Investigation of the composition of linear alkylbenzenes with emphasis on the identification and quantitation of some trace compounds using GC/MS system in both electron impact and chemical ionization modes

by

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In memory of my father, Ludomir Flejszer

"Niech mądrość twoja i wiedza nie opuszcza mnie nigdy...."

ABSTRACT

Linear alkylbenzenes, LAB, formed by the $AlCl_3$ or HF catalyzed alkylation of benzene are common raw materials for surfactant manufacture. Normally they are sulphonated using SO_3 or oleum to give the corresponding linear alkylbenzene sulphonates in >95 % yield.

As concern has grown about the environmental impact of surfactants, questions have been raised about the trace levels of unreacted raw materials, linear alkylbenzenes and minor impurities present in them. With the advent of modern analytical instruments and techniques, namely GC/MS, the opportunity has arisen to identify the exact nature of these impurities and to determine the actual levels of them present in the commercial linear alkylbenzenes.

The object of the proposed study was to separate, identify and quantify major and minor components (1-10%) in commercial linear alkylbenzenes. The focus of this study was on the structure elucidation and determination of impurities and on the qualitative determination of them in all analyzed linear alkylbenzene samples.

A gas chromatography/mass spectrometry, (GC/MS) study was performed on five samples from the same manufacturer (different production dates) and then it was followed by the analyses of ten commercial linear alkylbenzenes from four different suppliers. All the major components, namely linear alkylbenzene isomers, followed the same elution pattern with the 2-phenyl isomer eluting last. The individual isomers were identified by interpretation of their electron impact and chemical ionization mass spectra. The percent isomer distribution was found to be different from sample to sample. Average molecular weights were calculated using two methods, GC and GC/MS, and compared with the results reported on the Certificate of Analyses (C.O.A.) provided by the manufacturers of commercial

linear alkylbenzenes. The GC results in most cases agreed with the reported values, whereas GC/MS results were significantly lower, between 0.41 and 3.29 amu.

The minor components, impurities such as branched alkylbenzenes and dialkyltetralins eluted according to their molecular weights. Their fragmentation patterns were studied using electron impact ionization mode and their molecular weight ions confirmed by a 'soft ionization technique', chemical ionization. The level of impurities present in the analyzed commercial linear alkylbenzenes was expressed as the percent of the total sample weight, as well as, in mg/g. The percent of impurities was observed to vary between 4.5 % and 16.8 % with the highest being in sample "I".

Quantitation (mg/g) of impurities such as branched alkylbenzenes and dialkyltetralins was done using cis/trans-1,4,6,7-tetramethyltetralin as an internal standard. Samples were analyzed using GC/MS system operating under full scan and single ion monitoring data acquisition modes. The latter data acquisition mode, which offers higher sensitivity, was used to analyze all samples under investigation for presence of linear dialkyltetralins. Dialkyltetralins were reported quantitatively, whereas branched alkylbenzenes were reported semi-qualitatively.

The GC/MS method that was developed during the course of this study allowed identification of some other trace impurities present in commercial LABs. Compounds such as non-linear dialkyltetralins, dialkylindanes, diphenylalkanes and alkylnaphthalenes were identified but their detailed structure elucidation and the quantitation was beyond the scope of this study. However, further investigation of these compounds will be the subject of a future study.

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INTRODUCTION

1. *Brief history of synthetic detergents*

Soap is the oldest surfactant and is believed to be one of the oldest chemical materials known to man obtained by reacting two substances to obtain a product with social significance. The word soap is derived either from the celtic "saipo"[1] or the latin "sapo", first used by Pliny The Elder about A.D. 75. Although Pliny is credited[2] with the first written reference to soap, its use is believed to have begun long before recorded history. Soap "per se" was probably never actually discovered but evolved rather from various crude mixtures of alkalis and fatty acids.

Over time it was learned that soap was not a mixture of alkali and fat but indeed resulted from a chemical reaction, later called saponification, and thus soap making changed from an art to a science. Soap remained the principal cleaning product, or surface active agent, well into the twentieth century.

Synthetic detergents or surfactants are more than 100 years old but they were insignificant until the early 1930's. Since their development, synthetic detergents dramatically reduced world dependence on soap for cleaning. A tremendous number of synthetic detergents were made and patented, particularly in Germany where the greatest application for these new products occurred in the textile industry. By the end of World War II it was estimated that production and consumption of synthetic detergents in Germany was 90-100 million pounds per year. This was still small compared to an annual soap production of 3 billion pounds.[3]

Starting in 1945 a very marked growth occurred in synthetic detergent production and by 1947 soap sales began to decline. Detergents based on synthetic surfactants continued to

displace soap powders due to the availability of petrochemical feedstocks and observations that synthetic surfactants are less sensitive to temperature and water hardness. In 1953 the synthetic detergent production surpassed the production of soap.[3]

It is interesting to note that the basic batchwise process for soapmaking remained practically unchanged for approximately 2000 years. Is was not until the late 1930's that continuous soapmaking processes were developed and installed in large-scale manufacturing plants. Ironically, this timing coincides with the early stages of the tremendous growth of the synthetic detergent products. Nonetheless, a significant market remains for soap-based products for both consumer cleaning, primarily bar soap and for industrial use[2].

2. *General nature of surfactants*

The theory of surfactants has been studied and developed as an important part of the field of surface chemistry. Many scientists have contributed to an understanding of the physical-chemical properties of surfactants. Concurrently with the scientific studies of surfactants by chemists, physicists, and biologists, a vast technology has developed related to the application of surfactants in many different industries. This work includes studies of the effect of surfactant structure on wetting, detergency, dispersion and foaming.

A surfactant can be defined as organic chemical molecule consisting of two parts: a water soluble "head group" and a water insoluble "long tail". Anthropomorphically, it can be said that the "head group" likes water and the term *hydrophilic* is used to describe the behaviour of the head group. Similarly, it can be said that a "tail" hates water and the term *hydrophobic* is applied to the character of the water incompatible tail. The schematic representation of the surfactant molecule with a "head group" and a zig-zag "tail" is shown below:

An example of a surfactant is dodecyl sulphate, the head group (*hydrophilic*) is the sulphate group and the tail (*hydrophobic*) consists of the dodecyl chain:

$$CH_3(CH_2)_{11}OSO_3Na$$

Another example of a surfactant molecule is sodium 2-phenyldodecane sulphonate:

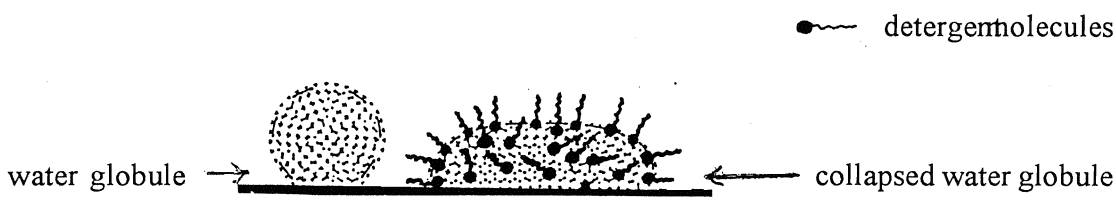
$$CH_3(CH_2)_8CH_2\text{-}\underset{\displaystyle C_6H_5SO_3Na}{\overset{|}{C}}H\text{-}CH_3$$

Looking at the above surfactant molecule, the *hydrophilic* group is the sulphonate group and the *hydrophobic* group is the "alkyl" group linked to a benzene ring. This material is the most widely used surfactant today and will be discussed further later.

A surfactant may be defined also as a material which reduces the surface energy of water or solvent. A good surfactant, for example, will reduce the surface tension of water from 72 to 30 dynes/cm at a concentration of less than 0.01 %.[3]

As stated above, the first reason why surfactants are effective detergents is that they lower the surface tension of water, enabling it to wet surfaces more effectively. Water alone does not wet well, a seeming contradiction in terms, and hence does not deterge effectively by itself. This is because water globules do not spread quickly on many comman surfaces. This is due to an imbalance of attractive forces between water molecules on the surface of the globule. In other words, there is a net force parallel to the surface, a kind of a "skin" which keeps the shape of the water globule. When a surfactant is introduced, the combined *hydrophobic* and *hydrophilic* moieties render the compound surface-active and thus able to concentrate at the surface between a surfactant solution and another phase, such as air, soil or textile. As a result, the *hydrophilic* head ends up in the surface layer and the *hydrophobic*

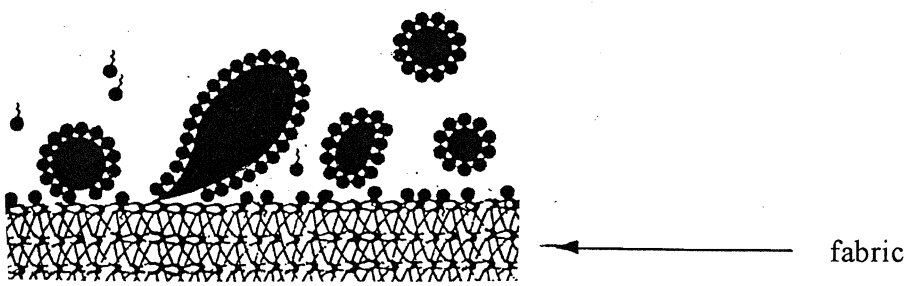
tail sticks out into the other phase. Such an orientation weakens the forces parallel to the surface (weakens the "skin") and the water globule collapses under the influence of gravity; as it spreads out and wets[4].



In water the surfactant molecules congregate at the surface, the water-air surface. There comes a point when all of the available surfaces are covered with surfactant molecules. As the number of surfactant molecules increases, they start to aggregate or cluster. These clusters are called micelles. All of the *hydrophobes* point into the centre of the micelle and all of the *hydrophilic* head groups point outward to the water. Micelles act as a reservoir of surfactant molecules; they also provide a "fatty" environment inside the water phase so the oily grease globules can actually be dissolved inside the micelles.

The second important function of a surfactant is that it helps to dislodge dirt from fabrics. Dirt is usually described as a mixture of fatty material and solid. The solids include any or all of the following: clay, pigment, carbon, and iron oxide. The fatty material on fabrics is mainly a natural skin constituent, sebum.

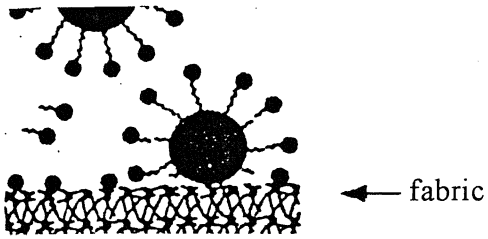
The "lift-off" mechanism of the fatty or oily globule from fabric can be represented scematically[4] ,where represents a surfactant molecule:



The surfactant molecules adsorb on the surface of the fat globule with the *hydrophobes*

pointing inside and the *hydrophillic* groups sticking into the water. As more and more surfactant molecules crowd around the fat globule, the globule is squeezed off the fabric and starts to float about in the wash water. The fact that the oil globules are covered with the charged groups, causes them to repel each other and hence they stay suspended.

The "lift-off" mechanism of the non-fatty globule, like a particle of rust, from fabric can also be represented schematically[4]:



The surfactant molecules first attach themselves with the head groups on the rust particles. The *hydrophobic* tails pointing outward provide a first layer, a "fatty" environment for the *hydrophobe* tails of the other surfactant molecules. Thus, a second layer of surfactant can surround the rust particle. The doubly surrounded rust particle is dislodged from fabric and, like the oil globule, is held in suspension by the repulsion of the charged groups.

In summary, surfactant function is to penetrate and wet soiled surfaces, to displace and solubilize various soils, and to disperse suspended soils in solution to prevent their redeposition.

3. ***Classification of surfactants***

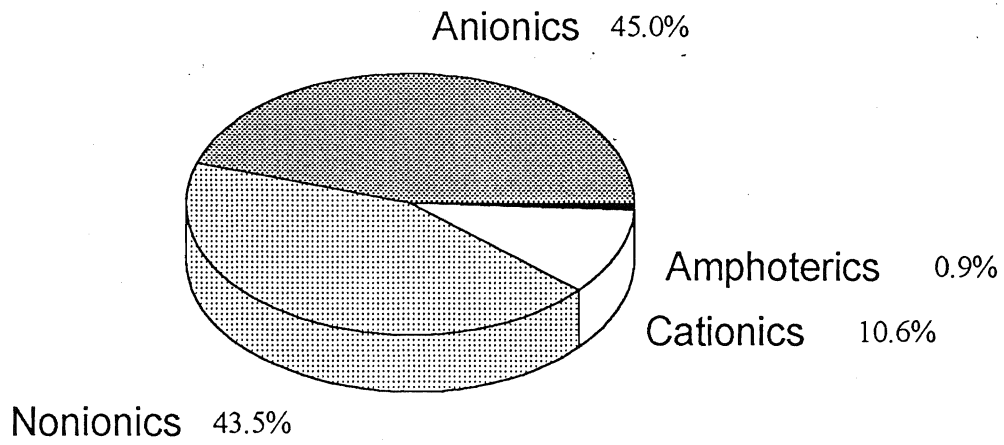
Surfactants are classified into four categories, depending on ionic activity or according to their electrical charge: i) *Anionic*, ii) *Nonionic*, iii) *Cationic*, and iv) *Amphoteric*.

i) *Anionic* surfactants, where the hydrophilic portion of the molecule carries a negative charge, account for 45.0 % of worldwide surfactant use (**Figure 1**)[5]. Generally, they are high-foaming and sensitive to hard water, and thus require the addition of substances to complex

Figure 1

Estimated Surfactant Consumption (1991)

(W.Europe, USA, Japan)

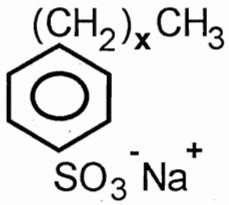


'000 Tns.

Anionics 2,255 Nonionics 2,180
Cationics 530 Amphoterics 44

calcium and magnesium ions. But they are more effective than other surfactants in particulate soil removal, especially for natural fabrics. As a rule, they are easily spray-dried and thus are favoured for detergent powders.[5] The most commonly used *anionic* surfactants are:

A. **Linear alkylbenzene sulphonates** (LAS),



(x ranges from 9 to 13)

which are synthesized by Fiedel-Crafts alkylation of benzene to produce linear alkylbenzene (LAB), followed by sulphonation with oleum or SO_3. Sulphonation produces mainly the para isomers.

B. **Linear alkyl sulphates**,

$$CH_3(CH_2)_yOSO_3^-Na^+$$ (y ranges from 9 to 17)

also called alcohol sulphates, are formed by making the sulphuric acid esters of linear alcohols followed by neutralization with base. The properties of the alkyl sulphates vary with the alkyl chain length distribution. The alcohol source can be either olechemical or petrochemical. Tallow-range and coconut-range alcohols come from both olechemical and petrochemical feedstocks.

C. **Linear alkyl ether sulphates**,

$$CH_3(CH_2)_z(O\text{-}CH_2\text{-}CH_2)_tOSO_3^-Na^+$$ (z ranges from 7 to 15) (t ranges from 0 to 11)

also called alcohol ethoxysulphates are prepared by addition of one to eleven oxyethylene groups to an alcohol, which is then sulphated and neutralized with base. Oxyethylation enhances water solubility, improves skin mildness and reduces sensitivity to temperature and water hardness. The raw materials for these products can be either olechemical fatty alcohols or primary or secondary synthetic alcohols.

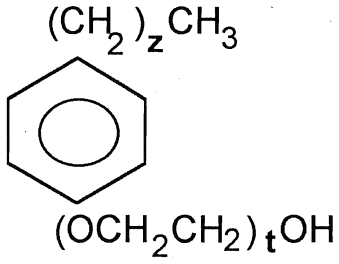
ii) *Nonionic* surfactants, which do not carry a charge but commonly derive their hydrophilic portion from polyhydroxy or polyethoxy structures, account for 43.5 % of worldwide surfactant use (**Figure 1**)[5]. This percentage is growing because *nonionics* are generally more tolerant of water hardness than *anionic*s, which makes the requirement for substances to complex calcium and magnesium ions in laundry detergents less demanding. They also tend to be more effective than other surfactants in removal of oily soil from synthetic fabrics. Most *nonionics* are considered low-foaming products and have good cold water solubility. The most commonly used *nonionic* surfactants are:

A. **Ethoxylated alcohols,**

$$CH_3(CH_2)_x(O\text{-}CH_2\text{-}CH_2)_yOH$$ (**x** ranges from 9 to 15) (**y** ranges from 4 to 20)

are generally made by solventless addition of ethylene oxide to fatty alcohols using alkaline catalysis. Most often, the alcohol starting material consists of a range of alkyl chain lengths, almost always linear. The most important surfactant properties are controlled by the average percent ethylene oxide units (EO) and the average chain length of the starting alcohol. The primary alcohol ethoxylates are the typical items of commerce.

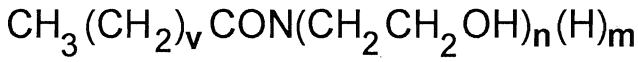
B. **Ethoxylated alkylphenols,**



(**z** ranges from 7 to 13)
(**t** ranges from 3 to 12)

are produced by alkaline-catalyzed ethoxylation of the alkylphenol. Their use is limited to special applications. They are excellent for the removal of oily soils and can be produced at a lower cost than more abundant alcohol ethoxylates, but have a less acceptable toxicological profile.

C. **Fatty acid alkanolamides,**



(**v** ranges from 9 to 17)
(**n** ranges from 1 to 2)
(**m** is 1 or 0)

are made by reation of an alkanolamine with either a fatty acid or a fatty acid ester, usually triglycerides or methyl esters. The most common examples of this class are the mono- and diethanolamides of linear alkyl acids. They are effective for increasing the viscosity of liquid formulations and are used to stabilize the foam formed by other surfactants. Although they are very effective surfactants in their own right, they are very sensitive to water hardness in the absence of other surfactants, as well as being subject to attack by acid or base. They are commonly used in liquid products where high foaming is required.

iii) *Cationic* surfactants, where the hydrophillic portion of the molecule carries a positive charge, account for 10.6 % of worldwide surfactant use (**Figure 1**)[5]. They are useful

as fabric softeners, corrosion inhibitors, and antimicrobial agents. They are not used in general-purpose detergents because they do not provide effective cleaning at neutral pH and they can absorb rapidly to textiles[6]. Commercially important *cationic* surfactants are:

A. **Quaternary ammonium salts,**

$$(C_nH_{2n+1})(CH_3)_3N^+Cl^-$$

are made from naturally occurring materials by reaction of methyl chloride with the dimethylalkylamine, wherein the alkyl group is C_{12} to C_{16} .

iv) *Amphoteric* surfactants, where the molecule carries a positive and negative charge locations, represent only 0.9 % of all surfactant produced (**Figure 1**)[5]. They are less irritating than the ionic surfactants and are used, for example, in children's shampoos[7]. Commercially important *amphoteric* surfactants are:

A. **Carboxybetaines** such as,

$$C_{12}H_{25}N^+(CH_2)_3CH_2COO^-$$

are most often made by quanternization of a tertiary amine with chloroacetic acid (they are internal salts). The commercial product is generally a mixture with alkyl chain lengths of C_8-C_{18}. Although there are a number of betaines classified as *amphoteric* surfactants, only the carboxybetaines are widely used, often in liquid soaps.

4. *Basic ingredients in the detergent formulation*

Typically, a laundry detergent formulation contains the following ingredients: a builder to soften water by complexing calcium and magnesium ions (trisodium nitrilotriacetate or sodium tripolyphosphate), a processing aid to improve product processing and handling(sodium sulphate), a corrosion inhibitor to protect washer parts (sodium silicate), an antiredepositioning agent, to prevent dirt from going back on cloths (carboxymethyl cellulose), a fluorescent whitening agent for a whiter looking wash, an enzyme to remove specific stains (protease), a perfume to provide scent, water, and last but not the least of the ingredients, a surfactant to lift dirt from cloths by helping water to penetrate the fabric and soil more easily for cleaning (alkylbenzene sulphonate).

5. *Linear alkylbenzene sulphonate (LAS), the sulphonated derivative of linear alkylbenzene*

Linear alkylbenzene sulphonates, LAS or LABS, the sulphonated derivative of linear alkylbenzene (LAB), is the most important surfactant, after soap, and is widely used in all kinds of formulations. After its introduction in the mid sixties LAS has been shown to have a remarkable number of attractive aspects with regard to formulability, performance, economics etc. which make this product the workhorse of the detergent industry. The overall credentials of LAS are unmatched by any other surfactant and therefore the predictions are that this product will continue to maintain its importance well into the 21st century.

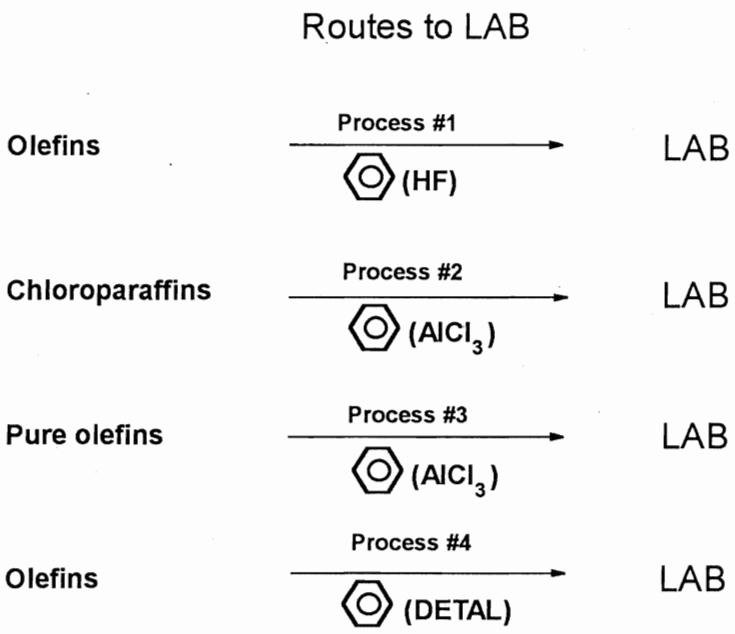
It has been observed that the composition of LAS[8,9] has a remarkable effect on solubility, viscosity, foaming, biodegradability and overall detergency performance.

The exact reaction mechanizm of alkylbenzene sulphonation is still not fully known. The key factor for an increasing efficiency performance in the production of LAS is

optimization of the sulphonation process. An important step involved in this optimization is the improvement in calculation of the actual molecular weight of raw material, namely linear alkylbenzenes, LAB.

6. *LAB production routes and typical composition of commercial LAB*

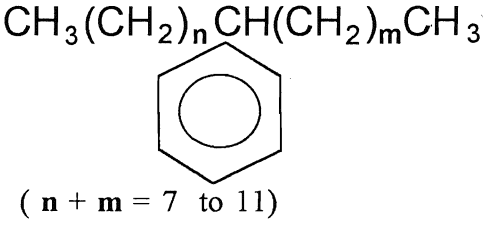
The production alternatives of linear alkylbenzenes (LAB) are differentiated by the alkylation catalyst used in the primary step of the production process, either HF (process **#1**) or $AlCl_3$ (process **#2** and **#3**). Aluminium chloride was the first catalyst used in the industry in the early 60's, HF was introduced later. The schematic representation of LAB production is shown below:



A third process, **#3** for production of LAB has recently been introduced. The new LAB process basically makes use of the same technology employed for the production route **#2**, but has been modified to use olefins. A **4th** route has also been developed which uses a new

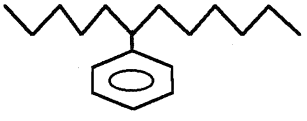
solid catalyst[10] (DETAL) in a fixed bed reactor operating in the liquid phase for the alkylation of benzene. The olefinic raw material used is the same as in the HF process **#1**, and operating conditions are very mild. A substantial advantage of the new technology is its simplicity compared to the HF route. The absence of HF catalyst is reflected not only on the process itself but also on other inherent aspects such as HF purification, regeneration, and neutralization of acidic effluents, etc.

The linear alkylbenzenes, LAB, whose structural representation for the linear components is shown below:

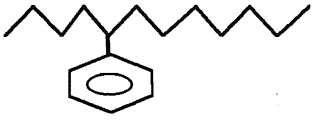


(**n** + **m** = 7 to 11)

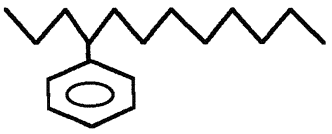
have different percent distribution of the phenyl position isomers along the linear alkyl chain as a function of the process. For example, for C_{12} LAB there are 5 (five) possible isomers: 6-, 5-, 4-, 3- and 2-phenyldodecane:



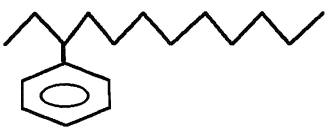
6-phenyldodecane



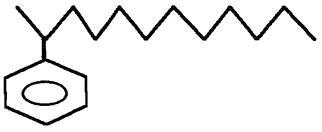
5-phenyldodecane



4-phenyldodecane

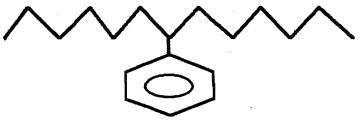


3-phenyldodecane



2-phenyldodecane

For C_{10} LAB there are only 4 (four) possible isomers: 5-, 4-, 3- and 2-phenyldecane, whereas for C_{13} and C_{14} LAB there are 6 (six) possible isomers: 2-, 3-, 4-, 5-, 6-, and 7-phenyltridecane, the latter being:



7-phenyldodecane

A further element of variation between LAB produced by alternative processes can be found in the different total amount of the linear alkylbenzenes, 2-phenyl isomer and in the impurities like *dialkyltetralins* and *branched* alkylbenzenes. The percent of the linear components present in the industrial LAB varies between **90** and **94 %** for the route via HF, **87** and **91 %** for the route via $AlCl_3$, around **98 %** for the route #3 and **91** and **93 %** for the 4th route. This is a consequence of the different amount of the by-products being formed along with the linear alkylbenzenes via the three production processes which were described

earlier. In the HF route, the *branched* alkylbenzenes vary between **5** and **8 %** with the low content of **0.5** to **2 %** of *dialkyltetralins*, whereas in the $AlCl_3$ route, process #2, *dialkyltetralins* vary between **6** and **10 %** with *branched* alkylbenze content of about **3 %**. The third route, using the top quality *n*-olefins leads to a low *dialkyltetralin* content of about **0.5 %** and the *branched* alkylbenzenes between **0.5** to **1.5 %**.

Typical LAB composition for the above processes, including percent of the total linear alkylbenzenes, percent of the *dialkyltetralins* and percent of the *branched* alkylbenzenes is presented in **Table 1**. The percent of 2-phenyl isomer, derived from four different processes is also presented in **Table 1**. It has been observed[8,11] that percent of 2-phenyl content markedly affects formulating properties of linear alkylbenzene sulphonate in liquid detergents, particularly solubility and viscosity.

The average molecular weight, which is the main parameter in the optimization of the sulphonation process of commercial LAB, is calculated based on percent carbon distribution in the LAB. **Table 2** represents a typical percent carbon distribution in commercialy produced LAB via the first three processes.

7. ***Impurities present in commercial linear alkylbenzenes***

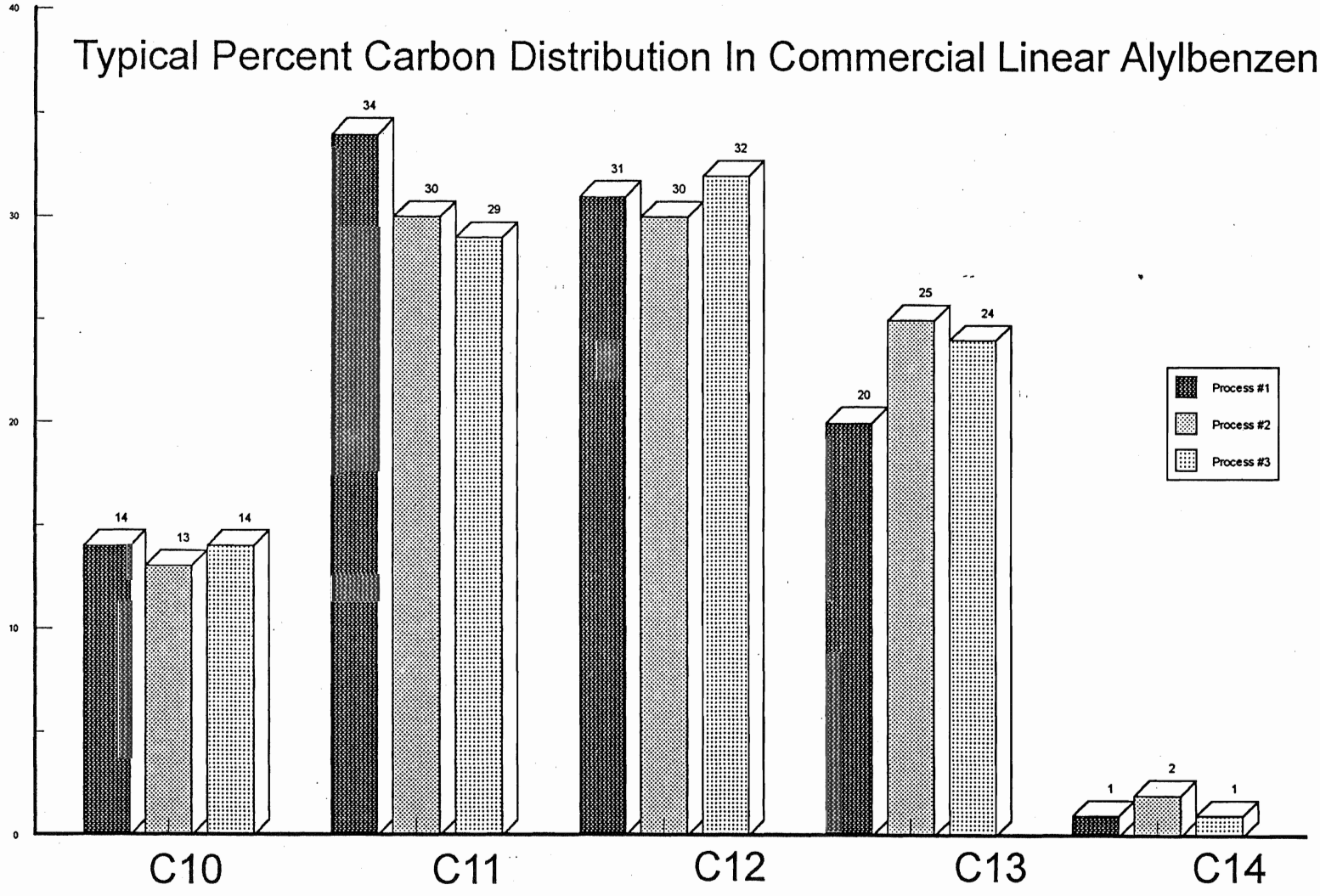
As mentioned in the previous paragraph, one class of compounds found as an impurity in the production of commercial linear alkylbenzenes, *dialkyltetralin*s, DAT, is formed as a by-product during the alkylation of benzene with chloroalkane/$AlCl_3$ (Process **#2**), or with olefin/HF (Process **#1**). A second class of compounds found as an impurity in the production of LAB via the $AlCl_3$ route, multi-branched alkylbenzenes is formed from skeletal rearrangement of the alkyl chains.

Table 1

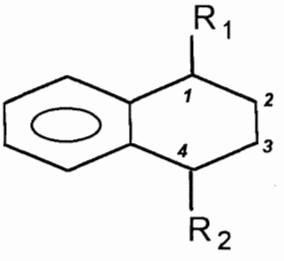
LAB characteristics - typical composition

Process	#1	#2	#3	#4
Catalist	HF	$AlCl_3$	$AlCl_3$	DETAL
	(%)	(%)	(%)	(%)
Linear isomers	**94**	**91**	**98**	**91 - 93**
Branched isomers	**5**	**3**	**1**	**6 - 8**
Dialkyltetralins	max **1**	**~6**	max **1**	max **1**
2-phenyl isomer	**~18**	**~29**	**~29**	**~29**
Average MW (amu)	**240**	**242**	**242**	**240**

Table 2


Typical Percent Carbon Distribution In Commercial Linear Alylbenzenes
40
30
20
10
0
14
13
14
34
30
29
31
30
32
20
25
24
1
2
1
C10
C11
C12
C13
C14
Process #1
Process #2
Process #3

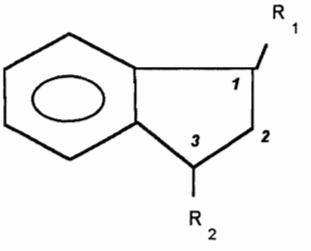
The number of *dialkyltetralin* isomers is restricted according to the chain length of the original paraffins. For example, the possible *dialkyltetralin* isomers coming from the C_{10} dichloroparaffins (Process **#2**) are six[12]:



R_1	R_2
CH_3	C_5H_{11}
C_2H_5	C_4H_9
C_3H_7	C_3H_7

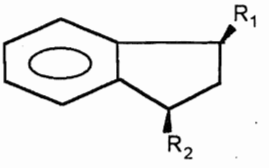
where R_1 and R_2 can be disposed in **cis** or **trans** positions, namely: **cis** and **trans**-1-methyl-4-pentyltetralin, **cis** and **trans**-1-ethyl-4-butyltetralin, and **cis** and **trans**-1,4-dipropyltetralin.

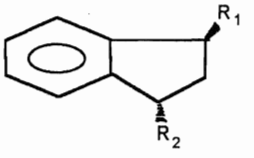
The third class of impurities, *dialkylindanes*, may be found in the production of commercial LAB. For the corresponding *dialkylindan*e isomers, there are still six possible isomers but the side chains R_1 and R_2 are different**:**



R_1	R_2
CH_3	C_6H_{13}
C_2H_5	C_5H_{11}
C_3H_7	C_4H_9

again with R_1 and R_2 in either **cis** or **trans** position, namely: **cis** and **trans**-1-methyl-3-hexylindane, **cis** and **trans**-1-ethyl-3-pentylindane, and **cis** and **trans**-1-propyl-3-butylindane.





In theory, one more possible isomer exists for each *dialkyltetralin* and *dialkylindane,* having R_1 = H and $R_2 = C_6H_{13}$ or C_7H_{15}. These isomers, however, are very unlikely. In fact the alkylation reaction involves the formation of carbonium-ion intermediates, which tend to rearrange to form more stable secondary carbonium ions. The absence of the 1-phenyl isomers in the alkylbenzenes is due to the same reason. For the remaining: C_{11} ,C_{12} , and C_{13} dichloroparaffins, the expected number of possible *dialkyltetralin* and *dialkylindane* isomers is as follows:

Dichloroparaffin	*Dialkyltetralin* isomers	*Dialkylindane* isomers
C_{11}	6	8
C_{12}	8	8
C_{13}	8	10

The number of *branched* alkylbenzene isomers formed during production of LAB is practically unknown. One can howener, easily differentiate a branched alkylbenzene from the corresponding linear alkylbenzene using GC/MS analytical instrument. The separation of linear from branched alkylbeznes will be discussed later.

8. ***Analysis of commercial linear alkylbenzenes (LAB)***

The so called "work horse" surfactant for manufacture of modern detergents, Linear alkylbenzene, LAB is synthetically produced from crude oil following different alternatives. At present LAB is, after soap, the most widely used surfactant feedstock in household products as well as in industrial formulations.

Since 1968 a number of significant advances have been made in the technology for the production of linear alkylbenzenes. These advances have been the result of detergent

industry's commitment to improve not only economic benefits but also the quality of the LAB produced.

With the steady increase of the world production and consumption of LAB, concern has grown about the environmental impact of surfactants, namely linear alkylbenzene sulphonates, LAS. Questions have been raised about the trace levels of starting materials, LAB and minor impurities present in them. With the advent of modern analytical instruments and techniques like gas chromatography or gas chromatography/mass spectrometry, the opportunity has arisen to identify the exact nature of these impurities and to determine the actual levels of them present in the commercially available LABs.

Analysis of commercial LAB is generally carried out using gas chromatography/flame ionization detection (GC/FID). This technique provides good information on the different homologues but other components like impurities, however, are not so easily identified. Gas chromatography/mass spectrometry (GC/MS) offers more information on the chemical composition of commercial LAB. It not only provides the identification of different homologues but also allows identification of the impurities, such as *dialkyltetralins* and *branched* alkylbenzenes. In order to evaluate their influence in the final LAB molecular weight, it is important to know the exact percentage of impurities. As mentioned before, the use of an accurate molecular weight is critical in the operation of sulphonation plants and therefore on the final yields obtained.

9. ***Summary of studies related to linear alkylbenzenes and to the impurities present in commercial alkylbenzenes, LAB and their sulponation derivatives***

As mentioned above, linear alkylbenzenes obtained via different processes, are not the same. They differ in the carbon chain length distribution, as well as, in isomer distribution,

with the phenyl group being distributed differently along the paraffin chain. The greatest difference is in the amount of 2-phenyl isomer (**Table 1**). Linear alkylbenzenes obtained from the $AlCl_3$ and HF processes are, therefore, commonly referred to as high and low 2-phenyl LAB, respectively, as are the linear alkylbenzene sulphonates (LAS). Drozd et al.[8] reported that differences in 2-phenyl content markedly affect formulating properties of linear alkylbenzene sulphonate (LAS) in liquid detergents, particularly solubility and viscosity. They reported the solubility of sodium and ammonium low 2-phenyl LAS to be lower than that of high 2-phenyl LAS, causing cloudy or hazy mixtures. Viscosities of solutions of the various salts of high and low 2-phenyl LAS were not the same but did not appear as significant as the solubility differences.

It is already well known in the detergent industry that LAB derived from the $AlCl_3$ alkylation process gives slurries with higher solubility than LAB derived from the HF process. This effect has been explained historically as a function only of the higher 2-phenyl alkane isomer content of the $AlCl_3$ derivative. Moreno et al.[11] reported that although the external isomers, 2- and 3-phenyl, of a given homologue have a different solubility than the internal ones, 4-, 5-, and 6-phenyl, the reason why $AlCl_3$ derivatives gave lower cloud points (higher solubility) than the HF ones, was also related to the higher tetralin content of the former. At the same time, authors observed that the higher the sulphonation severity, the SO_3 to LAB ratio, the poorer the solubility. This viscosity depressing effect was explained as a formation of dialkyltetralin sulphonates.

Cohen et al.[12] have reported that the alkyl chain length and the presence of tetralins have an important influence on solubility, viscosity and surface tension. They observed that tetralin content acts as a viscosity depressor. The lower the molecular weight of a similar type of LAB (same tetralin content), the lower the viscosity, and the better the solubility. It

is already well known that the optimum solubility is reached for a molecular weight of 232 - 235 (C_{11} homolog).

On the contrary, Matheson and Matson[13] reported that the carbon chain length, not phenyl isomer distribution, is the most important factor in determining detergency performance. According to these authors, LAS manufactured via both HF and $AlCl_3$ processes perform equally well and can be used interchangeably in high performance products.

Instrumental studies by GC/MS, of commercial LABs have been reported by Otvos et al.[14], Lesko et al.[15], Cavalli et al.[16]and Bravo and Vergara[17]. In 1973 Otvos et al.[14] tested the applicability of a simple GLC/MS system to obtain accurate data on the compositions of some commercial detergent alkylbenzenes, with a special emphasis on the major components. These authors identified all linear alkylbenzenes but for branched chain isomers, complete resolution of the individual components was unsuccessful. Alkyltetralins and alkylindanes were detected in each analyzed commercial LAB, but results were not reported.

Three years later, Lesko et al.[15] reported the analysis of commercial alkylbenzenes using GC, LC and GC/MS techniques. Although GC/MS analysis was carried out using a packed column that was incapable of separating all of the isomeric alkylbenzenes, the identification of these substances was successfully accomplished by taking the mass spectra of overlapping peaks. The quantitative analysis of alkylbenzenes was considerably influenced by dialkyltetralins and dialkylindanes present in the analyzed commercial products.

The same year, Cavalli et al.[16] investigated four commercial alkylbenzenes to obtain accurate and comparative data about the nature and concentration of minor components. A detailed analysis on laboratory synthesized model compounds and commercial linear alkylbenzenes, was carried out using both GC and GC/MS instruments. Besides the

identification of all the main peaks, which corresponded to the various phenyl isomers, several minor peaks were identified. Among these minor components, three different main types of compounds were recognized: branched alkylbenzenes, tetralins with linear side chains, and tetralins with branched side chains.

Bravo and Vergara[17] used both GC and GC/MS techniques to determine a detailed analytical composition of commercial linear alkylbenzenes derived from HF and $AlCl_3$ processes. They identified minor components as branched alkylbenzenes, dialkyltetralins, dialkylindanes and diphenylalkanes. These authors reported the same observations as Cavalli et al.[16], that minor components appearing in LAB derived from HF process were basically branched alkylbenzenes, while in the $AlCl_3$ process, dialkyltetralins constituted the most important impurities. In addition to identification of impurities, the authors reported the difference in homologues' distribution in commercial LAB comparing two analytical techniques, GC and GC/MS.

In 1988 Cavalli et al.[18] used high performance liquid chromatography, HPLC, in order to separate and concentrate impurities present as traces in industrially produced LABs. Apart from tetralins and branched alkylbenzenes, dinaphthenbenzenes, diphenylalkanes, and naphthalenes were identified and quantified as the "secondary components" using both GC and GC/MS techniques.

In 1982, Kuhne and Hesse[19] reviewed studies relating to the investigation of the reaction pathway in the radical cation of tetralin and related compounds. A special emphasis was placed on the occurrence of the formal retro-Diels-Alder reaction, a C_2H_4 loss. In the past, since the significance of the mass spectral retro-Diels-Alder fragmentation pattern was recognized, the "clean" RDA reaction of dialkyltetralins was accepted as being formally correct. Loudon et al.[20], Grutzmacher and Puschmann[21], Stolze and Budzikiewicz[22], and

Budzikiewicz et al.[23] observed that the RDA fragmentation pattern was not "clean" and that the other fragmentation pathways were possible.

Budzikiewicz et al.[23] in their study in 1965, under EI conditions, discussed the fragmentation reaction of organic molecules corresponding formally to the retro-Diels-Alder reaction. From thermodynamic data (the energy necessary for the decomposition), they showed that it was possible to predict whether an ionized *ene*- or *diene*-fragment would be formed preferentially. These predictions held true for complicated molecules such as dialkyltetralins.

More evidence with respect to RDA reaction emerged from the field ionization kinetic studies by Levsen et al.[24]. They investigated loss of C_2H_4 from the molecular ion of tetralin and revealed some hydrogen exchange prior to ethylene loss. They reported that loss of ethylene occurs via competing processes, not just via a single process, a "clean" RDA fragmentation pattern as had been suggested in the earlier studies.

Sindona et al.[25] used the field ionization kinetic (FIK) technique to reinvestigate the hydrogen exchange reactions in tetralin molecular ions prior to loss of ethylene. For their studies they used the suitable deuterium-labelled precursors.

Wojinski and Gross[26] reported that ionized 1- and 2-substituted phenyltetralins exhibit highly specific, 1,4 and 1,3 eliminations of small neutrals from position 1 and 4, and 2 and 4, respectively.

The cyclization of open-chain structures to cyclic isomers of tetralin or indane type was observed by Andrews et al.[27] as the overall trend and a preferred way of isomerization of these radical cations. Dass and Grass[28] also observed a pronounced trend to form cyclized isomers from open-chain, nonconjugated alkylbenzene ions.

10. *Scope of this study*

Though a number of analytical reports have been published from all over the world on production of LAB and LAS, to date there are only a handful of papers published in which the presence of minor impurities like *branched alkylbenzenes* and *dialkyltetralins* in commercially available LABs, is discussed. Most studies have focussed on the identification of impurities and have paid less or no attention to the quantitative aspects. Moreover, all of the qualitative studies that have been published, reported impurities as per cent (%) of the total weight of the analyzed LAB samples. No published study was carried out with *dialkyltetralins* (DAT) standard mix and with the internal standard technique using *cis/trans-1,4,6,7-tetramethyltetralin*.

The objective of the proposed study was to separate, identify and quantify major and minor components (1-10 %) in ten (10) commercial linear alkylbenzenes. The focus of this study was on the structure elucidation and determination of impurities levels in all analyzed linear alkylbenzenes samples, using both GC/MS and IS techniques.

The results of this study will provide firsthand information regarding the composition of all analyzed linear alkylbenzene samples including the identity and quantity of some impurities present in them. The qualitative results of impurities such as *dialkyltetralins* and *branched* alkylbenzenes will provide accurate calculation of the actual average molecular weights which are critical in the operation of the sulphonation plants in the production of very important surfactant, linear alkylbenzene sulphonate, LAS.

EXPERIMENTAL

I. Materials and Reagents

1. Types of analyzed linear alkylbenzenes, LAB

1) Initial study

For the initial part of this study, the following five (5) samples from Company #1 were analyzed:

Sample "A1" from January 31, 1991,

Sample "A2" from April 23, 1991,

Sample "A3" from April 13, 1992,

Sample "A4" from January 28, 1993,

Sample "A5" from April 15, 1993.

2) Main study

For the main part of this study, the following ten (10) samples of commercial linear alkylbenzenes from Company #1, #2, #3, and #4 were analyzed:

Company #1	Sample "A"
Company #1	Sample "B"
Company #2	Sample "C"
Company #2	Sample "D"
Company #2	Sample "E"
Company #3	Sample "F"
Company #3	Sample "G"
Company #4	Sample "H"
Company #4	Sample "I"

Company #4 Sample "J"

2. *Solvents*

The following solvents were used in this study:

Acetone, certified ACS grade, A18-4 from Fisher Scientific,

Dichloromethane, distilled in glass, 3601-2 from Caledon Laboratories,

Toluene, HPLC grade, certified ACS, A998-4 from Fisher Scientific,

Petroleum Ether, certified ACS, E139-4 from Fisher Scientific.

3. *Preparation of linear alkylbenzene samples*

1) Initial study

All analyzed samples of commercial LAB were provided by Company #1:

Sample "A1" - 0.0740 g in 5 ml of methylene chloride, a total of 14.8 ug/ul,

Sample "A2" - 0.0700 g was dissolved in 5 ml of methylene chloride, a total of 14.0 ug/ul,

Sample "A3" - 0.0680 g was dissolved in 5 ml of methylene chloride, a total of 13.6 ug/ul,

Sample "A4" - 0.0480 g was dissolved in 5 ml of methylene chloride, a total of 9.6 ug/ul,

Sample "A5" - 0.0670 g was dissolved in 5 ml of methylene chloride, a total of 13.4 ug/ul.

2) Main study

Company #1, Sample "A" from April 15/93, 0.043 g was dissolved in 5 ml of acetone, a total of 8.6 ug/ul,

Company #1, Sample "B", 0.0345 g was dissolved in 5 ml of acetone, a total of 6.9 ug/ul,

Company #2, Sample "C", 0.0280 g was dissolved in 5 ml of acetone, a total of 5.6 ug/ul,

Company #2, Sample "D", 0.0265 g was dissolved in 5 ml of acetone, a total of 5.3 ug/ul,

Company #2, Sample "E", 0.0325 g was dissolved in 5 ml of acetone, a total of 6.5 ug/ul , Company #3, Sample "F", 0.0310 g was dissolved in 5 ml of acetone, a total of 6.2 ug/ul, Company #3, Sample "G", 0.0305 g was dissolved in 5 ml of acetone, a total of 6.1 ug/ul, Company #3, Sample "H", 0.0335 g was dissolved in 5 ml of acetone, a total of 6.7 ug/ul, Company #4, Sample "I", 0.0285 g was dissolved in 5 ml of acetone, a total of 5.7 ug/ul, Company #4, Sample "J", 0.0405 g was dissolved in 5 ml of acetone, a total of 8.1 ug/ul.

4. Preparation of internal standard solutions

In the main part of this study, the following organic compounds were used as the internal standards:

- cis/trans-1,4,6,7-Tetramethyltetralin (cis/trans-1,4,6,7-Tetramethyl-1,2,3,4-tetrahydronaphthalene), 8673.00-1, from Wiley Organics, 1245 South Sixth St., Coshocton, Ohio 43812, USA,
- 1-phenyldecane, 98 %, 11,321-2 from Aldrich Chemical Company, P.O Box 355, Milw., WI 53201, USA,
- 1-Phenyldodecane, 97%, 11,-323-9 from Aldrich Chemical Company, P.O Box 355, Milw., WI 533201, USA.

i) Full Scan

a) Working solution

A working solution of 1-phenyldecane @ 50 ug/ul was prepared by dissolving 0.050 g in 1.0 ml of acetone. 1-phenyldodecane @ 50 ug/ul was also prepared in acetone by dissolving 0.050 g in 1.0 ml of solvent. All samples were prepared at final volume of 1.0 ml after spiking 10 ul of each internal standard solution. Final concentration of internal standards in

each sample was @ 500 ng/ul.

ii) Single Ion Monitoring

a) Working solution

A working solution of cis/trans-1,4,6,7-tetramethyltetralin @ 50 ug/ul was prepared by dissolving 0.050 g in 1.0 ml of acetone. All samples were at a final volume of 1.0 ml and were spiked with 10 ul of above internal standard solution. Final concentration of internal standard in each sample was @ 500 ng/ul.

5. Preparation of dialkyltetralins standard solutions

a) Stock solution

A stock solution @ 100 ug/ul was prepared by dissolving 0.037 g of dialkyltetralins mixture, DAT, in 0.37 ml of acetone.

b) Working solution

A working solution of dialkyltetralins @ 500 ng/ul was prepared by diluting a stock solution; 5.0 ul of the stock solution was measured accurately and added into 1.0 ml of acetone.

For both acquisition modes, the full scan and SIM, the same amount of internal standard, 10 ul was added to all samples which were at a final volume of 1.0 ml. Final concentration of internal standard in each sample was @ 500 ng/ul.

II. Gas Chromatography/Mass Spectrometry (GC/MS) as an analytical technique for identification and quantification of commercial linear alkylbenzene (LAB) isomers and impurities present in LABs.

1. Mass spectrometer tuning

Before any analytical data are acquired it is necessary that the mass spectrometer be tuned satisfactorily. Source pressure is a significant factor affecting tuning, and so it is desirable to tune the instrument under ~1.5 x 10^{-5} Torr. The purpose of tuning is to achieve the best mass spectrometer sensitivity across the selected mass range. Mass setting and measurement must be repeatable on a scan-to scan and run-to run basis.

Calibration gas, PFTBA, perfluorotributylamine was used to tune the GC/MS system. Since PFTBA was introduced via the gas chromatograph as a GC/MS sample, it was therefore indicating the overall system performance under routine operating conditions. The optimum peak shape, optimum peak intensity, optimum sensitivity throughout the mass range, optimum mass resolution, and the following abundances for selected PFTBA ions:

m/z 69	base peak
m/z 219	40-70 % of 69
m/z 502	2-5 % of 69

were required and determined during each GC/MS tuning. PFTBA resolution check was also performed, where m/z 502 and m/z 503 ions had to be fully resolved.

Mass resolution, R, is a measure of the GC/MS system, (mass analyzer's) ability to separate (resolve) masses that are close together:

$R = m / \Delta m$ where for example; m = m/z 502

Δm = m/z 503-502

Since the quadrupole recognizes only a full unit of mass difference, it has a unit mass resolution and therefore it is called a low resolution mass spectrometer.

2. *Quadrupole mass spectrometer and its scan characteristics*

The quadrupole consists of four cylindrical or hyperbolic rods set parallel to each other. The *rf* and *dc* voltages are applied to two pairs of rods to set up an electric field. Quadrupole operates with a fixed accelerating voltage. All ions oscillate in the electric field, but for a given fixed set of voltages, only one ion at a time reaches the detector.

Since quadrupole is essentially an electrostatic device, it has a very low inductance and a relatively low capacitance and can therefore be scanned at high rates. The amplitude, from minimum to maximum, of both *rf* and *dc* voltages can be changed extremely quickly, in a few milliseconds. Quadrupole is therefore suitable for both fast scanning work and selected ion monitoring.

In other words, the setting of a suitable mass spectrometer scan can be considered as the selection of two variables, mass and time. The mass/time function may be continuous or not, often called selected. A smooth transition from one mass to the next at a defined rate, called a full scan mode, gives an integrated signal indicative to the total amount of the analytes. This fast acquisition mode gives the full mass spectra across the defined mass range, usually between 45 to 500 amu.

Where the analytes in the sample are known and are at low levels, it is often preferable to monitor selected masses, unique to each analyte. In the latter mode the *rf* and *dc* voltages are rapidly switched among a number of values corresponding to the selected masses.

In the initial study, all data were acquired using only a full scan mode.

In the main part of this study all samples, from "A" to "J", were scanned using both acquisition modes. Linear and *branched* alkylbenzenes were analyzed and quantified using a full scan mode, whereas *dialkyltetralins* were analyzed and quantified using a selected ion monitoring acquisition mode.

3. Gas chromatograph injectors and capillary columns

The injector port of a gas chromatograph fulfils a number of purposes. The injector acts as a point of anchorage for the gas chromatography column and as the carrier gas connection to it. The injection assembly is usually contained in a heated block which serves to preheat the carrier gas as well as flash evaporating the injected sample.

The GC column is the heart of a GC/MS system. Without its separating power the mass spectral data would be impossible to interpret. Capillary column chromatographic resolution is very important. The degree of resolution required for adequate separation depends on the complexity of the sample being analyzed. Complex mixtures like linear alkylbenzenes or dialkyltetralins require the high resolution of capillary columns. Capillary columns have no packing material like the old type packed columns which were filled with fine particles of packing material coated with different kinds of liquid phases. The liquid phase in the capillary columns is bonded either directly to the column walls or to a support material coating the inner wall surface. To maintain the effective interaction between the liquid and gas phases, the internal diameters (ID) need to be small, typically 0.2 to 0.5 mm. Small internal diameters allow gas flow rates between 0.1 to 2 ml/min, which permits a direct connection to the mass spectrometer system via the GC/MS interface. Capillary columns usually range in length from 25 to 100 meters.

Unfortunately, capillary columns are limited in their sample- and solvent-carrying

capacity. It is often necessary to split the sample at the injector to prevent column damage by a relatively large injection of solvent. To overcome the problem of sample loss due to split injection, a number of splitless injectors and injection techniques have been developed[29]. A packed column injector was used for the first part of the initial study. For the rest of the initial part and for the main part of this study a splitless injector was used exclusively.

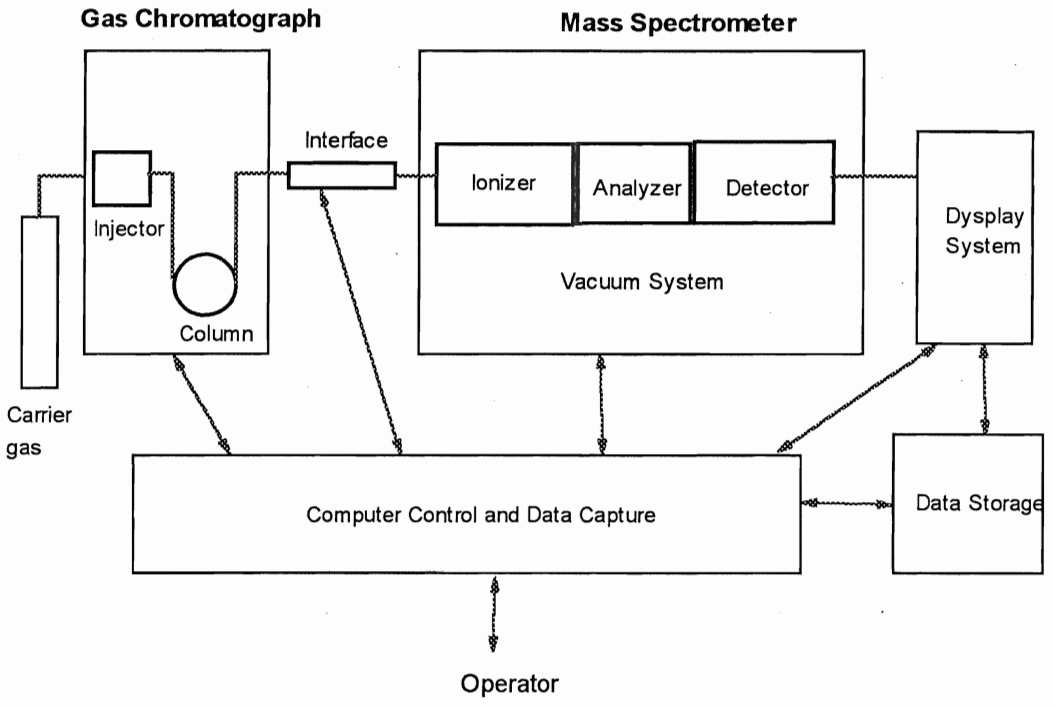
The following columns were used:

- J&W capillary column DB-5, 30 m, 0.25 mm I.D, 0.25 u film thickness,
- J&W capillary column SPB-20, 30 m, 0.25 mm I.D, 0.25 u film thickness,
- Restek's capillary column Rt_x-20, 60 m, 0.32 mm I.D, 1.0 u film thickness.

4. Gas chromatograph/mass spectrometer, GC/MS

GC/MS is an established technique for the analysis of complex matrices, holding a prime position in analytical chemistry because of its combination of sensitivity, wide range of applicability and versatility[30].

A gas chromatograph/mass spectrometer, GC/MS, comprises the gas chromatograph for admitting and separating components of analyzed mixtures, a mass spectrometer, for mass analysis of each component and an interface for transferring components between the two environments of gas chromatograph and mass spectrometer. A carrier gas, typically Helium, is passed through the system in order to achieve sample transfer and separation. A block diagram of a typical GC/MS system is shown below:



In general terms, the GC/MS has to perform one of two tasks: identification of unknown compounds or the detection of the known compounds.

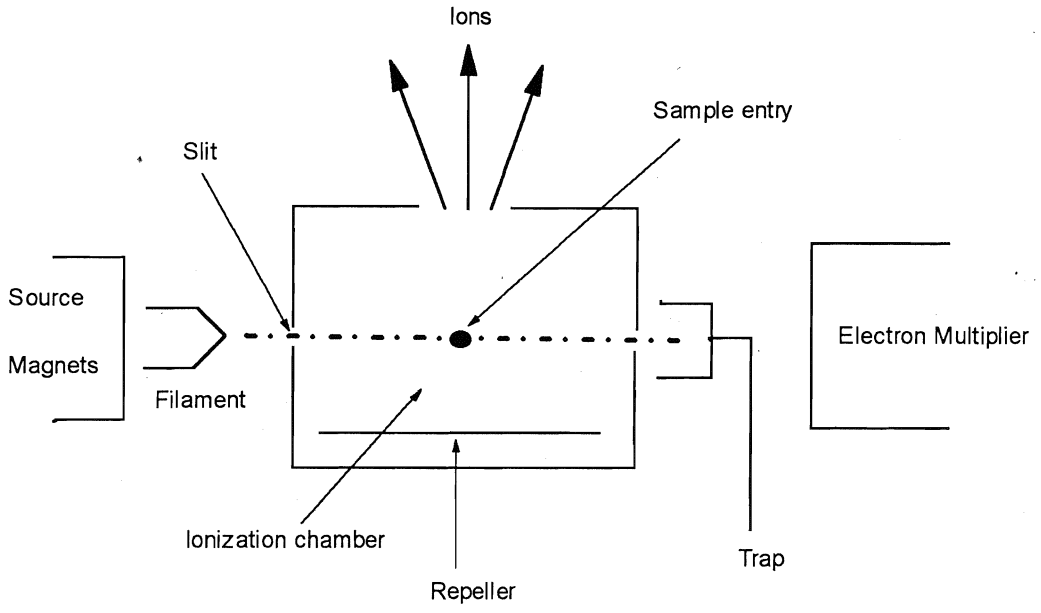
For this study a Hewlett-Packard gas chromatograph 5980 Series II was directly interfaced, via a direct GC/MS interface, to Hewlett-Packard mass spectrometer 5989A, called ENGINE. Both instruments were controlled via Hewlett-Packard MS ChemStation 59940A, UNIX series equipped with B.04.04 version of the software.

Before the mass spectrometer can analyze a sample it is necessary that the sample molecules be ionized. A number of techniques have been used to impart the charge on the molecules. The most common methods employed are *Electron Impact Ionization* and *Chemical Ionization*. Both ionization techniques were used in this study.

5. ***Methods of Ionization***

a) *Electron Impact (EI) Ionization*

In an *Electron Impact*, EI source,



electrons from a heated filament are accelerated across the ionization chamber. The effluent from the gas chromatograph also passes through the same chamber. The electrons interact with these gas molecules, transferring energy to them in the inelastic collisions that take place. If sufficient energy is transferred, the molecule of alkylbenzene or dialkyltetralin, R - H, will become significantly excited and may release an electron, giving rise to a molecular ion, $R - H^+$:

$$R - H + e^- \rightarrow R - H^{+\cdot} + 2\,e^- \quad (70\ eV)$$

Usually the energy given to the molecule is such that it enters a very excited state and breaks up into ions of lesser mass. The resulting fragments, electrically charged, are drawn by the electrical fields in the ion source into the mass analyzer section where they are separated according to their mass-to-charge ratios. Under the scan conditions the masses leaving the

mass analyzer are transmitted to the detector. Because the ions created in the ion source are being transmitted to the detector, the system must necessarily operate under a high vacuum, ~10^{-5} Torr, otherwise, the ions would collide with neutral molecules and be dissipated.

Each ion normally carries only one electrical charge. The movement of these charges is equivalent to a current flowing. The current levels are usually very small, typically 10^{-11} to 10^{-10} A. Some form of amplification is needed to detect these extremely low levels. This usually takes the form of an electron multiplier giving a typical gain of 10^6. The electron multiplier is followed by an electron amplifier that gives a current-to-voltage conversion of about 10^7 V/A. The output is then fed to a preamplifier, an amplifier, and finally is passed directly to a computer which evaluates the incoming data and prints out the required information[31].

In the *Electron Impact* ionization technique, in the unimolecular decompositions of alkylbenzenes and dialkyltetralins, represented as R - H;

$$R - H + e^- \rightarrow R - H^{+\cdot} + 2e^-$$

$$R - H^{+\cdot} \rightarrow R^+ + H\cdot$$

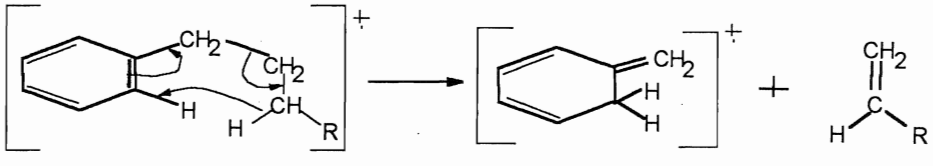
$$R - H^{+\cdot} \rightarrow R_1 - H^{+\cdot} + \text{neutral molecule}$$

the probability of cleavage of a particular bond is related to the bond strength, the possibility of low-energy transitions, and the stability of the fragments (charged and uncharged). There are some "General Rules" that apply to fragmentation patterns, some of which are applicable for the compounds under study, namely alkylbenzenes and *dialkyltetralins*:

- the relative height of the molecular ion is greatest for the straight chain compound and decreases as the degree of branching increases,
- the relative height of the molecular ion usually decreases with increasing molecular

weight (MW) in a homologous series, (C_{10} to C_{14}-alkylbenzenes),

- cleavage is favoured at branched carbon atoms (branched C_{10} to C_{14}-alkylbenzenes),
- the more branched, the more likely is the cleavage (branched C_{10} to C_{14}-alkylbenzenes and non-linear *dialkyltetralins*),
- generally, the largest substituent at a branch is eliminated, most readily as a radical,
- double bonds, cyclic structures and especially aromatic rings stabilize the molecular ions and increase the probability of its appearance (*dialkyltetralins*),
- in alkyl-substituted aromatic compounds, cleavage is very probable at the β-bond to the ring (C_{10} to $C_{1\,4}$-alkylbnzenes),
- cleavage is often associated with elimination of small stable neutral molecules,
- saturated rings tend to lose side chains at the α-bond and positive charge tends to stay with the ring fragment,
- in the McLafferty rearrangement, 6-membered ring transition is observed with the γ-H migration,



where for linear alkylbenzenes R is from C_7H_{15} to $C_{11}H_{23}$. The detailed fragmentation patterns of linear alkylbenzenes, *dialkyltetralins* and *branched* alkylbenzenes will be discussed further later.

b) *Chemical ionization* (CI)

Chemical Ionization is a "softer" technique than *Electron Impact Ionization.* There is less energy transferred to the sample molecule and consequently less fragmentation. In principal, the degree of fragmentation depends on the chemical nature of the sample, the reagent gas, and the source temperature. *Chemical Ionization* is used in two principal applications, the determination of molecular weight and the determination of chemical structure not normally available through *Electron Impact* ionization. Molecular weight information is an ideal complement to characteristic fragmentation patterns observed under *Electron Impact* conditions in the elucidation of the structure of unknown. Nowadays, many mass spectrometers are designed as combined EI/CI sources. With today's advanced computers, the combined source may be switched between EI and CI operation and vice versa in times of a very few seconds.

In a CI source, the collision of an ion and the reagent gas molecule leads to a reaction giving a new charged species. For effective ion/molecule reactions it is necessary to operate at source pressure of about 0.1 to 1.0 Torr, much greater than for EI source. The ion/molecule reaction between a methane ion and a methane molecule gives rise to the unusual but fairly stable CH_5^+ species in the following reactions:

$$CH_4 + e^- \rightarrow CH_4^{+\cdot} + 2\ e^-$$

$$CH_4^{+\cdot} \rightarrow CH_2^{+\cdot} + H_2$$

$$CH_4^{+\cdot} \rightarrow CH_3^+ + H\cdot$$

$$CH_4^{+\cdot} + CH_4 \rightarrow CH_5^+ + CH_3\cdot$$

The CH_3^+ ion can react with uncharged methane molecule to form $C_2H_5^+$:

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$$

Both ions, CH_5^+ and $C_2H_5^+$, along with $C_3H_5^+$ are the most prominent ions formed, accounting for approximately 95 % of the total ionization[29]. They are extremely reactive and attack molecules, passing charge to them. Furthermore, a proton or even the whole methane ion becomes attached to the sample molecule giving a pseudomolecular ion $(M+1)^+$, and two additional ions $(M+29)^+$ and $(M+41)^+$, where M is a molecular weight. The protonated and addition ions formed in the CI source, very often have greater stability than molecular ions formed in the EI source, so that positive identification of molecular weights can be confirmed with a great deal of confidence. The *Chemical Ionization* technique was used in the initial part of this study, using methane as a reagent gas. Another reagent gas, ammonia was also used in the initial part of this study but with much less success, mainly due to problems with the equipment.

6. Mass spectrum

In the quadrupole mass spectrometer, a mass spectrum is obtained by scanning the rod voltages from low mass to high mass. A compound's mass spectrum is a unique chemical fingerprint. It is possible to determine the compound's molecular weight from its mass spectrum. The cracking pattern resulting from collision-induced fragmentation in the ion source provides the analyst (operator) information about the compound's structure and enables the identity of an unknown compound to be determined. Once a mass spectrum is known, certain features of it can be recognized as being particulary representative of the compound, the mass spectrometer can then be operated so as to select these features, and if they are detected then the presence of the known compound can be confirmed. Furthermore, integration of the mass spectrum gives an output trace that is indicative of the amount of compound present. With suitable techniques like internal standard technique used in this

study, accurate quantitation of analyte even at very low levels is easily achieved.

7. *Internal standard technique, IS*

The Internal standard technique, IS, is a quantitative technique which requires the use of analyte's calibration standards and the addition of internal and/or surrogate standards. It offers the highest quantitative accuracy compared to other techniques, since it allows for minor variation in instrument response and injection size. It is commonly used for many environmental monitoring methods as well as forensic, clinical and industrial analyses. It is usually used when each analyte has a unique detector response, when the detector response varies slightly over time, when analyte retention times very slightly from run to run, and finally when injection size varies slightly over time.

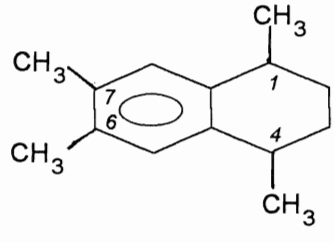
An internal standard is a substance that is added to the sample just prior to the instrumental analysis. Selection of the most appropriate internal standard is critical to obtaining accurate quantitative results. An internal standard must be completely resolved from all other peaks in the chromatogram, whilst at the same time being as similar as possible in terms of chemical and physical properties to the analyte being measured, consequently, the detector response is similar to the solute to be quantified. The internal standard should not be present or be a potential degradation product of the sample. It should be stable during the period of analysis and it should be available in reasonable high purity. Substances that are commonly used as internal standards include analogues, homologues, and isomers of the analyte. For the GC/MS analyses, internal standards are typically deuterium or ^{13}C labelled analogue of the analytes[32].

When analyzed compounds encompass a wide range of boiling points, molecular weight discrimination is observed. Therefore, it is advisable to select multiple internal

standards which encompass a wide boiling point range and elute from the chromatographic capillary column at various retention times (early, middle,late).

For this study, based on the general criteria in selecting internal standards and a wide range of boiling points of the analyzed compounds, three internal standards were selected. Both *1-phenyldecane* ($C_{16}H_{26}$) and *1-phenyldodecane* ($C_{18}H_{28}$) were used to calculate final concentration of linear and branched alkylbenzenes. Their structures are presented below:

A *cis/trans-1,4,6,7-tetramethyltetralin* was used to calculate final concentrations of dialkyltetralins and other impurities like branched dialkyltetralins and dialkylindanes:



To determine the linear responses for the analytes, the calibration standards which contained the analytes at various concentration levels and identical amount of internal standard, were injected into the instrument and the resultant retention times and peak areas were recorded for each analyte and the internal standard.

Relative response factors, RRF, were then calculated for each analyzed compound. Relative retention times, although more accurate, since they take into account slight shifts in

absolute retention time that occur from run-to-run, were not calculated due to an excellent repeatability of the manual injections.

$$RRT = \frac{\text{retention time (analyzed compound)}}{\text{retention time (Internal standard)}}$$

$$RRF = \frac{\text{area (analyzed compound) x concentration (IS)}}{\text{area (IS) x concentration (analyzed compound)}}$$

When analyzed compound exhibits a desired linear response over the concentration range, the relative response factors, RRFs, should have almost identical calculated values. In the final step, concentration of the analyzed compounds were calculated as shown below:

$$\text{Concentration} = \frac{\text{area (analyzed compound) x concentration (IS)}}{\text{area (IS) x RRF}}$$

III. GC/MS instrument operating parameters and conditions

1. Gas Chromatograph, GC

1) Initial study - analysis of samples "A1", "A2", "A3", "A4", and "A5"

In the initial study two capillary columns were used:

- J&W capillary column DB-5, 30 m, 0.25 mm I.D, 0.25 u film thickness,
- J&W capillary column SPB-20, 30 m, 0.25 mm I.D, 0.25 u film thickness.

Two injectors were used for this part of the study. Shortly after the experimental part was started, the packed column injector was upgraded to split/splitless to allow better peak separation and specificity.

For this part of the study, both injector port and GC/MS direct transfer line

temperatures were kept constant at 260 °C. The initial temperature for GC oven was set separately for each solvent in which sample "A5" was dissolved. Each oven temperature was set at the boiling point temperature plus approximately 20 °C as follows:

dichloromethane	60 °C	(b.p 39.4 °C)
toluene	130 °C	(b.p 111 C)
acetone	80 °C	(b.p 56.5 °C)

Different GC temperature programs were tested to determine the optimum peak resolution for sample "A5", as well as, to determine the overall analysis time. For the sample "A5" dissolved in dichloro methane, two temperature programs were tested.

Program I

Initial temperature: 60 °C

Initial time: 2 min

	Rate (°C/min)	Final temperature (°C)	Final time (min)
Level 1	15.0	100	0
Level 2	3.0	260	10

Program II

Initial temperature: 60 °C

Initial time: 2 min

	Rate (°C/min)	Final temperature (°C)	Final time (min)
Level 1	10.0	120	0
Level 2	1.0	260	10.0

The splitless injector's purge valve off time was tested for the optimum sample transfer

time. For the J&W SPB-20, 30 m, 0.25 mm I.D, 0.25 u film thickness capillary column, and for injection of 1 ul of a solvent and 1 ul of a sample, the purge valve was turned on at 1.0 minute. Column head pressure was set at 7 psi and remained constant throughout this part of the study.

2) Main study - analysis of "A" to "J" samples

Restek Rt_x-20 capillary column, 60 m, 0.32 mm I.D, 1.0 u film thickness was used exclusively for this part of the study. All the analyzed linear alkylbenzenes, were dissolved in acetone.

Both injector and GC/MS direct transfer line were set at 250 °C. The GC temperature program for the capillary column, was set as follows:

Initial temperature: 80 °C

Initial time: 2 min

	Rate (°C/min)	Final temperature (°C)	Final time (min)
Level 1	20.0	130	0
Level 2	1.0	230	0
Level 3	10.0	280	10.0

Total run time: 119 min

For 60 m Restek Rt_x-20 capillary column and for injection of 1 ul of a solvent and 1 ul of each sample, the purge valve was turned on at 1.5 minute. Column head pressure was set at 20 psi and remained constant throughout this part of the study.

2. ***Mass spectrometer in EI mode***

1) Initial study

i) Full Scan mode, FS

The ion source temperature, quadrupoles temperature, and electron energy were kept constant throughout the study, and were set as follows:.

Ion source:	200 °C
Quadrupoles temperature:	100 °C
Electron energy:	70 eV

The electron multiplier was kept at the autotune value plus 250 V, resulting in a total of ~ 2600 V to 2800 V. The instrument was scanned from 45 amu to 500 amu at the scan rate of 1.16 scans/second, and the acquisition threshold @ 35. The filament was turned on at 20 min (solvent delay).

2) Main study

i) Full Scan mode

ii) Single Ion Monitoring mode

Temperature and ion source parameters were kept the same as for a full scan acquisition mode, except for the scan range. Five groups of ions and the time descriptors were selected as follows:

Group #	Start time(min)	# ions	Dwell time(usec)	Cycles /sec	Ions (m/z)
1	20.0	20	50	0.8	117,131,145,159,173,187 216,230,146,188,160,168

					167,165,210,185,214, 218,232,246
2	68.0	19	50	0.8	117, 131, 145, 159, 173 187,201,215,168,167,165 210,216,230,214,185,244 246,260
3	78.0	13	80	0.8	117,131,145,159,173 187,201,215,244,260 274,229,230
4	88.0	13	80	0.8	117,131,145,159,173 187,201,215,229,258 274,243,244
5	98.0	13	80	0.8	117,131,145,159,173 187,201,215,229,243 272,257,260

The filament was also turned on at 20 min (solvent delay).

3. Mass spectrometer in CI mode

1) Initial study

i) Full scan, FS

A J&W capillary column SPB-20, was used for this part of the study. GC/MS transfer line and quadropule temperatures were kept constant throughout the initial study and were set as follows:

Quadrupoles temperature:	100 °C
Interface:	260 °C

The electron multiplier was kept at the autotune value plus 600 V, resulting in a total of ~ 2600 V. The instrument was scan from 45 amu to 500 amu at the scan rate of 1.16 scans/second, and the acquisition threshold was set at 10. The filament was turned on at 6.5 min (solvent delay).

Both methane and ammonia were used as reagent gases. Ion energy, ion source temperature and reagent gas pressure were optimized and set at:

Ion energy:	100 eV
Ion source temperature:	250 °C
Reagent gas pressure:	0.8 Torr

RESULTS AND DISCUSSION

I. Investigation of commercial linear alkylbenzenes, GC vs GC/MS techniques

The investigation of alkylbenzenes has been a central focus of mass spectrometry since its application to the analysis of petroleum and gasoline in the mid-twentieth century, and has provided much insight into the stability and reactivity of organic ions. Besides, and in connection with, for example, the $C_7H_7^+/C_7H_8^{+\cdot}$ ion problem and the McLafferty rearrangement, new information has emerged during the last few decades of investigating the mass spectrometry of alkylbenzenes.

Mass spectrometry of alkylbenzenes was reviewed for the first time in 1963 by Grubb et al[34]. Within ten years after the first review, the literature was deluged with reports on intermolecular rearrangements in gaseous organic ions. In 1973 Bursay et al.[35] collected and published this phenomena in a comprehensive review. The latest review was done by Kuck[36] and published in 1990.

The quantitative analysis of commercial linear alkylbenzenes, LAB, is carried out using gas chromatography, GC. Suppliers of the raw material use this analytical technique to provide customers with the Certificate of Analysis (C.O.A.) which guarantees its laboratory results within predefined specifications and limits. Generally, the GC technique provides enough information on the different homologues of alkylbenzenes, but it is deficient in identification of impurities present in commercially available linear alkylbenzenes.

Gas chromatography/mass spectrometry, GC/MS, on the other hand gives more detailed information on the chemical composition of commercial linear alkylbenzenes.

It not only provides the qualitative information on linear alkylbenzene isomers but also allows identification of the undesired compounds like branched alkylbenzenes and dialkyltetralins. It is important to know the exact percentage of impurities, in order to evaluate their influence in the final molecular weight (M.W) calculation of linear alkylbenzenes. The use of an accurate molecular weight is critical in the operation of the sulphonation plant and therefore on the final yield of the linear alkylbenzene sulphonates.

The initial part of this study was to find out if the reported results from the raw material supplier for the average molecular weight (MW) and for the percent 2-phenyl isomer were correct in the sense that they could be repeated in our laboratory by analyzing the same samples. The most accurate way to determine their values was to develop a GC/MS analytical method as a part of this study to determine actual average molecular weight and actual percent of 2-phenyl isomer in the commercial LAB.

II. Investigation of linear alkylbenzenes (LAB) in company #1's sample "A5"

1. *Separation of linear alkylbenzenes, LAB, using packed column and splitless GC injection ports*

This study was performed on the Hewlett-Packard's ENGINE 5980 II/5989 A GC/MS system with the direct interface between gas chromatograph and mass spectrometer. The first goal was to obtain a good chromatographic separation of the major eluting peaks. At the start of the study the Gas Chromatograph was only equipped with a packed column injection port. This gave separation of the major components, linear alkylbenzenes isomers in sample "A5" except for 6- and 5-phenyl isomers of C_{10}-

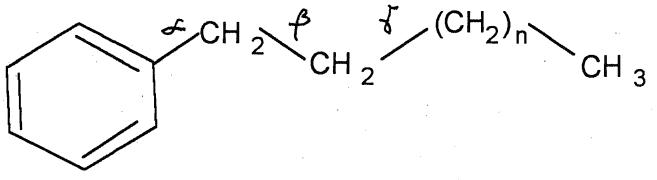
C_{13} alkylbenzenes. The arrows in the **Figure 2** point to the unresolved peaks.

As soon as the packed column injector port was replaced with the split/splitless injection port, the baseline separation of the major peaks improved dramatically (**Figure 3**).

2. ***Identification of linear alkylbenzene isomers using mass spectral interpretation of fragmentation patterns obtained via electron impact ionization mode.***

The molecular weights of alkylbenzenes fall into the series; $C_6H_5(CH_2)_nCH_3$, $C_6H_5(CH_2)_{n+1}CH_3$, $C_6H_5(CH_2)_{n+2}CH_3$, and etc., differing by 14 or CH_2. The parent ion, of mass equal to the molecular weight, is the heaviest ion produced in the mass spectrometer except for those containing heavy isotopes. Peaks at $(MW + 1)^+$ and at $(MW +2)^+$ result from parent ion that contains one or two heavy isotopes of ^{13}C. The heights of these peaks relative to that of the parent peak can be calculated from the known natural abundance of ^{13}C and ^{2}H.

Among the dissociation products of alkylbenzenes, the most abundant ions derive from the cleavage of bonds β to the benzene ring:



The number and lengths of the substituents on the α-carbon atom largely determine the

Figure 2

TIC Chromatogram of sample "A5" using packed column injection port and SPB-20 capillary column

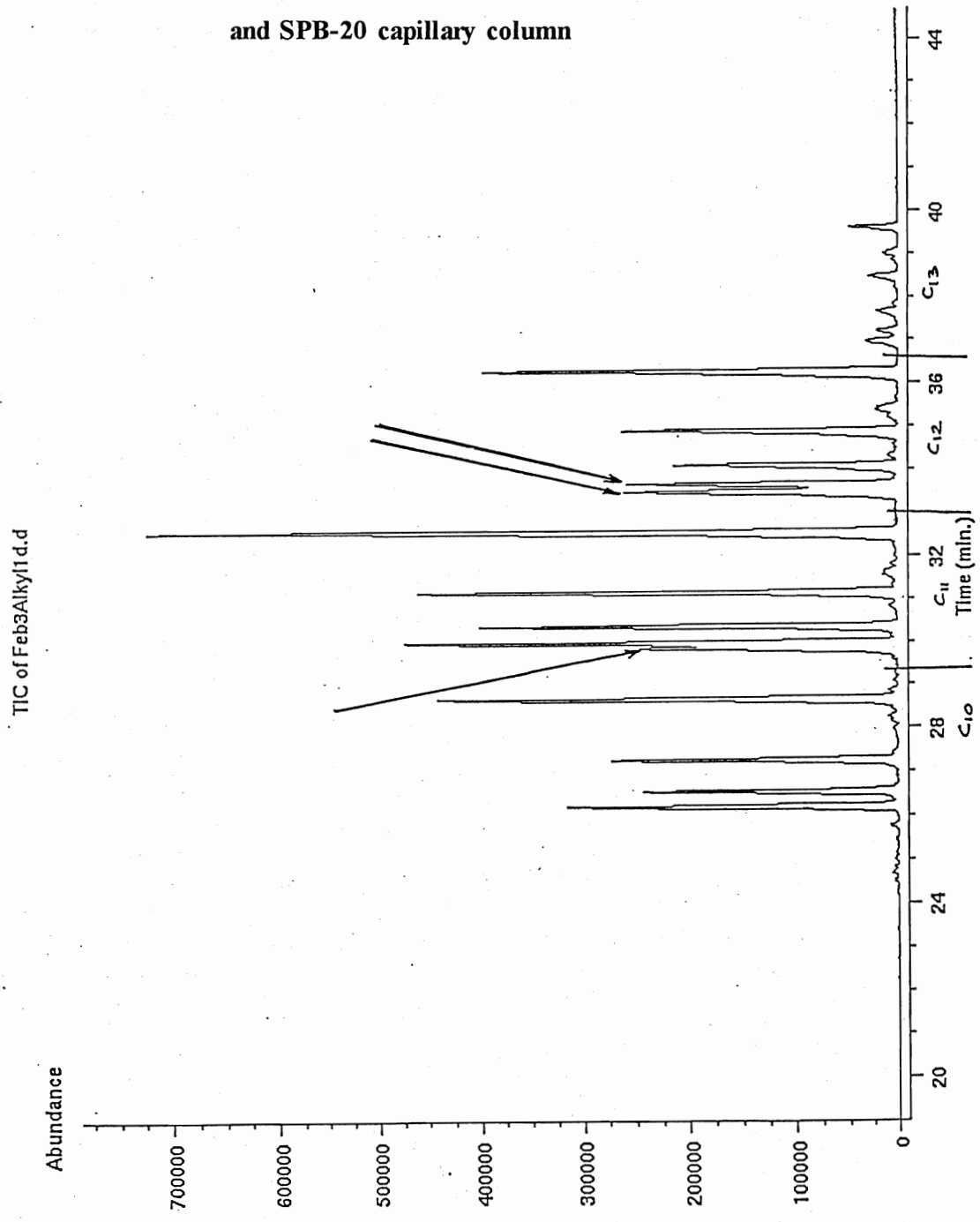
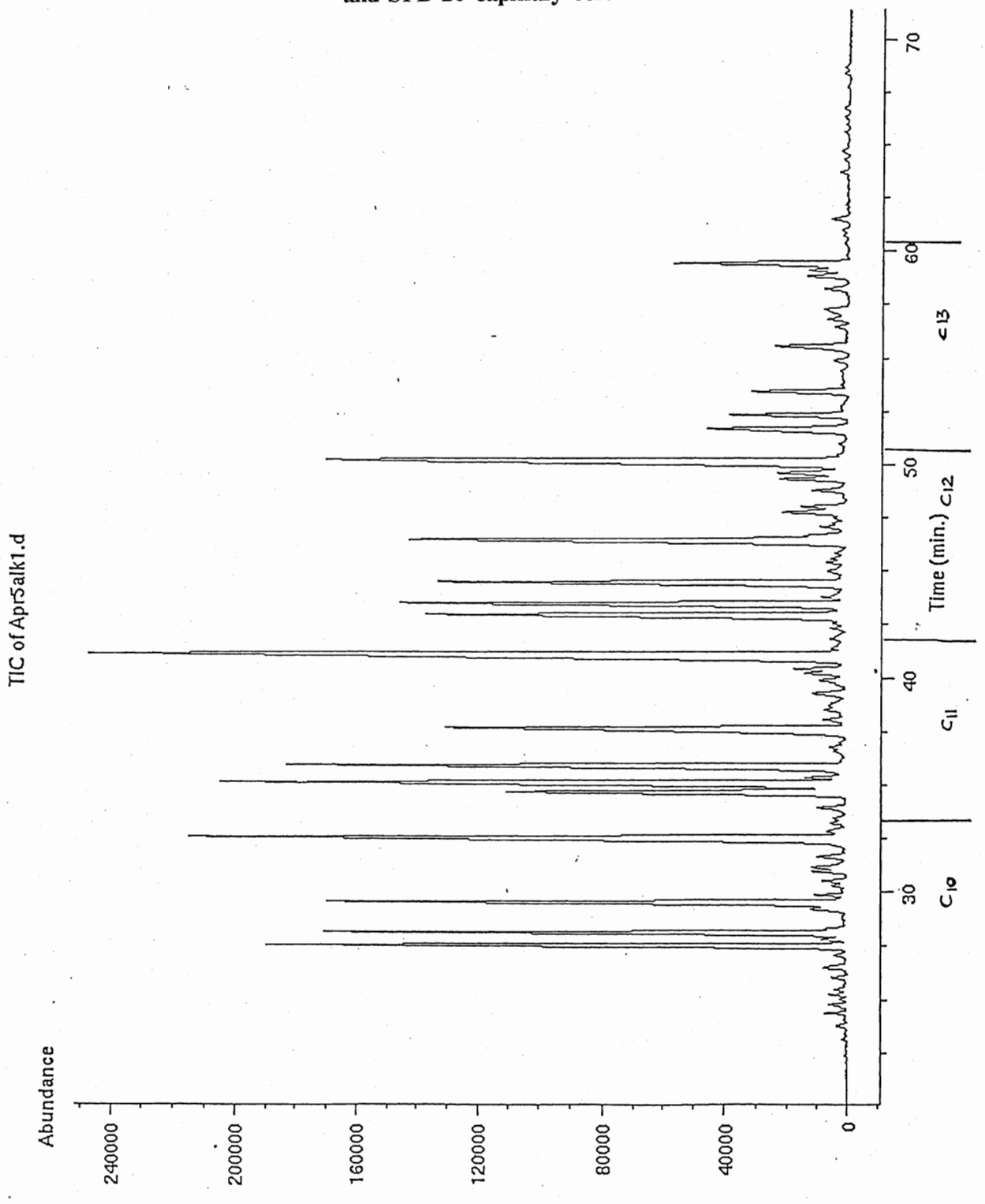
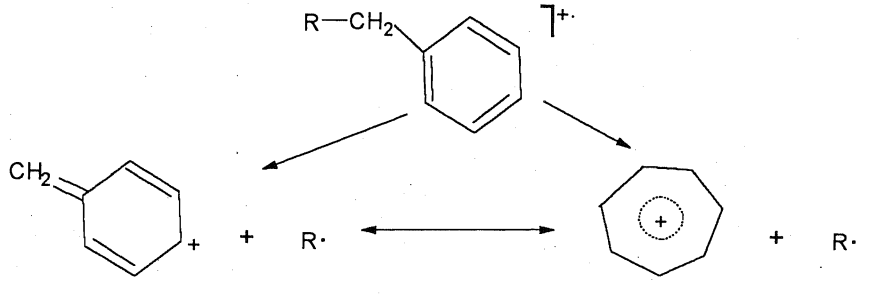


Figure 3

TIC Chromatogram of sample "A5" using splitless injection port and SPB-20 capillary column



product distribution. Increase in length of these groups promotes decomposition of the parent ion, the breaking of carbon-carbon bonds in competition with carbon-hydrogen bonds, and the breaking of β-bonds in competition with α-bonds. In any homologous series, as the side-chain length increases, the peaks at the parent mass $MW^{+\cdot}$, at $(MW + 1)^{+}$, and at the m/z 77/78/79 region decrease. The β-bond breakage alone produces the m/z 91 peak. The stability of the m/z 91 ion, benzyl ion (**a**), the product of cleavage of $C_7H_8^{+\cdot}$ and homologous ionized alkylbenzenes, has been shown to be less than that of the isomeric tropylium ion (**b**). According to the thermochemistry studies[37,38,39] the tropylium ion represents the thermodynamically controlled product of fragmentation of the unsubstituted alkylbenzenes.

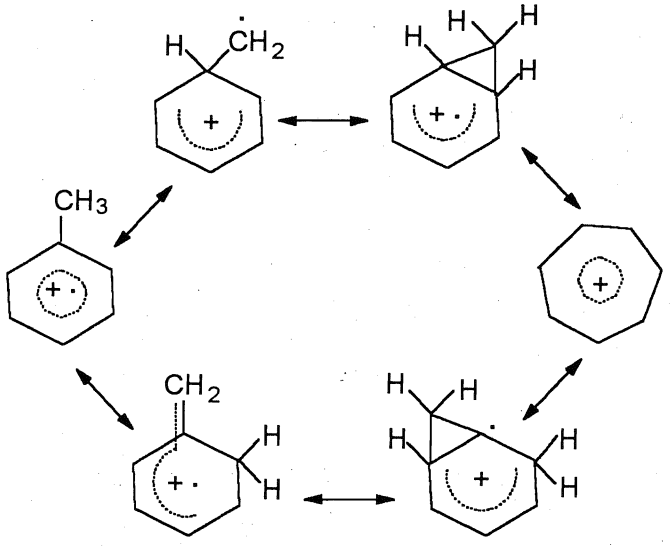


a **b**

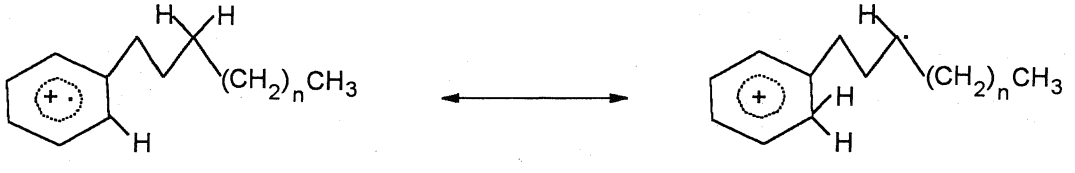
In 1990 Kuck[36] reviewed a number of studies related to the presence and stability of the m/z 91 ion. In his view, for most interpretive mechanisms it is not important to make a distinction between the resonance-stabilized benzyl ion and similarly stabilized tropylium ion.

From the semiempirical calculations and reliable models the following

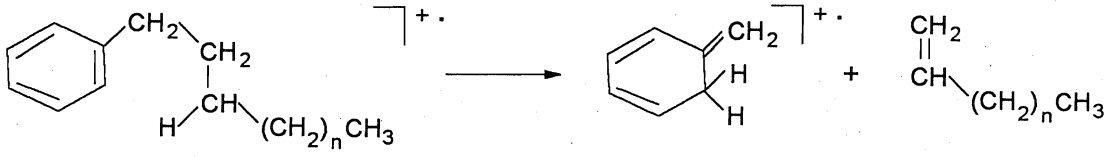
rearrangements for the m/z 92 ion were suggested by Pujado et al.[33]:



When the β-bond breakage is accompanied by hydrogen migration, it produces the m/z 92 peak. This reaction was uncovered in the early days of organic mass spectrometry but proposed much later[34] to proceed via a six-member transition state, hence representing a variant of the McLafferty rearrangement via formation of distonic ion (**c**) as a crucial intermediate:



c



In 1988 Kingston et al.[40] reported conditions when the rearrangement is not favourable because either the γ- or the ortho-position are completely substituted or virtually suppressed if there is also a para-substituent in the molecule.

A year later, Kuck[41] published a letter to stress the role of the distonic ion isomers and to corroborate Kingston's[40] observations. He demonstrated that, under favourable conditions the McLafferty rearrangement may even generate the base peak in the 70 eV mass spectrum on the "ortho-blocked' alkylbenzene. He observed a "paradox", a para-methyl group suppresses the McLafferty rearrangement whereas two ortho-methyl groups do not.

Evidence in support of the McLafferty rearrangement comes also from the isotopic labelling which showed that 5- 6- and 7-membered-ring transition states could be involved[36], as well as, from observations of structure-specific ion-molecule reactions in an ion-cyclotron resonance spectrometer[42].

Based on the above, on the "General Rules" mentioned in the experimental paragraph and on electron impact mass spectra, the identification of the different homologues of alkylbenzenes in sample "A5" became possible. Each linear isomer

showed characteristic homologous series corresponding to m/z 77, 91, 105, 119, etc., as well as, quite high parent ions, $MW^{+\cdot}$ ions. Molecular weight ions were identified as m/z 218, 232, 246, and 260, corresponding to C_{10}, C_{11}, C_{12}, and C_{13} homologous series, respectively. In each mass spectrum, peaks at $(MW + 1)^+$ were identified as m/z 219, 233, 247 and 261. The 77/78 region was analyzed but not in great detail.

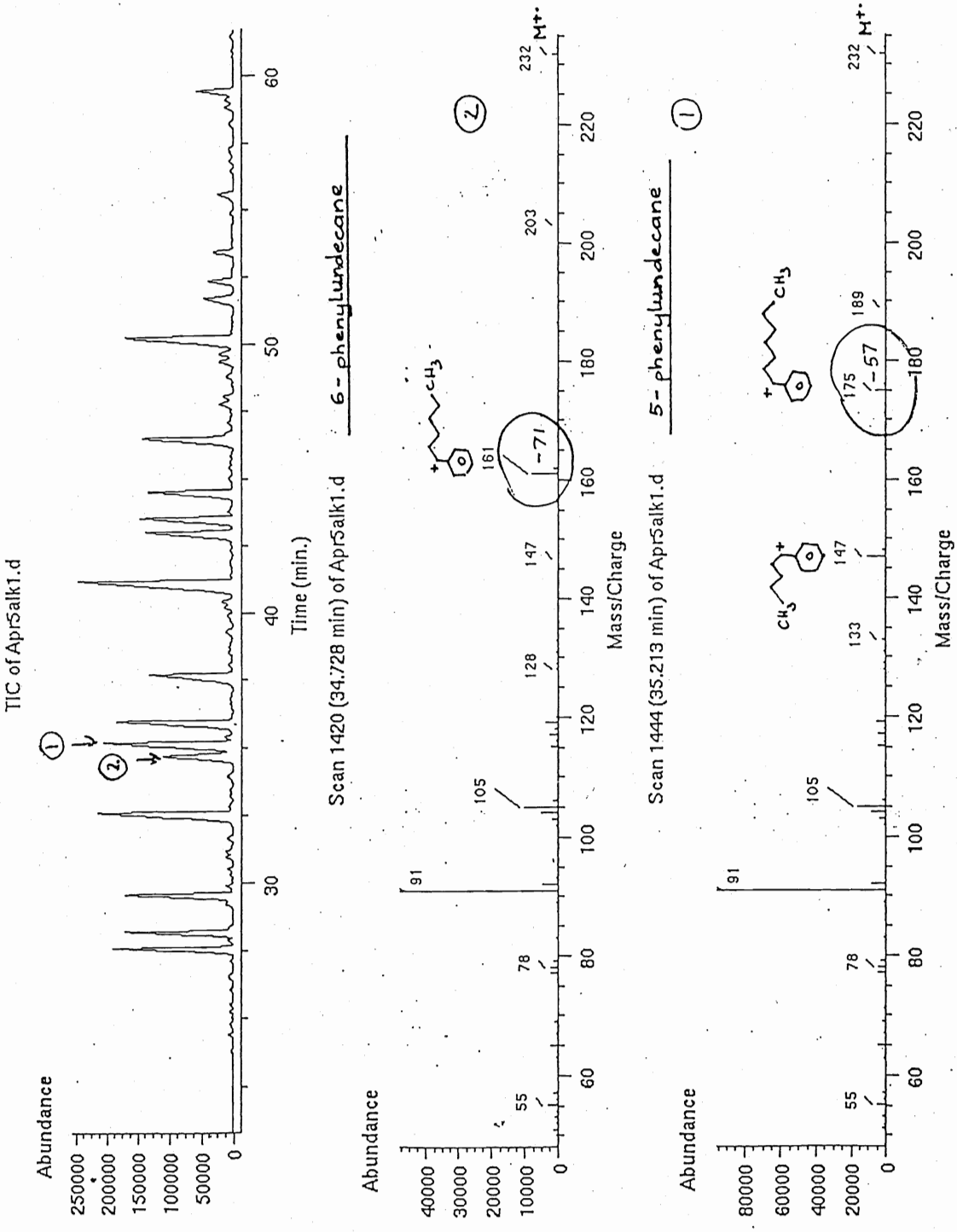
The base peak at m/z 91 which is $C_7H_7^+$ was found to be common to all isomers except one, the 2-phenyl which has a base peak at m/z 105 (**Figure 4**). The position of the benzene ring in the linear isomers was assigned by examining β-bond cleavage and the formation of the characteristic ions via favourable radical loses. In all 6-phenyl isomers for C_{11} - C_{13} alkylbenzenes, $(MW-71)^+$ ion, representing a C_5H_{11} radical loss was observed. The same β-bond cleavage was observed in all 5-phenyl isomers for C_{10} - C_{13} alkylbenzenes with the formation of $(MW-57)^+$ ion, representing C_4H_9 radical loss (**Figure 5**). The remaining 4- and 3-phenyl isomers for C_{10} - C_{13} alkylbenzenes showed $(MW-43)^+$ and $(MW-29)^+$ ions, representing C_3H_7 and C_2H_5 radical losses (**Figure 6**). The same fragmentation pattern for 2-phenyl isomer was also observed for all C_{10} - C_{13} alkylbenzenes with an exception for a much lower abundance of $(MW-15)^+$ ion or rather a lack of it (**Figure 4**). The summarized β-bond cleavage for C_{10} - C_{13} linear alkylbenzenes isomers is presented below:

Sample "A5"

Homolog	C_{10}	C_{11}	C_{12}	C_{13}
Molecular weight (amu)	218	232	246	260

Figure 4

EI mass spectra of 6-phenylundecane and 5-phenylundecane



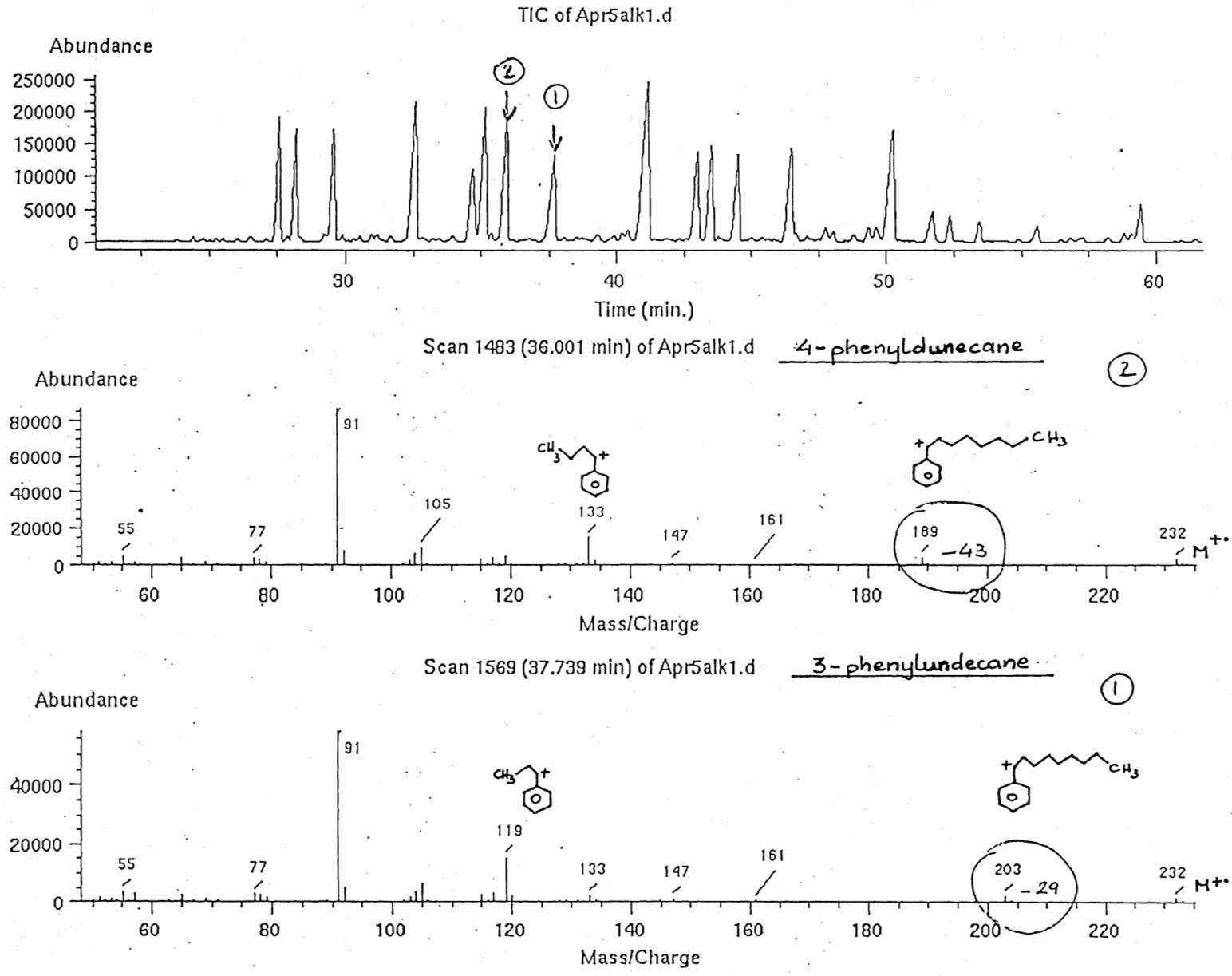
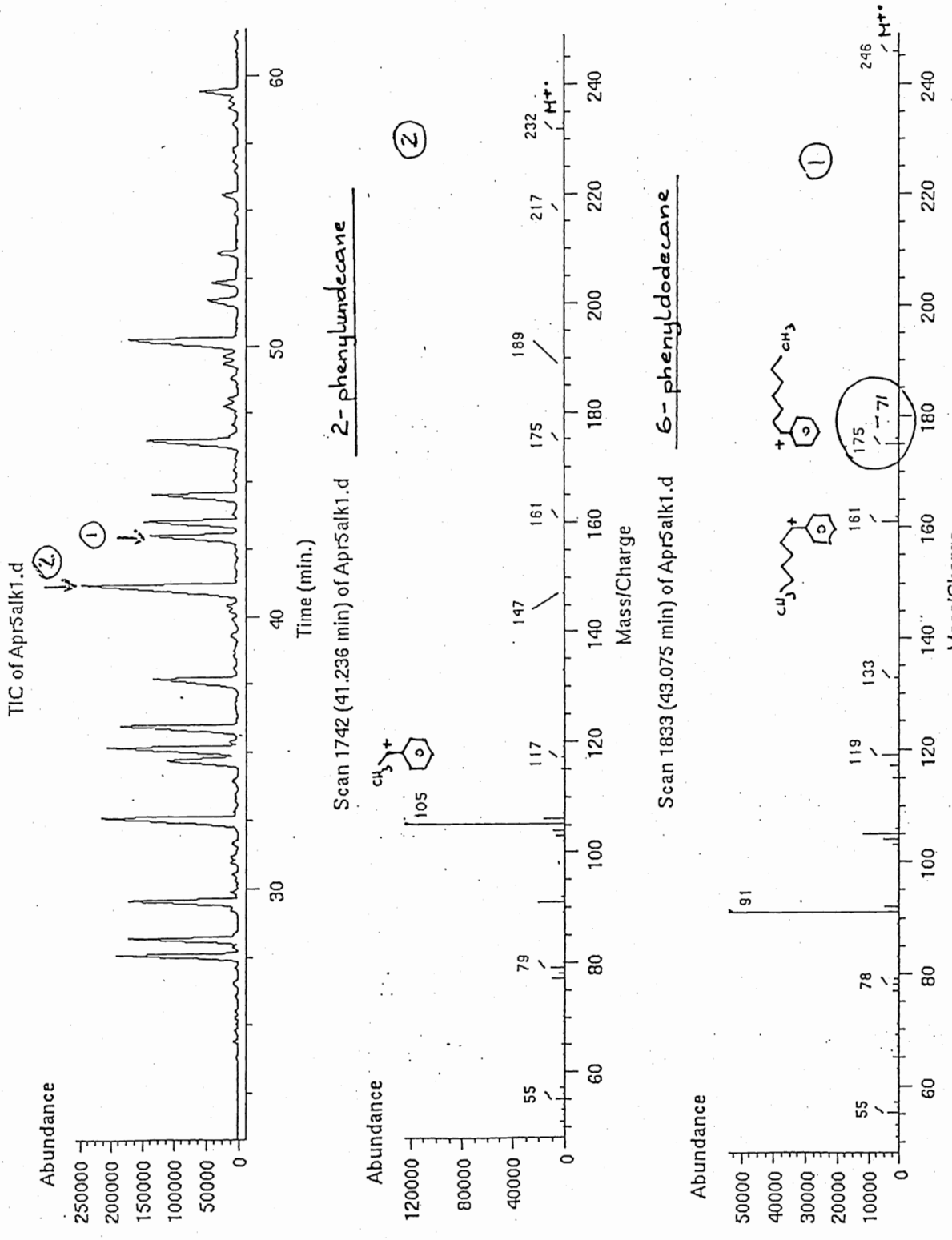


Figure 5

EI mass spectra of 4-phenylundecane and 3-phenylundecane

Figure 6
EI mass spectra of 2-phenylundecane and 6-phenyldodecane



Ion (m/z)				
6-phenyl $(MW-71)^+$	---	161	175	189
5-phenyl $(MW-57)^+$	161	175	189	203
4-phenyl $(MW-43)^+$	175	189	203	217
3-phenyl $(MW-29)^+$	189	203	217	231
2-phenyl $(MW-15)^+$	203	217	231	245

A 6-membered-ring transition state rearrangement, with the γ-H migration and formation of the m/z 92 ion was also observed in mass spectra of all linear alkylbenzenes in the analyzed sample "A5".

The retention times, RT for linear alkylbenzene isomers using a small bore capillary column, are represented in the tabulated form below:

Retention Times (min) for Sample "A5"

Alkyl group	C_{10}	C_{11}	C_{12}	C_{13}
6/7-phenyl	-----	-----	-----	51.40
6-phenyl	-----	34.42	42.78	-----
5-phenyl	27.32	34.97	43.37	52.04
4-phenyl	27.94	35.77	44.31	53.12
3-phenyl	29.37	37.51	46.28	55.26
2-phenyl	32.36	41.02	50.05	59.12

Some degree of separation for the other peaks, representing impurities had also

become possible with the upgraded injector port and the right choice of the capillary column, namely SPB-20 (**Figure 7** and **Figure 8**).

Leško et al.[15] in their published study followed the same general rules and reported mass spectral fragmentation assignments for 4-phenyldecane, 3-phenyldecane and 2-phenyldecane. Bravo and Vergara[17] in their study published a GC/MS chromatogram of the commercially available LAB with assigned chromatographic peaks but without mass spectral interpretation.

3. Identification of branched alkylbenzenes using electron impact mass spectral interpretation patterns

The same capillary column, J & W SPB-20 and GC/MS system allowed for the identification of some impurities present in the sample "A5" as branched alkylbenzenes and dialkyltetralins.

Although the mass spectrum of a branched alkylbenzene is definitely more complex than that of a linear isomer, it can be easily differentiated from the corresponding linear alkylbenzene. As stated earlier, the mass spectrum reflects the influence of each group present in the analyzed organic molecule. Thus a spectrum of a branched alkylbenzene exhibits many similarities to a linear alkylbenzene but also exhibits many anomalies which are caused by the highly branched side chains. Branching on the α-carbon promotes the cleavage of the α-bond in competition with β-bonds and formation of a m/z 119 ion:

Figure 7

TIC Chromatogram of sample "A5" - linear alkylbenzene isomers

elution order

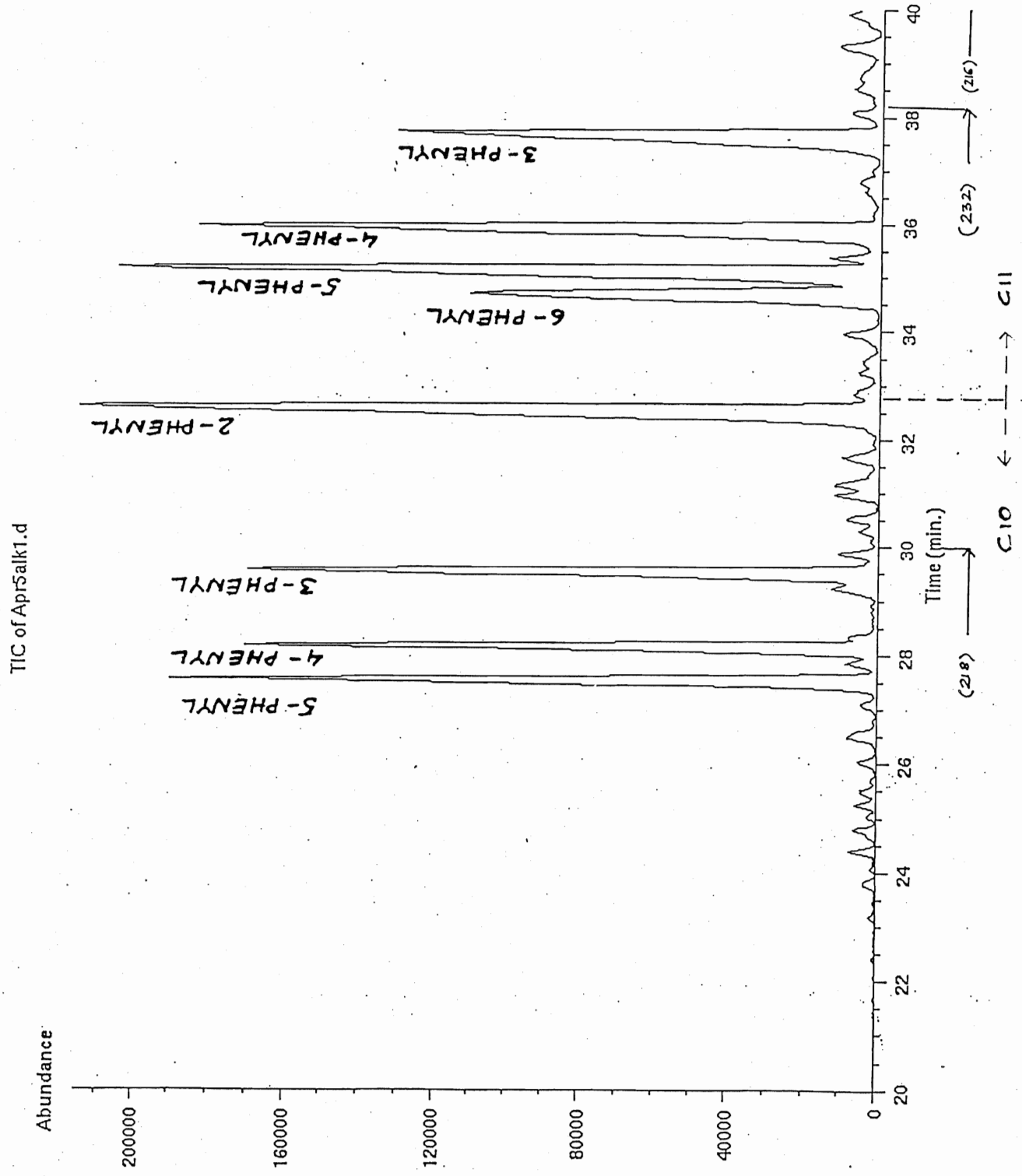
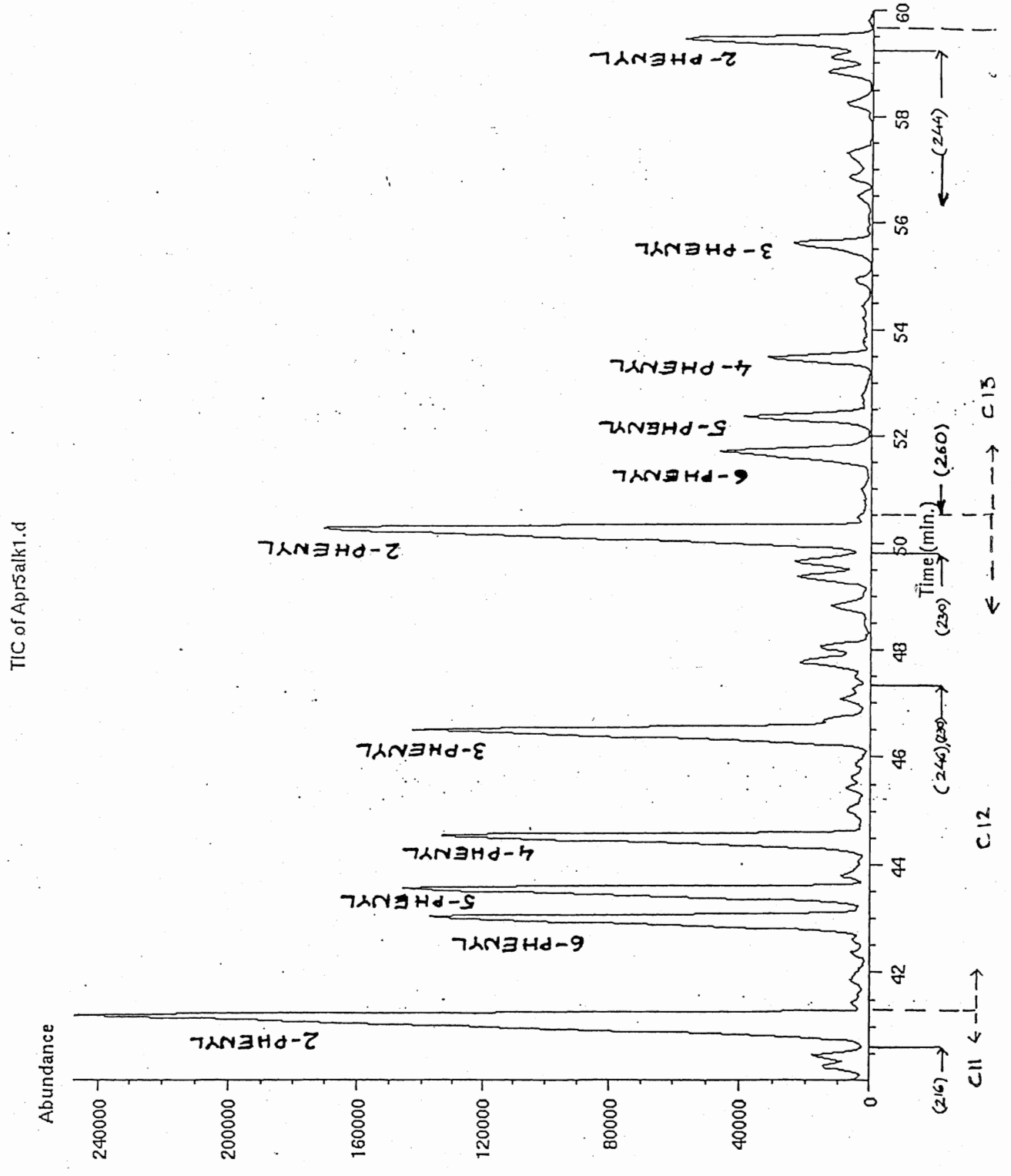
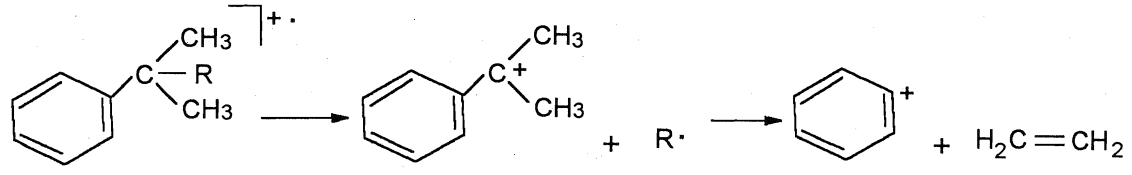


Figure 8

TIC Chromatogram of sample "A5" - linear alkylbenzene isomers

elution order - continued





Combinations of α-bond and β-bond breakage in different side chains result in profiles at m/z 91/92 and m/z 105/106, similar to that of m/z 77/78. Parent peaks, as well as, $(M + 1)^+$ are evident but are much smaller than for the linear alkylbenzenes. Ion series at m/z 77, 91, 105, 119, 133, etc., is a clear demonstration that the compound is an alkylbenzene. Other peaks, however, are present with unpredictable intensity. Consequently, it is difficult on the basis of the mass spectrum alone to state the exact structure of a branched alkylbenzene, only the total carbon number of the alkyl group can be given, for example C_{11}.

Again, based on the above, on the "General Rules" mentioned in the experimental paragraph and on the electron impact mass spectra, the identification of some branched alkylbenzenes as a total carbon number of the C_{10} to C_{13} alkyl groups in sample "A5" became possible. Parent peaks at m/z 218, 232, 246, and 260, as well as, $(M + 1)^+$ ions were evident. Ion series at m/z 77, 91, 105, 119, 133, etc., were observed. Similarly to the linear isomers, all branched alkylbenzenes with benzene in 6 to 3 positions, showed m/z 91 ion as a base peak (**Figure 9**), whereas for benzene in 2 position an ion m/z 105 was observed as a base peak (**Figure 10**).

Figure 9

EI mass spectra of two C_{10}-branched alkylbanzenes (MW = 218)

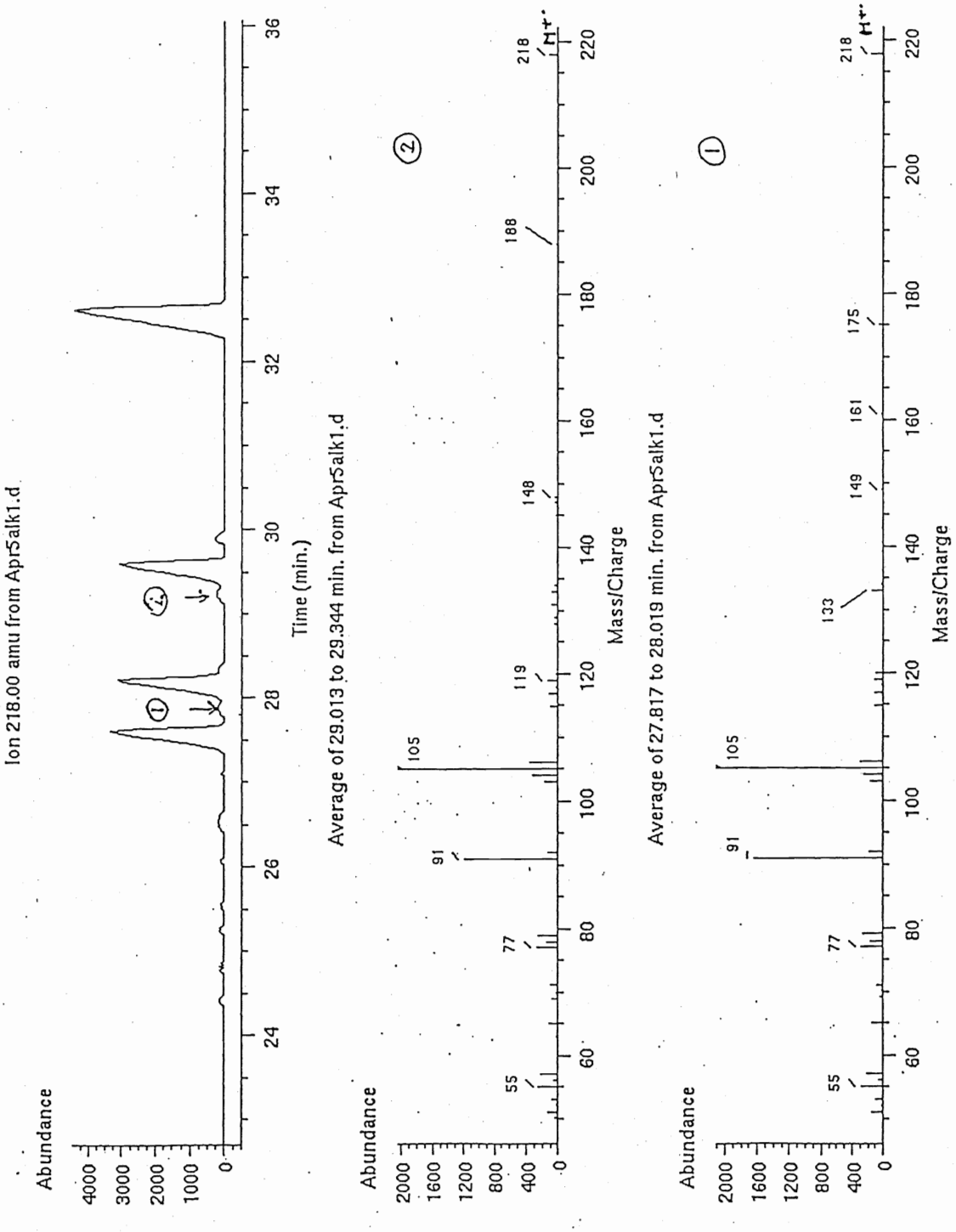
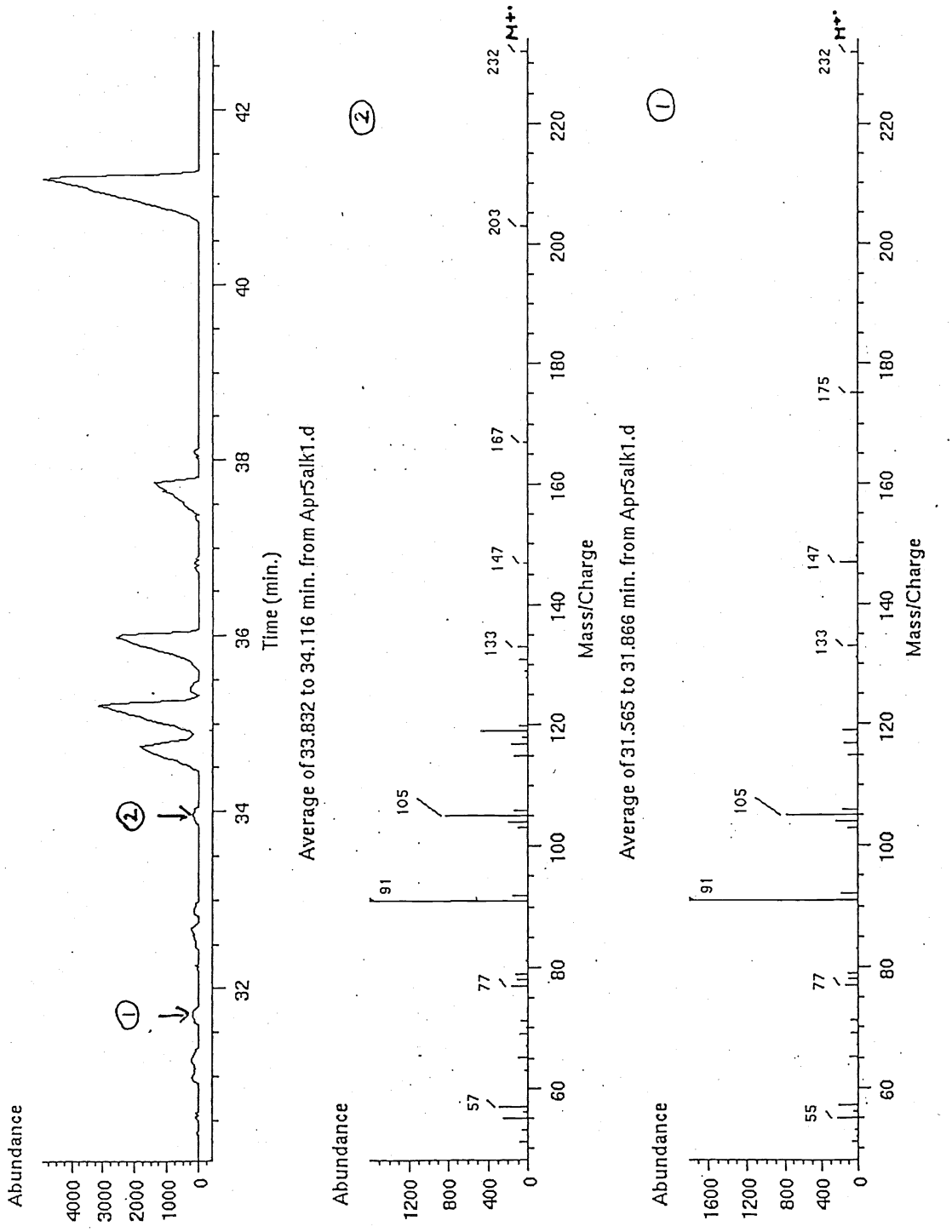


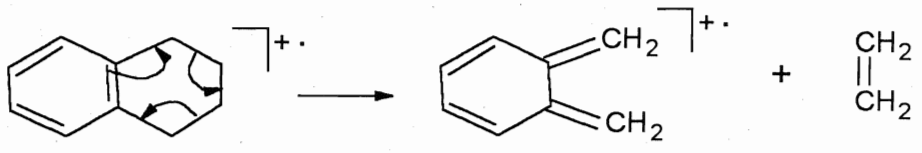
Figure 10

EI mass spectra of two C_{11}-branched alkylbenzenes (MW = 232)

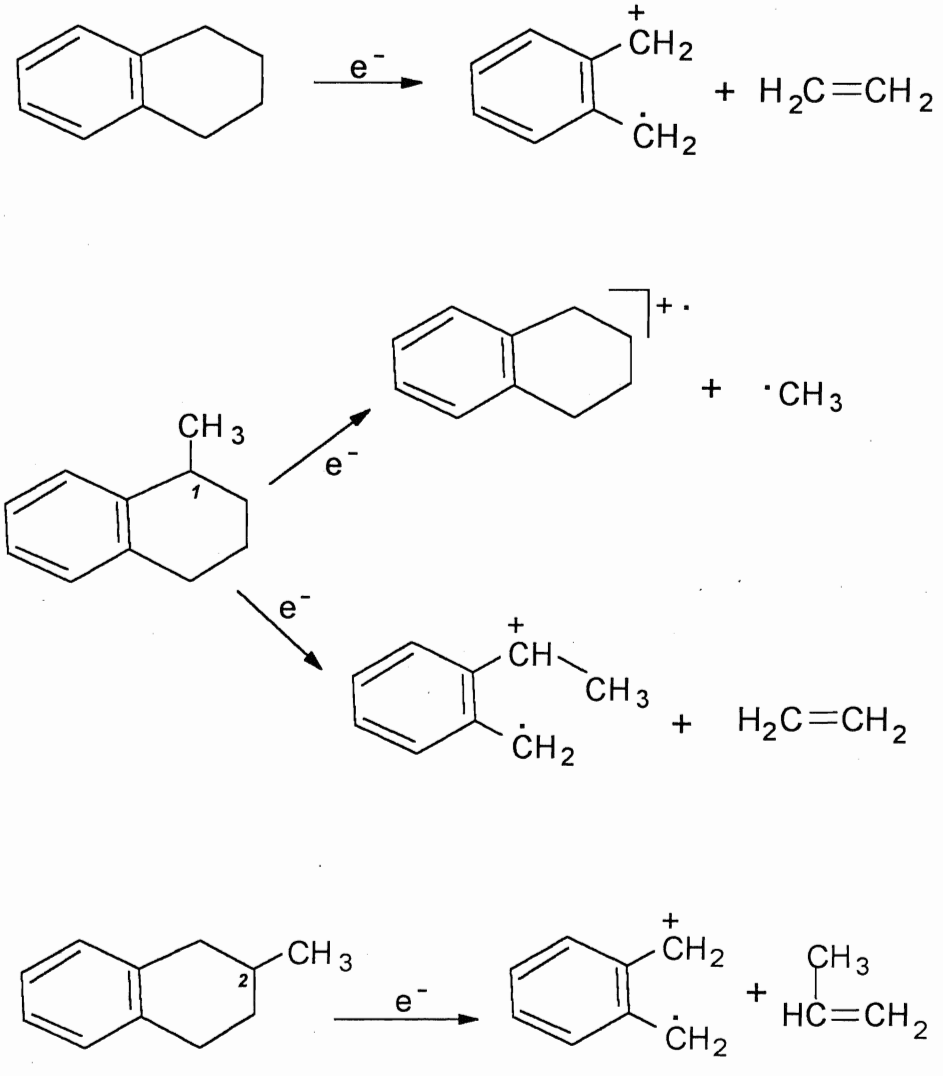


4. *Identification of dialkyltetralins using electron impact mass spectral interpretation of fragmentation patterns*

Certain rules governing mass spectral fragmentation for cyclic alkylbenzenes were put forward around 1960. Since then their validity has not been questioned, but subsequent studies have suggested that a rather aesthetic point of view had been taken in the formulation of many fragment ions. As an example, the retro-Diels-Alder reaction, RDA:



and its significance was first recognized by Biemann[43] in 1962. The reactions of 1,2,3,4-tetrahydronaphthalene, tetralin and its derivatives like dialkyltetralins, were therefore regarded as being more reliable, and as being especially favoured from energetic considerations. These compounds were thus said to undergo a clean RDA reaction. In a subsequent review, Budzikiewicz et al.[23] examined the fragmentation reaction of tetralin and 1- and 2-methyl substituted methyltetralins. They reported the RDA reaction mechanism as being formally correct. 1-Methyl-tetralin eliminates $CH_3^{\cdot}$ preferentially (base peak) rather than ethylene (ca. 18 %). In the latter case the stepwise elimination of (C-2)(C-3)H_4 seems probable, resulting from ready rupture of (C-1)-(C-2) bond. The ^{13}C-labelled methyl substituent remains with the diene part. Quite different behaviour is shown by 2-methyltetralin, which forms its base peak by loss of propylene as 93 % RDA reaction as shown below:

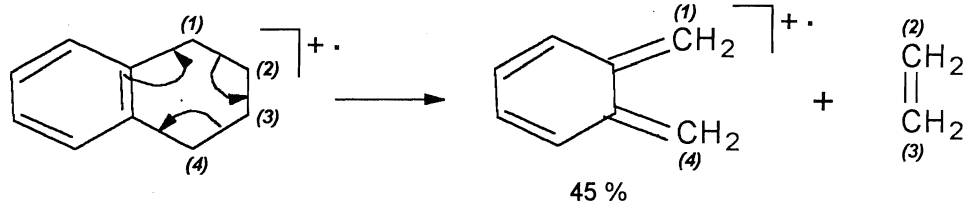


Further studies on tetralin fragmentation have been carried out using ^{2}H- and ^{13}C-labelled tetralin molecules. These investigations clearly excluded fragmentation by a formal RDA mechanism. This findings stimulated further work involving the labelling of substituted and unsubstituted tetralins[23].

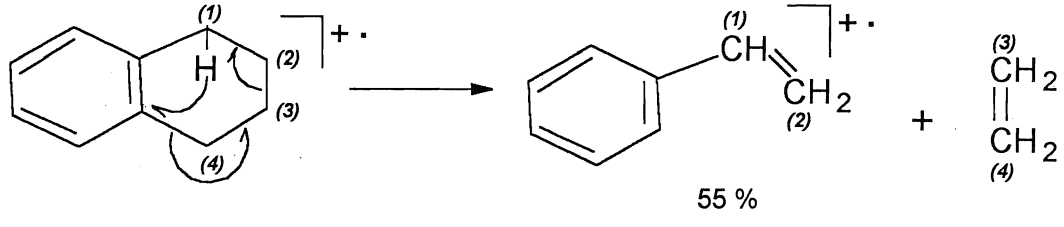
The first experimental results came from Loudon et al.[20] in 1970. The part of the ethylene caused by the RDA mechanism could be determined by peak shift in the

spectrum of D_2-1,4-tetralin. Without taking into consideration mass spectral H/D exchange reactions, a 45 % RDA loss of (C-2)(C-3)H_4 has been calculated based on mechanism A. The remaining 55 % loss resulted from elimination of (C-1)(C-2)H_4 via mechanism B. These fragmentation reactions and their proportions have been confirmed by metastable ion transitions.

Mechanism A



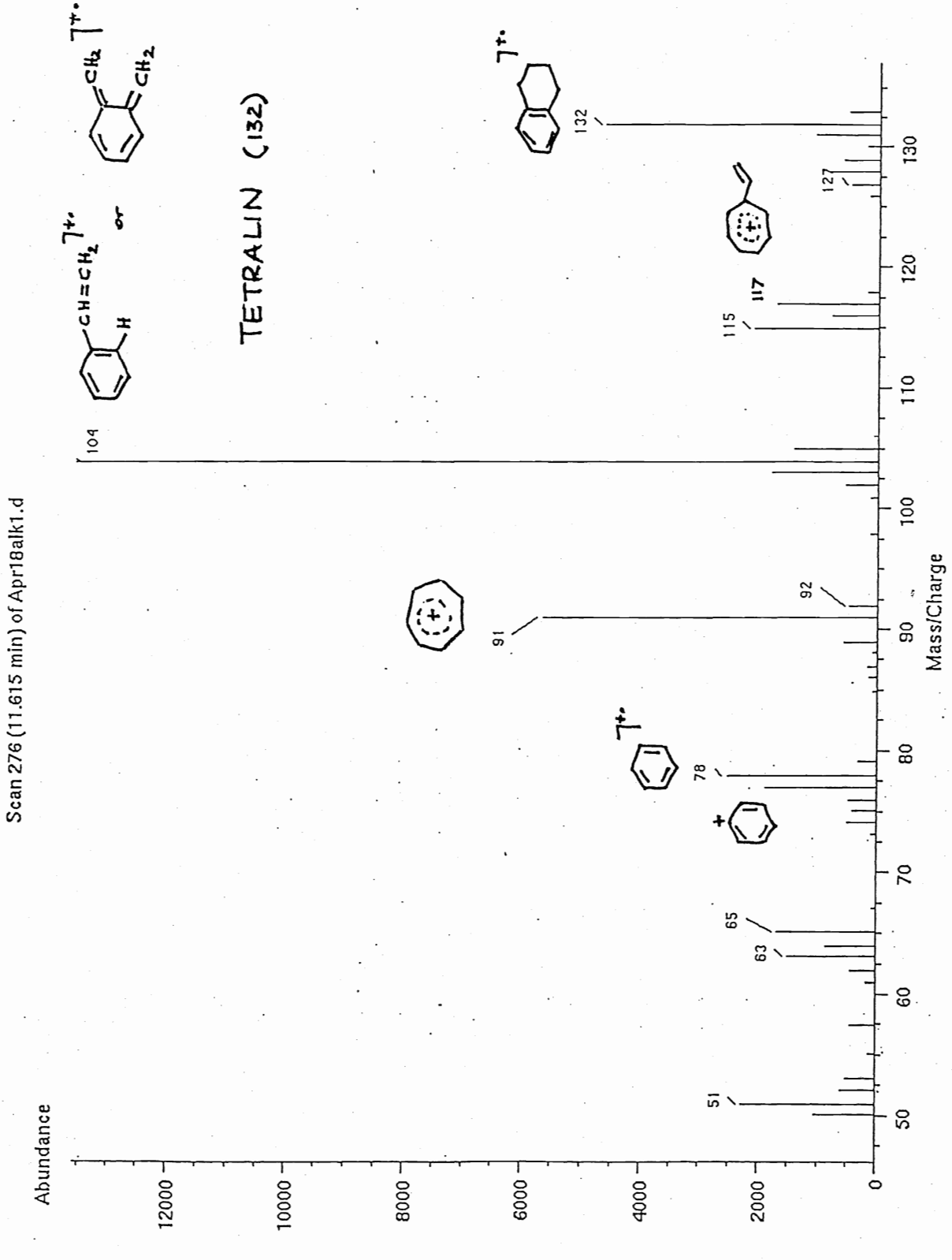
Mechanism B



A year later, Grutzmacher and Puschmann[21] in an investigation into the influence of 1,4-substitution on the RDA reaction of tetralins, observed the loss of substituted ethylenes. In an attempt to elucidate this loss, they studied the fragmentation of deuterated tetralin, D_4-1,1,2,2-tetralin. Instead of m/z 104 ion (**Figure 11**), they observed m/z 104, 106 and 108 ions in the approximate ratio of 1 : 2 : 1 (with a remarkably intense

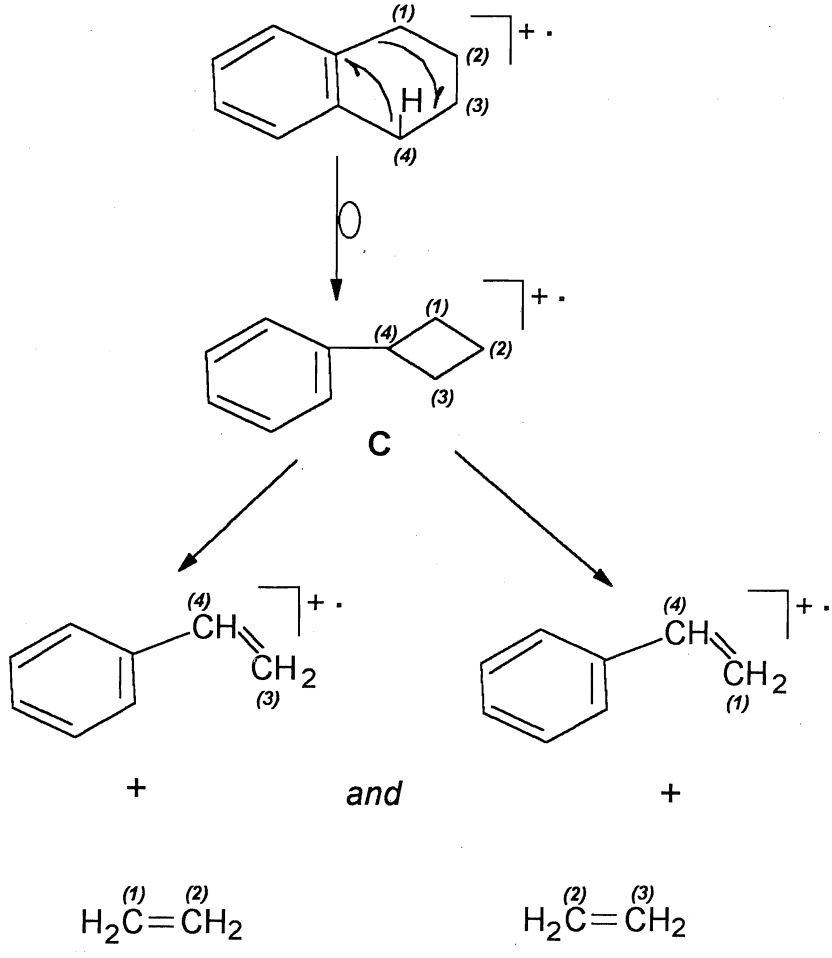
Figure 11

Mass spectrum of 1,2,3,4-tetrahydronaphthalene

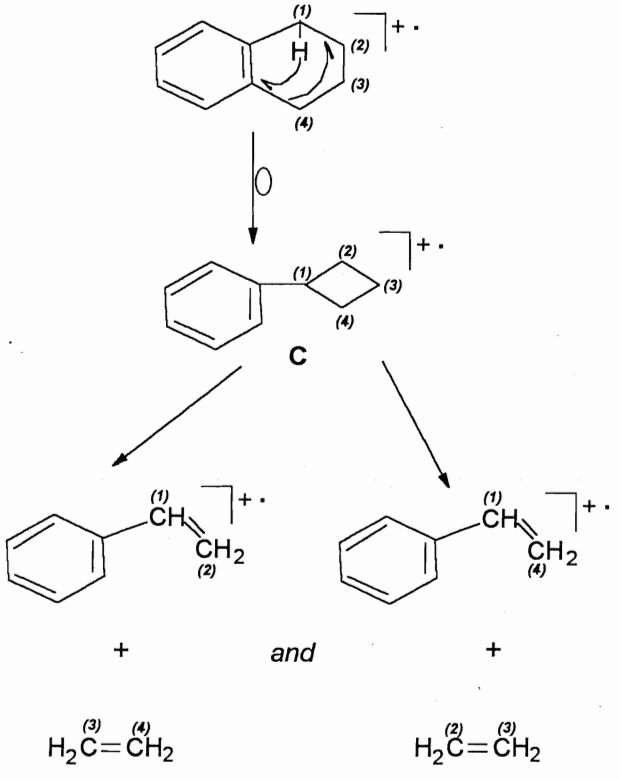


signals at m/z 105 and m/z 107). The ratio was nearly constant between 12 and 70 eV, so that the superposition of two different mechanisms was considered very unlikely. As a consequence, they proposed two fragmentation mechanisms, mechanism **C** and **D**, with phenylcyclobutane (**C**) and tetrahydroazulene (**D**) as intermediates which because of their symmetry resulted in the observed intensity ratio.

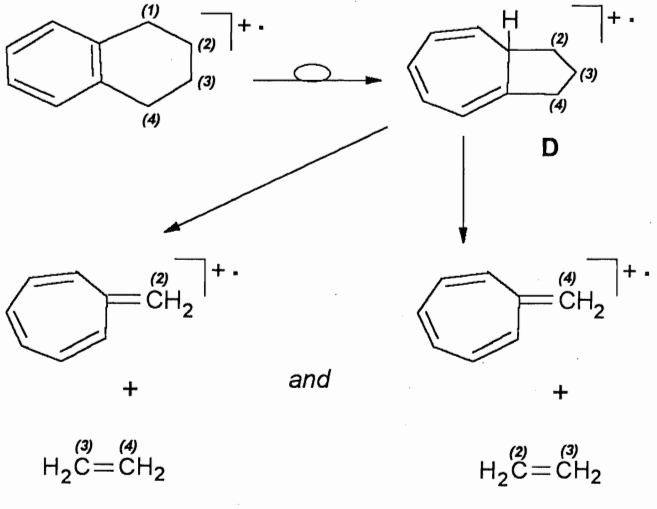
Mechanism C



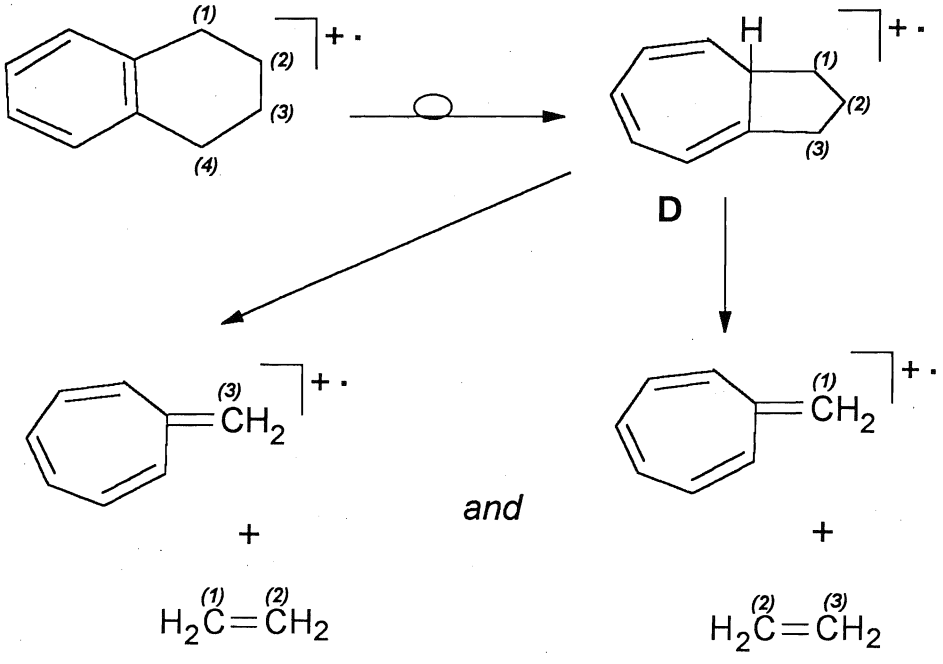
Mechanism C - continued



Mechanism D



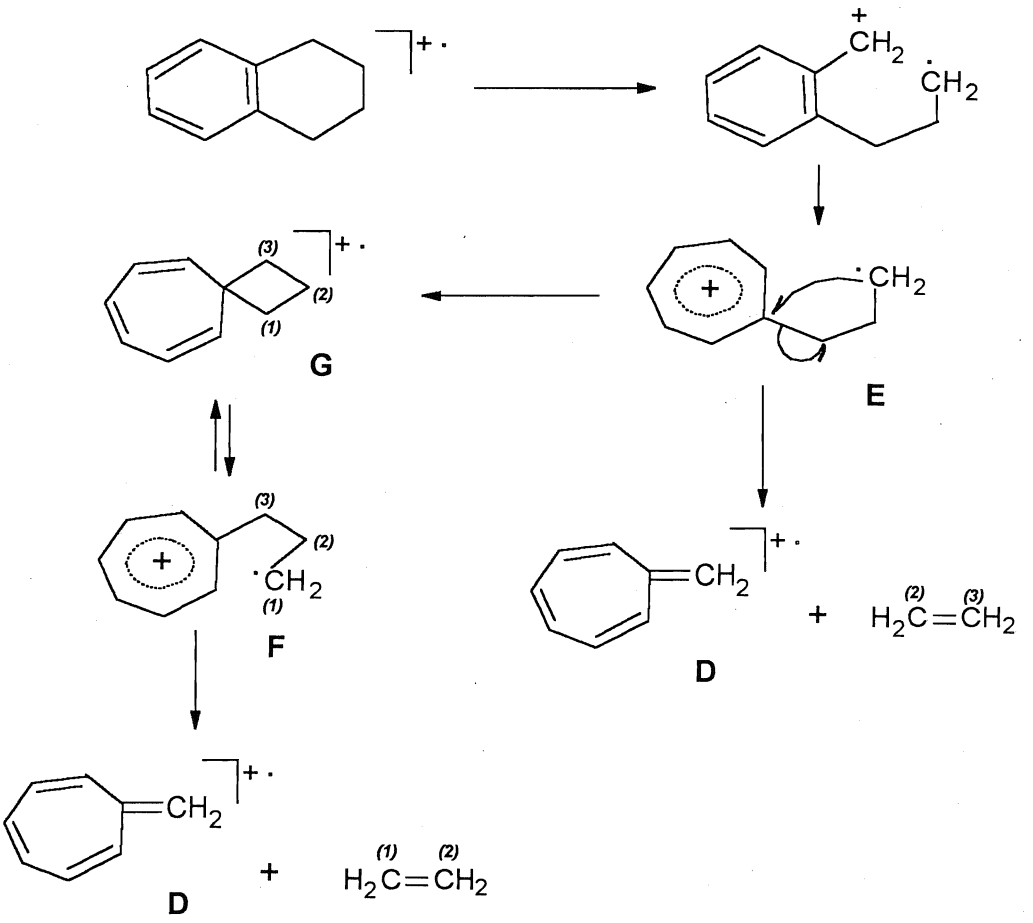
Mechanism D - continued



Though it is known from studies by Grutzmacher and Puschmann[21] on D_4-5,6,7,8-tetralin that H/D exchange reactions take place, quantitative statements are difficult to make. Furthermore, exchange reactions within the aliphatic part are not taken into consideration. Nevertheless the peak pattern at m/z 104-108 could have been influenced by such process.

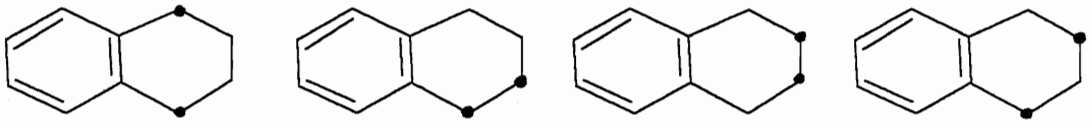
Gorfinkel and Bugreeva[44] have synthesized and studied ^{13}C-1-tetralin and ^{13}C-2-tetralin. Their observations, namely the loss of ethylene to the extent of 31 % or 66 %, respectively, of the ^{13}C label, agree with the results reported by Loudon et al.[20]. Apart from calculation of the relative proportions due to the mechanism **A** and **B**, no conclusion could be drawn.

Gretler et al.[45] in their studies reported a possible fragmentation pathway as mechanism **E**:



After the opening of an aliphatic ring and rearrangement to a propyltropylium radical cation, **E**, ethylene is lost directly via formal RDA reaction, or alternatively rearrangement to the inverted propyltropylium radical cation **F**, takes place. Loss of ethylene from **F** corresponds formally to the loss of carbon atoms (C-1)(C-2) or (C-3)(C-4) and results in a heptafulvene radical ion **D**, similarly to mechanism **D** proposed by Grutzmacher and

Puschmann[21]. Good agreement with the observed values was found for all four doubly ^{13}C-labelled tetralins, where "•" represents ^{13}C:

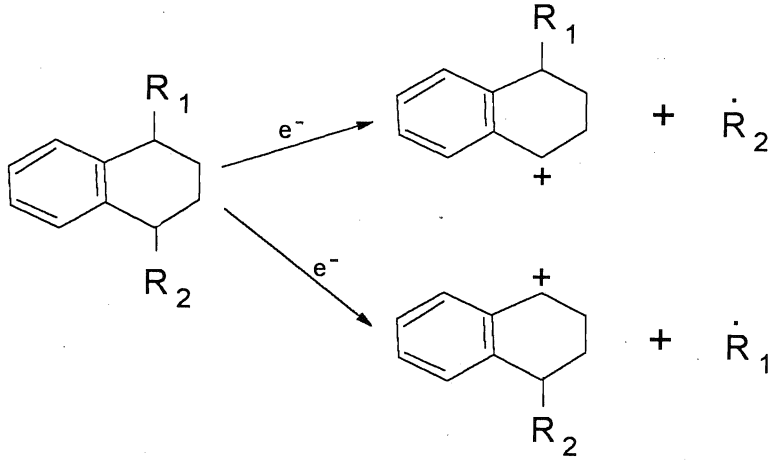


with a ratio of 2:3 for rearrangement and 1:3 for RDA reaction. The reason for the rearrangement being preferred over direct elimination of ethylene was left open to question. If, however, a symmetrical ion **G** were involved in the rearrangement, the contribution of the RDA reaction should always be at least 50 %.

Tetralins doubly labelled with ^{13}C have been examined by Stolze and Budzikiewicz[22]. The values are in good agreement with the assumption of superposition of the fragmentation via mechanism **A** and mechanism **B**, combined with a small proportion of complete C scrambling. The proportion of scrambling is almost constant (9-12 %) at all electron energies, but the ratio of the two decomposition reactions to each other is dependent on such energy. The same year, in 1978, results published by Levsen et al.[24] not only confirmed the loss of ethylene from the molecular ion of tetralin but also that the decomposition did not occur via a single process as had been suggested earlier by Biemann[43] and Budzikiewicz et al.[23]. According to their results, about 11 % of the molecular ions lose C_2H_4 after complete, but independent, C and H scrambling. About 32 % eliminate ethylene from the position (C-2) and (C-3) as a classical RDA

decomposition and the remainder 56 % from positions (C-1) and (C-2) or (C-3) and (C-4). The occurrence of competing processes was corroborated by the observation that lowering the electron energy resulted in a change of the ratio of the various decomposition modes. At 13 eV the percentage of scrambling was about 10 %, RDA was about 20 %, and loss from positions (C-1) and (C-2) and (C-3) and (C-4) was about 70 %.

Based on the discussed literature review, dialkyltetralins mass spectra can be interpreted similarly to the alkyl substituted tetralins or just tetralin. When dialkyltetralins contain linear side chains, besides a relatively high molecular weight or parent peak, benzylic bond rupture predominates and favourers the appearance of $(MW - R_1)^+$ and $(MW - R_2)^+$ fragments.



The dialkyltetralin skeleton structure gives a fragment at m/z 131. The m/z 117 is observed in all dialkyltetralins, as well as, the presence of m/z 145, m/z 173, and m/z 187 due to the characteristic losses at 1 ad 4 positions. The $(MW - 15)^+$ fragment comes from the rupture of one of the benzylic bonds (**Figure 12**).

Figure 12

EI mass spectrum fragmentation pattern of 1-methyl-4-pentyltetralin and 1-methyl-4-hexyltetralin

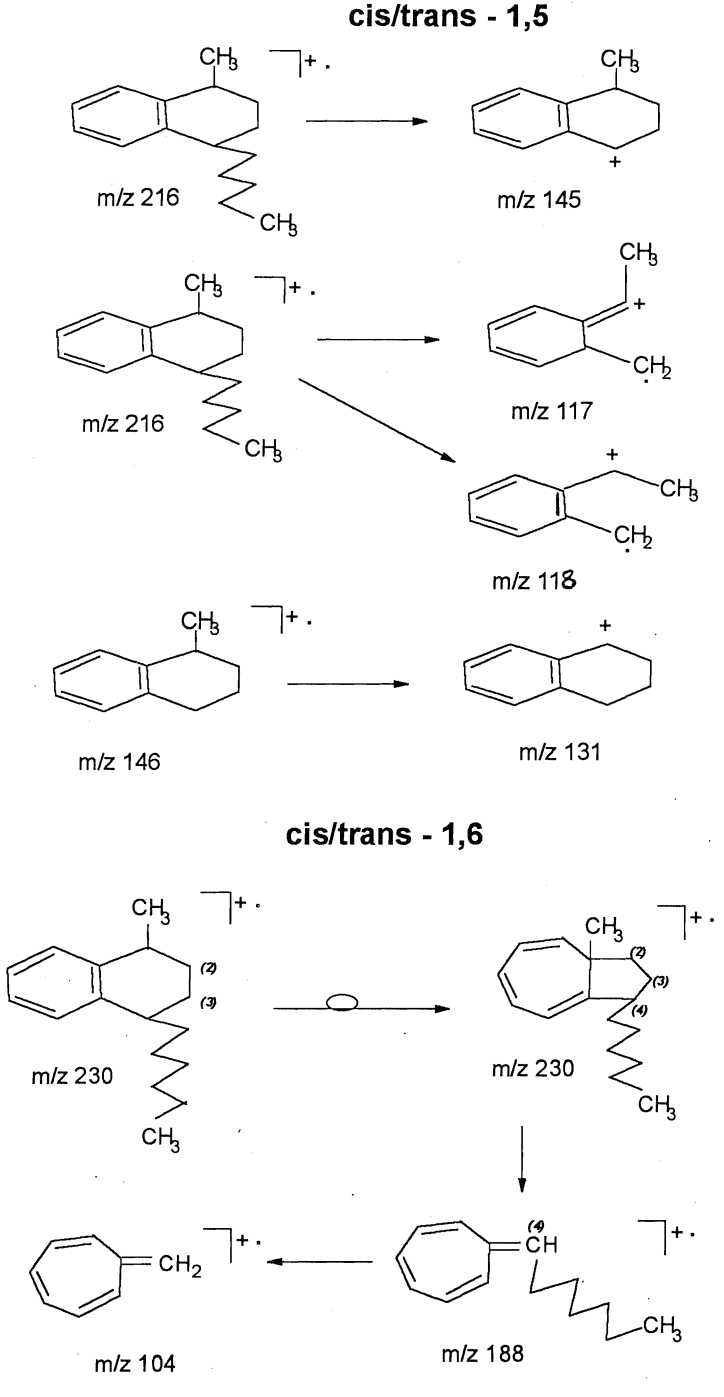
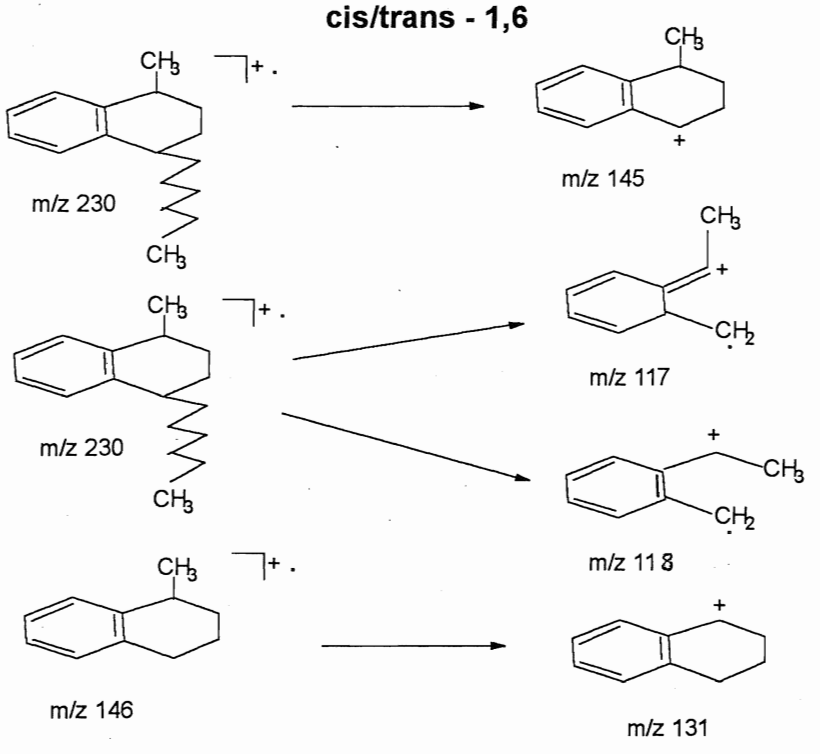


Figure 12 - continued

EI mass spectrum fragmentation pattern of 1-methyl-4-hexyltrtralin - continued



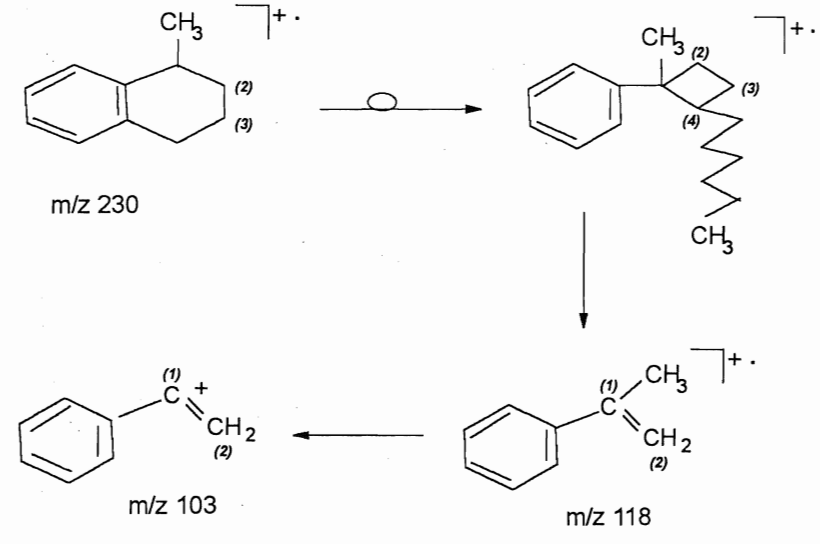
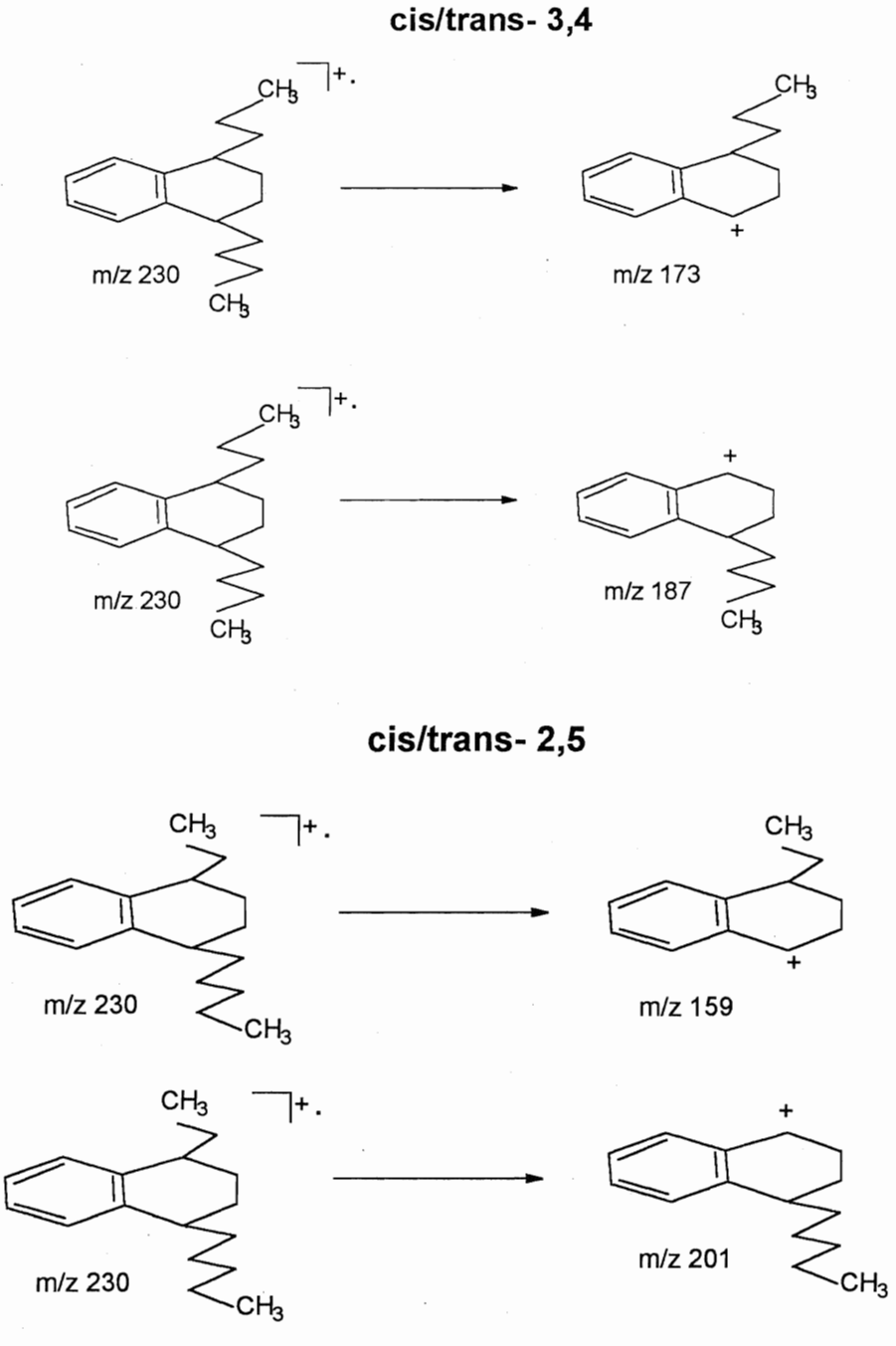


Figure 12 - continued

EI mass spectrum fragmentation pattern of 1-propyl-4-butyltrtralin and 1-ethyl-4-pentyltetralin



5. *Confirmation of linear alkylbenzene isomers and impurities such as branched alkylbenzenes and dialkyltetralins using Chemical Ionization mass spectra fragmentation patterns*

To complete the *initial* part of this study, confirmation of the molecular weight for all linear and branched alkylbenzenes, as well as, for dialkyltetralins was conducted using a much "softer" mass spectral ionization technique, *chemical ionization*, (*CI*).

First *chemical ionization* mass spectra of aromatic hydrocarbons were reported 1967[46]. Several subsequent studies of the proton transfer *CI* of alkylbenzenes have been reported since then. Aromatic molecules with no alkyl substituents show only MH^+ ions and the cluster ions $(M + C_2H_5)^+$ and $(M + C_3H_5)^+$. With the introduction of methyl groups, hydride abstraction also becomes possible and increases in importance with increasing size of the alkyl substituent. Hydride abstraction phenomenon are also observed for other compounds containing linear or branched alkyl chains in their molecules, as in branched alkylbenzenes and dialkyltetralins. Hydride abstraction is generally described as:

$$M + CH_5^+ \rightarrow (M - H)^+ + CH_4 + H_2$$

or

$$M + NH_4^+ \rightarrow (M - H)^+ + NH_3 + H_2$$

Both methane and ammonia were used as a reagent gas, the latter one however with less success due to instrumental problems. Ammonia is generally used for *chemical ionization* when less fragmentation is desired in the chemical ionization spectrum. This is because the proton affinity of ammonia is higher than that of methane; hence, less energy is

transferred in the ionization reaction. Because many compounds of interest have insufficient proton affinities, ammonia chemical ionization spectra often result from the addition of NH_4^+. This, together with M^+, $(M + H)^+$ and hydride abstraction ion $(M - H)^+$, was observed in chemical ionization mass spectra for alkylbenzenes (**Figure 13**, **14**, and **15**), as well as in chemical ionization mass spectra for dialkyltetralins (**Figure 16**, **17**, and **18**).

Molecular weight information via *chemical ionization* is an ideal complement of characteristic fragmentation patterns observed under *electron impact* conditions in the elucidation of the structure of unknown or the confirmation of the known compound. Methane gas was used to confirm molecular weight ions of impurities like branched alkylbenzenes and dialkyltetralins, as well as molecular weight ions of linear alkylbenzenes. For the linear isomers of C_{10}, C_{11}, and C_{12} alkylbenzene homologues, M^+, $(M + H)^+$ and $(M - H)^+$ ions (**Figure 19**, **20** and **21**) were observed but at a much smaller intensities than in the branched alkylbenzenes (**Figure 22** and **23**). These two observations are due to the vast difference in concentration between linear and branched isomers entering the ionization chamber in the mass spectrometer.

Chemical ionization mass spectra for dialkyltetralins showed characteristic adduct ions of methane, $(M + H)^+$ and $(M + C_2H_5)^+$ (**Figure 24**, **25**, **26** and **27**). The other ions, M^+, and $(M - H)^+$ were also observed.

The cis- and trans- assignment follows the results obtained by NMR study conducted by Cavalli et al.[16] of a model compound cis- and trans-1,4-dialkyltetralin. The

Figure 13

CI mass spectrum of C_{10} linear alkylbenzene (MW=218)

using ammonia as a reagent gas

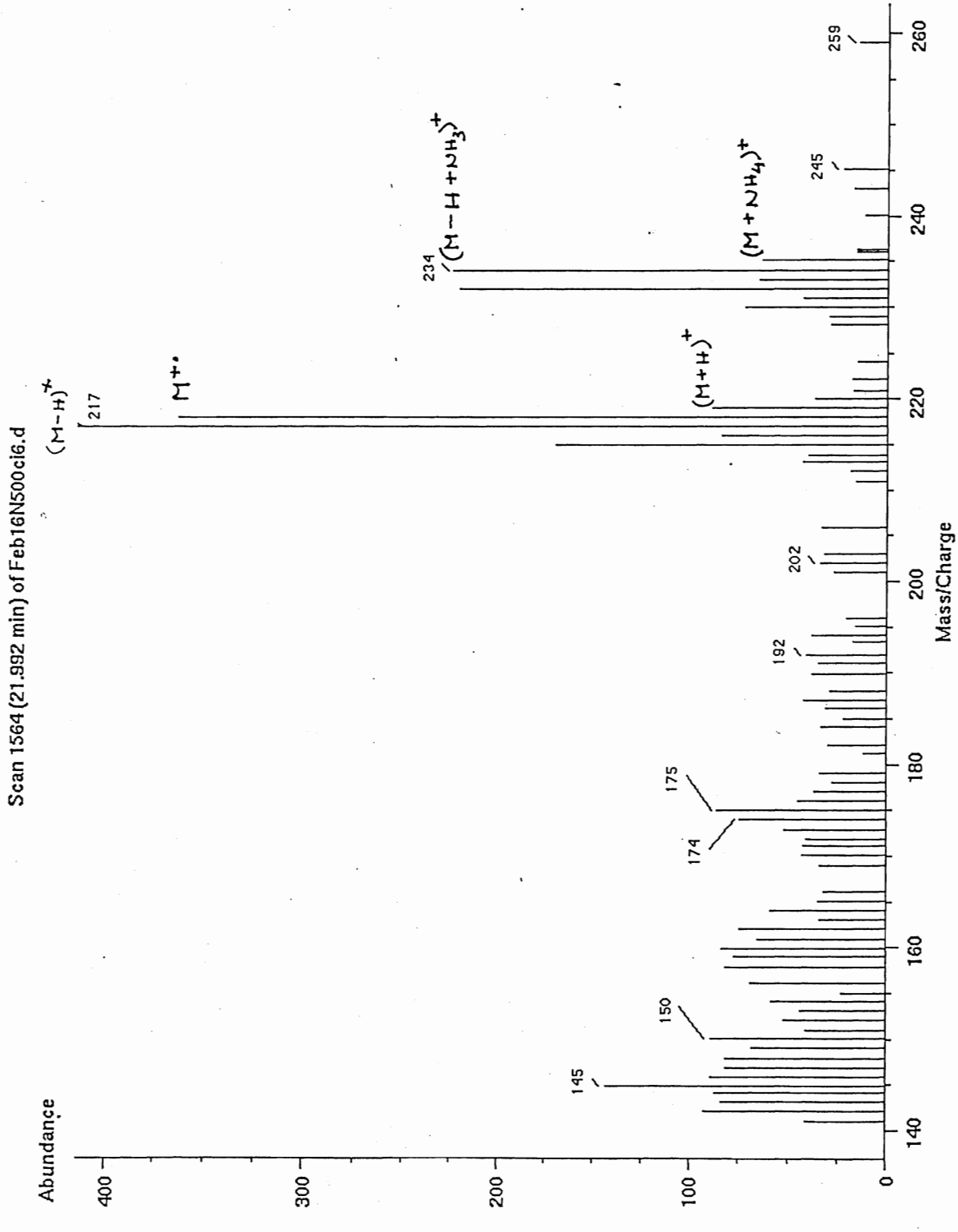


Figure 14

CI mass spectrum of C_{11} linear alkylbenzene (MW=232)

using ammonia as a reagent gas

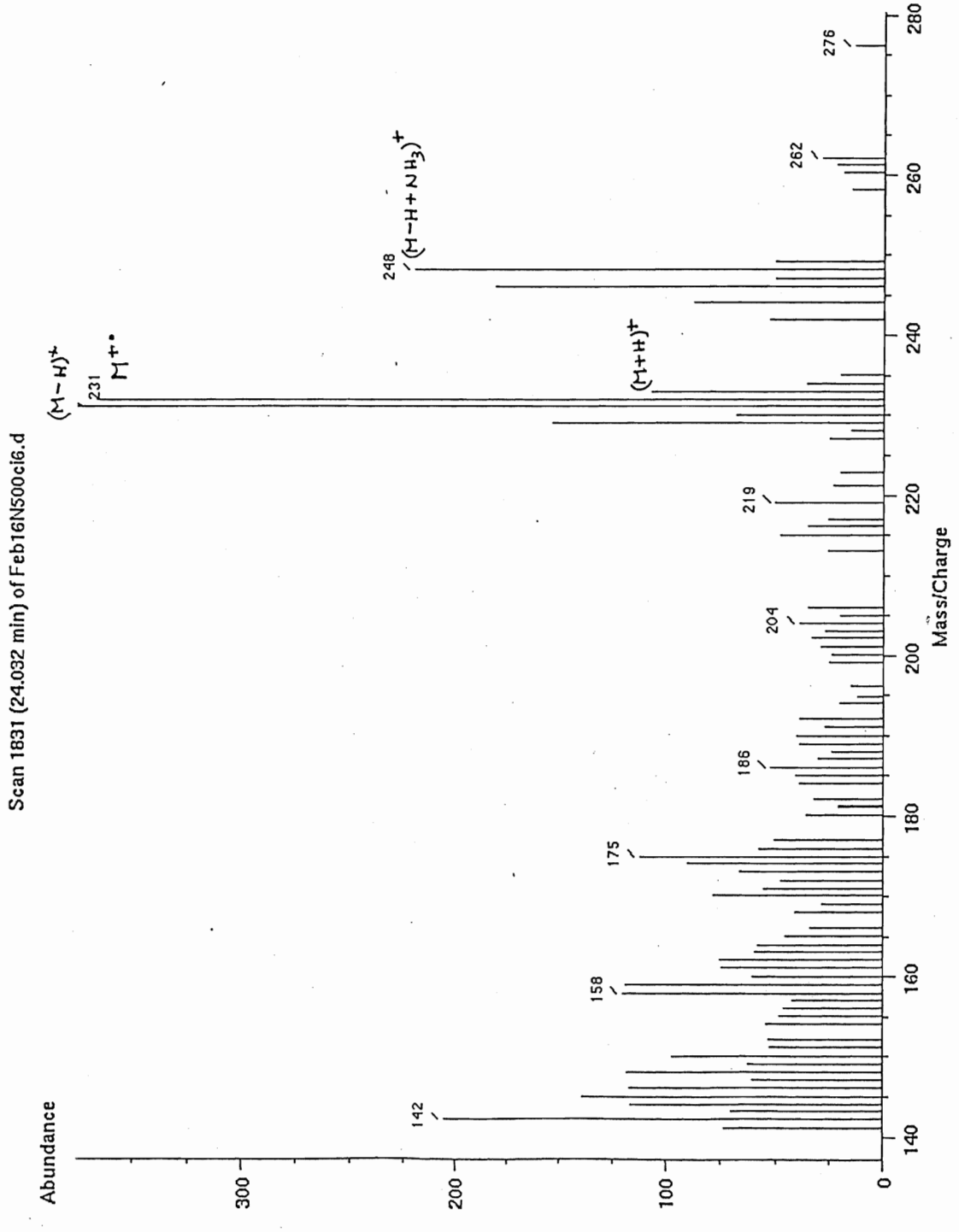


Figure 15

CI mass spectrum of C_{12} linear alkylbenzene (MW=246)

using ammonia as a reagent gas

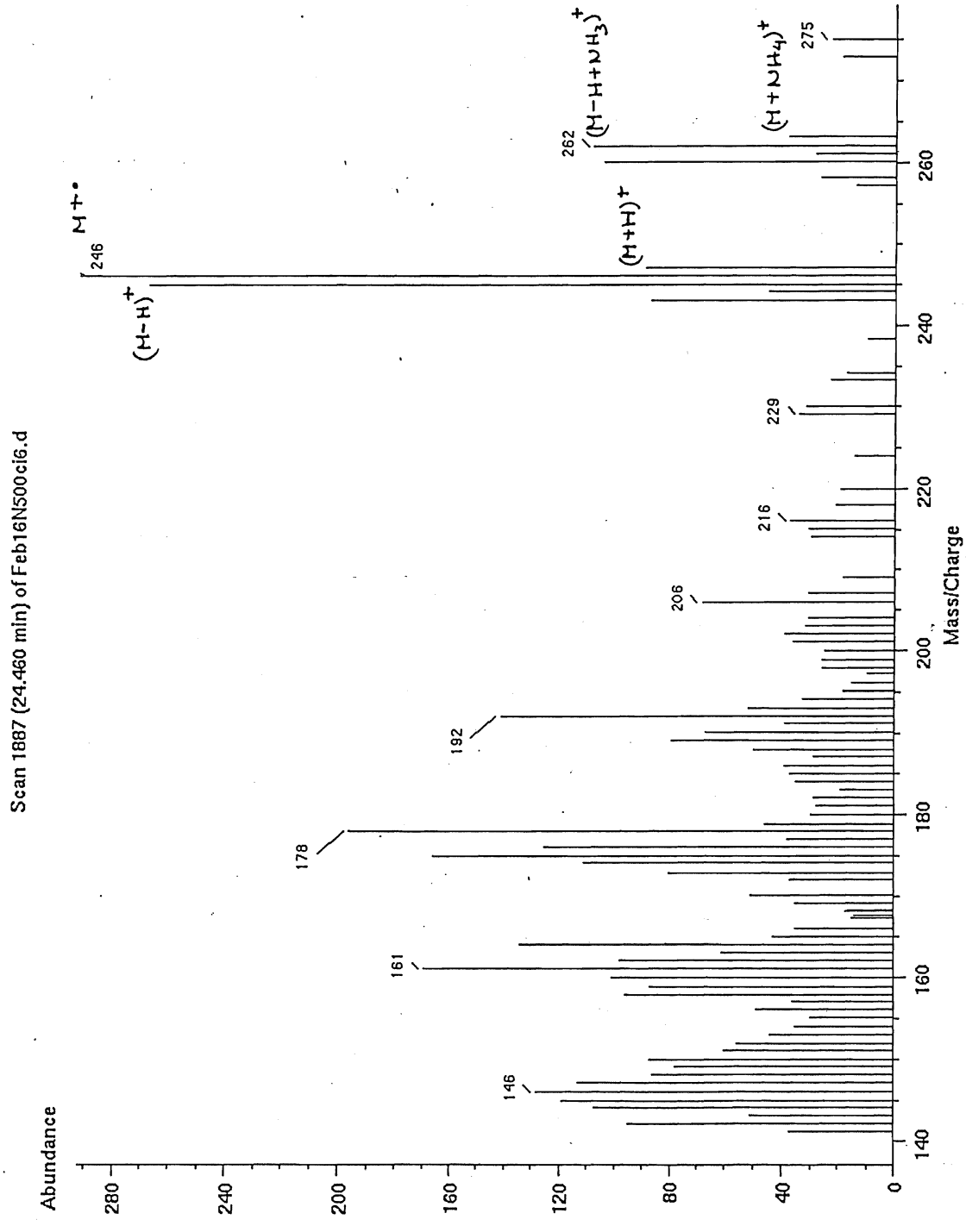


Figure 16

CI mass spectrum of 1-methyl-4-pentyltetralin (MW = 216)

using ammonia as a reagent gas

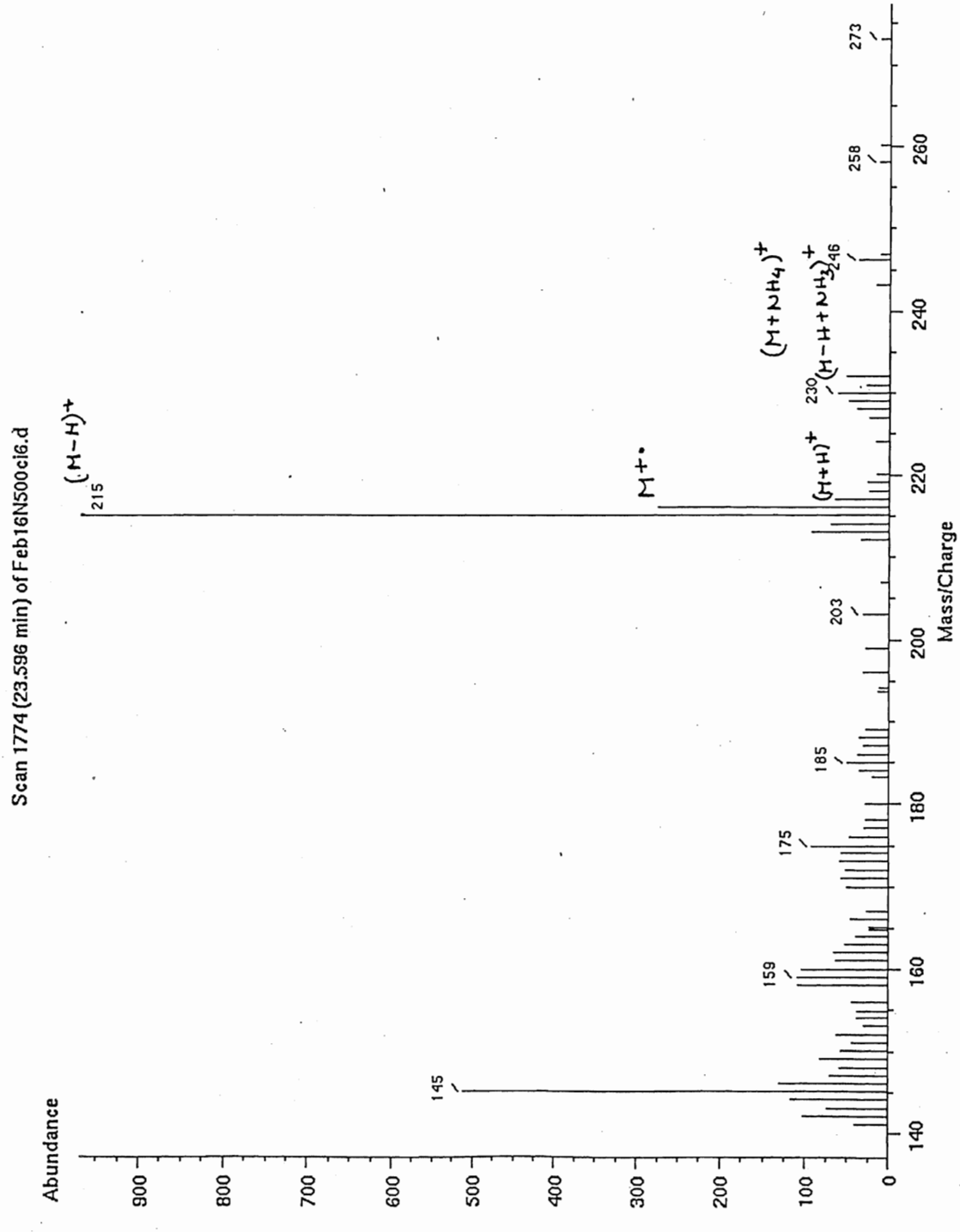


Figure 17

CI mass spectrum of 1-methyl-4-hexyltetralin (MW = 230)

using ammonia as a reagent gas

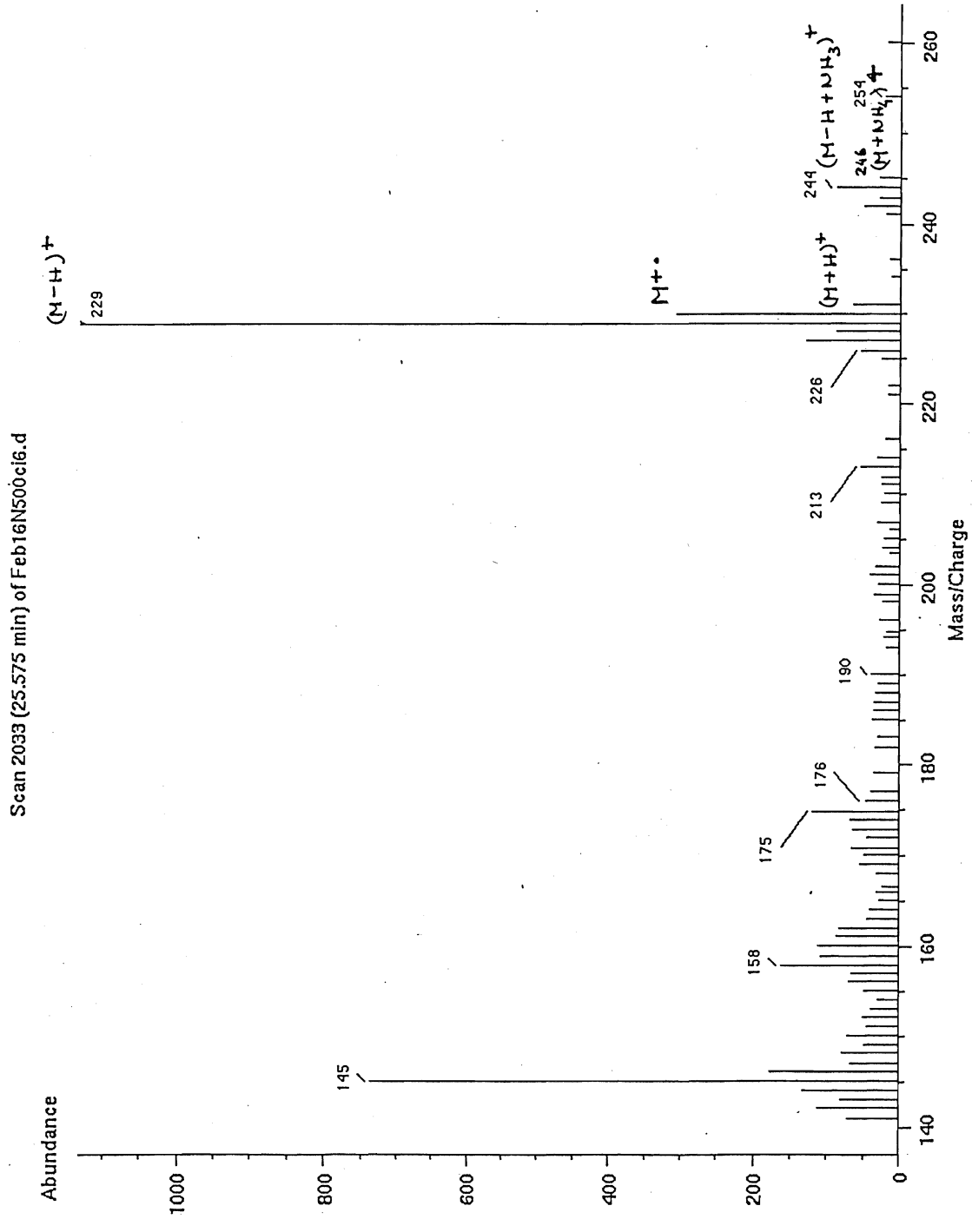


Figure 18

CI mass spectrum of 1-methyl-4-heptyltetralin (MW = 244)

using ammonia as a reagent gas

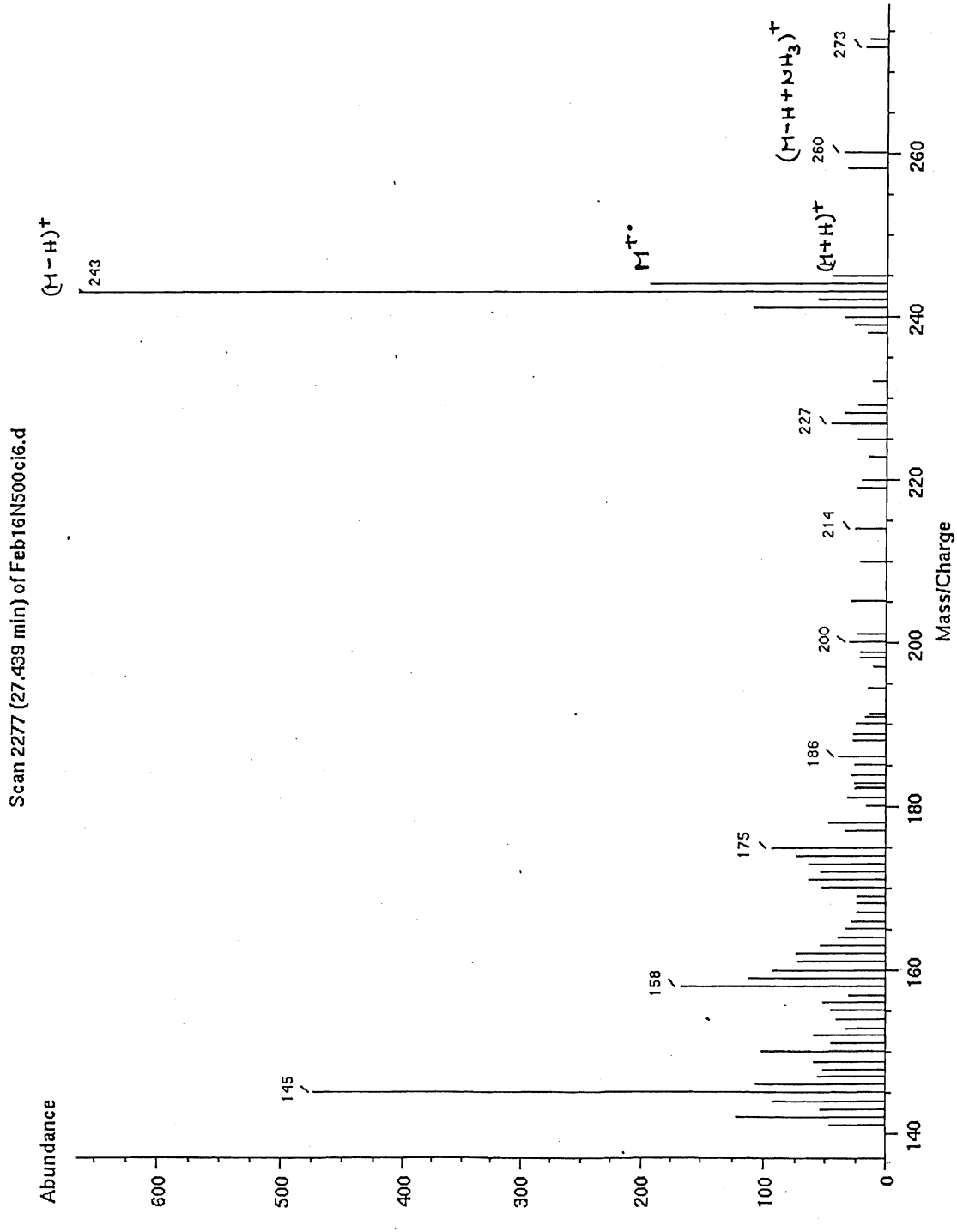


Figure 19

CI mass spectrum of 3-phenyldecane and 2-phenyldecane

using methane as a reagent gas

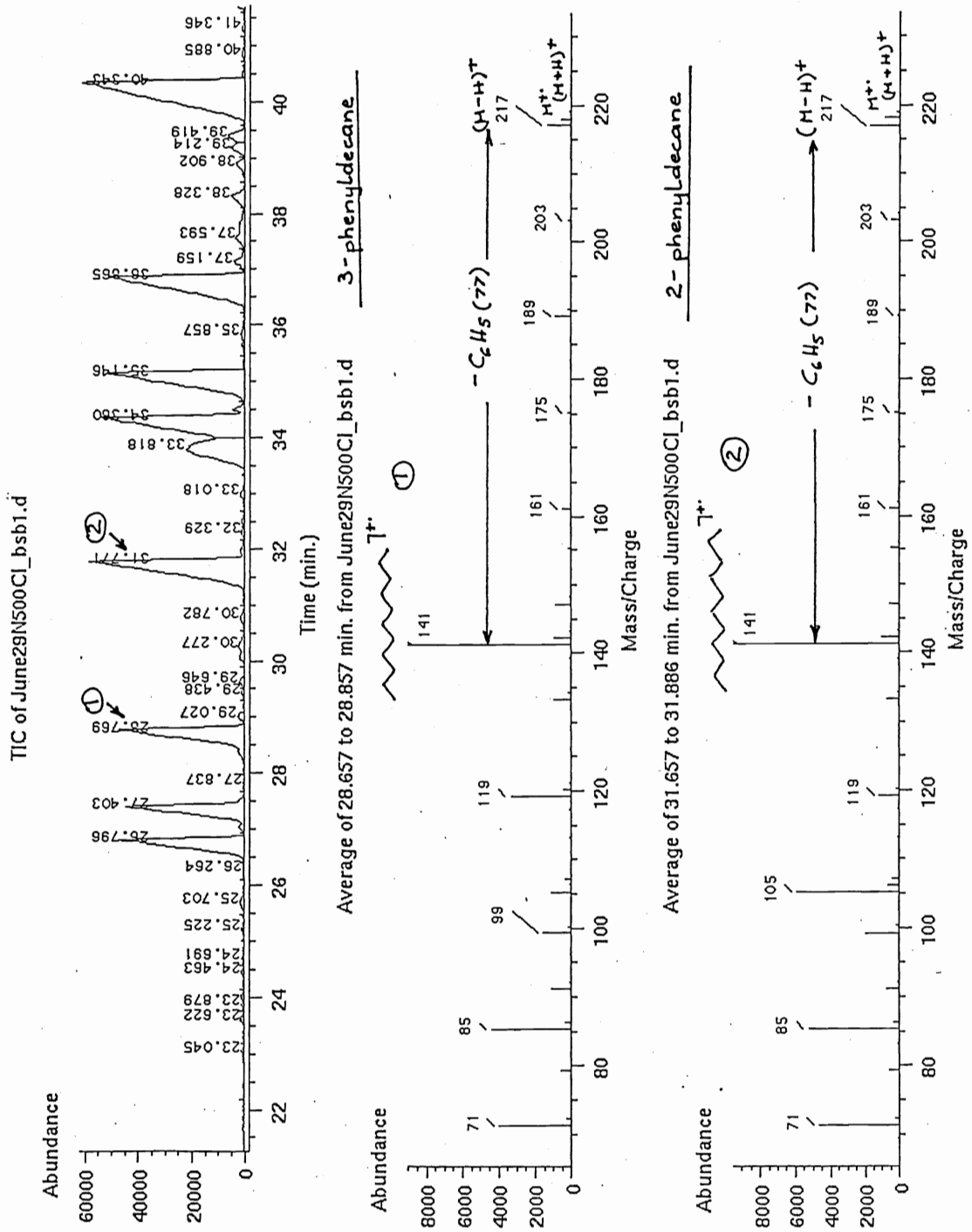


Figure 20

CI mass spectrum of C_{11}-4-phenylundecane and 3-phenylundecane using methane as a reagent gas

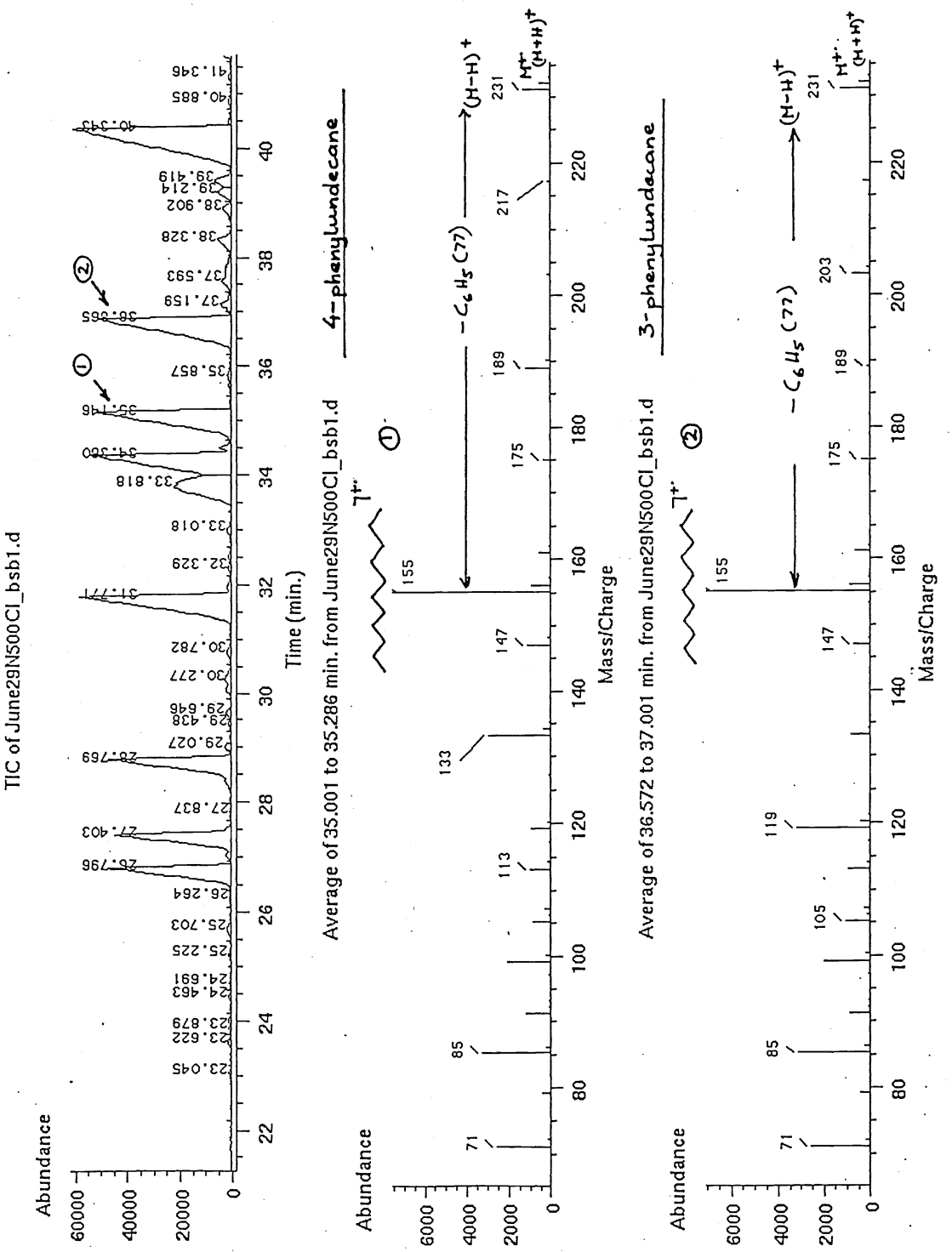


Figure 21

CI mass spectrum of C_{12}-4-phenyldodecane and 3-phenyldodecane using methane as a reagent gas

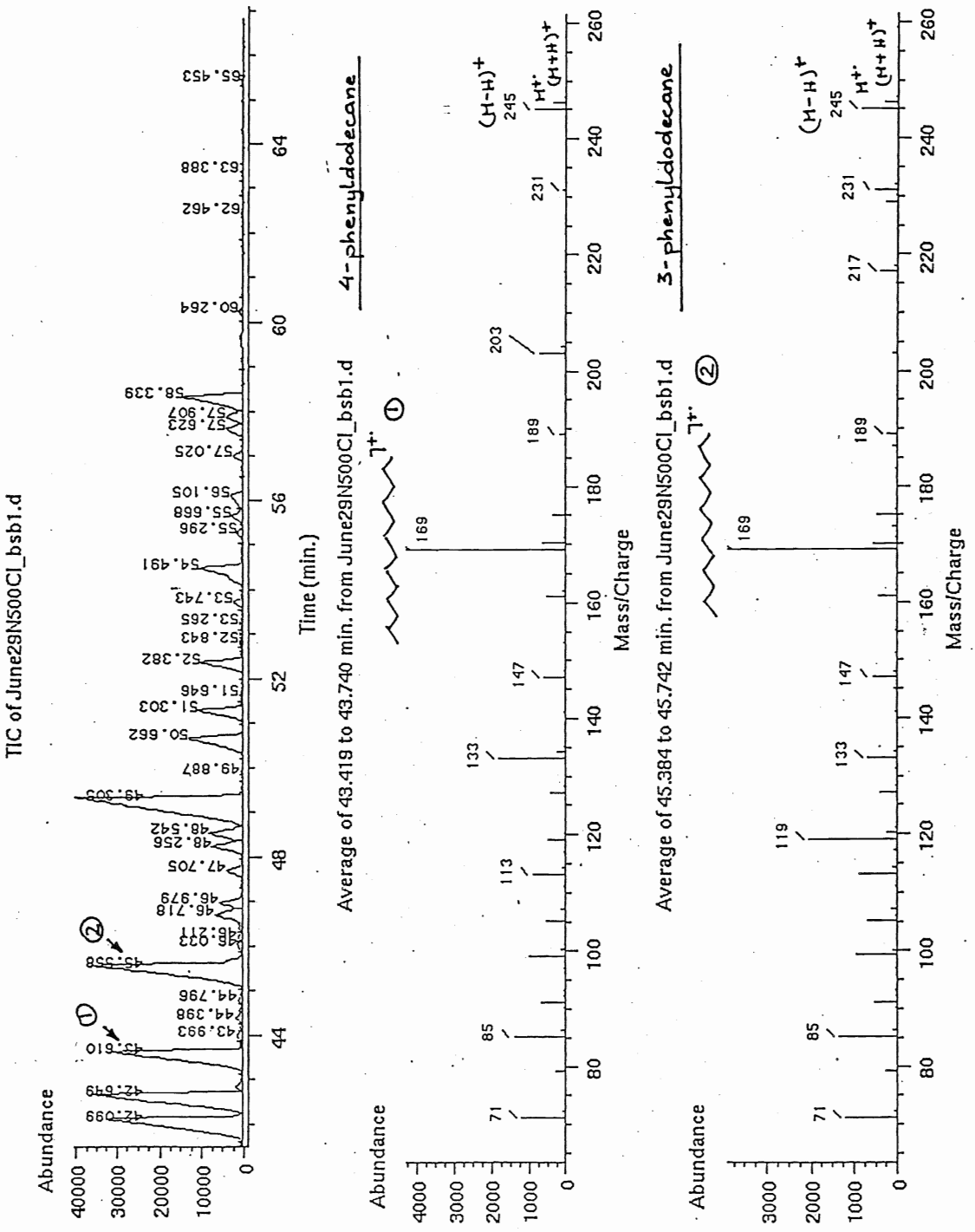


Figure 22

CI mass spectrum of C_{11}-branched alkylbenzene (MW = 232)

using methane as a reagent gas

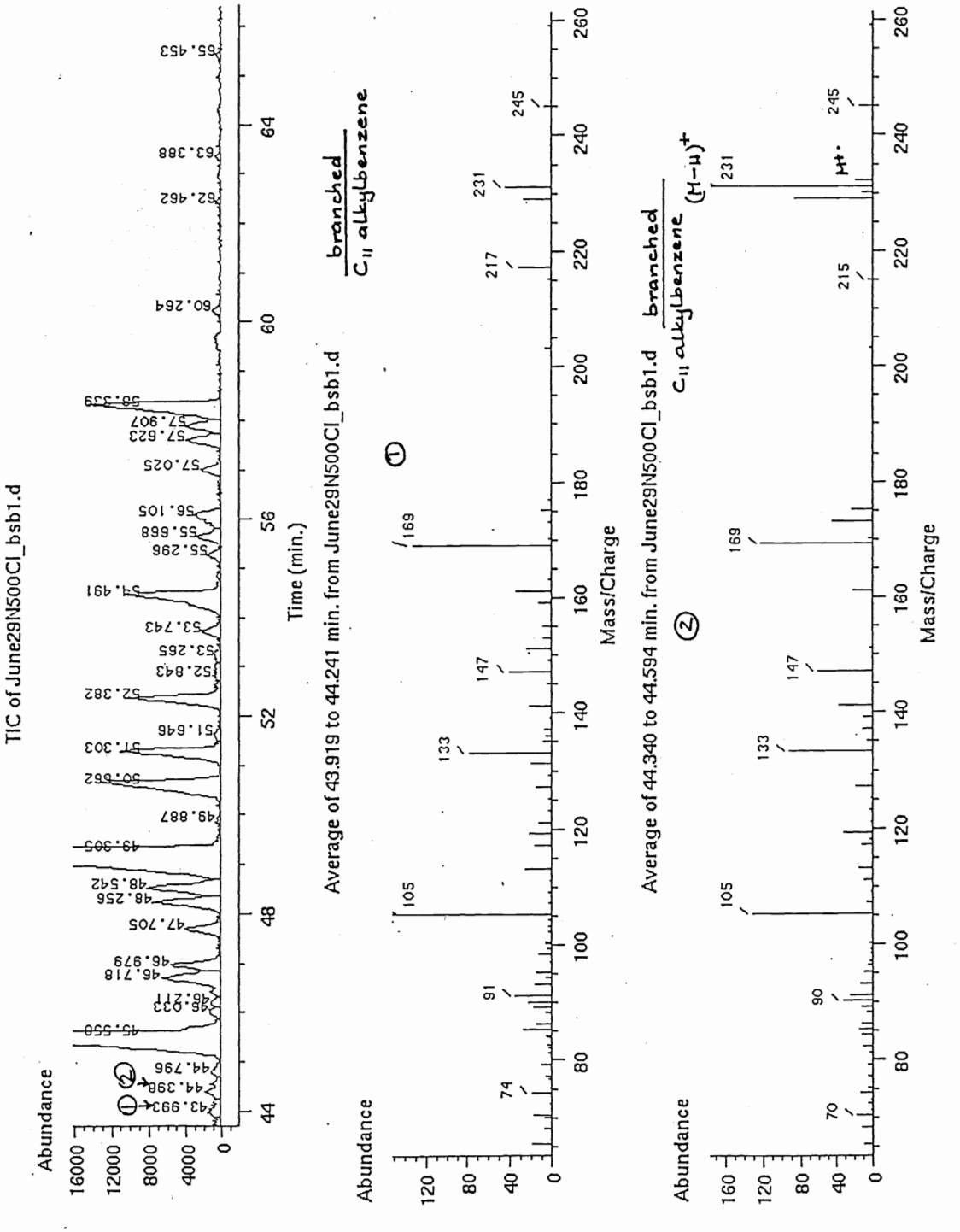


Figure 23

CI mass spectrum of C_{11} -branched alkylbenzene (MW = 232)

using methane as a reagent gas

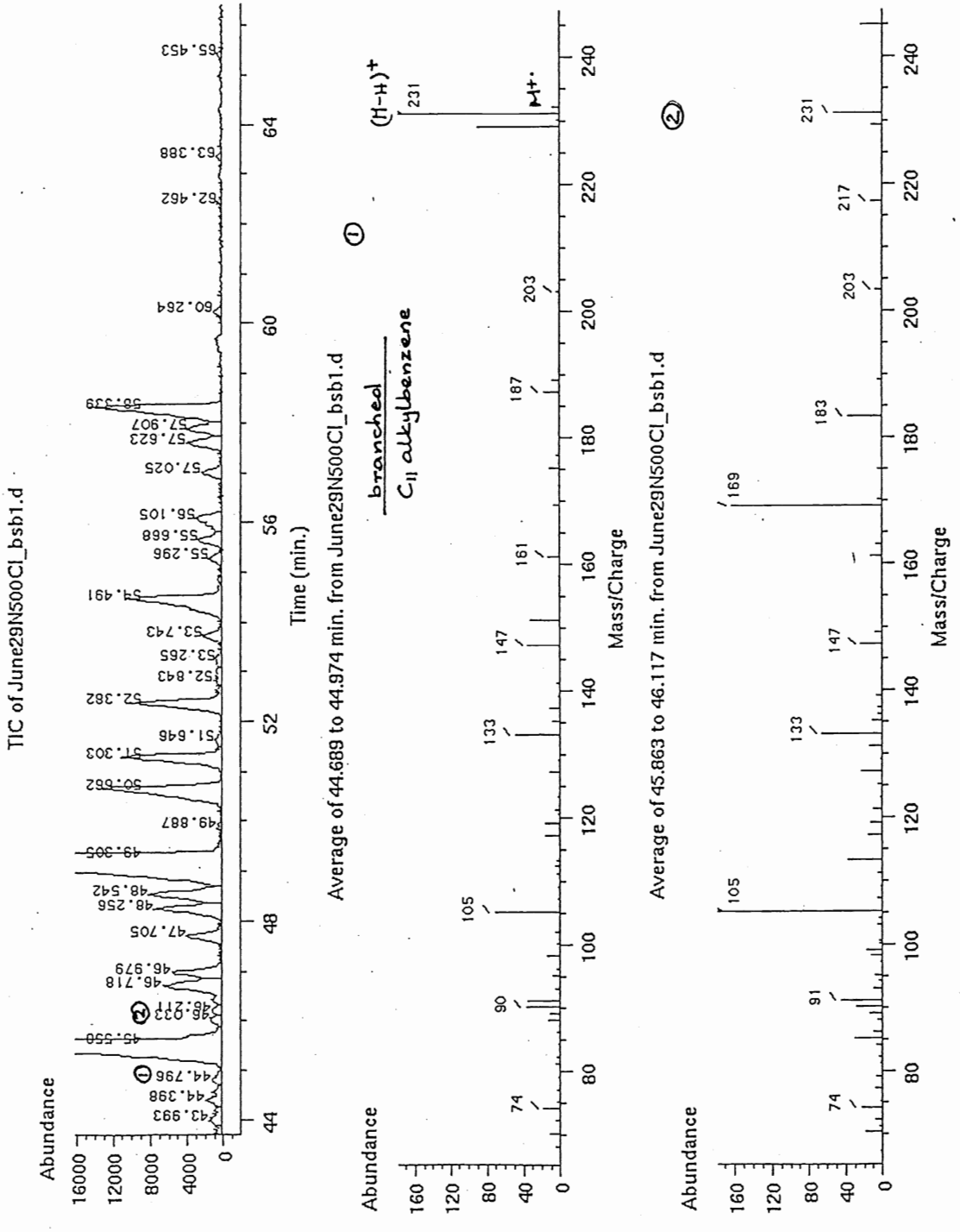


Figure 24

CI mass spectra of cis-1-ethyl-4-butyltetralin and trans-1,4-dipropyltetralin using methane as a reagent gas

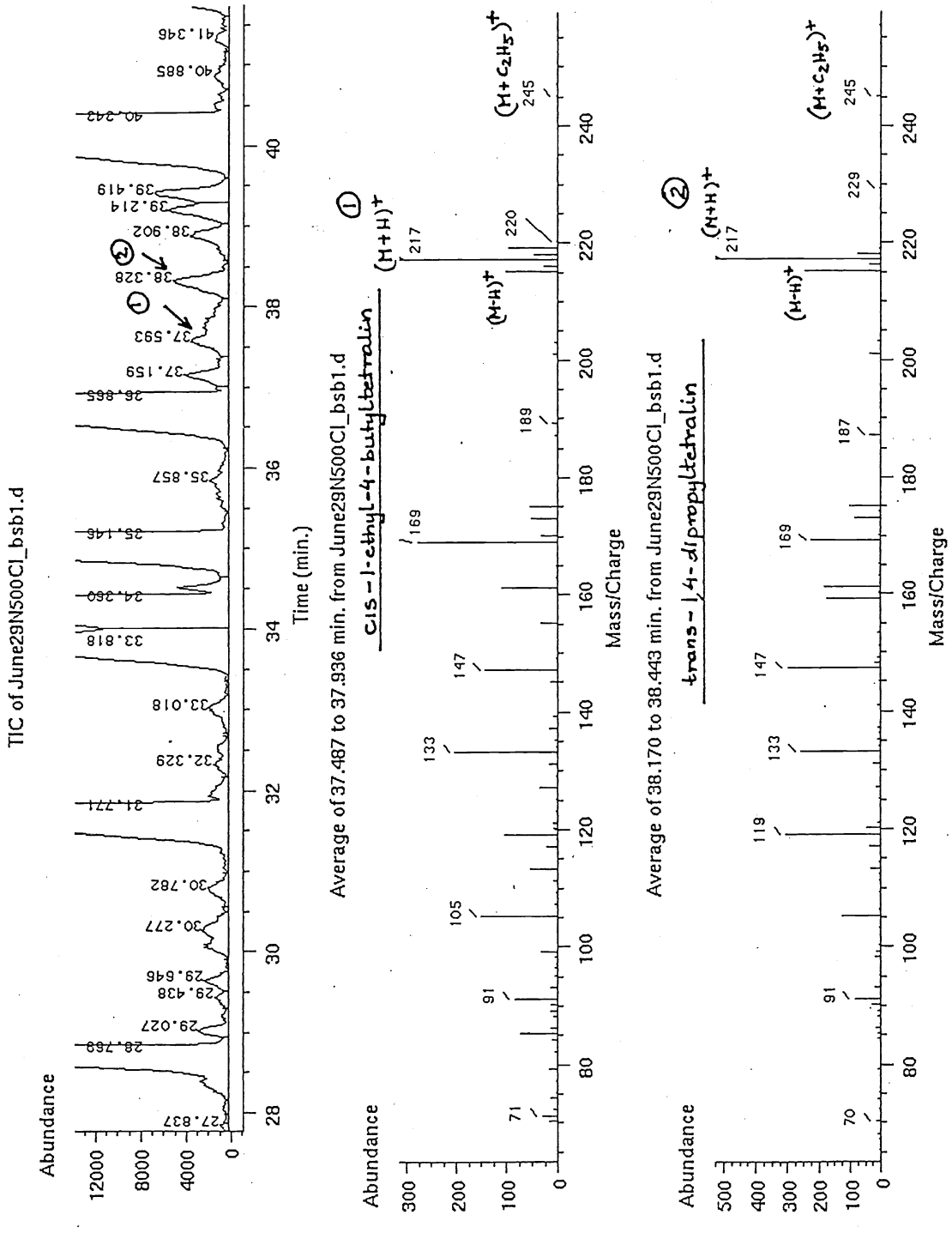


Figure 25

CI mass spectra of trans-1-ethyl-4-butyltetralin and trans-1-methyl-4-pentyltetralin using methane as a reagent gas

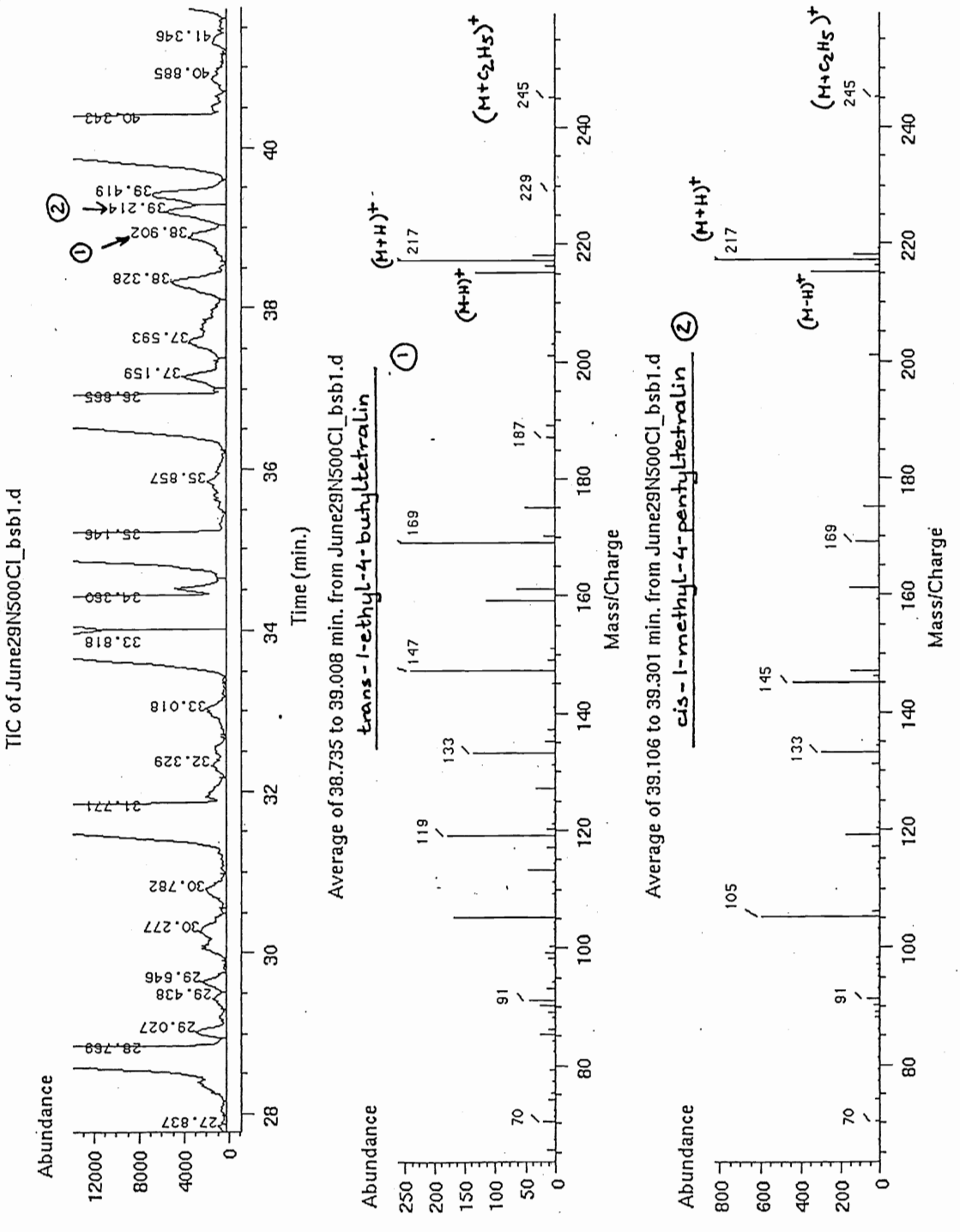


Figure 26

CI mass spectra of cis and trans-1-methyl-4-hexyltetralin

using methane as a reagent gas

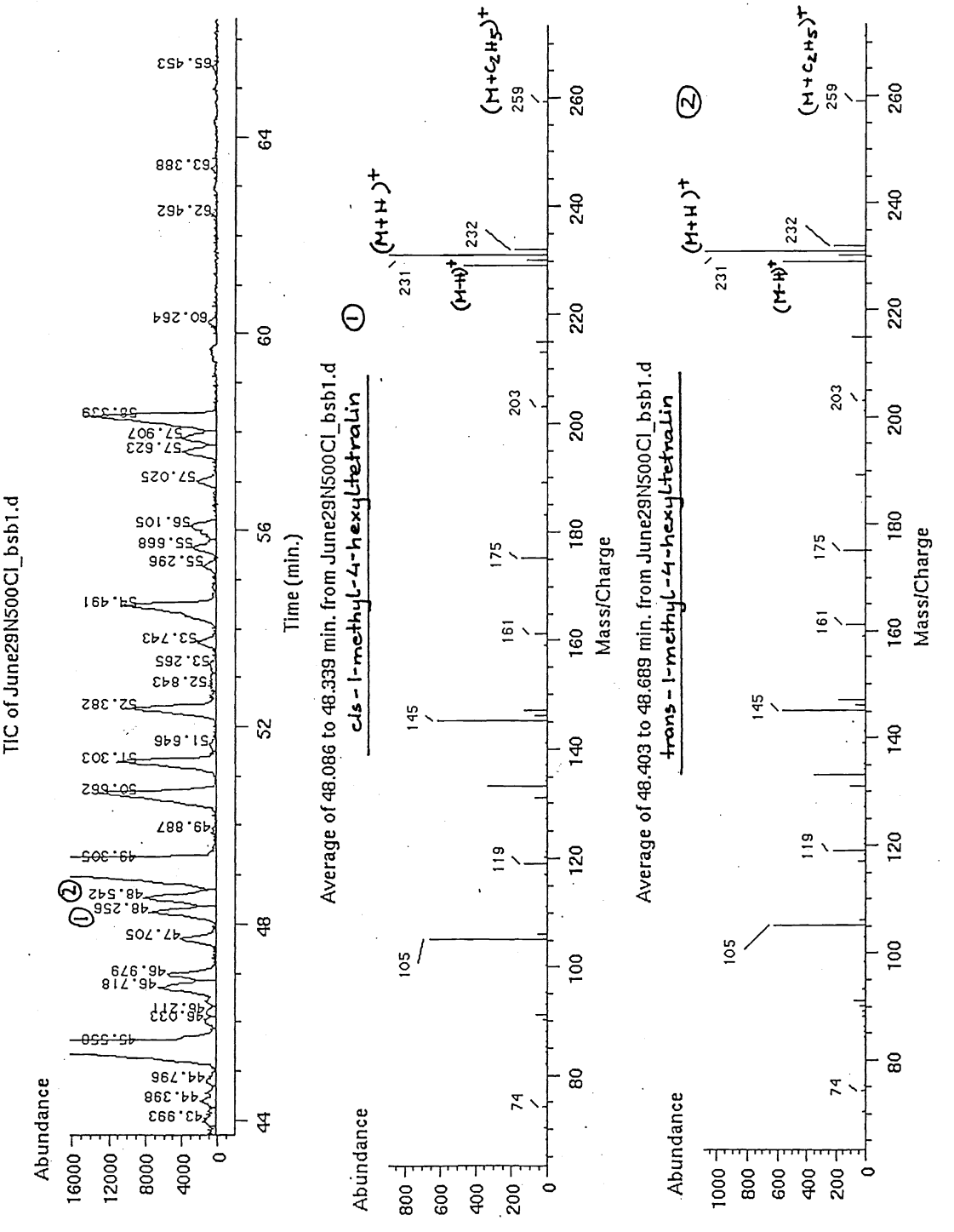
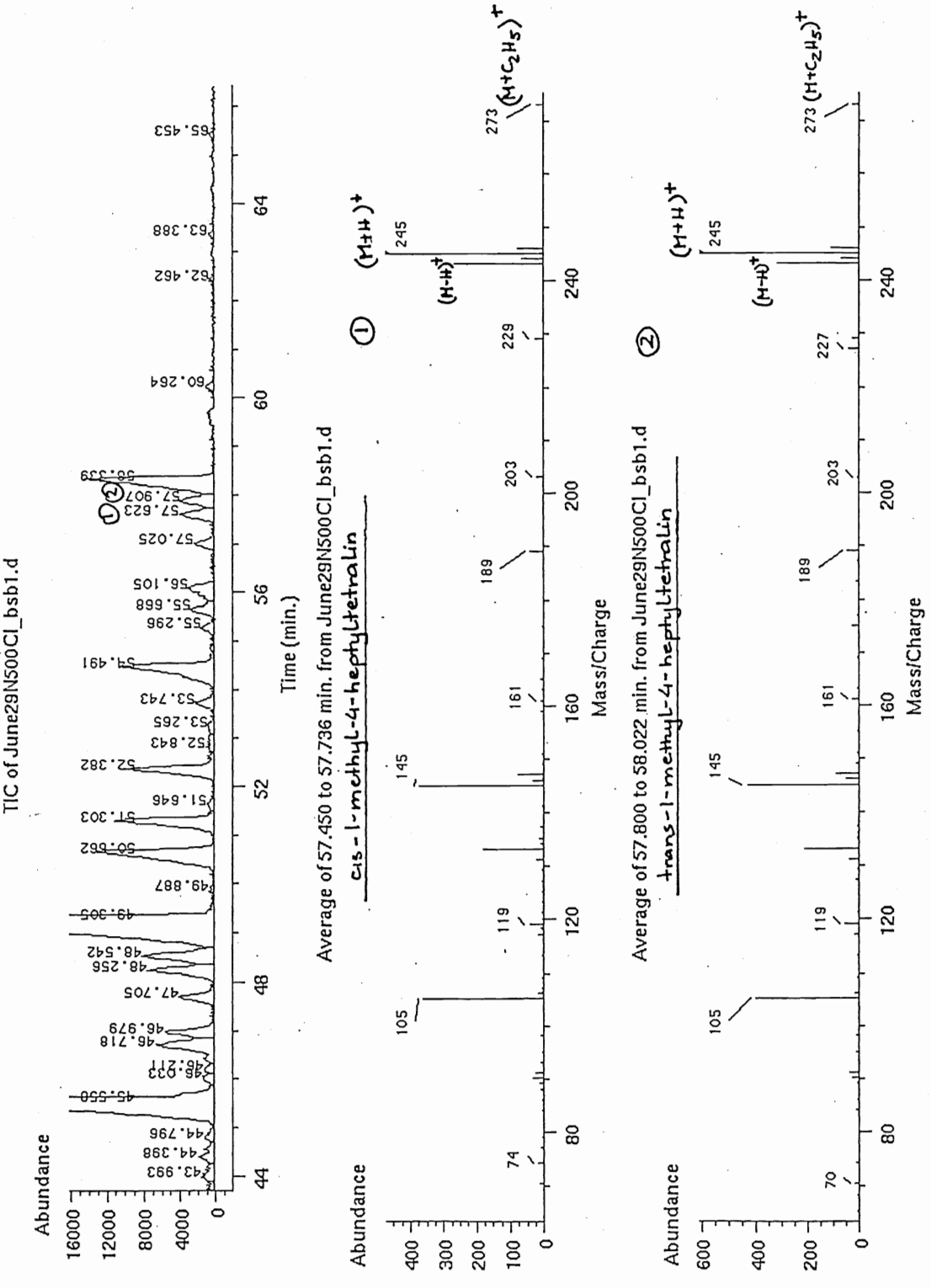


Figure 27

CI mass spectra of cis and trans-1-methyl-4-heptyltetralin

using methane as a reagent gas



NMR study allowed assignment of the cis structure to the more abundant isomer. The more abundant isomer of a model compound, 1-methyl-4-heptyltetralin was eluted first with a very short retention time. This finding can be confidently extended to all other linear dialkyltetralins.

II. Analyses of sample from "A1" to "A5"

1. *Alkylbenzene homologues' distribution - GC technique vs GC/MS technique*

As mentioned earlier, the determination of homologues distribution in commercial linear alkylbenzenes was carried out by gas chromatography. Suppliers of the raw material, LAB, for the molecular weight calculation purposes assume that all compounds included between the most external and most internal isomer of a given homologue have the same molecular weight. However, this assumption substantially changes when using the GC/MS technique results, because the mass distribution does not coincide with the GC results. By expanding a Total Ion Chromatogram, TIC, (**Figure 28**) it was observed that branched alkylbenzenes of a given number of carbon atoms are distributed between the corresponding linear isomers of the same number of carbon atoms and one carbon atom lighter. In other words, C_{12}-branched alkylbenzenes are eluted with C_{12} and C_{11} linear isomers, but in particular within C_{11} isomers. The same pattern was observed for the other homologues in all analyzed samples, "A1" to "A5". Another observation was that 2-phenyl isomer represents the highest percent of the total percent of all linear alkylbenzene isomers.

For the *initial* part of this study, results (**Table 3**, **4** and **5**) for the two analytical

Figure 28

Expanded TIC Chromatogram of sample "A5"

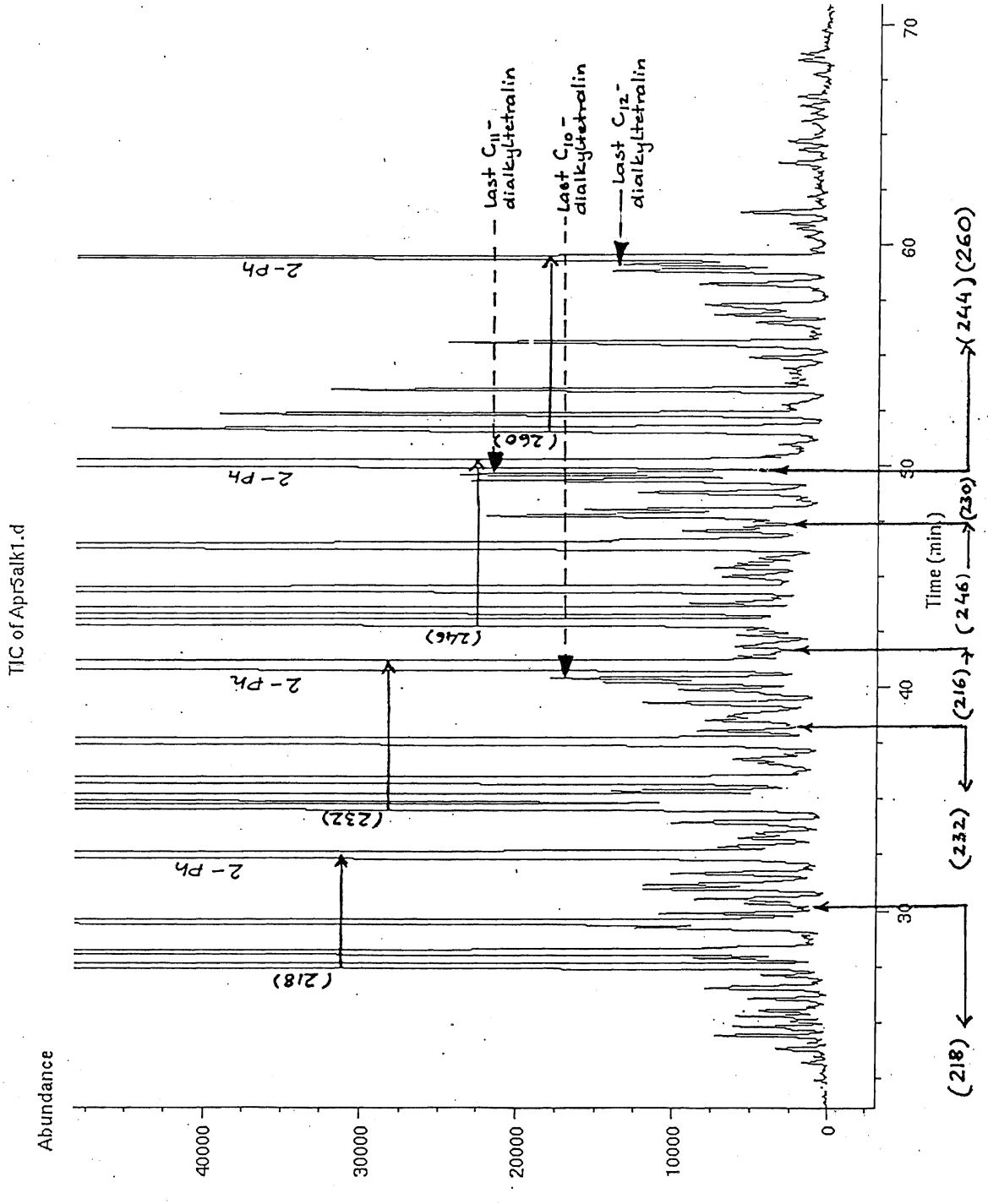


Table 3

Linear alkylbenzene distribution in sample "A3"

Sample: "A3" (April 13/92)

	between isomers		actual
	% Total Area		% Total Area
		2-Phenyl	
C10 (218)	8.72		7.85
C11 (232)	12.68		12.45
C12 (246)	6.83		6.70
C13 (260)	1.25		1.23
Total %	29.48		28.23
		3-Phenyl	
C10 (218)	4.94		4.85
C11 (232)	7.87		7.73
C12 (246)	4.65		4.56
C13 (260)	1.01		1.04
Total %	18.47		18.18
		4-Phenyl	
C10 (218)	4.81		4.72
C11 (232)	7.32		7.45
C12 (246)	3.81		3.74
C13 (260)	0.78		0.77
Total %	16.72		16.68
		5-Phenyl	
C10 (218)	5.02		4.93
C11 (232)	7.97		7.83
C12 (246)	4.43		4.45
C13 (260)	0.93		0.93
Total %	18.35		18.14
		6-Phenyl or 6/7-Phenyl	
C11 (232)	3.52		3.46
C12 (246)	4.25		4.17
C13 (260)	1.43		1.41
Total %	9.2		9.04

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Table 4

Linear alkylbenzene distribution in sample "A4"

Sample: "A4" (January 28/93)

	between isomers		actual
	% Total Area		% Total Area
		2-Phenyl	
C10 (218)	7.54		7.32
C11 (232)	11.25		10.93
C12 (246)	7.44		7.23
C13 (260)	1.75		1.70
Total %	27.98		27.18
		3-Phenyl	
C10 (218)	4.68		4.55
C11 (232)	4.97		4.83
C12 (246)	5.36		5.21
C13 (260)	0.83		0.80
Total %	15.84		15.39
		4-Phenyl	
C10 (218)	4.31		4.19
C11 (232)	6.06		5.89
C12 (246)	4.29		4.17
C13 (260)	0.90		0.88
Total %	15.56		15.13
		5-Phenyl	
C10 (218)	4.85		4.71
C11 (232)	7.01		6.81
C12 (246)	4.67		4.54
C13 (260)	1.14		1.10
Total %	17.67		17.16
		6-Phenyl or 6/7-Phenyl	
C11 (232)	4.03		3.92
C12 (246)	4.65		4.52
C13 (260)	1.78		1.73
Total %	10.46		10.17

Table 5

Linear alkylbenzene distribution in sample "A5"

Sample: "A5" (April 15/93)

	between isomers		actual
	% Total Area		% Total Area
		2-Phenyl	
C10 (218)	7.09		6.98
C11 (232)	12.98		12.79
C12 (246)	7.61		7.50
C13 (260)	1.54		1.52
Total %	29.22		28.79
		3-Phenyl	
C10 (218)	4.1		4.04
C11 (232)	7.94		7.82
C12 (246)	4.91		4.83
C13 (260)	1.09		1.08
Total %	18.04		17.77
		4-Phenyl	
C10 (218)	4.00		3.94
C11 (232)	7.77		7.65
C12 (246)	4.13		4.07
C13 (260)	0.87		0.86
Total %	16.77		16.52
		5-Phenyl	
C10 (218)	3.80		3.75
C11 (232)	7.98		7.86
C12 (246)	4.71		4.63
C13 (260)	1.04		1.03
Total %	17.53		17.27
		6-Phenyl or 6/7-Phenyl	
C11 (232)	3.4		3.35
C12 (246)	4.41		4.34
C13 (260)	1.58		1.56
Total %	9.39		9.25

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techniques were reported as follows: for GC technique as **"between isomers"** and for GC/MS technique as **"actual"**. The summarized results for percent linear alkylbenzene distributions are presented in **Table 6**. The difference between supplier's analytical data and GC/MS data for linear isomers was observed to be between 0.14 % and 0.43 %.

2. ***Determination of dialkyltetralins distribution using GC/MS technique***

For the impurities like dialkyltetralins, observation was that dialkyltetralins of molecular weight corresponding to a given linear alkylbenzene homologue are eluted within the linear isomers having a molecular weight of one carbon atom higher. In other words, C_{11} dialkyltetralins are eluted with C_{12} linear alkylbenzene isomers. For the 30 m, SPB-20 capillary column, all dialkyltetralins corresponding to a given linear alkylbenzene homologue are eluted just before 2-phenyl isomer of the one carbon higher alkylbenzene homologue (**Figure 28**).

3. ***Determination of a total percent of impurities using GC/MS technique***

The total percent of impurities including all non-linear (branched) alkylbenzenes and dialkyltetralin (cyclic) is presented in **Table 7**. According to GC/MS results, sample "A4" from January 28, 1993, contains the highest amount of the impurities, at 14.82 %. Second highest, from April 15, 1993, contains over 10 % of branched alkylbenzenes and dialkyltetralins. According to GC method, results for the same two samples are not the highest amongst them all. As expected, reported results using GC/MS method differ from

Table 6

Percent linear isomer distribution - comparison of two methods:

GC (between isomers) and GC/MS (actual)

Linear Isomers Distribution (%)

between isomers

Position of Phenyl Group	Sample "A1" (January 31/91)	Sample "A2" (April 23/91)	Sample "A3" (April 13/92)	Sample "A4" (January 28/93)	Sample "A5" (April 15/93)
2-Phenyl	28.08	28.63	29.48	27.98	29.22
3-Phenyl	18.71	18.64	18.47	15.84	18.04
4-Phenyl	16.78	16.98	16.72	15.56	16.77
5-Phenyl	18.10	18.57	18.35	17.67	17.53
6 or 6/7-Phenyl	9.29	8.66	9.20	10.46	9.39

actual

Position of Phenyl Group	Sample "A1" (January 31/91)	Sample "A2" (April 23/91)	Sample "A3" (April 13/92)	Sample "A4" (January 28/93)	Sample "A5" (April 15/93)
2-Phenyl	27.48	28.1	28.23	27.18	28.79
3-Phenyl	18.31	18.23	18.18	15.39	17.77
4-Phenyl	16.44	16.54	16.68	15.13	16.52
5-Phenyl	17.71	18.16	18.14	17.16	17.27
6 or 6/7-Phenyl	9.09	8.47	9.04	10.17	9.25

Difference

Position of Phenyl Group	Sample "A1" (January 31/91)	Sample "A2" (April 23/91)	Sample "A3" (April 13/92)	Sample "A4" (January 28/93)	Sample "A5" (April 15/93)
2-Phenyl	-0.60	-0.53	-1.25	-0.80	-0.43
3-Phenyl	-0.40	-0.41	-0.29	-0.45	-0.27
4-Phenyl	-0.34	-0.44	-0.04	-0.43	-0.25
5-Phenyl	-0.39	-0.41	-0.21	-0.51	-0.26
6 or 6/7-Phenyl	-0.20	-0.19	-0.16	-0.29	-0.14

Table 7

Comparison of percent impurities such as branched alkylbenzenes and cyclic using two methods GC (between isomers) and GC/MS (actual)

Total % branched Alkylbanzenes

		between isomers	actual	Difference
Sample "A1"	(January 31/91	8.17	4.32	-3.85
Sample "A2"	(April 23/91)	7.76	4.31	-3.45
Sample "A3"	(April 13/92)	7.67	3.89	-3.78
Sample "A4"	(January 28/93	11.07	6.40	-4.67
Sample "A5"	(April 15/93)	7.82	4.63	-3.19

Total % Cyclic

		between isomers	actual
Sample "A1"	(January 31/91)		6.1
Sample "A2"	(April 23/91)		5.88
Sample "A3"	(April 13/92)		5.71
Sample "A4"	(January 28/93)		8.42
Sample "A5"	(April 15/93)		5.82

Total % branched Alkylbenzenes /Cyclic

		between isomers	actual	Difference
Sample "A1"	(January 31/91	8.17	10.42	2.25
Sample "A2"	(April 23/91)	7.76	9.89	2.13
Sample "A3"	(April 13/92)	7.67	9.60	1.93
Sample "A4"	(January 28/93	11.07	14.82	3.75
Sample "A5"	(April 15/93)	7.82	10.45	2.63

GC method. The methods agree only for one sample, sample "A4" with respect to level of impurities. Both report them as being the highest in all analyzed samples, at 14.82% and 11.07 %. .

4. ***Determination of molecular weight distribution and the average molecular weight***

Having observed the above differences, linear alkylbenzene molecular weight determination results, as well as, the calculated percentage of the total non-linear and cyclic compounds, should not be the same using GC/MS vs GC technique (**Table 8**, **9**, **10**, **11** and **12**). The higher the content of impurities, like branched alkylbenzenes and dialkyltetralins in commercial LAB, the bigger difference should be observed in the final molecular weight calculations. Indeed, the difference in results from 1.28 up to 2.00 was observed (**Table 13**) with results being on the lower side using the GC/MS technique.

5. ***Determination of a total percent of 2-phenyl isomers and comparison to the reported values***

Drozd and Gorman[8], Moreno et al.[11], Cohen et al.[12], and Matheson and Matson[13] reported that total percent of 2-phenyl isomer is very important to know in formulation of every detergent product. As part of the specifications, the percent of 2-phenyl isomer is reported on the C.O.A with every shipment of commercial linear alkylbenzene. **Table 13** summarizes the total percent of 2-phenyl isomer present in the analyzed samples "A1" to "A5". The comparison with the C.O.A. results is not complete since some of the

Table 8

Moleculr weight distribution of LAB in sample "A1" (GC vs GC/MS)

Sample: "A1" (January 31/91)

	between isomers		actual	
			Linear Alkylbenzenes	
	Area (M)	%	Area (M)	%
C10 (218)	208.1	21.00	210	21.61
C11 (232)	400.7	40.44	391.3	40.28
C12 (246)	250.3	25.26	234.8	24.17
C13 (260)	50.80	5.13	34.26	3.53
			Branched Alkylbenzenes	
C10 (218)	13.15	1.33	15.42	1.59
C11 (232)	26.96	2.72	17.63	1.81
C12 (246)	24.35	2.46	8.88	0.91
C13 (260)	16.54	1.67		
			Cyclic	
Dialkyltetralins (216)			17.10	1.76
Dialkyltetralins (230)			18.15	1.87
Dialkyltetralins (244)			24.02	2.47
Total Area (M)	990.9		971.56	
Total %		100		100
Total NON-Linear Area (M)	81.00		41.93	
Total Cyclic Area (M)			59.27	
Total NON-Linear (%)		8.17		4.32
Total Cyclic (%)		0		6.10
Total NON-Linear/Cyclic (%)		**8.17**		**10.42**
Average Molecular Weight		**234.66**		**233.23**

Table 9

Moleculr weight distribution of LAB in sample "A2" (GC vs GC/MS)

Sample: "A2" (April 23/91)

	between isomers		actual	
			Linear Alkylbenzenes	
	Area (M)	%	Area (M)	%
C10 (218)	224.6	23.37	226.3	23.89
C11 (232)	393.7	40.96	385.7	40.71
C12 (246)	229.2	23.85	216.7	22.87
C13 (260)	38.99	4.06	24.94	2.63
			Branched Alkylbenzenes	
C10 (218)	12.36	1.29	14.06	1.48
C11 (232)	25.91	2.70	17.97	1.90
C12 (246)	22.30	2.32	8.81	0.93
C13 (260)	14.05	1.46		
			Cyclic	
Dialkyltetralins (216)			16.65	1.76
Dialkyltetralins (230)			16.47	1.74
Dialkyltetralins (244)			19.78	2.09
Total Area (M)	961.11		947.38	
Total %		100		100
Total NON-Linear Area (M)	74.62		40.84	
Total Cyclic Area (M)			52.90	
Total NON-Linear (%)		7.76		4.31
Total Cyclic (%)		0		5.58
Total NON-Linear/Cyclic (%)		**7.76**		**9.89**
Average Molecular Weight		**233.76**		**232.45**

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Table 10

Moleculr weight distribution of LAB in sample "A3" (GC vs GC/MS)

Sample: "A3" (April 13/92)

	between isomers		actual	
			Linear Alkylbenzenes	
	Area (M)	%	Area (M)	%
C10 (218)	202.8	22.18	205.4	22.95
C11 (232)	358.3	39.19	347.4	38.82
C12 (246)	223.3	24.43	210.2	23.49
C13 (260)	59.71	6.53	45.94	5.13
			Branched Alkylbenzenes	
C10 (218)	10.62	1.16	13.13	1.47
C11 (232)	24.78	2.71	13.86	1.55
C12 (246)	20.92	2.29	7.83	0.88
C13 (260)	13.77	1.51		
			Cyclic	
Dialkyltetralins (216)			13.92	1.56
Dialkyltetralins (230)			16.11	1.80
Dialkyltetralins (244)			21.02	2.35
Total Area (M)	914.2		894.81	
Total %		100		100
Total NON-Linear Area (M)	70.09		34.82	
Total Cyclic Area (M)			51.05	
Total NON-Linear (%)		7.67		3.89
Total Cyclic (%)		0		5.71
Total NON-Linear/Cyclic (%)		**7.67**		**9.60**
Average Molecular Weight		**234.72**		**233.43**

Table 11

Moleculr weight distribution of LAB in sample "A4" (GC vs GC/MS)

Sample: "A4" (January 28/93)

	between isomers		actual	
			Linear Alkylbenzenes	
	Area (M)	%	Area (M)	%
C10 (218)	80.6	20.69	81.87	21.48
C11 (232)	127.1	32.62	124.5	32.67
C12 (246)	106.9	27.44	96.03	25.20
C13 (260)	31.89	8.18	22.2	5.83
			Branched Alkylbenzenes	
C10 (218)	6.5	1.67	7.68	2.02
C11 (232)	11.6	2.98	9.03	2.37
C12 (246)	15.36	3.94	7.68	2.02
C13 (260)	9.69	2.49		
			Cyclic	
Dialkyltetralins (216)			6.92	1.82
Dialkyltetralins (230)			10.87	2.85
Dialkyltetralins (244)			14.28	3.75
Total Area (M)	389.64		381.06	
Total %		100		100
Total NON-Linear Area (M)	43.15		24.39	
Total Cyclic Area (M)			32.07	
Total NON-Linear (%)		11.07		6.40
Total Cyclic (%)				8.42
Total NON-Linear/Cyclic (%)		**11.07**		**14.82**
Average Molecular Weight		**236.25**		**234.25**

Table 12

Moleculr weight distribution of LAB in sample "A5" (GC vs GC/MS)

Sample: "A5" (April 15/93)

	between isomers		actual	
			Linear Alkylbenzenes	
	Area (M)	%	Area (M)	%
C10 (218)	184.2	22.31	185.3	22.59
C11 (232)	331.9	40.19	328.6	40.06
C12 (246)	193.6	23.45	182.2	22.21
C13 (260)	51.48	6.23	38.48	4.69
			Branched Alkylbenzenes	
C10 (218)	11.46	1.39	12.55	1.53
C11 (232)	21.65	2.62	18.34	2.24
C12 (246)	18.47	2.24	7.10	0.87
C13 (260)	13.00	1.57		
			Cyclic	
Dialkyltetralins (216)			13.47	1.64
Dialkyltetralins (230)			13.29	1.62
Dialkyltetralins (244)			21.00	2.56
Total Area (M)	825.76		820.33	
Total (%)		100		100
Total NON-Linear Area (M)	64.58		37.99	
Total Cyclic Area (M)			47.76	5.82
Total NON-Linear (%)		7.82		4.63
Total Cyclic (%)				5.82
Total NON-Linear/Cyclic (%)		**7.82**		**10.45**
Average Molecular Weight		**234.46**		**233.18**

Table 13

LAB molecular weight and percent of the 2-phenyl isomer - comparison between two methods GC and GC/MS

		Molecular Weight				
		between isomers	actual	Difference	C.O.A. (Certificate of Analysis)	
Sample "A1"	(January 31/91)	234.66	233.23	1.43	*	
Sample "A2"	(April 23/91)	233.76	232.45	1.31	*	
Sample "A3"	(April 13/92)	234.72	233.43	1.29	*	
Sample "A4"	(January 28/93)	236.25	234.25	2.00		236.3
Sample "A5"	(April 15/93)	234.46	233.18	1.28		236.5

		Total % 2-Phenyl Isomer		
		actual	C.O.A. (Certificate of Analysis)	Difference
Sample "A1"	(January 31/91)	27.48	*	
Sample "A2"	(April 23/91)	28.10	*	
Sample "A3"	(April 13/92)	28.23	*	
Sample "A4"	(January 28/93)	27.18	28.5	-1.32
Sample "A5"	(April 15/93)	28.79	28.6	0.19

NOTE: * - not available

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C.O.A., especially from 1991 and 1992 were no longer available.

Actual average molecular weight calculations were repeated for sample "A5" with different amount of sample dissolved in the same amount of solvent. Results are almost identical, 234.46 vs 234.37 and are presented in **Table 14** and **Table 15**.

III. Analyses of samples from "A" to "J"

1. *Distribution of linear alkylbenzene isomers*

The *main* part of this study was extended to other commercial linear alkylbenzenes. A total of ten raw material samples, sample "A" to "J", from four different suppliers, company #1 to company #4, were analyzed on GC/MS system. Reported molecular weights (C.O.A.) varied from 231.6 amu to 242.0 amu, and percent of 2-phenyl isomer varied from 13.0 % to 31.0 %. Graphical representations of the analyzed samples, the TIC chromatograms are presented in **Figure 29a&b**, **30a&b**, **31a&b**, **32a&b**, **33a&b**, **34a&b**, **35a&b**, **36a&b**, **37a&b**, and **38a&b**. All peaks in each chromatogram were labelled as follows: for example, for C_{10} homologue "5-Ph" represents 5-phenyldecane, "4-Ph" represents 4-phenyldecane, "3-Ph" represents 3-phenyldecane, and "2-Ph" represents 2-phenyldecane. Also, a letter "B" and a letter "T" were used to label all *branched* alkylbenzenes and all *dialkyltetralins*, respectively. Full scan mode did not allow for complete separation of all *dialkyltetralins* thus on the TIC chromatograms there are only a few peaks labelled with a letter "T".

Instrumentally the *main* part was a continuation of the *initial* part of this study with an exception for a different capillary column, Restek's Rt_x-20. With the use of a

Table 14

Molecular weight distribution of LAB in sample "A5"

Sample: "A5" (April 15/93) Total weight: 0.045 g

	between isomers		actual	
			Linear Alkylbenzenes	
	Area (M)	%	Area (M)	%
C10 (218)	333.7	18.86	330.9	19.22
C11 (232)	706.1	39.90	688.7	40.00
C12 (246)	460.1	26.00	435.1	25.27
C13 (260)	124.5	7.04	100.1	5.81
			Branched Alkylbenzenes	
C10 (218)	24.61	1.39	21.80	1.27
C11 (232)	53.44	3.02	36.07	2.10
C12 (246)	40.78	2.30	15.84	0.92
C13 (260)	26.44	1.49		
			Cyclic	
Dialkyltetralins (216)			23.45	1.36
Dialkyltetralins (230)			28.21	1.64
Dialkyltetralins (244)			41.42	2.41
Total Area (M)	1769.67		1721.59	
Total %		100		100
Total NON-Linear	145.27		73.71	
Total Cyclic			93.08	5.41
Total NON-Linear (%)		8.21		4.28
Total Cyclic (%)				5.41
Total NON-Linear/Cyclic (%)		**8.21**		**9.69**
Average Molecular Weight		**235.52**		**234.46**

Table 15

Molecular weight distribution of LAB in sample "A5" - continued

Sample: "A5" (April 15/93) **Total weight: 0.067 g**

	between isomers		actual	
			Linear Alkylbenzenes	
	Area (M)	%	Area (M)	%
C10 (218)	623	19.19	616.4	19.52
C11 (232)	1290.7	39.75	1259.4	39.88
C12 (246)	845.8	26.05	801.3	25.37
C13 (260)	225.5	6.95	176.8	5.60
			Branched Alkylbenzenes	
C10 (218)	40.3	1.24	33.69	1.07
C11 (232)	96.8	2.98	65.65	2.08
C12 (246)	75.92	2.34	31.46	1.00
C13 (260)	48.65	1.50		
			Cyclic	
Dialkyltetralins (216)			49.98	1.58
Dialkyltetralins (230)			49.99	1.58
Dialkyltetralins (244)			73.4	2.32
Total Area (M)	3246.67		3158.07	
Total %		100		100
Total NON-Linear Area (M)	261.67		130.80	
Total Cyclic Area (M)			173.37	
Total NON-Linear (%)		8.06		4.14
Total Cyclic (%)				5.49
Total NON-Linear/Cyclic (%)		**8.06**		**9.63**
Average Molecular Weight		**235.48**		**234.37**

Figure 29 a

TIC Chromatogram of sample "A"

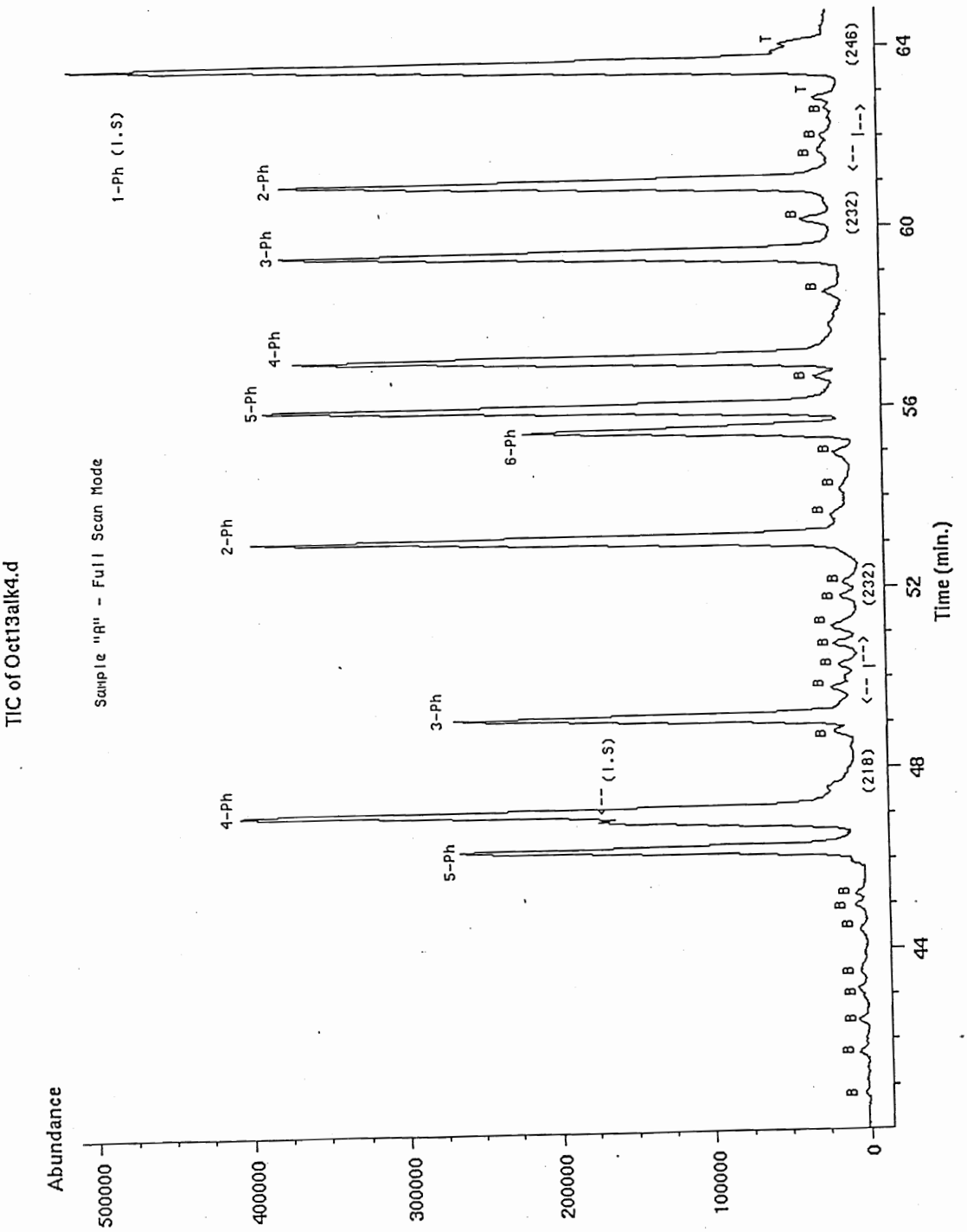
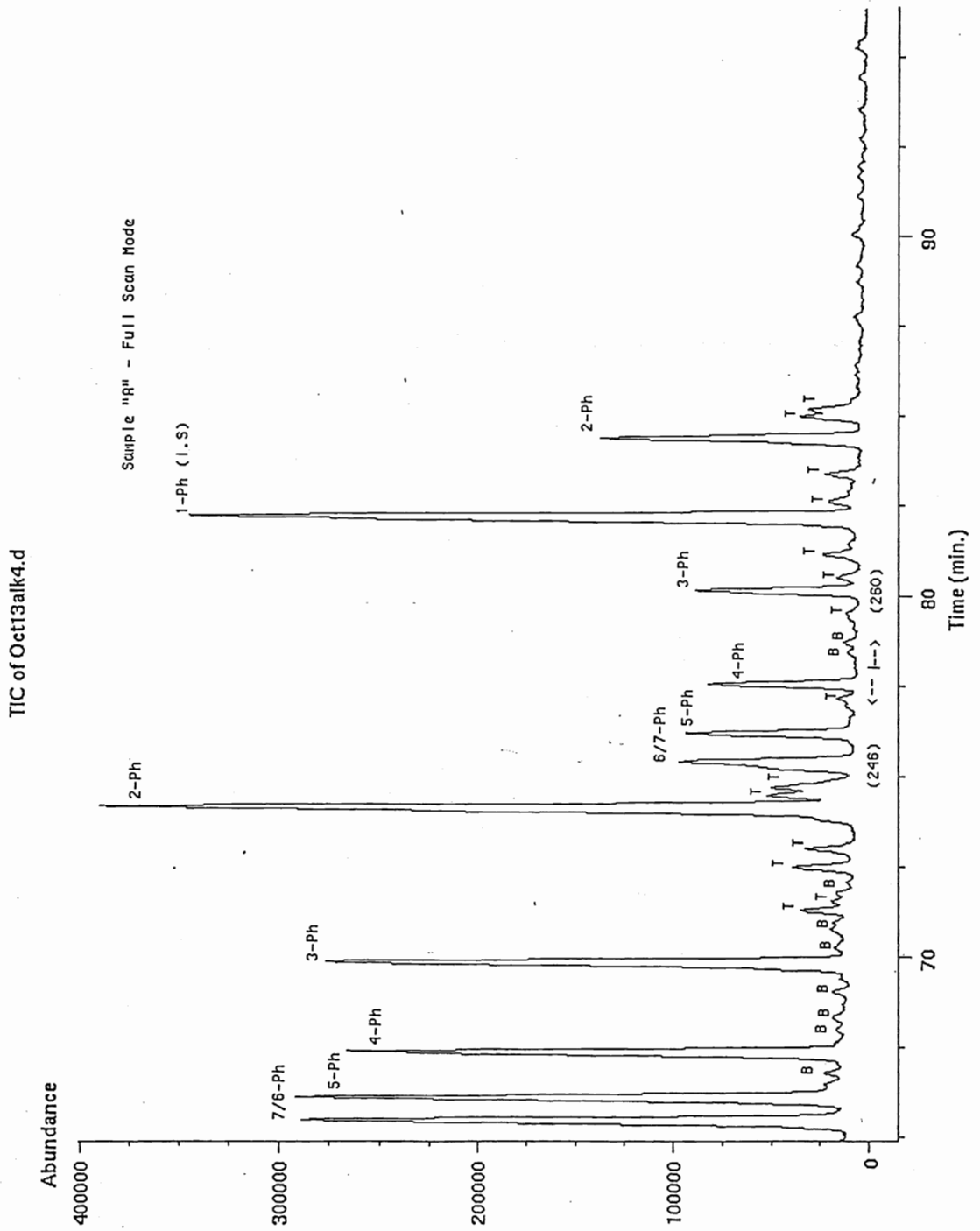


Figure 29 b

TIC Chromatogram of sample "A" - continued



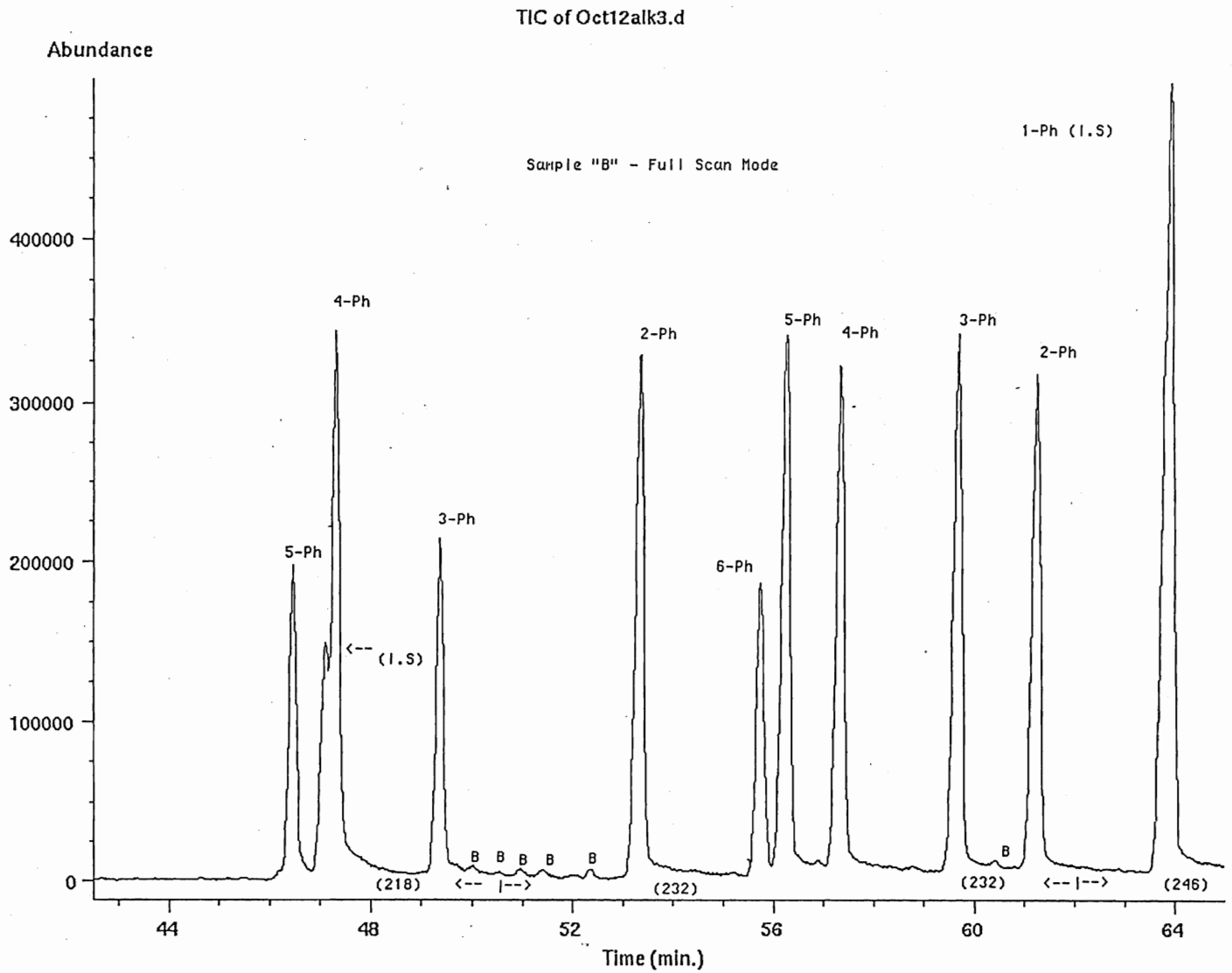


Figure 30 a

TIC Chromatogram of sample "B"

Figure 30 b

TIC Chromatogram of sample "B" - continued

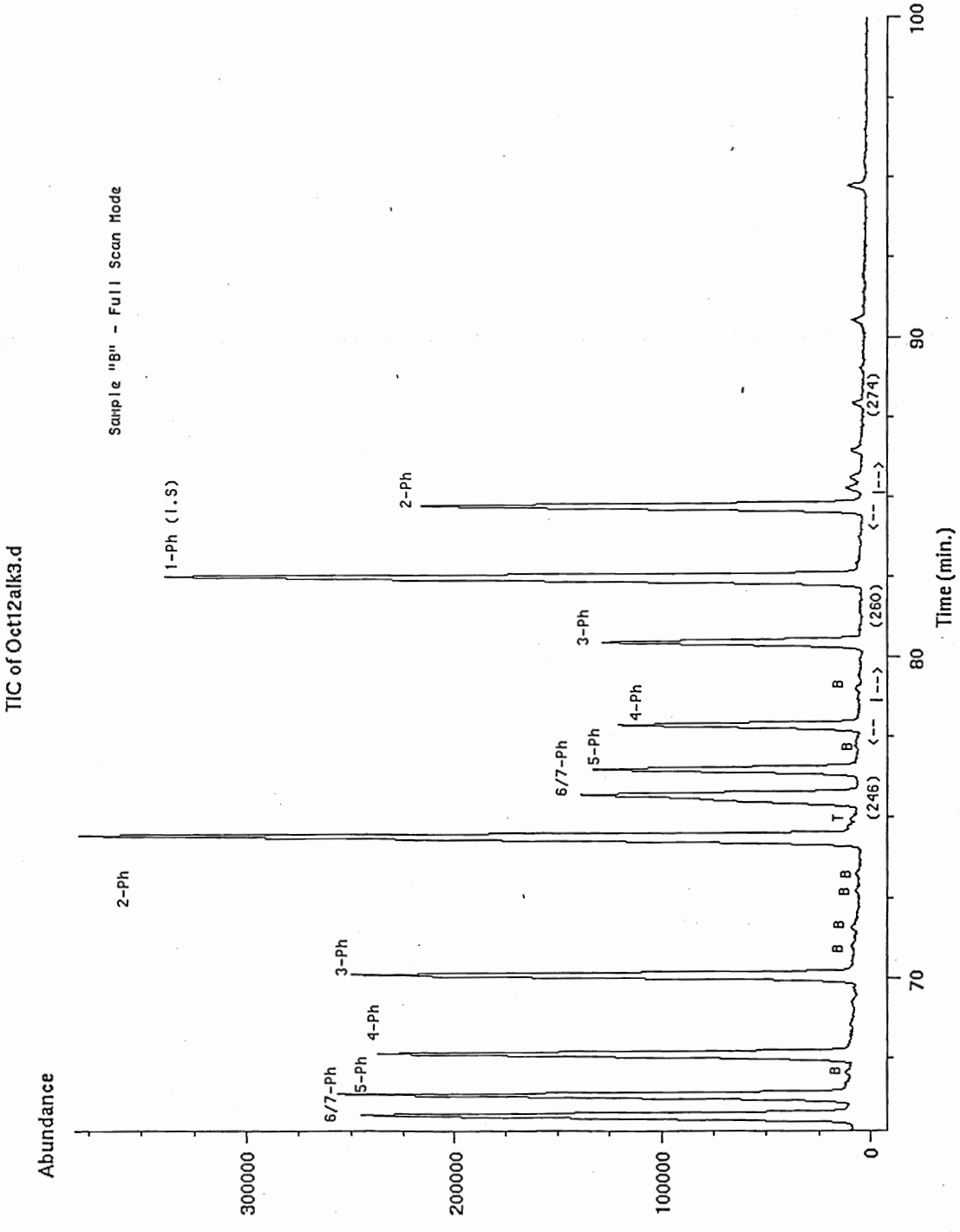


Figure 31 a

TIC Chromatogram of sample "C"

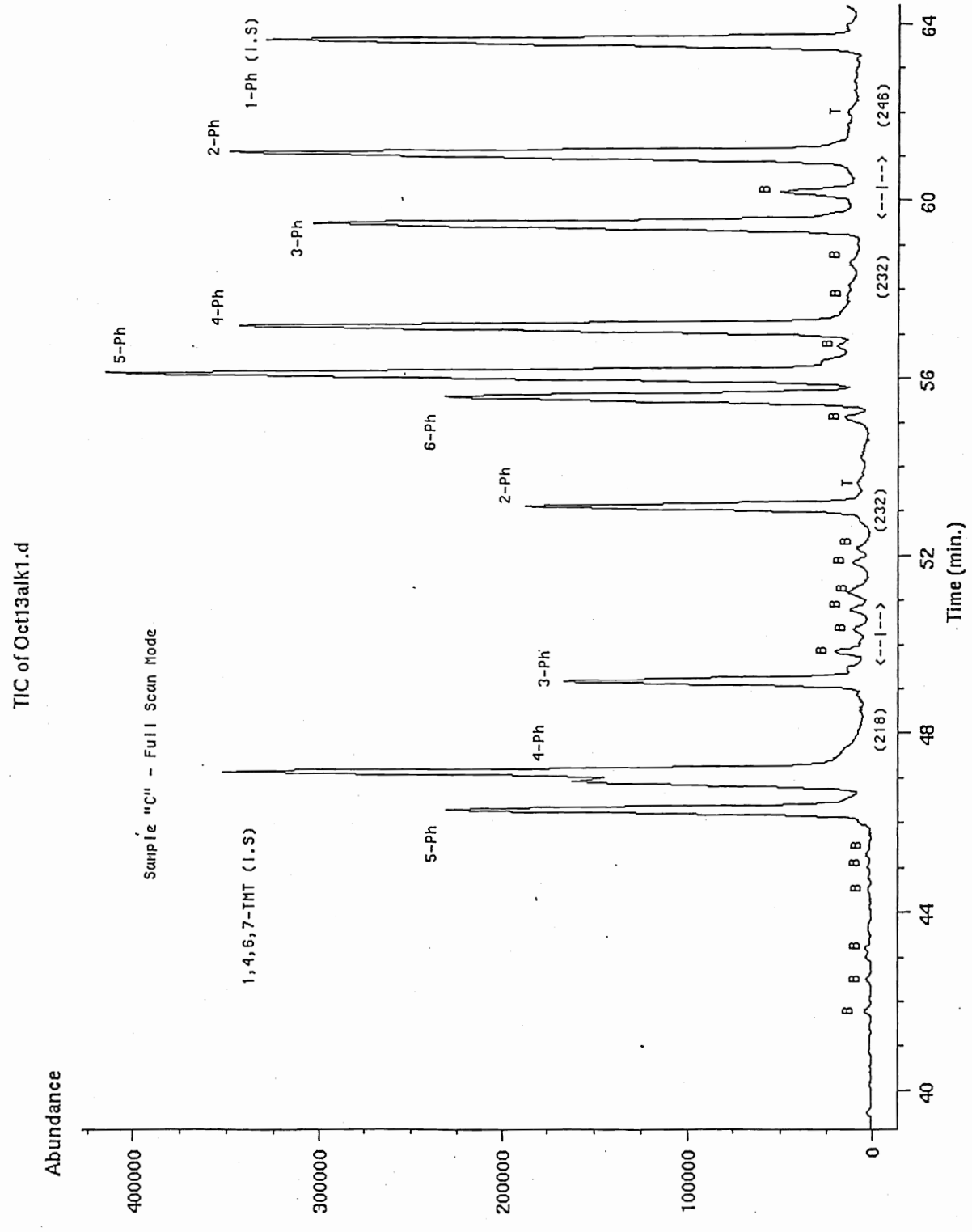
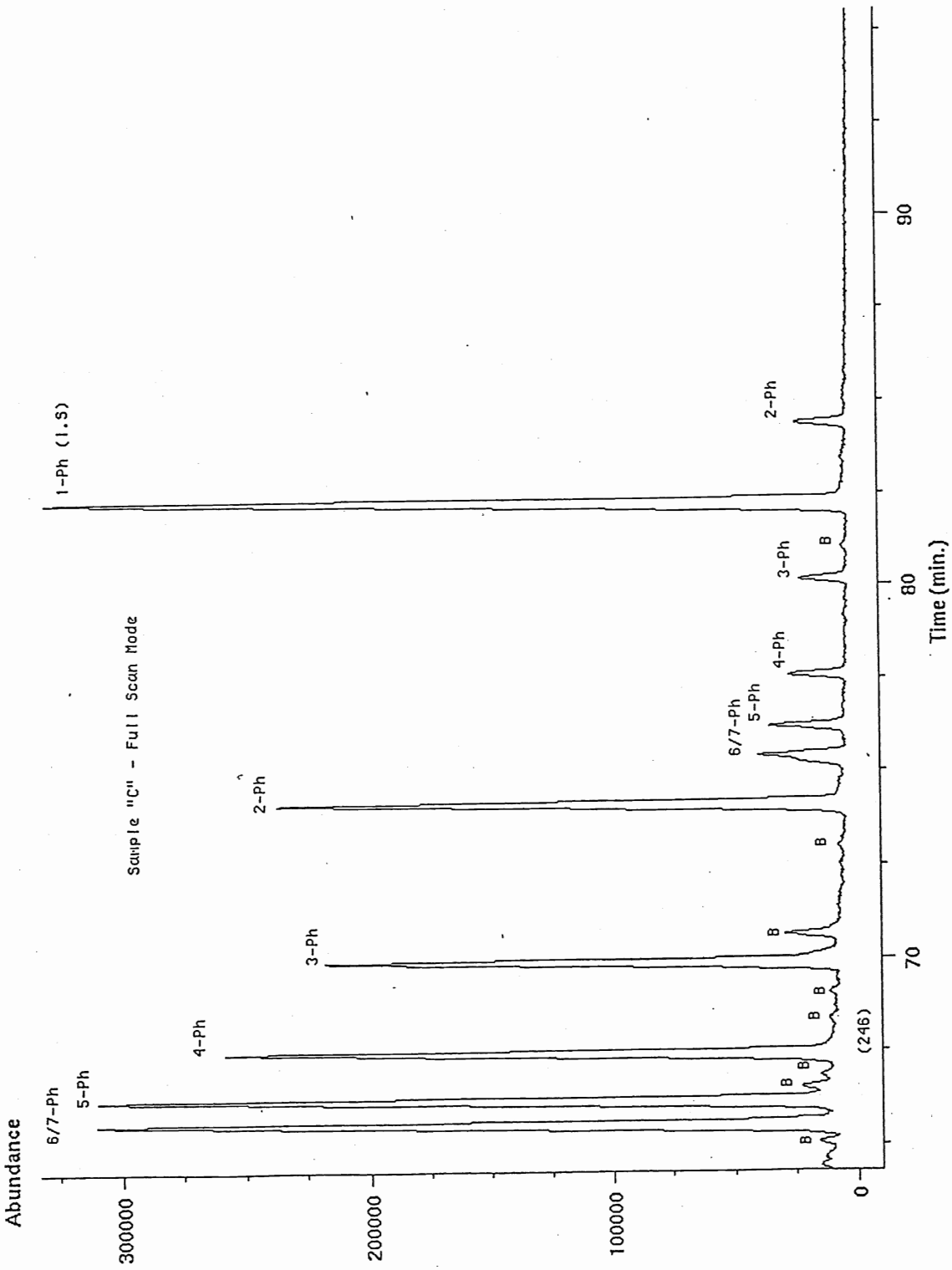


Figure 31 b

TIC Chromatogram of sample "C" - continued



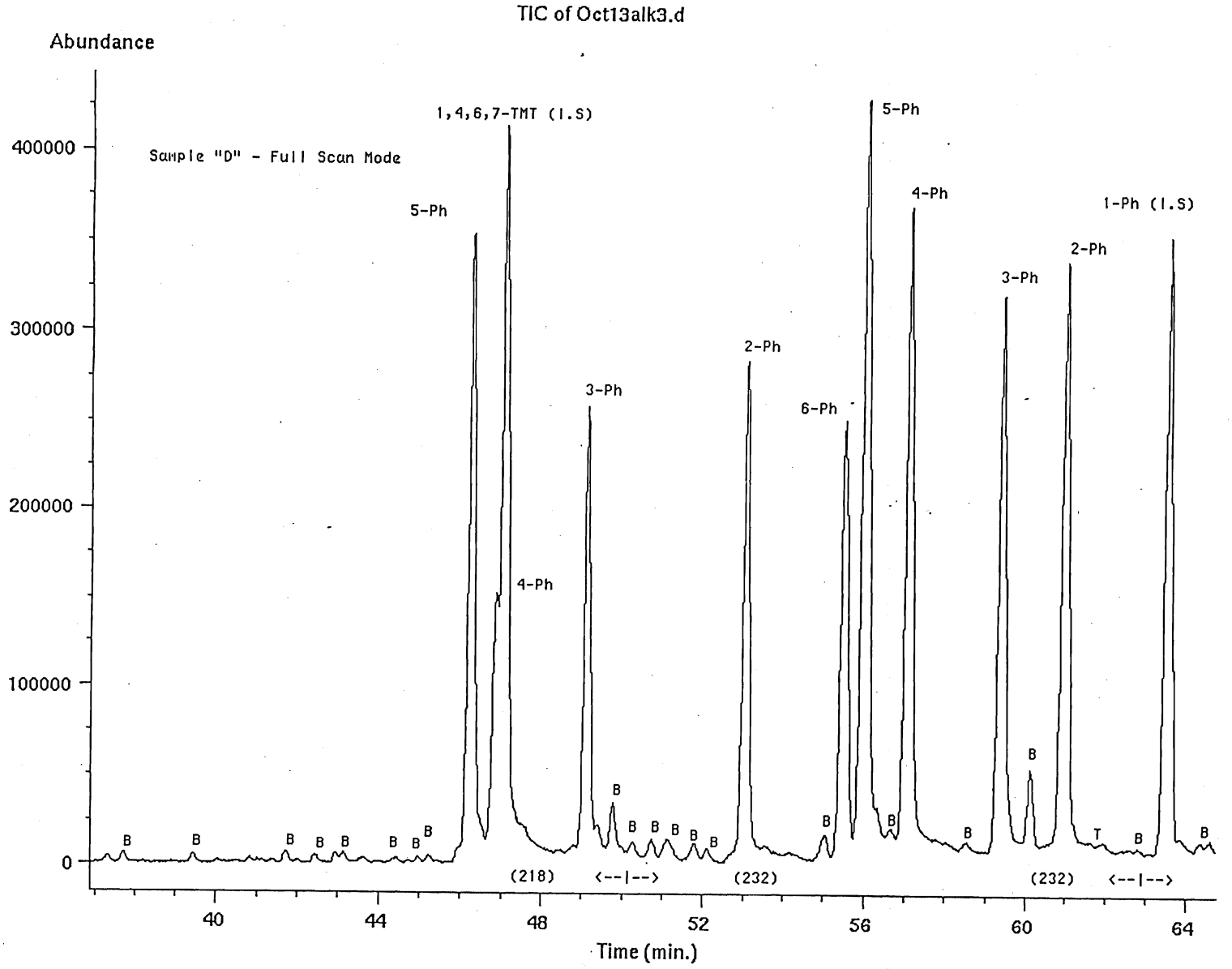
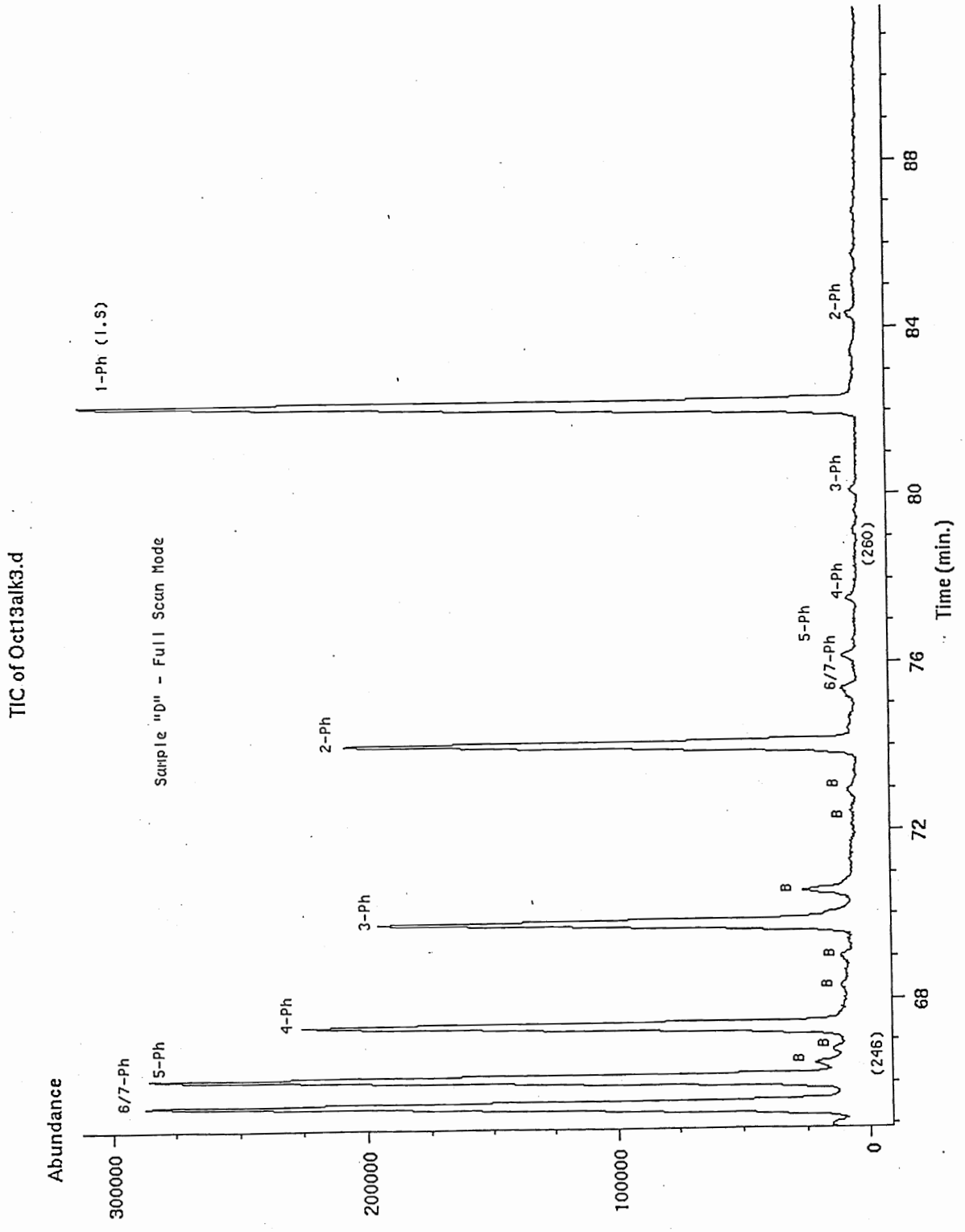


Figure 32 a

TIC Chromatogram of sample "D"

Figure 32 b

TIC Chromatogram of sample "D" - continued



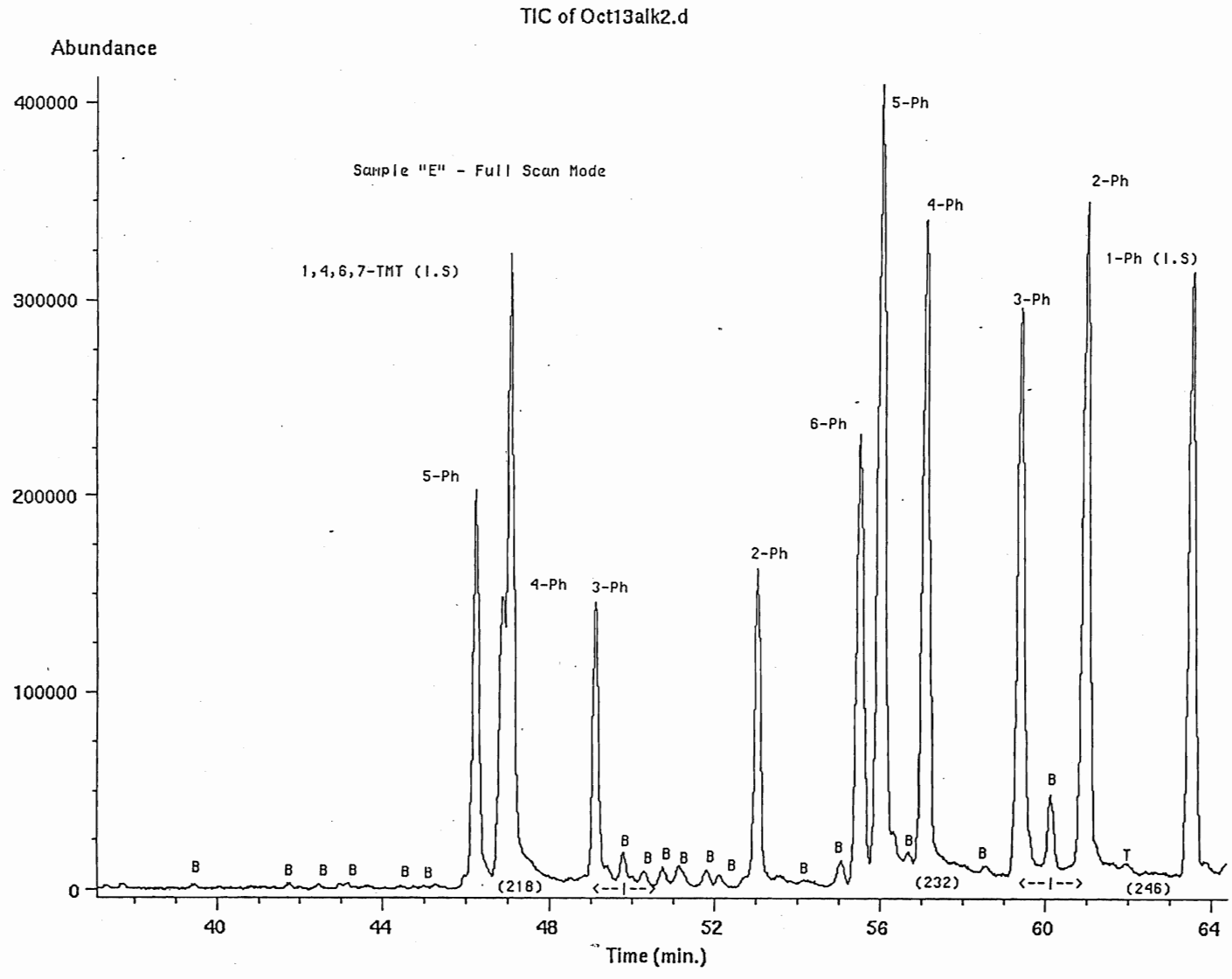


Figure 33a

TIC Chromatogram of sample 'E"

Figure 33 b

TIC Chromatogram of sample "E" - continued

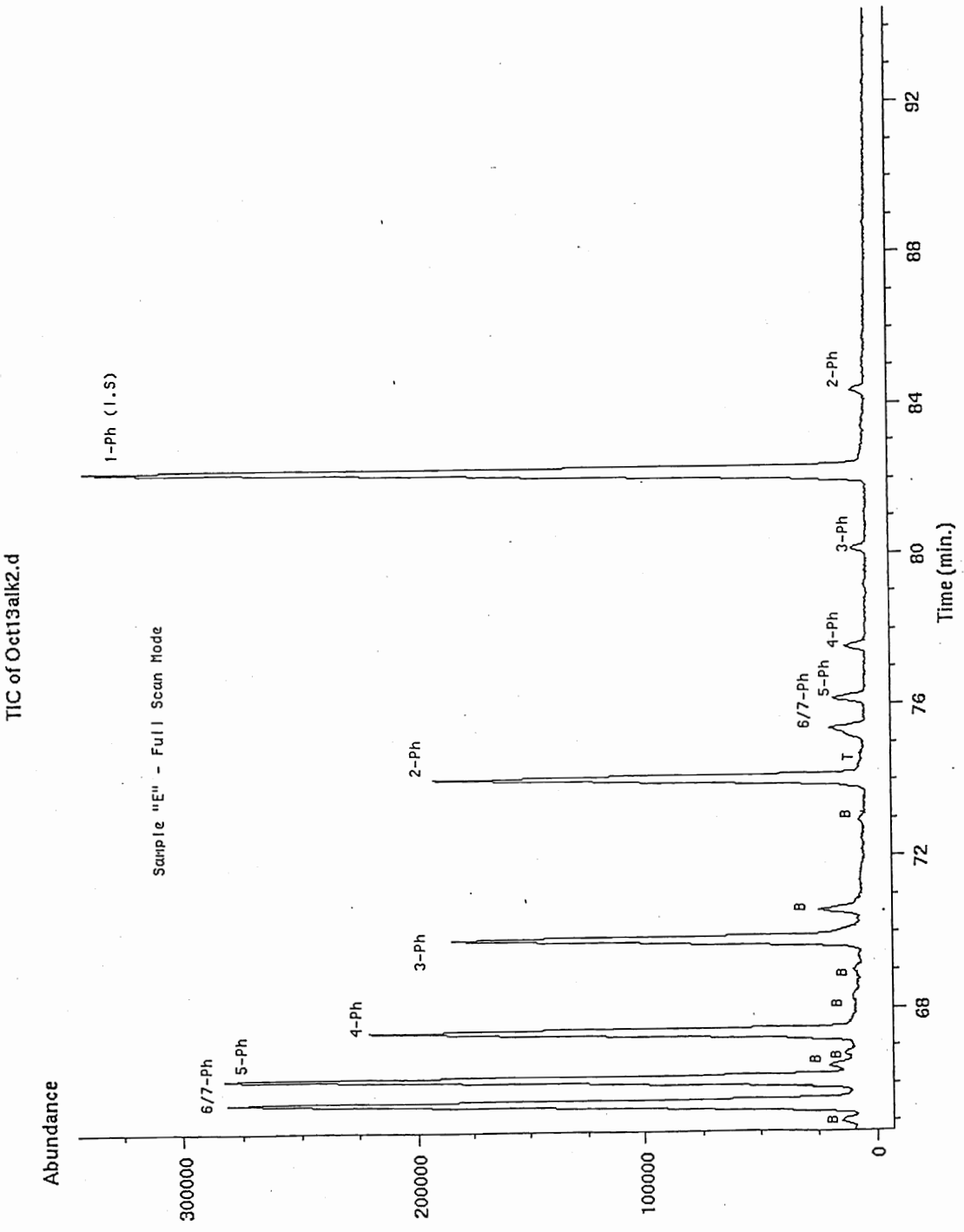


Figure 34 a

TIC Chromatogram of sample "F"

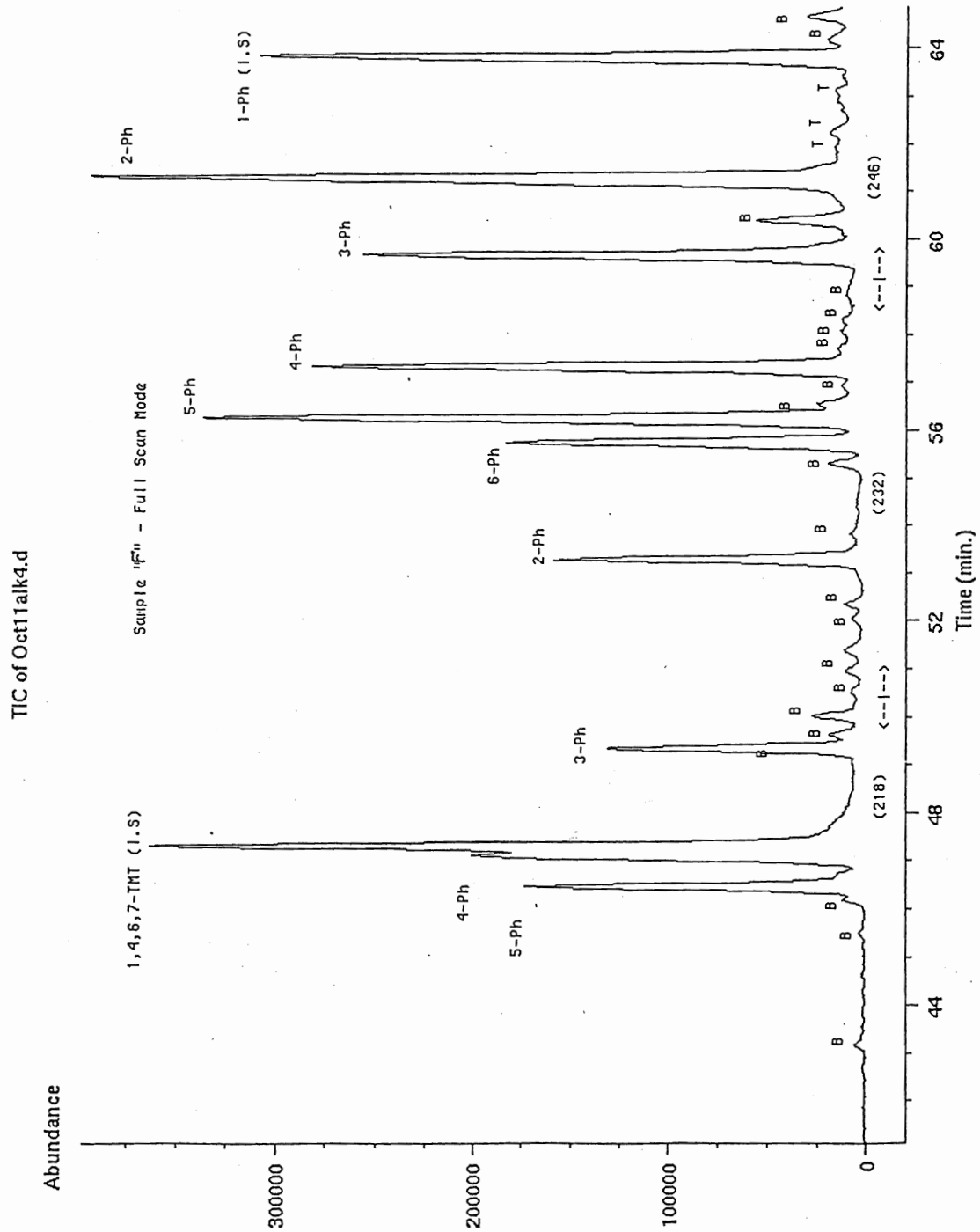


Figure 34 b

TIC Chromatogram of sample "F" - continued

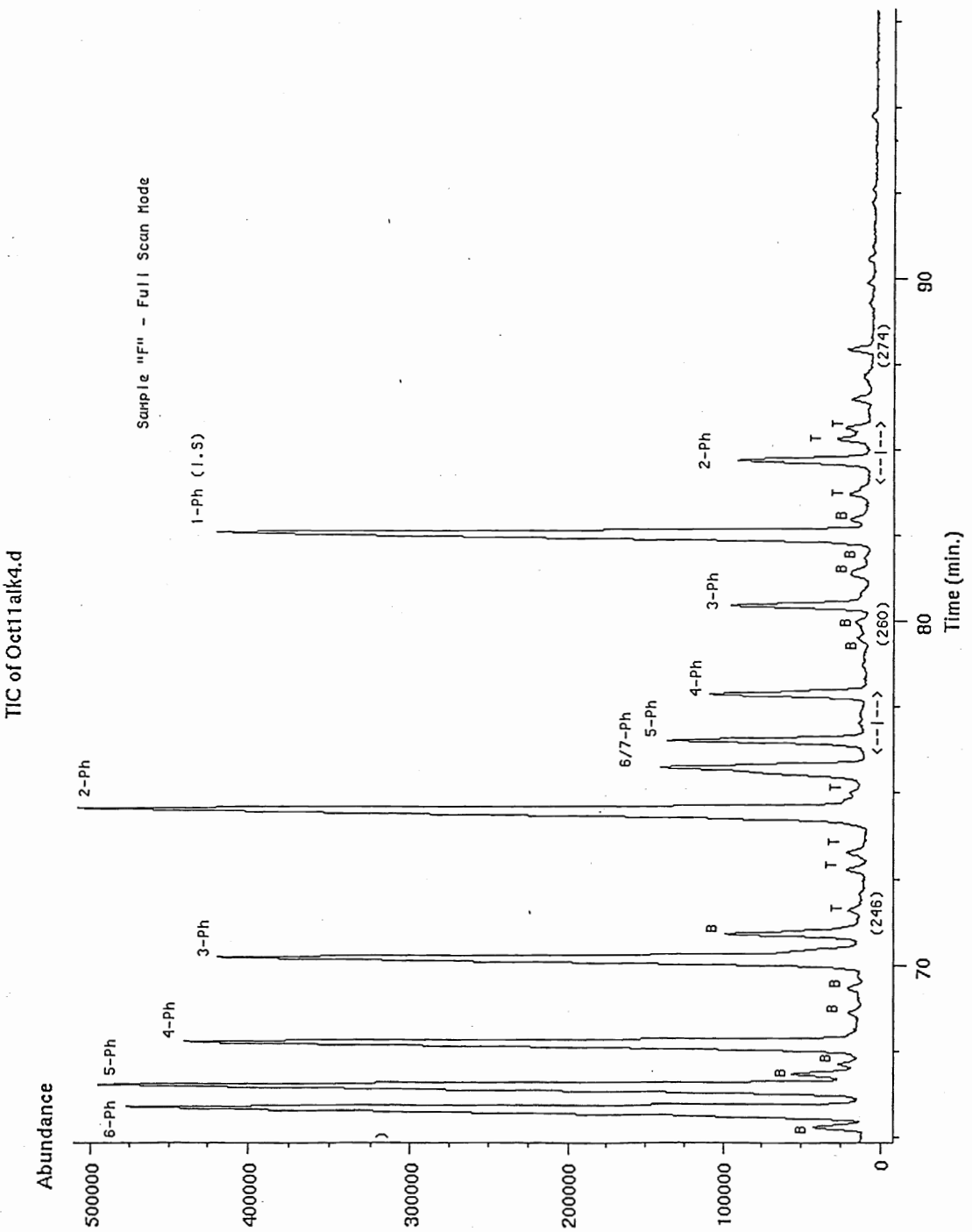


Figure 35 a

TIC Chromatogram of sample "G"

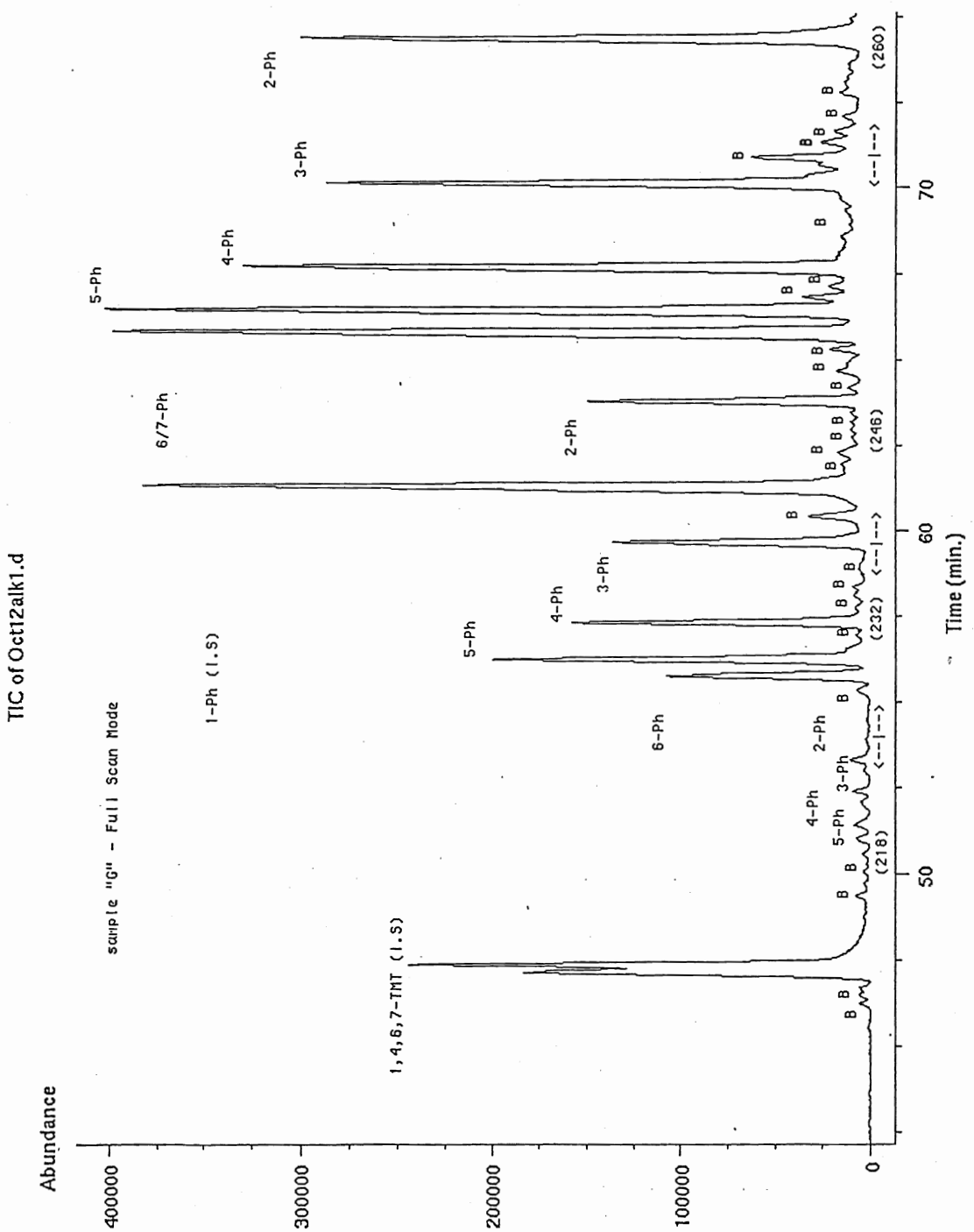
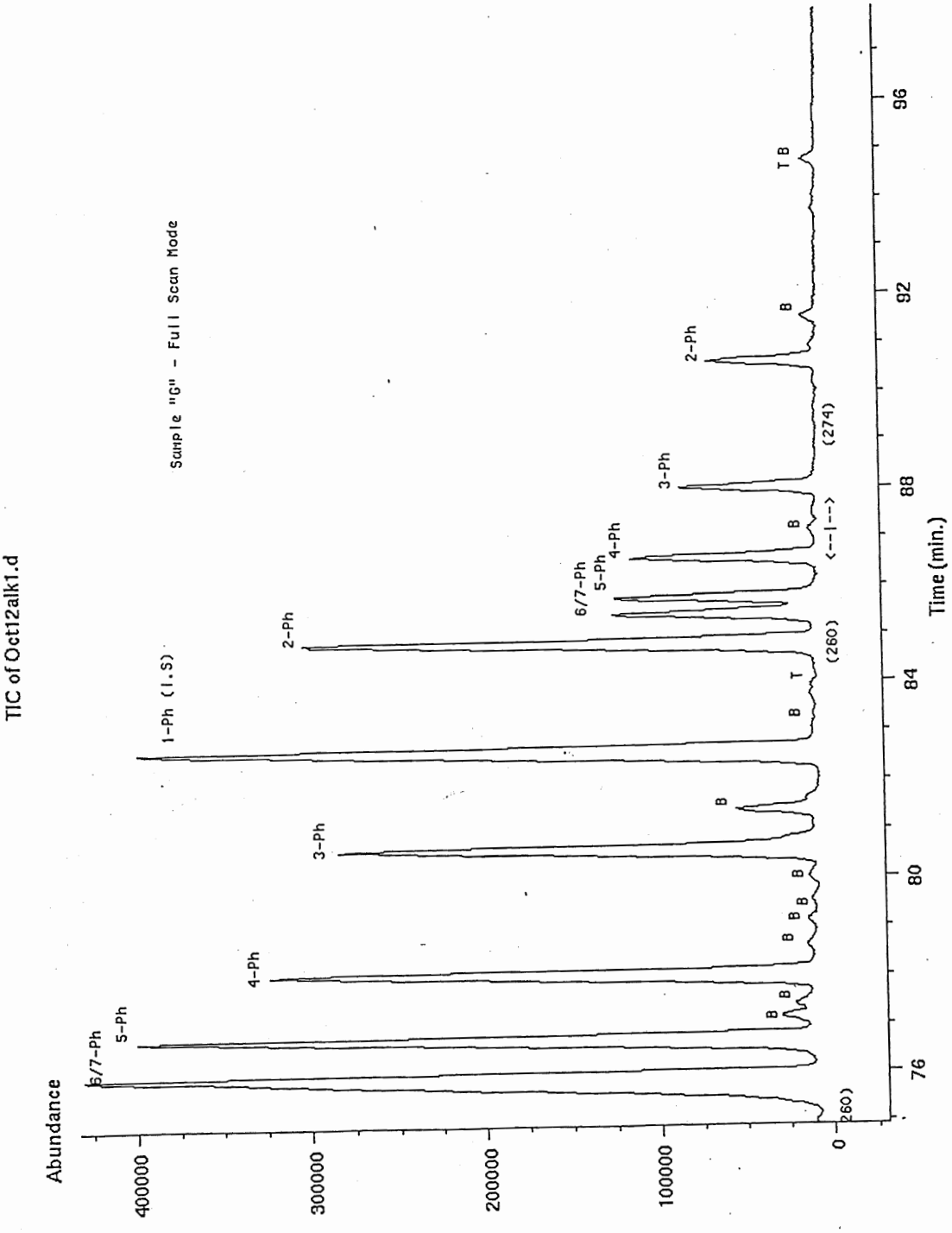


Figure 35 b

TIC Chromatogram of sample "G" - continued



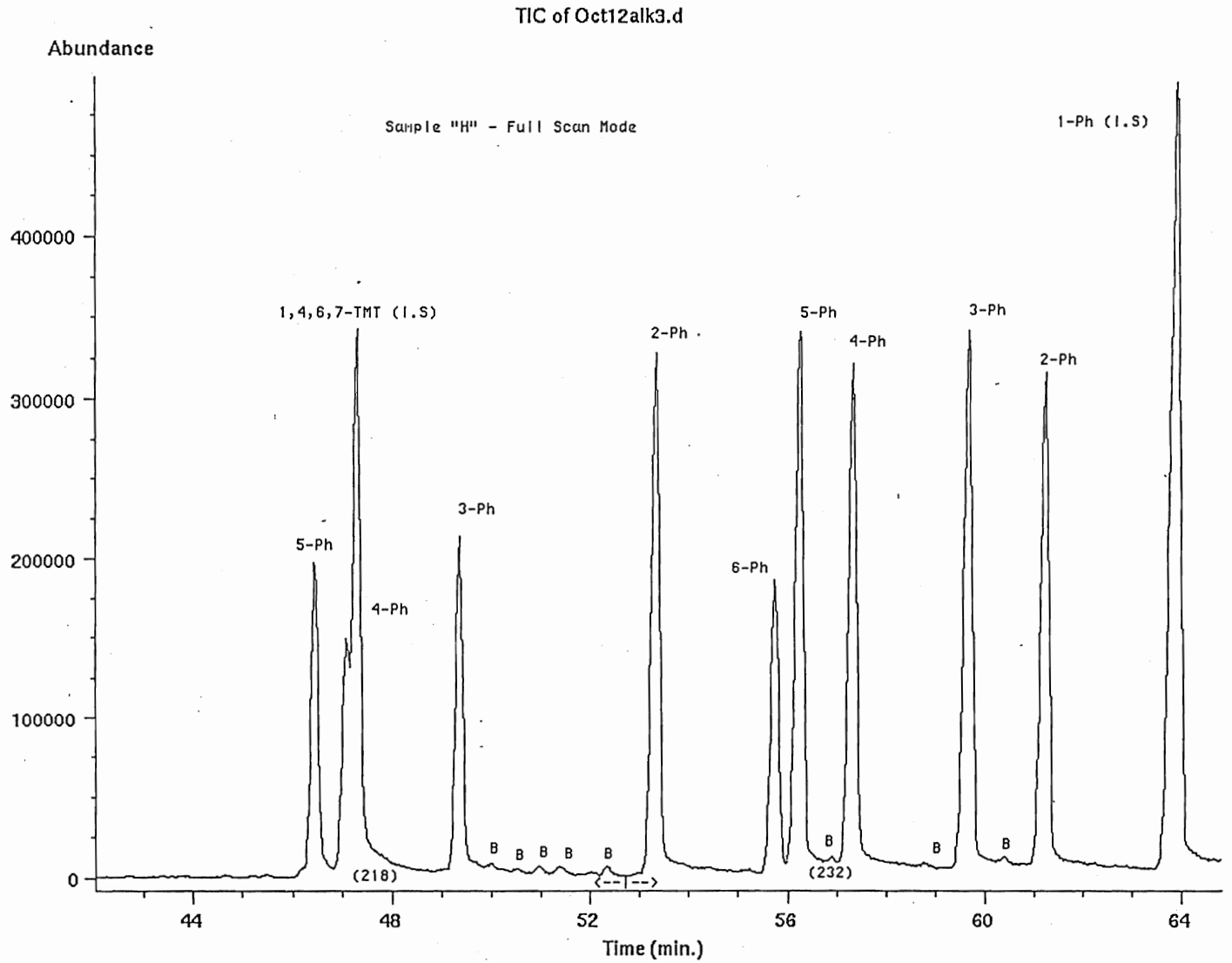


Figure 36 a

TIC Chromatogram of sample 'H"

Figure 36 b

TIC Chromatogram of sample "H" -continued

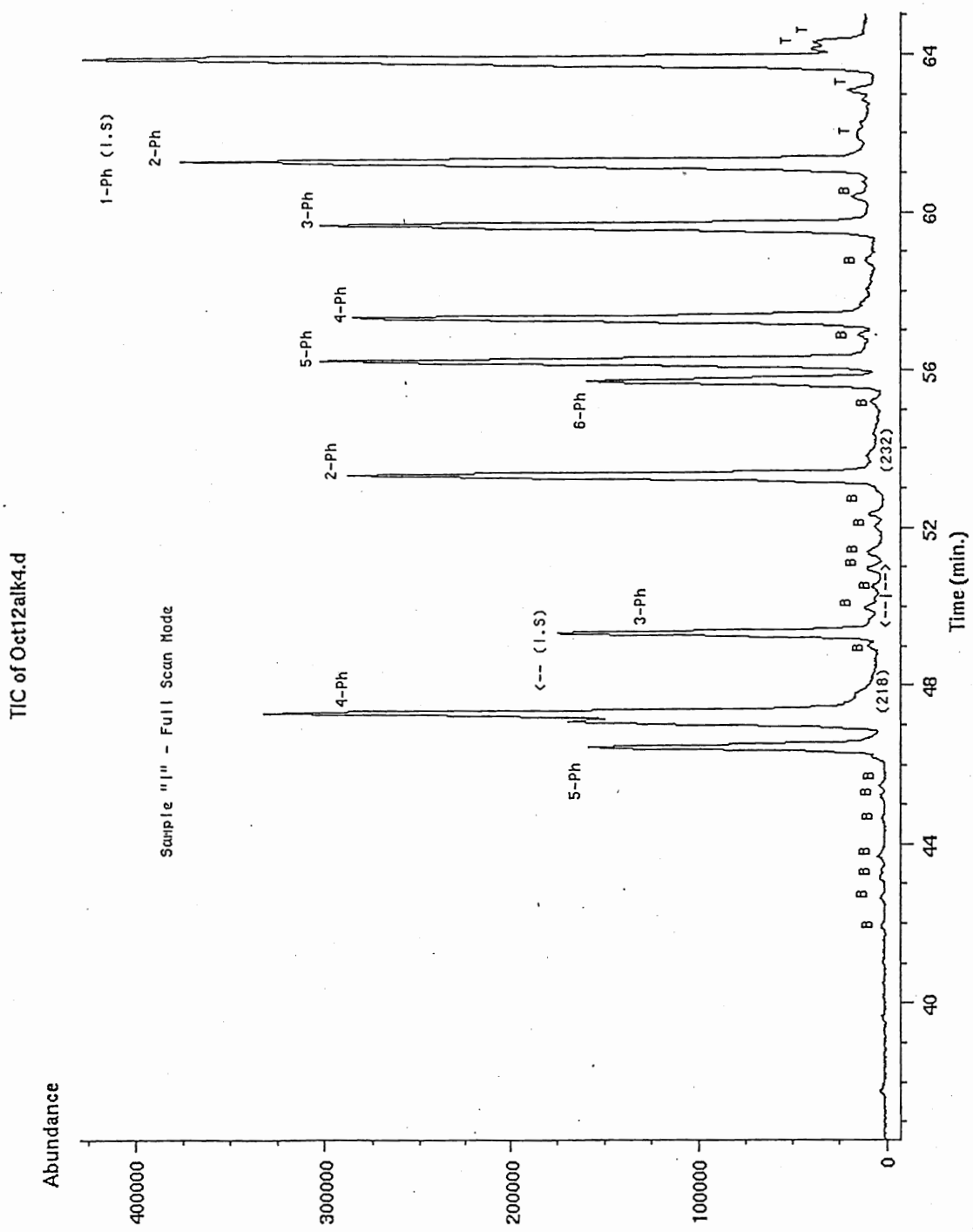


Figure 37 a

TIC Chromatogram of sample "T"

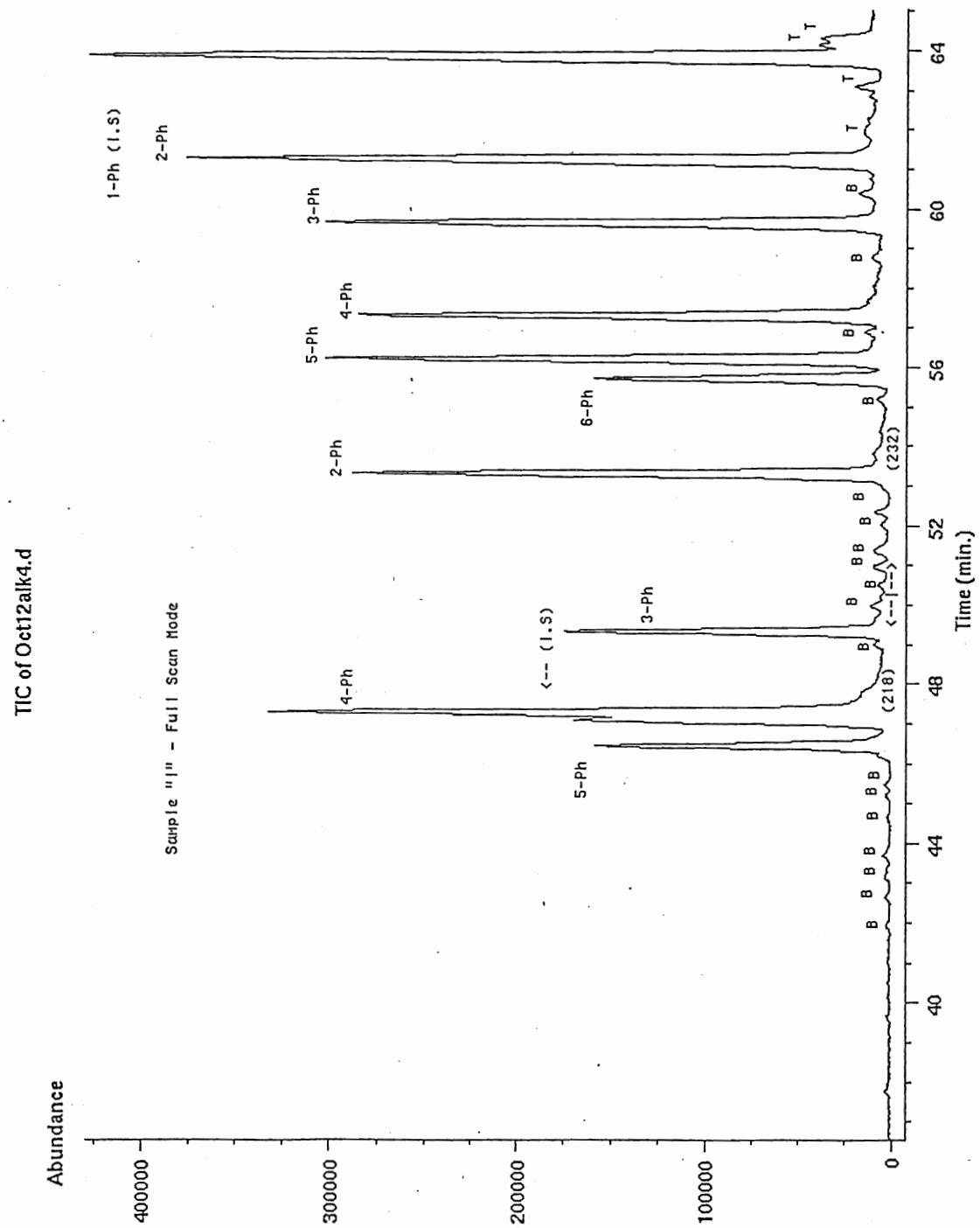


Figure 37 b

TIC Chromatogram of sample "I" - continued

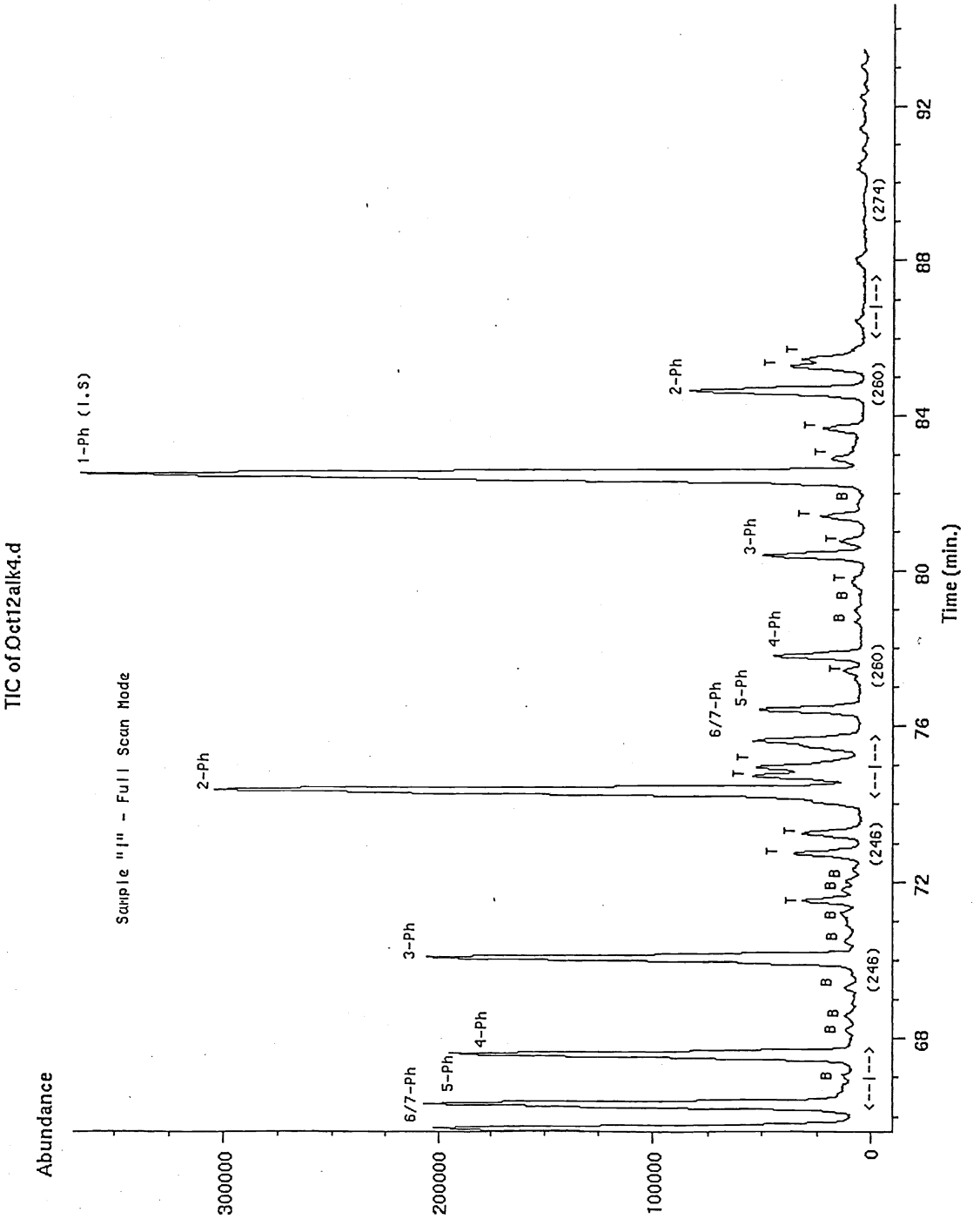


Figure 38 a

TIC Chromatogram of sample "J"

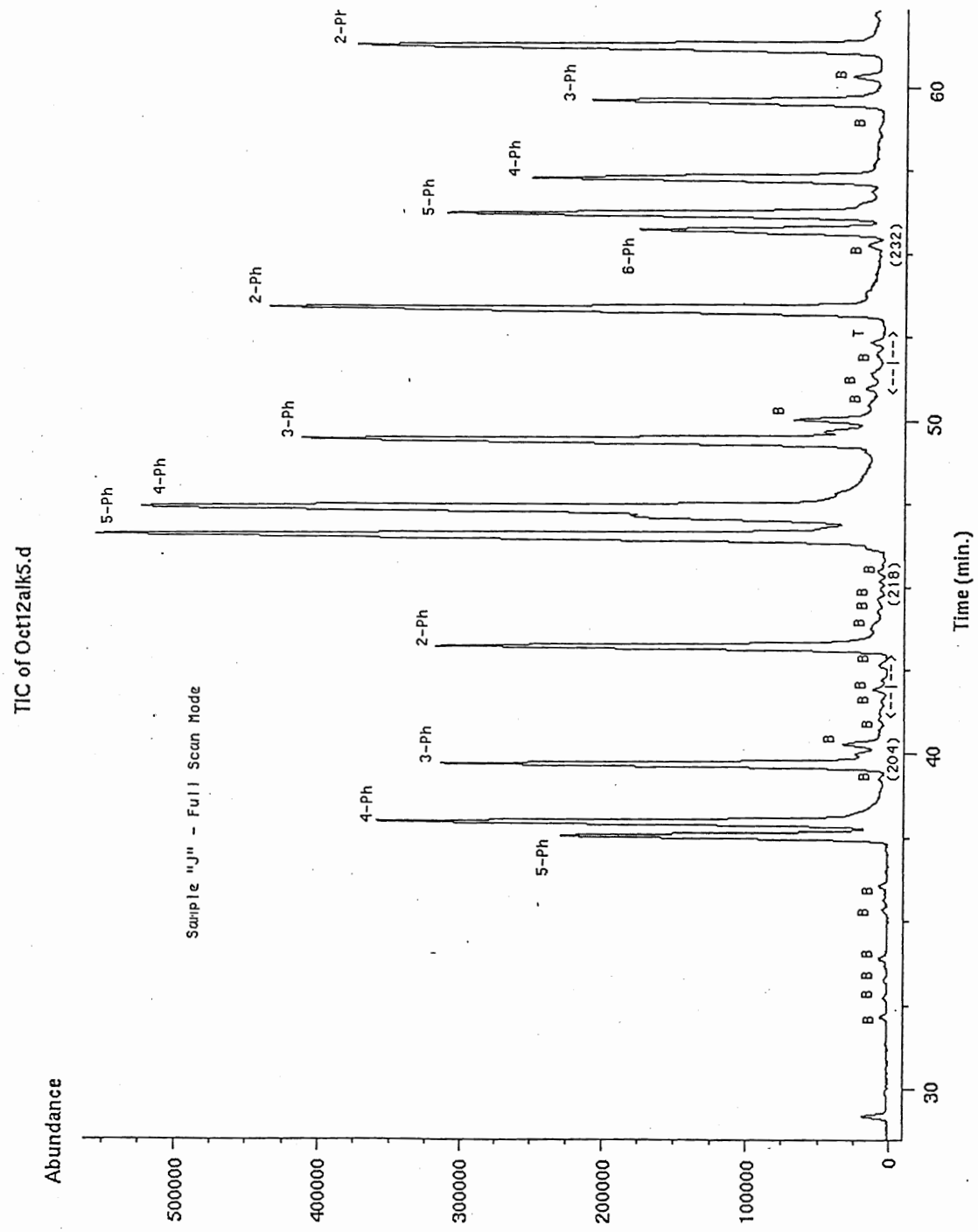
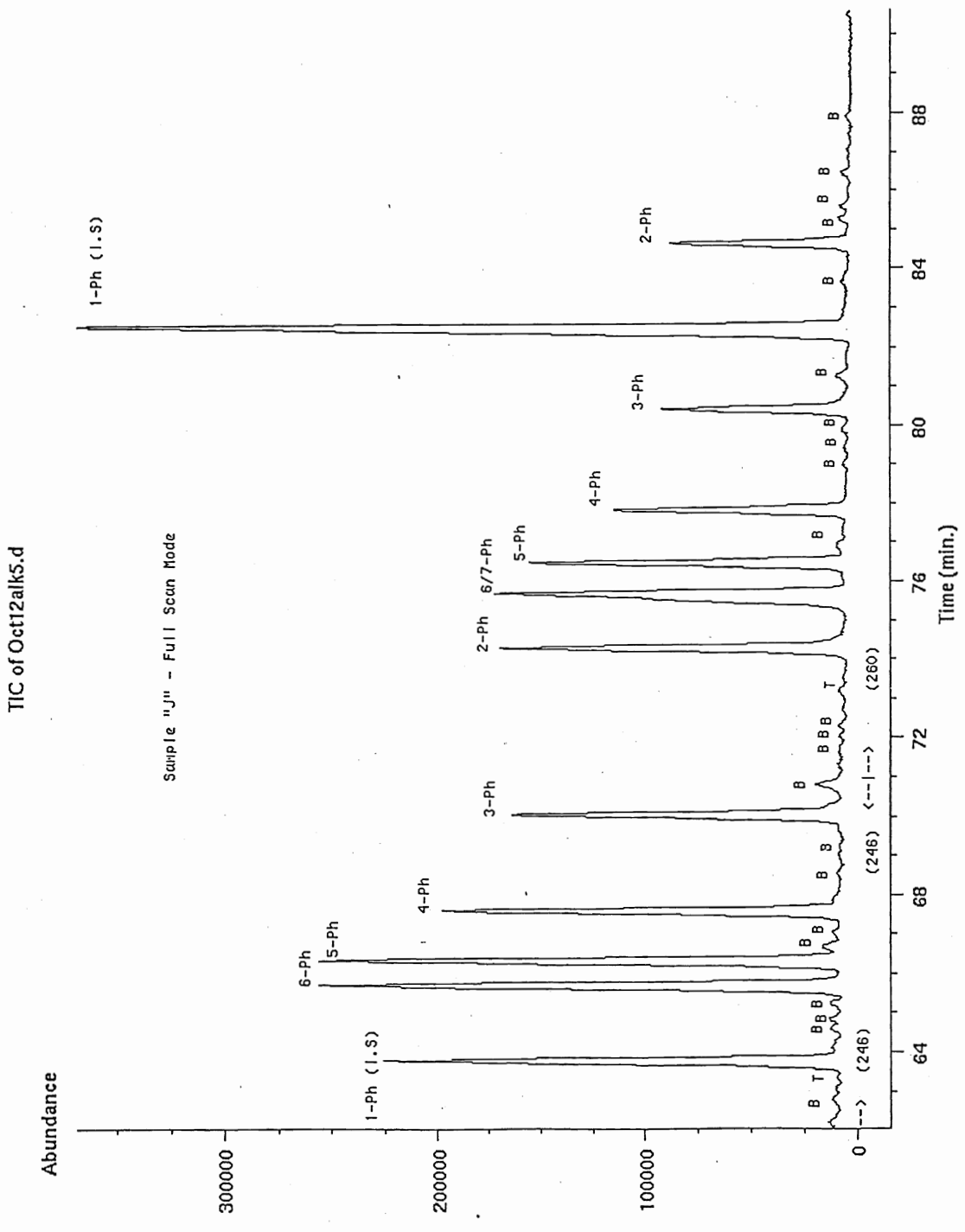


Figure 38 b

TIC Chromatogram of sample "J" - continued



new column the detailed composition of the alkylbenzene isomers was clearly identified. In addition, more sensitive GC/MS data acquisition technique, SIM, and more accurate data integration technique, IS, were employed.

Similarly to the *initial* part of this study, the percent of each linear isomer present in the analyzed LAB samples (from "A" to "J"), as well as, the total linear alkylbenzene isomers distribution were calculated and are presented in **Table 16**.

2. *Average molecular weights and distribution of molecular weights*

In order to calculate molecular weight distributions for all the selected commercial alkylbenzenes, the percent of the linear isomers, percent of the *branched* alkylbenzenes and percent of *dialkyltetralins* had to be calculated first. For this exercise, *branched* alkylbenzenes and *dialkyltetralins* were called ***non-linear*** and ***cyclic***, respectively. Results for the percent of the *non-linear* alkylbenzenes in samples "A" to "J" were tabulated and are presented in **Table 17**, **18**, **19** and **20**. Molecular weight distribution and actual average molecular weights for all analyzed samples are presented in **Table 21**, **22**, **23** and **24**.

The molecular weights and percent of 2-phenyl isomers are summarized and compared to the C.O.A. results in **Table 25**. Using a GC/MS method, molecular weights for all analyzed samples were found to be lower than reported values on each Certificate of Analysis. The difference in amu varied from 0.12 to 3.29. For the percent of 2-phenyl isomer, on the other hand, results were found to be higher than reported with the biggest difference for sample "G" at 4.25 % and the smallest for sample "A" at 0.31 %.

Table 16

Comparison of percent linear alkylbenzene isomers distribution in samples from "A" to "J"

% Total

Isomer	Sample "A"	Sample "B"	Sample "C"	Sample "D"	Sample "E"	Sample "F"	Sample "G"	Sample "H"	Sample "I"	Sample "J"
m/z 204										
5-Phenyl										3.63
4-Phenyl										6.36
3-Phenyl										5.17
2-Phenyl										6.28
Total m/z 204										21.44
m/z 218										
5-Phenyl	3.95	3.73	5.39	8.37	5.25	2.81	0.06	6.57	3.31	10.84
4-Phenyl	3.64	3.31	3.88	6.26	4.13	2.24	0.08	4.92	3.19	8.35
3-Phenyl	4.08	4.17	3.73	5.59	3.74	2.08	0.08	4.10	3.79	7.43
2-Phenyl	7.50	9.47	4.78	7.28	4.79	2.95	0.12	5.80	8.14	8.58
Total m/z 218	19.17	20.68	17.78	27.50	17.91	10.08	0.34	21.39	18.43	35.20
m/z 232										
6-Phenyl	3.25	3.41	5.65	5.88	6.50	2.91	1.79	5.31	3.23	2.30
5-Phenyl	6.62	7.02	11.26	11.65	12.92	6.03	3.67	10.75	6.85	4.61
4-Phenyl	6.76	6.43	9.80	9.14	10.39	4.85	2.67	8.52	6.28	3.42
3-Phenyl	6.81	7.19	7.90	7.49	8.35	4.33	2.40	6.89	7.35	2.85
2-Phenyl	12.17	14.79	10.08	9.08	10.27	6.23	2.96	7.82	14.09	3.49
Total m/z 232	35.61	38.84	44.69	43.24	48.43	24.35	13.49	39.29	37.80	16.67
m/z 246										
6-Phenyl	3.86	4.27	7.20	5.76	7.06	10.06	8.77	9.26	3.86	3.37
5-Phenyl	3.82	4.34	6.96	5.51	6.77	9.93	8.33	8.79	3.94	3.27
4-Phenyl	3.62	4.12	5.67	4.29	5.41	8.43	6.52	6.41	3.87	2.54
3-Phenyl	4.07	4.58	4.81	3.70	4.31	8.16	5.19	4.14	4.16	2.12
2-Phenyl	7.49	9.60	5.85	4.67	4.97	13.73	6.70	2.23	8.20	2.44
Total m/z 246	22.86	26.91	30.49	23.93	28.52	50.31	35.51	30.83	24.03	13.74
m/z 260										
7/6-Phenyl	1.31	2.65	0.70	0.17	0.35	2.25	12.86	0.29	0.97	2.62
5-Phenyl	0.87	1.76	0.44		0.19	1.47	8.09	0.13	0.65	1.66
4-Phenyl	0.78	1.54	0.32		0.12	1.14	5.94		0.57	1.14
3-Phenyl	0.86	1.76	0.27			1.00	4.98		0.63	0.89
2-Phenyl	1.75	4.14	0.36			1.16	6.78		1.39	1.04
Total m/z 260	5.57	11.85	2.09	0.17	0.66	7.02	38.65	0.42	4.21	7.35
m/z 274										
7/6-Phenyl	0.04	0.08				0.48	1.46		0.03	0.07
5-Phenyl							1.41			
4-Phenyl							1.26			
3-Phenyl							0.89			
2-Phenyl							0.69			
Total m/z 274	0.04	0.08				0.48	5.71		0.03	0.07
Total Linear	**83.25**	**98.36**	**95.05**	**94.84**	**95.52**	**92.24**	**93.70**	**91.93**	**84.50**	**76.66**

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Branched ALKYLBENZENES

Table 17

Percent non-linear (branched) alkylbenzene isomers distribution in samples "A" and "B"

	Sample "A"				Sample "B"			
	RT (min)	Area (k)	% Total	% Total NON	RT (min)	Area (k)	% Total	% Total NON
m/z 218	41.73	21.9	0.07	0.89				
	42.43	26.1	0.08	1.06				
	43.14	23.5	0.07	0.95				
	44.97	28.0	0.08	1.14				
	45.23	30.1	0.09	1.22				
	47.59	131.0	0.39	5.32	47.73	36.9	0.14	9.59
	48.80	74.9	0.22	3.04				
	49.75	182.0	0.54	7.39	50.05	66.4	0.25	17.25
	53.93	53.9	0.16	2.19				
m/z 232	50.29	23.5	0.07	0.95				
	50.76	42.1	0.13	1.71				
	51.13	82.6	0.25	3.35				
	51.81	54.8	0.16	2.23				
	52.87	81.7	0.24	3.32				
	53.14	42.5	0.13	1.73				
	53.63	39.4	0.12	1.60				
	55.00	56.8	0.17	2.31				
	56.7	157.0	0.47	6.38	56.93	50.5	0.19	13.12
	58.55	139.0	0.41	5.65				
	60.18	303.0	0.90	12.31	60.43	45.2	0.17	11.74
	65.11	42.9	0.13	1.74				
	71.56	73.5	0.22	2.98				
	74.22	38.6	0.12	1.57	74.4	49.9	0.19	12.96
	80.17	89.6	0.27	3.64	80.46	136.0	0.52	35.33
m/z 246	60.71	62.8	0.19	2.55				
	61.22	30.8	0.09	1.25				
	61.67	38.2	0.11	1.55				
	62.05	31.6	0.09	1.28				
	63.93	29.4	0.09	1.19				
	66.47	56.7	0.17	2.30				
	66.82	63.6	0.19	2.58				
	68.34	63.6	0.19	2.58				
	69.05	41.0	0.12	1.67				
	70.80	85.6	0.26	3.48				
	71.35	60.1	0.18	2.44				
	74.55	60.6	0.18	2.46				
NON-Linear; % Total area				100				100
NON-Linear; Total area (k)		2462.35				384.9		
Total area (k)		33556.2				26243.2		
% Total area			7.19				1.47	

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Table 18

Percent non-linear (branched) alkylbenzene isomers distribution in samples "C", "D" and "E"

Branched ALKYLBENZENES

	Sample "C"				Sample "D"				Sample "E"			
	RT (min)	Area (k)	% Total	% Total NON	RT (min)	Area (k)	% Total	% Total NON	RT (min)	Area (k)	% Total	% Total NON
m/z 218												
					41.75	25.6	0.11	2.34				
					42.44	15.1	0.07	1.38				
					43.16	25.9	0.11	2.36				
	47.55	42.8	0.20	3.35	47.58	52.2	0.23	4.76	47.61	61.1	0.32	7.28
	49.85	95.6	0.44	7.48	49.79	131	0.58	11.95	49.79	83.1	0.44	9.90
					53.16	41.7	0.18	3.80				
m/z 232												
					50.31	22.5	0.10	2.05				
	50.84	25.2	0.12	1.97	50.78	27.9	0.12	2.55	50.77	22.7	0.12	2.70
	51.17	51.5	0.24	4.03	51.11	58.4	0.26	5.33				
	51.87	46.9	0.21	3.67	51.81	52.2	0.23	4.76	51.13	50	0.27	5.96
	52.83	44.3	0.20	3.46	52.84	51.1	0.23	4.66	51.82	43.4	0.23	5.17
	55.13	43.6	0.20	3.41	53.11	37.5	0.17	3.42	52.75	38.3	0.20	4.56
					55.05	46.4	0.20	4.23	55.07	40.3	0.21	4.80
	56.73	107.0	0.49	8.37	56.69	115	0.51	10.49	56.71	89.1	0.47	10.62
	58.67	123.0	0.56	9.62					58.57	58.9	0.31	7.02
	60.22	227.0	1.04	17.75	60.16	161.0	0.71	14.69	60.16	145	0.77	17.28
					64.00	16.0	0.07	1.46				
	64.48	55.9	0.26	4.37								
m/z 246	60.76	38.1	0.17	2.98	60.69	38.4	0.17	3.50	60.68	18.1	0.10	2.16
	61.26	22.9	0.10	1.79	61.24	20.9	0.09	1.91				
	62.07	21.7	0.10	1.70								
	66.54	74.9	0.34	5.86	66.5	20.5	0.09	1.87	66.42	55.6	0.30	6.63
	66.87	52.4	0.24	4.10					66.81	43.5	0.23	5.18
					68.33	47.8	0.21	4.36				
	69.1	82.0	0.38	6.41								
	70.64	124.0	0.57	9.70	70.59	88.9	0.39	8.11	70.59	90.1	0.48	10.74
NON-Linear; % Total area				100				100				100
NON-Linear; Total area (k)		1278.8				1096				839.2		
Total area (k)		21815.1				22682.9				18835.3		
% Total area			5.86				4.83				4.46	

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Table 19

Percent non-linear (branched) alkylbenzene isomers distribution in samples "F", "G" and "H"

Branched ALKYLBENZENES

	Sample "F"				Sample "G"				Sample "H"			
	RT (min)	Area (k)	% Total	% Total NON	RT (min)	Area (k)	% Total	% Total NON	RT (min)	Area (k)	% Total	% Total NON
m/z 218												
					46.51	15.6	0.06	0.75				
	47.77	49.9	0.15	3.09	47.32	22.7	0.08	1.09	47.86	136	0.55	7.96
	49.64	43.8	0.13	2.71	49.37	20.6	0.08	0.99	50.04	105	0.42	6.15
					53.31	33.6	0.12	1.62				
m/z 232												
									51.36	36.3	0.15	2.13
									52.07	33.4	0.13	1.96
	55.32	42.8	0.13	2.65								
									55.33	50.7	0.20	2.97
	56.92	55.4	0.17	3.43	56.96	38.8	0.14	1.87	56.97	70.4	0.28	4.12
	60.41	141.0	0.43	8.72	60.45	73.8	0.27	3.56	60.41	153	0.61	8.96
	74.57	59.8	0.18	3.70	64.00	16.0	0.06	0.77				
	80.49	103.0	0.32	6.37								
					88.05	71.1	0.26	3.43				
m/z 246												
	60.42	71.8	0.22	4.44	60.47	70.4	0.26	3.39	60.45	63.9	0.26	3.74
	60.94	97.1	0.30	6.01	60.96	100	0.37	4.82	60.92	76.6	0.31	4.48
	61.49	61.4	0.19	3.80	61.52	54.2	0.20	2.61	61.49	47.7	0.19	2.79
	61.96	48.3	0.15	2.99	61.98	54.9	0.20	2.65				
	62.26	61.9	0.19	3.83	62.28	56.9	0.21	2.74	62.26	51.6	0.21	3.02
	64.17	34.9	0.11	2.16	64.21	25.3	0.09	1.22	64.64	45.2	0.18	2.65
	64.69	53.9	0.17	3.33	64.72	41.6	0.15	2.00	65.3	44.7	0.18	2.62
	65.05	23.4	0.07	1.45					66.81	93.2	0.37	5.46
	65.32	59.9	0.18	3.70	65.32	30.1	0.11	1.45	67.1	62.1	0.25	3.64
	66.85	142	0.44	8.78	66.84	90.2	0.33	4.35	70.88	83.3	0.33	4.88
					67.14	67.4	0.25	3.25	74.32	555	2.23	32.49
	68.64	106	0.33	6.56	68.64	59.2	0.22	2.85				
	69.37	51.3	0.16	3.17	69.39	29.1	0.11	1.40				
	70.95	281	0.86	17.38	70.95	162	0.59	7.81				
	80.48	28.3	0.09	1.75								
m/z 260												
					69.84	64.7	0.24	3.12				
					70.72	137	0.50	6.60				
					71.41	90.6	0.33	4.37				
					71.72	42.6	0.16	2.05				
					72.15	24.3	0.09	1.17				
					73.13	79.9	0.29	3.85				
					74.63	70.5	0.26	3.40				
					77.19	54.9	0.20	2.65				
					77.43	79.1	0.29	3.81				
					78.65	74.99	0.28	3.61				
					79.17	46.7	0.17	2.25				
					79.99	37.2	0.14	1.79				
					81.41	118	0.43	5.69				
m/z 274												
					94.8	21.3	0.08	1.03				
NON-Linear; % Total area				100				100				100
NON-Linear; Total area (k)		1616.9				2075.29				1708.1		
Total area (k)		32592.7				27267.7				24937.3		
% Total area			4.67				7.39				5.88	

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Branched ALKYLBENZENES

Sample "I"

	RT (min)	Area (k)	% Total	% Total NON
m/z 204				
m/z 218				
	47.81	74.7	0.33	11.52
	49.03	37.8	0.17	5.83
	49.99	82.9	0.37	12.78
	53.93	53.9	0.24	8.31
m/z 232	51.37	27.7	0.12	4.27
	53.03	26.4	0.12	4.07
	55.23	21.1	0.09	3.25
	56.93	44.2	0.20	6.81
	58.82	52.3	0.23	8.06
	60.44	60.7	0.27	9.36
m/z 246	66.73	30.9	0.14	4.76
	68.59	56.4	0.25	8.70
	69.32	31.9	0.14	4.92
	71.05	47.7	0.21	7.35
NON-Linear; % Total area				100
NON-Linear; Total area (k)		648.6		
Total area (k)		22580.7		
% Total area			2.87	

Sample "J"

RT (min)	Area (k)	% Total	% Total NON
33.92	24.5	0.07	1.34
36.09	30.9	0.09	1.69
40.33	151	0.43	8.27
53.43	26.2	0.07	1.44
59.65	223	0.63	12.22
41.96	40.7	0.12	2.23
42.69	25.6	0.07	1.40
43.39	40.4	0.11	2.21
43.86	36.3	0.10	1.99
44.67	24.7	0.07	1.35
45.23	23.3	0.07	1.28
45.49	39.4	0.11	2.16
47.86	251	0.71	13.75
49.04	66.9	0.19	3.67
50.07	421	1.19	23.06
54.49	14.4	0.04	0.79
55.28	26.7	0.08	1.46
56.87	35.4	0.10	1.94
60.38	103	0.29	5.64
80.43	89.4	0.25	4.90
66.71	59.3	0.17	3.25
70.83	72.2	0.20	3.96
			100
	1825.3		
	35242.5		
		5.18	

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Table 20

Percent non-linear (branched) alkylbenzene isomers distribution in samples "I and "J"

Table 21

Molecular weight distribution of LAB in samples "A" and "B"

Company #1

Isomer	Sample "A" Area (k)	%	Sample "B" Area (k)	%
		Linear ALKYLBENZENES		
m/z 218				
5-Phenyl	1324	3.95	979	3.73
4-Phenyl	1221	3.64	868	3.31
3-Phenyl	1368	4.08	1095	4.17
2-Phenyl	2518	7.50	2485	9.47
m/z 232				
6-Phenyl	1089	3.25	896	3.41
5-Phenyl	2221	6.62	1841	7.02
4-Phenyl	2268	6.76	1688	6.43
3-Phenyl	2285	6.81	1887	7.19
2-Phenyl	4083	12.17	3882	14.79
m/z 246				
6-Phenyl	1295	3.86	1121	4.27
5-Phenyl	1283	3.82	1139	4.34
4-Phenyl	1216	3.62	1080	4.12
3-Phenyl	1365	4.07	1201	4.58
2-Phenyl	2514	7.49	2519	9.60
m/z 260				
7/6-Phenyl	438	1.31	696	2.65
5-Phenyl	293	0.87	463	1.76
4-Phenyl	261	0.78	404	1.54
3-Phenyl	288	0.86	463	1.76
2-Phenyl	587	1.75	1087	4.14
m/z 274	11.8	0.04	22.3	0.08
		Branched ALKYLBENZENES		
m/z 218	571	1.70	103	0.39
m/z 232	1267	3.78	282	1.07
m/z 246	624	1.86		
		Cyclic		
m/z 216	937	2.79	14.9	0.06
m/z 230	1428	4.26	22.3	0.08
m/z 244	753	2.24	4.7	0.02
m/z 258	47.4	0.14		
Total area (k)	33556.2		26243.2	
Total %		100		100
Average M.W	**233.89**		**236.16**	

Table 22

Molecular weight distribution of LAB in samples "C", "D" and "E"

Company #2

	Sample "C"		Sample "D"		Sample "E"	
Isomer	Area (k)	%	Area (k)	%	Area (k)	%
		Linear ALKYLBENZENES				
m/z 218						
5-Phenyl	1176	5.39	1898	8.37	988	5.25
4-Phenyl	847	3.88	1419	6.26	777	4.13
3-Phenyl	813	3.73	1269	5.59	704	3.74
2-Phenyl	1042	4.78	1652	7.28	902	4.79
m/z 232						
6-Phenyl	1233	5.65	1334	5.88	1224	6.50
5-Phenyl	2457	11.26	2642	11.65	2433	12.92
4-Phenyl	2137	9.80	2073	9.14	1957	10.39
3-Phenyl	1723	7.90	1699	7.49	1573	8.35
2-Phenyl	2199	10.08	2060	9.08	1934	10.27
m/z 246						
6-Phenyl	1570	7.20	1307	5.76	1329	7.06
5-Phenyl	1519	6.96	1249	5.51	1276	6.77
4-Phenyl	1237	5.67	973	4.29	1019	5.41
3-Phenyl	1049	4.81	840	3.70	812	4.31
2-Phenyl	1276	5.85	1060	4.67	936	4.97
m/z 260						
7/6-Phenyl	152	0.70	37.9	0.17	65.3	0.35
5-Phenyl	96.5	0.44			35.0	0.19
4-Phenyl	68.8	0.32			21.7	0.12
3-Phenyl	59.4	0.27				
2-Phenyl	77.6	0.36				
		Branched ALKYLBENZENES				
m/z 218	97.4	0.45	292	1.29	144	0.76
m/z 232	502	2.30	588	2.59	488	2.59
m/z 246	458	2.10	217	0.96	207	1.10
		Cyclic				
m/z 216	7.2	0.03	36.3	0.16	3.0	0.02
m/z 230	16.1	0.07	30.2	0.13	7.3	0.04
m/z 244	2.1	0.01	6.5	0.03		
Total area (k)	21815.1		22682.9		18835.3	
Total %		100		100		100
Average M.W	**234.59**		**231.48**		**233.71**	

Table 23

Molecular weight distribution of LAB in samples "F", "G" and "H"

Company #3

Isomer	Sample "F" Area (k)	%	Sample "G" Area (k)	%	Sample "H" Area (k)	%
		Linear ALKYLBENZENES				
m/z 218						
5-Phenyl	917	2.81	15.6	0.06	1638	6.57
4-Phenyl	730	2.24	22.7	0.08	1228	4.92
3-Phenyl	678	2.08	20.6	0.08	1022	4.10
2-Phenyl	962	2.95	33.6	0.12	1447	5.80
m/z 232						
6-Phenyl	947	2.91	487	1.79	1325	5.31
5-Phenyl	1965	6.03	1000	3.67	2681	10.75
4-Phenyl	1581	4.85	729	2.67	2125	8.52
3-Phenyl	1412	4.33	654	2.40	1718	6.89
2-Phenyl	2031	6.23	808	2.96	1949	7.82
m/z 246						
6-Phenyl	3280	10.06	2391	8.77	2310	9.26
5-Phenyl	3236	9.93	2271	8.33	2193	8.79
4-Phenyl	2747	8.43	1779	6.52	1599	6.41
3-Phenyl	2658	8.16	1414	5.19	1033	4.14
2-Phenyl	4476	13.73	1828	6.70	555	2.23
m/z 260						
7/6-Phenyl	733	2.25	3507	12.86	71.9	0.29
5-Phenyl	479	1.47	2207	8.09	33.5	0.13
4-Phenyl	372	1.14	1621	5.94		
3-Phenyl	326	1.00	1358	4.98		
2-Phenyl	378	1.16	1848	6.78		
m/z 274						
7/6-Phenyl	155	0.48	399	1.46		
5-Phenyl			384	1.41		
4-Phenyl			344	1.26		
3-Phenyl			242	0.89		
2-Phenyl			187	0.69		
		Branched ALKYLBENZENES				
m/z 218	93.7	0.29	92.5	0.34	241	0.97
m/z 232	402	1.23	129	0.47	344	1.38
m/z 246	1121	3.44	437	1.60	1124	4.51
m/z 260			920	3.37		
m/z 274			21.3	0.08		
Total		**4.96**		**5.87**		**6.85**
		Dialkyltetralins				
m/z 216	184	0.56	12.7	0.05	210	0.84
m/z 230	330	1.01	36.2	0.13	89.9	0.36
m/z 244	399	1.22	29.9	0.11		
m/z 258			38.6	0.14		
Total		**2.80**		**0.43**		**1.20**
Total area (k)	32592.7		27267.7		24937.3	
Total %		100.00		100.00		100.00
Average M.W	**240.27**		**251.34**		**233.79**	

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Table 24

Molecular weight distribution of LAB in samples "I" and "J"

Company #4

Isomer	Sample "I" Area (k)	%	Sample "J" Area (k)	%
Linear ALKYLBENZENES				
m/z 204				
5-Phenyl			1279	3.63
4-Phenyl			2241	6.36
3-Phenyl			1823	5.17
2-Phenyl			2213	6.28
m/z 218				
5-Phenyl	748	3.31	3821	10.84
4-Phenyl	721	3.19	2943	8.35
3-Phenyl	856	3.79	2619	7.43
2-Phenyl	1838	8.14	3021	8.57
m/z 232				
6-Phenyl	729	3.23	811	2.30
5-Phenyl	1546	6.85	1626	4.61
4-Phenyl	1419	6.28	1205	3.42
3-Phenyl	1659	7.35	1005	2.85
2-Phenyl	3181	14.09	1229	3.49
m/z 246				
6-Phenyl	871	3.86	1189	3.37
5-Phenyl	889	3.94	1151	3.27
4-Phenyl	875	3.87	894	2.54
3-Phenyl	939	4.16	747	2.12
2-Phenyl	1852	8.20	859	2.44
m/z 260				
7/6-Phenyl	220	0.97	923	2.62
5-Phenyl	147	0.65	584	1.66
4-Phenyl	128	0.57	401	1.14
3-Phenyl	142	0.63	313	0.89
2-Phenyl	315	1.39	366	1.04
m/z 274				
7/6-Phenyl	5.8	0.03	25.9	0.07
NON-Linear ALKYLBENZENES				
m/z 204			456	1.29
m/z 218	249	1.10	984	2.79
m/z 232	232	1.03	165	0.47
m/z 246	167	0.74	132	0.37
Cyclic				
m/z 216	708	3.14	103	0.29
m/z 230	1387	6.14	106	0.30
m/z 244	741	3.28	7.6	0.02
m/z 258	15.9	0.07		
Total area (k)	22580.7		35242.5	
Total %		100		100
Average M.W	233.71		224.33	

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Table 25

Molecular weight of LAB and percent of 2-phenyl isomer in LAB - comparison of actual results and reported by the suppliers

Molecular Weight

Full Scan mode - using Molecular Weight Ion's (m/z) area counts

	Actual	C.O.A. (Certificate of Analysis)	Difference
Sample "A"	233.89	236.5	2.61
Sample "B"	236.16	237.5	1.34
Sample "C"	234.59	235.0	0.41
Sample "D"	231.48	231.6	0.12
Sample "E"	233.71	234.0	0.29
Sample "F"	240.27	242.0	1.73
Sample "G"	251.34	252.0	0.66
Sample "H"	233.79	235.0	1.21
Sample "I"	233.71	237.0	3.29
Sample "J"	224.33	225.7	1.37

Total % 2-phenyl isomer

Full Scan mode - using Molecular Weight Ion's (m/z) area counts

	Actual	C.O.A. (Certificate of Analysis)	Difference
Sample "A"	28.9	28.6	-0.31
Sample "B"	38.0	31.0	-7.00
Sample "C"	21.1	17.8	-3.27
Sample "D"	21.2	18.5	-2.70
Sample "E"	20.2	17.0	-3.15
Sample "F"	24.1	21.0	-3.07
Sample "G"	17.3	13.0	-4.25
Sample "H"	15.9	13.0	-2.85
Sample "I"	31.8	29.0	-2.82
Sample "J"	26.3	18.5	-7.80

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The same observations were published by Ötvös et al.[14]. They used GLC/MS method and reported the average molecular weight for the analyzed commercial linear alkylbenzene to be 2.5 lower. In 1988 Bravo et al.[17] in their studies compared GC and GC/MS methods and reported the difference of 2.00 amu lower in average molecular weights using GC/MS method. Another interesting observation was done by the same authors that for the commercial alkylbenzenes obtained via HF route, an actual molecular weight was higher when using GC/MS technique.

3. *Influence of LAB actual molecular weight on the calculation of the percent active ingredient in LAS*

The main parameter in the calculation of active ingredient content in linear alkylbenzene sulphonic acid is the LAB molecular weight. Thus, the exact determination of the linear alkylbenzenes average molecular weight is of major importance. The active ingredient content of an anionic surfactant (LAS) titrated with a cationic is given by the following formula:

$$\% A = C \times MW \times 100 \%$$

where, A - active ingredient,

C - constant related to the cationic concentration and volume consumed during titration (laboratory data indicates that $C \approx 0.003$),

MW - molecular weight of linear alkylbenzene sulphonic acid.

Taking both molecular weights, using GC and GC/MS techniques, the effect on the active ingredient calculation is presented below:

MW (GC method) = 237.00 (**Table 25**) + 80 (SO_3) = 317.00

% A = 317.00 x 0.003 x 100 % = 95.10 %

MW (GC/MS method) = 233.71 (**Table 25**) + 80 (SO_3) = 313.71

% A = 313.71 x 0.003 x 100 % = 94.11 %

In view of these differences two conclusions were made. First, the actual active ingredient content based on the GC/MS technique was substantially lower that the active ingredient calculated using the GC technique. The second, a difference in active ingredient content up to 0.99 % was observed in one of the analyzed linear alkylbenzene samples. An accurate linear alkylbenzene molecular weight calculation using the GC/MS technique was found to contribute greatly to a better understanding of differences observed in the sulphonation yield.

4. ***Semi-quantitative determination of branched alkylbenzenes***

In addition to the *initial* part of this study, the use of an Internal Standard technique allowed for the semi-quantitative results for *non-linear* alkylbenzenes. First of all, samples from "B" to "J" were analyzed under a full scan mode. Since a standard blend of linear alkylbenzenes was not available, sample "A" was used as a standard. Two internal standards, 1-phenyldecane and 1-phenyldodecane were used to calculate relative response factors, RRF, for all *non-linear* alkylbenzenes. Since there were only two internal standards available, the following assumptions were made; for all C_{10} and C_{11} *non-linear* alkylbenzenes, the 1-phenyldecane's molecular ion at m/z 218 was used as a quantitative ion, and for all C_{12} , C_{13} and C_{14} *non-linear* alkylbenzenes, the 1-phenyldodecane's molecular ion at m/z 246 was used

as a quantitative ion and for all C_{12} , C_{13} and C_{14} *non-linear* alkylbenzenes, the 1-phenyldodecane's molecular ion at m/z 246 was used as a quantitative ion. The summarized results for samples from "B" to "J" are presented in **Table 26**, **27**, **28** and **29**. The highest concentration of the first class of impurities, branched alkylbenzenes was observed in sample "G" at 81.32 mg/g whereas the lowest concentration was observed in sample "B" at 18.10 mg/g.

5. *Analysis of dialkyltetralins standard using both full scan and single ion monitoring modes*

With the longer column, a higher percentage of the phenyl groups in the bounding phase, 20 % vs 5 %, and a much thicker bounding phase, a greater degree of separation was achieved between *non-linear* alkylbenzenes and *dialkyltetralins*. Most peaks eluted in the same order, except for all cis/trans isomers of 1,5- , 1,6- , 1,7- and 1,8-dialkyltetralins which eluted after 2-phenyl alkylbenzene in comparison to just before 2-phenyl isomer peak using SPB-20 column.

In this part of study a more sensitive GC/MS data acquisition mode, a single ion monitoring mode was used to analyze all samples from "A" to "J" for the second class of impurities, *dialkyltetralins*. By monitoring ions of specific mass instead of the whole spectrum, a hundred to a thousand-fold increase in sensitivity is usually attained. Before any compound can be analyzed quantitatively, its mass spectrum must be examined for the best mass peaks suitable for selective monitoring. The selected ions should be abundant and characteristic for each analyzed compound. *Dialkyltetralins* mixture, a blend

Branched Alkylbenzenes (mg/g)

Internal Standard Technique

Isomer	Sample "A" As a Standard RT (min)	Area (k)	ug/ul	RRF	Sample "B" RT (min)	Area (k)	mg/g
m/z 218	41.73	21.9	0.0056	0.6217352			
	42.43	26.1	0.0067	0.6193199			
	43.14	23.5	0.0060	0.6226815			
	44.97	28.0	0.0072	0.6182653			
	45.23	30.1	0.0077	0.6214771			
	47.59	131.0	0.0336	0.6198425	47.73	36.9	1.74
	48.80	74.9	0.0192	0.6201974			
	49.75	182.0	0.0466	0.6209188	50.05	66.4	3.12
	53.93	53.9	0.0138	0.6209534			
m/z 232	50.29	23.5	0.0060	0.6226815			
	50.76	42.1	0.0108	0.6197374			
	51.13	82.6	0.0212	0.6194319			
	51.81	54.8	0.0140	0.6223030			
	52.87	81.7	0.0209	0.6214771			
	53.14	42.5	0.0109	0.6198859			
	53.63	39.4	0.0101	0.6201892			
	55.00	56.8	0.0146	0.6185073			
	56.70	157.0	0.0402	0.6209019	56.93	50.5	2.37
	58.55	139.0	0.0356	0.6207463			
	60.18	303.0	0.0777	0.6199704	60.43	45.2	2.13
	65.11	42.9	0.0110	0.6200318			
	71.56	73.5	0.0188	0.6215540			
	74.22	38.6	0.0099	0.6198712	74.40	49.9	2.35
	80.17	89.6	0.0230	0.6193406	80.46	136.0	6.40
m/z 246	60.71	62.8	0.0161	0.6144646			
	61.22	30.8	0.0079	0.6141673			
	61.67	38.2	0.0098	0.6140452			
	62.05	31.6	0.0081	0.6135888			
	63.93	29.4	0.0075	0.6175173			
	66.47	56.7	0.0145	0.6159963			
	66.82	63.6	0.0163	0.6146567			
	68.34	63.6	0.0163	0.6146567			
	69.05	41.0	0.0105	0.6151169			
	70.80	85.6	0.0219	0.6157334			
	71.35	60.1	0.0154	0.6147759			
	74.55	60.6	0.0155	0.6158912			
I.S 1-Phen (m/z 218)	61.09	3145			61.29	2485	
I.S 1-Pheny (m/z 24	82.31	3174			82.55	3054	
Total area (k)		33556.2				26243.2	

Total (mg/g) **18.10**

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Table 26

Comparison of non-linear (branched) alkylbenzenes in sample "B" using an internal standard technique

Table 27

Comparison of non-linear (branched) alkylbenzenes in sample "C", "D" and "E" using an internal standard technique

Branched Alkylbenzenes (mg/g)

Internal Standard Technique

	Sample "A" As a Standard				Sample "C"			Sample "D"			Sample "E"		
Isomer	RT (min)	Area (k)	ug/ul	RRF	RT (min)	Area (k)	mg/g	RT (min)	Area (k)	mg/g	RT (min)	Area (k)	mg/g
m/z 218	41.73	21.9	0.0056	0.62174				41.75	25.6	1.35			
	42.43	26.1	0.0067	0.61932				42.44	15.1	0.80			
	43.14	23.5	0.0060	0.62268				43.16	25.9	1.36			
	44.97	28.0	0.0072	0.61827									
	45.23	30.1	0.0077	0.62148									
	47.59	131.0	0.0336	0.61984	47.55	42.8	2.48	47.58	52.2	2.76	47.61	61.1	2.63
	48.80	74.9	0.0192	0.62020									
	49.75	182.0	0.0466	0.62092	49.85	95.6	5.53	49.79	131	6.91	49.79	83.1	3.58
	53.93	53.9	0.0138	0.62095				53.16	41.7	2.20			
m/z 232	50.29	23.5	0.0060	0.62268				50.31	22.5	1.18			
	50.76	42.1	0.0108	0.61974	50.84	25.2	1.46	50.78	27.9	1.47	50.77	22.7	0.98
	51.13	82.6	0.0212	0.61943	51.17	51.5	2.99	51.11	58.4	3.09	51.13	50	2.16
	51.81	54.8	0.0140	0.62230	51.87	46.9	2.71	51.81	52.2	2.75	51.82	43.4	1.86
	52.87	81.7	0.0209	0.62148	52.83	44.3	2.56	52.84	51.1	2.69	52.75	38.3	1.65
	53.14	42.5	0.0109	0.61989				53.11	37.5	1.98			
	53.63	39.4	0.0101	0.62019									
	55.00	56.8	0.0146	0.61851	55.13	43.6	2.53	55.05	46.4	2.46	55.07	40.3	1.74
	56.70	157.0	0.0402	0.62090	56.73	107.0	6.19	56.69	115	6.06	56.71	89.1	3.83
	58.55	139.0	0.0356	0.62075	58.67	123.0	7.12				58.57	58.9	2.54
	60.18	303.0	0.0777	0.61997	60.22	227.0	13.16	60.16	161.0	8.50	60.16	145	6.25
	65.11	42.9	0.0110	0.62003	64.48	55.9	3.24	65.48	55.9	2.95			
	71.56	73.5	0.0188	0.62155									
	74.22	38.6	0.0099	0.61987									
	80.17	89.6	0.0230	0.61934				64.00	16.0	0.85			
m/z 246	60.71	62.8	0.0161	0.61446	60.76	38.1	2.23	60.69	38.4	2.05	60.68	18.1	0.79
	61.22	30.8	0.0079	0.61417	61.26	22.9	1.34	61.24	20.9	1.11			
	61.67	38.2	0.0098	0.61405	62.07	21.7	1.27						
	62.05	31.6	0.0081	0.61359									
	63.93	29.4	0.0075	0.61752									
	66.47	56.7	0.0145	0.61600	66.54	74.9	4.37	66.5	20.5	1.09	66.42	55.6	2.41
	66.82	63.6	0.0163	0.61466	66.87	52.4	3.06				66.81	43.5	1.89
	68.34	63.6	0.0163	0.61466				68.33	47.8	2.55			
	69.05	41.0	0.0105	0.61512	69.1	82.0	4.79						
	70.80	85.6	0.0219	0.61573	70.64	124.0	7.24	70.59	88.9	4.73	70.59	90.1	3.91
	71.35	60.1	0.0154	0.61478									
	74.55	60.6	0.0155	0.61589									
I.S 1-Phen (m/z 218)	61.09	3145			61.29	2485		61.14	2881		61.08	2879	
I.S 1-Pheny (m/z 246	82.31	3174			82.55	3054		82.33	2959		82.29	3037	
Total area (k)		33556.2				21815.1			22682.9			18835.3	
Total (mg/g)							74.26			60.89			36.21

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Table 28

Comparison of non-linear (branched) alkylbenzenes in sample "F", "G" and "H" using an internal standard technique

Branched Alkylbenzenes (mg/g)

Internal Standard Technique

	Sample "A" As a Standard				Sample "F"			Sample "G"			Sample "H"		
Isomer	RT (min)	Area (k)	ug/ul	RRF	RT (min)	Area (k)	mg/g	RT (min)	Area (k)	mg/g	RT (min)	Area (k)	mg/g
m/z 218	41.73	21.9	0.0056	0.62174									
	42.43	26.1	0.0067	0.61932									
	43.14	23.5	0.0060	0.62268									
	44.97	28.0	0.0072	0.61827									
	45.23	30.1	0.0077	0.62148				45.51	15.6	0.59			
	47.59	131.0	0.0336	0.61984	47.77	49.9	1.73	47.32	22.7	0.86	47.86	136	5.17
	48.80	74.9	0.0192	0.62020									
	49.75	182.0	0.0466	0.62092	49.64	43.8	1.52	49.37	20.6	0.78	50.04	105	3.98
	53.93	53.9	0.0138	0.62095				53.31	33.6	1.27			
m/z 232	50.29	23.5	0.0060	0.62268									
	50.76	42.1	0.0108	0.61974									
	51.13	82.6	0.0212	0.61943							51.36	36.3	1.38
	51.81	54.8	0.0140	0.62230							52.07	33.4	1.26
	52.87	81.7	0.0209	0.62148									
	53.14	42.5	0.0109	0.61989									
	53.63	39.4	0.0101	0.62019									
	55.00	56.8	0.0146	0.61851	55.32	42.8	1.49				55.33	50.7	1.93
	56.70	157.0	0.0402	0.62090	56.92	55.4	1.92	56.96	38.8	1.47	56.97	70.4	2.67
	58.55	139.0	0.0356	0.62075	60.41	141.0	4.88						
	60.18	303.0	0.0777	0.61997				60.45	73.8	2.79	60.41	153	5.81
	65.11	42.9	0.0110	0.62003									
	71.56	73.5	0.0188	0.62155									
	74.22	38.6	0.0099	0.61987	74.57	59.8	2.07						
	80.17	89.6	0.0230	0.61934	80.49	103.0	3.57						
				0.61934				64.00	16.0	0.61			
m/z 246	60.71	62.8	0.0161	0.61446	60.42	71.8	2.51	60.96	100	3.82	60.45	63.9	2.45
	61.22	30.8	0.0079	0.61417	61.49	61.4	2.15	61.52	54.2	2.07	61.49	47.7	1.83
	61.67	38.2	0.0098	0.61405	61.96	48.3	1.69	61.98	54.9	2.10	62.26	51.6	1.98
	62.05	31.6	0.0081	0.61359	62.26	61.9	2.17	62.28	56.9	2.17			
	63.93	29.4	0.0075	0.61752	64.17	34.9	1.21	64.21	25.3	0.96			
	66.47	56.7	0.0145	0.61600									
	66.82	63.6	0.0163	0.61466	66.85	142	4.97	66.84	90.2	3.44	66.81	93.2	3.57
	68.34	63.6	0.0163	0.61466	68.64	106	3.71	68.64	59.2	2.26			
	69.05	41.0	0.0105	0.61512	69.37	51.3	1.79						
	70.80	85.6	0.0219	0.61573	70.95	281	9.81	70.95	162	6.17	70.88	83.3	3.19
	71.35	60.1	0.0154	0.61478									
	74.55	60.6	0.0155	0.61589							74.32	555	21.23
				0.61589	60.94	97.1	3.39	60.47	70.4	2.68	60.92	76.6	2.93
				0.61589	64.69	53.9	1.88	64.72	41.6	1.58	64.64	45.2	1.73
				0.61589	65.05	23.4	0.82	67.14	67.4	2.57	65.30	44.7	1.71
				0.61589	65.32	59.9	2.09	69.39	29.1	1.11	67.10	62.1	2.38
				0.61589	80.48	28.3	0.99	70.95	162	6.17			
m/z 260				0.61589				69.84	64.7	2.46			
				0.61589				70.72	137	5.22			
				0.61589				71.41	90.6	3.45			
				0.61589				71.72	42.6	1.62			
				0.61589				72.15	24.3	0.93			
				0.61589				73.13	79.9	3.04			
				0.61589				74.63	70.5	2.68			
				0.61589				77.19	54.9	2.09			
				0.61589				77.43	79.1	3.01			
				0.61589				78.65	74.99	2.86			
				0.61589				79.17	46.7	1.78			
				0.61589				79.99	37.2	1.42			
				0.61589				81.41	118	4.49			
m/z 274				0.61589				94.81	21.3	0.81			
I.S 1-Phen (m/z 218)	61.09	3145			61.35	3752		61.38	3495		61.08	3168	
I.S 1-Pheny (m/z 24	82.31	3174			82.64	4654		82.68	4105		82.29	3737	
Total area (k)		33556.2				32597.2			27267.7			24937.3	
Total (mg/g)							56.35			81.32			65.20

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Table 29

Comparison of non-linear (branched) alkylbenzenes in sample "I" and "J" using an internal standard technique

Branched Alkylbenzenes (ug/g)

Internal Standard Technique

	Sample "A" As a Standard				Sample "I"			Sample "J"		
Isomer	RT (min)	Area (k)	ug/ul	RRF	RT (min)	Area (k)	mg/g	RT (min)	Area (k)	mg/g
m/z 204				0.62174				33.93	24.5	0.74
				0.61932				36.09	30.9	0.93
				0.62268				40.33	151	4.53
				0.61827				53.43	26.2	0.79
				0.62148				59.65	223	6.70
m/z 218	41.73	21.9	0.0056	0.62174				41.96	40.7	1.22
	42.43	26.1	0.0067	0.61932				42.69	25.6	0.77
	43.14	23.5	0.0060	0.62268				43.39	40.4	1.21
	44.97	28.0	0.0072	0.61827				43.86	36.3	1.10
	45.23	30.1	0.0077	0.62148				44.67	24.7	0.74
	47.59	131.0	0.0336	0.61984	47.81	74.7	3.09	45.23	23.3	0.70
	48.80	74.9	0.0192	0.62020	49.03	37.8	1.56	45.49	39.4	1.19
	49.75	182.0	0.0466	0.62092	49.99	82.9	3.42	47.86	251	7.55
	53.93	53.9	0.0138	0.62095	53.93	53.9	2.23	49.04	66.9	2.01
				0.62090				50.07	421	12.66
				0.92095				54.49	14.4	0.29
m/z 232	50.29	23.5	0.0060	0.62268						
	50.76	42.1	0.0108	0.61974						
	51.13	82.6	0.0212	0.61943						
	51.81	54.8	0.0140	0.62230	51.37	27.7	1.14			
	52.87	81.7	0.0209	0.62148						
	53.14	42.5	0.0109	0.61989						
	53.63	39.4	0.0101	0.62019	53.03	26.4	1.09			
	55.00	56.8	0.0146	0.61851	55.23	21.1	0.87	55.28	26.7	0.81
	56.70	157.0	0.0402	0.62090	56.93	44.2	1.82	56.87	35.4	1.06
	58.55	139.0	0.0356	0.62075	58.82	52.3	2.16			
	60.18	303.0	0.0777	0.61997	60.44	60.7	2.51	60.38	103	3.10
	65.11	42.9	0.0110	0.62003						
	71.56	73.5	0.0188	0.62155						
	74.22	38.6	0.0099	0.61987						
	80.17	89.6	0.0230	0.61934				80.43	89.4	2.70
m/z 246	60.71	62.8	0.0161	0.61446						
	61.22	30.8	0.0079	0.61417						
	61.67	38.2	0.0098	0.61405						
	62.05	31.6	0.0081	0.61359						
	63.93	29.4	0.0075	0.61752						
	66.47	56.7	0.0145	0.61600						
	66.82	63.6	0.0163	0.61466	66.73	30.9	1.29	66.71	59.3	1.80
	68.34	63.6	0.0163	0.61466	68.59	56.4	2.35			
	69.05	41.0	0.0105	0.61512	69.32	31.9	1.33			
	70.80	85.6	0.0219	0.61573				70.83	72.2	2.19
	71.35	60.1	0.0154	0.61478	71.05	47.7	1.99			
	74.55	60.6	0.0155	0.61589						
I.S 1-Phen (m/z 218)	61.09	3145			61.34	3422		60.31	3308	
I.S 1-Pheny (m/z 246	82.31	3174			82.58	3466		82.56	3480	
Total area (k)		33556.2								
Total (ug/g)							26.86			54.79

of *dialkyltetralins* was synthesized by company #1 and a few drops of it were kindly offered to me. Mass spectra for all compounds present in the *dialkyltetralin* blend were acquired under a full scan mode (**Figure 39** to **Figure 51**) and carefully examined for the best suitable peaks. The following mass peaks were selected: $M^{+\cdot}$ representing molecular weight ion, $(M - R_1)^+$ ion representing R_1 loss from 1- or 4-position, and $(M - R_2)^+$ also representing loss from 1- or 4-position but for R_2. The same blend of *dialkyltetralins* containing an internal standard, cis/trans-1,4,6,7-tetramethyltetralin was rerun under the single ion monitoring mode (**Figure 52** and **53**). Relative response factors were calculated and used for the final calculation of the *dialkyltetralins*.

6. *Quantitative analysis of dialkyltetralins*

All samples under investigation, sample from "A" to "J", were then analyzed under the same instrumental conditions. **Figures 54** to **67** correspond to sample "A" where the top portion of each figure represent molecular weight ion chromatograms at m/z 216, 230, 244 and 258 corresponding to C_{10}, C_{11}, C_{12} and C_{13} *dialkyltetralin* homologues. The middle and the bottom portions of the same figures represent *dialkyltetralin* mass spectra. Results were calculated (**Table 30**, **31**, **32** and **33**) using an internal standard technique and m/z 173 ion (common fragmentation ion to the most *dialkyltetralins*) of *cis/trans-1,4,6,7-tetramethyltetralin* as a quantitation ion (**Figure 68**). All *dialkyltetralins* identified in the standard blend, DAT, were found in the following samples: "A" and "B" manufactured by company #1, and "I" and "J" manufactured by company #4. The remaining analyzed samples contained most but not all of the *dialkyltetralins*. The highest

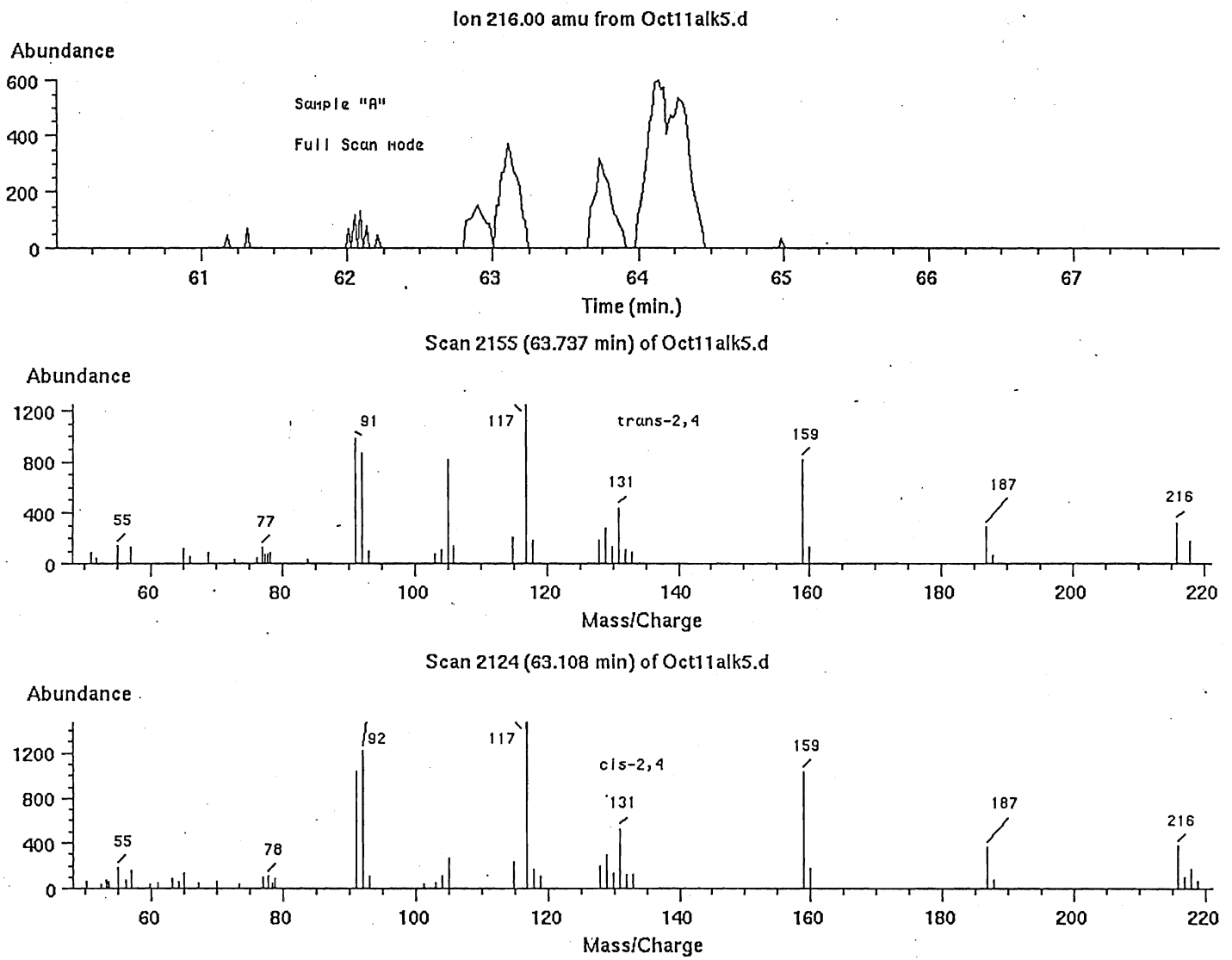


Figure 39

Full scan EI mass spectra of cis and trans 1-ethyl-4-butyltetralin

Figure 40

Full scan EI mass spectra of cis and trans 1-methyl-4-pentyltetralin

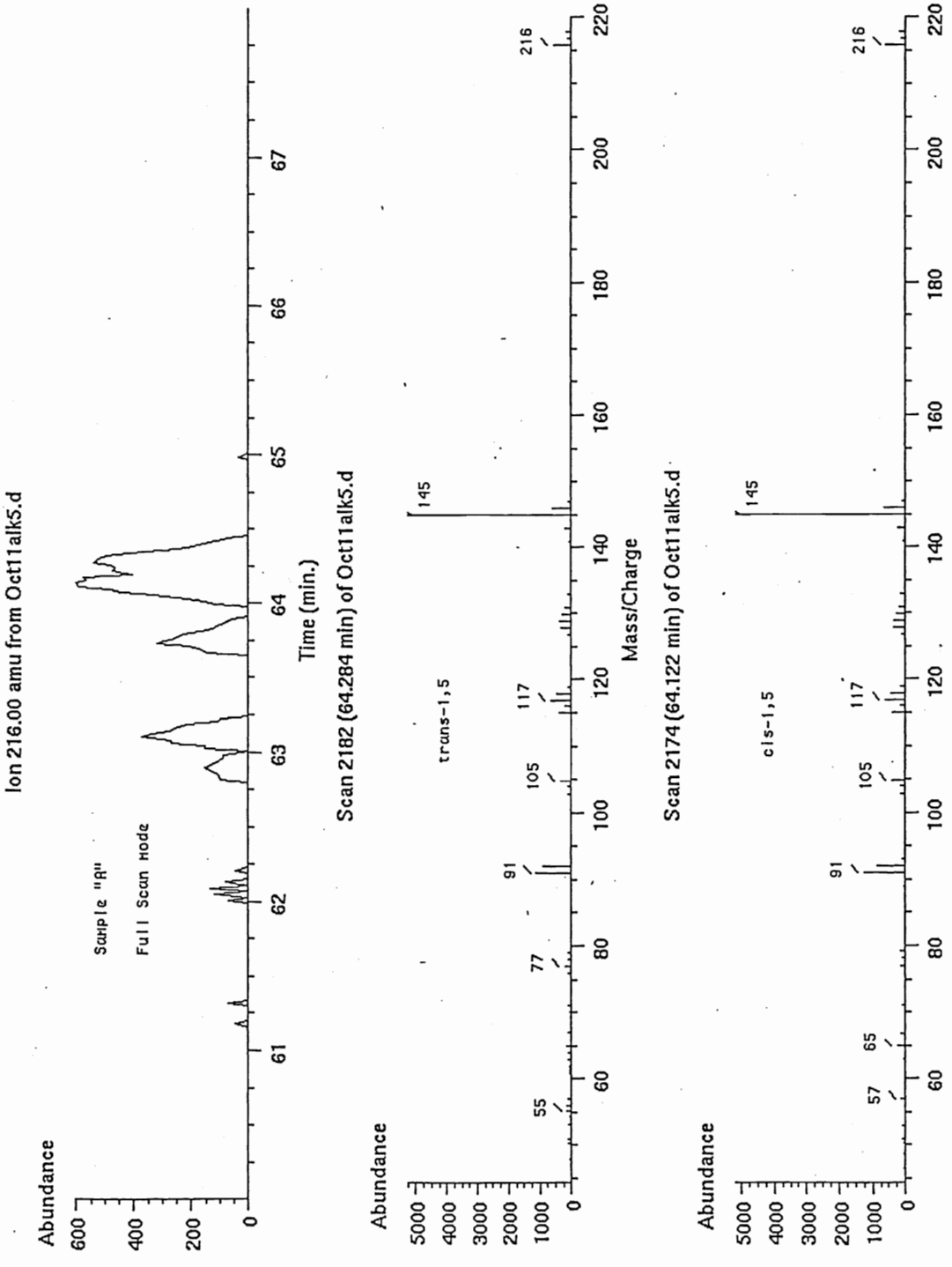


Figure 41

Full scan EI mass spectra of cis and trans 1-ethyl-4-pentyltetralin

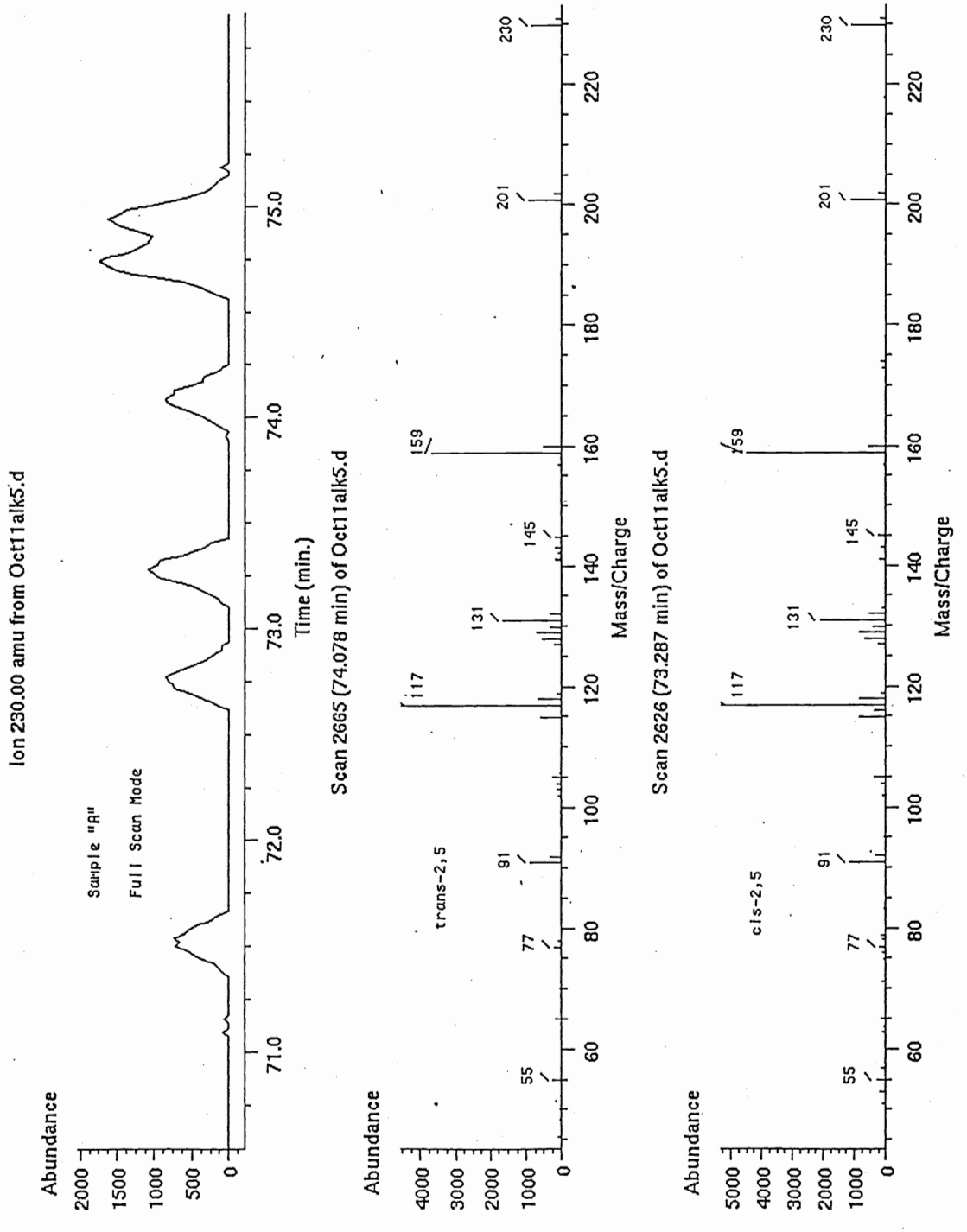
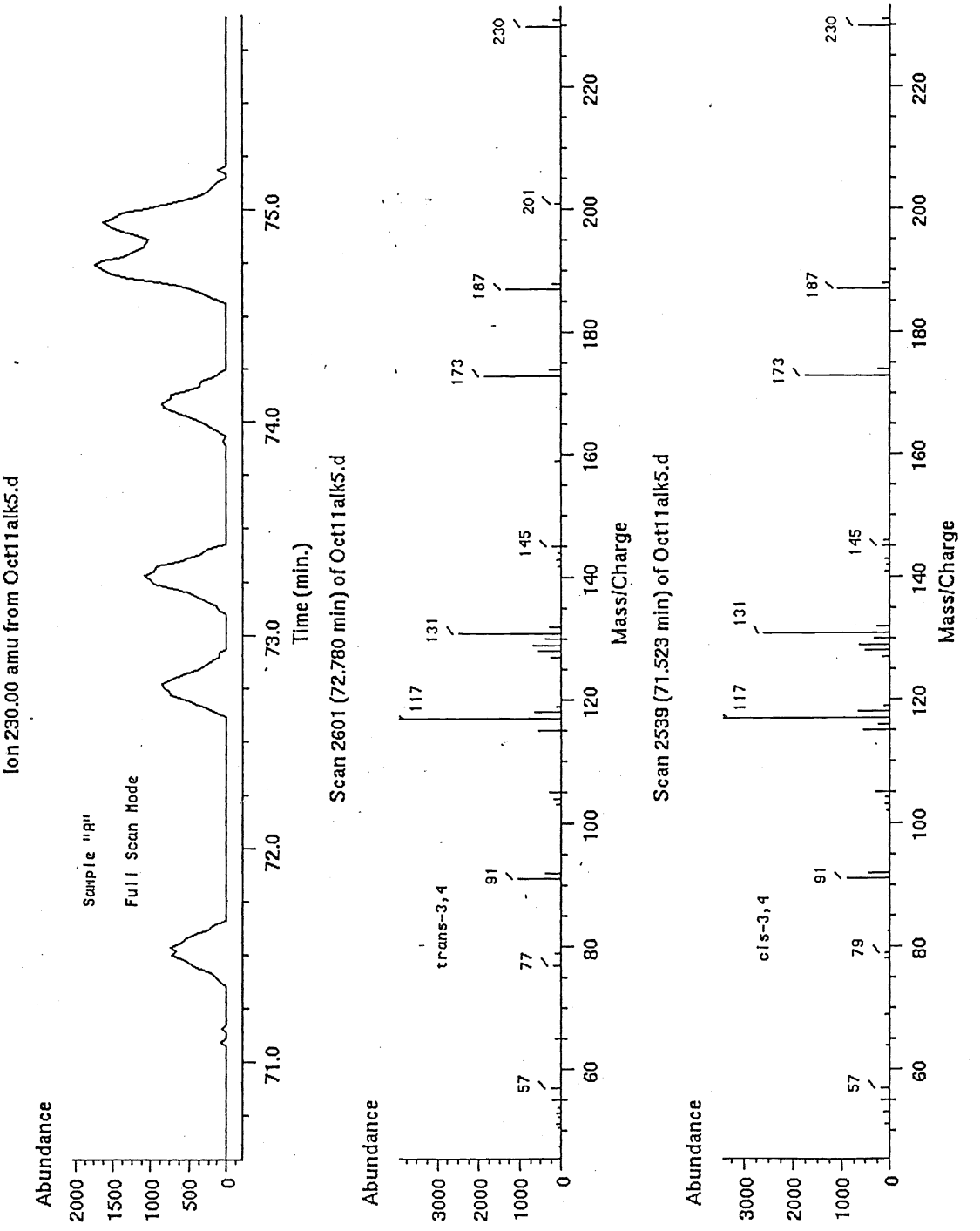


Figure 42

Full scan EI mass spectra of cis and trans 1-propyl-4-butyltetralin



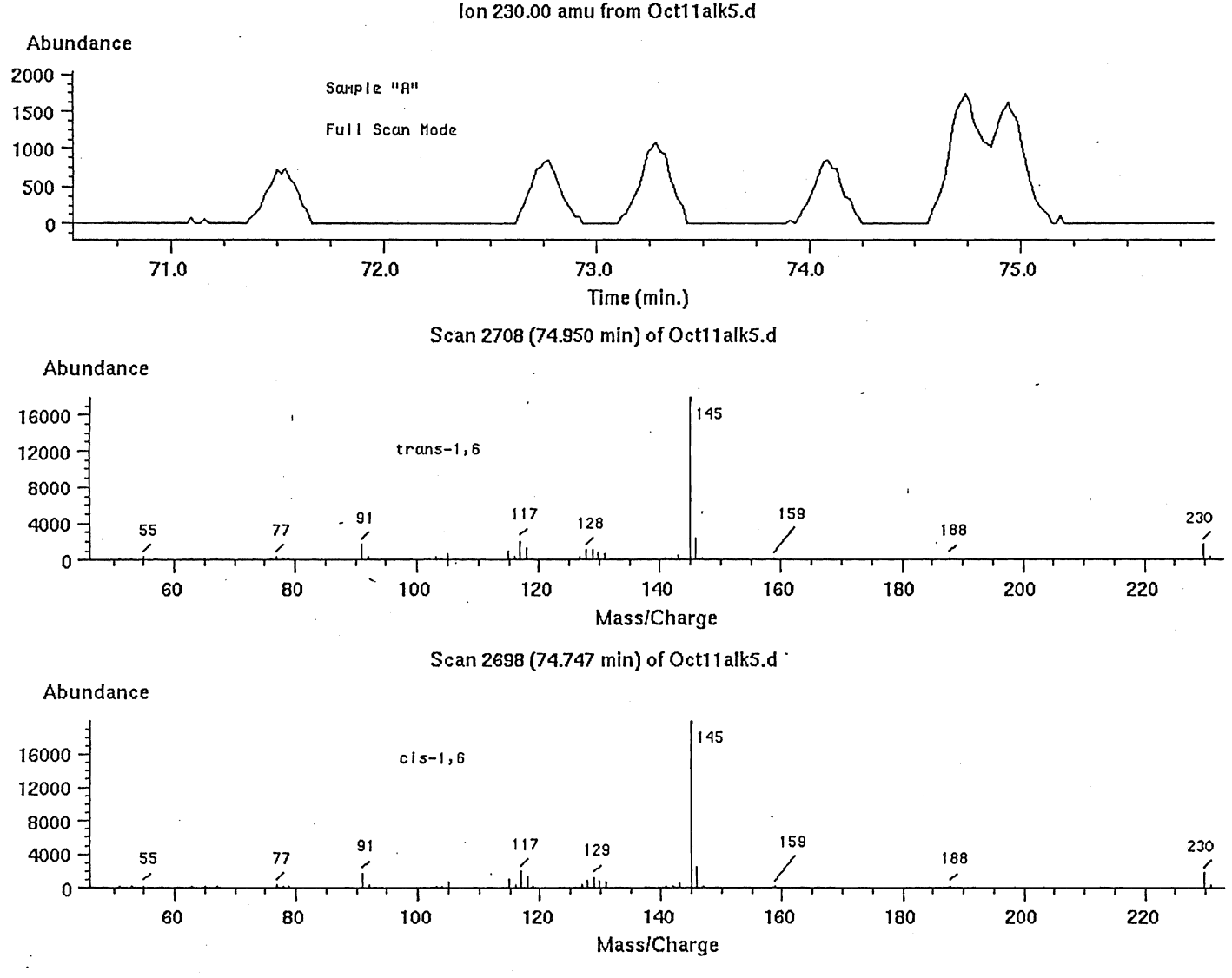


Figure 43

Full scan EI mass spectra of cis and trans 1-methyl-4-hexyltetralin

Figure 44

Full scan EI mass spectra of cis and trans 1,4-dibutyltetralin

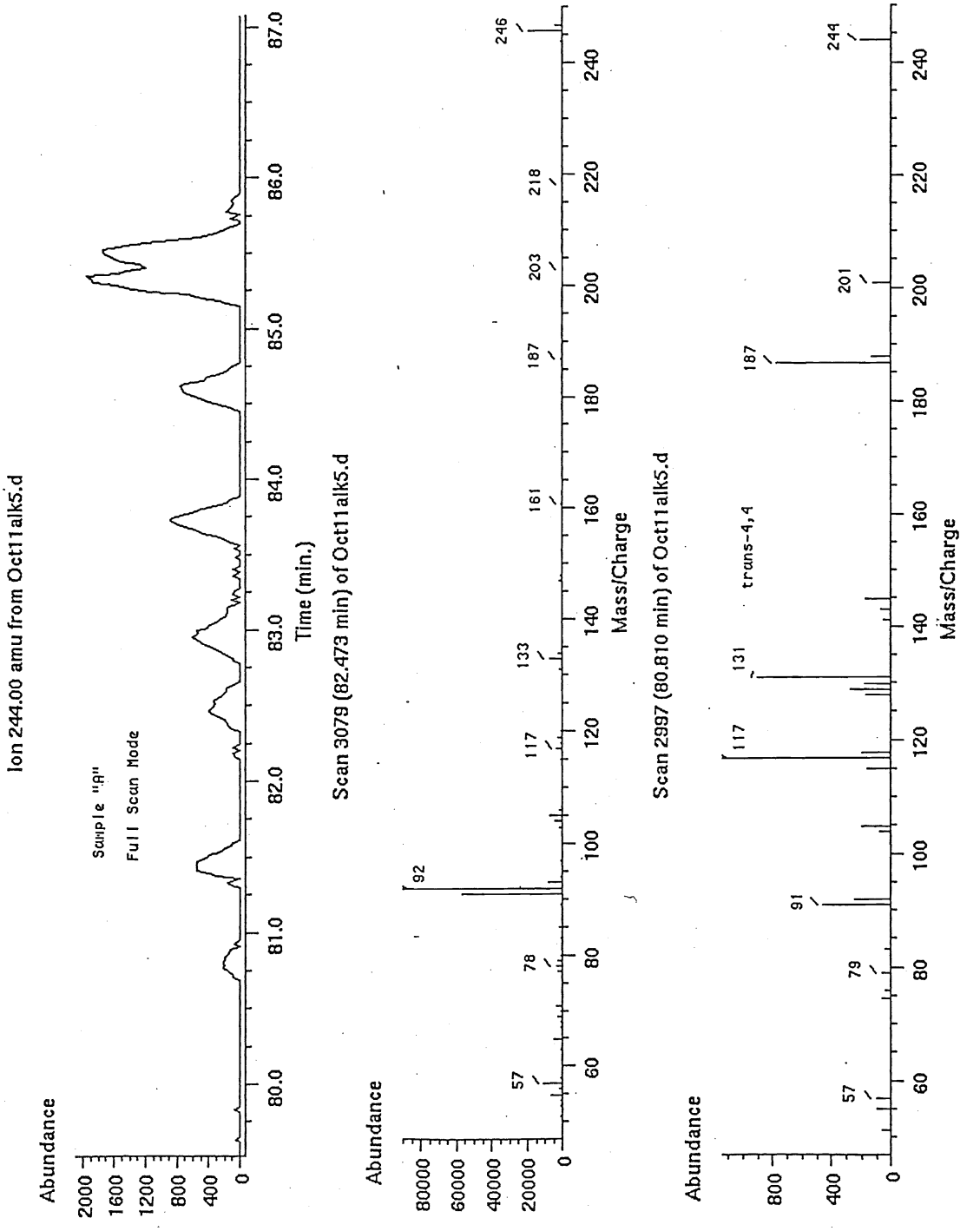


Figure 45

Full scan EI mass spectra of cis and trans 1-propyl-4-pentyltetralin

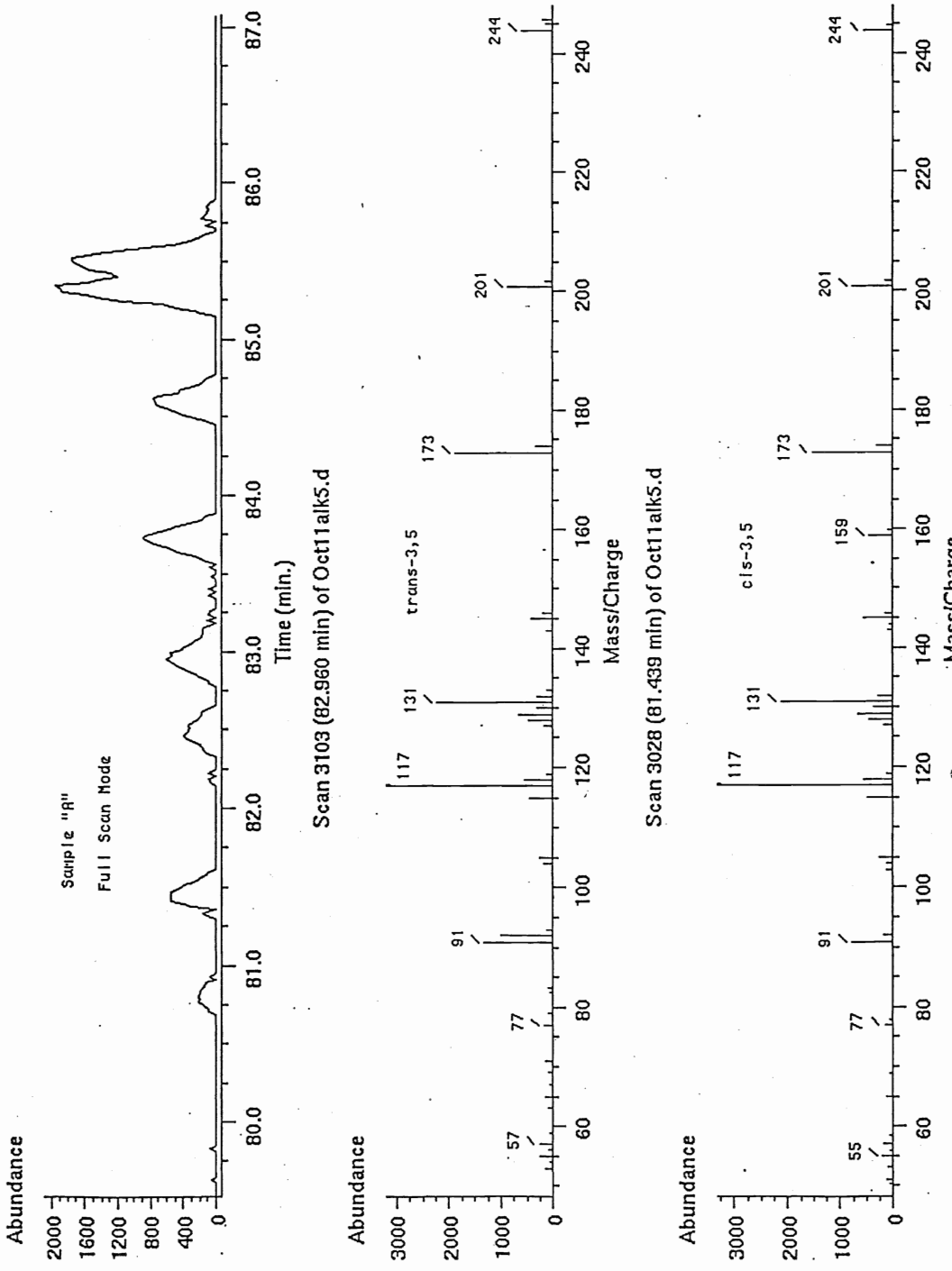
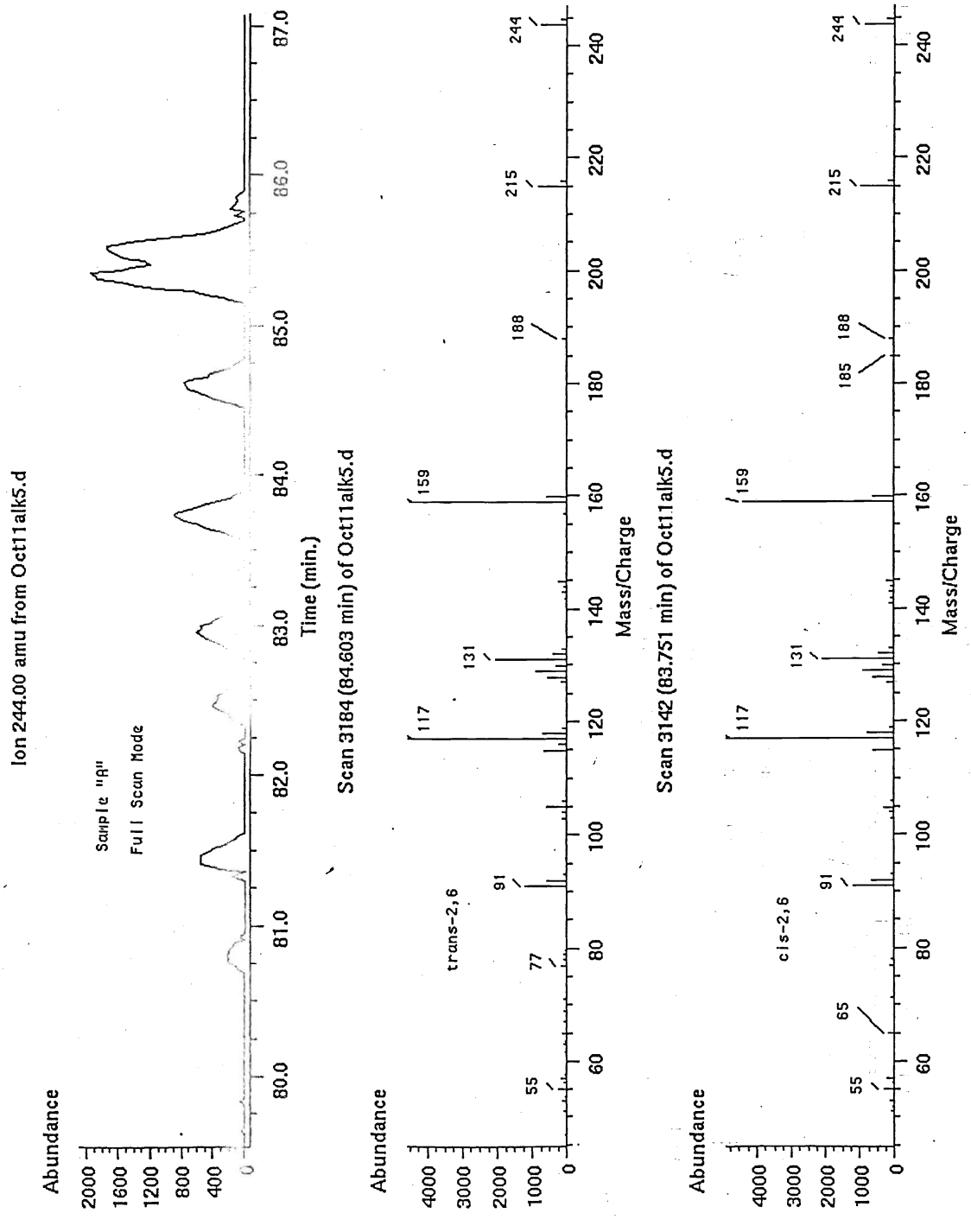


Figure 46

Full scan EI mass spectra of cis and trans 1-ethyl-4-hexyltetralin



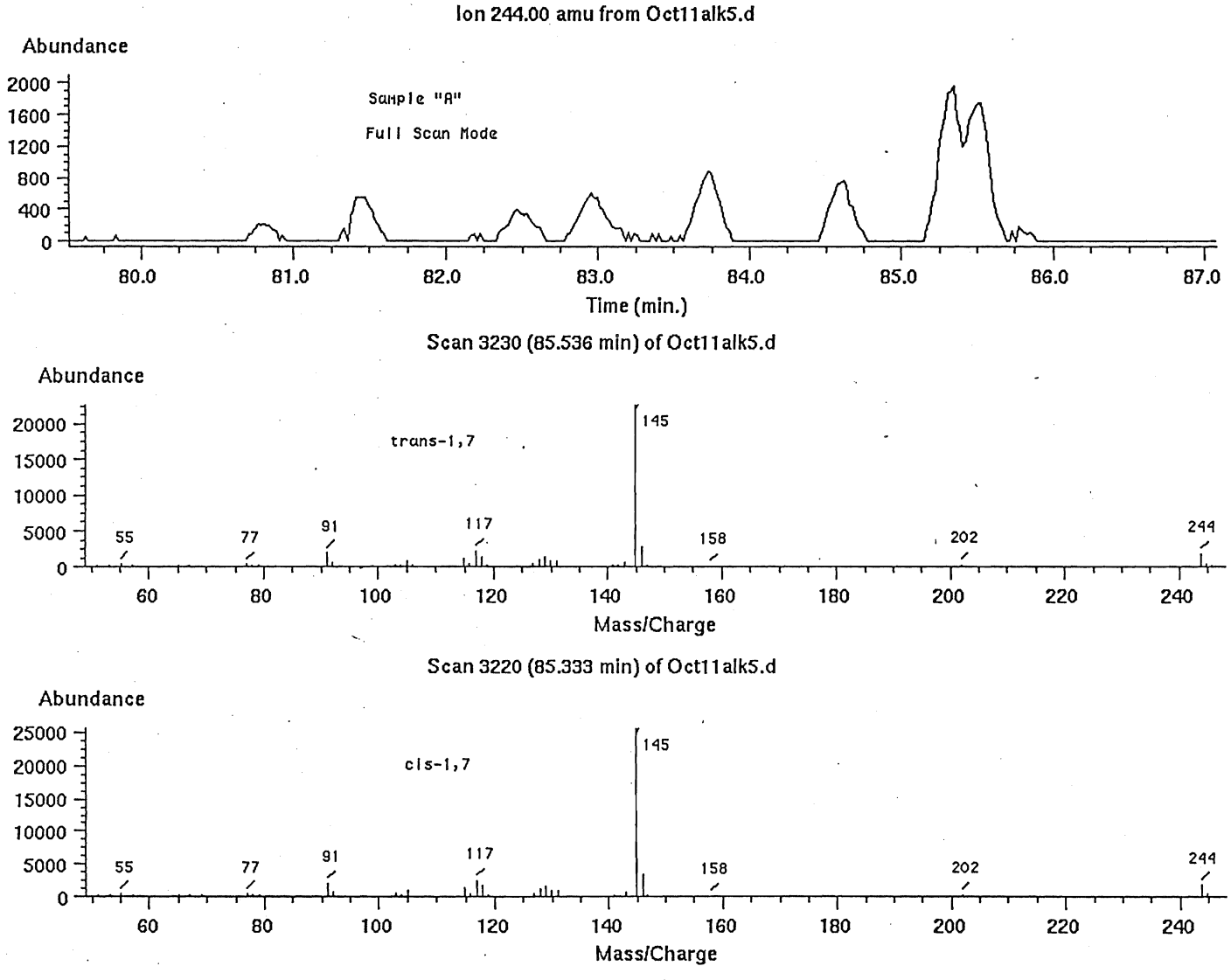


Figure 47

Full scan EI mass spectra of cis and trans 1-methyl-4-heptyltetralin

Figure 48

Full scan EI mass spectra of cis and trans 1-butyl-4-pentyltetralin

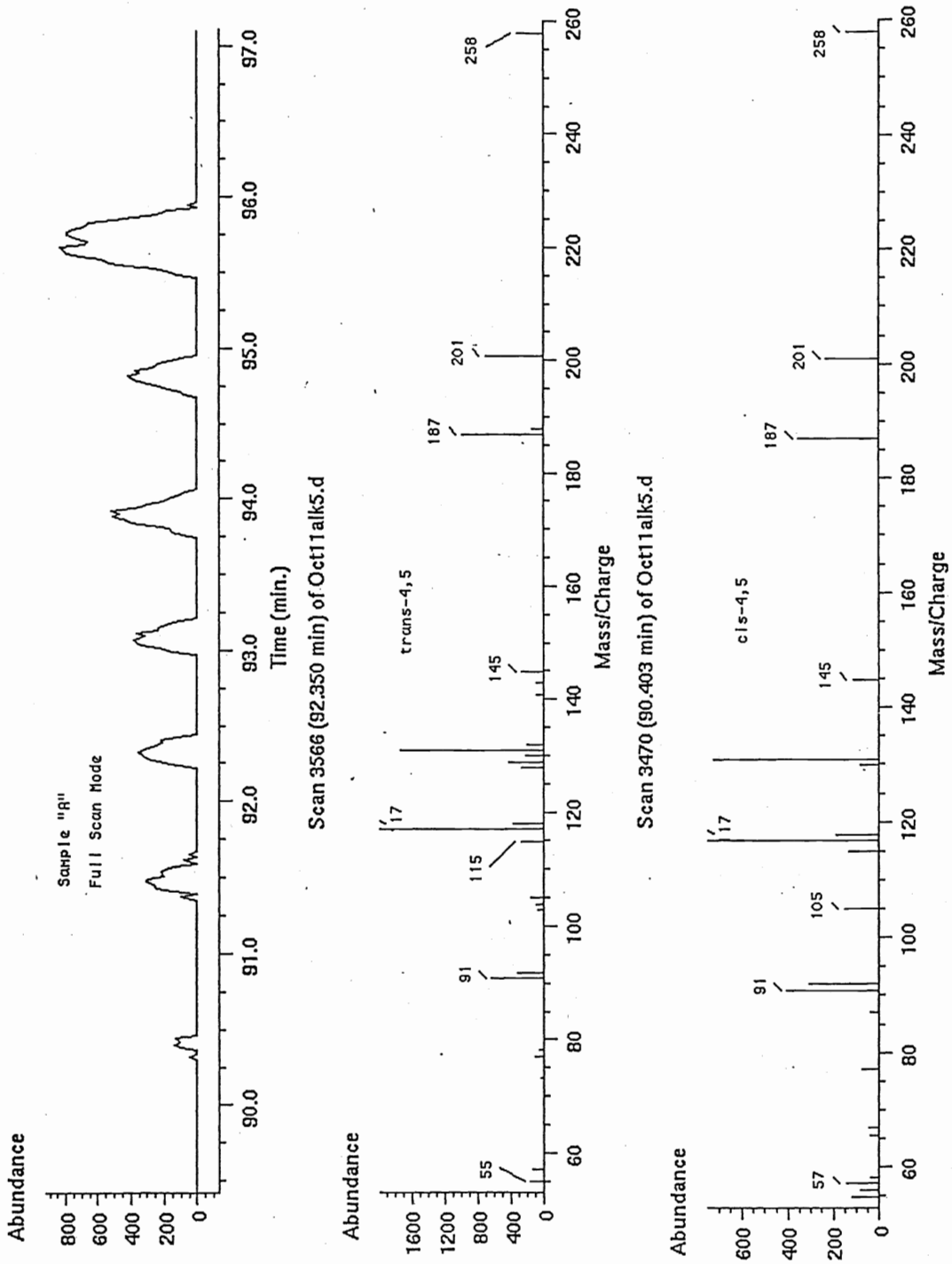


Figure 49

Full scan EI mass spectra of cis and trans 1-propyl-4-hexyltetralin

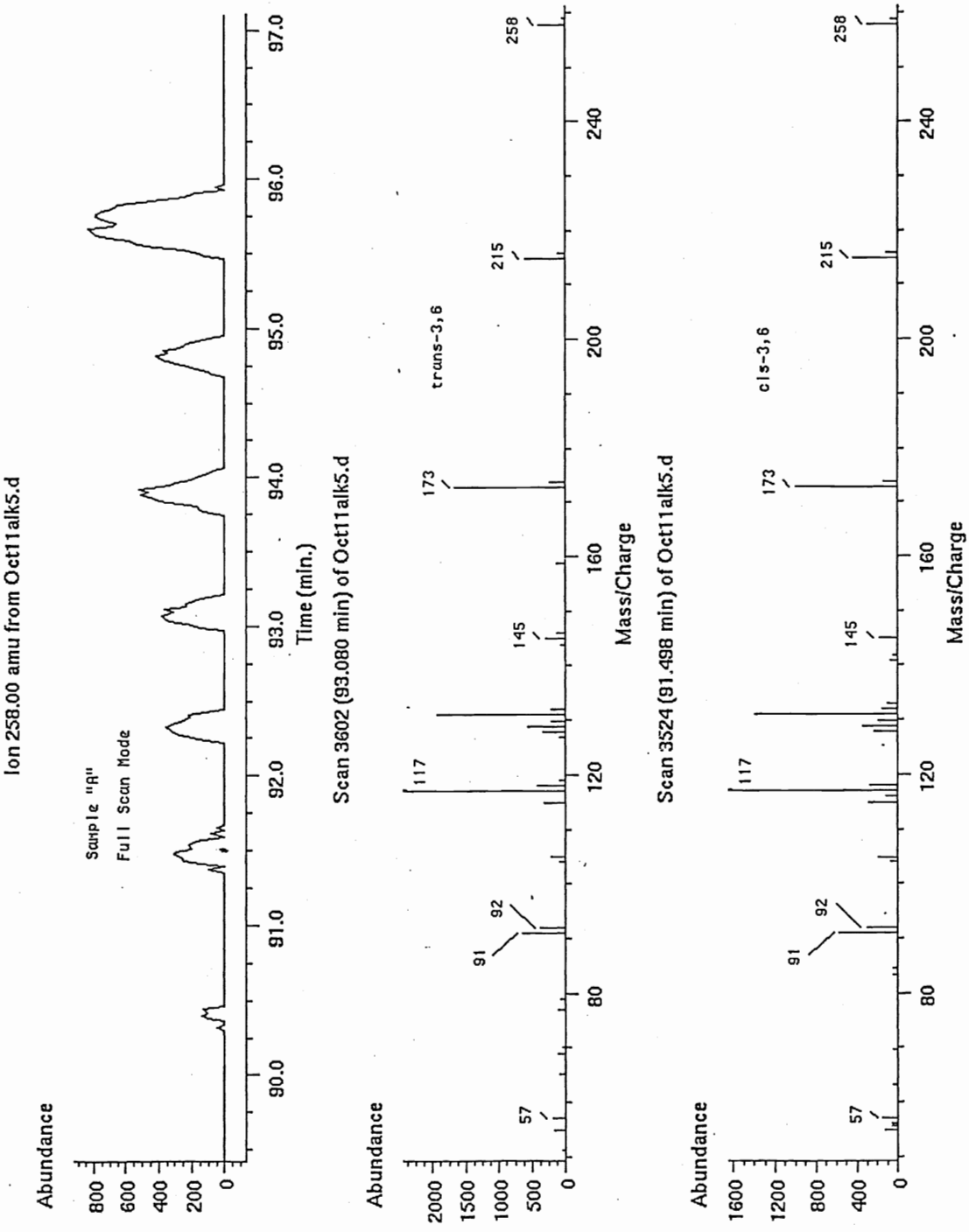


Figure 50

Full scan EI mass spectra of cis and trans 1-ethyl-4-heptyltetralin

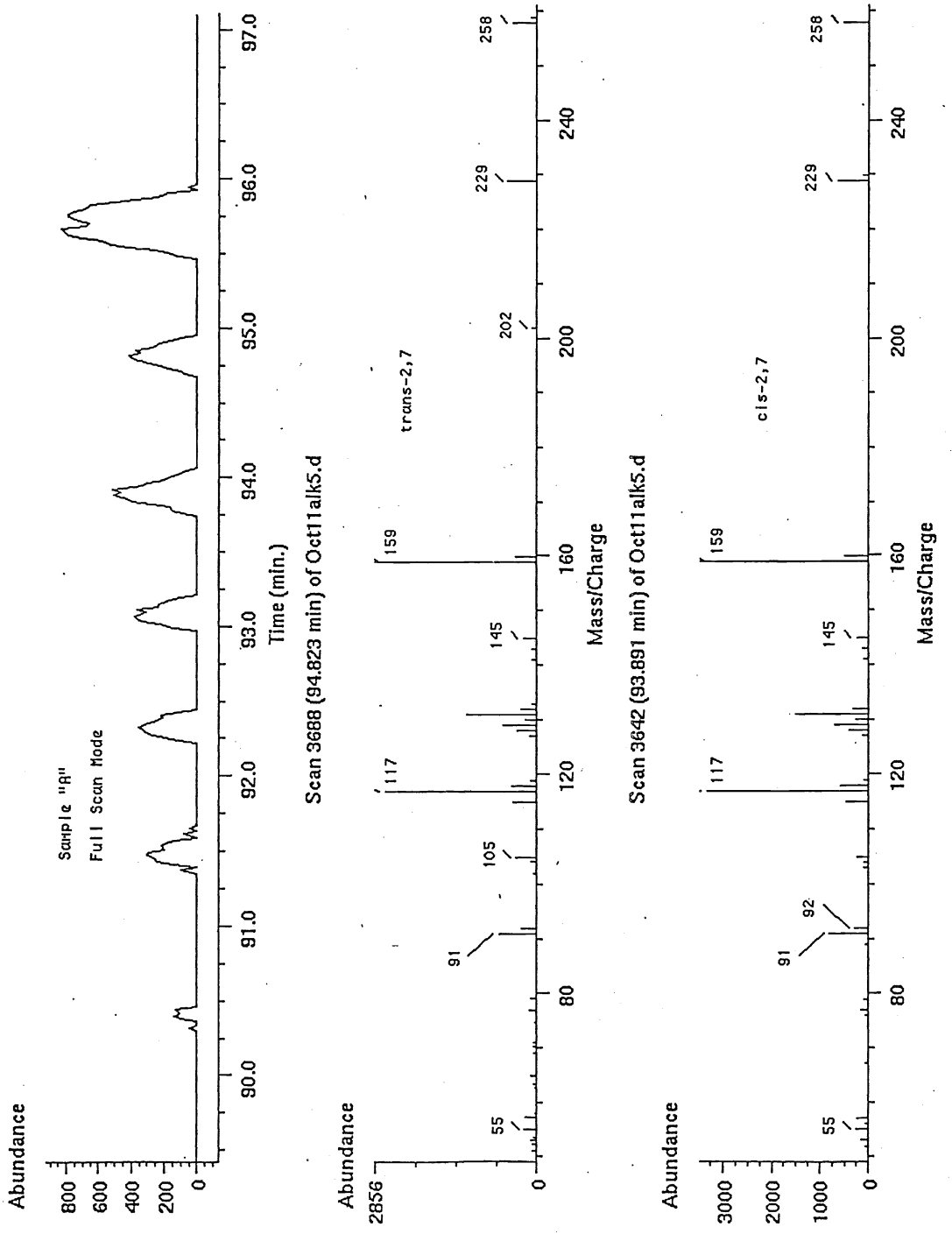


Figure 51

Full scan EI mass spectra of cis and trans 1-methyl-4-octyltetralin

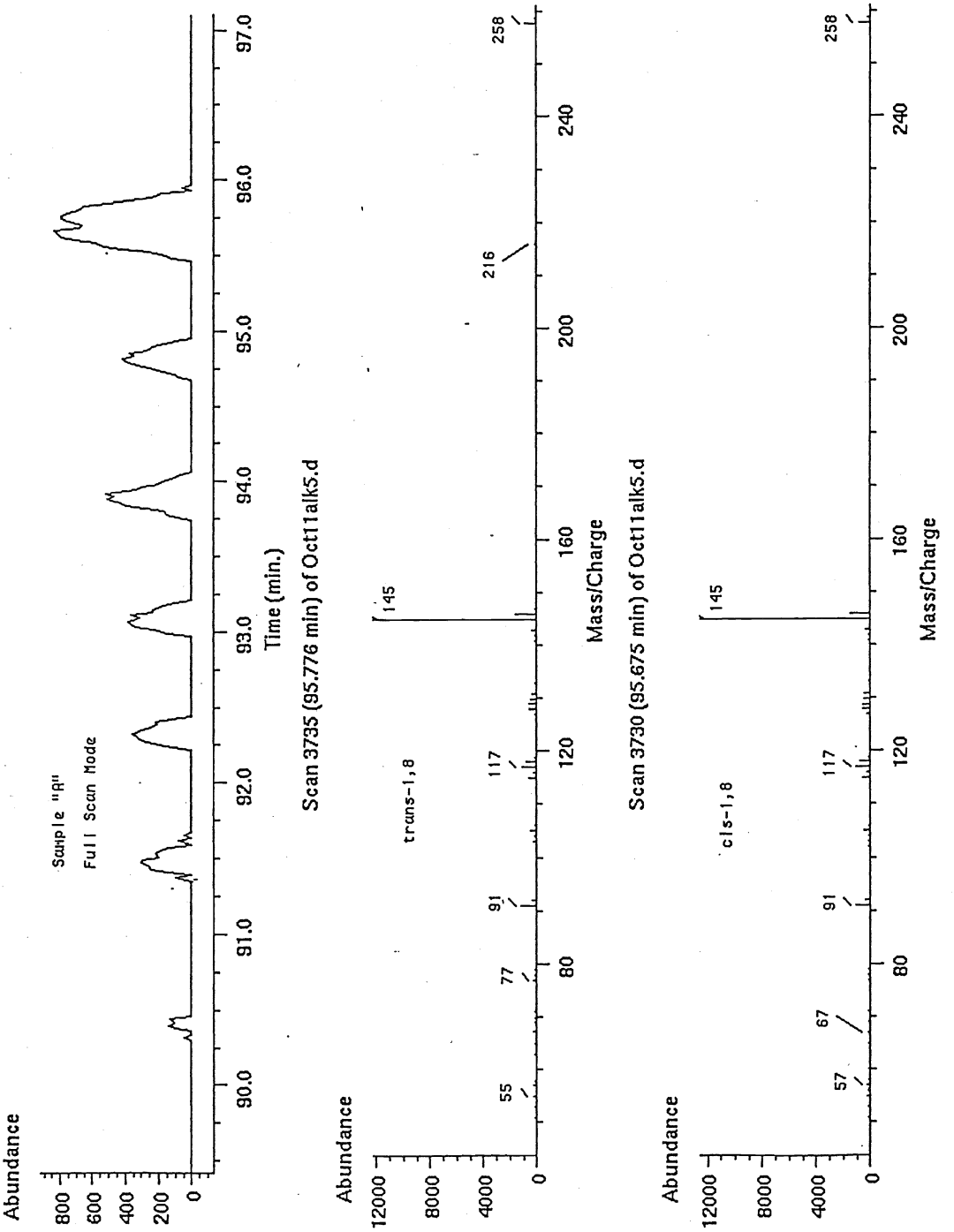


Figure 52

Ion Chromatograms of selected ions of dialkyltetralins standard, DAT, using SIM mode

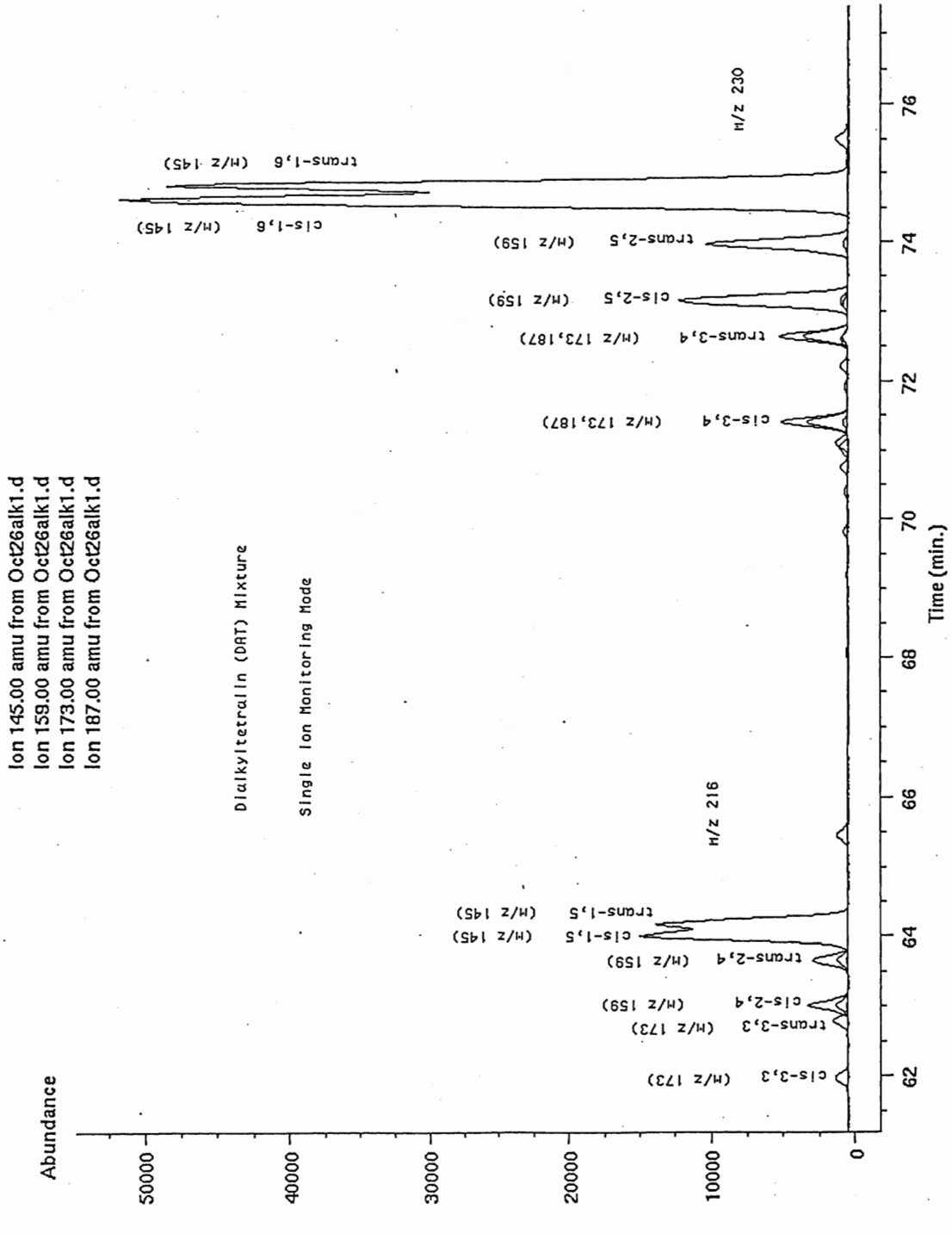


Figure 53

Ion Chromatograms of selected ions of dialkyltetralins standard, DAT, using SIM mode - continued

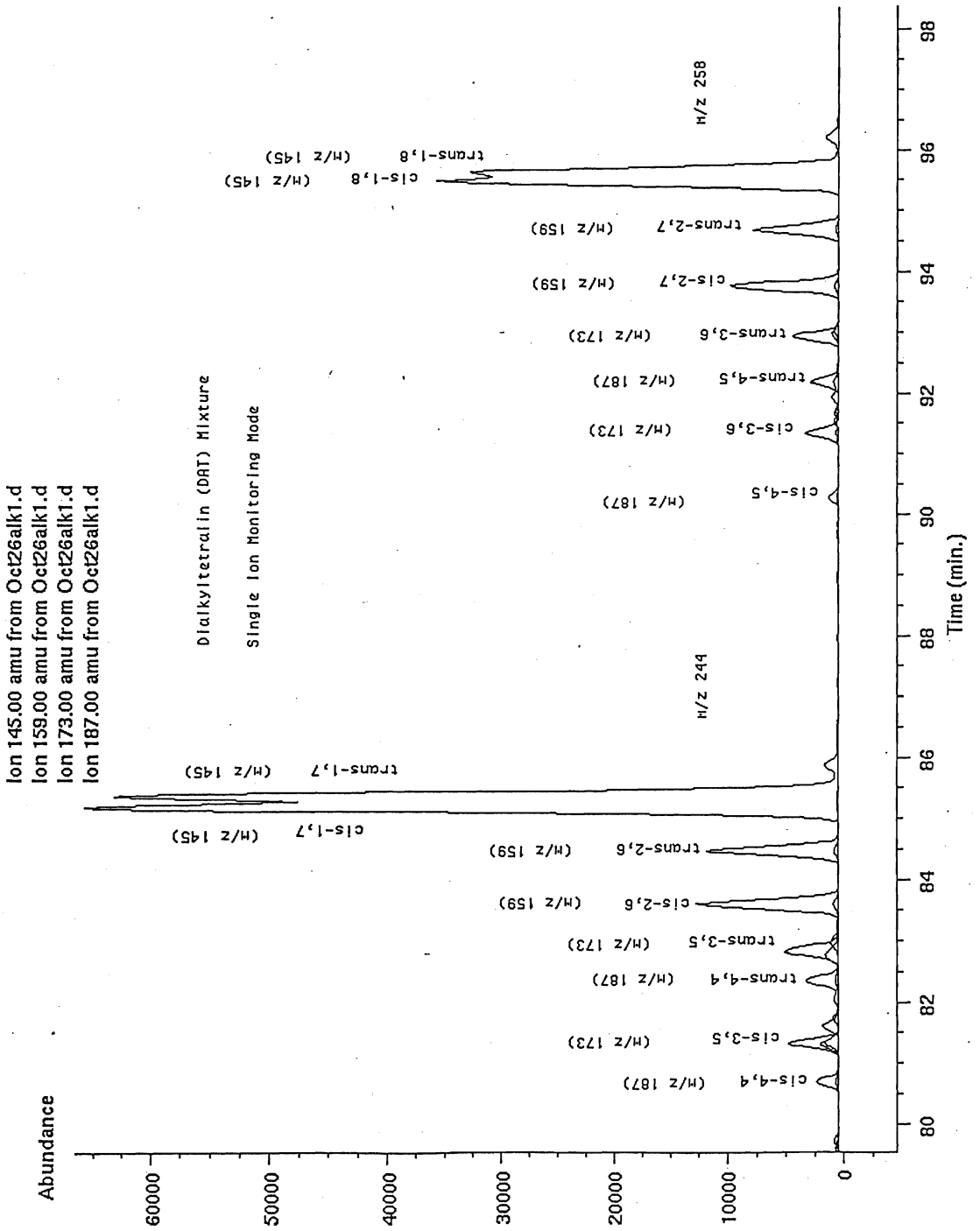


Figure 54

EI mass spectra of cis and trans 1,4-dipropyltetralin present in sample "A" using SIM mode

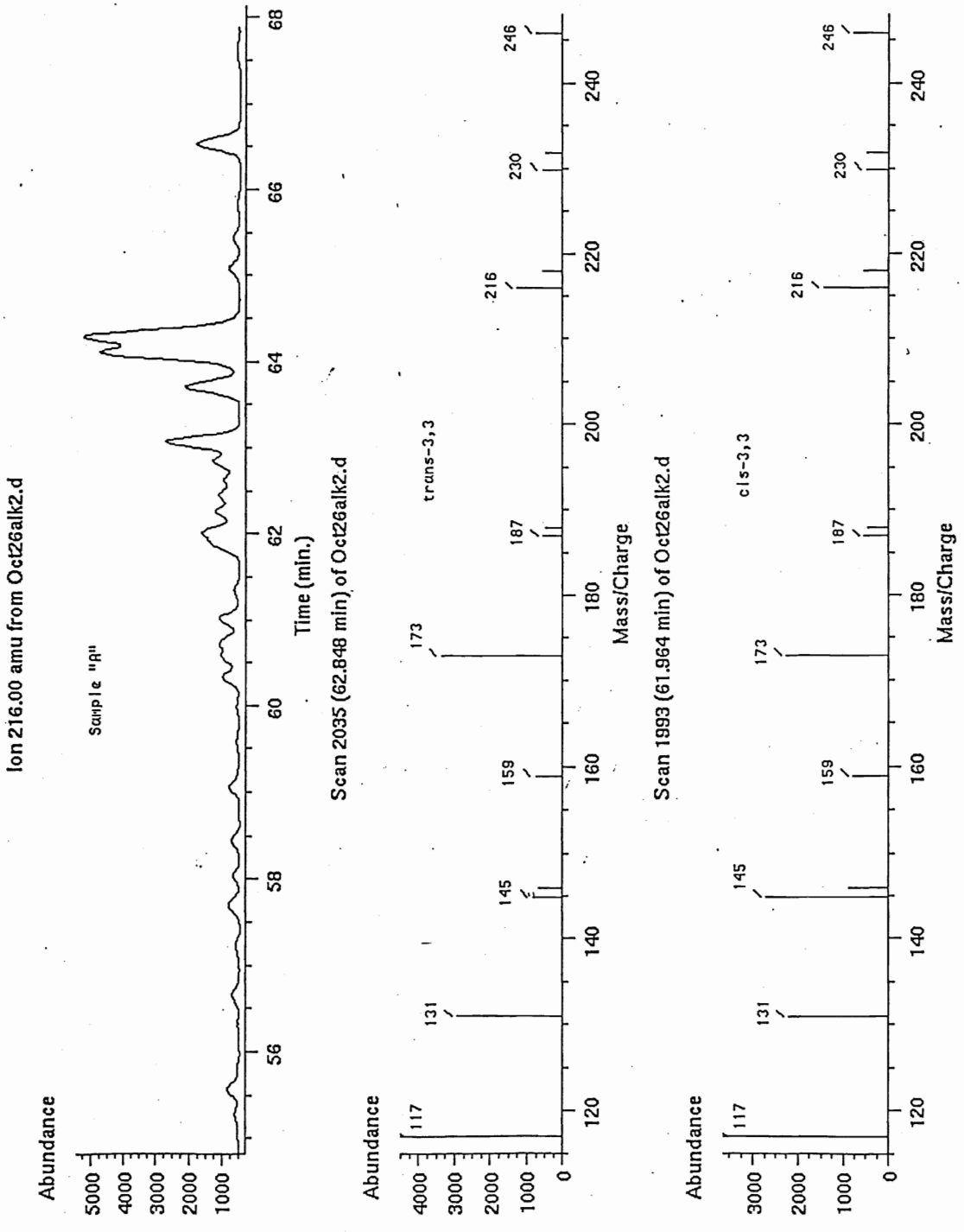


Figure 55

EI mass spectra of cis and trans 1-ethyl-4-butyltetralin present in sample "A" using SIM mode

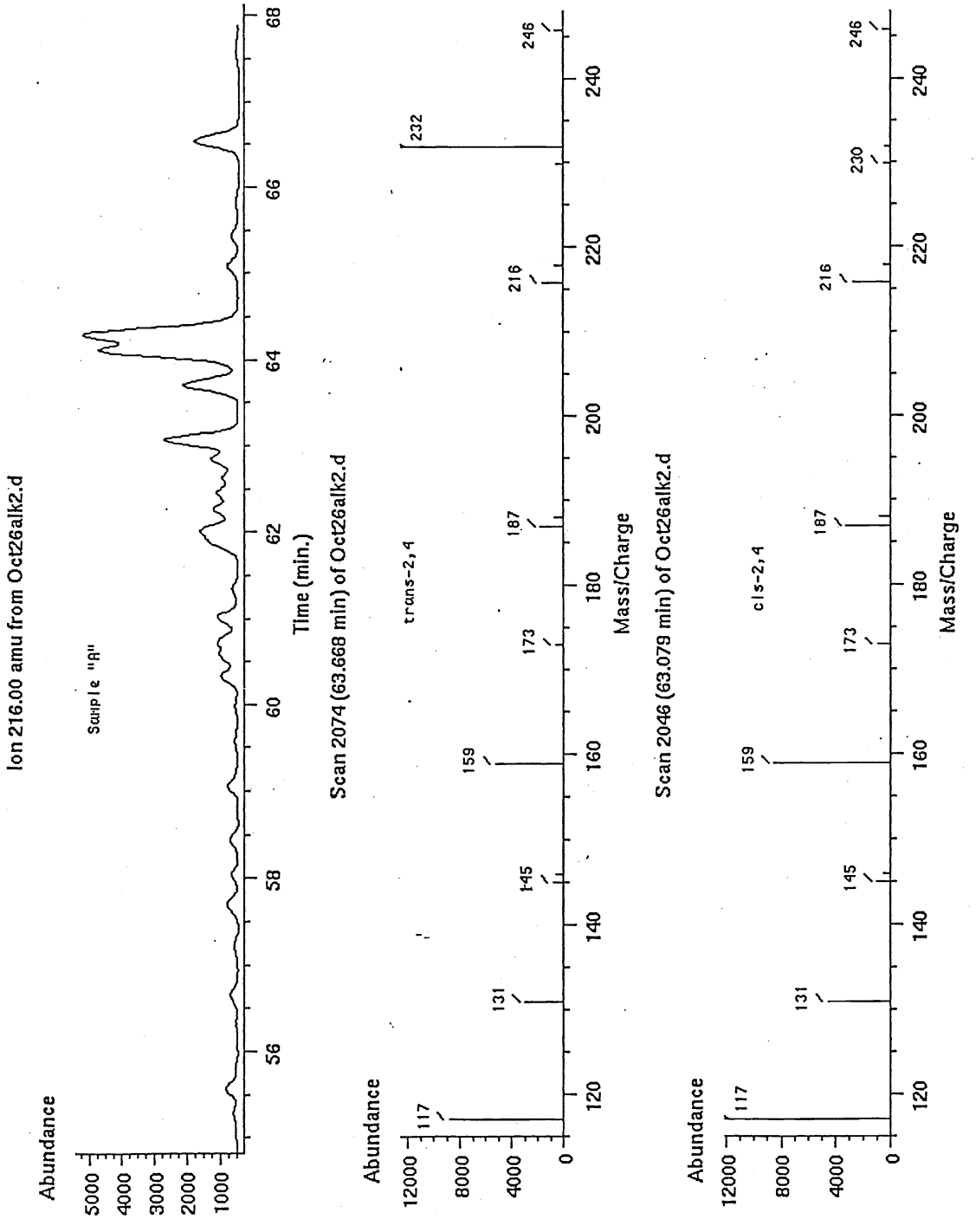


Figure 56

EI mass spectra of cis and trans 1-methyl-4-pentyltetralin present in sample "A" using SIM mode

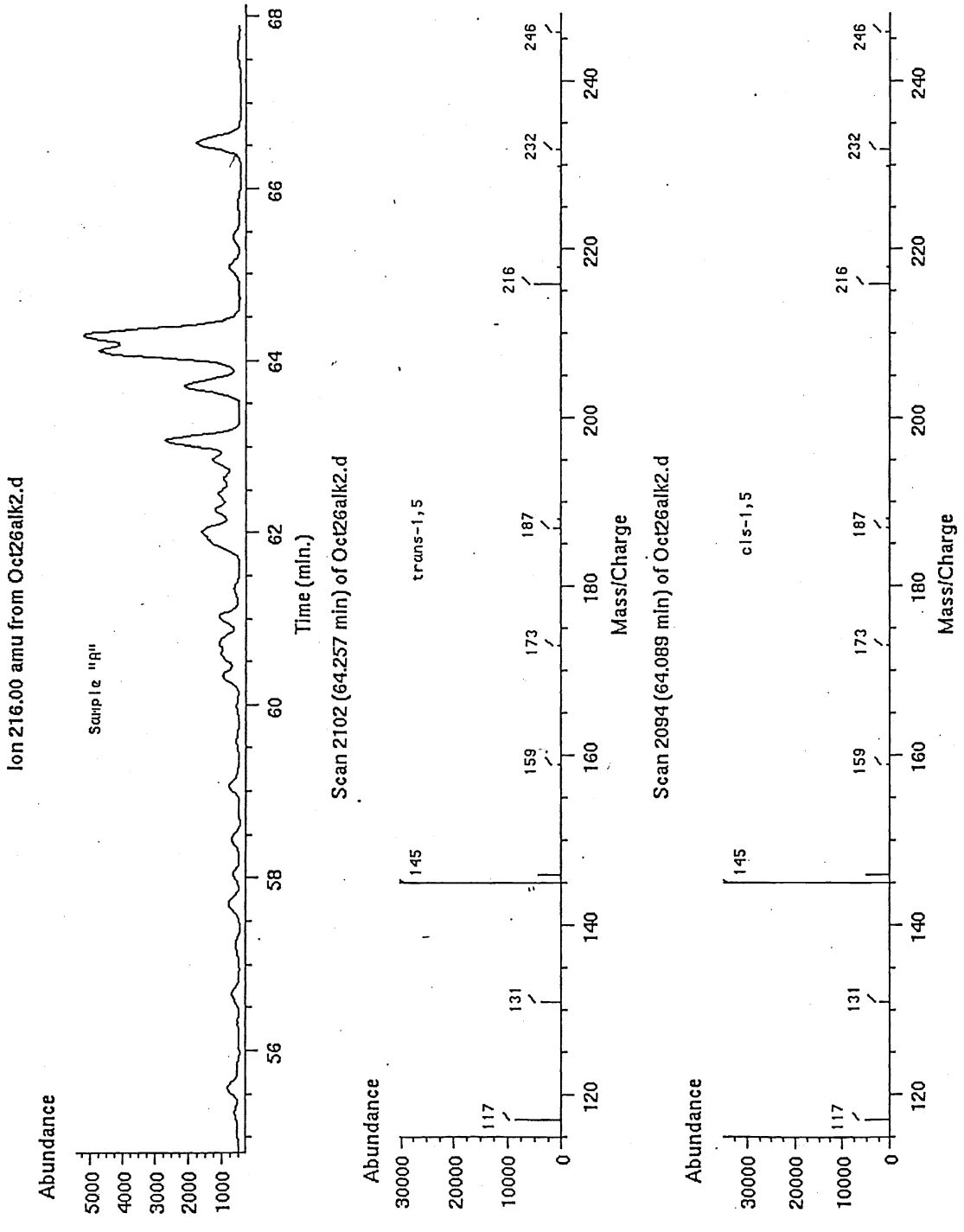


Figure 57

EI mass spectra of cis and trans 1-propyl-4-butyltetralin present in sample "A" using SIM mode

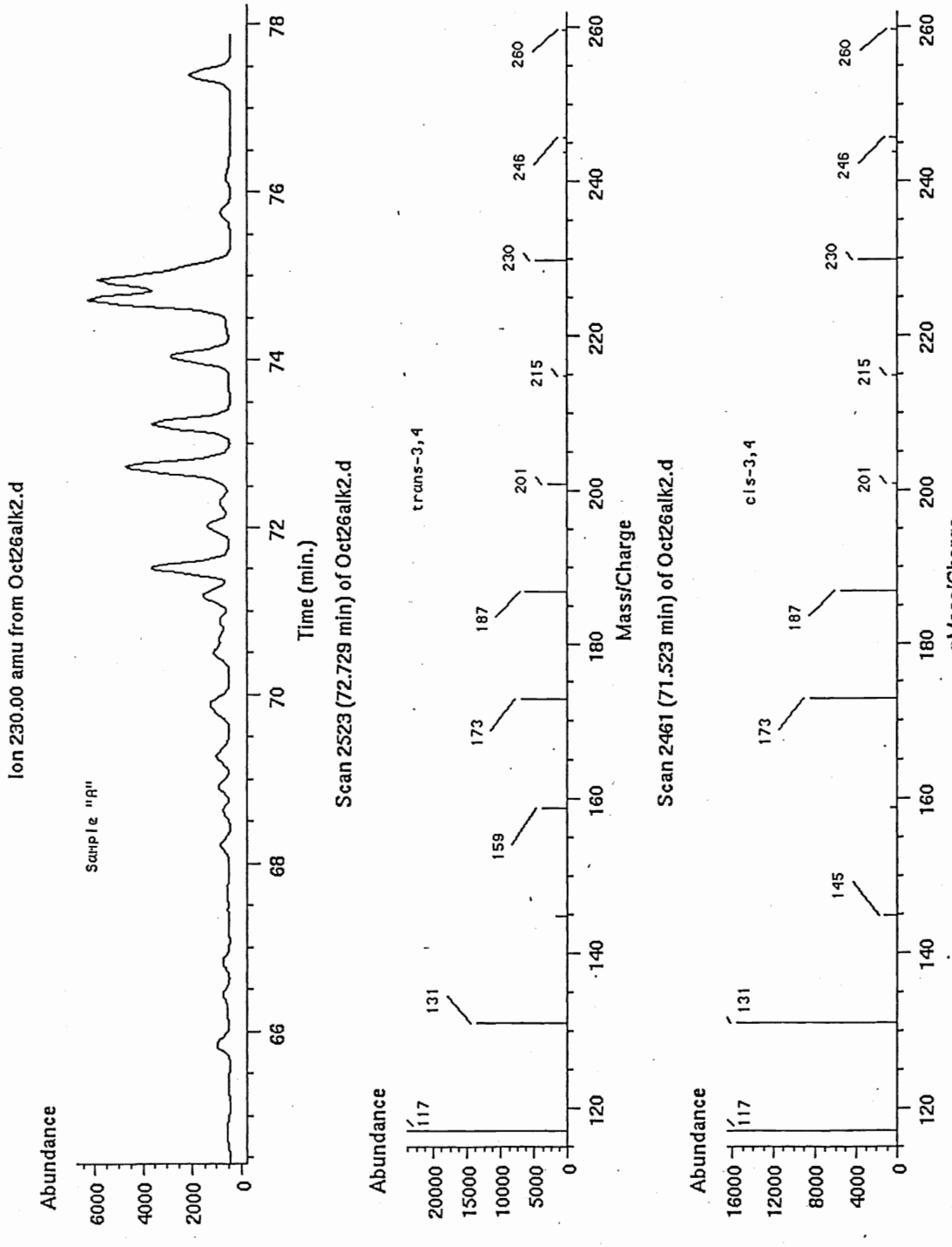


Figure 58

EI mass spectra of cis and trans 1-ethyl-4-pentyltetralin present in sample "A" using SIM mode

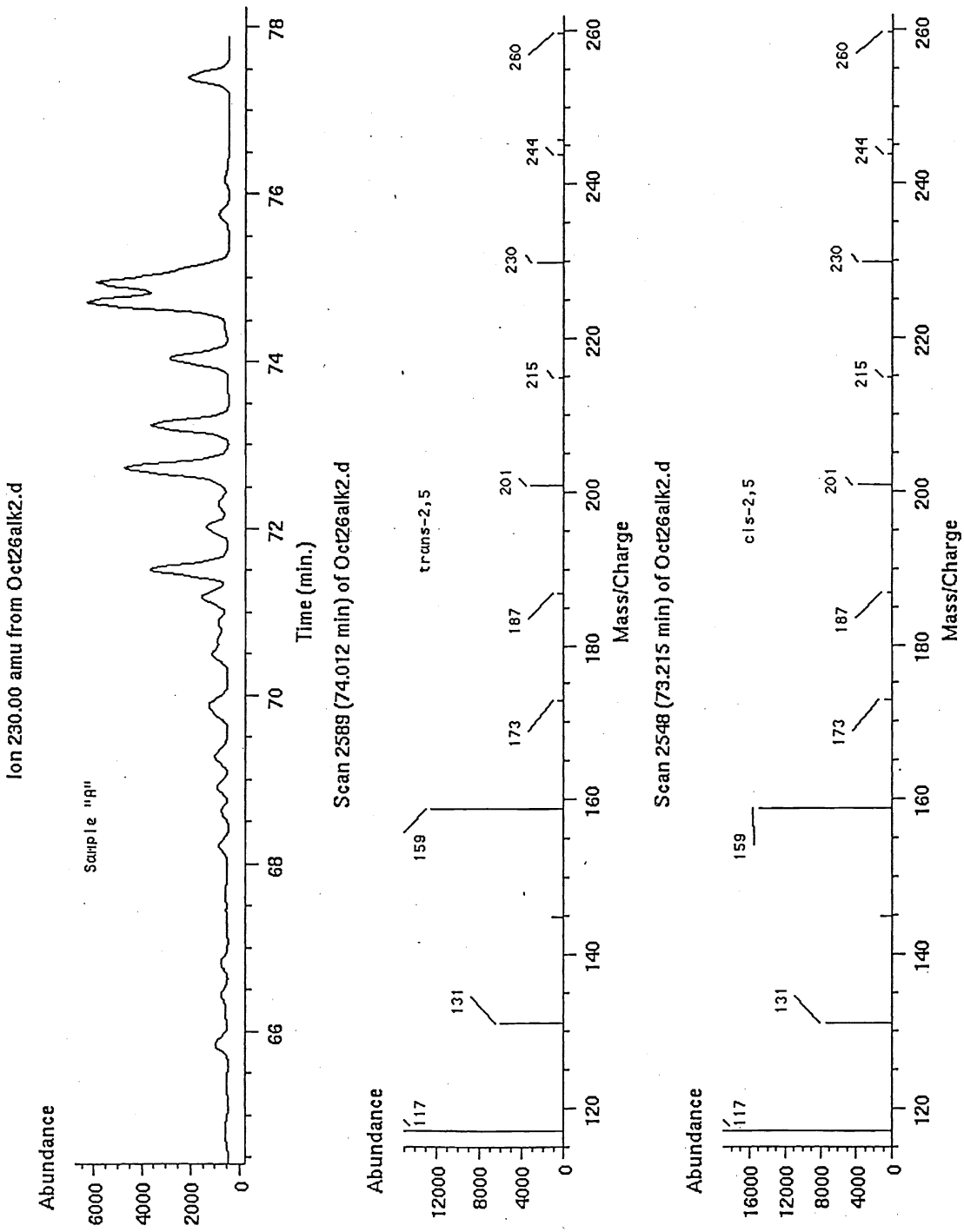


Figure 59

EI mass spectra of cis and trans 1-methyl-4-hexyltetralin present in sample "A" using SIM mode

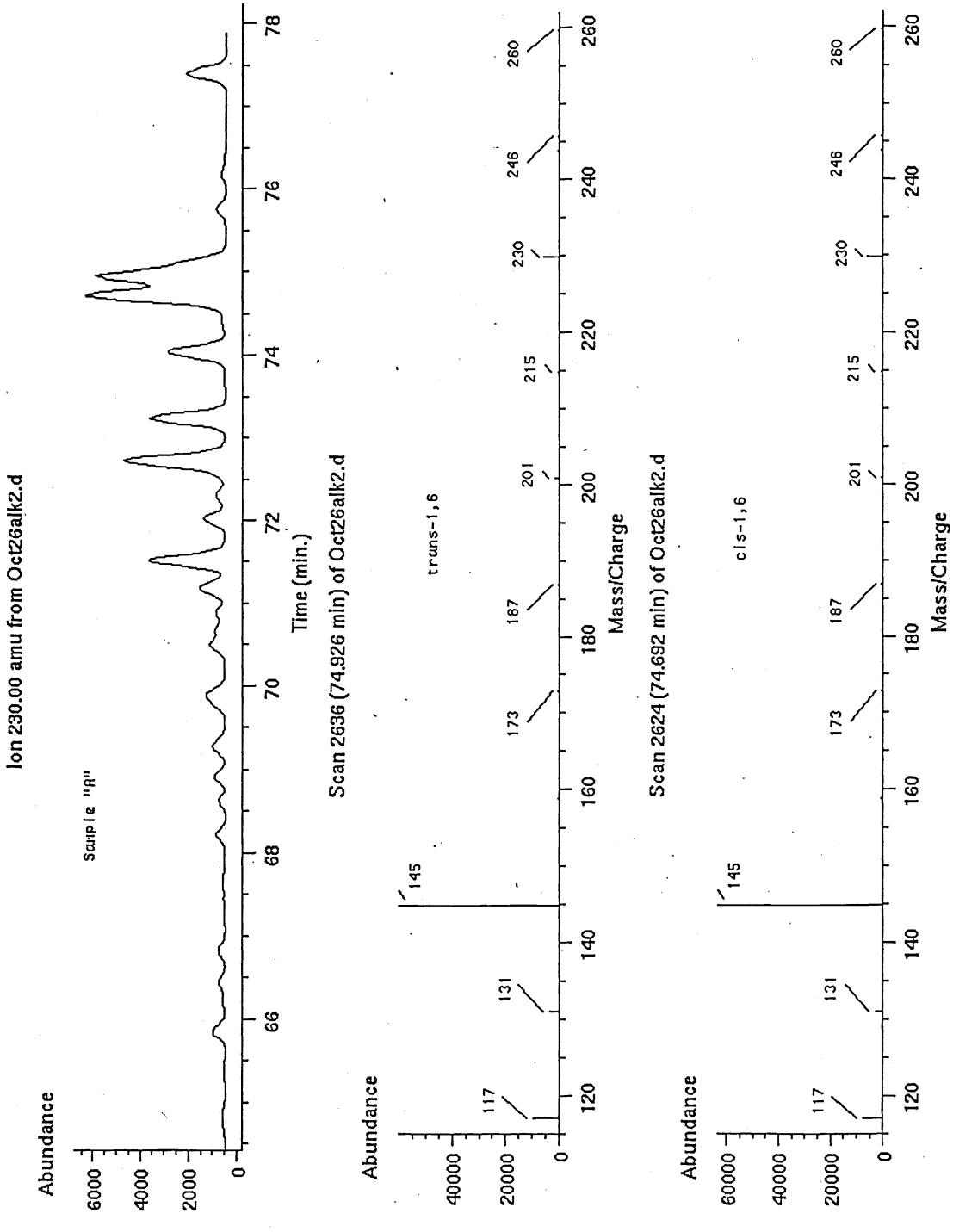


Figure 60

EI mass spectra of cis and trans 1,4-dibutyltetralin present in sample "A" using SIM mode

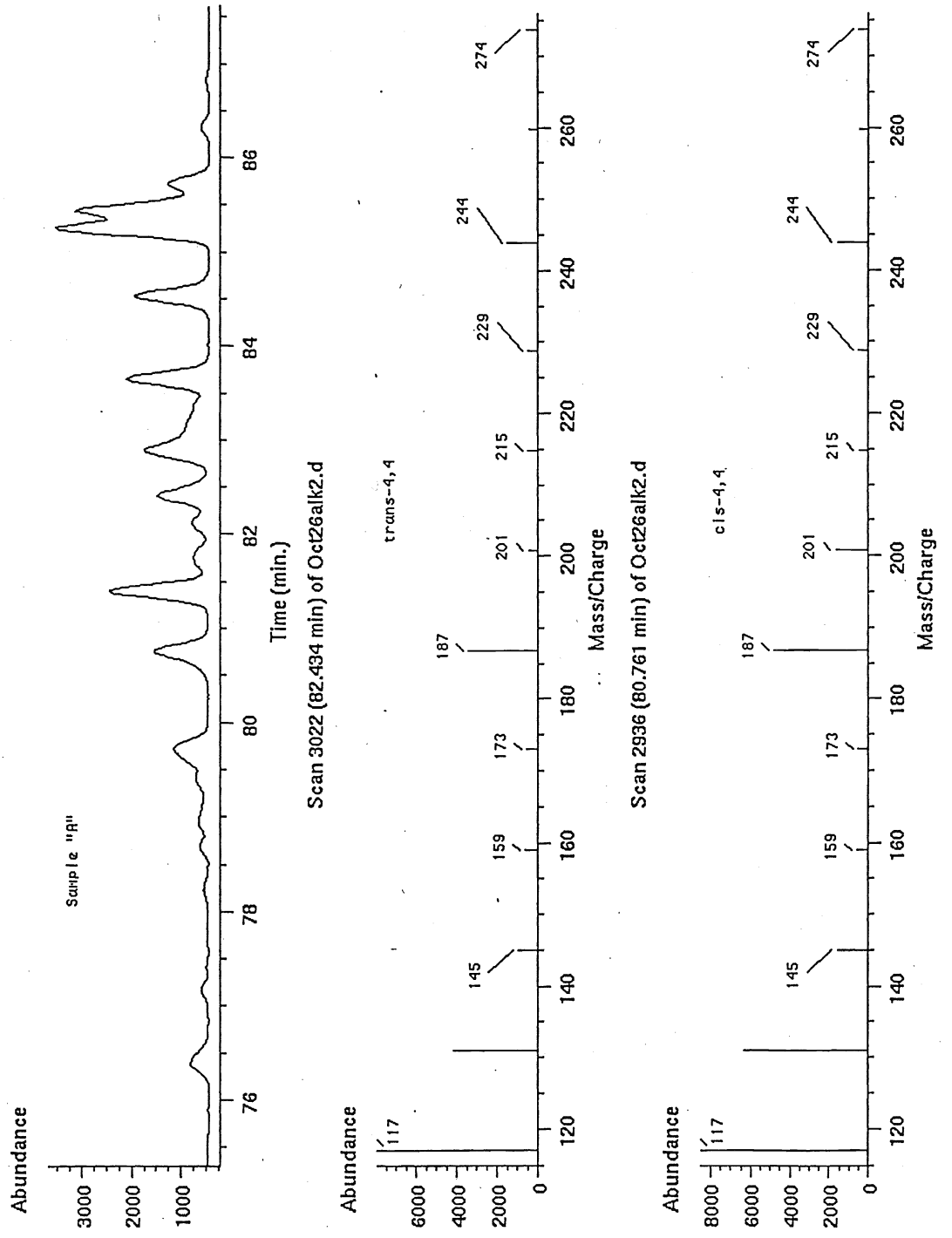


Figure 61

EI mass spectra of cis and trans 1-propyl-4-pentyltetralin present in sample "A" using SIM mode

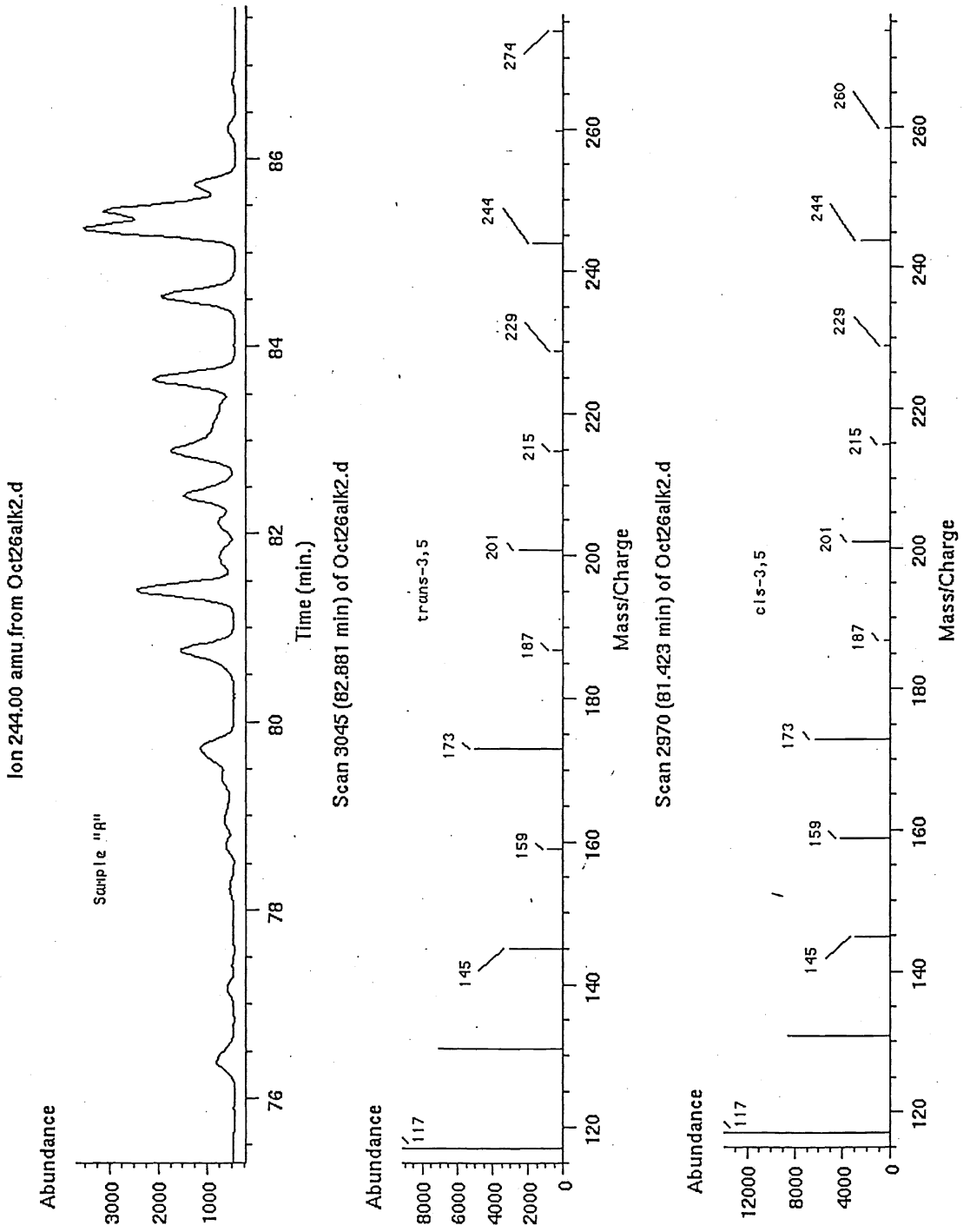


Figure 62

EI mass spectra of cis and trans 1-ethyl-4-hexyltetralin present in sample "A" using SIM mode

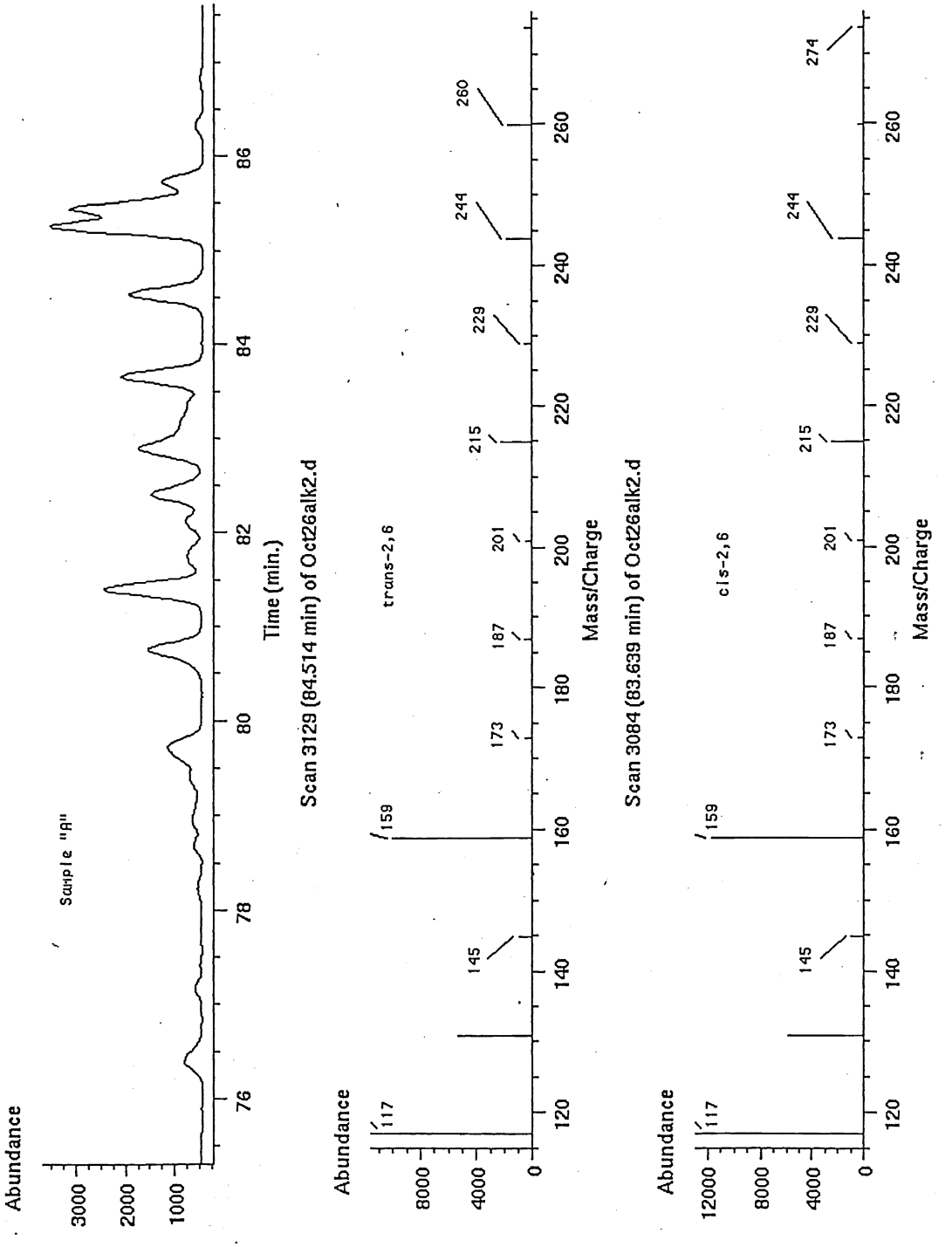


Figure 63

EI mass spectra of cis and trans 1-methyl-4-heptyltetralin present in sample "A" using SIM mode

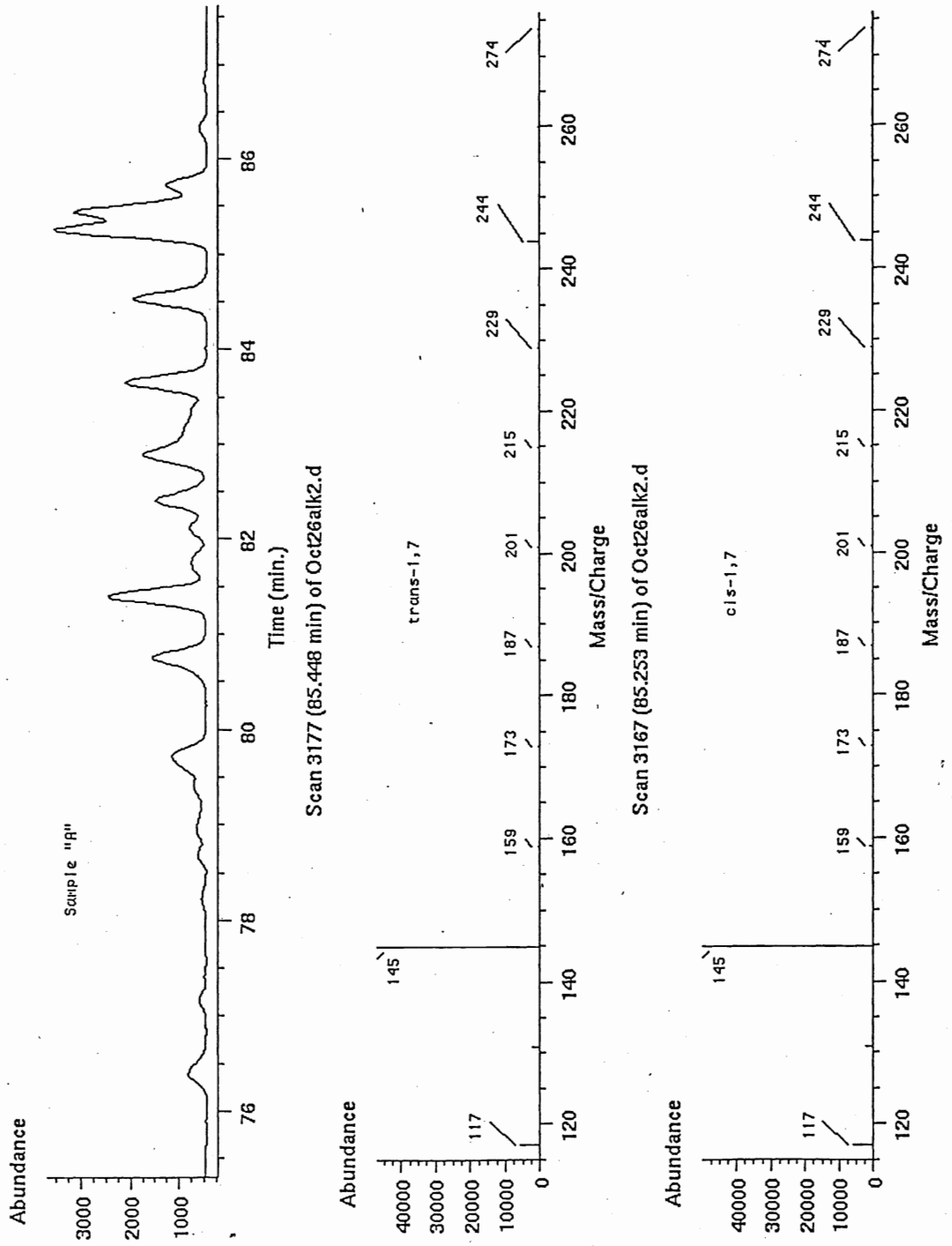


Figure 64

EI mass spectra of cis and trans 1-butyl-4-pentyltetralin present in sample "A" using SIM mode

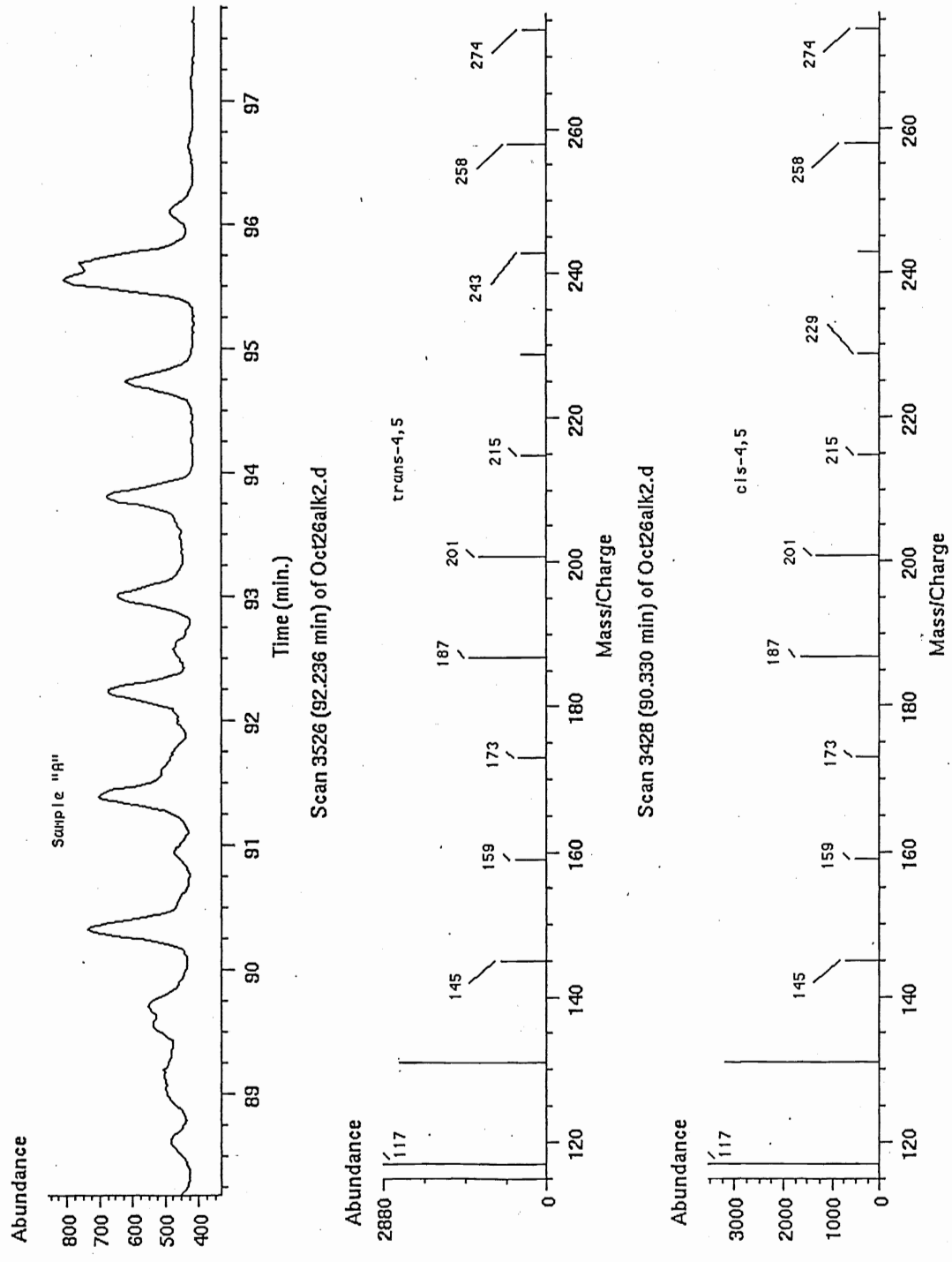


Figure 65

EI mass spectra of cis and trans 1-propyl-4-hexyltetralin present in sample "A" using SIM mode

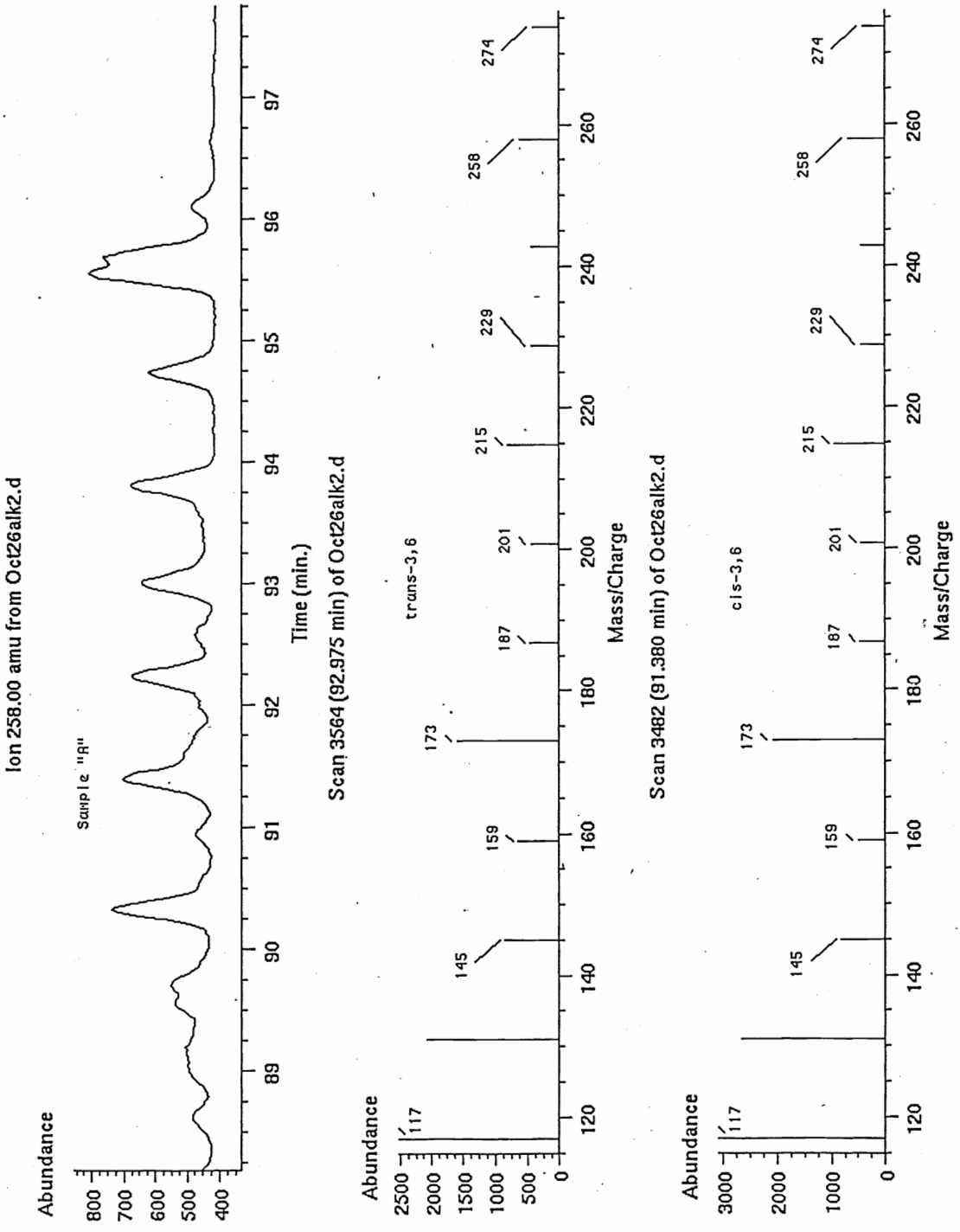


Figure 66

EI mass spectra of cis and trans 1-ethyl-4-heptyltetralin present in sample "A" using SIM mode

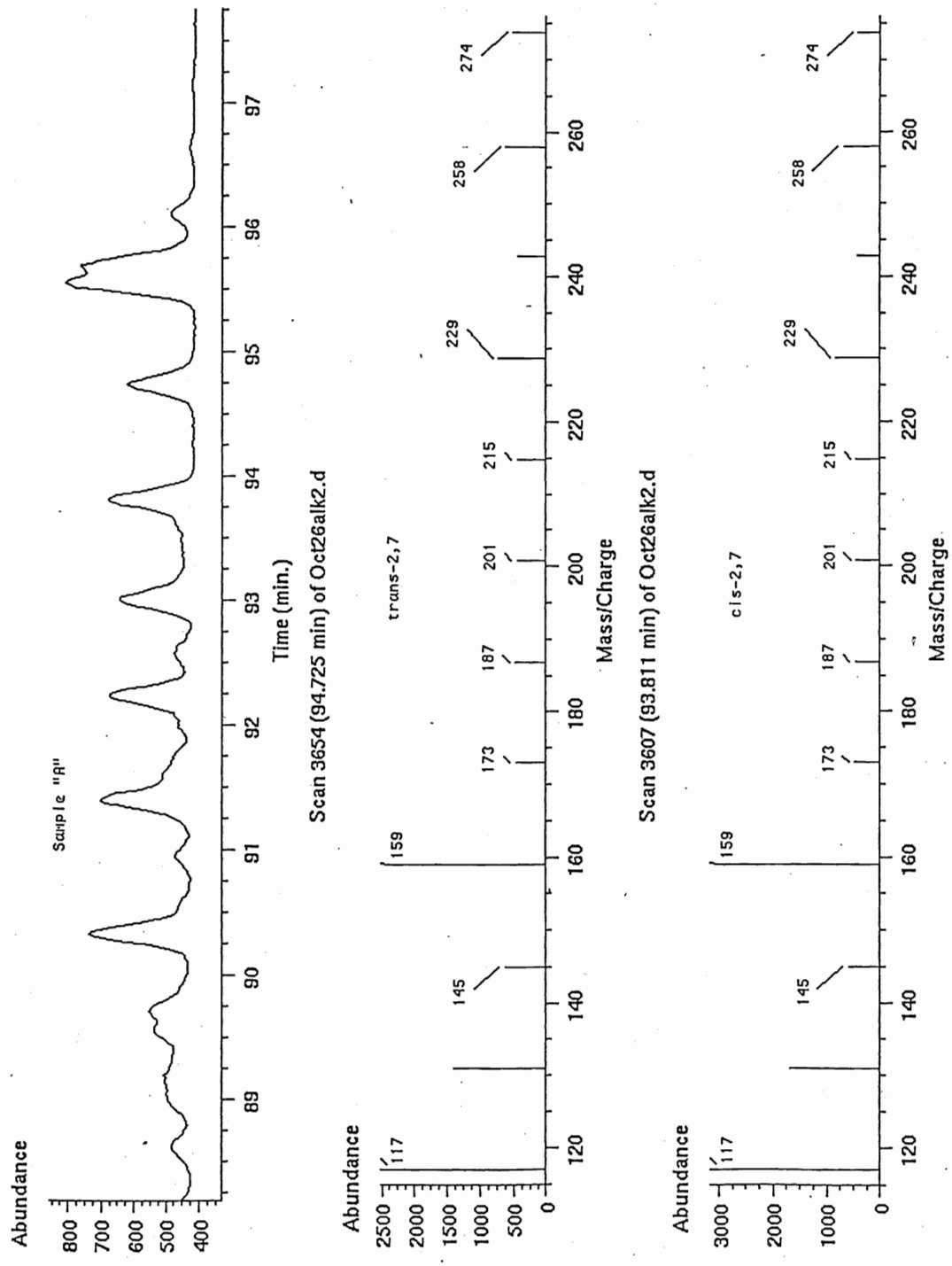
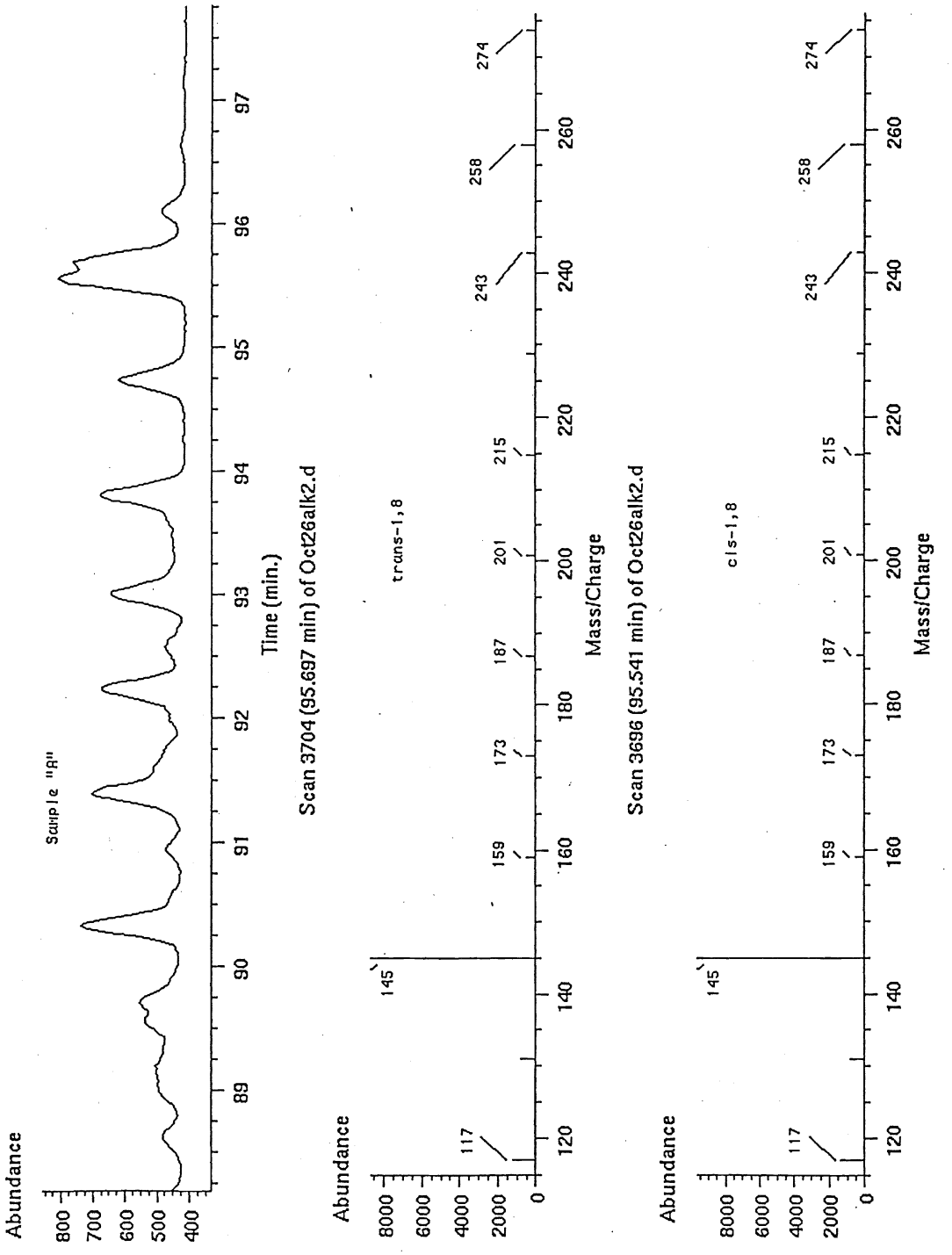


Figure 67

EI mass spectra of cis and trans 1-methyl-4-octyltetralin present in sample "A" using SIM mode



Dialkyltetralins - SIM mode

Internal Standard Technique

total-1,4,6,7-Tetramethyltetralin as an Internal Standard

Isomer	m/z	RT (min)	DAT Std. Total: 0.5 ug/ul Area (k)	DAT Std. ug/ul	RRF	Sample "A" RT (min)	Sample "A" Area (k)	Sample "A" mg/g	Sample "B" RT (min)	Sample "B" Area (k)	Sample "B" mg/g
cis-3,3	173	61.98	100	0.00117	1.35364	61.97	255	0.42	61.98	19.4	0.04
trans-3,3	173	62.79	105	0.00123	1.35254	62.78	216	0.36	62.79	14.8	0.03
cis-2,4	159	63.02	270	0.00317	1.35194	63.07	788	1.31	63.02	48.3	0.10
trans-2,4	159	63.66	239	0.00281	1.35855	63.72	624	1.03	63.66	47.2	0.10
cis-1,5	145	64.02	1393	0.01635	1.35260	64.12	3845	6.37	64.05	217	0.45
trans-1,5	145	64.18	1215	0.01426	1.35241	64.3	3361	5.57	64.23	162	0.34
cis-3,4	173	71.41	469	0.00551	1.35222	71.52	783	1.30	71.46	50.5	0.10
trans-3,4	173	72.65	489	0.00574	1.35134	72.73	659	1.09	72.66	42.5	0.09
cis-2,5	159	73.16	1189	0.01396	1.35269	73.24	1599	2.65	73.18	108	0.22
trans-2,5	159	73.98	988	0.01160	1.35229	74.04	1329	2.20	73.97	87.4	0.18
cis-1,6	145	74.63	5318	0.06242	1.35218	74.71	7344	12.17	74.63	429	0.89
trans-1,6	145	74.83	4699	0.05516	1.35213	74.94	6519	10.80	74.87	359	0.74
cis-4,4	187	80.71	191	0.00224	1.34992	80.77	446	0.74	80.74	29.8	0.06
cis-3,5	173	81.33	433	0.00508	1.35348	81.39	654	1.08	81.36	41.1	0.09
trans-4,4	187	82.36	318	0.00373	1.35090	82.41	338	0.56	82.39	23.5	0.05
trans-3,5	173	82.85	547	0.00642	1.35250	82.89	521	0.86	82.85	33.5	0.07
cis-2,6	159	83.61	1322	0.01552	1.35187	83.66	1254	2.08	83.61	84.6	0.18
trans-2,6	159	84.49	1138	0.01336	1.35247	84.53	1000	1.66	84.48	73.9	0.15
cis-1,7	145	85.21	7011	0.08230	1.35216	85.25	5220	8.65	85.21	316	0.66
trans-1,7	145	85.39	5890	0.06914	1.35231	85.45	4603	7.63	85.39	265	0.55
cis-4,5	187	90.29	92.5	0.00109	1.35550	90.28	101	0.17	90.29	16.6	0.03
cis-3,6	173	91.36	288	0.00338	1.35699	91.34	162	0.27	91.36	21.3	0.04
trans-4,5	187	92.12	247	0.00290	1.35578	92.19	71.7	0.12	92.21	13.1	0.03
trans-3,6	173	92.96	405	0.00475	1.35619	92.94	84.7	0.14	92.97	16.7	0.03
cis-2,7	159	93.78	961	0.01128	1.35481	93.81	282	0.47	93.77	41.1	0.09
trans-2,7	159	94.71	758	0.00890	1.35582	94.73	207	0.34	94.7	35.5	0.07
cis-1,8	145	95.52	3548	0.04165	1.35514	95.54	929	1.54	95.51	142	0.29
trans-1,8	145	95.66	2973	0.03490	1.35524	95.68	725	1.20	95.65	113	0.23
Total area (k)			42596.5								
cis-1467-TMT	173	47.07	15615			47.07	13643		47.03	13446	
trans-1467-TMT	173	47.29	15688			47.28	12306		47.24	12380	
total 1467-TMT (I.S)			31303				25949			25826	
Total DAT (mg/g)								**72.76**			**5.91**

impdmt1.wk3

Table 30

Concentrations of dialkyltetralins in sample "A" and "B" using an internal standard technique

Table 31

Concentrations of dialkyltetralins in sample "C", "D" and "E" using an internal standard technique

Dialkyltetralins - SIM mode

Internal Standard Technique

total-1,4,6,7-Tetramethyltetralin as an Internal Standard

			DAT Std. Total: 0.5 ug/ul	DAT Std.		Sample "C"			Sample "D"			Sample "E"		
Isomer	m/z	RT (min)	Area (k)	ug/ul	RRF	RT (min)	Area (k)	mg/g	RT (min)	Area (k)	mg/g	RT (min)	Area (k)	mg/g
cis-3,3	173	61.98	100	0.00117	1.35364	62.04	36.7	0.09	62.06	64.4	0.19	62.05	37.7	0.08
trans-3,3	173	62.79	105	0.00123	1.35254	62.83	32.3	0.08	62.85	72.8	0.21	62.84	32.9	0.07
cis-2,4	159	63.02	270	0.00317	1.35194	63.06	56.4	0.14	63.09	109	0.32	63.06	60.3	0.12
trans-2,4	159	63.66	239	0.00281	1.35855	63.7	62.2	0.16	63.72	118	0.34	63.70	66.7	0.14
cis-1,5	145	64.02	1393	0.01635	1.35260	64.08	137	0.34	64.11	241	0.71	64.08	112.0	0.23
trans-1,5	145	64.18	1215	0.01426	1.35241	64.25	122	0.31	64.28	242	0.71	64.26	123.0	0.25
cis-3,4	173	71.41	469	0.00551	1.35222	71.5	27.2	0.07	71.51	23	0.07	71.49	27.1	0.06
trans-3,4	173	72.65	489	0.00574	1.35134	72.7	28.2	0.07	72.71	32.1	0.09	72.69	28.9	0.06
cis-2,5	159	73.16	1189	0.01396	1.35269	73.21	55.8	0.14	73.23	63.6	0.19	73.21	51.4	0.11
trans-2,5	159	73.98	988	0.01160	1.35229	74.02	63.1	0.16	74.04	67.7	0.20	74.02	51.7	0.11
cis-1,6	145	74.63	5318	0.06242	1.35218	74.67	163	0.41	74.69	187	0.55	74.67	140.0	0.29
trans-1,6	145	74.83	4699	0.05516	1.35213	74.89	187	0.47	74.9	216	0.63	74.88	163.0	0.33
cis-4,4	187	80.71	191	0.00224	1.34992	80.74	18.3	0.05	80.76	16.8	0.05	80.75	13.9	0.03
cis-3,5	173	81.33	433	0.00508	1.35348	81.36	26.4	0.07	81.38	23.3	0.07	81.37	19.4	0.04
trans-4,4	187	82.36	318	0.00373	1.35090	82.39	24.9	0.06	82.41	20.9	0.06	82.88	21.4	0.04
trans-3,5	173	82.85	547	0.00642	1.35250	82.87	30.3	0.08	82.88	25.4	0.07	82.39	17.6	0.04
cis-2,6	159	83.61	1322	0.01552	1.35187	83.63	48.6	0.12	83.64	44.6	0.13	83.64	34.1	0.07
trans-2,6	159	84.49	1138	0.01336	1.35247	84.51	58.7	0.15	84.52	49.2	0.14	84.51	40.9	0.08
cis-1,7	145	85.21	7011	0.08230	1.35216	85.23	122	0.31	85.23	108	0.32	85.23	85.1	0.17
trans-1,7	145	85.39	5890	0.06914	1.35231	85.41	162	0.41	85.41	140	0.41	85.39	112.0	0.23
cis-4,5	187	90.29	92.5	0.00109	1.35550									
cis-3,6	173	91.36	288	0.00338	1.35699									
trans-4,5	187	92.12	247	0.00290	1.35578									
trans-3,6	173	92.96	405	0.00475	1.35619									
cis-2,7	159	93.78	961	0.01128	1.35481									
trans-2,7	159	94.71	758	0.00890	1.35582									
cis-1,8	145	95.52	3548	0.04165	1.35514	95.66	11.6	0.03						
trans-1,8	145	95.66	2973	0.03490	1.35524	95.67	15.9	0.04						
Total area (k)			42596.5											
cis-1467-TMT	173	47.07	15615			47.07	13515		47.11	12698		47.09	14622.0	
trans-1467-TMT	173	47.29	15688			47.29	12721		47.32	11055		47.31	13202.0	
total 1467-TMT (I.S)			31303				26236			23753			27824	
Total DAT (mg/g)								**3.75**			**5.48**			**2.53**

impdmt2.wk3

Table 32

Concentrations of dialkyltetralins in sample "F", "G" and "H" using an internal standard technique

Dialkyltetralins - SIM mode

Internal Standard Technique

total-1,4,6,7-Tetramethyltetralin as an Internal Standard

			DAT Std. Total: 0.5 ug/ul	DAT Std.		Sample "F"			Sample "G"			Sample "H"		
Isomer	m/z	RT (min)	Area (k)	ug/ul	RRF	RT (min)	Area (k)	mg/g	RT (min)	Area (k)	mg/g	RT (min)	Area (k)	mg/g
cis-3,3	173	61.98	100	0.00116	1.34766	61.98	107	0.24				62.01	144	0.29
trans-3,3	173	62.79	105	0.00122	1.34545	62.78	138	0.31				62.79	204	0.41
cis-2,4	159	63.02	273	0.00317	1.34630	63.01	196	0.45	62.99	10.6	0.03	63.03	256	0.51
trans-2,4	159	63.66	241	0.00280	1.34554	63.65	242	0.55	63.65	18.2	0.04	63.67	294	0.59
cis-1,5	145	64.02	1341	0.01556	1.34728	64.03	372	0.85	64.01	22.7	0.06	64.05	572	1.14
trans-1,5	145	64.18	1217	0.01412	1.34739	64.2	472	1.07	64.16	20.3	0.05	64.22	708	1.41
cis-3,4	173	71.42	101	0.00117	1.34950	71.5	216	0.49	71.45	66.8	0.16	71.47	145	0.29
trans-3,4	173	72.65	501	0.00581	1.34803	72.68	287	0.65	72.65	81.7	0.20	72.67	151	0.30
cis-2,5	159	73.17	1189	0.01379	1.34789	73.19	328	0.75	73.17	82.0	0.20	73.18	175	0.35
trans-2,5	159	73.98	993	0.01152	1.34752	73.99	467	1.06	73.98	101.0	0.25	73.99	201	0.40
cis-1,6	145	74.63	6169	0.07156	1.34766	74.66	783	1.78	74.63	115.0	0.28	74.63	269	0.54
trans-1,6	145	74.74	4685	0.05434	1.34781	74.88	910	2.07	74.84	141.0	0.34	74.84	309	0.62
cis-4,4	187	80.71	201	0.00233	1.34858	80.72	178	0.40	80.75	20.4	0.05			
cis-3,5	173	81.33	449	0.00521	1.34724	81.35	258	0.59	81.38	22.2	0.05			
trans-4,4	187	82.37	318	0.00369	1.34722	82.37	266	0.61	82.38	25.4	0.06			
trans-3,5	173	82.85	553	0.00641	1.34867	82.85	346	0.79	82.86	26.7	0.06			
cis-2,6	159	83.61	1333	0.01546	1.34790	83.61	372	0.85	83.61	35.4	0.09			
trans-2,6	159	84.49	1148	0.01332	1.34733	84.49	523	1.19	84.48	46.6	0.11			
cis-1,7	145	85.21	6837	0.07931	1.34764	85.19	717	1.63	85.21	84.2	0.20			
trans-1,7	145	85.39	5958	0.06911	1.34771	85.38	951	2.16	85.39	118.0	0.29			
cis-4,5	187	90.29	92.6	0.00107	1.35290				90.31	14.6	0.04			
cis-3,6	173	91.35	311	0.00361	1.34676				91.36	19.4	0.05			
trans-4,5	187	92.20	261	0.00303	1.34659				92.19	18.7	0.05			
trans-3,6	173	92.95	422	0.00490	1.34634				92.95	18.3	0.04			
cis-2,7	159	93.77	982	0.01139	1.34780				93.77	34.3	0.08			
trans-2,7	159	94.70	794	0.00921	1.34772				94.69	43.6	0.11			
cis-1,8	145	95.51	3541	0.04107	1.34784				95.49	98.8	0.24			
trans-1,8	145	95.65	2989	0.03467	1.34775				95.65	112.0	0.27			
Total area (k)			43104.6											
cis-1467-TMT	173	47.06	15998			47.03	13422		47.00	12285		47.05	14686	
trans-1467-TMT	173	47.28	15986			47.24	12865		47.22	12771		47.27	13056	
total 1467-TMT (I.S)			31984				26287			25056			27742	
Total DAT (mg/g)								**18.51**			**3.39**			**6.84**

impdmt4.wk3

Dialkyltetralins - SIM mode

Internal Standard Technique

total-1,4,6,7-Tetramethyltetralin as an Internal Standard

			DAT Std. Total: 0.5 ug/ul	DAT Std.		Sample "I"			Sample "J"		
Isomer	m/z	RT (min)	Area (k)	ug/ul	RRF	RT (min)	Area (k)	mg/g	RT (min)	Area (k)	mg/g
cis-3,3	173	62.09	84.1	0.00112	1.38772	92.08	253	0.64	62.07	33.4	0.06
trans-3,3	173	62.91	86.1	0.00115	1.38365	62.89	213	0.54	62.86	48.1	0.09
cis-2,4	159	63.13	235	0.00313	1.38754	63.12	614	1.54	63.11	39.5	0.07
trans-2,4	159	63.77	207	0.00276	1.38607	63.76	614	1.54	63.75	61.9	0.12
cis-1,5	145	64.14	1198	0.01596	1.38722	64.15	3441	8.65	64.12	194	0.36
trans-1,5	145	64.29	1075	0.01433	1.38639	64.33	2939	7.39	64.29	210	0.39
cis-3,4	173	71.53	403	0.00537	1.38693	71.56	737	1.85	71.54	11.3	0.02
trans-3,4	173	72.77	422	0.00562	1.38771	72.77	623	1.56	72.75	17.8	0.03
cis-2,5	159	73.29	1032	0.01375	1.38707	73.28	1520	3.82	73.25	37.1	0.07
trans-2,5	159	74.09	855	0.01139	1.38728	74.09	1259	3.16	74.08	36.8	0.07
cis-1,6	145	74.74	4666	0.06218	1.38681	74.76	7394	18.58	74.72	108	0.20
trans-1,6	145	74.95	4147	0.05526	1.38690	74.97	6671	16.77	74.93	115	0.21
cis-4,4	187	80.83	161	0.00215	1.38392	80.82	370	0.93	80.81	13.2	0.02
cis-3,5	173	81.45	376	0.00501	1.38699	81.44	553	1.39	81.44	18.5	0.03
trans-4,4	187	82.48	280	0.00373	1.38730	82.47	291	0.73	82.45	15.9	0.03
trans-3,5	173	82.97	473	0.00630	1.38753	82.94	448	1.13	83.62	21.1	0.04
cis-2,6	159	83.73	1150	0.01533	1.38637	83.71	1046	2.63	83.7	38.6	0.07
trans-2,6	159	84.61	989	0.01318	1.38677	84.58	855	2.15	84.58	43.3	0.08
cis-1,7	145	85.32	6116	0.08150	1.38686	85.31	4737	11.91	85.29	87.9	0.16
trans-1,7	145	85.51	5382	0.07172	1.38684	85.49	4225	10.62	85.48	109	0.20
cis-4,5	187	90.41	72.4	0.00096	1.39377	90.38	90.2	0.23	90.55	11.6	0.02
cis-3,6	173	91.49	253	0.00337	1.38744	91.45	143	0.36	91.44	12	0.02
trans-4,5	187	92.32	208	0.00277	1.38773	92.29	68.4	0.17	92.29	10.8	0.02
trans-3,6	173	93.07	349	0.00465	1.38706	93.05	92.5	0.23	93.05	12.5	0.02
cis-2,7	159	93.89	839	0.01118	1.38689	93.86	218	0.55	93.86	18	0.03
trans-2,7	159	94.82	661	0.00881	1.38659	94.78	179	0.45	94.79	21.5	0.04
cis-1,8	145	95.64	3176	0.04232	1.38694	95.6	906	2.28	95.6	109	0.20
trans-1,8	145	95.36	2624	0.03497	1.38673	95.74	802	2.02	95.74	49.4	0.09
Total area (k)			37519.6								
cis-1467-TMT	173	47.15	13261			47.11	12825		47.16	12578	
trans-1467-TMT	173	47.37	13794			47.34	12342		47.37	11230	
total 1467-TMT (I.S)			27055				25167			23808	
Total DAT (mg/g)								**103.80**			**2.81**

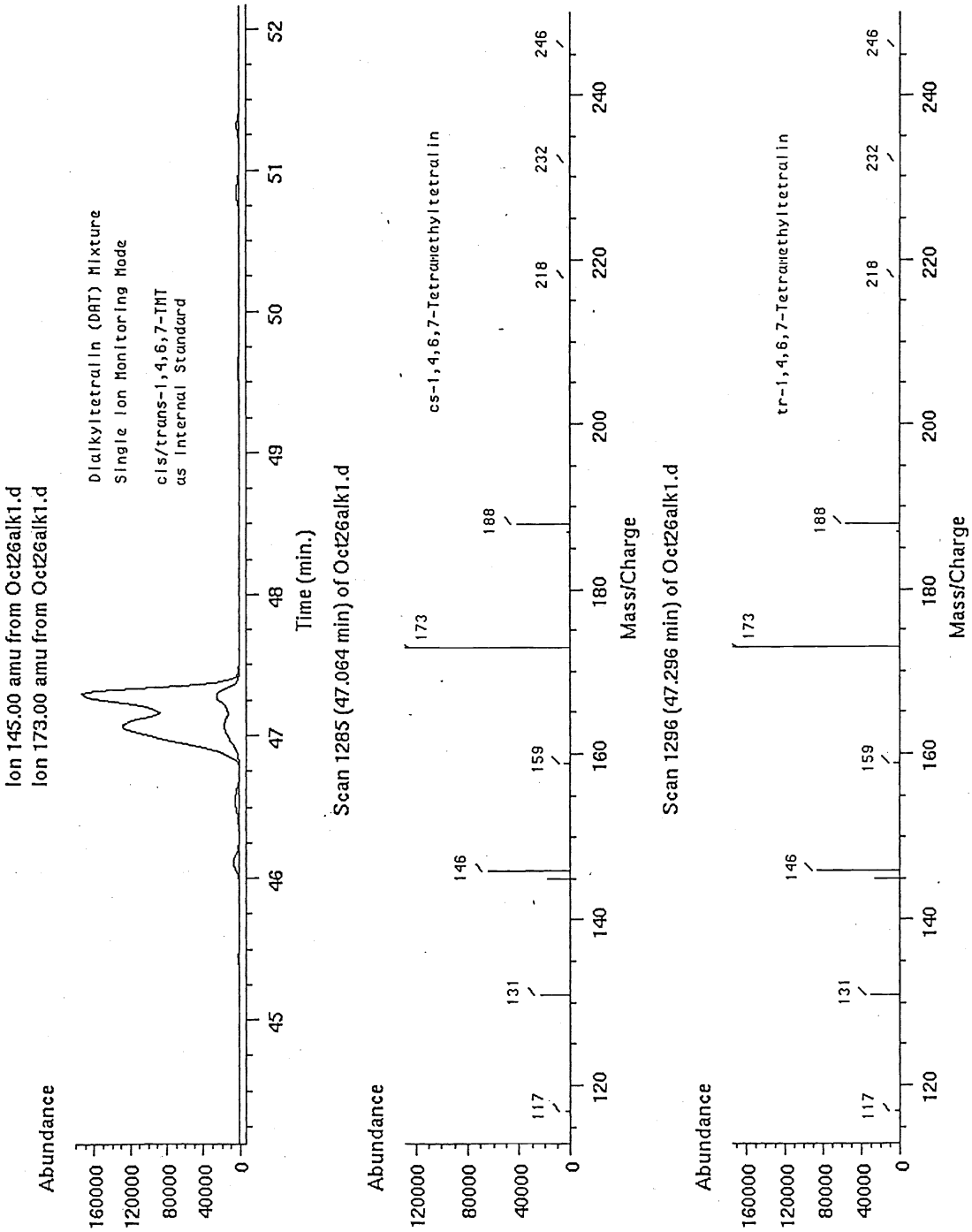
impdmt3.wk3

Table 33

Concentrations of dialkyltetralins in sample "I and "J" using an internal standard technique

Figure 68

EI mass spectra of internal standard, cis-1,4,6,7-tetramethyltetralin and trans-1,4,6,7-tetramethyltetralin



concentration of a total *dialkyltetralins* was found in the sample "I" at 103.80 mg/g (10.38 %), followed by sample "A" at 72.76 mg/g (7.28 %). The lowest concentration of the same class of impurities was found in the sample "E" manufactured by company #2, at 2.53 mg/g (0.25 %).

As mentioned earlier, no published study was carried out with the actual standard, dialkyltetralins blend, DAT, and with an internal standard, cis/trans-1,4,6,7-tetramethyltetralin, chemically similar to the compounds under investigation.

In 1991, Unilever was asked to take part in a round-robin test of a tentative method for determination of *dialkyltetralins* in linear alkylbenzenes. Results of the test were never published due to method's sensitivity and precision problems. A tentative result for a total concentration of *dialkyltetralins* (65283 ppm) present in one of the analyzed commercial LABs became available via personal communication.

The method that was developed as a result of this study proved to be not only sensitive but also precise. The summarized qualitative results, in % (mg/g for IS technique), for *dialkyltetralins* in all ten analyzed samples are presented below:

Sample	**%** **(by total weight of sample)**	**% (mg/g) (by IS technique)**
"A"	9.43	7.28 (72.76)
"B"	0.16	0.59 (5.92)
"C"	0.11	0.38 (3.75)
"D"	0.32	0.55 (5.48)

"E"	0.06	0.25 (2.53)
"F"	2.79	1.85 (18.51)
"G"	0.53	0.34 (3.39)
"H"	1.20	0.69 (6.85)
"I"	12.63	10.38 (103.80)
"J"	0.61	0.28 (2.84)

For samples containing high concentration of *dialkyltetralins*, calculated results using an internal standard technique were found to be lower of about ~2 %. The difference represents some other impurities present as traces in industrially produced linear alkylbenzenes. Identification and quantitation of them was beyond the scope of this study. However, some of them representing the following class of compounds: diphenylalkanes, alkylnaphthalenes, non-linear dialkyltetralins and dialkylindanes, were identified and their mass spectra are presented in the appendix. The detailed structure elucidation and quantitation of them will take place in the near future.

6. ***Summary of the identified impurities in commercial linear alkylbenzenes***

The summary of the total concentration of impurities present in analyzed commercial linear alkylbenzene samples are presented in **Table 34**. The highest concentration was observed in sample "I" at 13.07 % (130.66 mg/g). The similarily high level of impurities would be observed for sample "A" if it hadn't been used as a standard. The lowest concentration of the total impurities was found in sample "B" produced by company #1 at 2.40 % (24.02 mg/g).

Table 34

Comparison of total impurities' concentration in analyzed commercial LABs using an internal standard technique

Total Impurities in Commercial Linear Alkylbenzenes (mg/g)

		Branched Alkylbenzenes	Dialkyltetralins (Cyclic)	Total (mg/g)
Sample "A"	Company #1	*	72.76	
Sample "B"	Company #1	18.10	5.92	24.02
Sample "C"	Company #2	74.26	3.75	78.01
Sample "D"	Company #2	60.89	5.48	66.36
Sample "E"	Company #2	36.21	2.53	38.75
Sample "F"	Company #3	56.35	18.51	74.86
Sample "G"	Company #3	81.32	3.39	84.71
Sample "H"	Company #3	65.20	6.85	72.05
Sample "I"	Company #4	26.86	103.80	130.66
Sample "J"	Company #4	54.79	2.84	57.63

Note: * - Sample "A" was used as a STANDARD to calculate concentrations for branched Alkylbenzenes

As mentioned in the experimental paragraph, five consecutive time windows (descriptors) were set in the SIM mode to monitor selected ions for all dialkyltetralins and the internal standard. In addition, each time window was set to monitor other possible impurities such as dialkylindanes, diphenylalkanes and alkylnaphthalenes. Selected mass apectra of these compounds are presented in the appendix.

IV. Linearity studies

1. *Accuracy and precision in the method used for determination of dialkyltetralins*

There are two basic indicators of measurement quality: precision and accuracy. Generally, the accuracy of an analytical method is a degree of agreement of the test results generated by the method to the true value. The true value for accuracy assessment can be obtained in two ways. They can be compared with results of an established reference material or the sample itself is spiked with a known concentration of reference material. Since for this study a reference material was not available, the provision of accurate results was by the use of internal standard. The use of internal standard, chemically similar to the analytes, assumes that both the internal standard and analyte are affected to the same extent by the analysis conditions. For this work, three internal standards were used.

Precision of a method is the degree of agreement among individual test results when the procedure is applied repeatedly to multiple samplings. For this study, precision was measured by injecting a series of standards, DAT standards at five different concentrations: at 50, 100, 250, 500 and 1000 ng/ul (**Table 35**). Relative standard

Linear Range using 1,4,6,7-TMT as an Internal Standard @ 500 ng/ul

Total conc.	50 ng/	100 ng/	250 ng/	500 ng/	1000 ng/	50 ng/ul	100 ng/	250 ng/	500 ng/	1000 ng/ul			
Compound	Area (k)	Area (k)	Area (k)	Area (k)	Area (k)	RF	RF	RF	RF	RF	Average	STD	RSD (%)
cis-3,3	20.1	57.8	214.5	413.4	871.2	0.0034	0.0038	0.0049	0.0047	0.00489	0.0043	0.0006	13.5
trans-3,3	20.3	48.8	177.5	350.9	757.6	0.0034	0.0032	0.0041	0.004	0.00425	0.0038	0.0004	9.8
cis-2,4	66.6	157.1	554.2	1102	2277	0.0111	0.0104	0.0128	0.0126	0.01277	0.0119	0.0009	7.6
trans-2,4	55.2	137.4	481.3	965.6	2033	0.0092	0.0091	0.0111	0.011	0.0114	0.0104	0.0009	8.8
cis-1,5	122.2	293.7	1089	2094	4502	0.0204	0.0194	0.0251	0.0239	0.02526	0.0228	0.0022	9.8
trans-1,5	101	278.9	955	2013	4103	0.0168	0.0185	0.022	0.023	0.02302	0.0207	0.0023	11.2
cis-3,4	157.4	385.7	1392	2814	5805	0.0262	0.0255	0.0321	0.0321	0.03257	0.0297	0.0029	9.6
trans-3,4	185.9	460.1	1670	3420	7010	0.031	0.0305	0.0385	0.039	0.03933	0.0357	0.0037	10.4
cis-2,5	285	646	2187	4426	8927	0.0475	0.0428	0.0504	0.0505	0.05008	0.0483	0.0027	5.6
trans-2,5	202.9	499.2	1774	3677	7458	0.0338	0.033	0.0409	0.042	0.04184	0.0383	0.0037	9.6
cis-1,6	417.7	1030	3748	7897	15775	0.0696	0.0682	0.0864	0.0901	0.0885	0.0806	0.0088	10.9
trans-1,6	402.3	999.4	3567	7222	14721	0.0671	0.0662	0.0822	0.0824	0.08258	0.0761	0.0071	9.3
cis-4,4	56	141.5	492.9	1032	2120	0.0093	0.0094	0.0114	0.0118	0.01189	0.0107	0.0011	9.8
cis-3,5	163.2	396.7	1442	3017	6120	0.0272	0.0263	0.0332	0.0344	0.03433	0.0311	0.0033	10.6
trans-4,4	85.6	210	750.9	1573	3190	0.0143	0.0139	0.0173	0.018	0.0179	0.0163	0.0016	10.1
trans-3,5	193.6	476.7	1727	3606	7270	0.0323	0.0316	0.0398	0.0412	0.04078	0.0371	0.0039	10.5
cis-2,6	252.3	629.3	2269	4755	9563	0.0421	0.0417	0.0523	0.0543	0.05365	0.0488	0.0052	10.7
trans-2,6	215.8	540	1929	4048	8183	0.036	0.0357	0.0445	0.0462	0.04591	0.0417	0.0044	10.5
cis-1,7	526.2	1339	4796	9987	20254	0.0877	0.0886	0.1106	0.114	0.11362	0.1029	0.011	10.7
trans-1,7	492.1	1284	4561	9441	18864	0.082	0.085	0.1052	0.1078	0.10583	0.0972	0.0102	10.5
cis-4,5	38.7	93.3	334.6	698.1	1434	0.0065	0.0062	0.0077	0.008	0.00804	0.0073	0.0007	10.0
cis-3,6	108.7	268.2	932.6	1963	3974	0.0181	0.0178	0.0215	0.0224	0.02229	0.0204	0.0019	9.2
trans-4,5	126.6	312.8	1095	2294	4671	0.0211	0.0207	0.0252	0.0262	0.0262	0.0239	0.0022	9.4
trans-3,6	135.9	331.8	1166	2446	4935	0.0227	0.022	0.0269	0.0279	0.02768	0.0254	0.0023	9.2
cis-2,7	195	457.9	1618	3377	6806	0.0325	0.0303	0.0373	0.0385	0.03818	0.0354	0.003	8.6
trans-2,7	142.1	357.2	1242	2596	5239	0.0237	0.0236	0.0286	0.0296	0.02939	0.027	0.0025	9.3
cis-1,8	259	686.2	2440	4757	10332	0.0432	0.0454	0.0563	0.0543	0.05796	0.0514	0.0055	10.6
trans-1,8	259	607.8	2100	4758	8712	0.0432	0.0402	0.0484	0.0543	0.04887	0.047	0.0045	9.5
c/t-1,4-DMT	4311	5557	6739	6811	7069								
c/t-1467-TM	59979	75538	86738	87607	89128								

LINEAR1A.WK3

Table 35

Linear range for dialkyltetralins (DAT standard) using cis/trans-1,4,6,7-tetramethyltetralin as an internal standard

deviation for all linear dialkyltetralin isomers using cis/trans-1,4,6,7-tetramethyltetralin was around 10 %, namely between 7.6 % and 13.5 %. At the time of the accuracy and precision study, a second internal standard, cis/trans-1,4-dimethyltetralin became available. Using latter internal standard, relative standard deviations for all *dialkyltetralin* isomers except one, cis-1,4-dipropyltetralin, were calculated to be lower, at 6 % to 7 % (**Table 36**). Percent relative standard deviation at such low levels confirms a good accuracy and precision of analytical method used in this study, a GC/MS technique.

2. *Linearity study of dialkyltetralins standard, DAT*

The linearity of the detector response (GC/MS system) measured in the analytical method used in this study was directly proportional to the concentrations of analytes in sample within a given range. The response should be linearly related to the concentrations of standards.

Generally, linearity is determined by a series of injections of standards at about five different concentrations that span 50 - 150 % of the expected working range assay. A linear regression equation applied to the results should have an intercept not significantly different from zero.

DAT standard was prepared at five different concentration: at 50, 100, 250, 500, and 1000 ng/ul. Tabulated results are presented in **Table 36**. The response for each dialkyltetralin isomers was linear, as can be seen in **Figure 69**, **70**, **71**, **72**, **73**, **74** and **75**.

Linear Range using 1,4-DMT as an Internal Standard @ 50 ng/ul

Total conc.	50 ng/	100 ng/	250 ng/	500 ng/	1000 ng/	50 ng/ul	100 ng/	250 ng/	500 ng/	1000 ng/ul			
Compound	Area (k)	Area (k)	Area (k)	Area (k)	Area (k)	RF	RF	RF	RF	RF	Average	STD	RSD (%)
cis-3,3	20.1	57.8	214.5	413.4	871.2	0.0047	0.0052	0.0064	0.0061	0.0062	0.0057	0.0006	10.4
trans-3,3	20.3	48.8	177.5	350.9	757.6	0.0047	0.0044	0.0053	0.0052	0.0054	0.0050	0.0003	6.7
cis-2,4	66.6	157.1	554.2	1102	2277	0.0154	0.0141	0.0164	0.0162	0.0161	0.0157	0.0008	4.8
trans-2,4	55.2	137.4	481.3	965.6	2033	0.0128	0.0124	0.0143	0.0142	0.0144	0.0136	0.0008	5.7
cis-1,5	122.2	293.7	1089	2094	4502	0.0283	0.0264	0.0323	0.0307	0.0318	0.0299	0.0020	6.8
trans-1,5	101	278.9	955	2013	4103	0.0234	0.0251	0.0283	0.0296	0.0290	0.0271	0.0022	8.1
cis-3,4	157.4	385.7	1392	2814	5805	0.0365	0.0347	0.0413	0.0413	0.0411	0.0390	0.0026	6.6
trans-3,4	185.9	460.1	1670	3420	7010	0.0431	0.0414	0.0496	0.0502	0.0496	0.0468	0.0034	7.3
cis-2,5	285	646	2187	4426	8927	0.0661	0.0581	0.0649	0.0650	0.0631	0.0635	0.0026	4.1
trans-2,5	202.9	499.2	1774	3677	7458	0.0471	0.0449	0.0526	0.0540	0.0528	0.0503	0.0033	6.5
cis-1,6	417.7	1030	3748	7897	15775	0.0969	0.0927	0.1112	0.1159	0.1116	0.1057	0.0083	7.9
trans-1,6	402.3	999.4	3567	7222	14721	0.0933	0.0899	0.1059	0.1060	0.1041	0.0999	0.0062	6.3
cis-4,4	56	141.5	492.9	1032	2120	0.0130	0.0127	0.0146	0.0152	0.0150	0.0141	0.0009	6.7
cis-3,5	163.2	396.7	1442	3017	6120	0.0379	0.0357	0.0428	0.0443	0.0433	0.0408	0.0031	7.6
trans-4,4	85.6	210	750.9	1573	3190	0.0199	0.0189	0.0223	0.0231	0.0226	0.0213	0.0015	7.1
trans-3,5	193.6	476.7	1727	3606	7270	0.0449	0.0429	0.0513	0.0529	0.0514	0.0487	0.0037	7.5
cis-2,6	252.3	629.3	2269	4755	9563	0.0585	0.0566	0.0673	0.0698	0.0676	0.0640	0.0049	7.6
trans-2,6	215.8	540	1929	4048	8183	0.0501	0.0486	0.0572	0.0594	0.0579	0.0546	0.0040	7.4
cis-1,7	526.2	1339	4796	9987	20254	0.1221	0.1205	0.1423	0.1466	0.1433	0.1350	0.0103	7.6
trans-1,7	492.1	1284	4561	9441	18864	0.1141	0.1155	0.1354	0.1386	0.1334	0.1274	0.0095	7.5
cis-4,5	38.7	93.3	334.6	698.1	1434	0.0090	0.0084	0.0099	0.0102	0.0101	0.0095	0.0007	7.0
cis-3,6	108.7	268.2	932.6	1963	3974	0.0252	0.0241	0.0277	0.0288	0.0281	0.0268	0.0016	6.1
trans-4,5	126.6	312.8	1095	2294	4671	0.0294	0.0281	0.0325	0.0337	0.0330	0.0313	0.0020	6.4
trans-3,6	135.9	331.8	1166	2446	4935	0.0315	0.0299	0.0346	0.0359	0.0349	0.0334	0.0021	6.3
cis-2,7	195	457.9	1618	3377	6806	0.0452	0.0412	0.0480	0.0496	0.0481	0.0464	0.0027	5.8
trans-2,7	142.1	357.2	1242	2596	5239	0.0330	0.0321	0.0369	0.0381	0.0371	0.0354	0.0022	6.2
cis-1,8	259	686.2	2440	4757	10332	0.0601	0.0617	0.0724	0.0698	0.0731	0.0674	0.0050	7.4
trans-1,8	259	607.8	2100	4758	8712	0.0601	0.0547	0.0623	0.0699	0.0616	0.0617	0.0044	7.2
c/t-1,4-DM	4311	5557	6739	6811	7069								
c/t-1467-T	59979	75538	86738	87607	89128								

LINEAR1B.WK3

Table 36

Linear range for linear dialkyltetralins (DAT standard) using cis/trans-1,4-dimethyltetralin as an internal standard

Figure 69

DAT standard - linear range for cis and trans 1-ethyl-4-pentyltetralin and 1-methyl-4-hexyltetralin

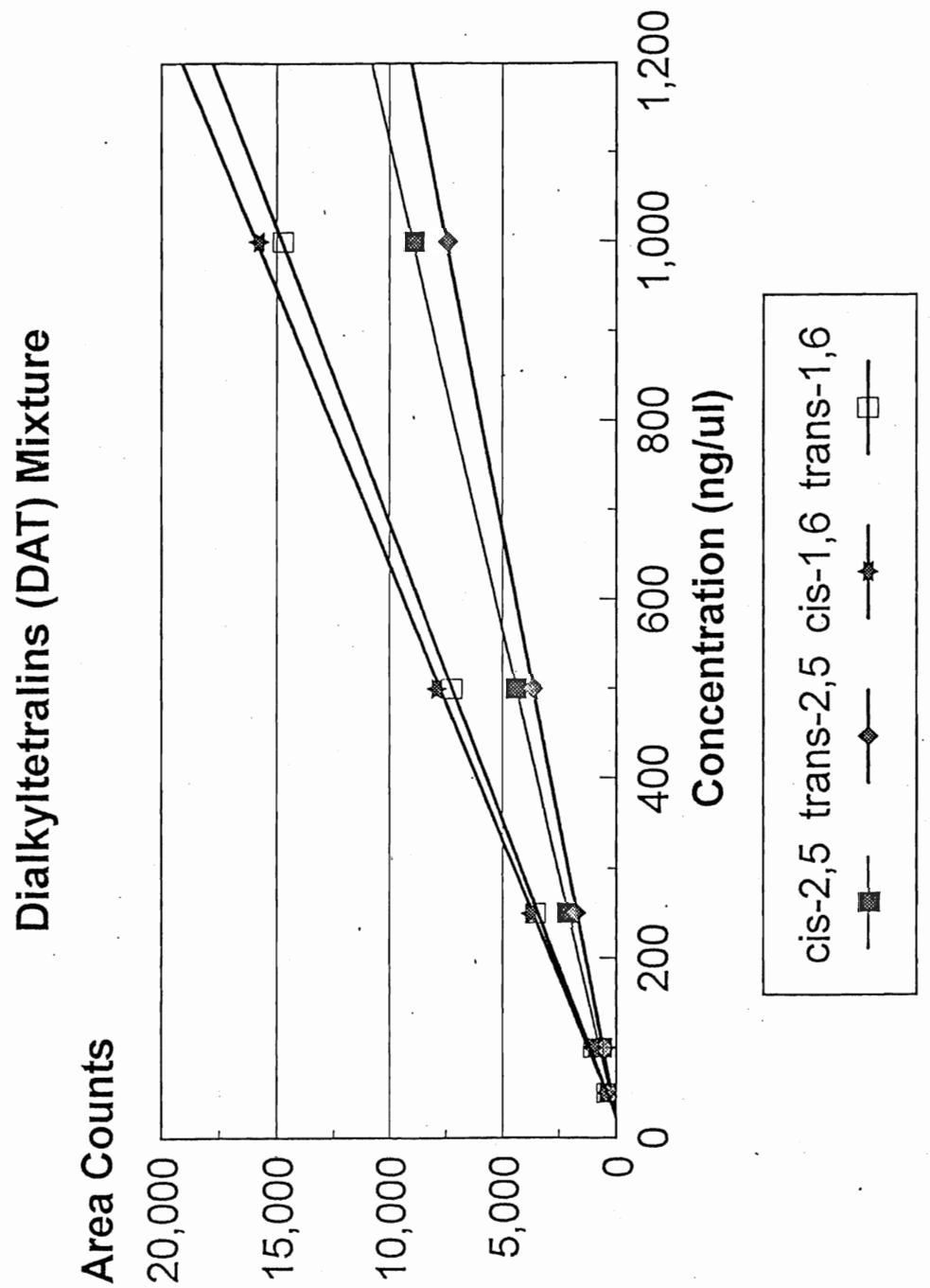


Figure 70

DAT standard - linear range for cis and trans 1-methyl-4-pentyltetralin and 1-propyl-4-butyltetralin

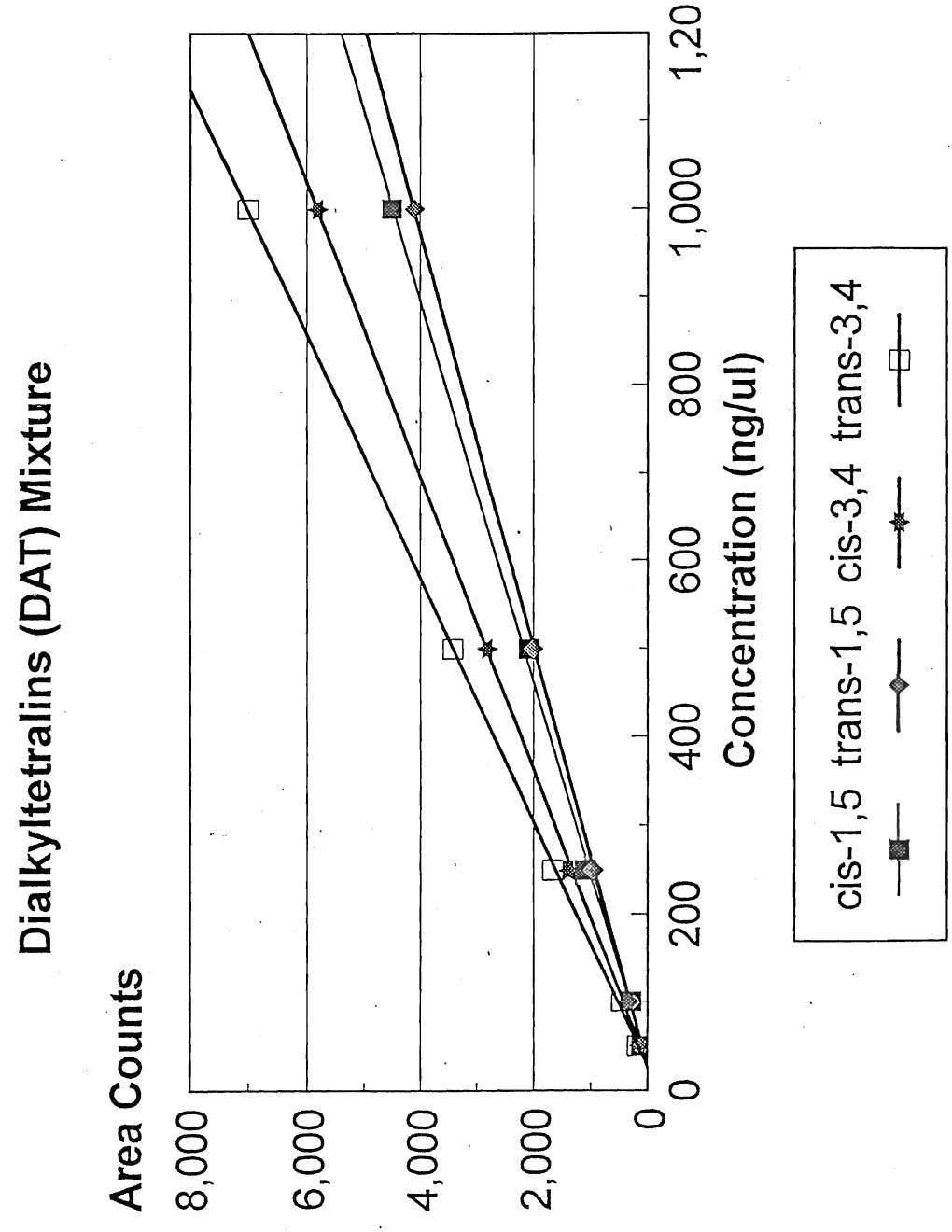


Figure 71

DAT standard - linear range for cis and trans 1,4-dipropyltetralin and 1-ethyl-4-butyltetralin

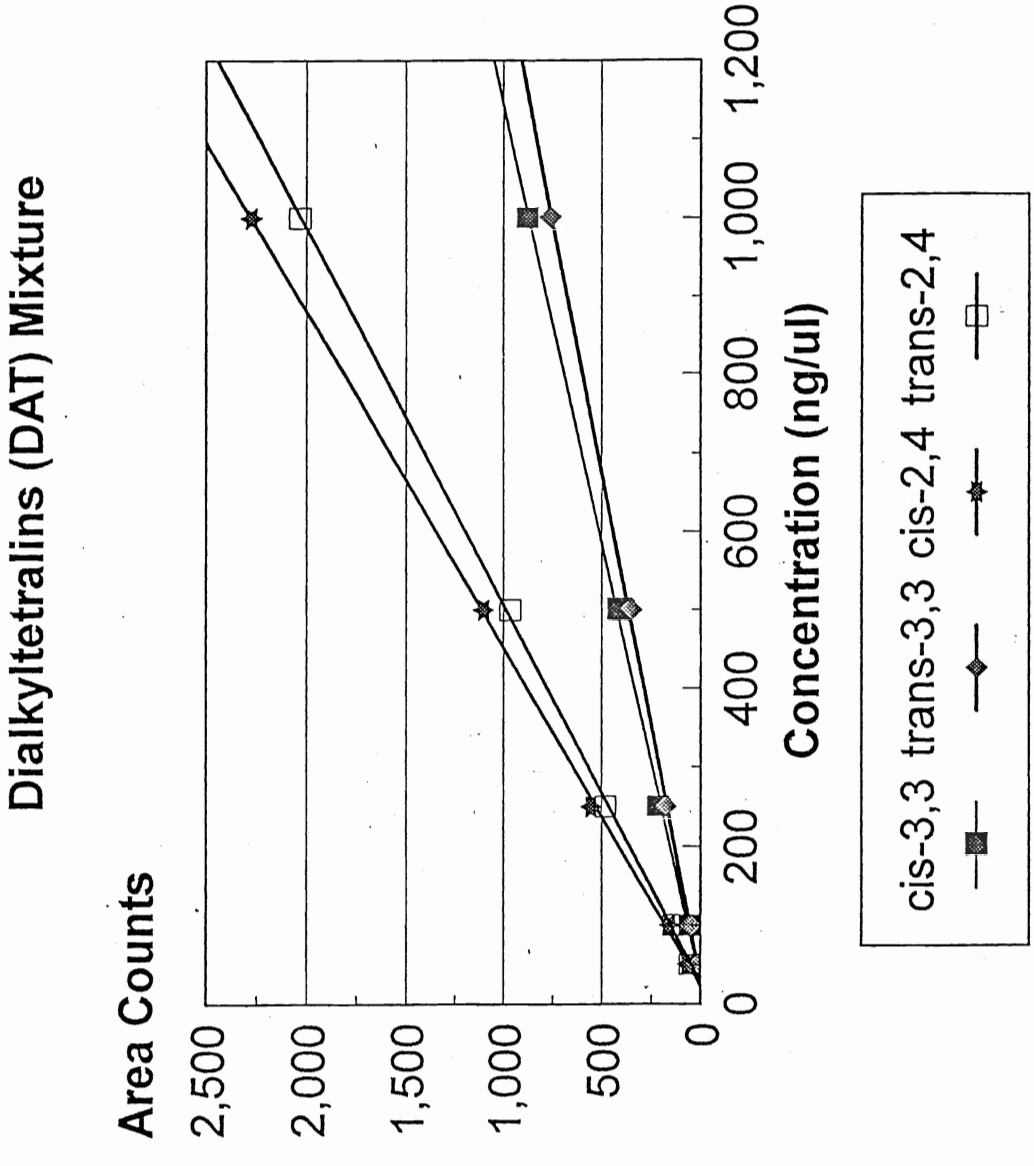


Figure 72

DAT standard - linear range for cis and trans 1,4-dibutyltetralin and 1-ethyl-4-pentyltetralin

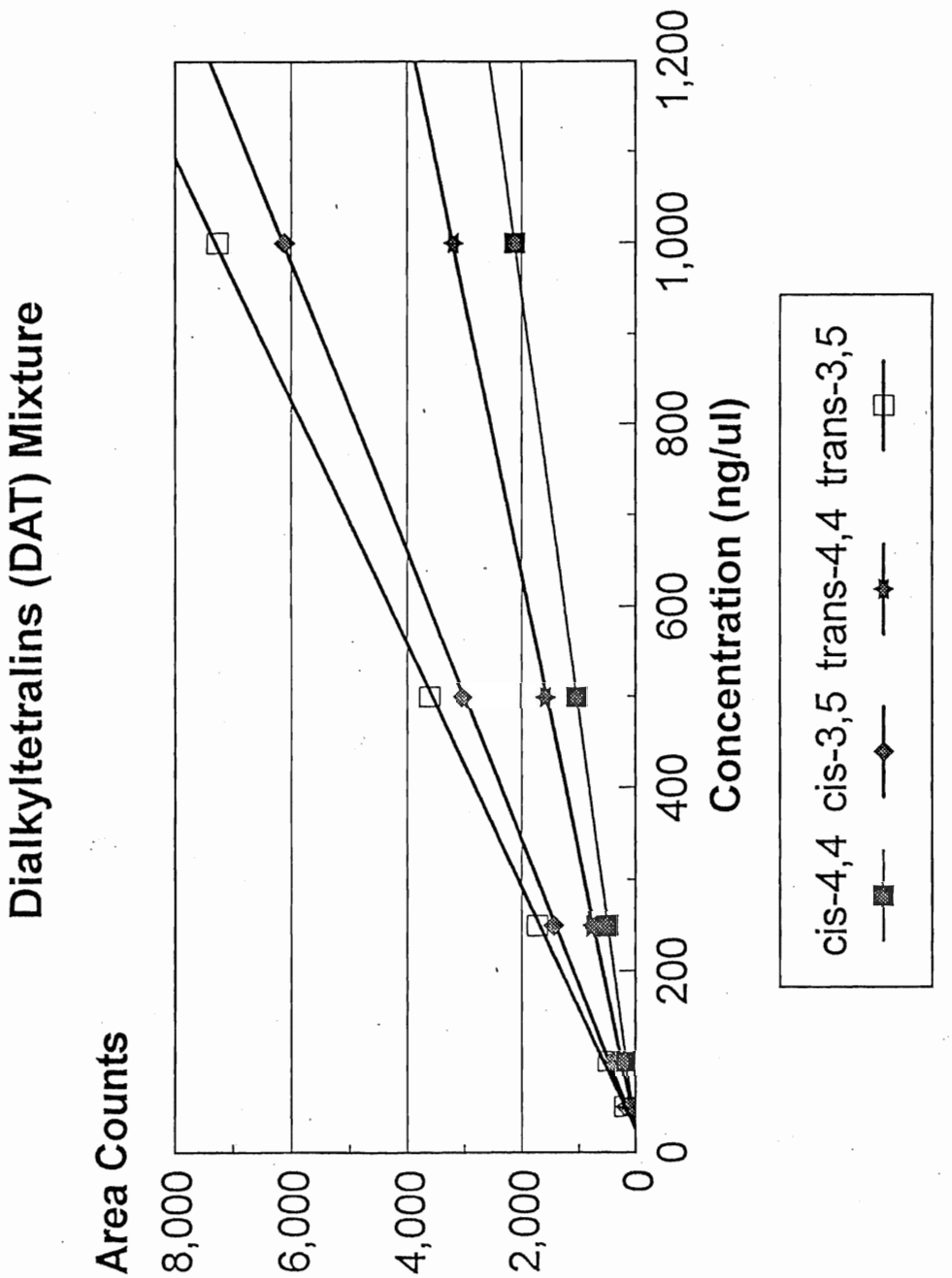


Figure 73

DAT standard - linear range for cis and trans 1-ethyl-4-hexyltetralin and 1-methyl-4-heptyltetralin

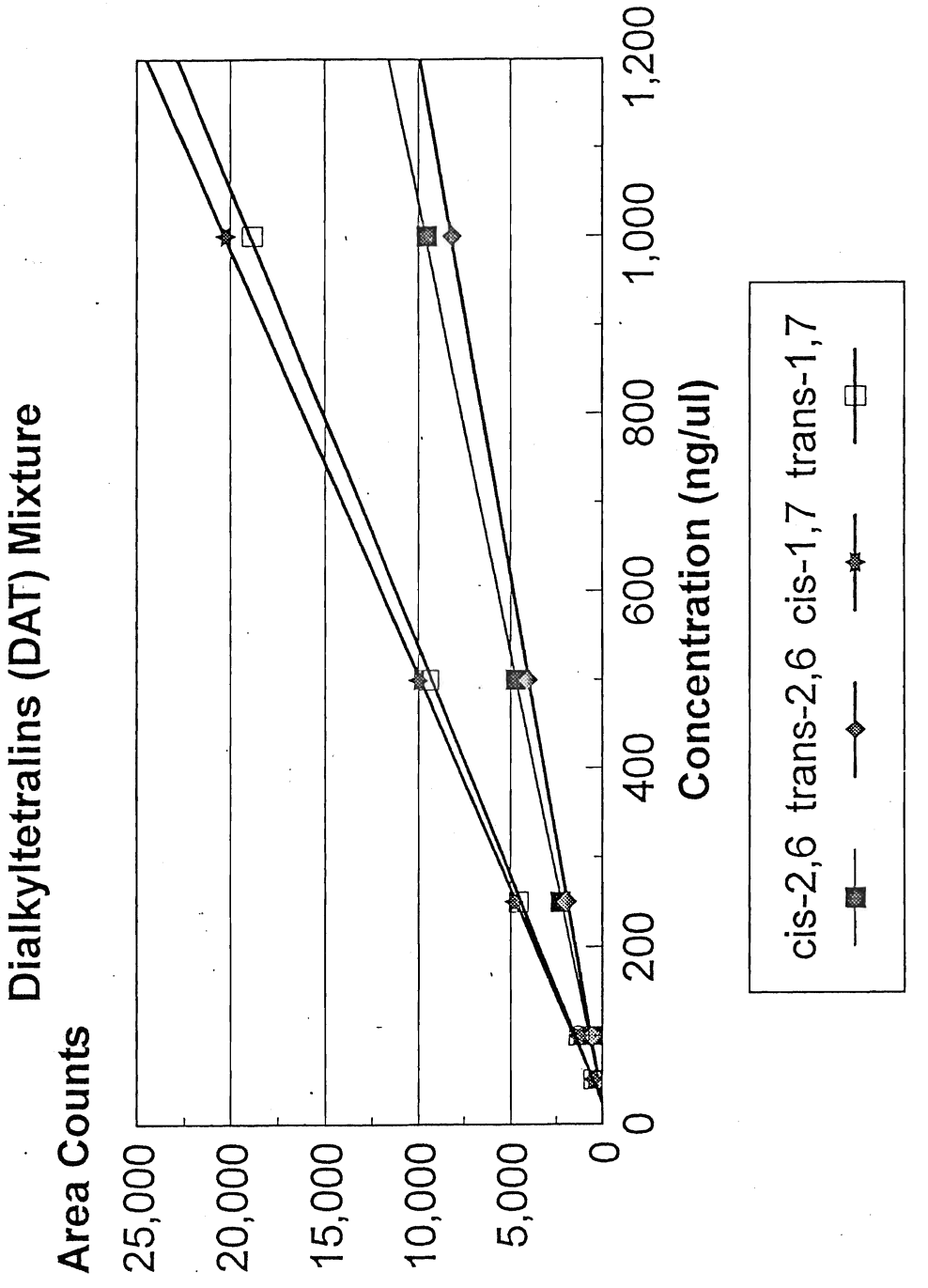


Figure 74

DAT standard - linear range for cis and trans 1-butyl-4-pentyltetralin and 1-propyl-4-hexyltetralin

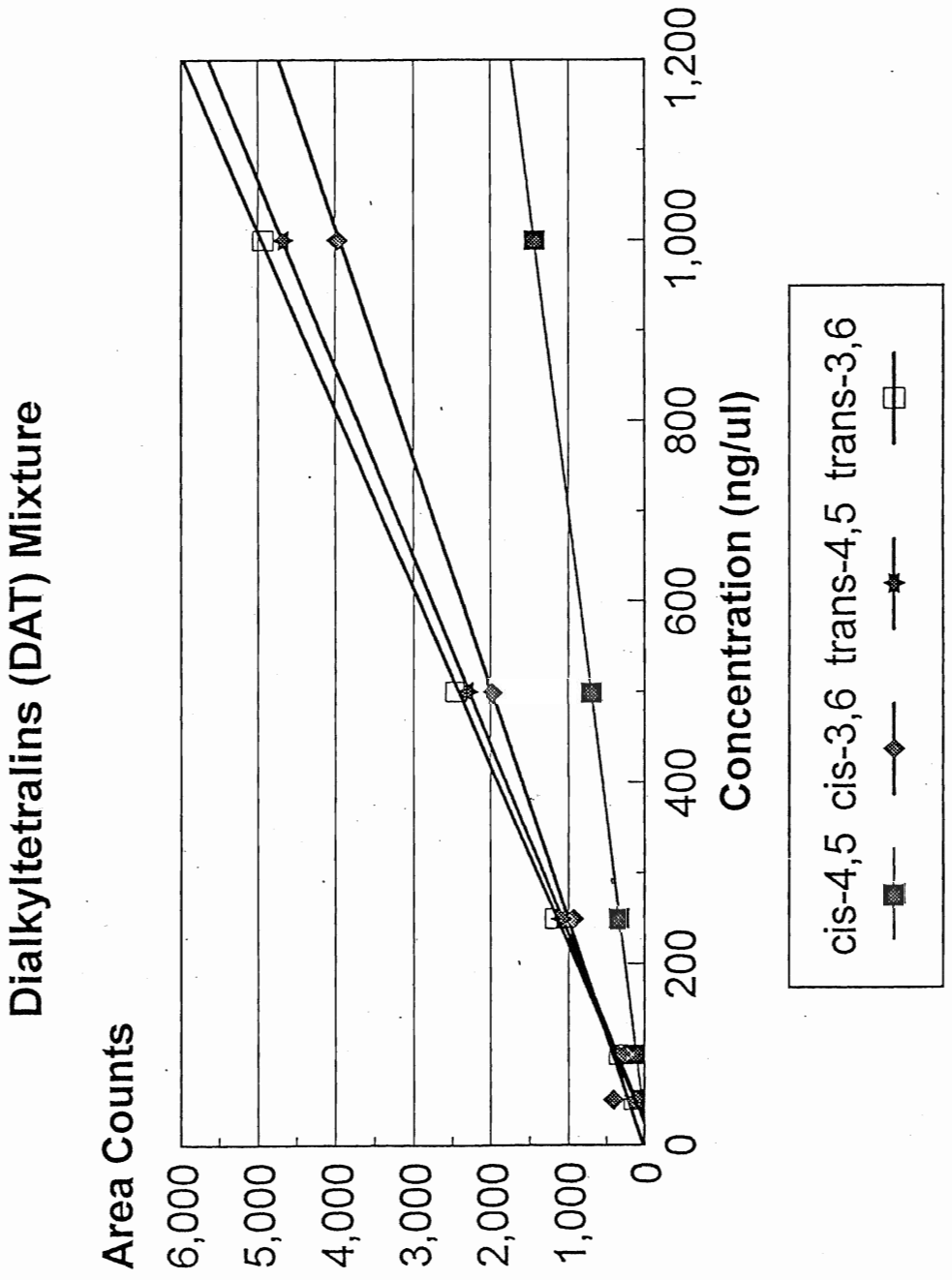
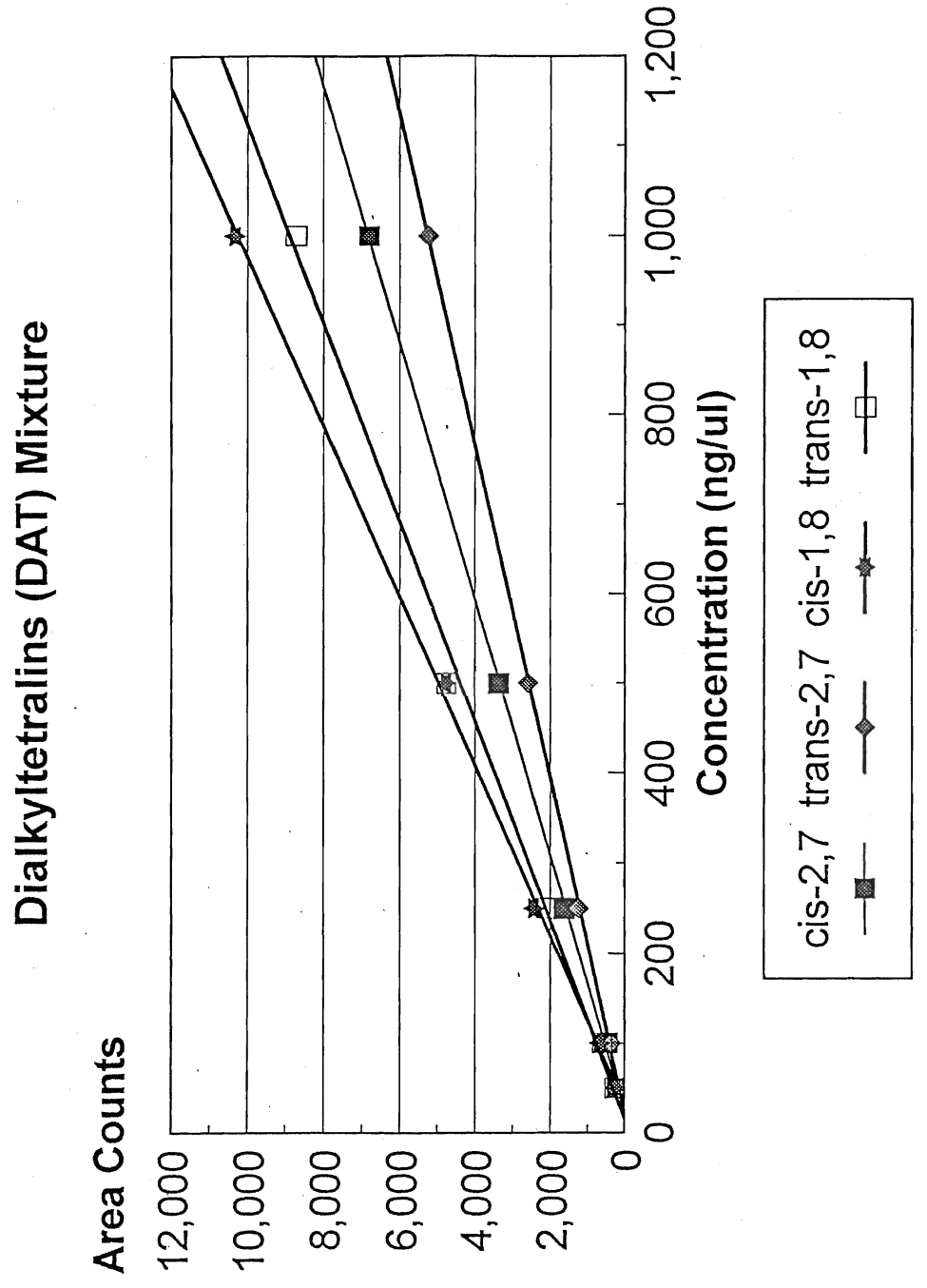


Figure 75

DAT standard - linear range for cis and trans 1-ethyl-4-heptyltetralin and 1-methyl-4-octyltetralin



3. ***Linearity study of dialkyltetralin isomers present in commercial linear alkylbenzenes, in sample "A"***

The same exercise was done for dialkyltetralin isomers present in commercial linear alkylbenzenes, sample "A". Five samples at different concentration of dialkyltetralins were prepared and analyzed using single ion monitoring data acquisition mode. Again, precision and accuracy for this method was very good, percent relative deviations were calculated and are presented in **Table 37**. The response for each dialkyltetralin isomer was observed to be linear and is presented in **Figure** from **76** to **82**.

4. ***Determination of precision and accuracy of the manual injections***

The percent of relative standard deviations for the retention times of all linear alkylbenzenes were calculated to determine precision and accuracy of the manual injections for all ten analyzed samples (**Table 38**). Results in **Table 38** confirmed a very good accuracy and precision of the manual injection technique with the percent standard deviation as low as 0.17 %. For the dialkyltetralins present in analyzed sample "A", a ten-fold lower (**Table 39**) percent relative standard deviations were observed for their retention times. Thus in each chromatogram of the analyzed commercial linear alkylbenzenes, all major peaks representing linear alkylbenzenes and minor peaks representing dialkyltetralins were identified with an excellent accuracy.

Table 37

Linear range for dialkyltetralin isomers present in sample "A" using cis/trans-1,4,6,7-tetramethyltetralin as an internal standard in SIM mode

Linear Range for Dialkyltetralin isomers using total cis- and trans-1,4,6,7-DMT as an Internal Standard @ 5 ng/ul

Sample "A"

Isomer	m/	RT	DAT Std. Total 0.5 ug/ Area (k)	DAT Std. Isomer ug/ul	0.0137 Area (k)	0.0286 Area (k)	0.0447 Area (k)	0.0601 Area (k)	0.0137 ug/g	0.0286 ug/g	0.0447 ug/g	0.0601 g ug/g	Average	STD	RSD (%)
cis-3,3	173	*****	21.6	0.00109	21.3	42.1	64.3	84.4	0.38	0.33	0.35	0.32	0.35	0.0243	7.0
trans-3,3	173	*****	22.3	0.00112	18.5	31.3	44.9	59.9	0.33	0.24	0.24	0.23	0.26	0.0417	15.9
cis-2,4	159	*****	68.4	0.00345	60.3	128	189	252	1.09	0.99	1.02	0.97	1.02	0.0450	4.4
trans-2,4	159	*****	61.2	0.00309	80.6	189	293	397	1.45	1.46	1.58	1.53	1.51	0.0518	3.4
cis-1,5	145	*****	365	0.01841	309	756	1231	1853	5.58	5.84	6.64	7.13	6.30	0.6207	9.9
trans-1,5	145	*****	323	0.01629	286	656	982	1429	5.16	5.07	5.30	5.50	5.26	0.1624	3.1
cis-3,4	173	*****	90.2	0.00455	44.9	98.1	145	191	0.81	0.76	0.78	0.74	0.77	0.0280	3.6
trans-3,4	173	*****	96.1	0.00485	40.8	84.7	124	161	0.74	0.65	0.67	0.62	0.67	0.0424	6.3
cis-2,5	159	*****	268	0.01352	111	244	359	465	2.00	1.88	1.94	1.79	1.90	0.0780	4.1
trans-2,5	159	*****	225	0.01135	102	196	287	366	1.84	1.51	1.55	1.41	1.58	0.1603	10.2
cis-1,6	145	*****	1347	0.06794	544	1264	1917	2546	9.82	9.76	10.34	9.80	9.93	0.2368	2.4
trans-1,6	145	*****	1164	0.05871	497	1161	1720	2263	8.97	8.97	9.28	8.71	8.98	0.2007	2.2
cis-4,4	187	*****	57.4	0.00290	24.8	50.1	71.1	89.1	0.45	0.39	0.38	0.34	0.39	0.0374	6.4
cis-3,5	173	*****	78.2	0.00394	36.3	75.1	108	136	0.66	0.58	0.58	0.52	0.59	0.0467	8.6
trans-4,4	187	*****	64.2	0.00324	32.4	71.8	102	128	0.58	0.55	0.55	0.49	0.55	0.0333	6.1
trans-3,5	173	*****	94.2	0.00475	24.9	59.6	79.7	99	0.45	0.46	0.43	0.38	0.43	0.0304	7.1
cis-2,6	159	*****	279	0.01407	76.9	168	242	302	1.39	1.30	1.31	1.16	1.29	0.0808	6.3
trans-2,6	159	*****	244	0.01231	67.7	157	226	280	1.22	1.21	1.22	1.08	1.18	0.0608	5.1
cis-1,7	145	*****	1683	0.08489	367	832	1201	1522	6.62	6.43	6.48	5.86	6.35	0.2911	4.6
trans-1,7	145	*****	1434	0.07233	311	714	1074	1312	5.61	5.52	5.79	5.05	5.49	0.2743	5.0
cis-4,5	187	*****	16.1	0.00081	8.1	14.9	20.3	24.1	0.15	0.12	0.11	0.09	0.12	0.0193	16.7
cis-3,6	173	*****	50.2	0.00253	11.7	22.9	32.2	38.7	0.21	0.18	0.17	0.15	0.18	0.0221	12.5
trans-4,5	187	*****	44.7	0.00225	5.4	11.9	15.7	17.1	0.10	0.09	0.08	0.07	0.08	0.0120	14.1
trans-3,6	173	*****	69.3	0.00350	7.3	13.1	18.7	21.4	0.13	0.10	0.10	0.08	0.10	0.0177	17.0
cis-2,7	159	*****	189	0.00953	18.2	37.5	56	65.1	0.33	0.29	0.30	0.25	0.29	0.0281	9.6
trans-2,7	159	*****	153	0.00772	13.3	26.8	36.8	43.5	0.24	0.21	0.20	0.17	0.20	0.0259	12.7
cis/trans-1,8	145	*****	1405	0.07087	109	234	324	376	1.97	1.81	1.75	1.45	1.74	0.1884	10.8
Total area			9913.1												
cis-1467-TMT	173	*****	46.4		42.9	40.6	36.9	36.2							
tr-1467-TMT	173	46.9	53.2		58.7	73.1	67.3	72.4							
total 1467-T	173		99.6		101.6	113.7	104.2	108.6							

DATLAB2.WK3

Figure 76

Sample "A" - linear range for cis and trans 1,4-dipropyltetralin and 1-ethyl-4-butyltetralin

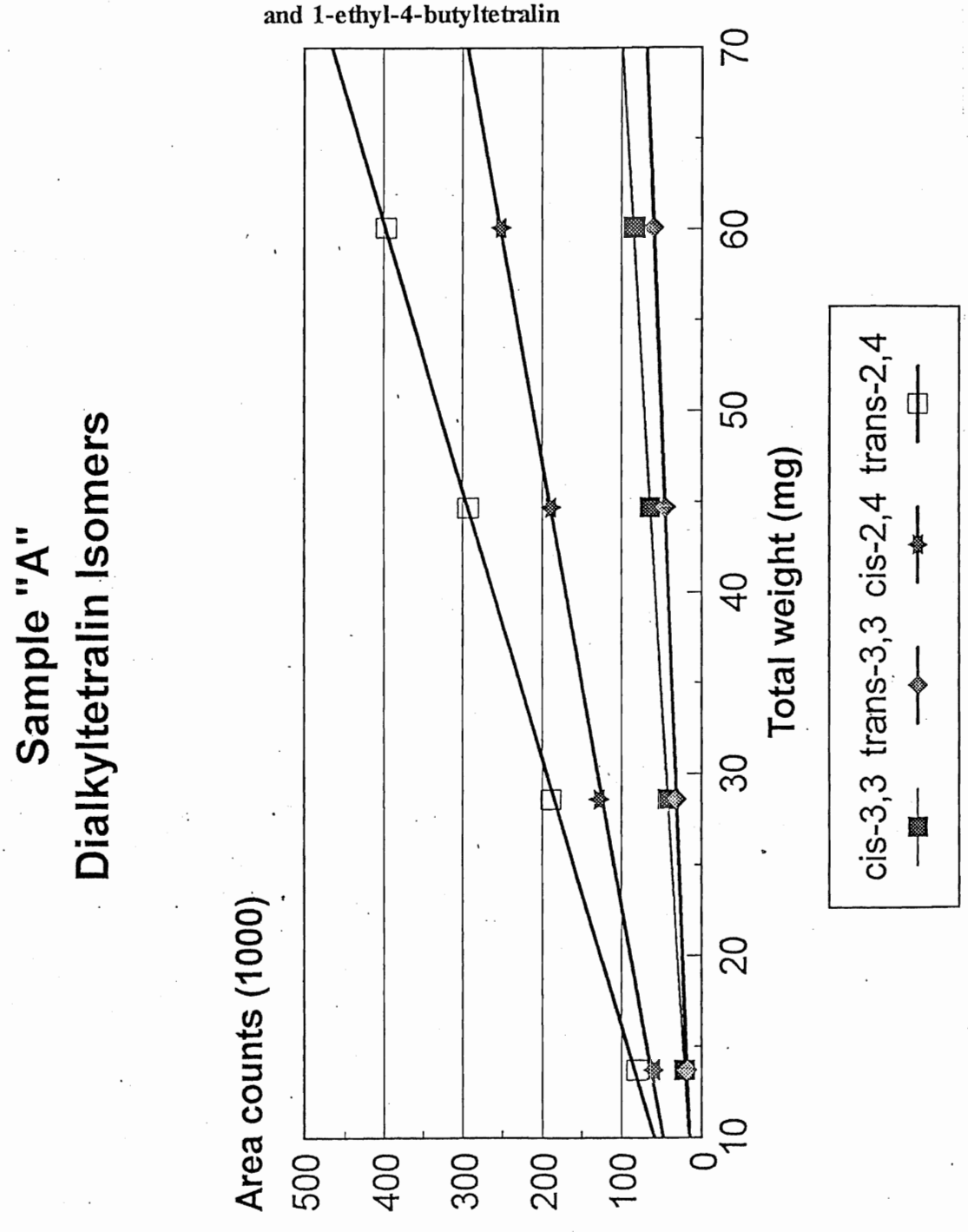


Figure 77

Sample "A" - linear range for cis and trans 1-propyl-4-butyltetralin and 1-methyl-4-pentyltetralin

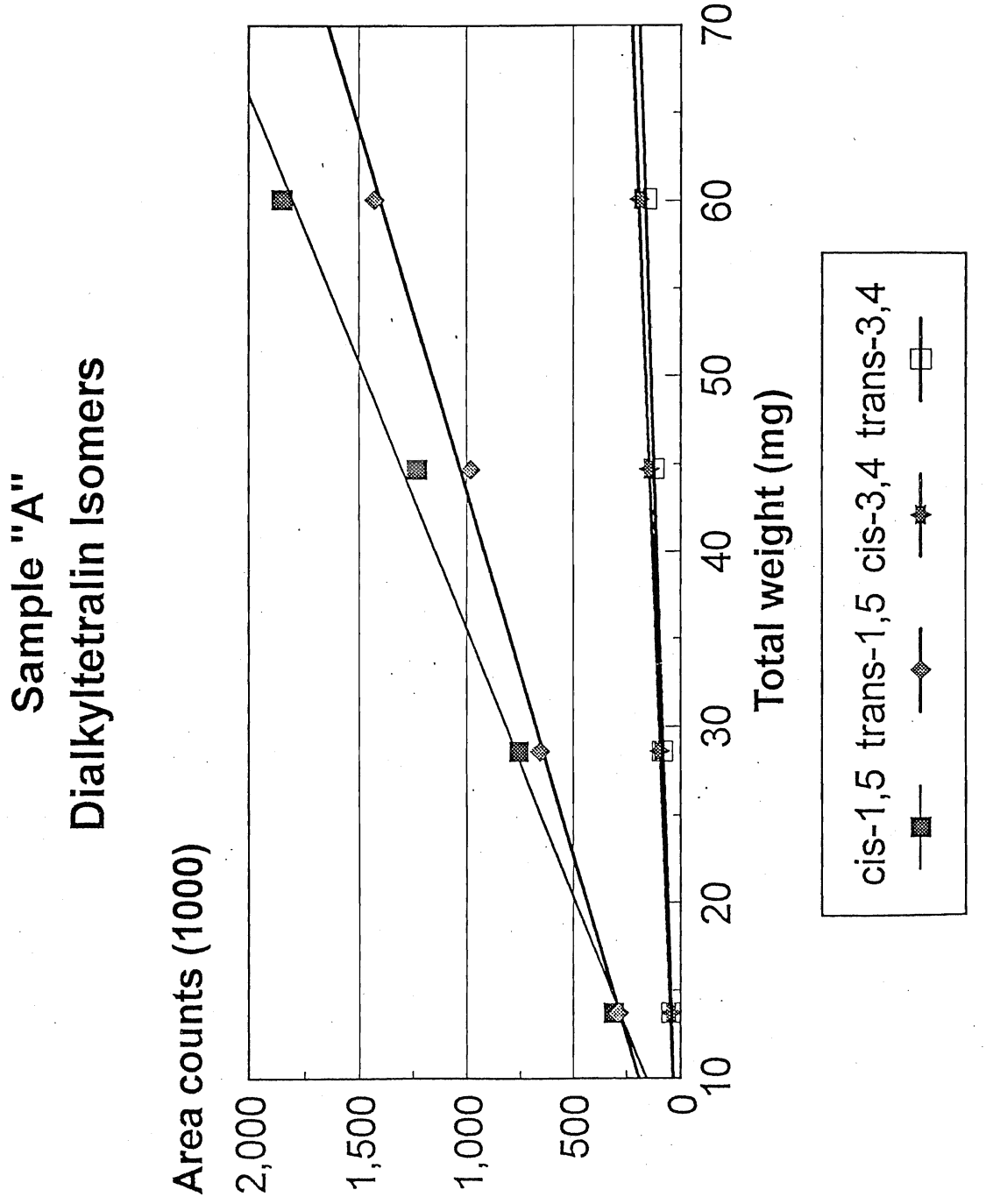


Figure 78

Sample "A" - linear range for cis and trans 1-ethyl-4-pentyltetralin and 1-methyl-4-hexyltetralin

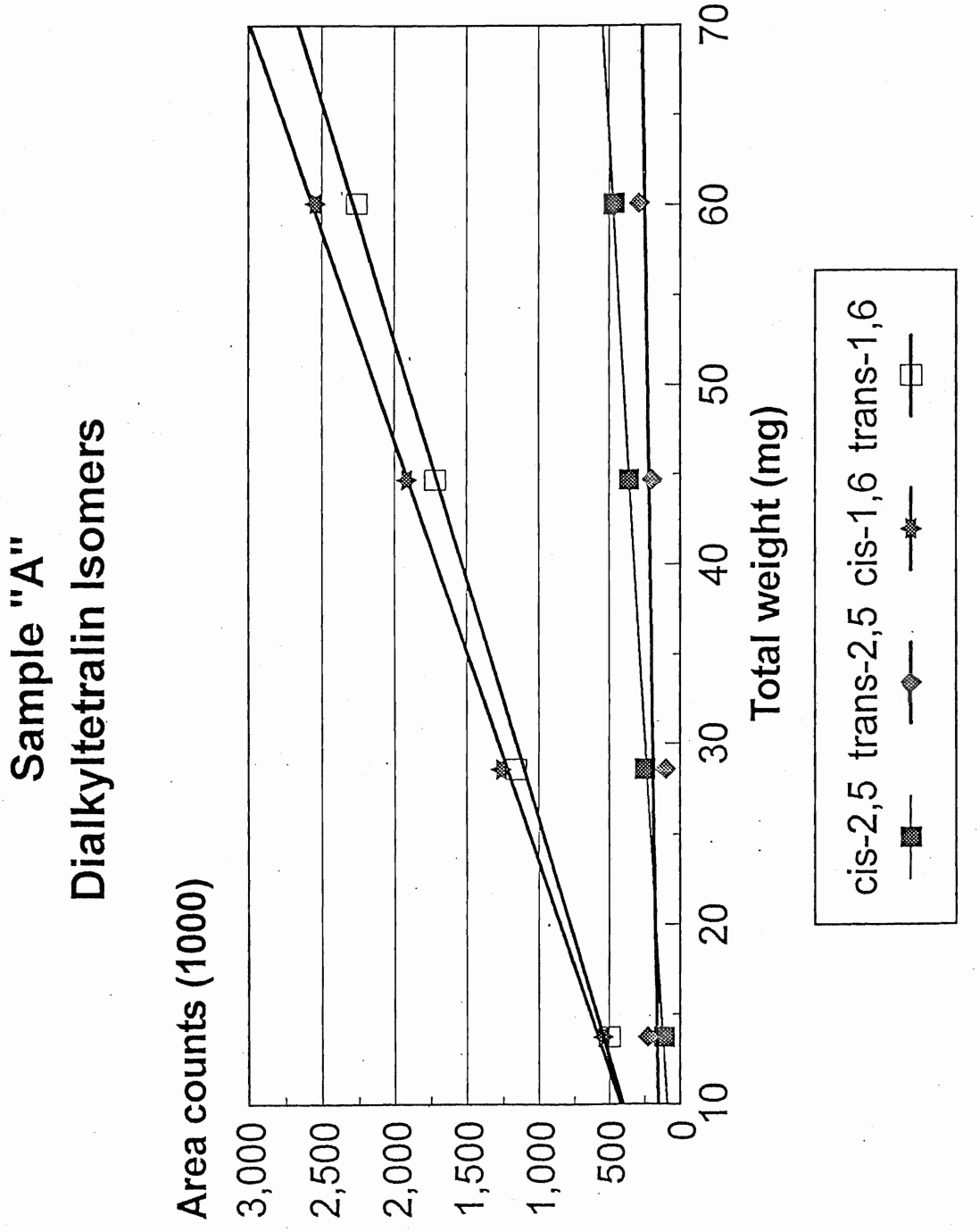


Figure 79

Sample "A" - linear range for cis and trans 1,4-dibutyltetralin and 1-propyl-4-pentyltetralin

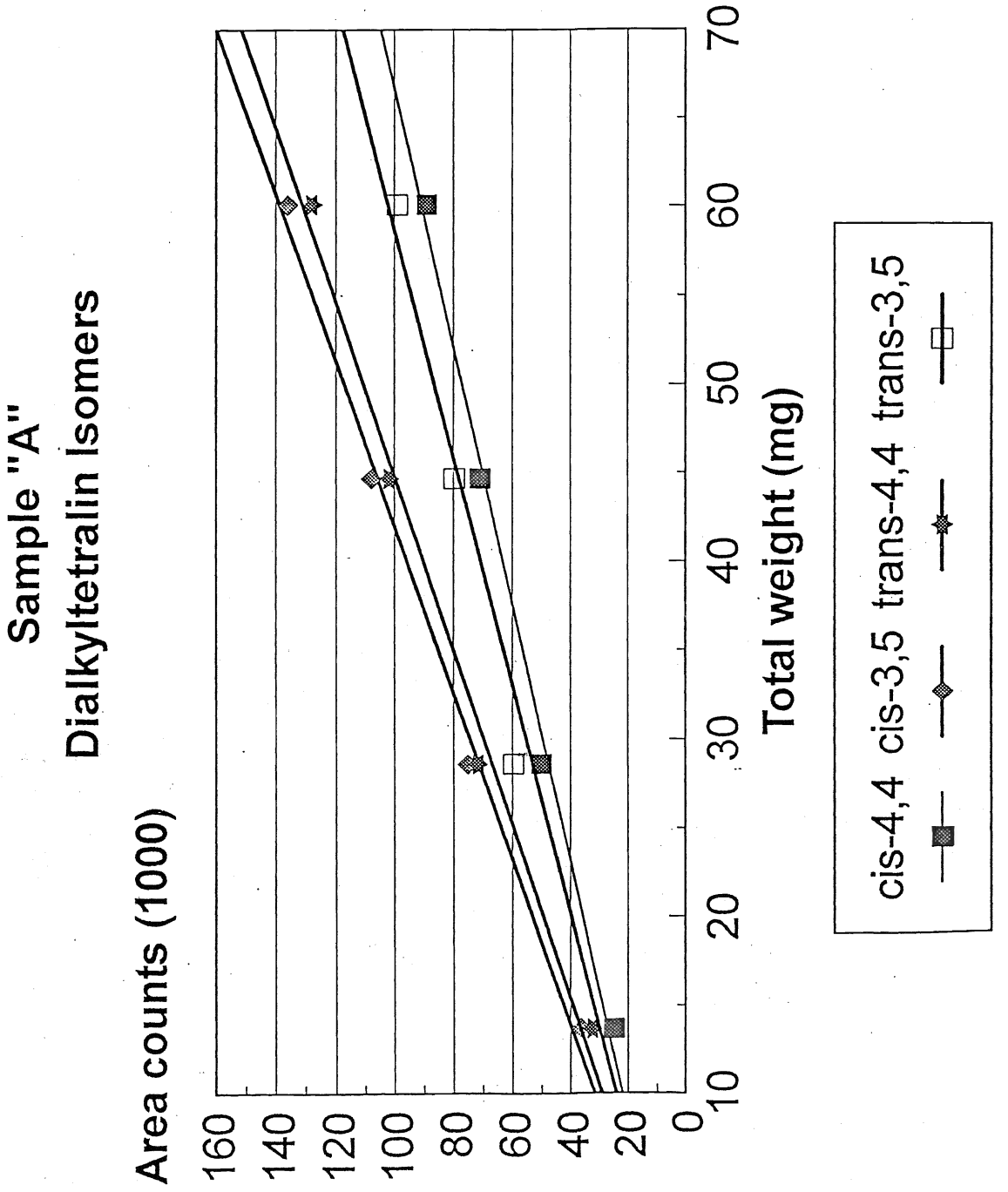


Figure 80

Sample "A" - linear range for cis and trans 1-ethyl-4-hexyltetralin and 1-methyl-4-heptyltetralin

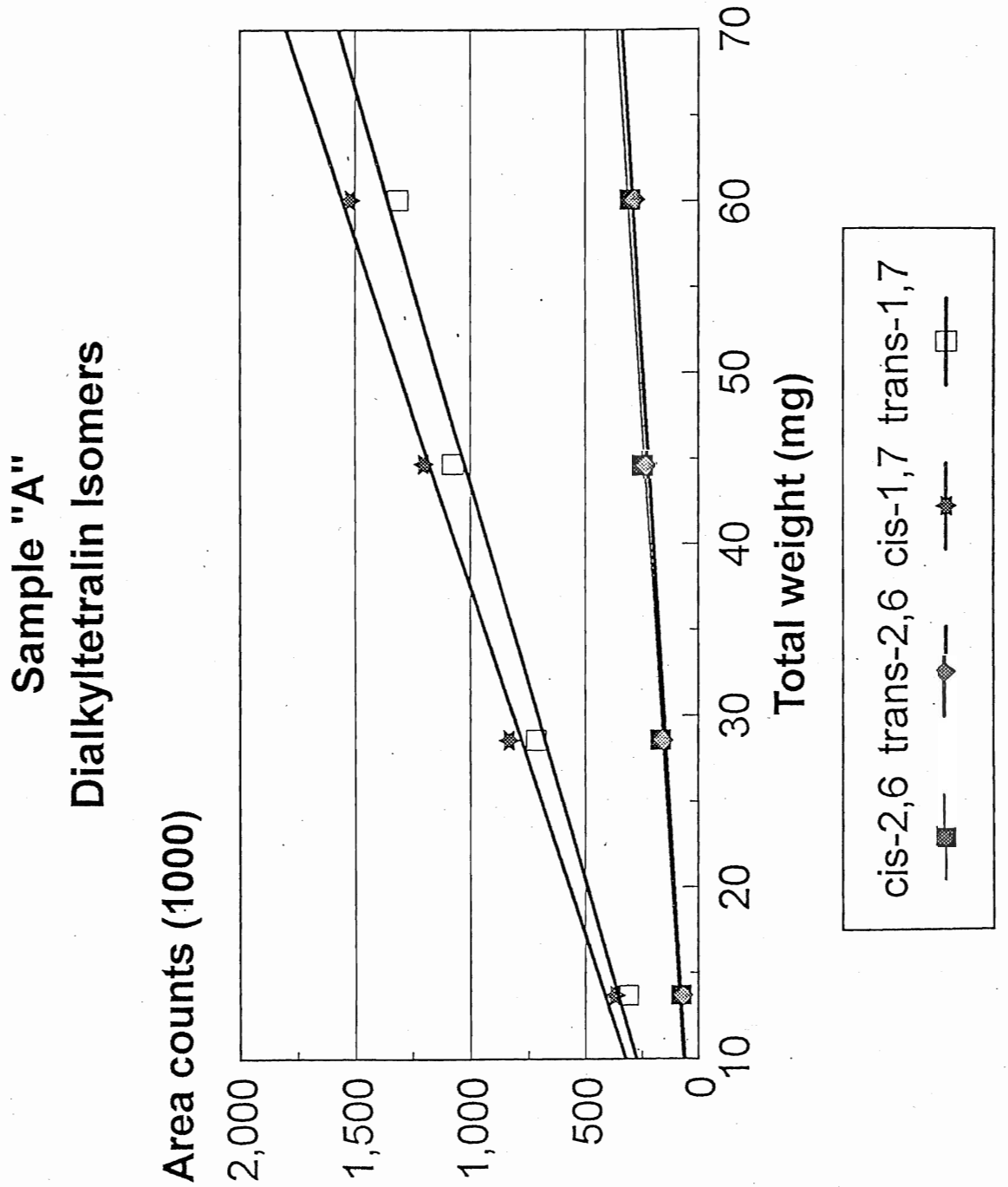


Figure 81

Sample "A" - linear range for cis and trans 1-butyl-4-pentyltetralin and 1-propyl-4-hexyltetralin

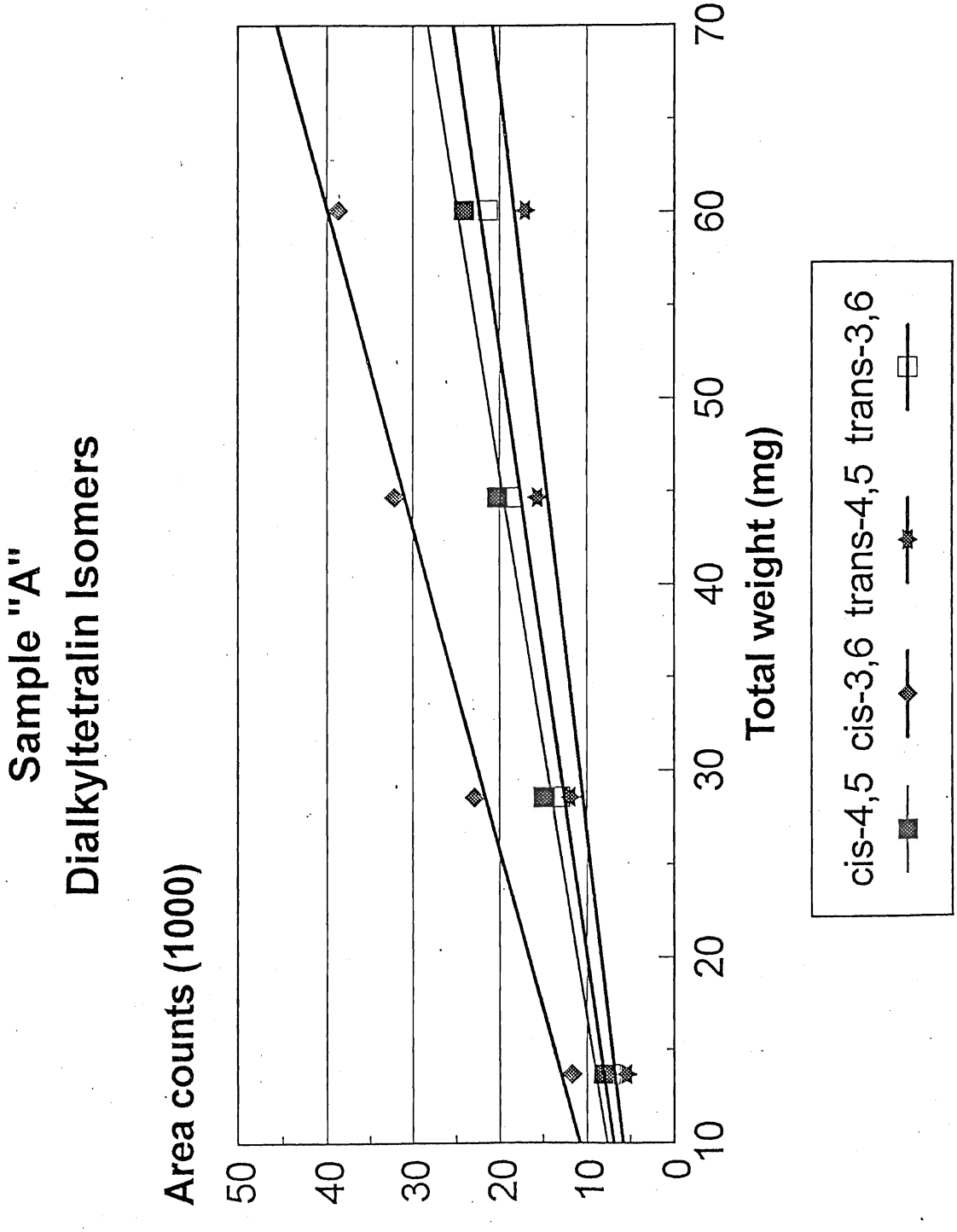


Figure 82

Sample "A" - linear range for cis and trans 1-ethyl-4-heptyltetralin and 1-methyl-4-octyltetralin

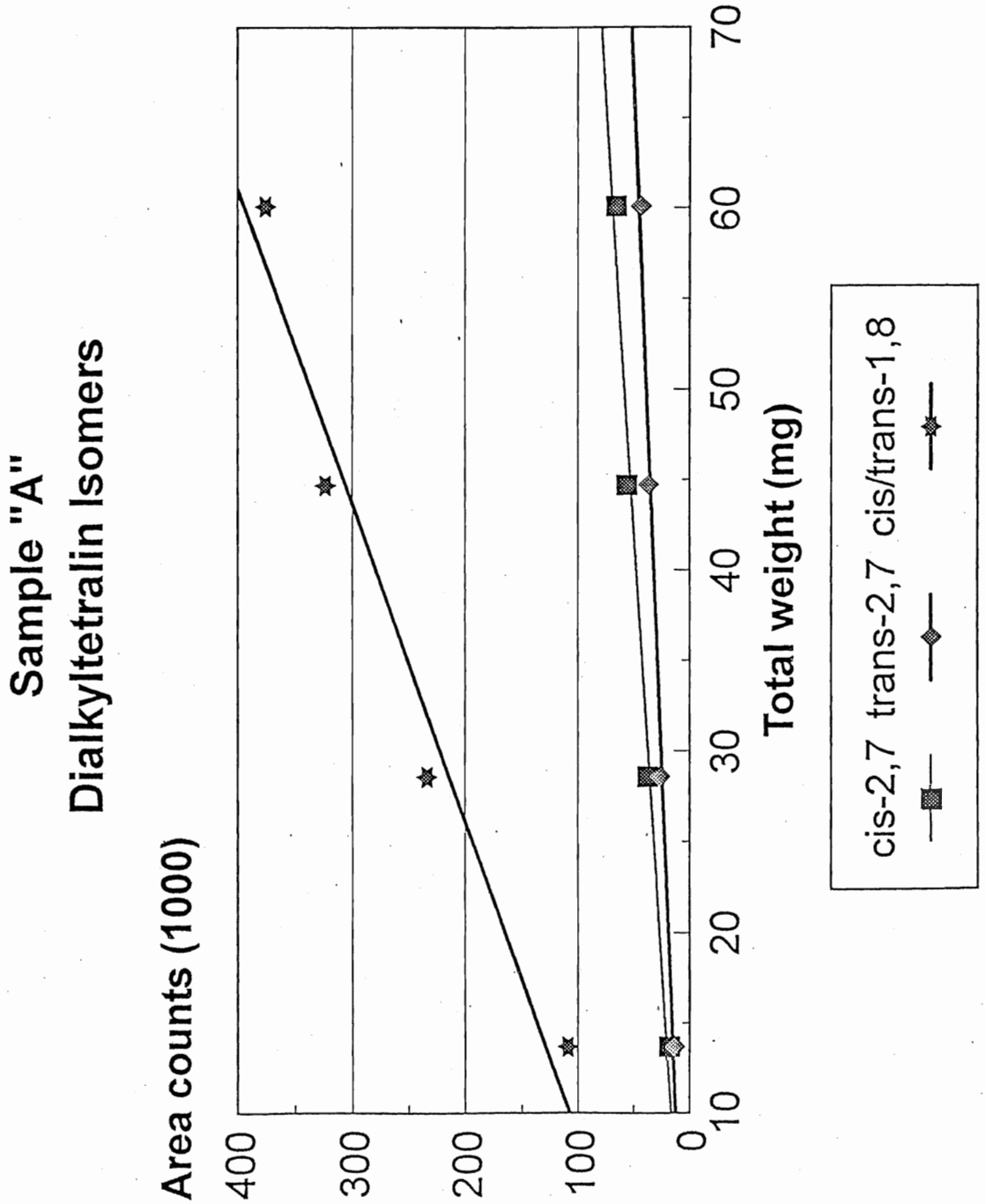


Table 38

Precision and accuracy of the manual injection - retention times for multiple injections of sample "A" using full scan

Isomer	Sample "B" RT (min)	Sample "C" RT (min)	Sample "D" RT (min)	Sample "E" RT (min)	Sample "F" RT (min)	Sample "G" RT (min)	Sample "H" RT (min)	Sample "I" RT (min)	Sample "J" RT (min)	Average RT (min)	STD	RSTD (%)
m/z 204												
5-Phenyl									37.59	37.59	0	0
4-Phenyl									38.02	38.02	0	0
3-Phenyl									39.75	39.75	0	0
2-Phenyl									43.27	43.27	0	0
m/z 218												
5-Phenyl	46.48	46.33	46.31	46.26	46.49	46.51	46.53	46.47	46.63	46.45	0.113	0.24
4-Phenyl	47.34	47.17	47.16	47.11	47.33	47.32	47.37	47.32	47.48	47.29	0.112	0.24
3-Phenyl	49.39	49.21	49.17	49.14	49.37	49.37	49.41	49.38	49.50	49.33	0.116	0.23
2-Phenyl	53.38	53.15	53.12	53.08	53.32	53.32	53.35	53.37	53.44	53.28	0.122	0.23
m/z 232												
6-Phenyl	55.77	55.63	55.56	55.57	55.79	55.79	55.82	55.76	55.76	55.72	0.095	0.17
5-Phenyl	56.30	56.17	56.12	56.12	56.31	56.59	56.34	56.28	56.28	56.28	0.135	0.24
4-Phenyl	57.39	57.23	57.19	57.18	57.38	57.36	57.43	57.38	57.35	57.32	0.089	0.16
3-Phenyl	59.73	59.54	59.49	59.48	59.71	59.69	59.74	59.71	59.67	59.64	0.100	0.17
2-Phenyl	63.97	63.68	63.64	63.62	63.88	63.84	63.88	63.95	63.80	63.81	0.124	0.19
m/z 246												
6-Phenyl	65.74	65.59	65.51	65.51	65.9	65.88	65.84	65.72	65.73	65.71	0.140	0.21
5-Phenyl	66.38	66.22	66.14	66.15	66.55	66.53	66.49	66.36	66.36	66.35	0.147	0.22
4-Phenyl	67.65	67.48	67.41	67.4	67.8	67.78	67.72	67.63	67.62	67.61	0.141	0.21
3-Phenyl	70.13	69.93	69.85	69.85	70.27	70.23	70.14	70.11	70.07	70.06	0.146	0.21
2-Phenyl	74.46	74.17	74.09	74.09	74.58	74.47	74.32	74.43	74.32	74.33	0.167	0.22
m/z 260												
7/6-Phenyl	75.73	75.47	75.38	75.38	75.75	75.97	75.68	75.68	75.73	75.64	0.184	0.24
5-Phenyl	76.51	76.23		76.18	76.56	76.75	76.44	76.47	76.52	67.96	0.309	0.46
4-Phenyl	77.88	77.61		77.54	77.91	78.08		77.86	77.86	60.53	0.360	0.60
3-Phenyl	80.47	80.2			80.51	80.63		80.43	80.45	68.96	0.205	0.30
2-Phenyl	84.76	84.43			84.73	84.87		84.69	84.67	72.59	0.245	0.34
m/z 274												
7/6-Phenyl						85.43				85.43	0	0
5-Phenyl						85.77				85.77	0	0
4-Phenyl						86.60				86.60	0	0
3-Phenyl						88.05				88.05	0	0
2-Phenyl						90.65				90.65	0	0
I.S 1-Phenyl (m/z 218)	61.29	61.14	61.06	61.08	61.35	61.38	61.08	61.34	61.31	61.23	0.125	0.20
I.S 1-Phenyl (m/z 246)	82.55	82.33	82.26	82.29	82.64	82.68	82.29	82.58	82.56	82.46	0.159	0.19

Table 39

Precision and accuracy of the manual injection for dialkyltetralins in sample "A" using SIM

Isomer	m/z	DAT Std. Total 0.5 ug/ul RT (min)	0.0137 g RT (min)	0.0286 g RT (min)	0.0447 g RT (min)	0.0601 g RT (min)	Average	STD	RSTD (%)
cis-3,3	173	61.612	61.671	61.713	61.693	61.688	61.675	0.0344	0.056
trans-3,3	173	62.460	62.480	62.519	62.502	62.071	62.406	0.1689	0.271
cis-2,4	159	62.679	62.700	62.743	62.717	62.707	62.709	0.0210	0.033
trans-2,4	159	63.335	63.359	63.398	63.375	63.367	63.367	0.0206	0.032
cis-1,5	145	63.703	63.715	63.768	63.758	63.697	63.728	0.0292	0.046
trans-1,5	145	63.866	63.882	63.941	63.934	63.935	63.912	0.0312	0.049
cis-3,4	173	71.109	71.110	71.162	71.157	71.154	71.138	0.0237	0.033
trans-3,4	173	72.344	72.331	72.376	72.364	72.359	72.355	0.0157	0.022
cis-2,5	159	72.857	72.841	72.883	72.866	72.859	72.861	0.0136	0.019
trans-2,5	159	73.664	73.649	73.686	73.665	73.656	73.664	0.0124	0.017
cis-1,6	145	74.313	74.297	74.347	74.340	74.339	74.327	0.0190	0.026
trans-1,6	145	74.520	74.510	74.654	74.562	74.654	74.580	0.0629	0.084
cis-4,4	187	80.390	80.381	80.409	80.392	80.385	80.391	0.0096	0.012
cis-3,5	173	81.014	81.007	81.035	81.019	81.013	81.018	0.0095	0.012
trans-4,4	187	82.043	82.053	82.078	82.057	82.044	82.055	0.0127	0.015
trans-3,5	173	82.477	82.518	82.541	82.519	82.505	82.512	0.0210	0.025
cis-2,6	159	83.219	83.272	83.305	83.273	83.256	83.265	0.0280	0.034
trans-2,6	159	84.127	84.157	84.188	84.158	84.146	84.155	0.0198	0.024
cis-1,7	145	84.861	84.855	84.890	84.871	84.860	84.867	0.0124	0.015
trans-1,7	145	85.049	85.039	85.076	85.058	85.049	85.054	0.0124	0.015
cis-4,5	187	89.965	89.958	89.969	89.944	89.927	89.953	0.0154	0.017
cis-3,6	173	91.028	91.008	91.028	91.003	90.984	91.010	0.0166	0.018
trans-4,5	187	91.879	91.867	91.877	91.855	91.837	91.863	0.0155	0.017
trans-3,6	173	92.627	92.617	92.625	92.601	92.584	92.611	0.0162	0.018
cis-2,7	159	93.438	93.426	93.441	93.415	93.398	93.424	0.0158	0.017
trans-2,7	159	94.362	94.354	94.364	94.343	94.324	94.349	0.0147	0.016
cis/trans-1,8	145	95.182	95.161	95.171	94.147	95.128	94.958	0.4058	0.427
cis-1467-TMT	173	46.692	46.669	46.707	46.689	46.682	46.688	0.0124	0.027
tr-1467-TMT	173	46.894	46.874	46.971	46.896	46.892	46.905	0.0337	0.072
Total 1467-TM	173	46.793	46.772	46.839	46.793	46.787	46.797	0.0226	0.048
Total 1,4-DMT	145	27.801	27.771	27.790	27.771	27.761	27.779	0.0145	0.052

DATRT.WK3

CONCLUSION

As a result of this study, an accurate GC/MS method was developed to separate, identify and quantify the major and some minor components of various commercial linear alkylbenzenes. Identification of linear alkylbenzene isomers and the structure elucidation of the impurities was done by the detailed analysis of electron impact mass spectral fragmentation patterns of the separated chromatographic peaks. Structure confirmation was conducted by analysis of the chemical ionization mass spectra, in particular the molecular and adduct ions.

This study afforded an opportunity to evaluate two analytical techniques, GC and GC/MS and confirmed earlier observations that the average molecular weight results were not the same when comparing these two techniques. It was observed that the higher the content of impurities, the bigger the difference in results. The GC/MS technique proved to provide more accurate average molecular weight determinations which are critical in the calculation of the percent of active ingredient content of the sulphonated product, linear alkylbenzene sulphonate, LAS.

As a result of this study, the GC/MS method and the data presented can be used by the suppliers of commercial linear alkylbenzenes as a method to evaluate the composition and purity of their products.

This study also proved that in the past some of the reported results, especially for *dialkyltetralins*, were incorrect. Most results reported were lower than the actual values. One of the reasons for this was that standards like dialkyltetralin blend, cis/trans-1,4,6,7-

tetramethyltetralin and cis/trans-1,4-dimethyltetralin were not used in previous studies. Also, in the previous studies, neither the more sensitive SIM technique nor the more accurate internal standard technique was used for the GC/MS analysis of commercial linear alkylbenzenes.

Further, the analytical data presented in this study can be utilized by other chemists for the identification and quantitation of the impurities such as *branched* alkylbenzenes and *dialkyltetralins* in all currently available linear alkylbenzenes. These data are useful and can help other scientists in their future studies to assess the environmental impact of these compounds and their sulphonated derivatives.

Lastly, the GC/MS method that was developed during the course of this study allowed identification of some other trace impurities present in industrially produced linear alkylbenzenes. Compounds such as dialkylindanes, alkylnaphthalenes and diphenylalkanes were identified without preparative HPLC separations. Further investigation of these impurities using GC/MS method will be the subject of a future study.

In summary, the results of this study provide a detailed picture of the composition of commercial linear alkylbenzenes, their actual molecular weights and the quantity of the impurities present.

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APPENDIX

Apart from *dialkyltetralins* and *branched* alkylbenzenes, other trace impurities that belong mainly to the following classes of compounds: dialkylindanes, diphenylalkanes and alkylnaphthalenes were identified using the GC/MS method that was developed in the course of this study.

Structure elucidation of diphenylalkanes; 1,1-diphenylmethane (MW=168) and 1,1-diphenylbutane (MW=210) was done using electron impact mass spectra. Their mass spectra are presented in **Figure 83** and **84**. Two alkylnaphtalenes were identified (MW= 212 and MW=226) and their EI mass spectra are presented in **Figure 85** and **86**. **Figure 87** represents the EI mass spectrum of dialkylindane with the base peak at m/z 131.

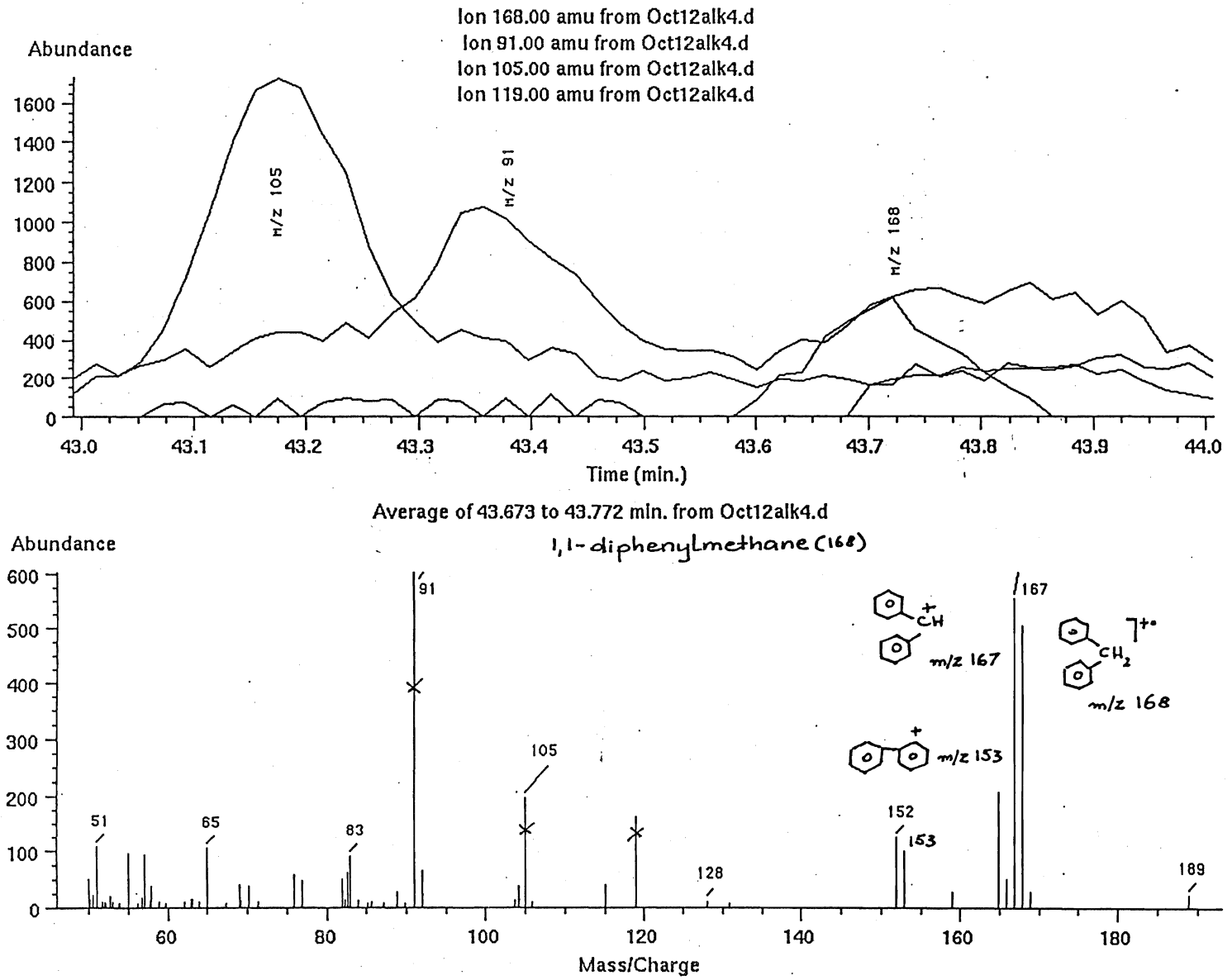


Figure 83

EI mass spectrum of 1,1-diphenylmethane

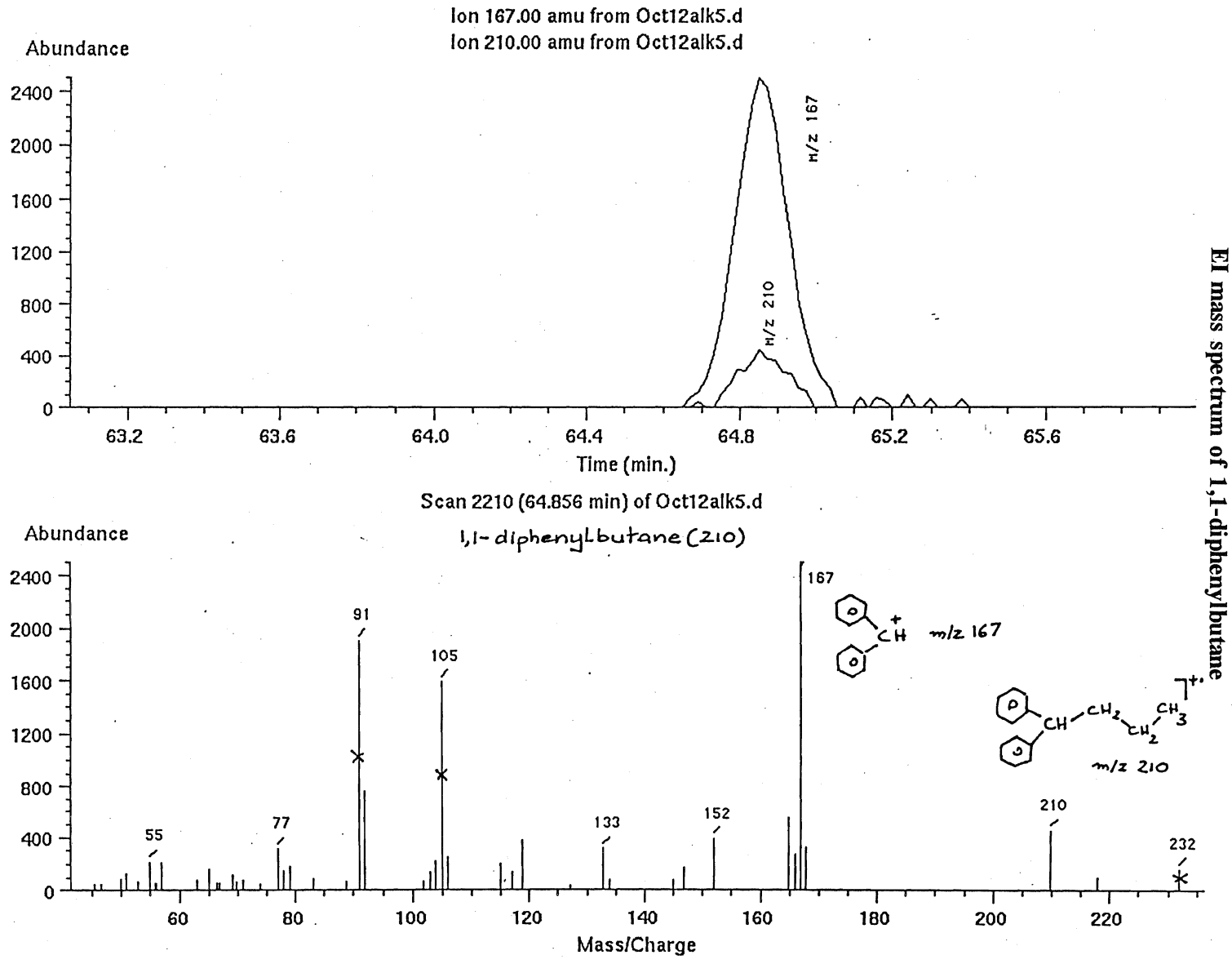


Figure 84

EI mass spectrum of 1,1-diphenylbutane

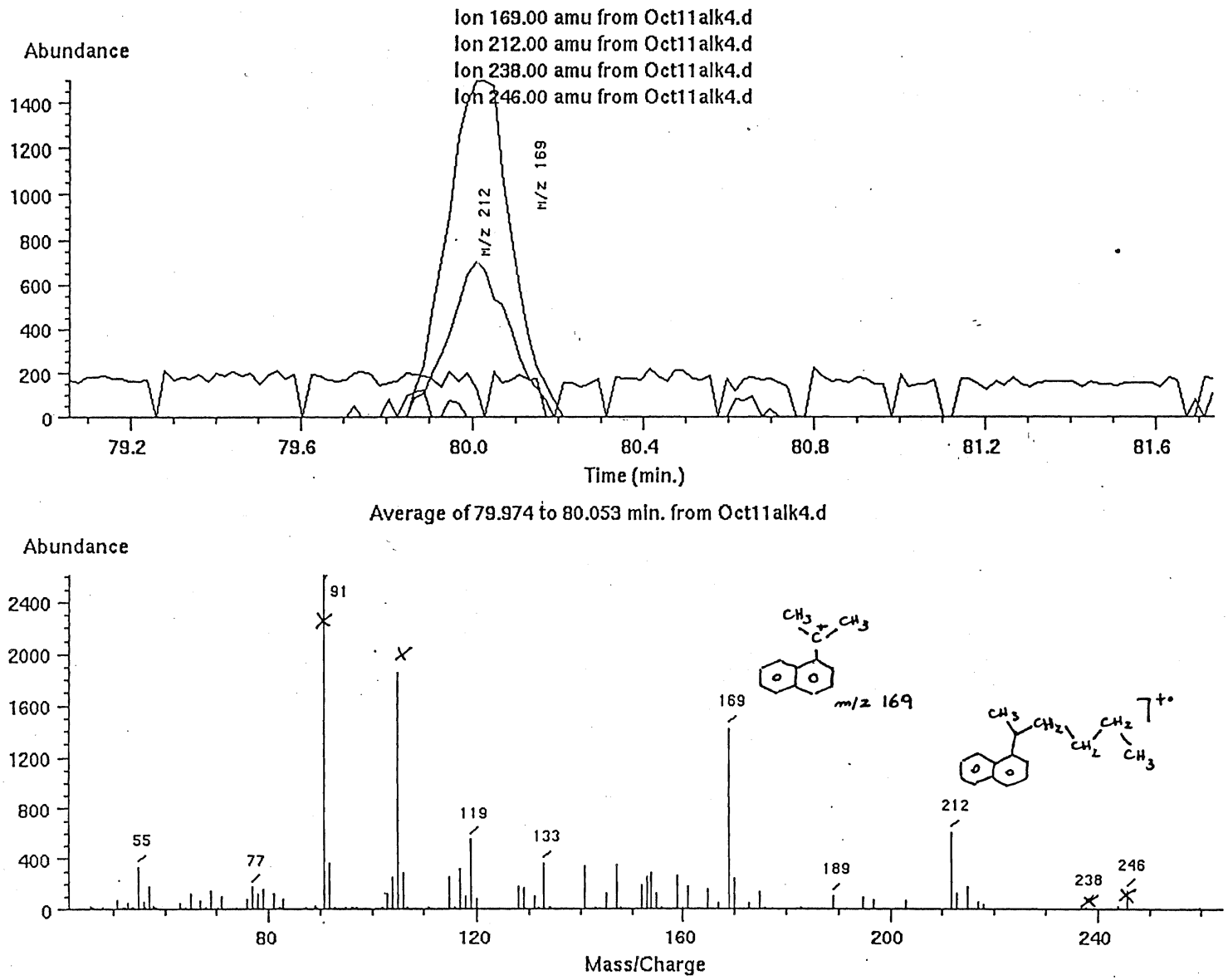
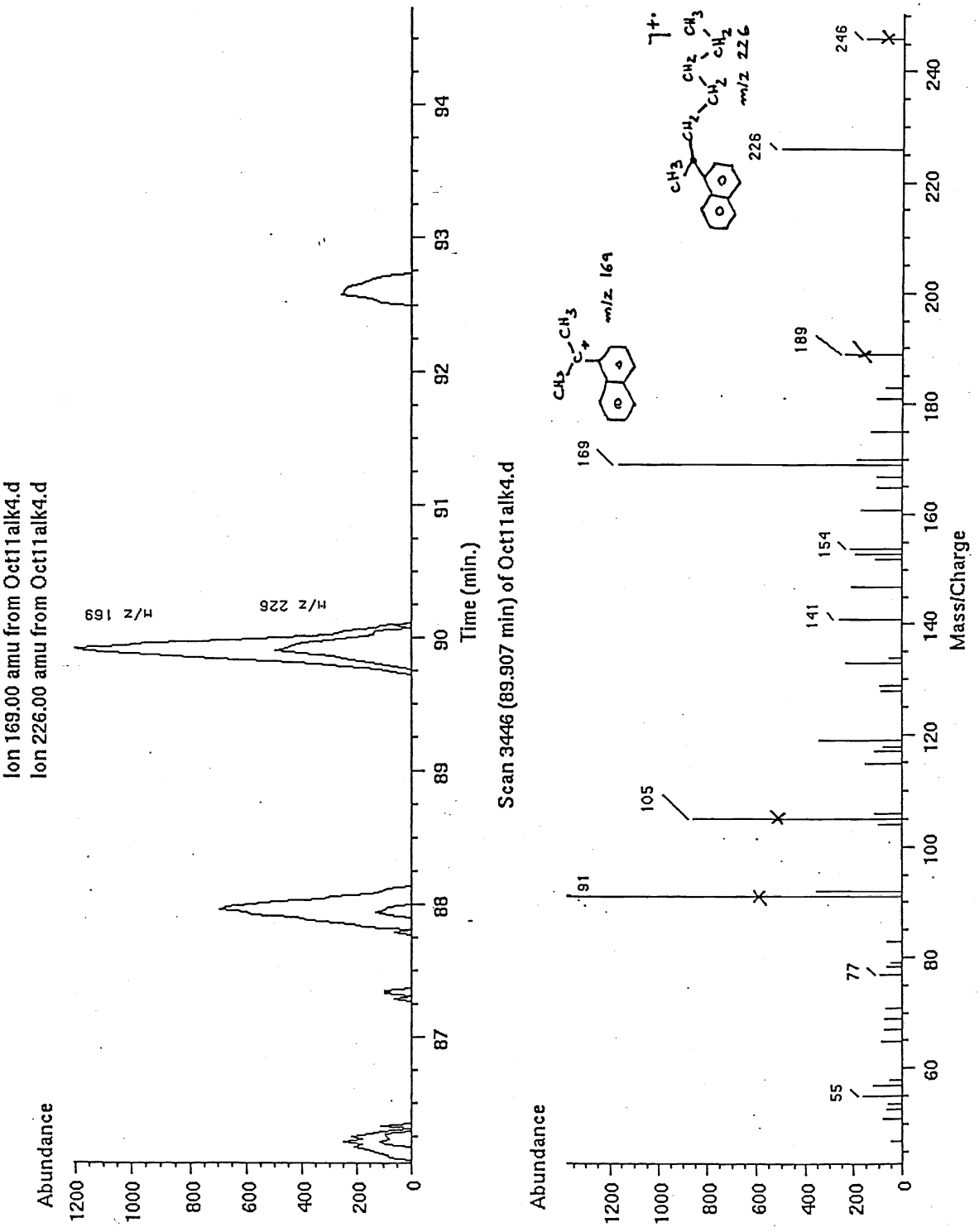


Figure 85

EI mass spectrum of C_6 - naphthalene

Figure 86

EI mass spectrum of C_7 - naphthalene



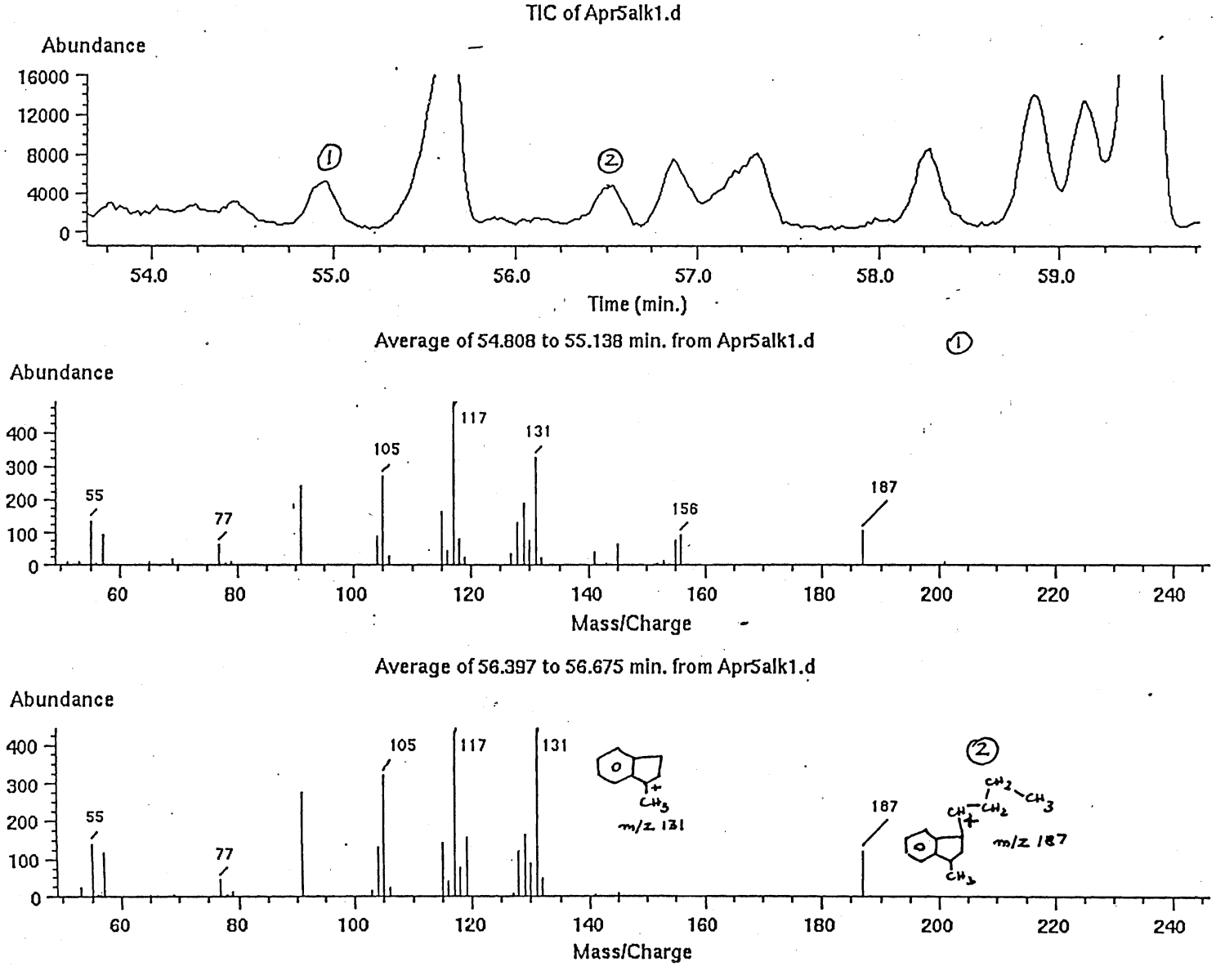


Figure 87

EI mass spectrum of a dialkylindane