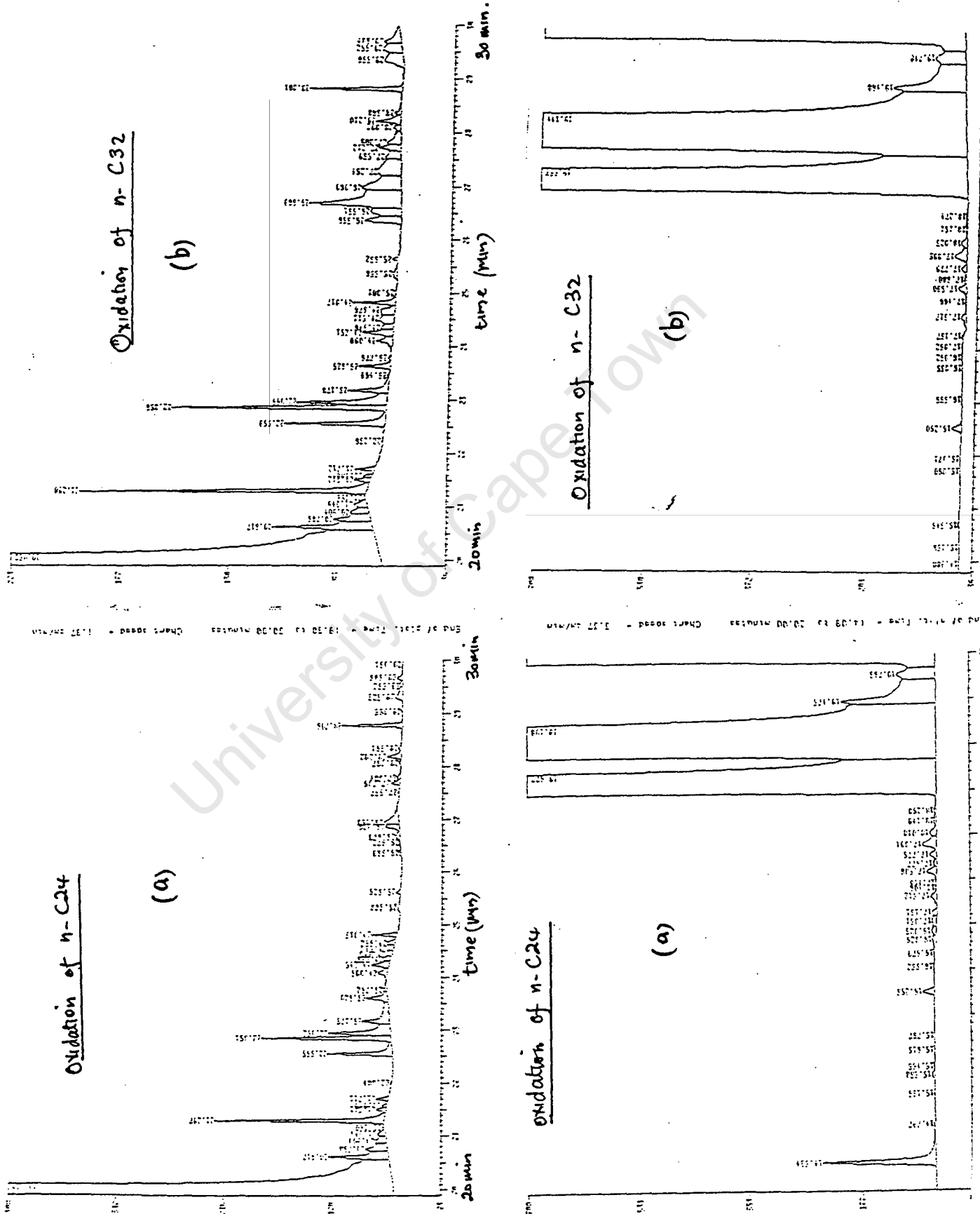


FIGURE 17: AED-GC chromatograms of the reaction mixture from the oxidation of (a) n-C24 and (b) n-C32 in the 0 to 30 minute region.

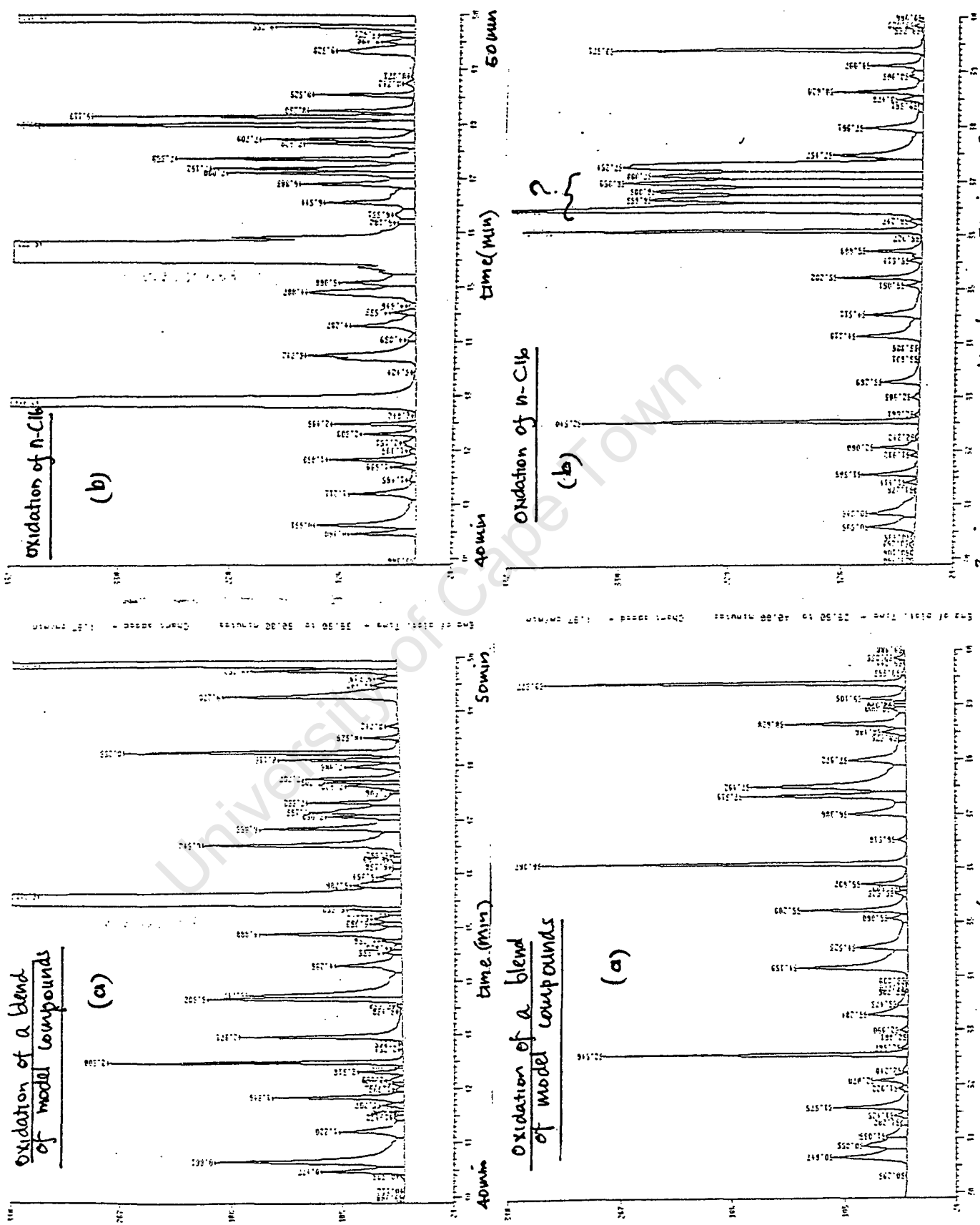


FIGURE 18 : AED-GC chromatograms of the reaction mixture from the oxidation of (a) a blend of model compounds and (b) n-C16 in the 30 to 50 minute region



*Region 70 to 90 minutes of Figure 15*

In Figure 20, the 'initial oxidation products' and a portion of the 'scission products' of the n-C32 oxidation are compared with those of the oxidised blend of model compounds. The oxidation products are similar except for concentration differences. Oxidation products from the oxidation of n-C32, present in both the 'scission' and 'initial oxidation products' region, are relatively more abundant when compared to the oxidation products from the blend. The 'initial oxidation products' and the 'scission products' from the oxidation of n-C32 in the blend appear to be oxidised further to shorter-chained oxidation products faster than for the n-C24 and n-C16 compounds.

The qualitative study which compared the oxidation products from the blend with those of the individual model compounds indicates that the respective oxidation products are practically identical. Whether they are oxidised individually or in a blend of model compounds similar oxidation products were formed. The following are some observations from the qualitative study done in this chapter:

- No 'new' additional products are formed during oxidation of the blend of hydrocarbons with different chain lengths. For instance, the 'initial oxidation products' from the n-C16 oxidation reaction would include the n-C16 alcohols and ketones whereas those for n-C24 would include the n-C24 ketones and alcohols. Oxidation products from the blend of hydrocarbons would have a similar composition with the 'initial oxidation products' of the highest carbon number hydrocarbon determining the highest molecular mass of the 'initial oxidation products'.
- The composition of the 'scission products' from the oxidation of the blend of straight-chain hydrocarbons will follow a similar pattern as given in Section 3.4.1 with respect to the identity of the products and to the maximum carbon numbers of the individual oxidation products. For example, the maximum carbon number of the acids being two less than the carbon number of

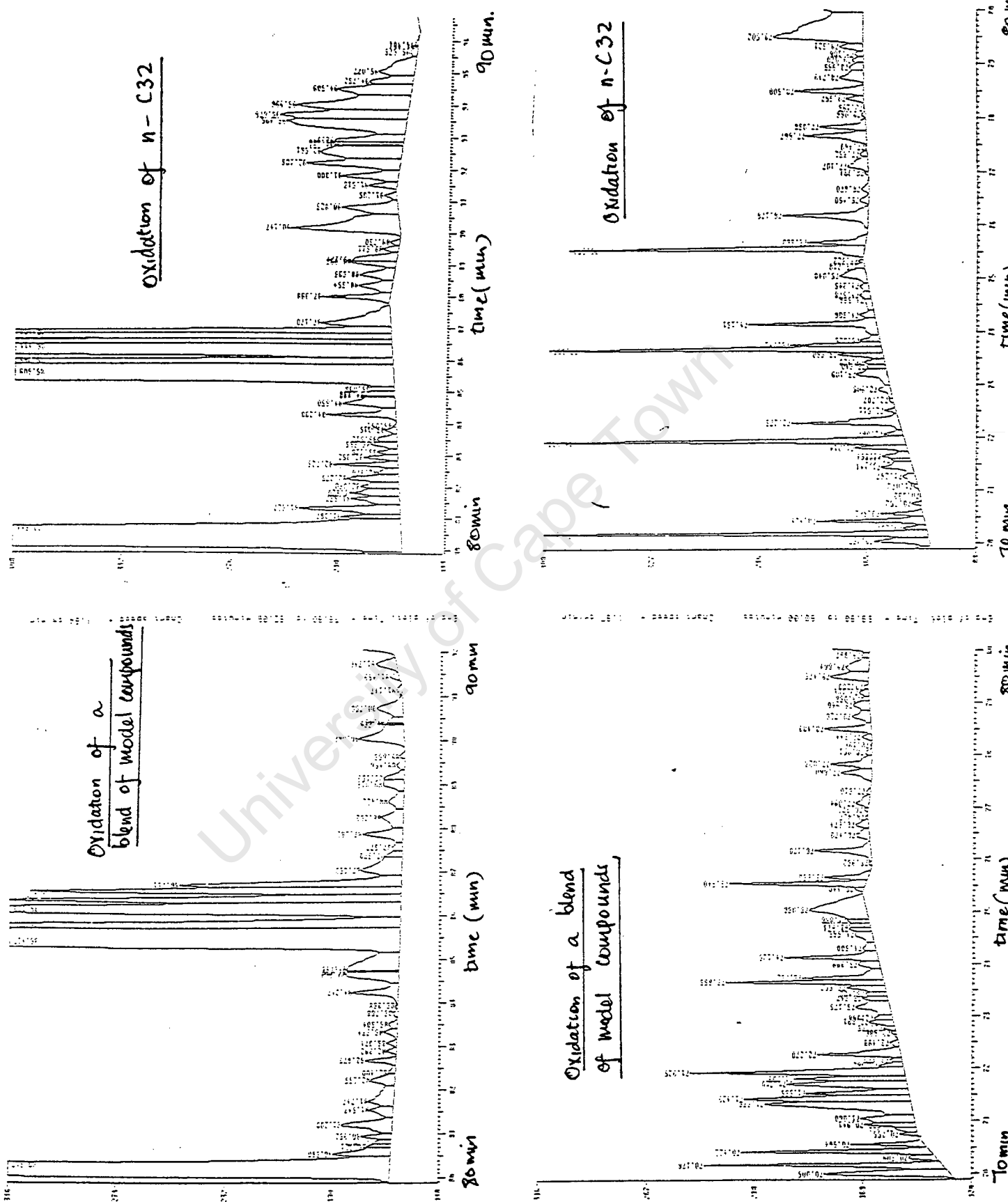


FIGURE 20: AED-GC chromatograms of the reaction mixture of the oxidation of (a) a blend of model compounds and (b) n-C32 in the 70 to 90 minute region

the parent hydrocarbon, etc.

- It appears that the chain length of the hydrocarbon is directly proportional to the rate with which it will be oxidised. The longer-chained hydrocarbons are oxidised at a faster rate.

### 3.4 Conclusions

It is possible from a study of the oxidation products of the model compounds to predict the results of the oxidation of Fischer-Tropsch hard wax assuming that these systems oxidise similarly. The Fischer-Tropsch oxidised hard wax should therefore consist of both 'initial oxidation products' and 'scission products' which should have similar general compositions to the model compounds except for differences in chain length.

The 'scission' products of the Fischer Tropsch hard wax should have the following composition:

- Alkanes ranging from C<sub>2</sub> to the alkane with the carbon number equal to that of the longest-chain hydrocarbon in the Fischer-Tropsch wax.
- Ketones and aldehydes ranging up to the carbon number equal to that of the longest-chain hydrocarbon in the Fischer-Tropsch wax.
- Lactones ranging from carbon 6 to two carbons less than that of the longest-chain hydrocarbon in the Fischer-Tropsch wax.
- Acids having carbon numbers ranging from two up to two less than the carbon number equal to that of the longest-chain hydrocarbon in the Fischer-Tropsch wax.
- Relatively smaller quantities of alcohols (all being primary alcohols) when compared to the other functional groups
- No straight chain esters.

The 'initial oxidation products' from the oxidation of Fischer-Tropsch hard wax will be similar to the 'initial oxidation products' from the model compound oxidation except that the carbon chain

lengths will differ. These 'initial oxidation products' have not been conclusively identified even for the model compounds, because of co-elution. However, the major components were identified. Based on the identity of the major oxidation products from the oxidation of model compound, these 'initial oxidation products' of the Fischer-Tropsch hard wax are considered to be composed mainly of the following major compounds:

- Ketone with the 2- and 3- isomers being predominant.
- Alcohols with the 2- isomer being predominant.
- Straight chain esters although their concentration and their identity could not be conclusively be determined due to co-elusion.

These 'initial oxidation products' will have molecular masses at least up to that of the that of the longest-chain hydrocarbon in the Fischer-Tropsch wax.

Other observations made during the oxidations of the model compounds are:

- The concentration of the components of the 'initial oxidation products' remained more or less constant throughout the oxidation once a certain maximum is reached. The 'scission products' on the other hand, increase as the oxidation progresses.
- A certain percentage of starting hydrocarbon chain remain unaffected by the oxidation process. As mentioned on page 37 and gleaned from the the various chromatographs in the dissertation especially Figure 9 on page 46, the 'initial oxidation products' will after a certain time interval, be oxidised to 'scission oxidation' products by the available oxygen, in preference to the oxidation of the unreacted starting hydrocarbon.

The complete identification of the components of the 'initial oxidation products' and quantification of the unreacted starting hydrocarbon will be attempted in subsequent research programs which will investigate techniques to reduce the amount unreacted starting hydrocarbon.

The composition of the oxidised Fischer-Tropsch wax as proposed in this chapter will be verified with the research findings reported in the remaining chapters of this dissertation.

## **4.0 COMPOSITION OF THE LIGHTER FRACTIONS IN OXIDISED FISCHER-TROPSCH HARD WAX**

### **4.1 INTRODUCTION**

A composition of the oxidised Fischer-Tropsch hard wax was proposed in Chapter 3 based on the results from the model compound oxidations and the oxidation of a blend of these model compounds. To verify this proposed composition of the oxidised Fischer-Tropsch hard wax, the lighter fraction of the oxidised Fischer-Tropsch hard wax was analysed to determine whether the proposed products were present in this lighter fraction. It was not possible to analyse the heavier fraction of the oxidised Fischer-Tropsch hard wax by GC-MS because the long-chain hydrocarbons have high boiling points. In order to analyse a compound by GC-MS, the sample must be volatilised to allow the gaseous molecules to elute through the column where they are separated prior to mass spectroscopic determination. The heavier fraction of the oxidised Fischer-Tropsch hard wax cannot be volatilised at the maximum temperature conditions (~250°C) that the GC column packing can tolerate and can therefore not be analysed using GC-MS techniques.

### **4.2 EXPERIMENTAL**

Oxidised Fischer-Tropsch hard wax was distilled under a vacuum of 5 mm Hg to a residue temperature of 100°C. The distillation flask was heated in a heating mantle. The condenser was cooled with tap water (~25°C). The distillate was analysed by GC-MS to identify the components in the lighter fraction of the oxidised wax.

The sample (1 µl) was analysed by a GC-MS system equipped with a 50 m PONA column. The GC-MS conditions to effect the separation are given in Section 3.2.3. The Wiley 138

database was used to assist in the identification of the compounds.

### 4.3 RESULTS AND DISCUSSION

A section of the GC-MS chromatogram of the distillate from the vacuum distillation of the oxidised Fischer-Tropsch hard wax is given in Figure 21. The component table and the complete set of GC-MS chromatograms are collated in Appendix 2. A distinguishing feature of the chromatogram is its remarkable similarity to the oxidation products identified for the model compounds oxidations. To summaries the most important features of the research findings:

- No normal straight chain esters were detected in the chromatograms. Cyclic esters, namely, substituted furanones or lactones were present.
- 2- ketones are present in fairly high concentrations. It is interesting to note that 2- ketones are the most abundant while the 3,5 and 6 isomers are present only in very small quantities. This is consistent with the literature<sup>(54)</sup> that the major products obtained from the oxidation of linear hydrocarbons were those formed by substitution at the 2- position.
- The aldehydes are present in very small quantities. This is to be expected because aldehydes can be further oxidised to form carboxylic acids<sup>(60)</sup>.
- Only minute quantities of alcohols were detected, e.g. referring to the component table of Appendix 2., 14 (a) decanol, 28 (a) tridecanol, etc.
- Carboxylic acids and alkanes are also present in substantial concentrations

Alkanes, ketones and carboxylic acids of consecutive chain lengths were detected. Similar results were obtained for the 'scission section' of the oxidation products from the model compound oxidation.

The distilled fraction was thus the 'scission products' of the oxidised Fischer-Tropsch Hard wax.

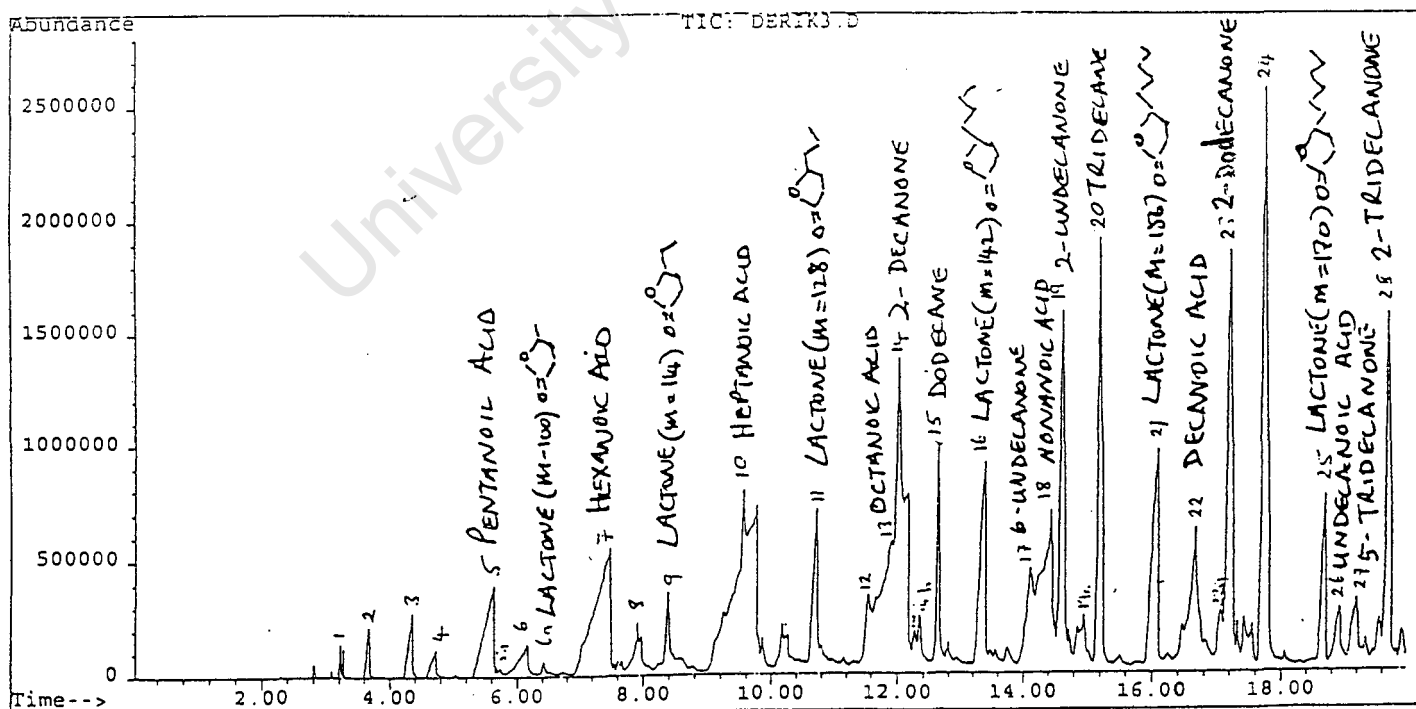
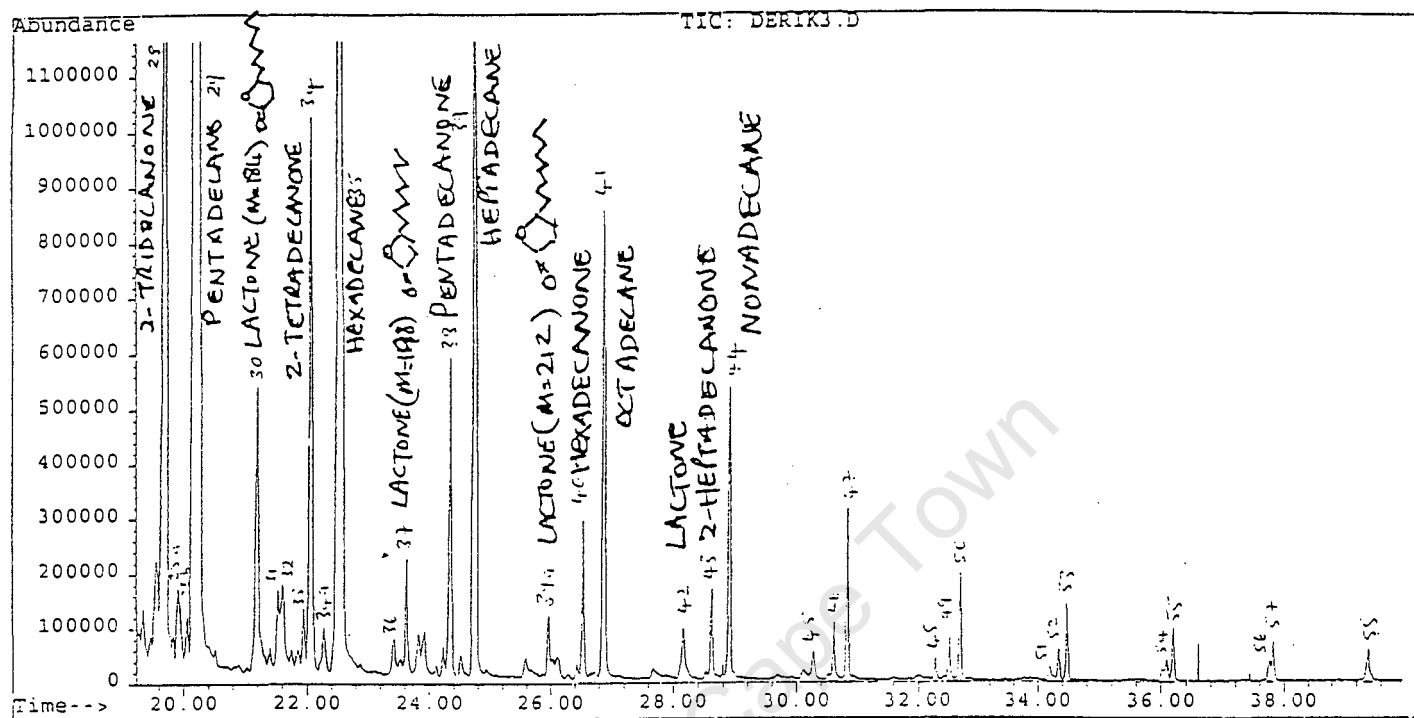


FIGURE 21 : GC-MS chromatograms from the distillate from the vacuum distillation of oxidised Fischer Tropsch hard wax.

It was remarkably similar to the products from the model compound oxidations, only differing in chain length. These results support the proposed composition of oxidised Fischer-Tropsch hard wax.

#### 4.4 CONCLUSIONS

The products isolated by the vacuum distillation were the lighter more volatile components of the oxidised wax. The Fischer-Tropsch hard wax range in chain length from approximately C30 to C100. The 'initial oxidation products' would therefore have chain lengths equal to or greater than approximately C30 and would not be distilled over under the experimental conditions. Therefore, the products which were detected are all 'scission products' of the oxidation.

The same pattern of the 'scission products' which were detected in the GC-MS chromatograms of the oxidation products from the model compounds oxidations, were also detected in the GC-MS chromatograms of the distillate from the vacuum distillation of oxidised Fischer-Tropsch hard wax (Figure 21). Each hydrocarbon chain in the Fischer-Tropsch hard wax was oxidised to yield products which were similar (except for differences in chain length) to the products obtained from the oxidation of a blend of model compounds.

Thus the 'scission products' of the oxidation of Fischer-Tropsch hard wax will be similar to those from the oxidation of model compound but will have longer chain lengths. Therefore, the bulk of the wax is expected to be composed of hydrocarbon chains with the same functional groups of the distilled lighter fraction, but have longer chain lengths.

As was stated previously, these results support the proposed composition of the 'scission products' of oxidised Fischer-Tropsch hard wax as outlined in Chapter 3

## 5.0 COLUMN SEPARATION OF OXIDISED FISCHER-TROPSCH HARD WAX

### 5.1 INTRODUCTION

Oxidised Fischer-Tropsch hard wax was separated on a silica column in an attempt to verify the structure proposed in Chapter 3. Hard wax consists of a normal distribution of carbon chains spanning 30 to 100 carbon atoms with an average of approximately 60 carbon atoms. The oxidation products of the Fischer-Tropsch hard wax form a complex mixture of functionalised and unfunctionalised chains. Until now, it is impossible to analyse this complex mixture of oxidised material using conventional analytical techniques.

To facilitate the analysis, oxidised Fischer-Tropsch hard wax was separated into fractions. It was hoped that the separated wax fractions could be analysed using conventional analytical techniques. However, the mass spectroscopic results and nuclear magnetic resonance spectra (both proton and carbon 13 NMR) of the fractionated oxidised wax were even then too complex to interpret. The only instrumental techniques which gave meaningful results were infrared spectroscopy, differential scanning calorimetry and high temperature gas chromatography.

The results from these analytical techniques indicate that the proposed composition of the oxidised Fischer-Tropsch hard wax as discussed in Chapter 3, correlates well with the actual composition of thermally oxidised Fischer-Tropsch hard wax.

### 5.2 EXPERIMENTAL

Materials used to effect the separation of the oxidised Fischer-Tropsch hard wax:

Dimethyl formamide, Analar grade (GLC assay : 99.5% min.) was obtained from BDH Chemicals Ltd in Poole England. Methanol, chemically pure, was obtained from CJ Chem, Johannesburg.

Xylene, chemically pure, was obtained from CJ Chem, Johannesburg.

Silica Gel 60 (200-400 mesh ASTM) was obtained from Merck, Germany.

All the solvents were distilled prior to use.

A diagram of the apparatus used for the column separation appears in Figure 22.

Merck silica gel 60 (300 g) was activated at 250°C for 12 hours. The activated silica gel was transferred in a xylene slurry to a jacketed glass column which was maintained at a temperature of 93°C- 95°C by circulating hot silicon oil (95°C) through the jacket. The column was compacted to remove air bubbles or 'channels' in the silica gel column along which the wax could flow without being adsorbed. The excess xylene was eluted until the level was ~1 cm above the silica gel.

Solid oxidised Fischer-Tropsch hard wax (Parafint A1) was transferred to the column and allowed to melt. Hot xylene was carefully added to the top of the column in order to adsorb the wax onto the silica gel while using the minimum amount of xylene. The oxidised wax was eluted through the silica gel column with hot xylene while maintaining a solvent level of not less than ~1 cm above the silica gel. The eluted xylene fractions were distilled to constant mass and the mass of the residue was recorded. This process was continued until the mass of the residue from the xylene fractions was negligible.

Thereafter, the polarity of the solvent was gradually increased to elute the more polar components of the oxidised Fischer-Tropsch hard wax which were adsorbed onto the silica gel. The polarity of the solvent was increased by adding DMF (which is relatively more polar than xylene) to xylene. Starting with 20 mls DMF per 400 mls xylene (5 % v/v DMF in xylene), the volume of DMF in xylene was gradually increased to 50% v/v DMF in xylene. The column was finally eluted with undiluted DMF to remove the highly polar components. Fractions of

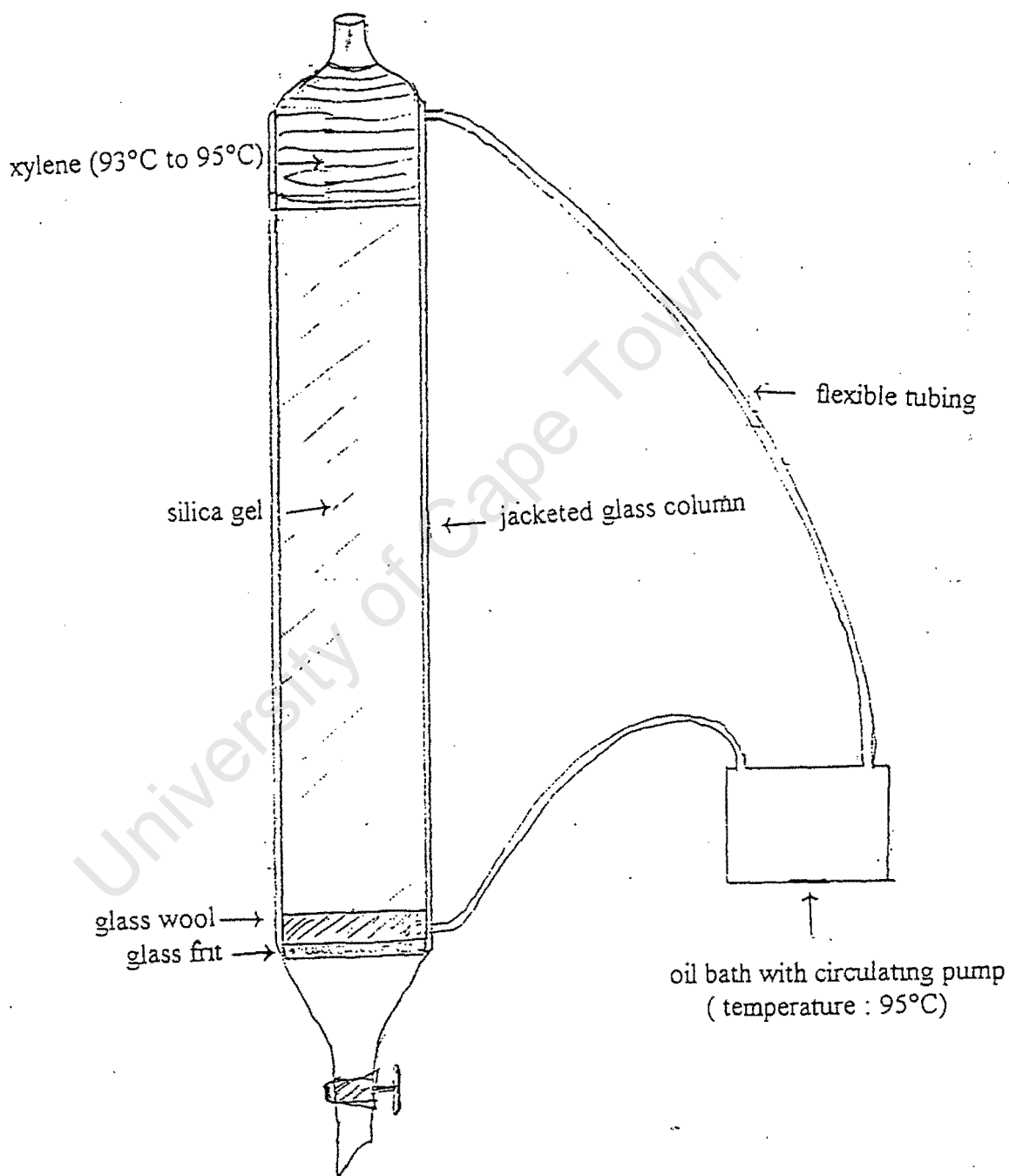


FIGURE 22: Diagram of the silica column for the fractionation of oxidised Fischer-Tropsch hard wax

approximately 100 to 200 cm<sup>3</sup> of the eluent were collected, the solvent was evaporated to constant mass under vacuum, and the mass of the various residues was recorded. The table specifying the masses and conditions under which the fractions were collected is given in Appendix 3(b). Selected samples were analysed for acid value. DSC, IR and HTGC analyses were also performed on selected samples. The acid values of the fractions were determined using ASTM D1386-83.

#### *DSC Conditions*

The thermal analysis of the oxidised wax fractions were done on a Perkin Elmer System 4 Differential Scanning Calorimeter using the following conditions:

sample weight: ~2 mg

initial temperature: 0°C

final temperature: 130°C

scan rate: 10°C min<sup>-1</sup>

The wax samples were analysed in aluminium sample pans with lids in a nitrogen atmosphere.

#### *IR Conditions*

The oxidised wax fractions were analysed on a Nicolet Fourier-Transform Infrared Spectrometer.

The samples were prepared as KBr discs and scanned from 4000 to 500 cm<sup>-1</sup>.

#### *HTGC Conditions*

Initial column temperature: 60°C for 5 minutes

Final column temperature: 440°C for 5 minutes

Injector temperature : 40°C for 0 minutes

Ramp rate for the column : 10°C min<sup>-1</sup>

Ramp rate for the injector : 70°C min<sup>-1</sup>

Detector temperature : 450°C for 48 minutes

Carrier gas : Hydrogen

Flow rate :  $5 \text{ cm}^3 \text{ min}^{-1}$

Solvent : xylene

### 5.3. RESULTS AND DISCUSSION

The silica gel column separated the wax into polar and non-polar components. The efficiency of the separation depends on the type of solvent used for the elution and the degree of adsorption of the oxidised wax onto the silica gel column.

#### *Fraction 1*

The outputs of the HTGC, IR and DSC analyses of the first fraction appear on Figure 23. The chromatogram of the HTGC analysis indicates that this wax fraction has an average carbon number of approximately 70. A standard with a chain length of 36 carbon atoms was co-injected with the fractionated oxidised wax sample. The position of hydrocarbon with 70 carbon atom (C70) is located on the chromatogram by counting the peaks starting from the C36 standard peak. Each peak represents one carbon atom.

The narrow melting range on the DSC plot indicates that this wax fraction is highly crystalline. The DSC maximum, which is an indication of the melting point of the wax, is approximately  $99^\circ\text{C}$ . The double peak on the DSC plot cannot be explained conclusively but it is thought that:

- (i) the first peak (at  $\sim 100^\circ\text{C}$ ) is due to the partial melting of less organised crystals,
- (ii) the trough is due to reorganising and crystallisation of hydrocarbon chains which results in the absorption of energy and
- (iii) the second peak (at  $\sim 110^\circ\text{C}$ ) is due to the melting of crystalline material including those that were formed in (ii) above.

The IR scan shows a small peak for carbonyls at  $1720 \text{ cm}^{-1}$ , a peak typical of straight chain

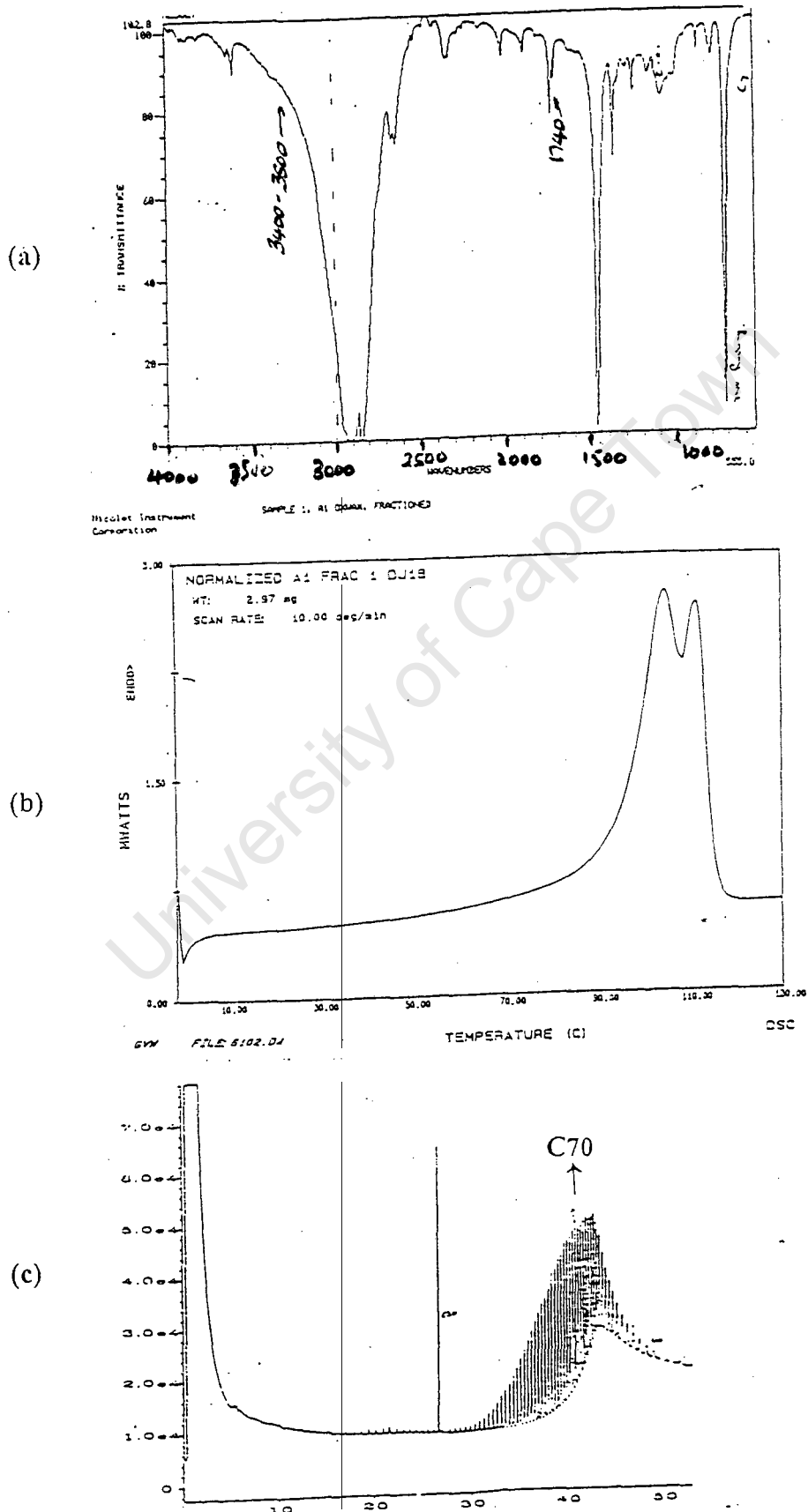


Figure 23: Fraction 1 from the column separation of oxidised Fischer-Tropsch hard wax. (a) IR scans (b) DSC plot (c) HTGC chromatogram

normal esters at  $1740\text{ cm}^{-1}$  and no peak at  $3400\text{-}3500\text{ cm}^{-1}$  for alcohols or acids.

The results from the three analytical techniques indicated that this fraction contains a small percentage of long chain esters and ketones but consists mostly of long chain unfunctionalised hydrocarbons. It does not contain any lactones, alcohols or acids. The functionalised hydrocarbon chains of this fraction is typical of the 'initial oxidation products' of the oxidised wax. The major components of this fraction however were long chain alkanes which could also be the 'scission products' of longer chain hydrocarbons or unreacted starting alkanes, as discussed in Chapter 3.

#### *Fractions 2 and 4*

The outputs of the instrumental analyses for fractions 2 and 4 appear in Figures 24 and 25 respectively.

These fractions have IR scans similar to the IR scan of fraction 1. The functional groups present on the hydrocarbon chains in fraction 1 were therefore similar to those present on the hydrocarbon chains in fractions 2 and 4.

The HTGC chromatograms indicate that the carbon number of the hydrocarbon chains becomes progressively smaller from fractions 1 to 4. Fraction 4 has more shorter-chain material than fraction 2 (average carbon chain lengths of approximate 36 and 45 respectively).

The DSC plots also indicate the presence of lower melting material which confirms the existence of shorter chain length material detected by HTGC. The DSC maximum shifted from approximately  $90^{\circ}\text{C}$  for fractions 2, to approximately  $70^{\circ}\text{C}$  for fraction 4. The above results imply that the hydrocarbon chains in these fractions have similar functional groups to those of fraction 1 but are of shorter chain length.

The combined fractions 1, 2 and 4 contained hydrocarbons having chain lengths representative of the entire normal distribution of chain lengths for a typical Fischer-Tropsch hard

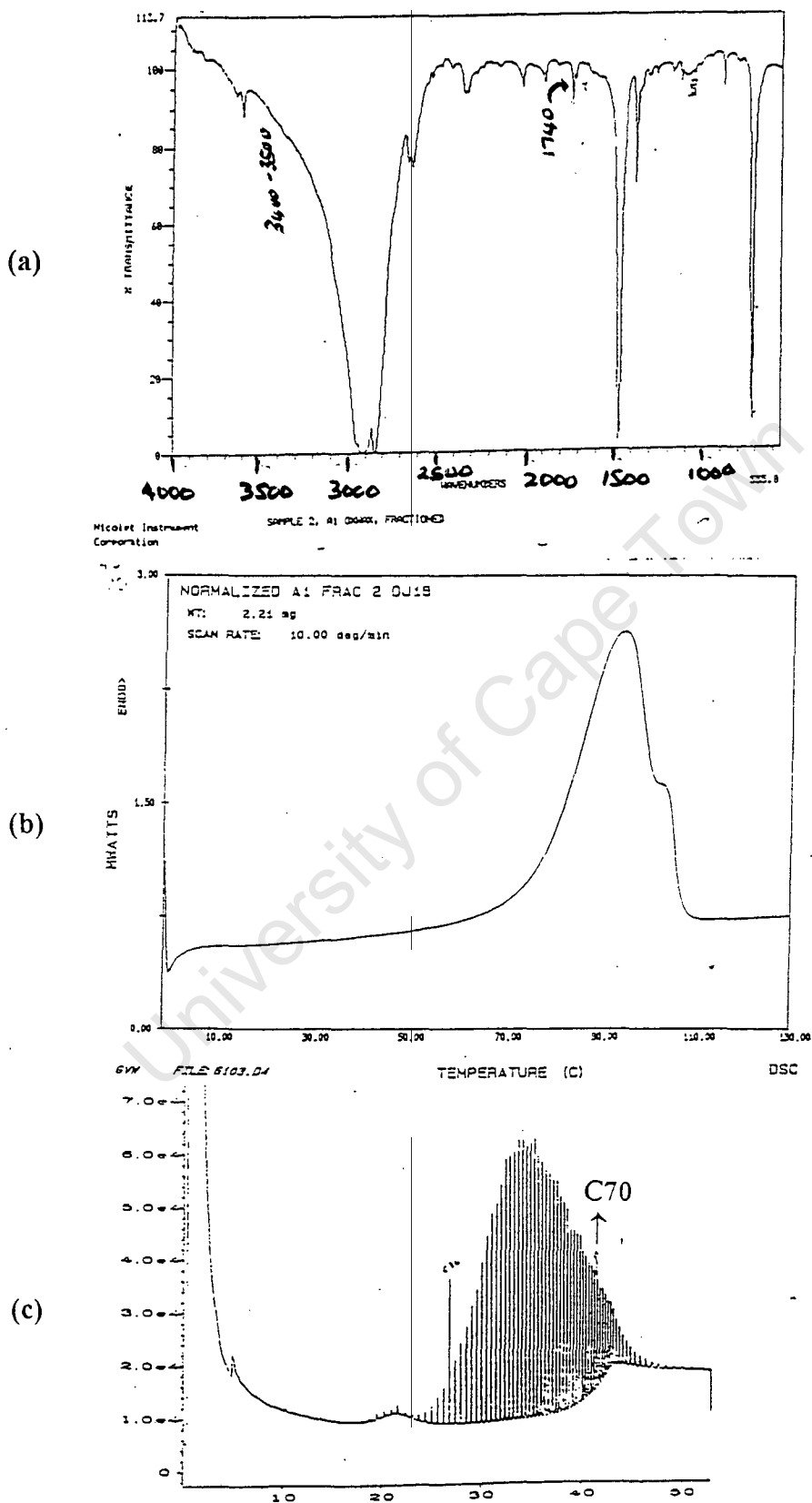


Figure 24: Fraction 2 from the column separation of oxidised Fischer-Tropsch hard wax. (a) IR scans (b) DSC plot (c) HTGC chromatogram

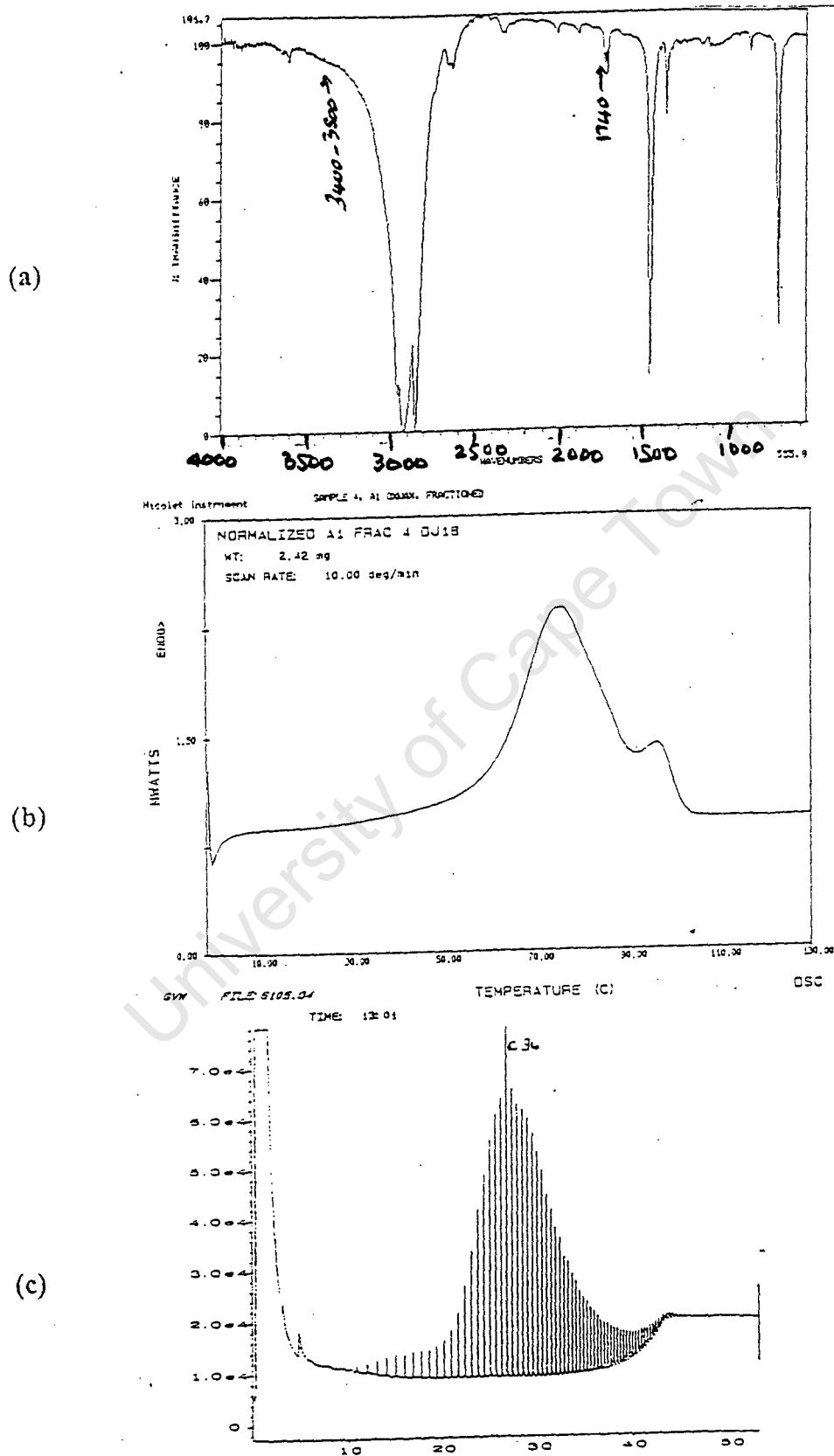


Figure 25: Fraction 4 from the column separation of oxidised Fischer-Tropsch hard wax. (a) IR scans (b) DSC plot (c) HTGC chromatogram

wax, i.e. they spanned from approximately C30 to C100. The combined fractions 1 to 4 contained the alkanes, long chain esters and ketones of the oxidised Fischer-Tropsch wax and represents approximately 10 percent of the starting mass. The long chained esters and ketones have predominantly more non-polar character and were adsorb onto the silica column to a similar degree as the non-functionalised alkanes. This could explain why the longer chained hydrocarbons containing ketone and ester functional groups, were eluted together with the non-polar alkanes. The DSC chromatograms indicated that the wax from these fractions were relatively more crystalline than subsequent fractions (sharp DSC peaks are characteristic of highly crystalline compounds).

#### *Fraction 8*

The outputs of the analytical analyses of fraction 8 appear in Figure 26. The hydrocarbons in this fraction had an acid value of zero and also had a strong carbonyl absorbance at  $1721\text{ cm}^{-1}$  due to ketones, and at  $1736\text{ cm}^{-1}$  due to normal straight chain esters. There was also a strong hydroxyl absorbance at  $3422\text{ cm}^{-1}$  which had to be due solely to alcohols and not to carboxylic acids because the acid value was zero.

The HTGC chromatograms indicated that the carbon chain length of the hydrocarbons averaged around C36. There were hydrocarbons containing different functional groups and of varying chain lengths whose normal distribution peaked at different times. Thus the separation was incomplete and caused the appearance of 'sets' in the HTGC trace. This fraction therefore contained the esters, alcohols and ketones groups of the entire range of hydrocarbon chains present in the Fischer-Tropsch wax before oxidation. No lactones and acids were detected in this fraction.

The 'initial oxidation products' (alcohols, esters and ketones) which form prior to chain

scission to shorter chain oxidation products, were present in this fraction. Their carbon numbers spanned the entire normal carbon chain distribution of typical Fischer-Tropsch hard wax. This implied all chain lengths of the hydrocarbons which were present in the Fischer-Tropsch hard wax, were oxidised to produce 'initial oxidation products'. This was also observed for the model compounds. The oxidation of Fischer-Tropsch hard wax were, therefore, not limited to the preferential oxidation of certain carbon chain lengths. The presence of these 'initial oxidation products' in the commercial product of oxidised Fischer-Tropsch wax indicated that the hydrocarbon chains were oxidised to 'initial oxidation products' for the entire duration of the oxidation.

As stated above, normal esters were detected in this fraction. They were not detected in the GC-MS chromatograms of the distillate of oxidised Fischer-Tropsch wax (Chapter 4) nor in the 'scission section' of the GC-MS chromatograms of the oxidised model compounds (Chapter 3). IR scans of the model compound oxidation (collated in Appendix 4), also indicated the presence of normal esters. These esters were detected in the unresolved complex 'initial oxidation product' section of the GC-MS chromatograms of the oxidation products from the model compound oxidation (Figure 6).

#### *Fraction 12*

The outputs of the instrumental analyses of fraction 12 appear in Figure 27, The HTGC chromatogram showed a shift to larger carbon numbers. The hydrocarbons in fraction 12 have longer chain lengths than those of fractions 2 to 8. These longer chained hydrocarbons were retained onto the silica gel column longer than the shorter-chain hydrocarbons which were eluted in the previous fractions. This was because they had more polar functional groups on the carbon chain. This fraction had a similar carbon distribution to fraction 1 in Figure 23.

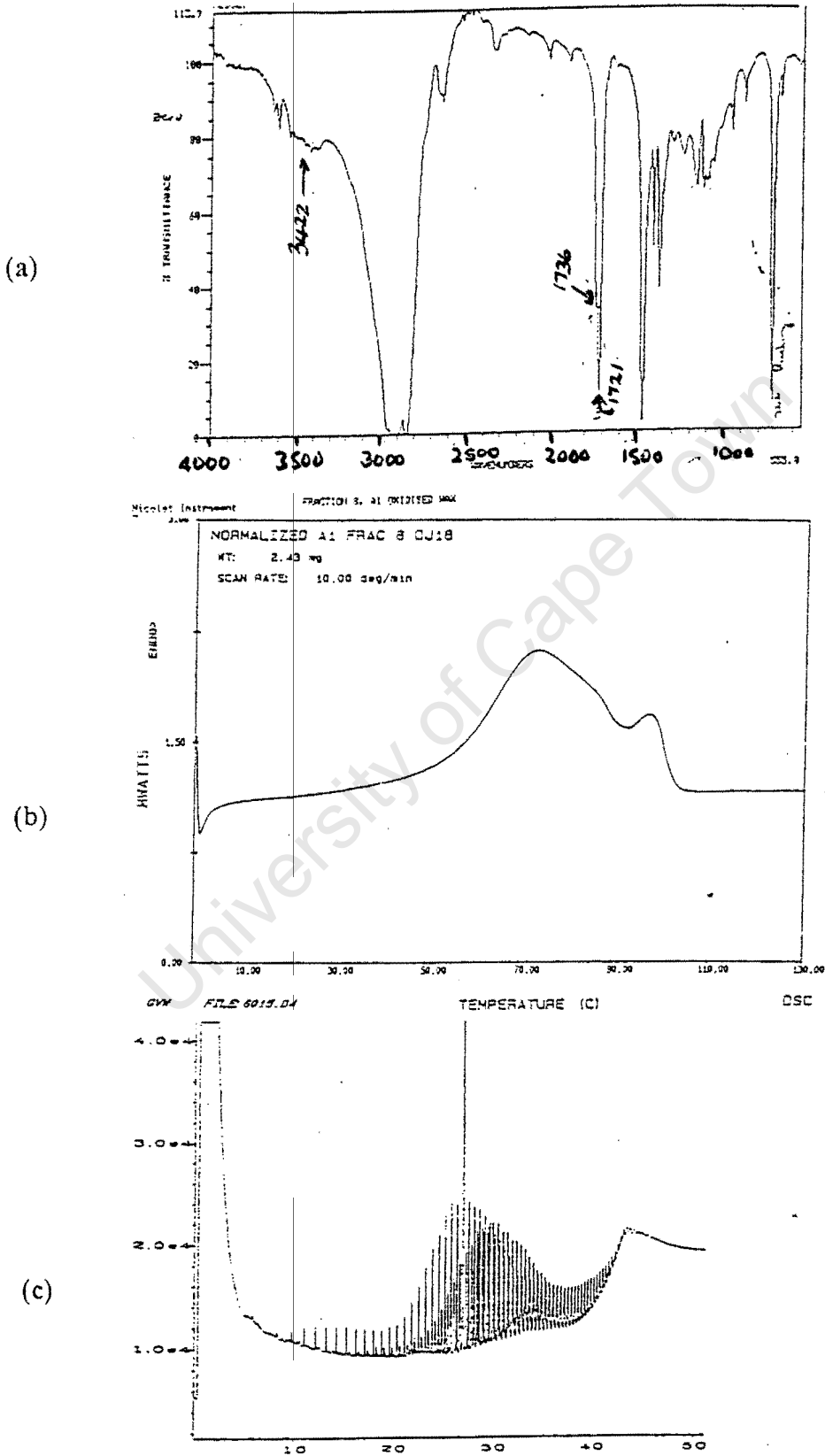


Figure 26: Fraction 8 from the column separation of oxidised Fischer-Tropsch hard wax.  
 (a) IR scans (b) DSC plot (c) HTGC chromatogram

The IR scan indicated the presence of lactones ( $1780\text{ cm}^{-1}$ ) and acids. The strong carbonyl peak, which together with the flatter peak at  $3452\text{ cm}^{-1}$  (cf. fraction 8 in Figure 22 ) indicate the presence of acids. The acid number of this fraction was 22 mg KOH/g. These are the longer chained acids and lactones which were produced by the oxidation of the longer chain hydrocarbons present in the Fischer-Tropsch hard wax. Acids and lactones are, by the definition used in this dissertation, the 'scission products' of the oxidation. They are formed by the oxidation or further reactions of the 'initial oxidation products'. When considering the model compound oxidation in Chapter 3, these were typically the products of the oxidation reaction which have carbon chain lengths close to that of the parent hydrocarbon. Longer chain length 'scission products', similar to those observed for the model compound oxidation, were present in the oxidised Fischer-Tropsch hard wax.

Therefore, the oxidation of hydrocarbon chains in the Fischer Tropsch hard wax and the oxidation of hydrocarbon chains of the model compounds formed similar oxidation products. These were therefore, the 'scission products' produced by the oxidation of the longer chained hydrocarbons of the Fischer-Tropsch hard wax.

The DSC plots indicated that, although the chain lengths of the hydrocarbons of this fraction were as high as that of fraction 1, the material was less crystalline. This is due to the presence of functional groups on the carbon chains which disrupted the crystal formation and therefore affected the crystallinity of the wax.

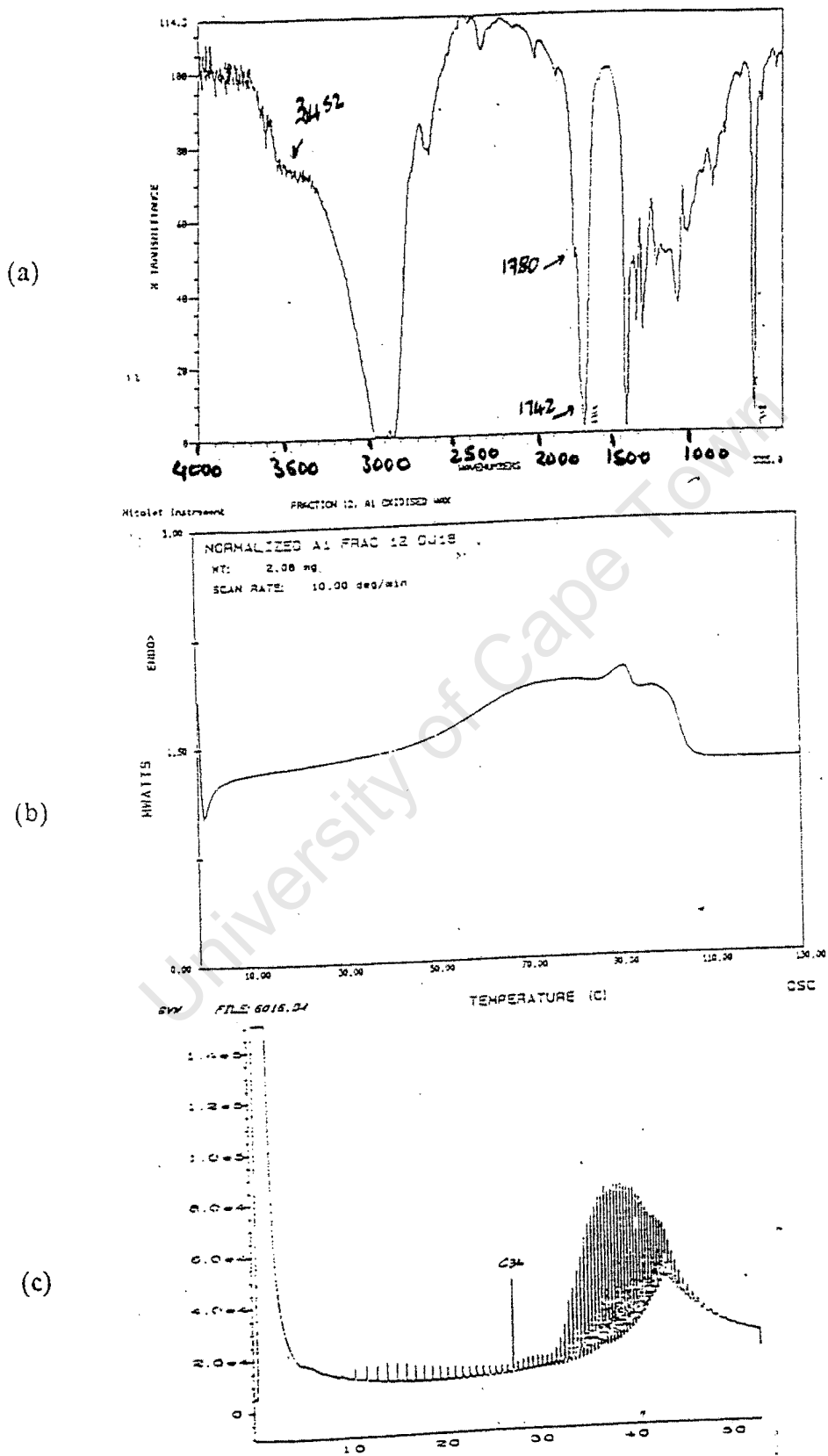


Figure 27: Fraction 12 from the column separation of oxidised Fischer-Tropsch hard wax.  
(a) IR scans (b) DSC plot (c) HTGC chromatogram

*Fractions 16 and 20*

The instrumental analyses output of fractions 16 and 20 appear in Figures 28 and 29 respectively. The DSC plots and IR scans were similar to those of fraction 12. The only difference was a shift to lower temperatures of the DSC maxima which indicated the presence of lower melting material. The IR scans again indicated the presence of acids, lactones and ketones. The HTGC chromatograms of these fractions showed that shorter chain lengths hydrocarbons were retained longer onto the silica gel.

Combined fractions 12 to 20 are composed of functionalised hydrocarbons with chain lengths which spans the entire range of chain lengths of the Fischer-Tropsch hard wax (i.e carbon numbers span ~20 to ~100). As stated above, the IR scans indicated that these fractions contained acids, ketones and lactones. These were therefore the 'initial oxidation products' of the oxidation and could contain acids with carbon numbers up to two less than the number of carbon atoms of the parent molecule (cf model compound oxidations in Chapter 3).

It is not expected that any of the fractions which were analysed contained any short chain acids. This is firstly because the more polar shorter chain acids are adsorbed onto the silica gel more strongly and secondly, the HTGC chromatograms (cf Figures 28 and 29) indicated that the longer chained hydrocarbons eluted before the shorter ones. The former is because the longer chain acids have a strong alkane character and therefore display more non-polar characteristics. They will therefore be retained onto the silica column to a lesser degree than the shorter chain acids.

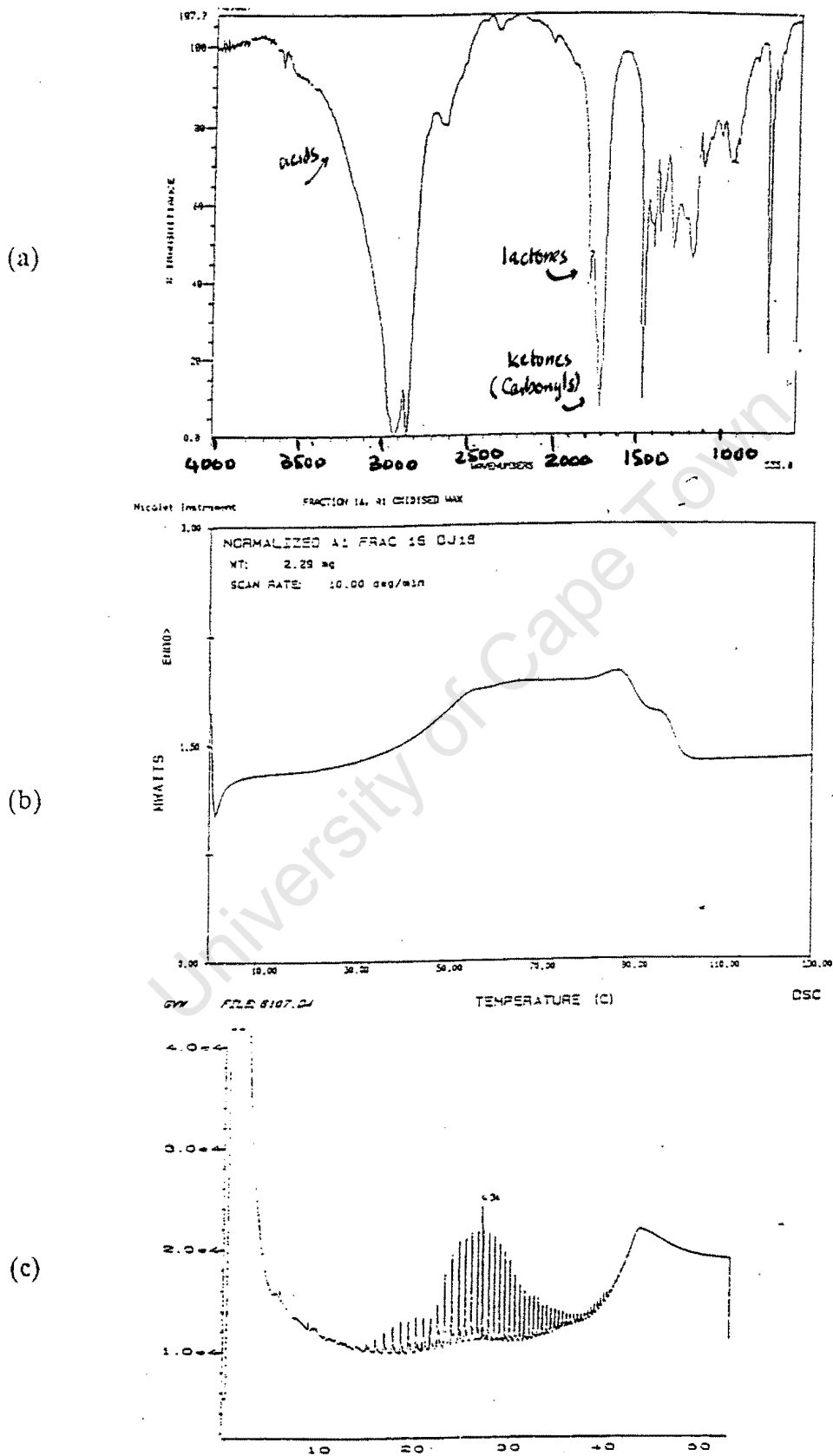


Figure 28: Fraction 16 from the column separation of oxidised Fischer-Tropsch hard wax.  
(a) IR scans (b) DSC plot (c) HTGC chromatogram

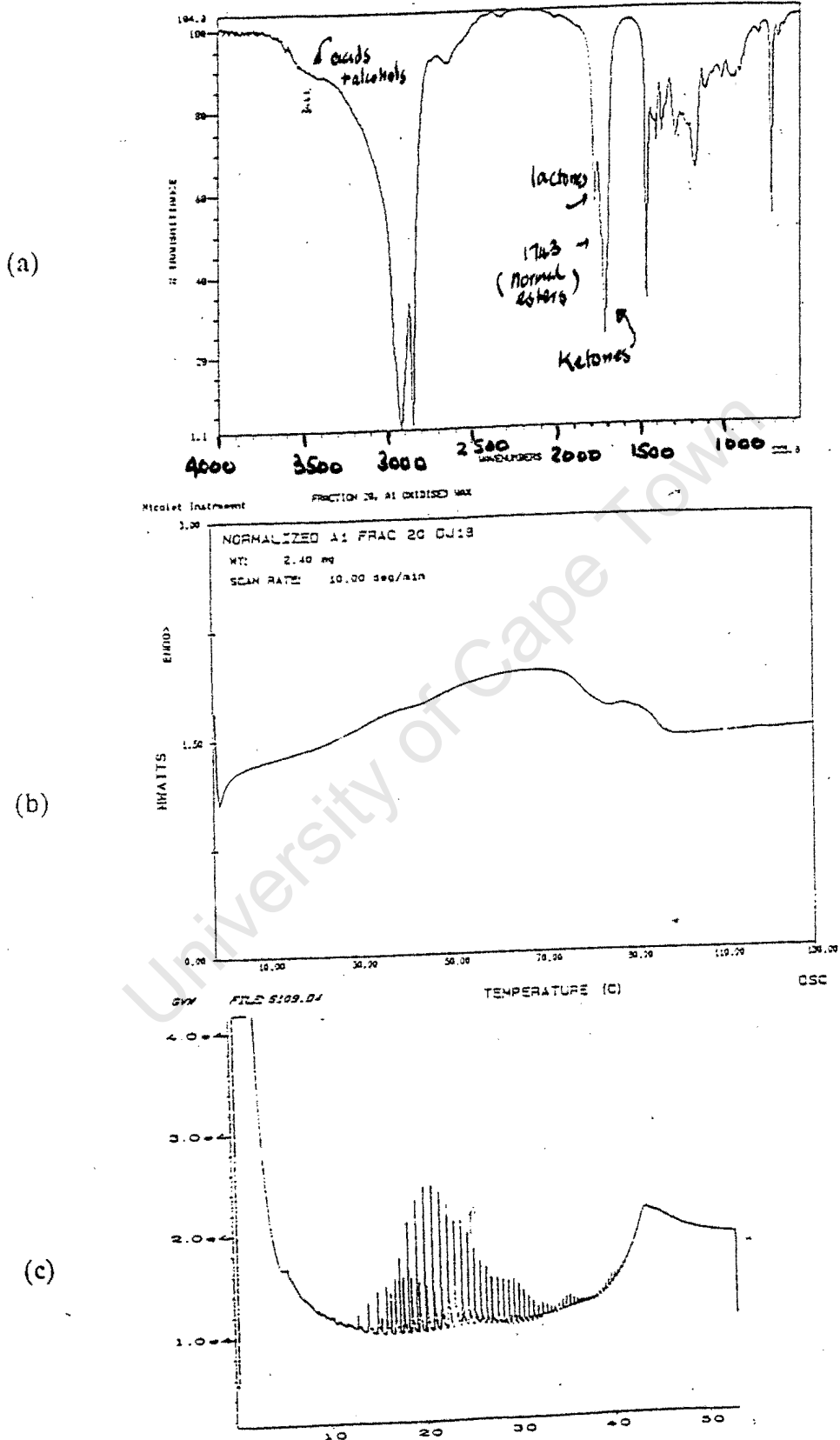


Figure 29: Fraction 20 from the column separation of oxidised Fischer-Tropsch hard wax. (a) IR scans (b) DSC plot (c) HTGC chromatogram

*Fractions 24, 28 and 32*

The instrumental outputs from fractions 24, 28 and 32 are collated in Appendix 3(a). These more polar components of the oxidised Fischer-Tropsch wax, were eluted from the silica column by increasing the polarity of the solvent. The colour of the waxy residue obtained from the distillation of the eluent, changed from a light yellow colour in fraction 24 to an orange-brown tacky waxlike substance in fraction 32. The fractions were highly acidic with acid values of approximately 60 mg KOH per gram. Both the DSC plots and the HTGC chromatograms were similar. The DSC plots are indicative of non-crystalline material.

The analyses of these fractions by HTGC gave very poor response signals as seen on the chromatograms. The peaks on the chromatograms were very small. The reason for this is that short chain acids or other highly polar compounds do not elute normally from the GC column. Instead they are decomposed or 'burnt off' from the GC columns as the temperature of the column increases to the final temperatures of 440°C. This appears on the chromatograms as small decomposition peaks.

The IR scans of all the fractions were similar and indicated the presence of lactones and acids. Normal esters ( $1743\text{ cm}^{-1}$ ) were identified on the IR scans. The normal esters were, by the definition used in this dissertation, the 'initial oxidation products' of shorter chain hydrocarbons which were formed during the early stages of the oxidation. As explained for fraction 8 on page, these normal esters must have carbon chain lengths which are close to that of the parent hydrocarbon before oxidation.

## 5.4 CONCLUSION

The silica column separated the oxidised Fischer-Tropsch wax into polar and non-polar components.

The non-polar components included the following:

- (i) long chain acids and lactones,
- (ii) alkanes which were present in the unoxidised Fischer-Tropsch hard wax and those that were formed during the oxidation due to hydrogen abstraction of alkyl radicals,
- (iii) long straight chain normal esters and
- (iv) ketones and the alcohols.

Long chain acids and long chain lactones were eluted together with the non-polar fractions because of their high paraffinic character. The composition of the non-polar components indicated that they were the 'initial oxidation products' from the thermal oxidation process (as discussed in the oxidation of the model compound in Section 3).

The more polar components were eluted with the xylene / DMF solvent mixture. These were oxidation products which would typically be present in the 'scission products' section of the GC-MS chromatograms of the products from the model compounds oxidation as per the definition used in this dissertation. They are the shorter chain cleavage products such as the acids, lactones, and possibly ketones and alcohols of the oxidation of the Fischer-Tropsch hard wax

The analyses of the fractionated oxidised wax indicated that all the functional groups which were formed during the oxidation of the longer chain Fischer-Tropsch hard wax were also formed during the oxidation of the shorter chain model compounds.

The composition of the oxidised Fischer-Tropsch hard wax could therefore be deduced with reasonable accuracy, from the composition of oxidised model compounds.

## 6.0 CONCLUSION

The aim of the research was to propose a composition for the thermally oxidised Fischer-Tropsch hard wax. A composition was proposed (Chapter 3, section 3.4) based on research results obtained when studying the composition of thermally oxidised model compounds.

The thermal oxidation of hydrocarbons yielded two types of products i.e., those that are formed without the rupture of the carbon chain ('initial oxidation products') and those that are produced by the further reaction of the 'initial oxidation products' usually with the rupture of the carbon chain ('scission products'). These terms (bracketed) are defined on page (v).

The research conducted in Chapters 4 and 5, was done to confirm that the proposed composition holds for thermally oxidised Fischer-Tropsch hard wax. The lighter fraction of oxidised Fischer-Tropsch hard wax was distilled under vacuum and was analysed using analytical techniques. This distilled lighter fraction although being of longer chain length than the model compounds which were chosen for the research, was found to be almost identical to the composition of the 'scission products' of the model compounds. No 'new' products were produced and the same pattern of functional groups were identified in both the Fischer-Tropsch hard wax and the model compound oxidations. Certain positions on the hydrocarbon chains were thus preferentially oxidised to produce functionalised hydrocarbons of reasonably fixed composition. This verified the composition for the 'scission products' of the thermally oxidised Fischer-Tropsch hard wax (Chapter 4).

The composition of both the 'scission products' and the 'initial oxidation products' of the thermally oxidised Fischer-Tropsch hard wax were confirmed in Chapter 5. Thermally oxidised Fischer-Tropsch hard wax was fractionated on a silica gel column and the fractions were analysed by analytical techniques. The analyses verified the proposed structure.

The most important conclusion that can be drawn from the research done for this dissertation in Chapters 4 and 5, is that none of the analytical results refuted the proposed composition as given in Chapter 3. Therefore the proposed composition can be regarded as accurate enough to be used for the following;

- (i) the further modification of oxidised Fischer-Tropsch hard wax,
- (ii) as a basis for studies to manipulate the oxidation process to produce waxes with specific functionalities or
- (iii) to explain the performance of oxidised Fischer-Tropsch hard wax in applications.

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## **APPENDICES**

### **Appendix 1**

These appendices relate to figures appearing in Chapter 3 of the text.

- (a) Complete GC-MS chromatograms of the C24 oxidation for 3 hours at 150°C and a table containing the identities of the numbered components of the chromatogram.
- (b) Complete GC-MS chromatograms of the C16 oxidation for 3 hours at 150°C
- (c) Complete chromatograms of the C16 oxidation using an expanded scale for improved identification of peaks in the 'initial oxidation product' section of the chromatogram
- (d) Complete GC-MS chromatograms of the C16 oxidation using a polar FFAP column

### **Appendix 2**

GC-MS chromatograms and the table of compounds corresponding to the numbers on the chromatograms of the distillate from the vacuum distillation of oxidised wax.

### **Appendix 3**

- (a) DSC and HTGC chromatograms and IR spectra of fractions 24, 28 and 32 of the column separation of oxidised waxes.
- (b) Table of fractions collected during the column separation of oxidised Fischer-Tropsch hard wax

### **Appendix 4**

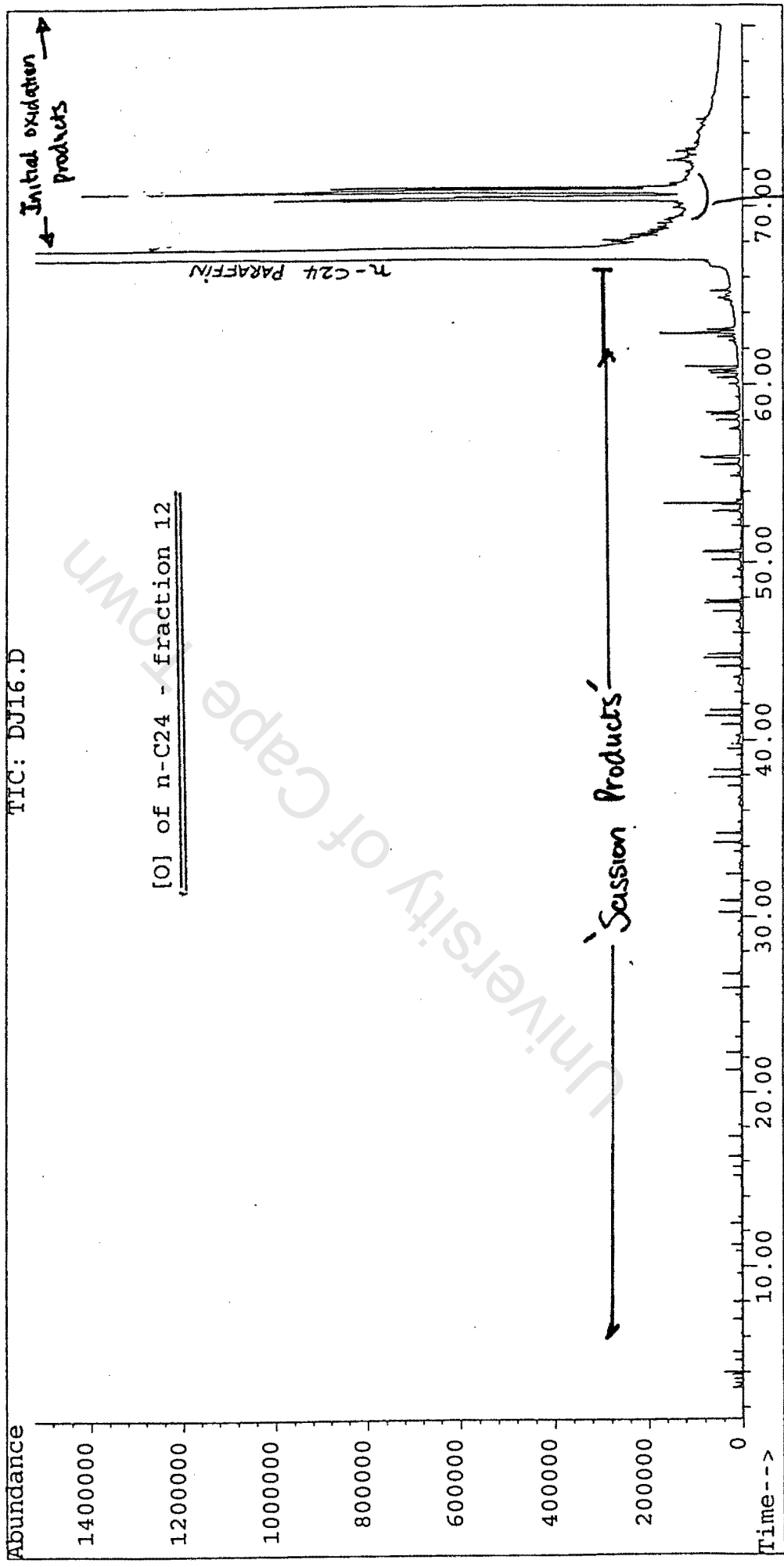
IR spectra of the oxidised model compounds namely, n-C16, n-C24 and n-C32, and a blend of these model compounds.

**APPENDIX 1 (a)**

**Complete GC-MS chromatograms of the C24 oxidation for 3 hours at 150°C and a table containing the identities of the numbered components of the chromatogram.**

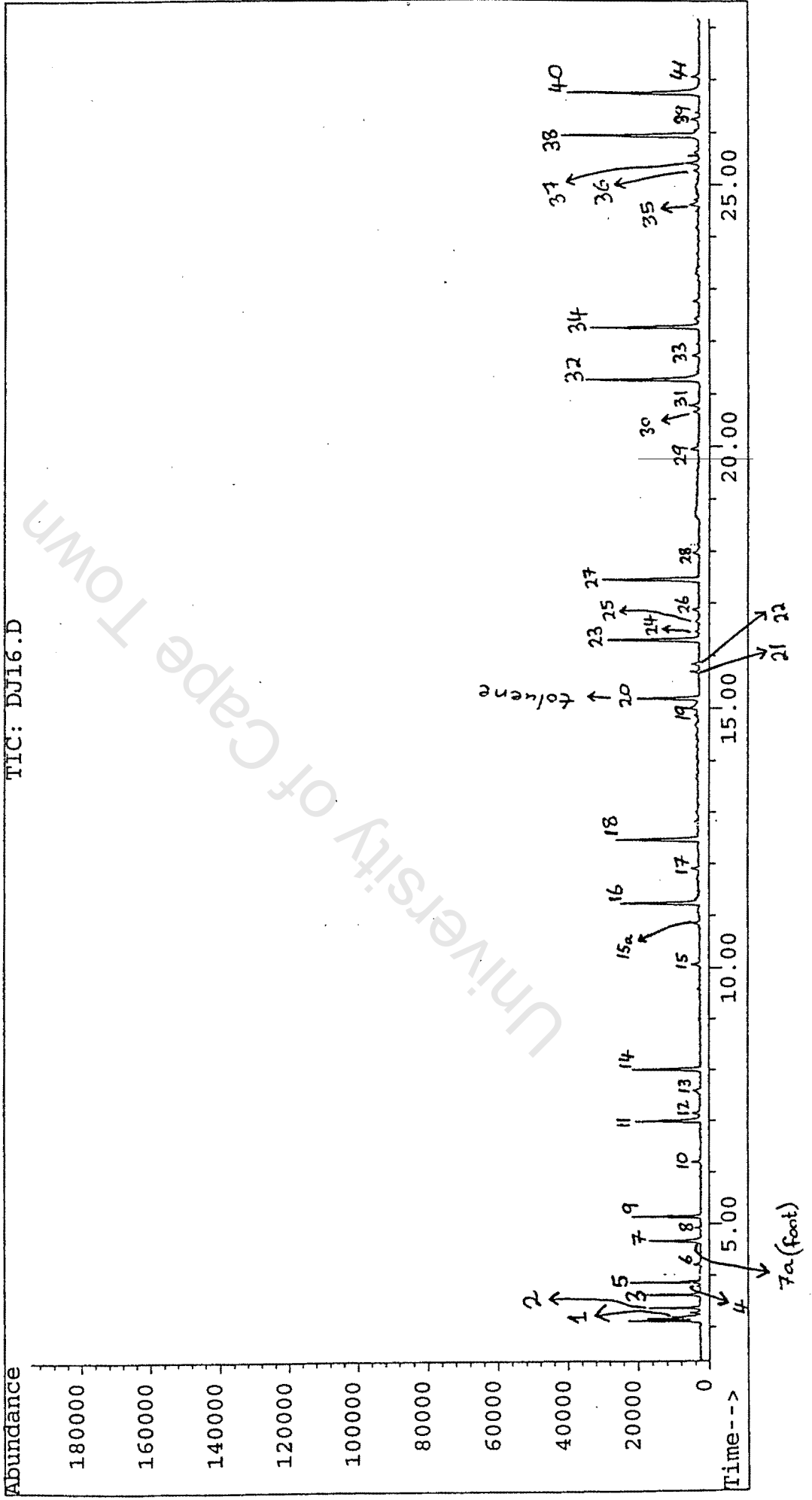
University of Cape Town

File : C:\HPCHEM\1\DATA\DJ16.D  
Operator :  
Acquired : 13 Nov 95 2:12 pm using AcqMethod PONA  
Instrument : 5972 - In  
Sample Name: [O] of n-C24 - fraction 12  
Misc Info :  
Vial Number: 1

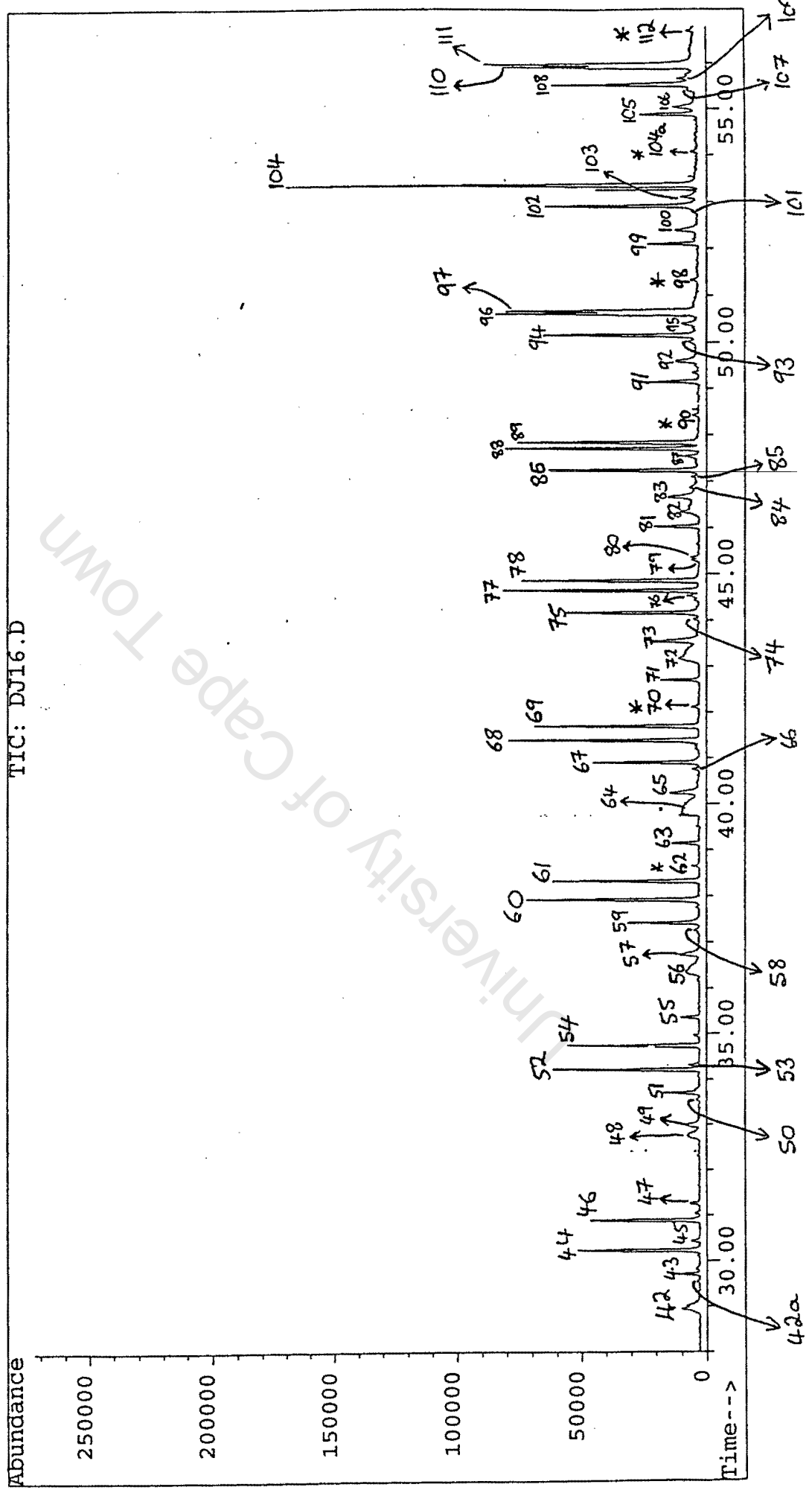


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Operator :  
Acquired : 13 Nov 95 2:12 pm using AcqMethod PONA  
Instrument : 5972 - In  
Sample Name: [O] of n-C24 - fraction 12  
Misc Info :  
Vial Number: 1

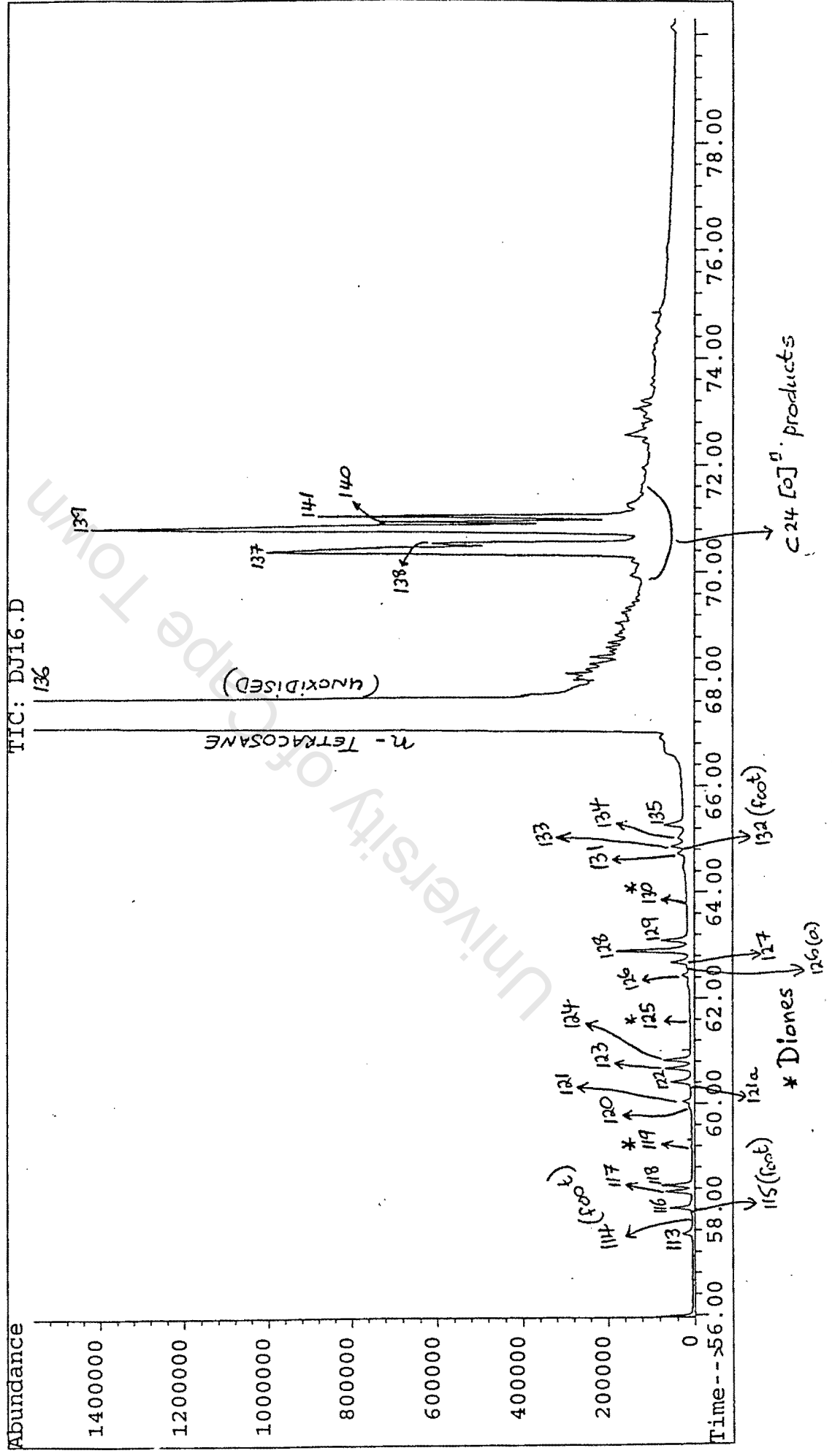
TIC: DJ16.D



File : C:\HPCHEM\1\DATA\DJ16.D  
 Operator :  
 Acquired : 13 Nov 95 2:12 pm using AcqMethod PONA  
 Instrument : 5972 - In  
 Sample Name: [O] of n-C24 - fraction 12  
 Misc Info :  
 Vial Number: 1



File : C:\HPCHEM\1\DATA\DJ16.D  
 Operator :  
 Acquired : 13 Nov 95 2:12 pm using AcqMethod PONA  
 Instrument : 5972 - In  
 Sample Name: [O] of n-C24 - fraction 12  
 Misc Info :  
 Vial Number: 1



**TABLE 1: IDENTIFICATION OF COMPONENTS IN n-C24 OXIDATION PRODUCT**

No.	Component / Possible isomer*
1	Ethane
2	Propane
3	Acetaldehyde
4	C4 Olefin (1-butene or isobutene)
5	n-Butane
6	Ethanol
7a	2-Propanone (acetone)
7	Propanal
8	1-Pentene
9	n-Pentane
10	1-Propanol
11	Butanal
12	2-Butanone (MEK)
13	1-Hexene
14	n-Hexane
15	1-Butanol
15a	2-Pentanone
16	Pentanal
17	1-Heptene + C5 branched alcohol
18	n-Heptane
19	1-Pentanol
20	Toluene
21	3-Hexanone
22	2-Hexanone
23	Hexanal
24	C6 Alcohol, branched (possibly 3-hexanol)
25	Unknown
26	1-Octene + a branched C6 alcohol
27	n-Octane
28	Unknown
29	1-Hexanol
30	3-Heptanone
31	2-Heptanone
32	Heptanal
33	1-Nonene + a branched C7 alcohol
34	n-Nonane
35	1-Heptanol
36	3-Octanone

\* Isomers listed are best library options

TABLE 1: IDENTIFICATION OF COMPONENTS IN n-C24 OXIDATION PRODUCT

No.	Component / Possible isomer*
37	2-Octanone
38	Octanal
39	C8 Branched alcohol + 1-decene
40	n-Decane
41	A C6 gamma-lactone
42	Heptanoic acid (C7 linear acid) + 1-octanol
43a	3-Nonanone
43	2-Nonanone
44	Nonanal
45	1-Undecene + C9 branched alcohol
46	n-Undecane
47	A C7 gamma-lactone
48	Octanoic acid
49	1-Nonanol
50	3-Decanone
51	2-Decanone
52	Decanal
53	1-Dodecene + C10 branched alcohol
54	n-Dodecane
55	A C8 gamma-lactone (5-butyldihydro-2(3H)-furanone best option)
56	Nonanoic acid
57	1-Decanol
58	3-Undecanone
59	2-Undecanone
60	Undecanal
61	n-Tridecane
62	A Dione (2,4-octanedione best option)
63	A C9 gamma-lactone (5-pentyldihydro-2(3H)-furanone best option)
64	Decanoic acid
65	1-Undecanol
66	3-Dodecanone
67	2-Dodecanone
68	Dodecanal
69	n-Tetradecane
70	A Dione (probably 2,4-nonanedione)
71	A C10 gamma-lactone (5-hexyldihydro-2(3H)-furanone best option)
72	Undecanoic acid
73	1-Dodecanol

\* Isomers listed are best library options

**TABLE 1: IDENTIFICATION OF COMPONENTS IN n-C24 OXIDATION PRODUCT**

No.	Component / Possible isomer*
74	3-Tridecanone
75	2-Tridecanone
76	1-Pentadecene + C13 branched alcohol
77	Tridecanal
78	n-Pentadecane
79	C13 branched alcohol
80	<i>A Dione (probably 2,4-decanedione)</i>
81	<i>A C11 gamma-lactone (5-heptyldihydro-2(3H)-furanone best option)</i>
82	Dodecanoic acid + unknown
83	1-Tridecanol
84	A C? delta-lactone or a C?-pyranone
85	3-Tetradecanone
86	2-Tetradecanone
87	1-Hexadecene + C14 branched alcohol
88	Tetradecanal
89	n-Hexadecane
90	<i>A Dione (probably 2,4-undecanedione)</i>
91	<i>A C12 gamma-lactone (probably 5-octyldihydro-2(3H)-furanone)</i>
92	1-Tetradecanol
93	3-Pentadecanone
94	2-Pentadecanone
95	1-Heptadecene + C15 branched alcohol
96	Pentadecanal
97	n-Heptadecane
98	<i>A Dione (probably 2,4-dodecanedione)</i>
99	<i>A C13 gamma-lactone (probably 5-nonyldihydro-2(3H)-furanone)</i>
100	1-Pentadecanol
101	3-Hexadecanone
102	2-Hexadecanone
103	1-Octadecene + C16 branched alcohol
104	n-Octadecane + hexadecanal
104a	<i>A Dione (probably 2,4-tridecanedione)</i>
105	<i>A C14 gamma-lactone (probably 5-decyldihydro-2(3H)-furanone)</i>
106	1-Hexadecanol
107	3-Heptadecanone
108	2-Heptadecanone
109	1-Nonadecene + C17 branched alcohol
110	n-Nonadecane

\* Isomers listed are best library options

**TABLE 1: IDENTIFICATION OF COMPONENTS IN n-C24 OXIDATION PRODUCT**

No.	Component / Possible isomer*
111	Heptadecanal
112	<i>A Dione (probably 2,4-tetradecanedione)</i>
113	A C15 gamma-lactone (probably 5-undecyldihydro-2(3H)-furanone)
114	1-Heptadecanol
115	3-Octadecanone
116	2-Octadecanone
117	n-Eicosane (linear C20 paraffin)
118	Octadecanal
119	<i>A Dione (probably 2,4-pentadecanedione)</i>
120	Unknown
121	A C16 gamma-lactone (probably 5-dodecyldihydro-2(3H)-furanone)
121a	3-Nonadecanone
122	2-Nonadecanone
123	n-Heneicosane (linear C21 paraffin)
124	Nonadecanal
125	<i>A Dione (probably 2,4-hexadecanedione)</i>
126	A C17 gamma-lactone (probably 5-tridecyldihydro-2(3H)-furanone)
126a	3-Eicosanone
127	2-Eicosanone
128	n-Docosane
129	Eicosanal (C20 n-aldehyde)
130	<i>A Dione (probably 2,4-heptadecanedione)</i>
131	A C18 gamma-lactone (probably 5-tetradecyldihydro-2(3H)-furanone)
132	3-Heneicosanone
133	2-Heneicosanone
134	n-Tricosane
135	Heneicosanal (C21 n-aldehyde)
136	n-Tetracosane (unoxidised feed material)
137	C24 Oxygenate (most probably a C24 aldehyde)
138	C24 Oxygenate (most probably a C24 ketone)
139	C24 Alcohol (C <sub>24</sub> H <sub>50</sub> O; M-18 ion, i.e. 336 amu ion detected) + C24 ketone
140	C24 Oxygenate (most probably a C24 ketone)
141	C24 Alcohol (C <sub>24</sub> H <sub>50</sub> O; M-18 ion, i.e. 336 amu ion detected)

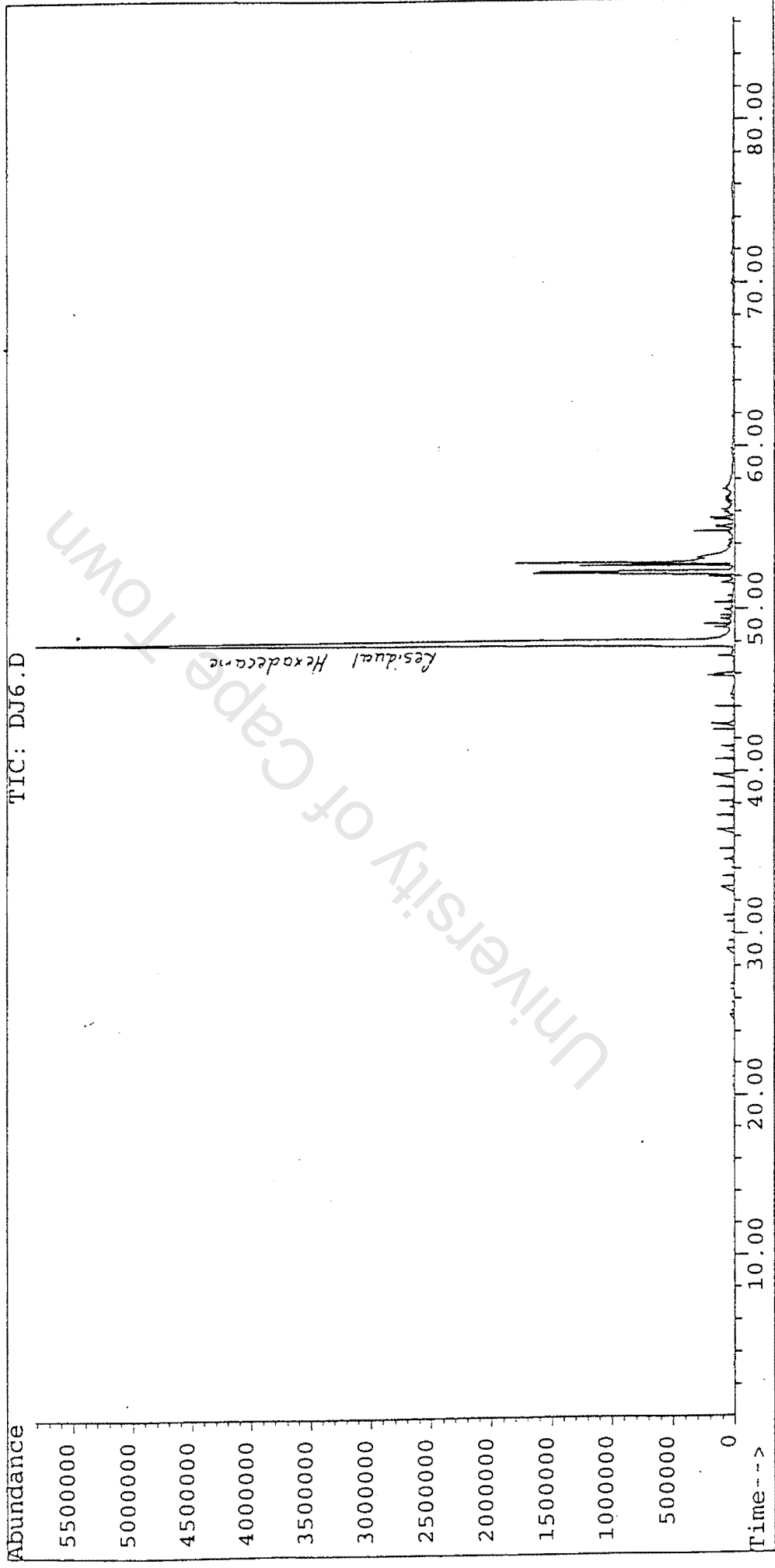
\* Isomers listed are best library options

**APPENDIX 1 (b)**

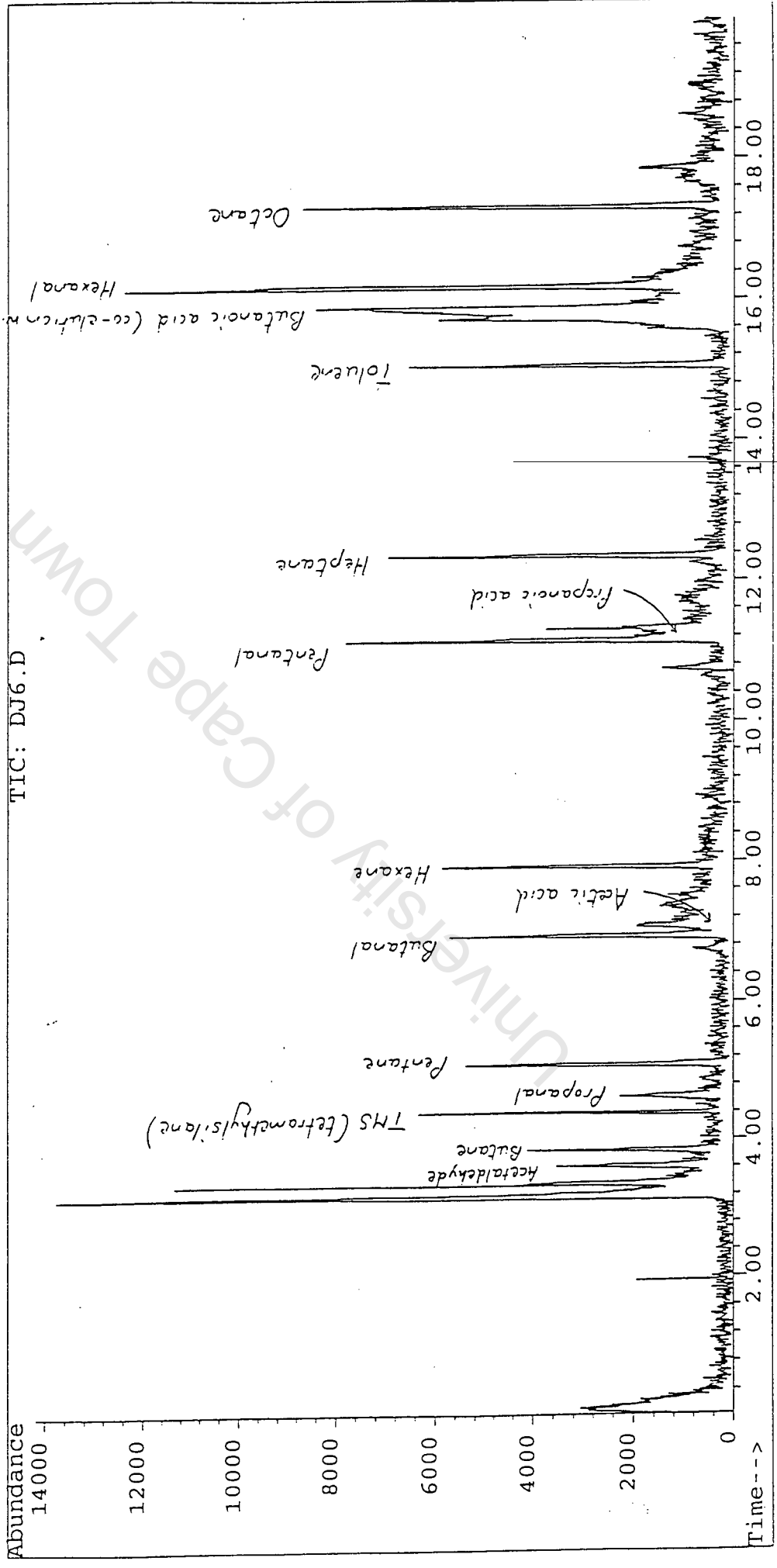
**Complete GC-MS chromatograms of the C16 oxidation at 150°C for 3 hours.**

University of Cape Town

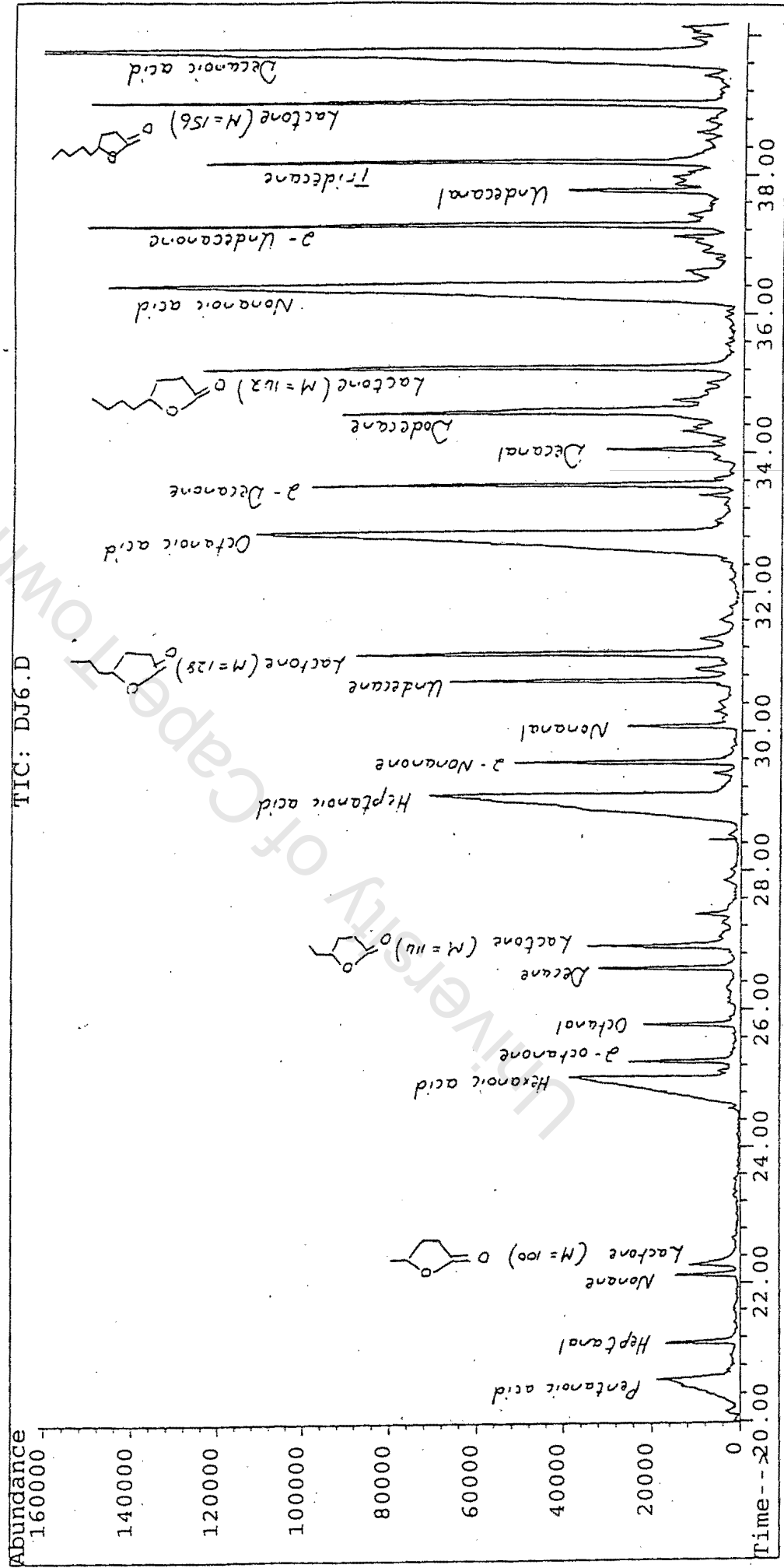
File : C:\HPCHEM\1\DATA\DJ6.D  
Operator : Nicky  
Acquired : 13 May 96 9:13 am using AcqMethod PONA  
Instrument : 5972 - In  
Sample Name: Oxidised C16  
Misc Info : C5234  
Vial Number: 1



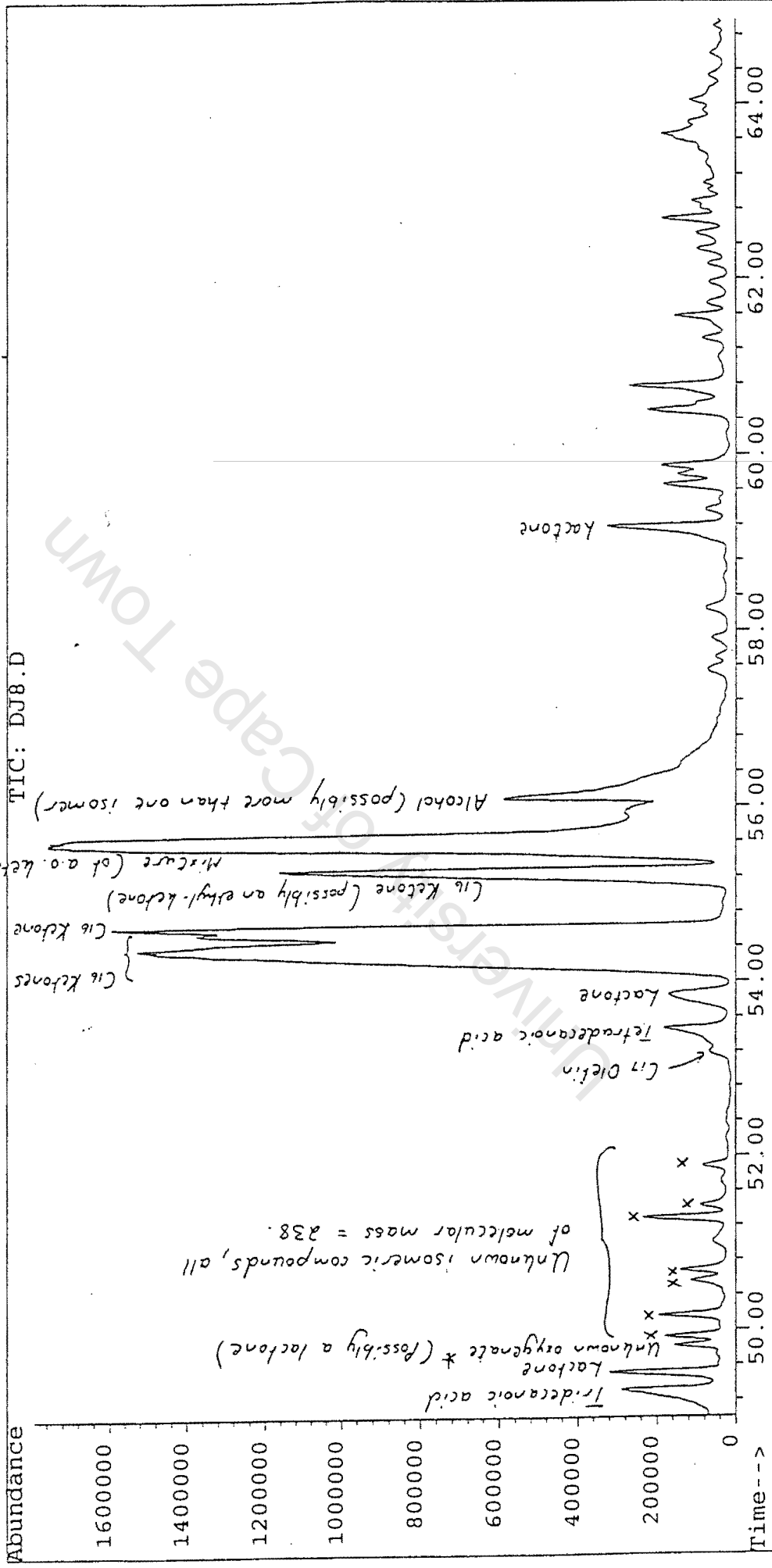
File : C:\HPCHEM\1\DATA\DJ6.D  
 Operator : Nicky  
 Acquired : 13 May 96 9:13 am using AcqMethod PONA  
 Instrument : 5972 - In  
 Sample Name: Oxidised C16  
 Misc Info : C523  
 Vial Number: 1



File : C:\HPCHEM\1\DATA\DJ6.D  
Operator : Nicky  
Acquired : 13 May 96 9:13 am using AcqMethod PONA  
Instrument : 5972 - In  
Sample Name : Oxidised C16  
Misc Info : C523  
Vial Number: 1



File : C:\HPCHEM\1\DATA\DJ8.D  
 Operator : Nicky  
 Acquired : 14 May 96 3:55 pm using AcqMethod PONA  
 Instrument : 5972 - In  
 Sample Name: Oxidised C16  
 Misc Info : C524  
 Vial Number: 1

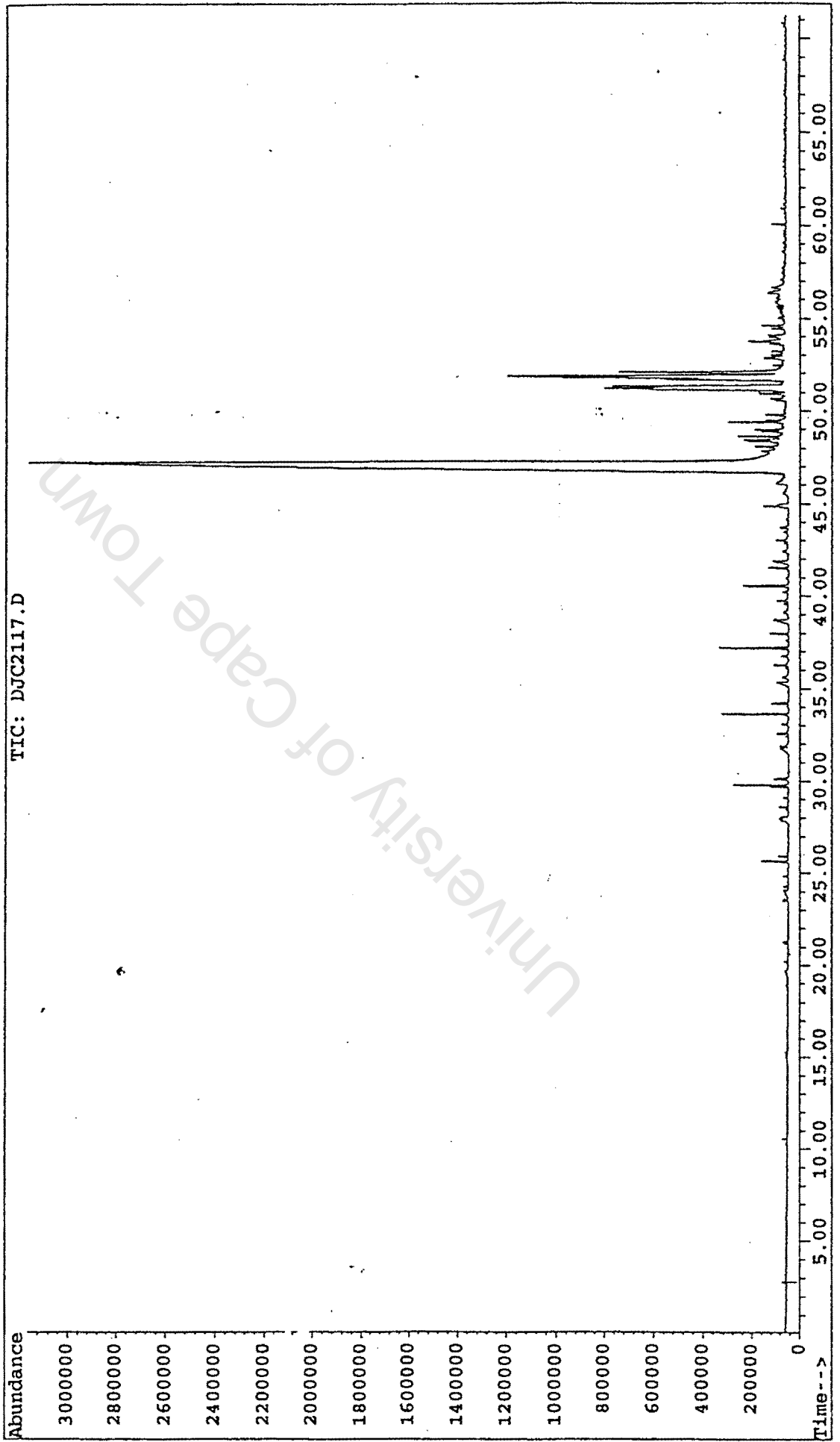


**APPENDIX 1 (c)**

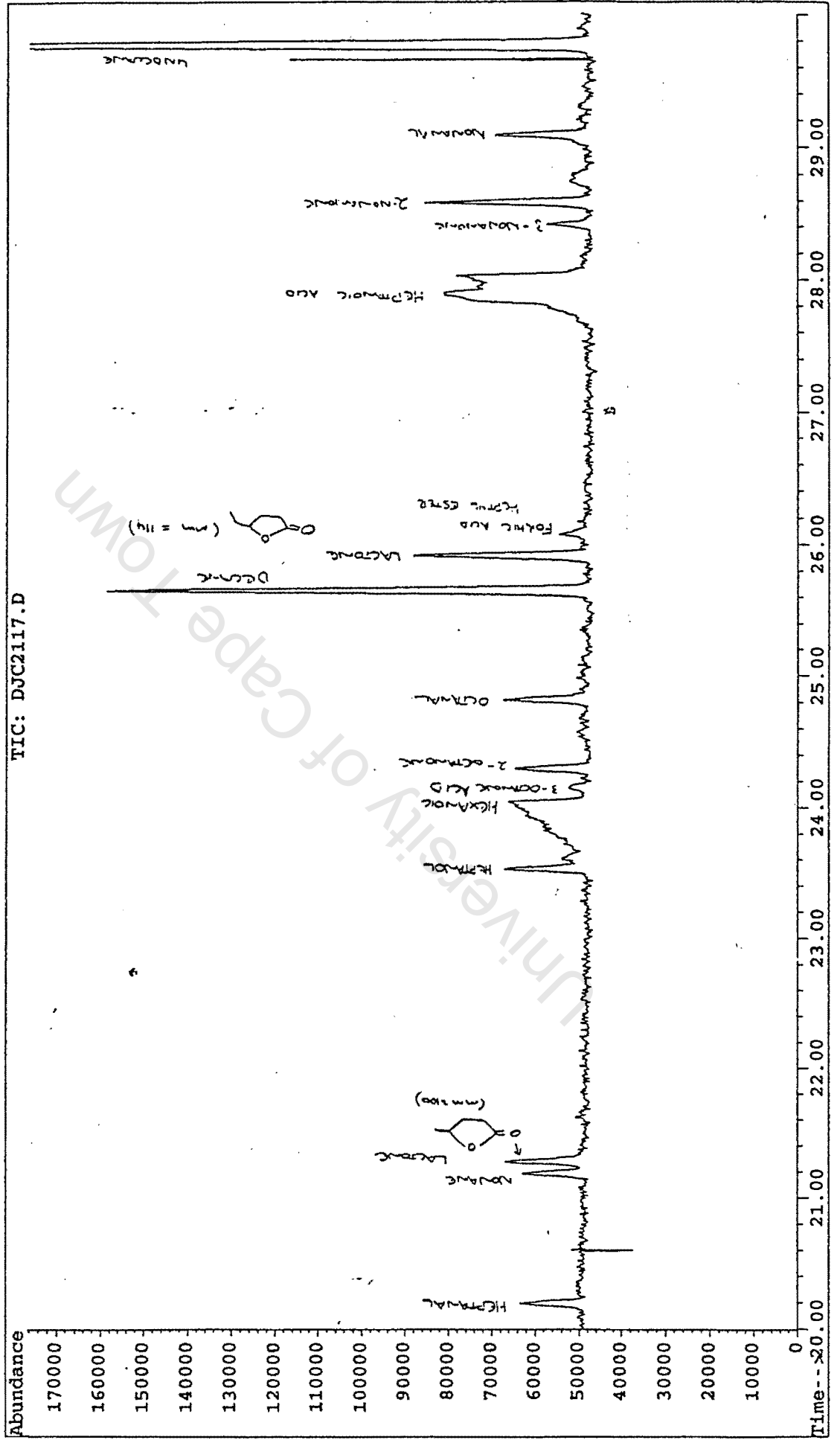
**Complete chromatograms of the C16 oxidation using an expanded scale for improved identification of peaks in the 'initial oxidation product' section of the chromatogram**

University of Capetown

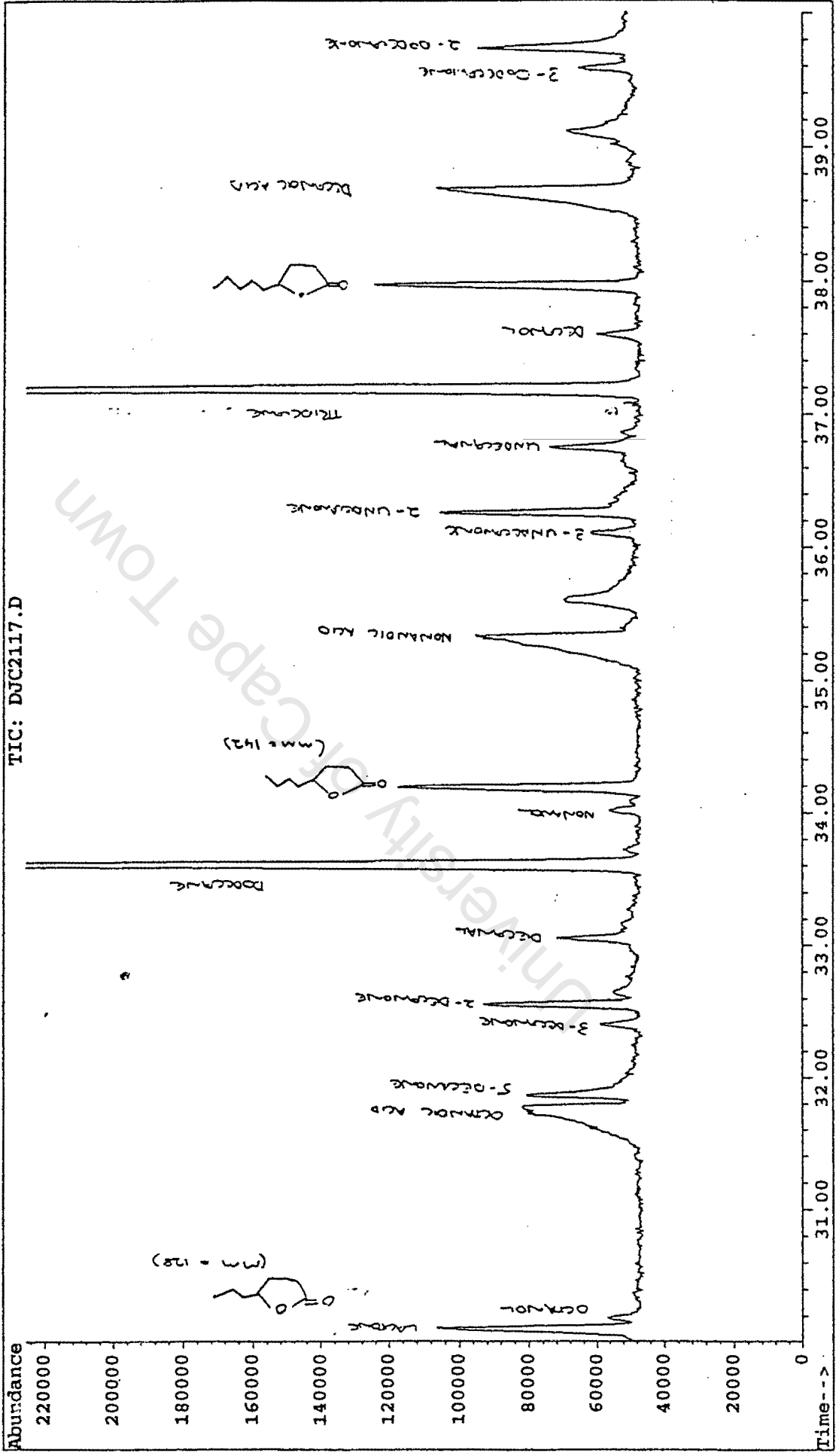
File : C:\HPCHEM\1\DATA\DJC2117.D  
Operator : Nicky  
Acquired : 9 Dec 96 12:21 pm using AcqMethod PONA  
Instrument : 5972 - In  
Sample Name: Oxidation of C16 @ 170°C DJ 3-3 4/10/96  
Misc Info : C2117  
Vial Number: 1



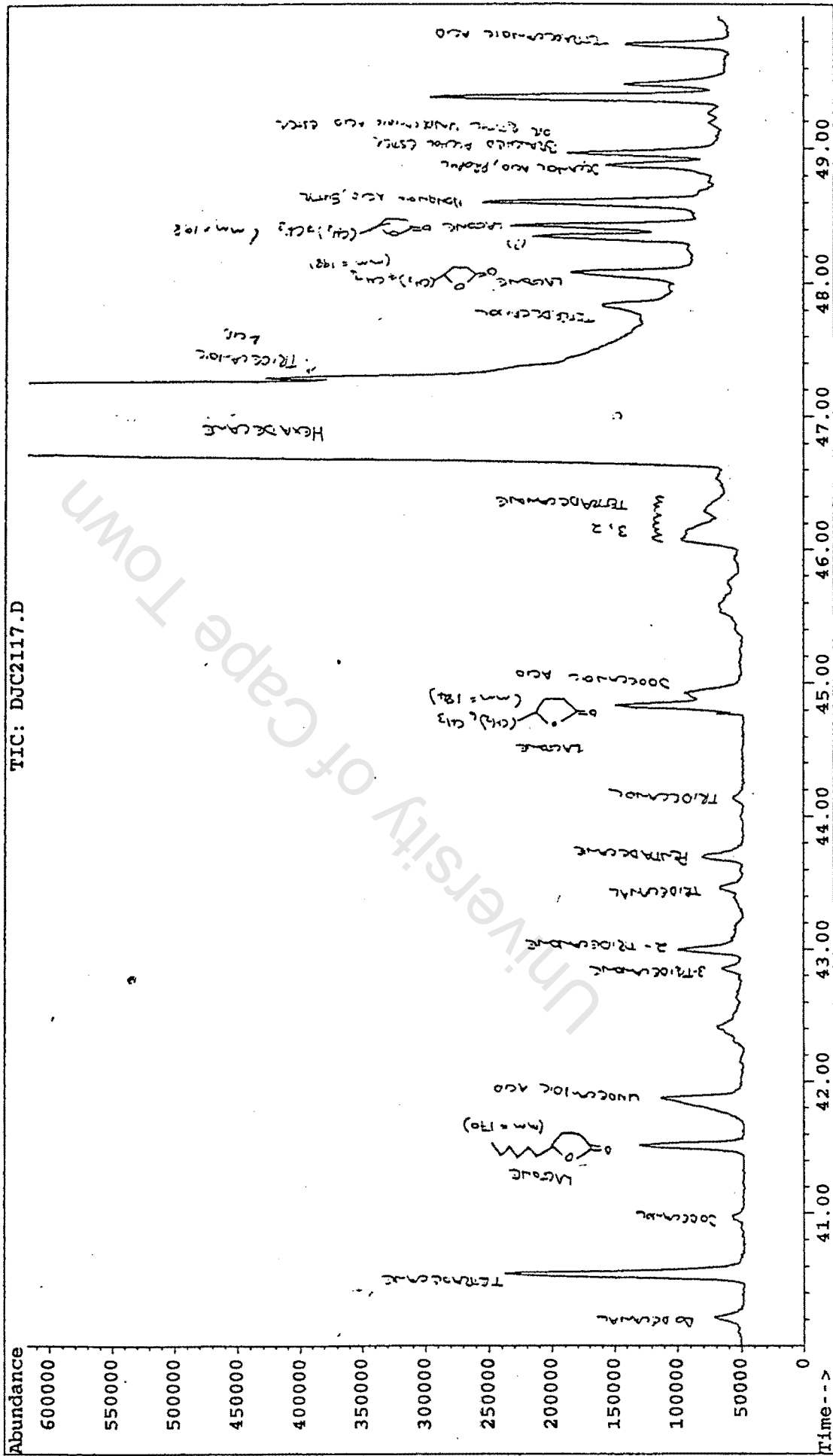
File : C:\HPCHEM\1\DATA\DJC21117.D  
 Operator : Nicky  
 Acquired : 9 Dec 96 12:21 pm using AcqMethod PONA  
 Instrument : 5972 - In  
 Sample Name: Oxidation of C16 @ 170°C DJ 3-3 4/10/96  
 Misc Info : C2117  
 Vial Number: 1



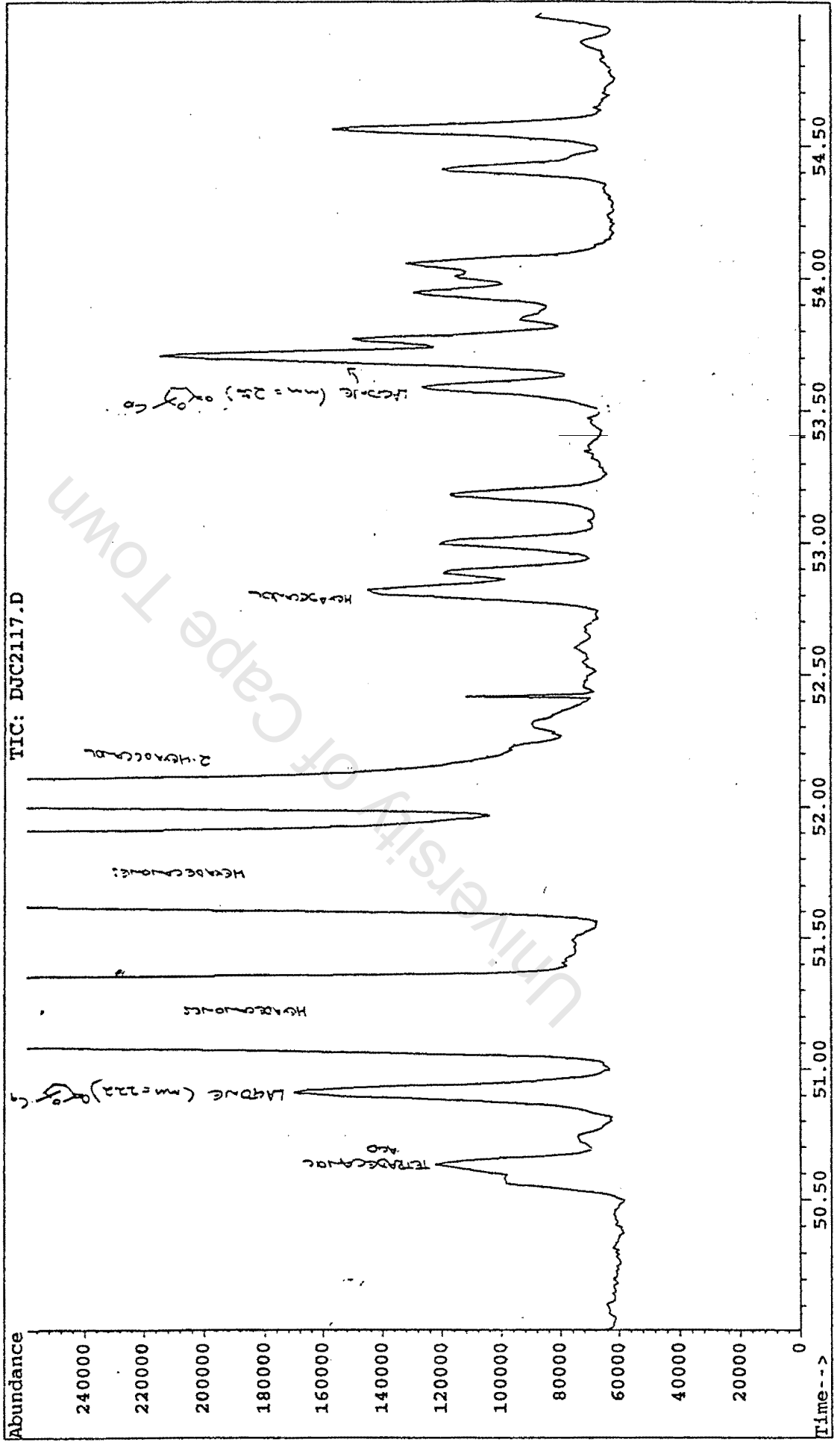
File : C:\HPCHEM\1\DATA\DJC2117.D  
 Operator : Nicky  
 Acquired : 9 Dec 96 12:21 pm using AcqMethod PONA  
 Instrument : 5972 - In  
 Sample Name : Oxidation of C16 @ 170°C DJ 3-3 4/10/96  
 Misc Info : C2117  
 Vial Number: 1



File : C:\HPCHEM\1\DATA\DJC21117.D  
 Operator : Nicky  
 Acquired : 9 Dec 96 12:21 pm using AcqMethod PONA  
 Instrument : 5972 - In  
 Sample Name: Oxidation of C16 @ 170°C DJ 3-3 4/10/96  
 Misc Info : C2117  
 Vial Number: 1



File : C:\HPCHEM\1\DATA\DJC2117.D  
Operator : Nicky  
Acquired : 9 Dec 96 12:21 pm using AcqMethod PONA  
Instrument : 5972 - In  
Sample Name: Oxidation of C16 @ 170°C DJ 3-3 4/10/96  
Misc Info : C2117  
Vial Number: 1



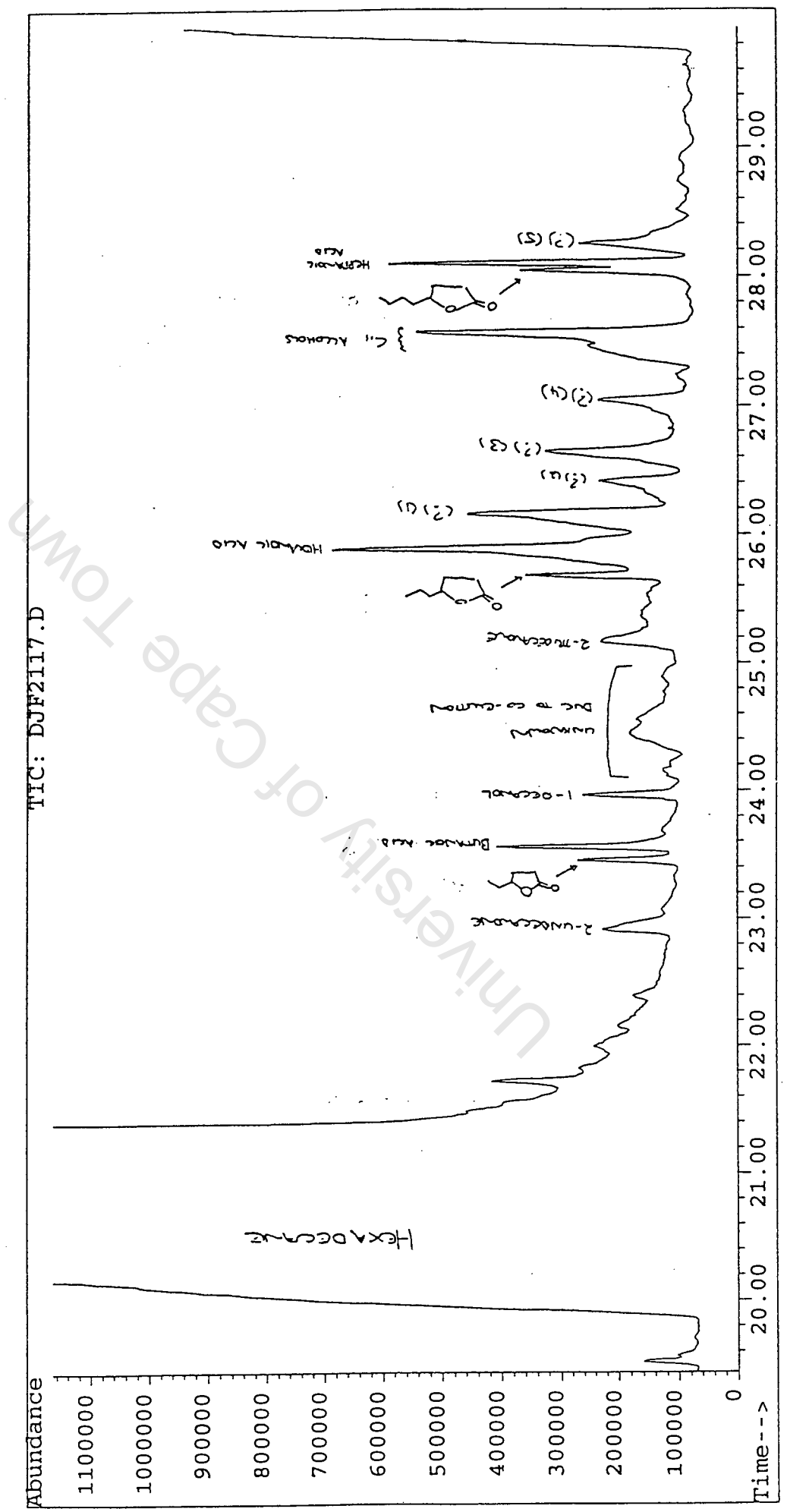
**APPENDIX 1 (d)**

**Complete GC-MS chromatograms of the C16 oxidation using a polar FFAP column**

University of Cape Town

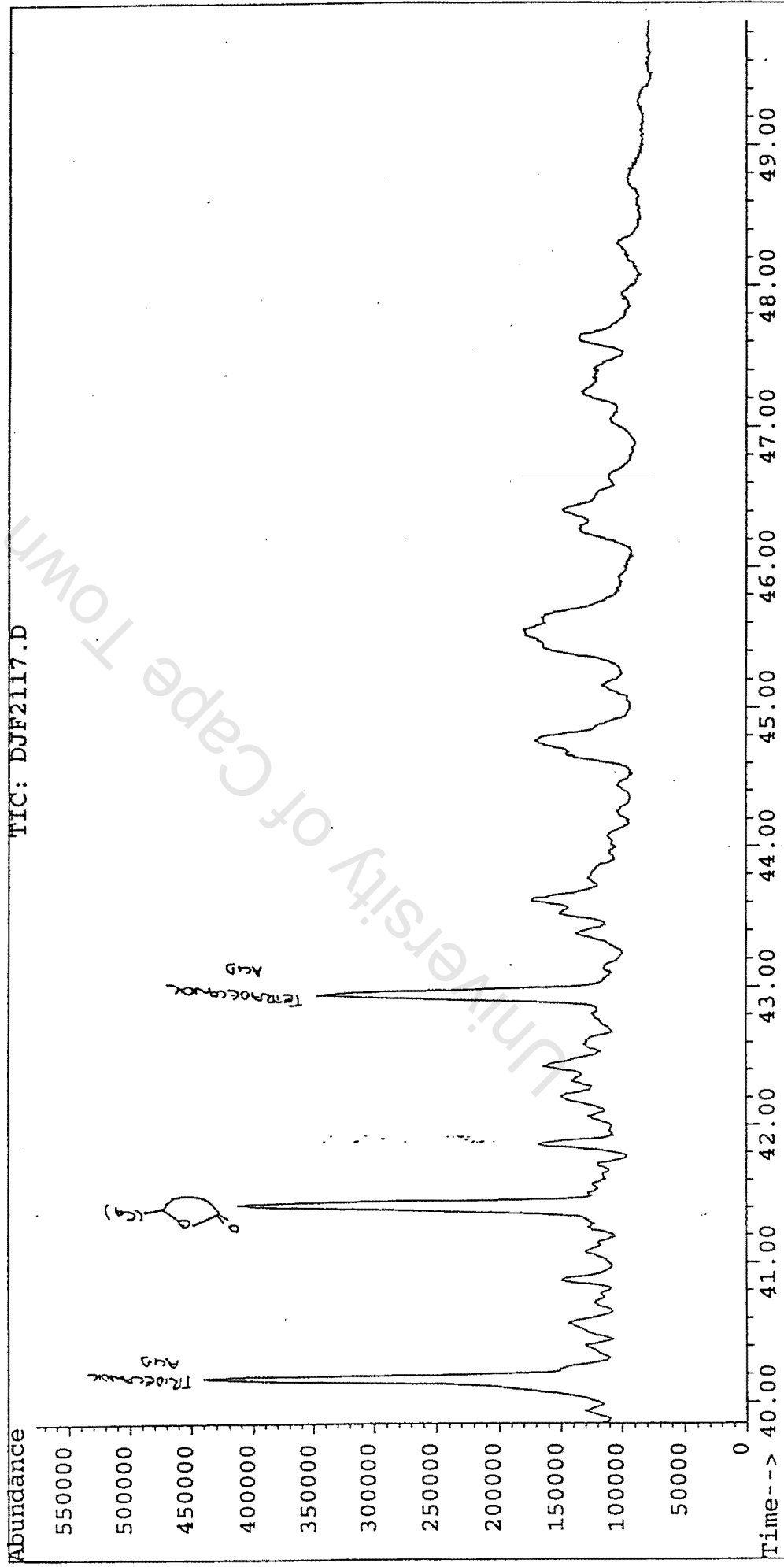


File : C:\HPCHEM\1\DATA\DJF2117.D  
 Operator : Nicky  
 Acquired : 18 Dec 96 4:30 pm using AcqMethod FFAP  
 Instrument : 5972 - In  
 Sample Name: C16 oxidised @ 170°C  
 Misc Info : C2117 on FFAP  
 Vial Number: 1





File : C:\HPCHEM\1\DATA\DJF2117.D  
Operator : Nicky  
Acquired : 18 Dec 96 4:30 pm using AcqMethod FFAP  
Instrument : 5972 - In  
Sample Name: C16 oxidised @ 170°C  
Misc Info : C2117 on FFAP  
Vial Number: 1

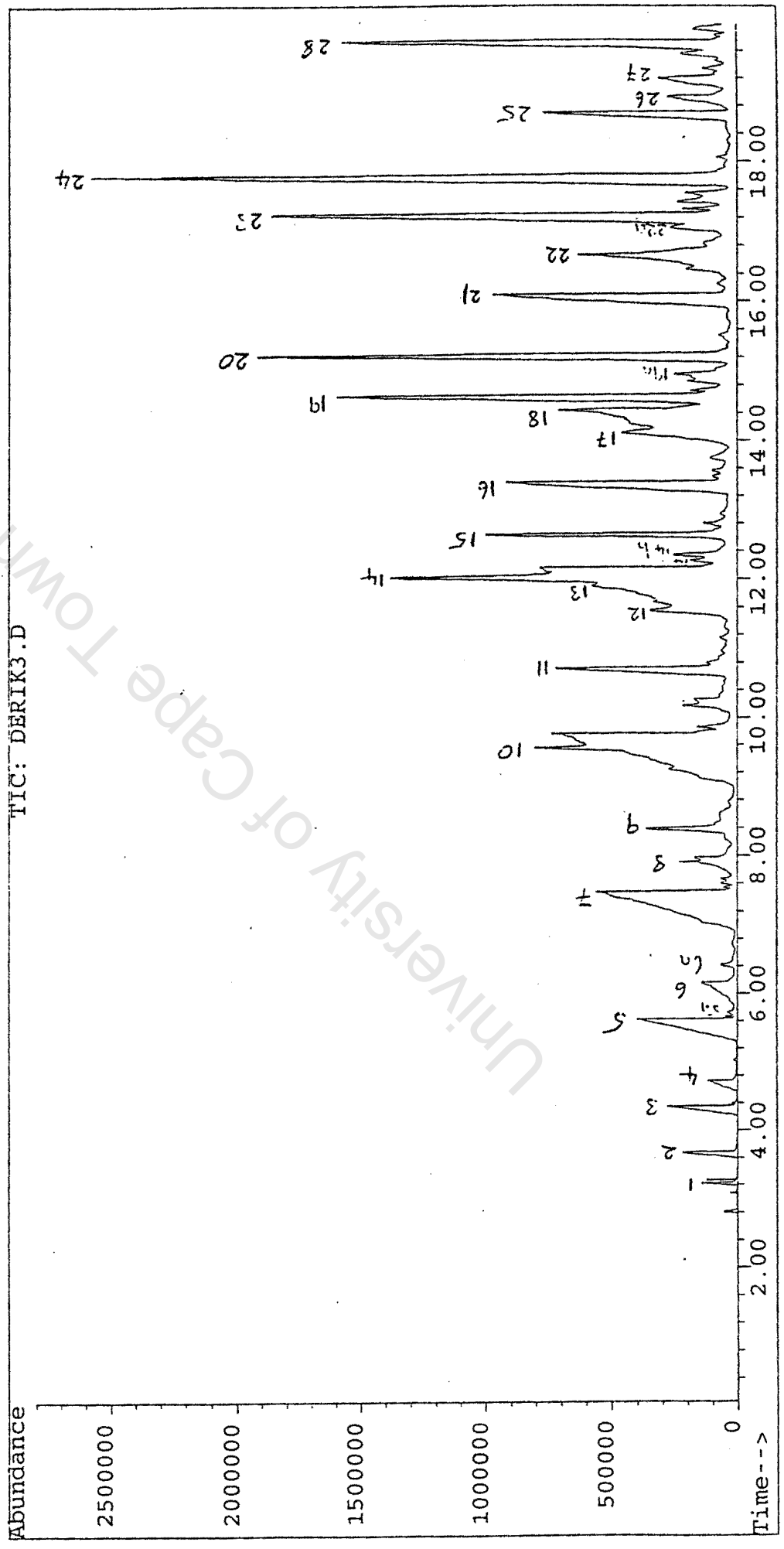


## APPENDIX 2

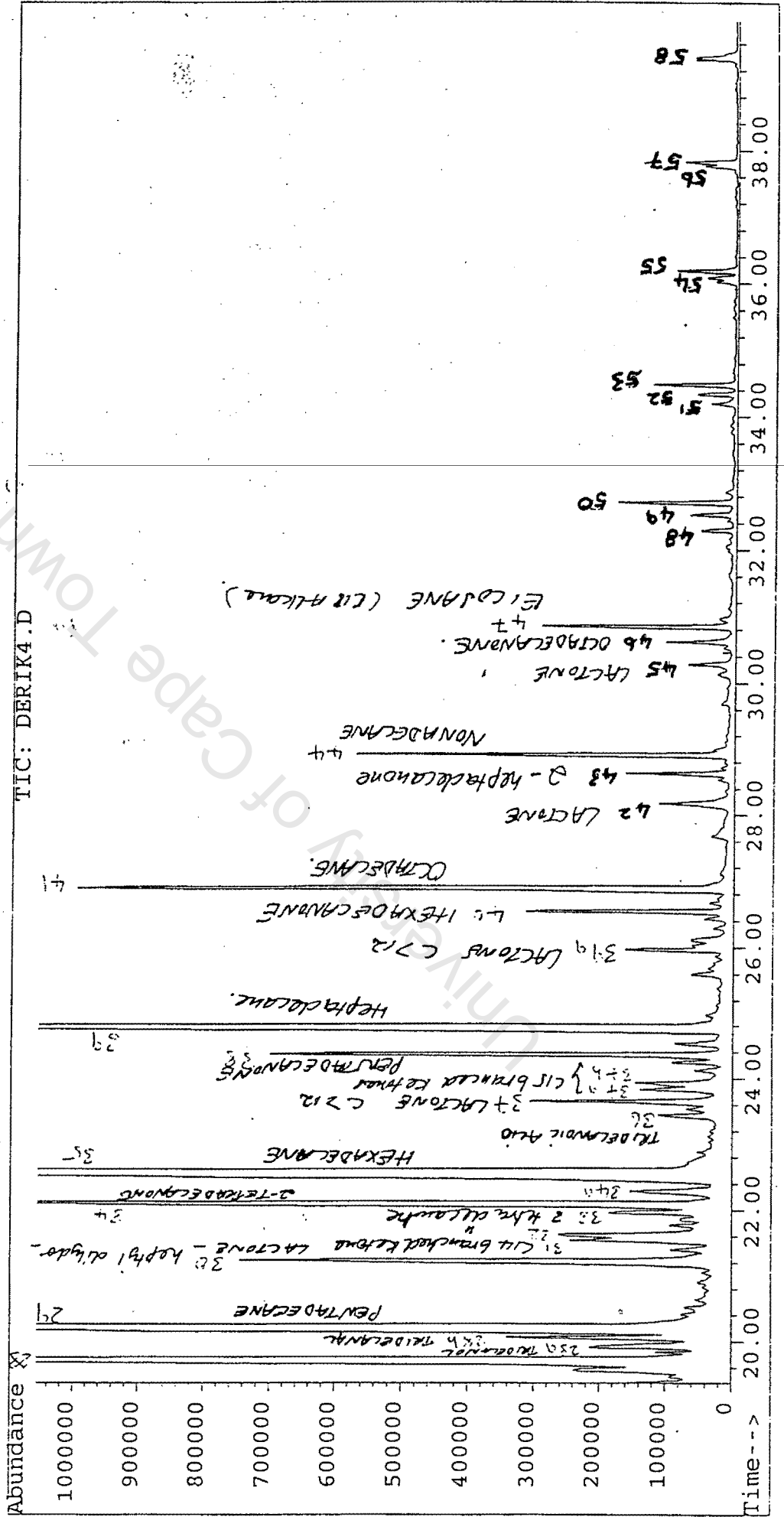
**GC-MS chromatograms and the table of compounds corresponding to the numbers on the chromatograms of the distillate from the vacuum distillation of oxidised wax.**

University of Cape Town

File : C:\HPCHEM\1\DATA\DERIK3.D  
Operator :  
Acquired : 18 Apr 95 4:50 pm using AcqMethod PONA  
Instrument : 5972 - In  
Sample Name: DJ 42 (heated)  
Misc Info :  
Vial Number: 1



File : C:\HPCHEM\1\DATA\DERIK4.D  
 Operator :  
 Acquired : 19 Apr 95 7:56 am using AcqMethod PONA  
 Instrument : 5972 - In  
 Sample Name: DJ 42 C60  
 Misc Info :  
 Vial Number: 1



File : C:\HPCHEM\1\DATA\DERIK4.D  
Operator :  
Acquired : 19 Apr 95 7:56 am using AcqMethod PONA  
Instrument : 5972 - In  
Sample Name: DJ 42 C60  
Misc Info :  
Vial Number: 1

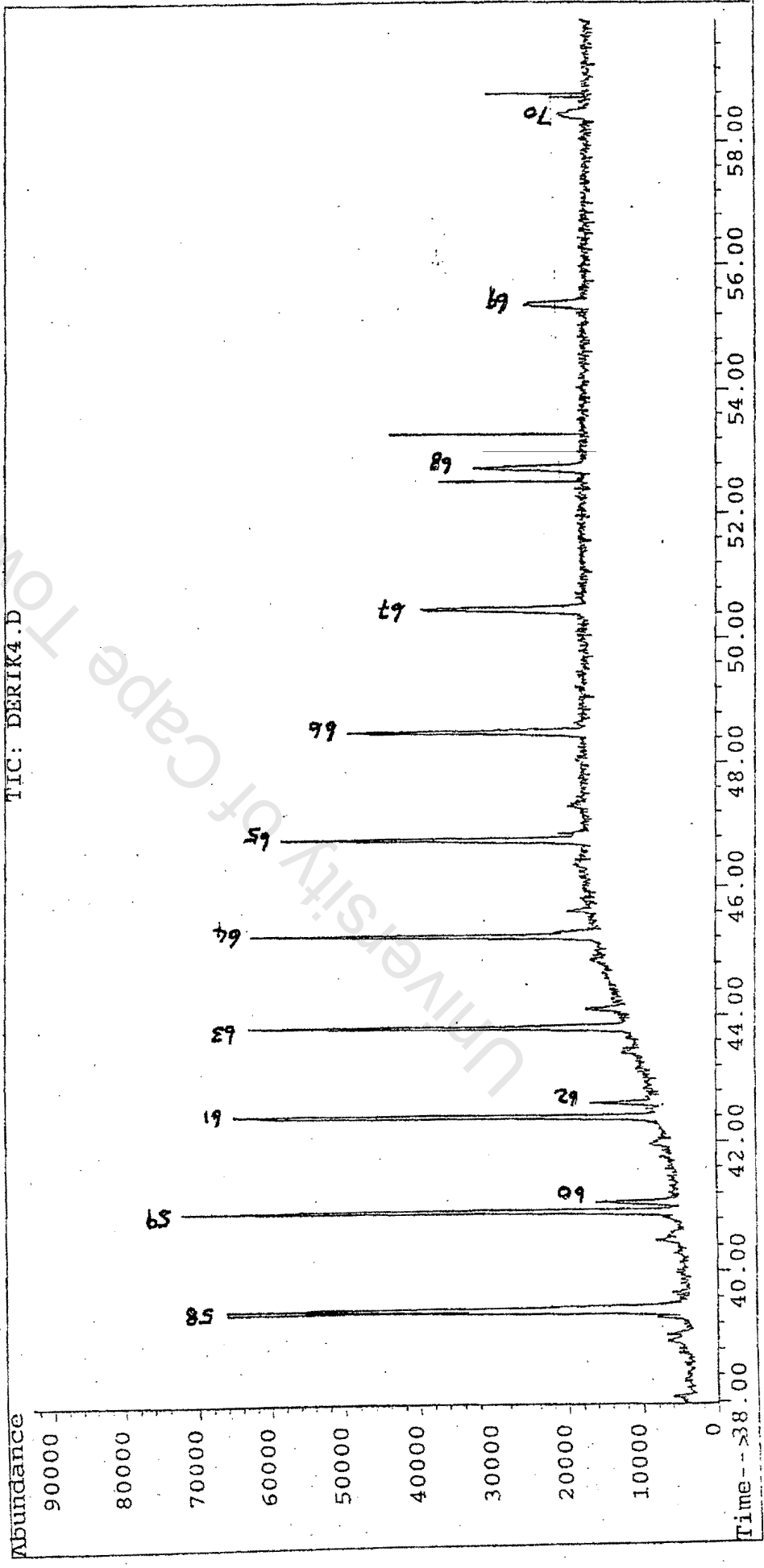


TABLE 1: IDENTIFICATION OF COMPONENTS IN SAMPLES DJ42 AND DJ42 C60

No.	Component/Possible isomer*
1	Acetic acid
2	Propanoic + 2-propenoic acid
3	Butanoic acid
4	2-Butenoic acid
5	Pentanoic acid
5a	Dihydro-2(3H)-furanone
6	2-Methyl-2-butenoic acid
6a	Dihydro-5-methyl-2(3H)-furanone (a lactone)
7	Hexanoic acid
8	2-Hexenoic acid
9	Dihydro-5-ethyl-2(3H)-furanone
10	Heptanoic acid
10a	Nonanal
10b	Undecane
11	Dihydro-5-propyl-2(3H)-furanone
12	Unknown (possibly a lactone)
13	Octanoic acid
14	2-Decanone
14a	Decanol
14b	Decanal
15	Dodecane
16	5-Butyldihydro-2(3H)-furanone
17	6-Undecanone
18	Nonanoic acid
19	2-Undecanone
19a	Undecanal
20	Tridecane
21	Dihydro-5-pentyl-2(3H)-furanone
22	Decanoic acid
22a	3-Dodecanone
23	2-Dodecanone
23a	Dodecanal
24	Tetradecane
25	5-Hexyldihydro-2(3H)-furanone
26	Undecanoic acid
27	5-Tridecanone
28	2-Tridecanone
28a	Tridecanol
28b	Tridecanal
29	Pentadecane
30	5-Heptyldihydro-2(3H)-furanone
31	C14 branched ketone

\* MSD cannot distinguish between geometrical isomers, therefore isomers listed here should only be taken as the best database options and not as absolute

TABLE 1: IDENTIFICATION OF COMPONENTS IN SAMPLES DJ42 AND DJ42 C60

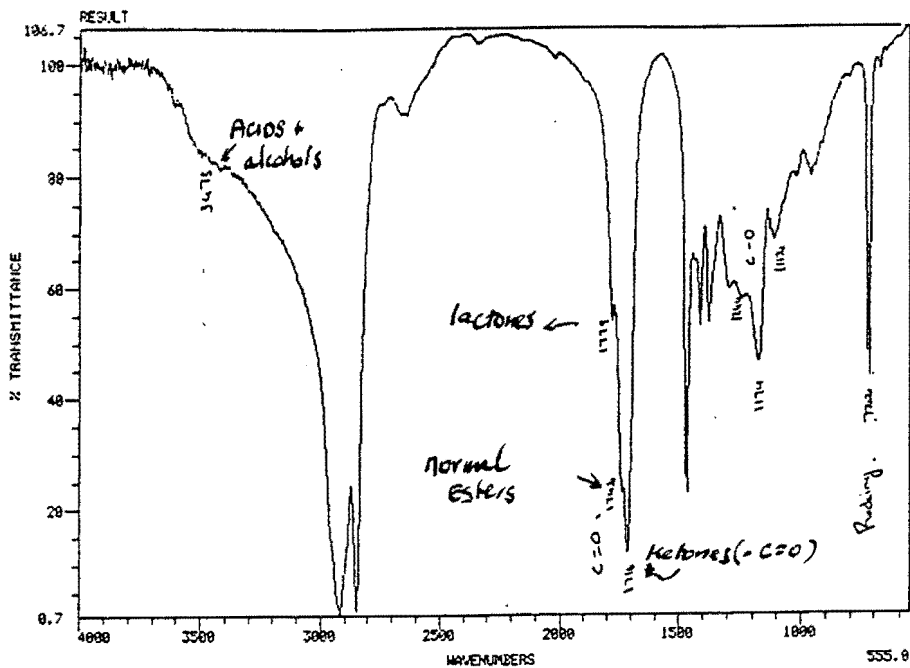
No.	Component/Possible isomer*
32	C14 branched ketone
33	3-Tetradecanone
34	2-Tetradecanone
34a	C14/C15 Alkene
35	Hexadecane
36	Tridecanoic acid
37	A lactone of carbon number > 12
37a	C15 branched ketone
37b	C15 branched ketone
38	Pentadecanone
39	Heptadecane
39a	A lactone of carbon number > 12
40	Hexadecanone
41	Octadecane
42	A lactone of carbon number > 12
43	2-Heptadecanone
44	Nonadecane
45	A lactone of carbon number > 12
46	Octadecanone
47	Eicosane
48	A lactone of carbon number > 12
49	2-Nonadecanone
50	Heneicosane
51	A lactone of carbon number > 12
52	C20 ketone
53	Docosane
54	C21 Ketone
55	Tricosane
56	Unknown (possibly a ketone)
57	Alkane (possibly C24)
58	Alkane (possibly C25)
59	Alkane (possibly C26)
60	Unknown (possibly an alkene)
61	Alkane (possibly C27)
62	Unknown
63	Alkane (possibly C28)
64	Alkane (possibly C29)
65	Alkane (possibly C30)
66	Alkane (possibly C31)
67	Alkane (possibly C32)

\* MSD cannot distinguish between geometrical isomers, therefore isomers listed here should only be taken as the best database options and not as absolute

**APPENDIX 3 (a)**

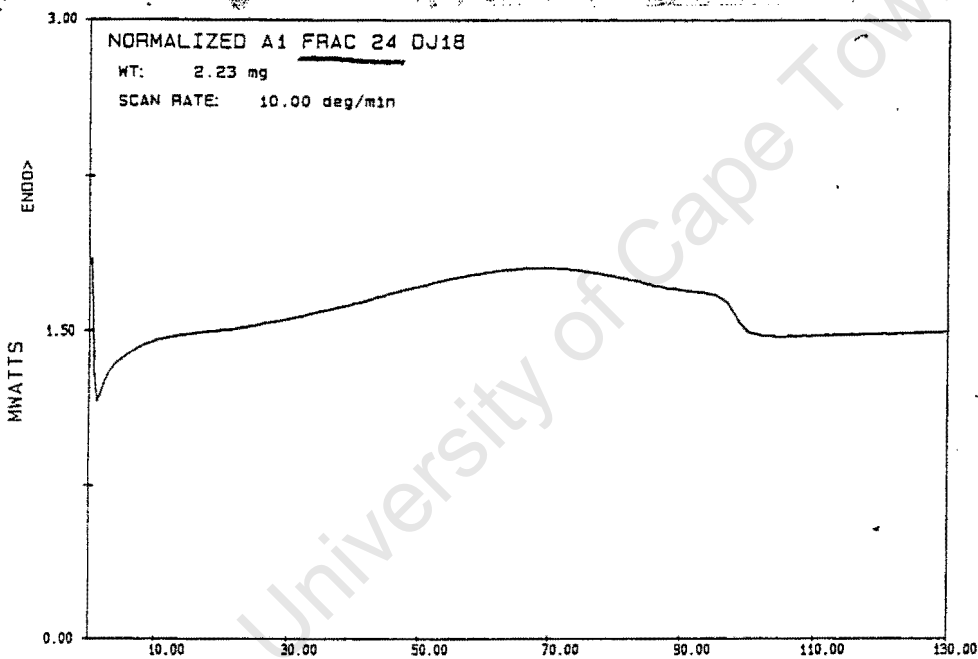
**DSC and HTGC chromatograms and IR spectra of fractions 24, 28 and 32 of the column separation of oxidised waxes.**

University of Cape Town



Nicolet Instrument Corporation

SAMPLE 24, A1 OAHX, FRACTIONED



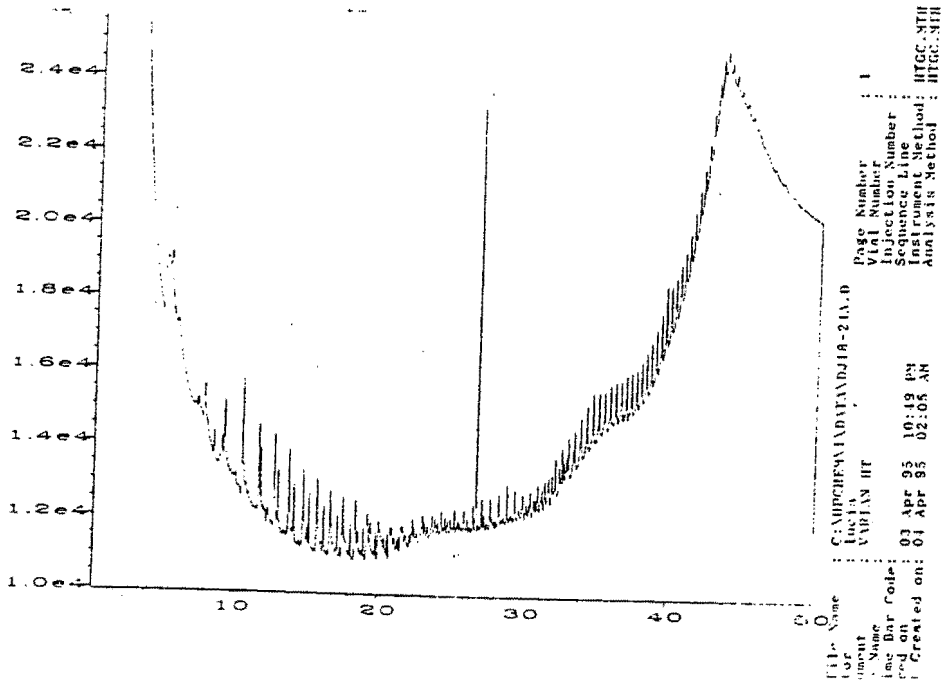
Fraction 24:  
Appendix 3

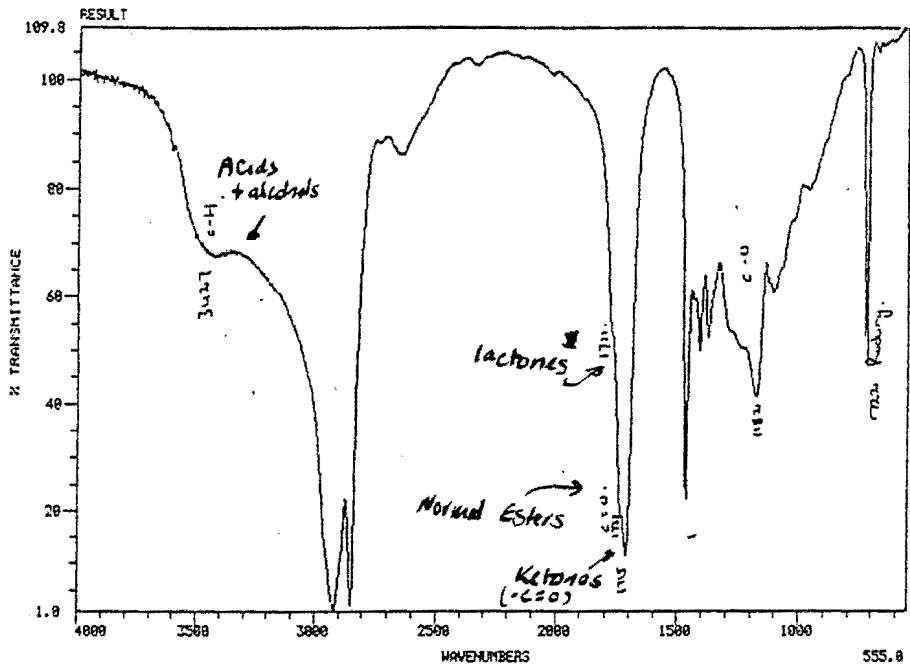
GVW FILE: 6111.D4

TEMPERATURE (C)

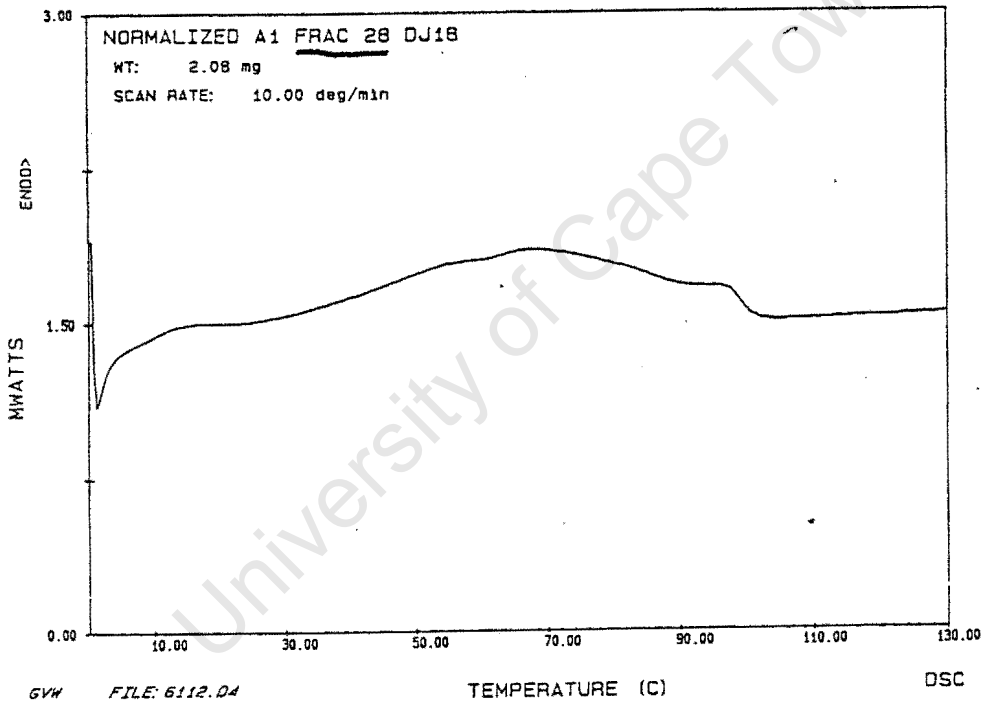
DSC

DATE: 95/03/13 TIME: 14:06

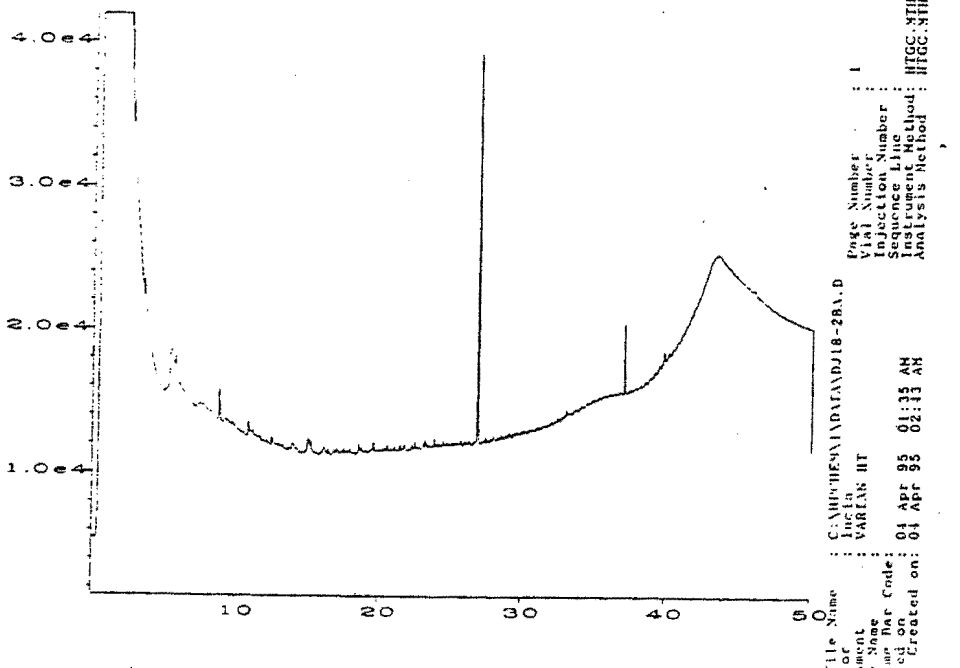




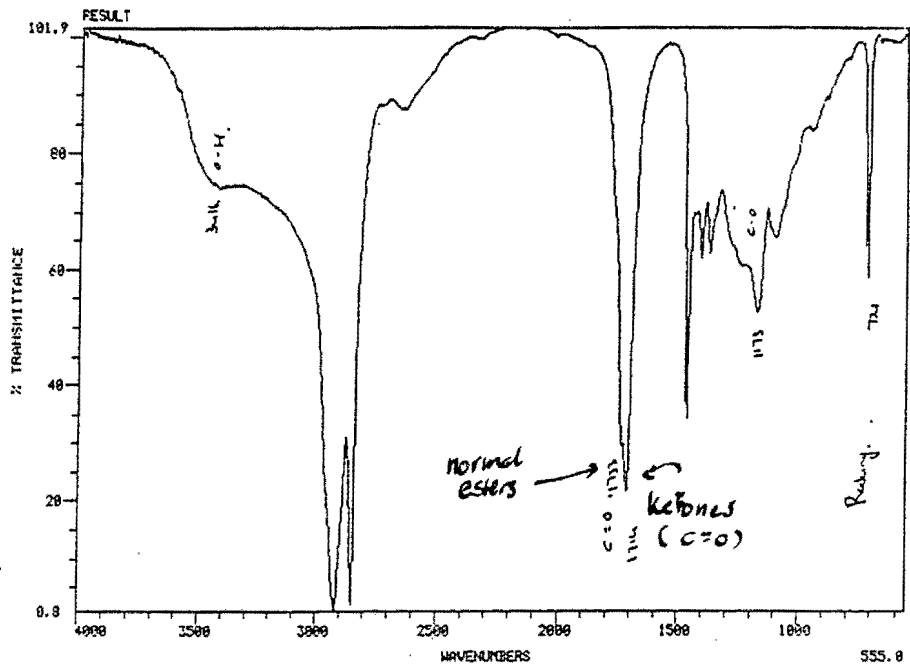
Nicolet Instrument Corporation  
FRACTION 28, A1 OXIDISED WAX



GVH FILE: 6112.D4  
DATE: 95/03/13 TIME: 15:30

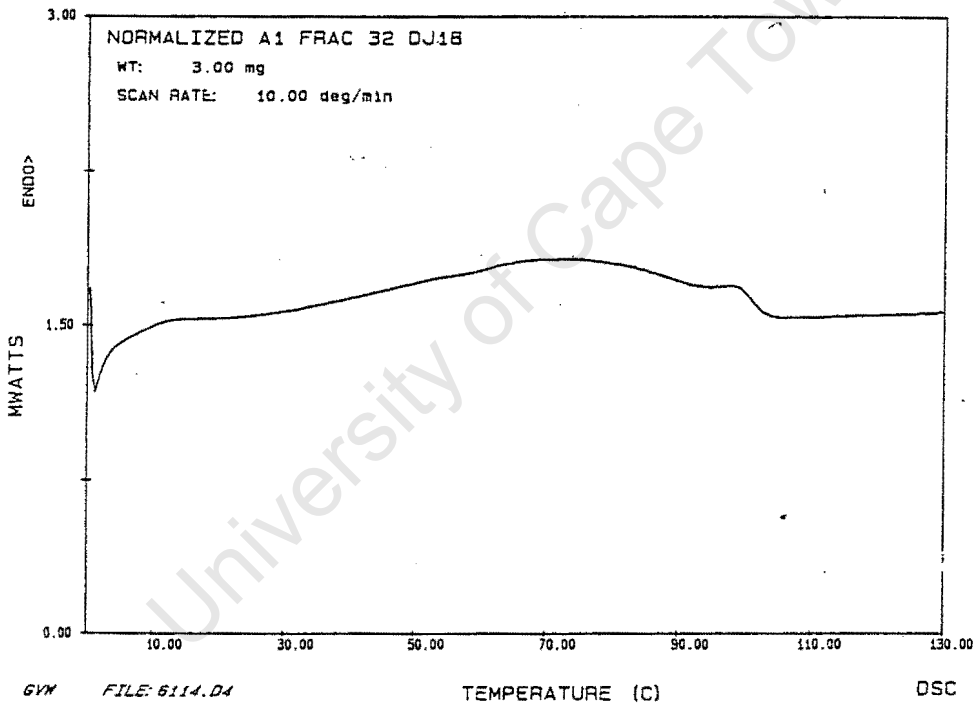


Fraction 28:  
Appendix 3



Nicolet Instrument Corporation

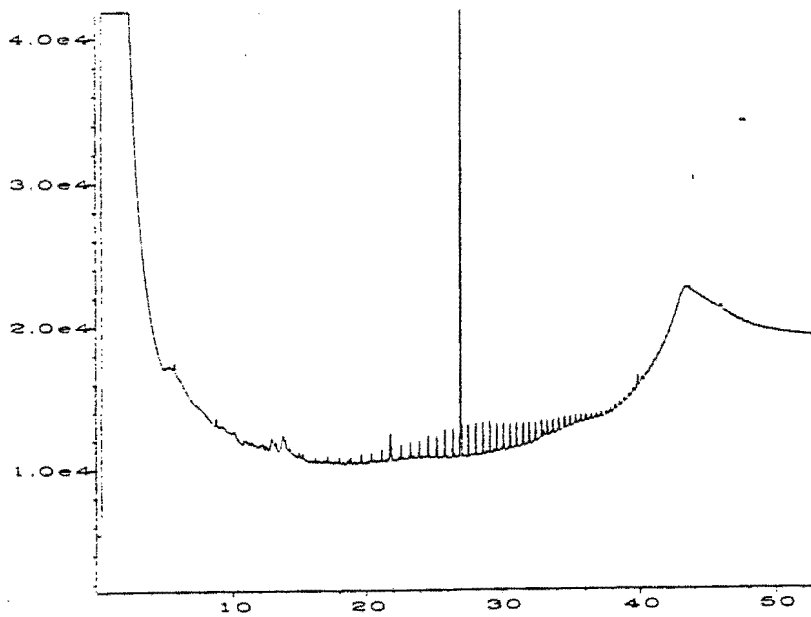
FRACTION 32, A1 OXIDISED MAX



Fraction 32:  
Appendix 3

GVV FILE: 6114.D4

DATE: 95/03/13 TIME: 16:35



C:\APCEN\1\DATA\DJ18-F32.D

Page Number

Vial Number

Injection Number

FILE: 6114.D4

DATE: 95/03/13

TIME: 16:35

File Name

File Path

File Size

**Appendix 3 (b)**

**Table of fractions collected during the column separation of oxidised Fischer-Tropsch hard wax**

University of Cape Town

**Table of fractions collected during the column separation of oxidised Fischer-Tropsch hard wax**

<b>Fraction</b>	<b>Mass ( g )</b>	<b>Comments</b>
1	0,2	Xylene elution
2	0,69	Xylene elution, volume = ~160ml
3	1,6	Xylene elution, volume = ~50ml
4	1,72	Xylene elution, volume = ~ 30ml
5	2,32	Xylene elution, volume = ~ 25 ml
6	4,02	Xylene elution, volume = ~ 50ml, AV*= zero
7	4,05	Xylene elution, volume = ~ 50ml
8	3,52	Xylene elution, volume = ~ 50ml
9	2,22	Xylene elution, volume = ~ 50ml, AV*= 0,5
10	3,92	Xylene elution, volume = ~ 50ml, AV*= 20
11	1,5	Xylene elution, volume = ~ 75ml
12	1,47	Xylene elution, volume = ~ 100ml, AV*=22
13	1,14	Xylene elution, volume = ~ 100ml
14	1,05	Xylene elution, volume = ~ 150ml
15	0,95	Xylene elution, volume = ~ 150ml
16	0,47	Xylene elution, volume = ~ 125ml
17	0,75	Xylene elution, volume = ~ 250ml
18	0,39	Xylene elution, volume = ~ 250ml
19	0,37	Xylene elution, volume = ~ 250ml
20	0,18	Start of xylene/DMF , volume=~ 200ml
21	0,42	Start of xylene/DMF , volume=~ 250ml
22	0,27	Xylene/DMF elutions, volume=~80ml
23	2,5	Xylene/DMF elutions, volume=~80ml
24	2,41	Xylene/DMF elutions, volume=~80ml, AV*=57
25	3,0	Xylene/DMF elutions, volume=~80ml
26	1,68	Xylene/DMF elutions, volume=~80ml
27	1,1	Xylene/DMF elutions, volume=~80ml

**Table of fractions collected during the column separation of oxidised wax (cont)**

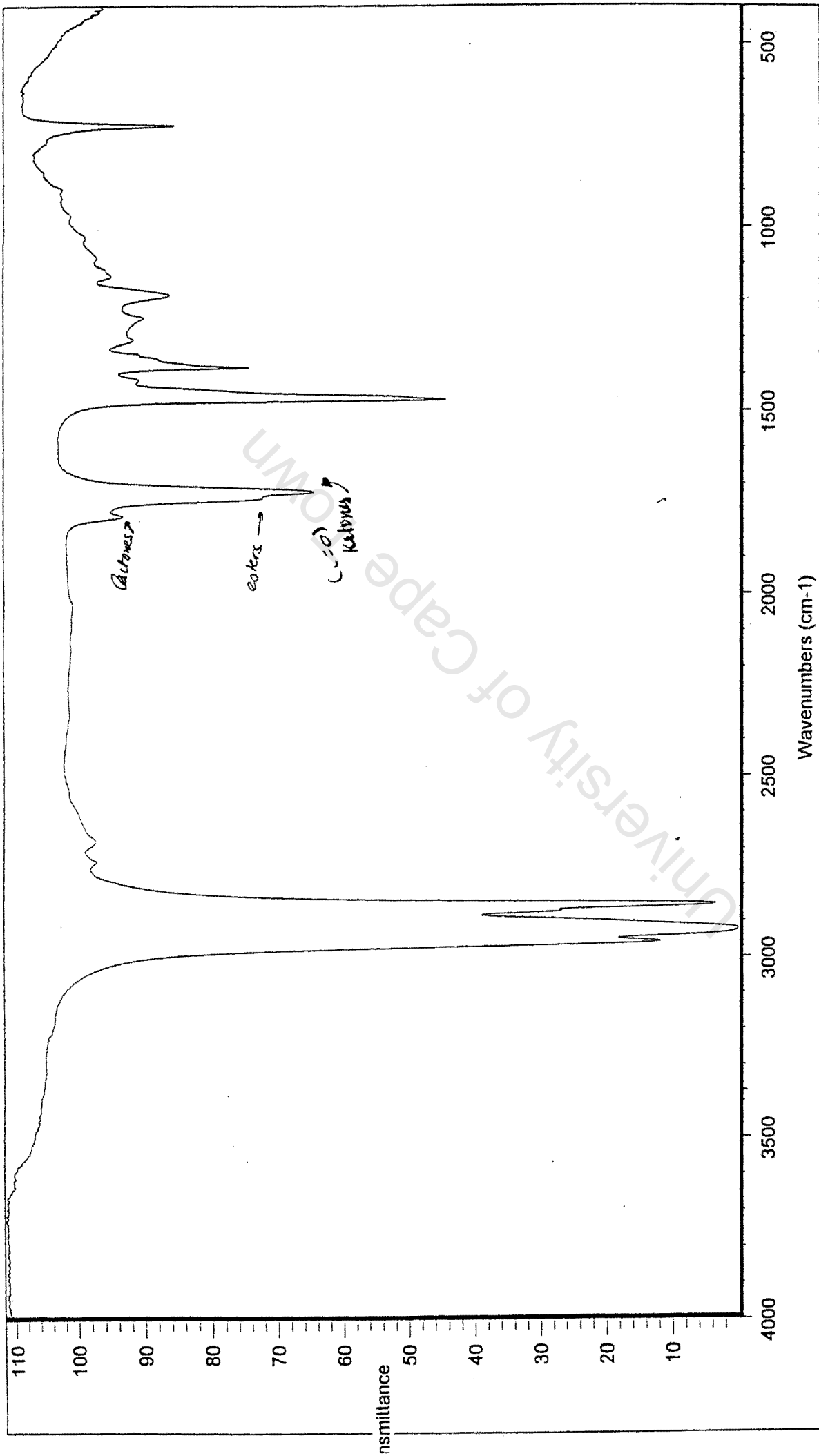
<b>Fraction</b>	<b>Mass ( g )</b>	<b>Comments</b>
28	0,48	Xylene/DMF elutions, volume≈80ml
29	0,43	Xylene/DMF elutions, volume≈80ml
30	0,27	Xylene/DMF elutions, volume≈80ml
31	0,46	Xylene/DMF elutions, volume≈100ml
32	0,26	Xylene/DMF elutions, volume≈60ml
33	0,47	DMF elutions, volume≈80ml
34	0,14	DMF elutions, volume≈80ml
35	0,2	DMF elutions, volume≈100ml
36	0,22	DMF elutions, volume≈150ml

\* AV- acid value expressed in mgKOH/g ( ASTM D1386-83 )

#### **APPENDIX 4**

**IR spectra of the oxidised model compounds namely, n-C16, n-C24 and n-C32, and a blend of these model compounds.**

University of Cape Town

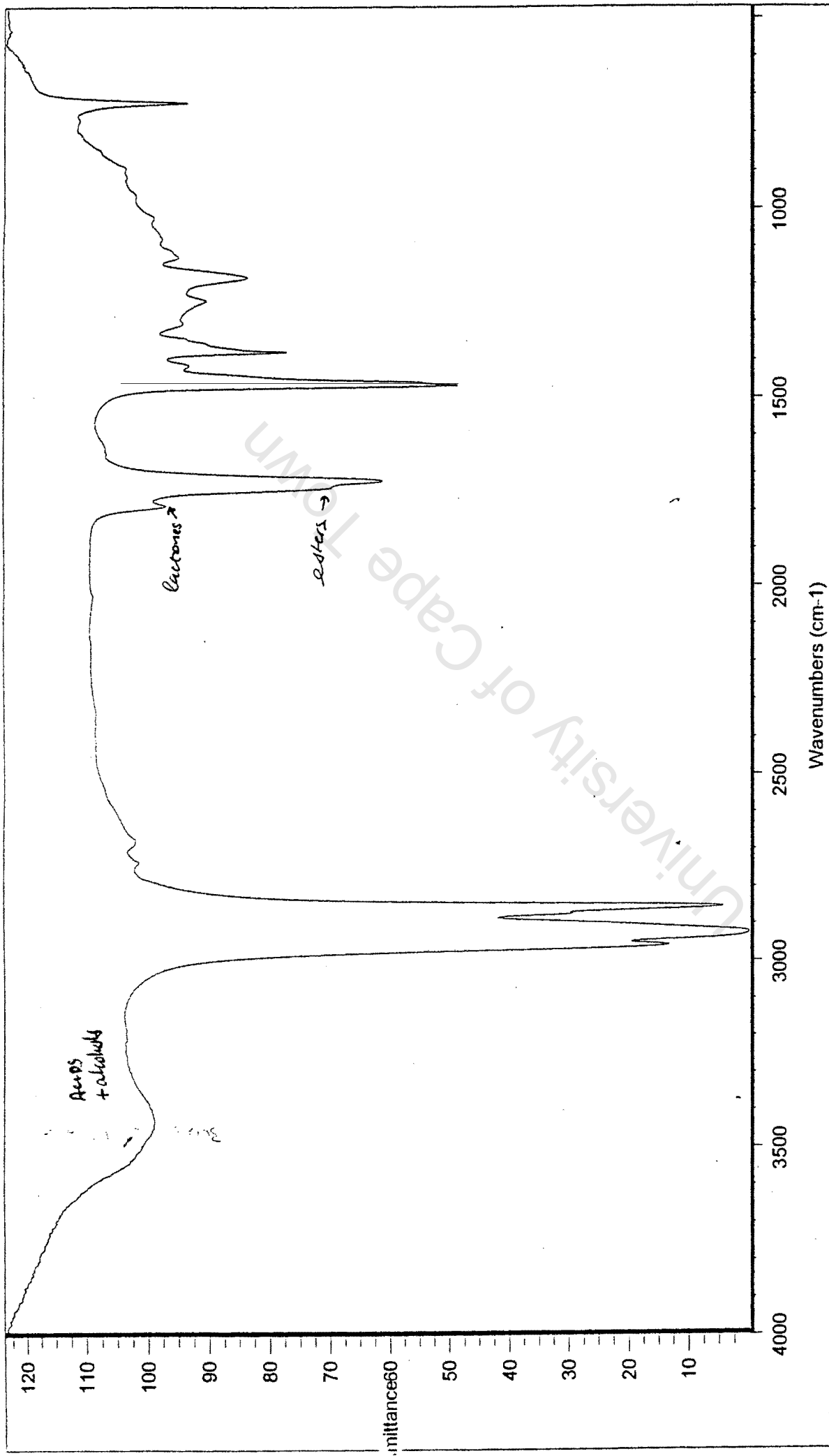


Date: Tue Dec 03 09:01:42 1996

Scans: 32

Resolution: 4.000

\*Oxidised C16, 170C, 4/10/96

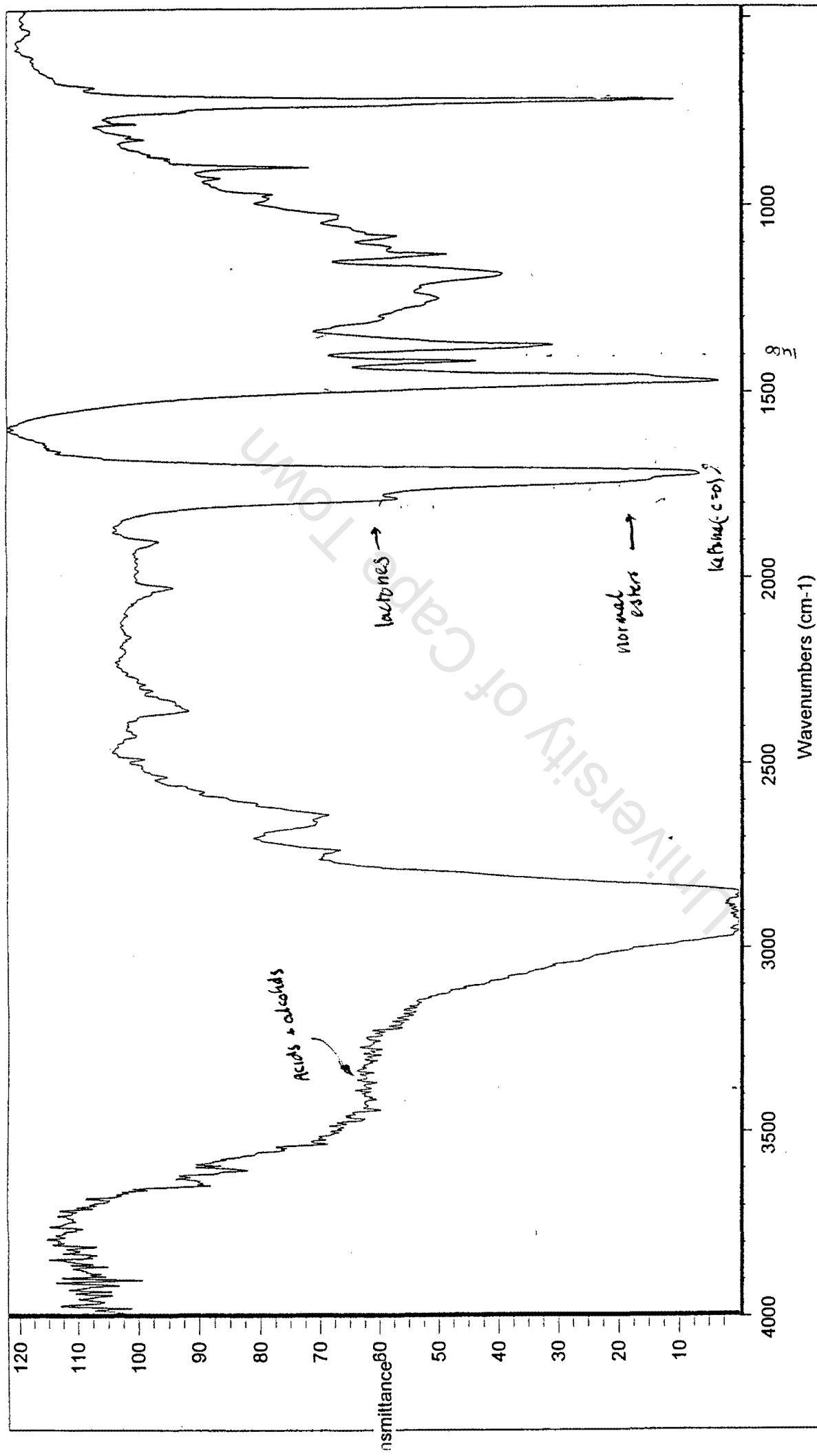


Date: Tue Dec 03 08:56:05 1996

\*\*Oxidised C16, 170C, 30/10/96

Scans: 32

Resolution: 4.000

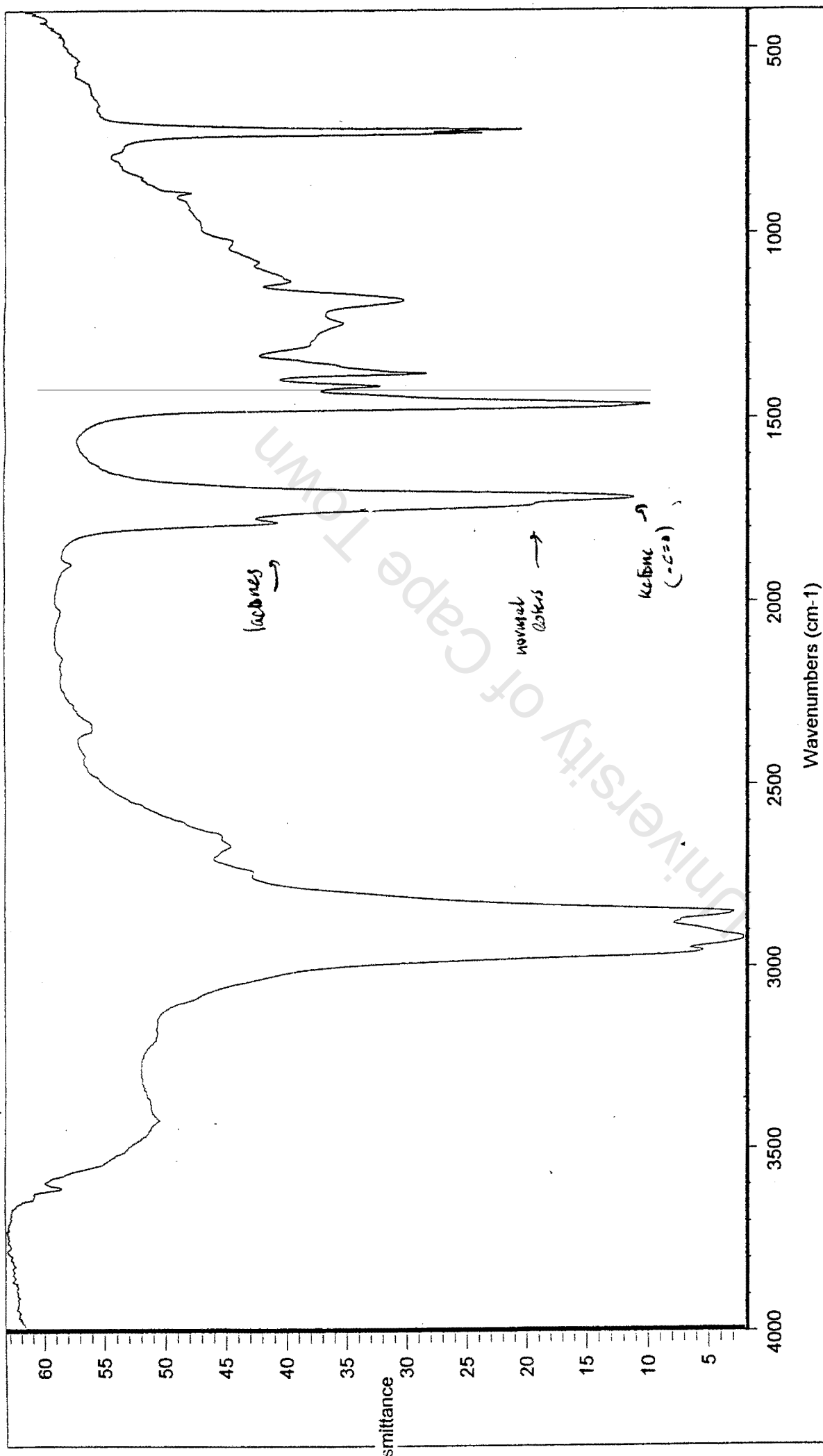


Date: Tue Dec 03 08:24:32 1996

\*Oxidised C24

Scans: 32

Resolution: 4.000

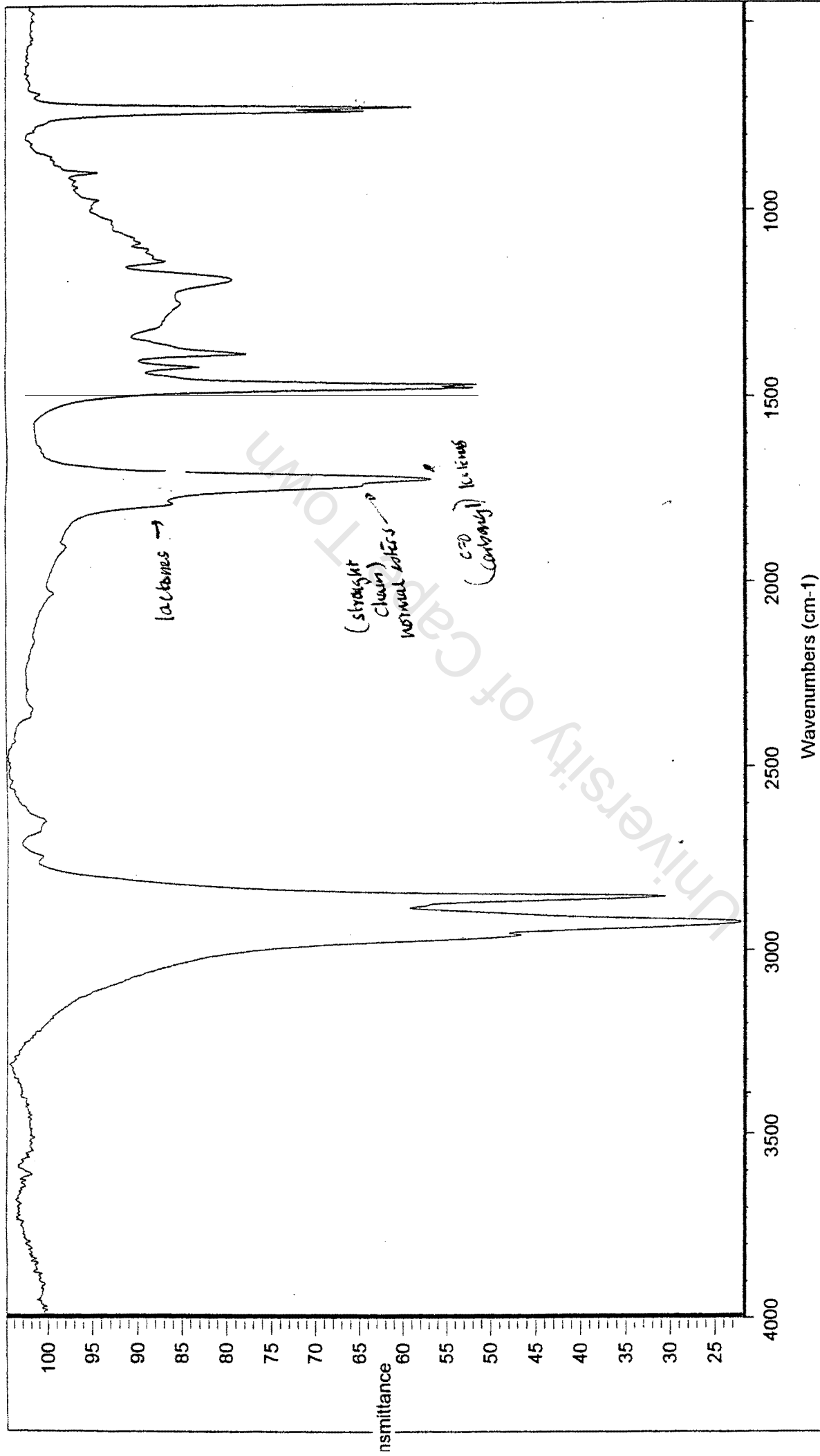


Date: Tue Dec 03 08:48:40 1996

Oxidised mixture: C16,C24,C32

Scans: 32

Resolution: 4.000



Date: Tue Dec 03 08:38:12 1996

\*Oxidised C32

Scans: 32

Resolution: 4.000