

1998

## Chemical Interaction of "Declorane Plus" with Antimony Trioxide in Nylon 66

Yum Min Kang

*College of William & Mary - Arts & Sciences*

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**CHEMICAL INTERACTION OF "DECHLORANE PLUS" WITH  
ANTIMONY TRIOXIDE IN NYLON 66**

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A Thesis

Presented to

The Faculty of the Department of Chemistry

The College of William and Mary in Virginia

In Partial Fulfillment

Of the Requirements for the Degree of

Master of Arts

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by

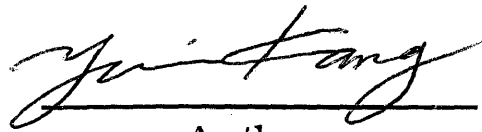
Yun Min Kang

1998

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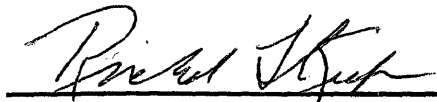
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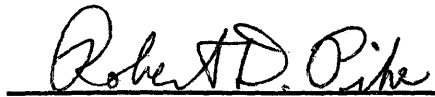
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Author

Approved, August 25, 1998

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Robert D. Pike

A handwritten signature in cursive script, appearing to read "William H. Starnes, Jr.", written over a horizontal line.

William H. Starnes, Jr.

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## ABSTRACT

Several products formed from heated mixtures of Nylon 66, antimony trioxide, and the important commercial fire retardant "Dechlorane Plus" ("Dech Plus") have been identified in an attempt to understand the unfavorable flame-retardant characteristics of this system, which are manifested by undesirable losses of mass upon pyrolysis. The chemistry that has been revealed by this work is strikingly novel and involves reductive dechlorination as well as an unusually rapid retro-Diels-Alder process. Preliminary attempts to elucidate the mechanisms of these reactions have been made by comparing the behavior of Dech Plus with that of hexachlorocyclopentadiene under similar reaction conditions.

**CHEMICAL INTERACTION OF "DECHLORANE PLUS" WITH  
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## I. INTRODUCTION

### A. General

In recent years there has been a considerable amount of interest in areas related to the flammability of plastics or other polymeric materials. Although synthetic polymers have become widely used in our everyday life, they are flammable and will burn readily in the air with sufficient heat. Annual fire costs around the world run into hundreds of millions of dollars, and burning polymeric materials and the smoke and combustion gases which are produced in fires cause the deaths of many fire victims.<sup>1</sup> In relation to this, polymer flammability has been recognized as an increasingly important social and scientific problem. Thus, the flame retardants are now the most widely used plastics additives, and Table 1 gives the principal groups of these chemicals and their relative extents of use.<sup>1</sup>

Group	1986, t	1991	
		t	\$ x 10 <sup>6</sup>
phosphate esters	20	18	50
halogenated phosphates	13	16	46
chlorinated hydrocarbons	15	15	31
brominated hydrocarbons	28	36	160
brominated Bisphenol A	16	18	37
antimony trioxide	22	25	85
borates	8	8	10
alumina trihydrate	140	170	85
magnesium hydroxide	2	3	6
Total	264	309	510

**Table 1.** Flame-Retardant Market Volume<sup>1</sup>

## **B. Stages in Burning Plastics**

The burning of a solid polymer or polymer composition involves four stages:<sup>2</sup>

1. Heating of the polymer
2. Decomposition
3. Ignition
4. Combustion

These stages are explained briefly in the following paragraphs.

### **Heating of the Polymer**

The application of a heat source, such as a flame, raises the temperature of the solid polymer at some rate that is dependent upon the temperature of the flame and of the polymer. The heated polymer can generate gaseous or condensed species which can react with gaseous or absorbed oxygen. Generally, the accumulation of energy by such chemical processes is initially slow.<sup>3</sup>

### **Decomposition**

Decomposition of the polymer occurs with the elimination of volatile gases or chemically degraded polymer fragments. The understanding of flammability and flame retardancy requires an understanding of the thermal decomposition processes of polymers.<sup>4</sup> Polymers degrade

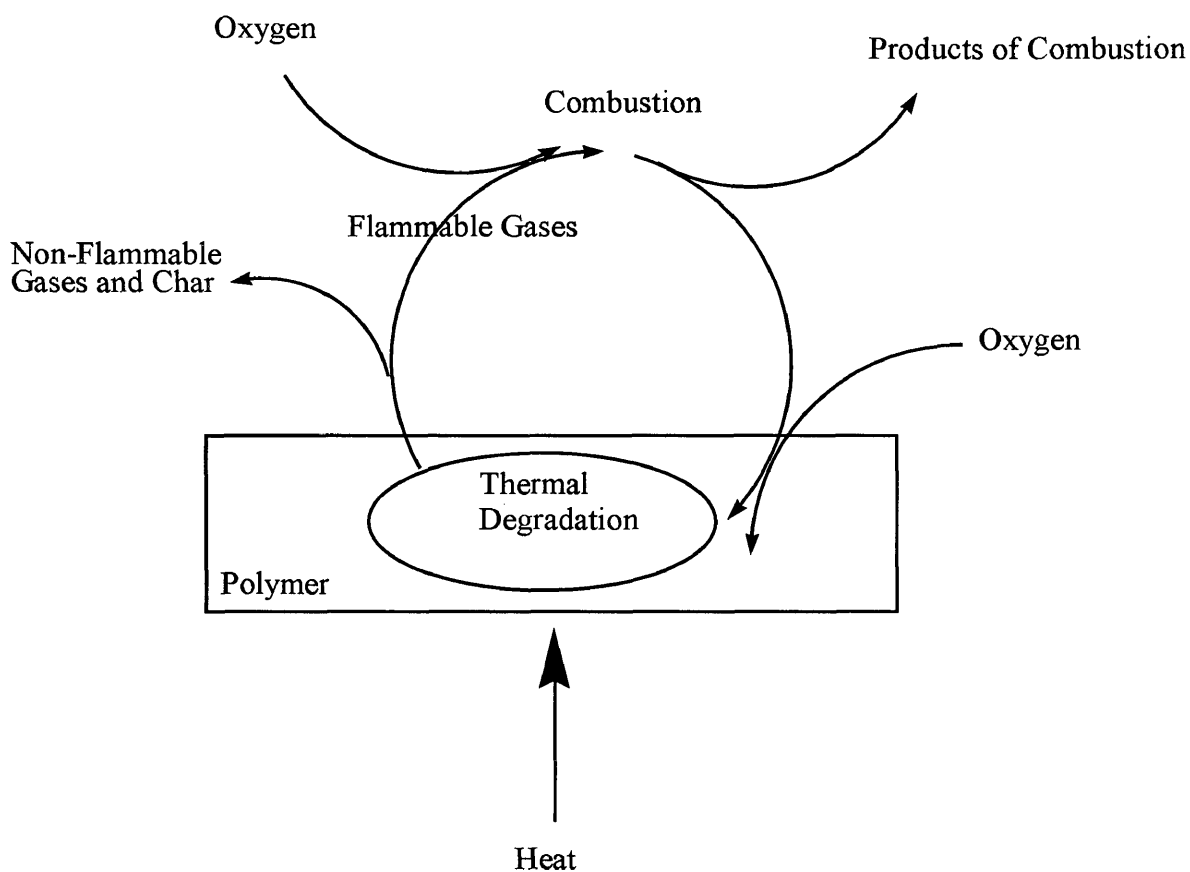
thermally in a different manner in inert atmospheres than they do under oxidative conditions, which result in more complex reactions.

### **Ignition**

As the temperature of the polymer increases and the flammable gases formed reach an appropriate ratio to the oxygen of the air, ignition occurs. At some point, the exothermic gas-phase reaction is sufficiently fast, generating enough energy to supply more fuel, that combustion is sustained.<sup>5</sup>

### **Combustion**

The combustion of a polymer is a very complex process involving a number of stages taking place in three interdependent regions, i.e., within the condensed phase, at the interface between the condensed phase and the gas phase, and in the gas phase.<sup>6</sup> It is thus possible to decrease the overall rate of polymer combustion by interfering with one or more of these stages.<sup>7,8</sup> This interference is usually achieved by the use of additives which may affect the various stages of the burning process in a number of ways.<sup>6</sup> Flaming combustion proceeds if the exothermic gas phase combustion reactions generate sufficient energy, in the form of heat transferred back to the condensed phase, to decompose the polymer further, thus producing more fuel and so maintaining the combustion cycle (Figure 1).<sup>9</sup>



**Figure 1.** The combustion cycle<sup>10</sup>

### C. Flame Retardants

Flame retardants can be divided into two general classes, additives and reactives.<sup>3,10</sup> The additives are generally added to the polymer during processing but do not react chemically with the other constituents of the composition. The reactive types, on the other hand, generally react chemically with the polymer at some processing stage. Basically, both additives and reactives function under heat to yield products that would be

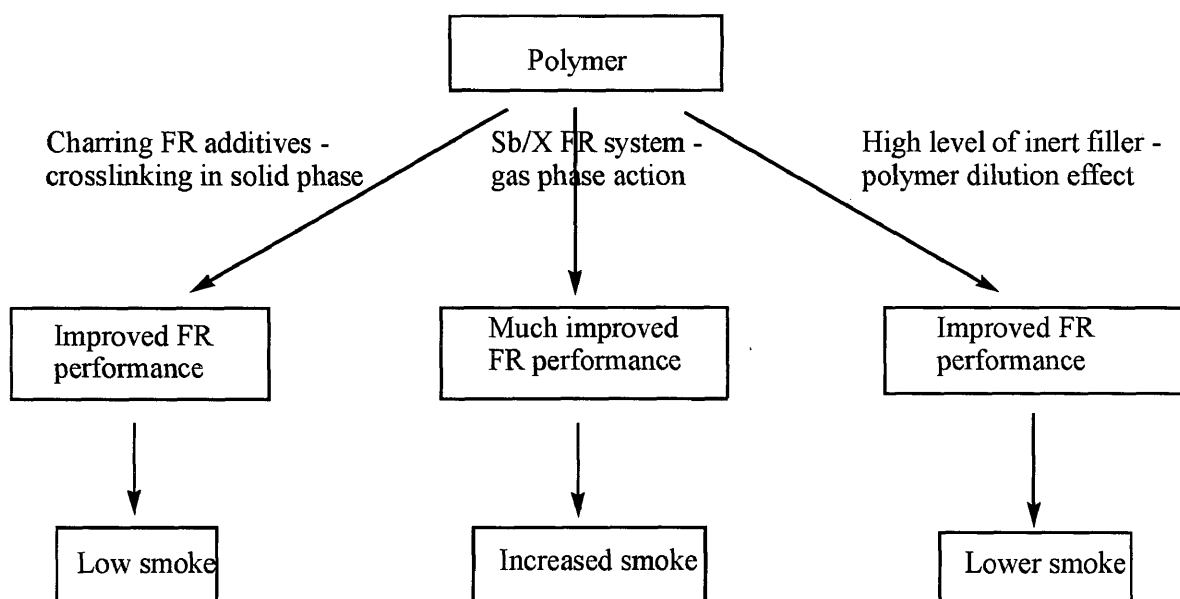


more difficult to ignite than the virgin plastics, or that do not propagate flame as readily. They function in one or more of the following ways:<sup>3</sup>

- By absorbing the heat, thereby making sustained burning more difficult.
- By forming a nonflammable char or coating that insulates the substrate from the heat, excludes oxygen, and slows the rate of diffusion of volatile, flammable pyrolysis fragments from the substrate.
- By enhancing the decomposition of the substrate, thereby accelerating its melting at lower temperatures so that it drips or flows away from the flame front.
- By evolving products that stop or slow flame propagation.
- By forming free radicals that convert a polymer into less combustible products.
- By excluding oxygen from possible burning sites by coating resin particles.

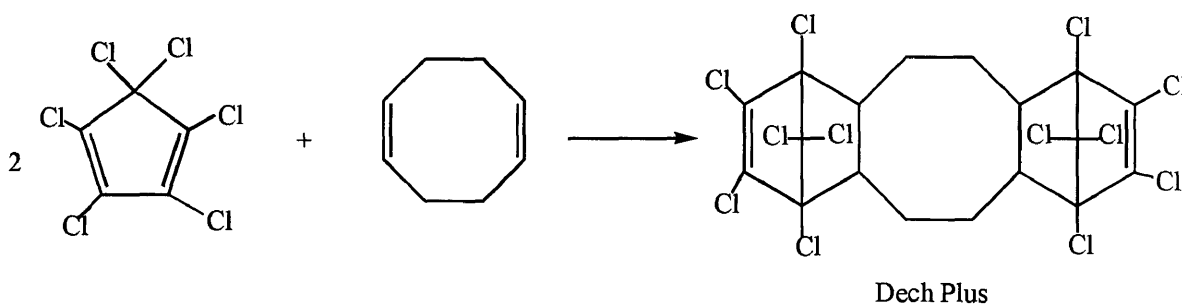
The most important commercial flame-retardant systems are summarized in Figure 2, which shows qualitatively the effects that flame retardants have on burning and on the production of smoke.<sup>10</sup>

Halogens occupy an important position today among the fire-extinguishing and flame-retardant agents. Some commercially important organohalogen flame retardants are given in Tables 2 and 3. Among

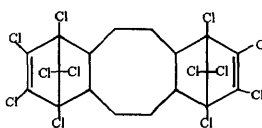
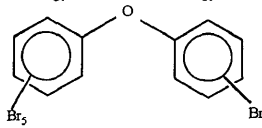
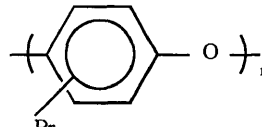


**Figure 2.** Flame retardants and their effect on smoke production<sup>10</sup>

these is “Dechlorane Plus” (“Dech Plus”), which is the second entry in Table 2. Dech Plus is the principal commercial flame retardant based upon hexachlorocyclopentadiene.<sup>11</sup> It is readily prepared by a Diels-Alder reaction of two equivalents of hexachlorocyclopentadiene with 1,5-cyclooctadiene, as shown in Figure 3. Dech Plus, a very stable flame-retardant additive, is especially suited for applications that require high-temperature processing characteristics, no weight loss, no plasticization, and good moisture resistance.<sup>11</sup>

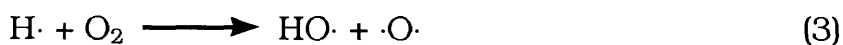
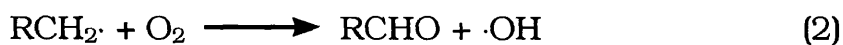


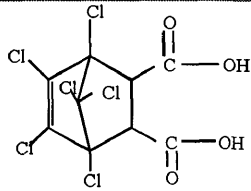
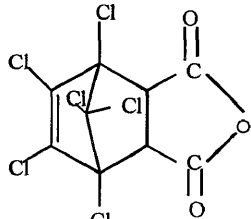
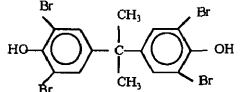
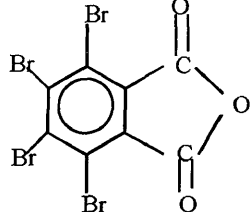
**Figure 3.** Dech Plus synthesis

Class	Example of structure	Halogen, %	MP, °C	Decomposition temp, °C
chlorinated paraffin	$\left( C_2H_{4-X} Cl_X \right)_n$	20-70	liquid to 175	175
chlorinated cycloaliphatic		65	350	350
brominated aromatic		83	300	400
brominated polyaromatic		60-80	200-250	440

**Table 2.** Halogenated Flame-Retardant Additives<sup>5</sup>

Bromine compounds are generally known to be more effective than the corresponding chlorinated ones, but they are more expensive and less thermally and photochemically stable because of the weak carbon-bromine bond.<sup>3,5</sup> Halogenated flame retardants may act in the condensed phase, but detailed research indicates that they are primarily vapor-phase retardants, interfering with the free-radical reactions involved in flame propagation.<sup>3,5,6,8,12</sup> Only a few reactions are critical for such propagation. The following ones are common to most flames:<sup>5,10,11</sup>



Compound	Structure	Halogen, %	MP, °C	Decomposition temp, °C
chlrendic acid		54	a	240
chlrendic anhydride		57	240	240
tetrabromoBisphenol A		58	180	300
tetrabromophthalic anhydride		69	280	350

<sup>a</sup> Decomposes to anhydride.

**Table 3.** Halogenated Reactive Flame Retardants<sup>5</sup>

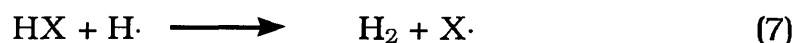


Reactions 3 and 4 are the most critical steps for combustion because HO· and H· radicals are responsible for propagation of combustion via kinetic chain branching.<sup>5,6,11</sup>

The mechanism of the inhibitory action of halogen compounds is believed to be based on the interaction of the halogen with some of the reactive moieties of the flame itself.<sup>13</sup> The active species is the hydrogen

halide (HX), which scavenges the critical chain-branching radicals.<sup>5,13</sup>

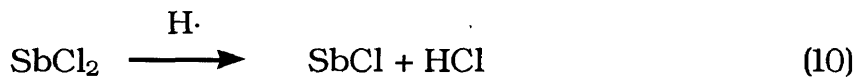
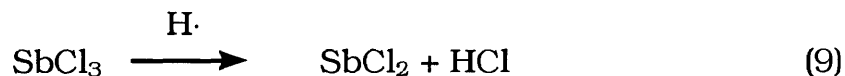
Halogen reactions are shown below:<sup>5,11</sup>



As is shown in equation 5, removal of OH· radicals has a further inhibiting effect, inasmuch as these radicals bring about the very exothermic conversion of carbon monoxide to carbon dioxide.<sup>6</sup>

The flame-retardant activity of organohalogens was found to be greatly enhanced by a number of compounds considered as synergists.<sup>13</sup>

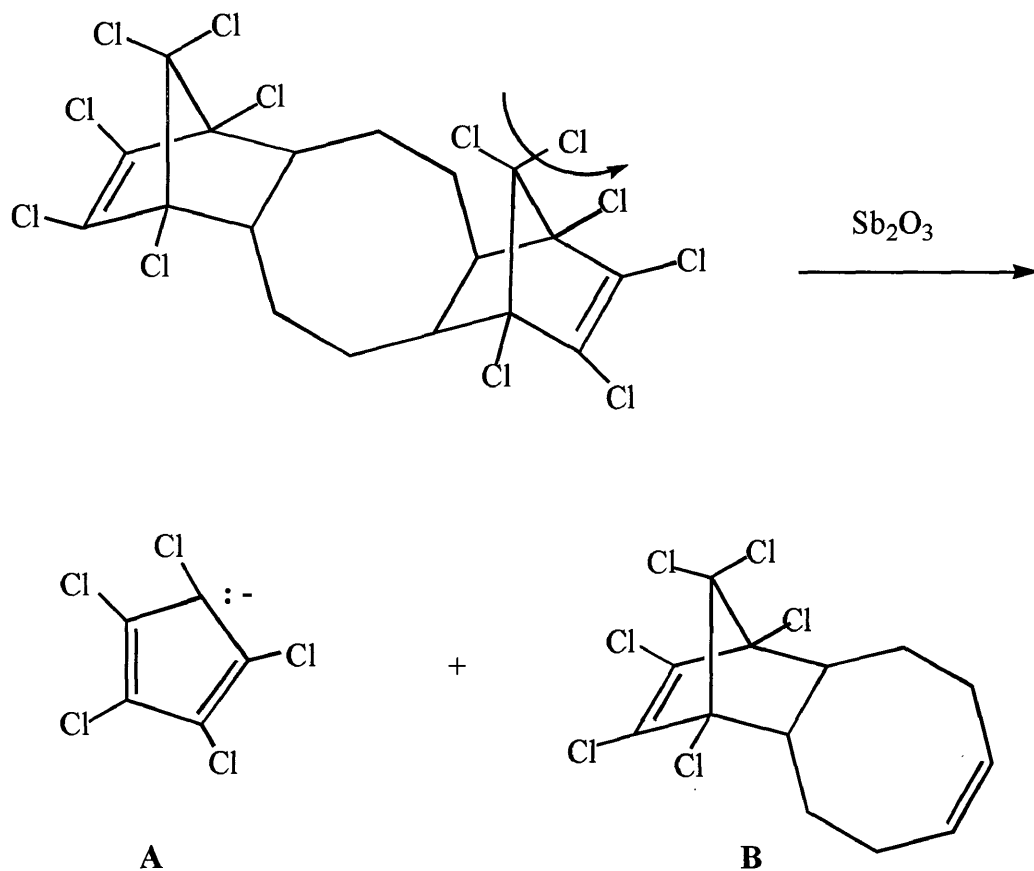
Antimony trioxide,  $\text{Sb}_2\text{O}_3$ , and antimony pentoxide,  $\text{Sb}_2\text{O}_5$ , are widely used synergists. They are often used with organohalogen compounds to create a flame-retardant effect that is greater than the sum of individual effects.<sup>5</sup> Antimony oxides by themselves function only as inert fillers, but the combined system is more effective than the organohalogen alone. Multimetallic flame retardants which contain antimony and other metallic salts also can be used to give the same performance as antimony oxide at lower cost.<sup>3</sup> It has been suggested that the mode of the antimony oxide-halogen system is primarily vapor phase and that the effectiveness is due to the formation of volatile antimony halides and oxyhalides.<sup>5</sup> For example, antimony halides scavenge H· radicals in the vapor phase:<sup>10</sup>



#### D. Interaction between Dechlorane Plus (Dech Plus) and Antimony Trioxide

A working mechanistic hypothesis for the effect of  $\text{Sb}_2\text{O}_3$  on Dech Plus, as shown in Figure 4, is that an antimony atom in the metal-containing additive is basic enough to abstract  $\text{Cl}^+$  from a  $-\text{CCl}_2-$  bridge. The resultant carbanion may then undergo a very rapid retrograde Diels-Alder reaction to give, as one of the products, the pentachlorocyclopentadienyl anion (**A**). Since this anion is an aromatic (six- $\pi$ -electron) species, its high stability would provide a very powerful driving force for its formation. In the polymeric system, the anion should be converted rapidly, however, into penta- or hexachlorocyclopentadiene, either of which would volatilize quickly from mixtures that had been heated to  $>300^\circ\text{C}$ . The other organic product (**B**) also would be much more volatile than the Dech Plus and might produce 1,5-cyclooctadiene and penta- or hexachlorocyclopentadiene via a similar sequence of steps.

The present research was designed to investigate these possibilities and other chemical aspects of the fire-retardant properties of Dech Plus and antimony trioxide in Nylon 66.



**Figure 4.** Possible interaction of Dech Plus with antimony trioxide

## II. EXPERIMENTAL

### A. Instrumentation

#### 1. Gas Chromatography/Mass Spectroscopy (GC/MS)

A Hewlett-Packard 5890 Series II GC instrument equipped with a crosslinked methyl siloxane capillary column (12 m x 0.2) mm was used in conjunction with a Hewlett-Packard 5971A Mass Selective Detector. Sample data were analyzed by using Hewlett-Packard G1034B software for the MS ChemStation (DOS series). The carrier gas was helium, and the GC parameters are shown in Table 4.

GC Parameters	
injector temp.	200 °C
detector temp.	200 °C
initial	2 min @ 50 °C
rate	20 °C/min to 300 °C
final	10 min @ 300 °C

**Table 4.** GC Parameters



## 2. Infrared Spectroscopy (IR)

The sublimed Dech Plus was examined on a Perkin-Elmer 1600 Series FTIR instrument. The samples were introduced in KBr pellets.

## 3. Melting Point Determination

Melting points (uncorrected) were determined by using a UniMelt (Thomas Hoover) capillary melting point apparatus.

## 4. Nuclear Magnetic Resonance (NMR)

The NMR spectra were acquired by using a General Electric QE-300 spectrometer. Data processing was performed using Tecmag MacNMR 5.4 software. Chemical shifts are reported in ppm ( $\delta$ ) at ambient temperature with TMS ( $\text{Me}_4\text{Si}$ ) as an internal reference ( $\delta = 0.00$ ), and tetrahydrofuran- $\text{d}_8$  was used as a solvent.

## 5. Thermogravimetric Analysis (TGA)

All experiments were conducted with a Seiko SSC 5040 thermal analysis system. This system included a TG/DTA 200 simultaneous

thermogravimetric/differential thermal analyzer with version 2.0 system software. All samples were either molded specimens supplied by OxyChem or mixtures prepared at William and Mary by grinding at liquid nitrogen temperature. Sample masses varied from 12 to 20 mg. The flow rate for nitrogen was 50 mL/min.

## **B. Materials**

OxyChem supplied Nylon 66, Dechlorane Plus (Dech Plus), antimony trioxide, and molded polymer-additive mixtures. Aldrich supplied the hexachlorocyclopentadiene, 98%; 1,5-cyclooctadiene, 99%; and pentachlorobenzene, 98%. Acros supplied tetrachloroethylene, 99%. Fisher supplied tetrahydrofuran (THF) with 0.031% of BHT added as an inhibitor.

## **C. Pyrolysis of Nylon 66/Additive Mixtures**

Pyrolysis studies were carried out in an open system with Dech Plus alone and with mixtures of (a) Dech Plus,  $\text{Sb}_2\text{O}_3$ , and Nylon 66; (b) Dech Plus and Nylon 66; (c)  $\text{Sb}_2\text{O}_3$  and Nylon 66; and (d) Dech Plus and  $\text{Sb}_2\text{O}_3$ . Into a 25-mL two-neck round-bottom flask, 2.0 g of sample was placed. The flask was then put into pre-heated Wood's metal, and the sample was pyrolyzed under flowing  $\text{N}_2$  for 30 min at  $325\text{ }^\circ\text{C} (\pm 5\text{ }^\circ\text{C})$ . The volatile

products were trapped in a U-tube immersed in an ethyl acetate/liquid nitrogen slush that kept the temperature at  $-85\text{ }^{\circ}\text{C}(\pm 5\text{ }^{\circ}\text{C})$ . The resulting condensate was treated with an amount of THF that was sufficient to produce a 5 - 15 wt % in the solution of trapped material, and this solution was subjected to GC/MS analysis.

#### **D. Preparation of KBr Pellets Containing Dech Plus or Sublimed**

##### **Dech Plus**

Two KBr pellets were prepared at ambient temperature by grinding 1 - 2 mg of Dech Plus or sublimed Dech Plus with 100 mg of KBr in a mortar for 3 - 5 min. Each pellet was placed in a die and analyzed by FTIR.

#### **E. Reaction of Hexachlorocyclopentadiene with $\text{Sb}_2\text{O}_3$**

##### **1. Experimental Procedure**

The experiments were carried out in pressure tubes (Ace Glass; catalog No.8648-76). Since hexachlorocyclopentadiene is moisture-sensitive, all manipulations were conducted in a glovebox under argon until the tubes were sealed. Two mixtures were prepared. First, into one

tube were added 3.4 g ( 2 mL) of hexachlorocyclopentadiene and 0.378 g of  $\text{Sb}_2\text{O}_3$ , so that the weight ratio of the two components was 90:10.

Second, 1.7 g ( 1 mL) of hexachlorocyclopentadiene and 1.7 g of  $\text{Sb}_2\text{O}_3$  were added to another tube, so that the weight ratio of the two components was 50:50. The sealed tubes were placed into a pre-heated Wood's metal container and heated at  $250\text{ }^\circ\text{C}$  ( $\pm 10\text{ }^\circ\text{C}$ ) for 2 - 20 h.

## **2. GC/MS Analysis**

It was necessary to treat the resulting suspensions with 3-5 mL of THF to avoid overloading the detector of the GC/MS instrument. The resultant product solutions were filtered and injected directly into the apparatus.

### **F. Reaction of Hexachlorocyclopentadiene with 1,5-Cyclooctadiene**

This reaction was carried out in an open system under ambient pressure. Into a 25-mL two-neck round-bottom flask were added 1.702 g (0.0062 mol) of hexachlorocyclopentadiene and 2.683 g (0.0248 mol) of 1,5-cyclooctadiene. The flask was then immersed in a magnetically stirred silicone oil bath held at  $100\text{ }^\circ\text{C}$  ( $\pm 1\text{ }^\circ\text{C}$ ), and the mixture was refluxed for 4 h under  $\text{N}_2$ . Power to a Nichrome wire coil within the bath was supplied

by a Variac. The resulting suspension was injected directly into the GC/MS apparatus for analysis.

### **G. Pyrolysis Studies via Thermogravimetric Analysis**

Thermogravimetric analysis (TGA) measurements involved two kinds of mixtures: molded blends obtained from OxyChem and hand-ground mixtures prepared in our laboratory. All of the blends made by us contained materials that OxyChem supplied and were prepared by grinding the ingredients together with a liquid-nitrogen-cooled mortar and pestle. For the TGA runs, a measured mass of the sample ( usually between 12 and 20 mg ) was placed in the platinum pan of the apparatus. Each experiment was conducted with a nitrogen flow rate of 50 mL/min. For the temperature study, all samples were pyrolyzed at 320 °C. The heating program consisted of an initial 10 °C/min increase to the desired temperature, followed by a 30 min hold, after which the temperature was reduced to room temperature at the rate of 50 °C/min. For the concentration study, a number of mixtures with different compositions were pyrolyzed.

### III. RESULTS AND DISCUSSION

#### A. General

The main objective of this research was to understand why there is an unfavorable flame-retardant interaction between Dechlorane Plus (Dech Plus) and  $\text{Sb}_2\text{O}_3$  that occurs in Nylon 66 formulations at high temperatures and causes large losses of mass upon pyrolysis. For this purpose, pyrolysis studies were carried out with Dech Plus alone and with mixtures of (a) Dech Plus,  $\text{Sb}_2\text{O}_3$ , and Nylon 66; (b) Nylon 66 and Dech Plus; (c) Nylon 66 and  $\text{Sb}_2\text{O}_3$ ; and (d) Dech Plus and  $\text{Sb}_2\text{O}_3$ . All of the pyrolysis experiments were conducted at 320 °C. The work involved programmed-temperature TGA measurements under nitrogen, and it also included preparative experiments that were designed to allow both the collection of the volatile pyrolysis products and their identification with the aid of modern spectroscopic techniques (GC/MS, FTIR, and  $^1\text{H}$  and  $^{13}\text{C}$  NMR). Among these, GC/MS was the single most useful technique for the identification of volatile compounds. Some of the products found by GC/MS were identified conclusively via spiking experiments and by comparisons of retention times and mass spectra with those of authentic substances that were commercially available. Other products were identified tentatively, if possible, by rationalizations based primarily on GC/MS comparisons with known materials. The identification of

chlorinated compounds was assisted greatly by determinations of the intensities of the multiple MS peaks that corresponded to ions bearing one or more atoms of  $^{35}\text{Cl}$  and/or  $^{37}\text{Cl}$ .

In order to acquire good and reproducible GC/MS data, it was necessary to use a solvent that dissolved the volatile pyrolysis products well. The search for such a solvent was based upon its ability to dissolve Dech Plus, whose pyrolysis products were our main interest. The solvents tested included acetone, chloroform, benzene, chlorobenzene, 1,2,4-trichlorobenzene, 1,1,2,2-tetrachloroethane, and tetrahydrofuran. None of these were satisfactory except tetrahydrofuran (THF). Thus, it was used exclusively to dissolve Dech Plus and the volatile pyrolysis products. However, it did not dissolve volatile inorganic products such as  $\text{SbOCl}$  and  $\text{SbCl}_3$ , and it may not have dissolved all of the volatile organic materials.

## **B. Thermogravimetric Analysis Results**

All samples were heated to  $320\text{ }^\circ\text{C}$  at the rate of  $10\text{ }^\circ\text{C}/\text{min}$  and held at that temperature for 30 min. The TGA curve of Dech Plus is shown in Figure 6 (see page 30). About 52% of the original mass was lost after the 30 min hold period. Considering the fairly high decomposition point,  $350\text{ }^\circ\text{C}$ , of Dech Plus, this weight loss was unexpectedly high.

In order to determine what caused the Dech Plus weight loss, the material trapped in the condenser was collected after the preparative

pyrolysis experiment and examined by determining both its melting point and its FTIR spectrum. The melting point of the trapped material was identical to that of pure Dech Plus. As is shown in Figures 7 and 8, the IR spectra of the trapped material and that of pure Dech Plus also were identical. These results indicate that the weight loss of Dech Plus at 320 °C is due mainly to sublimation, not to decomposition.

The TGA curve of Nylon 66 is shown in Figure 9. Nylon 66 alone only experiences very slow weight loss during the entire heating period. In Figure 10, the TGA curves of Nylon 66, 90:10 Nylon 66/antimony trioxide, 90:10 Nylon 66/Dech Plus, and 82:10:8 Nylon 66/Dech Plus/antimony trioxide are overlaid. These curves show that when Dech Plus or Dech Plus and antimony trioxide are present in the polymer formulation, there is more weight loss; and as shown in Table 5, the actual weight losses for these cases are up to twice the values expected from simple additivity. The TGA study alone does not show conclusively that antimony trioxide behaves antagonistically toward Dech Plus in the Nylon 66 formulation. However, it is clear from these results that Dech Plus, with or without antimony trioxide, may not be as effective as desired in Nylon 66.

TGA data for several formulations are summarized in Tables 5, 6, and 7. Table 7 shows data for several mixed-metal blends. As mentioned earlier, in some polymer formulations, multimetallic flame retardants which contain antimony and salts of other metals reportedly



give excellent performance at reduced cost. For this reason, the data in Table 7 were obtained for comparison purposes.

Formulation weight %	1	2	3	4	5	6	7	8
Nylon 66	100			80	90	88	86	84
Dech Plus		100		20	10	10	10	10
Sb <sub>2</sub> O <sub>3</sub>			100			2	4	6
Expected wt loss %, $\pm$ dev				15.3 $\pm$ 1.0	10.7 $\pm$ 0.6	10.6 $\pm$ 0.6	10.4 $\pm$ 0.6	10.3 $\pm$ 0.6
Mean wt loss <sup>a</sup> %, $\pm$ dev	6.1 $\pm$ 0.2	51.9 $\pm$ 4.4	0	23.6 $\pm$ 9.9	14.6 $\pm$ 2.8	16.2 $\pm$ 1.3	15.4 $\pm$ 1.8	19.0 $\pm$ 0.4
Mean wt. loss <sup>b</sup> %, $\pm$ dev				28.6 $\pm$ 4.8	21.4 $\pm$ 3.4	22.3 $\pm$ 2.0		

<sup>a</sup>Values of ground samples. <sup>b</sup>Values of molded samples.

**Table 5.** TGA Study (10 °C/min to 320 °C, 30 min hold)

Formulation weight %	9	10	11	12	13	14	15	16	17
Nylon 66	82	78	76	72	98	95	90		
Dech Plus	10	20	19	18				90	90
Sb <sub>2</sub> O <sub>3</sub>	8	2	5	10	2	5	10	10	
PPh <sub>3</sub>									10
Expected wt loss %, $\pm$ dev	10.2 $\pm$ 0.6	15.1 $\pm$ 1.0	14.5 $\pm$ 1.0	13.7 $\pm$ 0.9	6.0 $\pm$ 0.2	5.8 $\pm$ 0.2	5.5 $\pm$ 0.2	46.7 $\pm$ 4.0	
Mean wt loss <sup>a</sup> %, $\pm$ dev	18.5 $\pm$ 1.6	25.1 $\pm$ 12.0	25.8 $\pm$ 5.2	28.0 $\pm$ 6.1	5.3 <sup>c</sup>	5.4 <sup>c</sup>	4.8 $\pm$ 1.6	40.8 $\pm$ 6.1	49.3 <sup>c</sup>
Mean wt loss <sup>b</sup> %, $\pm$ dev	21.6 $\pm$ 0						4.2 $\pm$ 1.0		

<sup>a</sup>Values of ground samples. <sup>b</sup>Values of molded samples. <sup>c</sup>Single run.

**Table 6.** TGA Study (10 °C/min to 320 °C, 30 min hold)

Forulation weight %	18	19	20	21	22	23	24	25	26
Nylon 66	70	70	70	70	70	70	70	70	70
Dech Plus	20	20	20	20	20	20	20	20	20
Sb <sub>2</sub> O <sub>3</sub>			10				5		5
Zinc borate	10					5	5	5	
Kemguard 981		10			5	5			5
Sodium antimonate				10	5			5	
Mean wt loss <sup>a</sup> %, ± dev	24.8 <sub>±</sub> 7.7	37.8 <sub>±</sub> 6.0	36.2 <sub>±</sub> 4.1	31.2 <sub>±</sub> 5.0	24.4 <sub>±</sub> 1.6	25.4 <sub>±</sub> 15.0	34.3 <sub>±</sub> 2.6	29.4 <sub>±</sub> 1.6	25.4 <sub>±</sub> 4.1

<sup>a</sup>Values of molded samples.

**Table 7.** TGA Study (10 °C/min to 320 °C, 30 min hold)

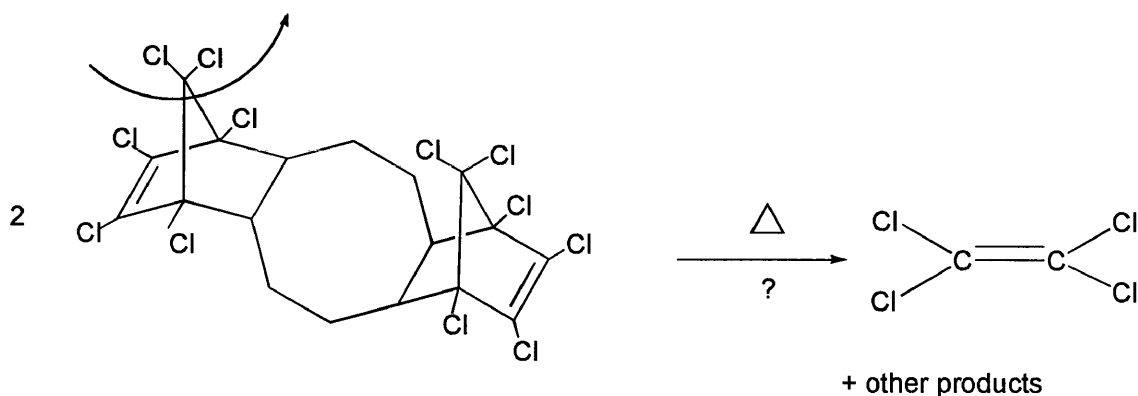
### **C. (Gas Chromatography)/(Mass Spectroscopy) Results**

GC/MS results for the volatile pyrolysate from Nylon 66 are shown in Figures 11-1 and 11-2. The peak with the retention time of 1.35 min was conclusively identified as cyclopentanone. This ketone is well known to be a pyrolysis product of Nylon 66, and we found it to be present in all of our preparative pyrolysis experiments with the nylon. The peak with the retention time of 8.21 min is “butylated hydroxy toluene (BHT)”, an oxidation inhibitor in THF. This peak appeared in all of our chromatograms, as expected.

GC/MS results for pure Dech Plus are shown in Figures 12-1 and 12-2. The two peaks with the retention times of 20.16 and 21.14 min seem to be isomers of Dech Plus itself.

GC/MS results for the nonvolatile residue from Dech Plus heated in a sealed tube at 320-370 °C for 22 h are shown in Figures 13-1 through 13-7. The peak with the retention time of 8.21 min is pentachlorobenzene. The three peaks with retention times of 11.99, 12.53, and 13.08 min are believed to be isomers of compounds resulting from the loss of a cyclopentadiene moiety from Dech Plus.

GC/MS results for the volatile products from pyrolyzed Dech Plus are shown in Figure 14. The peak with the retention time of 1.76 min is tetrachloroethylene. As is shown in Figure 5, tetrachloroethylene conceivably could result from the formation and dimerization of dichlorocarbene. We emphasize, however, that this mechanism is only speculative at this time.



**Figure 5.** Possible mechanism for the formation of tetrachloroethylene

Figures 15-1 through 15-7 show GC/MS results for the volatile products of a pyrolyzed 90:10 Nylon 66/Dech Plus mixture. The peak with the retention time of 3.32 min is 1,5-cyclooctadiene. The peak with the retention time of 7.98 min is yet to be identified, but, interestingly, this peak disappears when  $\text{Sb}_2\text{O}_3$  is present in the pyrolyzed polymer formulation. The peaks with the retention times of 11.56, 11.80, and 12.08 min also seem to be isomers of Dech Plus without one cyclopentadiene ring (see above).

GC/MS results for the volatile products of a pyrolyzed 90:10 Nylon 66/ $\text{Sb}_2\text{O}_3$  mixture are shown in Figures 16-1 and 16-2. As noted earlier, the peak with the retention time of 1.36 min is cyclopentanone, and the peak with the retention time of 8.22 min is BHT.

GC/MS results for the volatile products from a pyrolyzed 82:10:8 Nylon 66/Dech Plus/ $\text{Sb}_2\text{O}_3$  mixture are shown in Figures 17-1 through 17-9. As indicated above, the peaks with the retention times of 1.32, 3.30, and 8.21 min are cyclopentanone, 1,5-cyclooctadiene, and BHT, respectively. The peaks with the retention times of 10.84, 11.05, 11.55, and 11.79 min seem to be isomers of Dech Plus without one cyclopentadiene ring, but, very importantly, most (or all) of these materials have been partially dechlorinated. That is, one or more of the original six chlorines has been replaced by hydrogen. The peaks with retention times near 18 min seem to be isomers of Dech Plus.

The residue from the pyrolysis just described was extracted with THF, and the resultant solution was analyzed by GC/MS. The chromatograms and mass spectra are shown in Figures 18-1 through 18-7. Peaks with retention times of 11.52 and 11.76 min apparently are isomers of reduced Dech Plus that has lost a cyclopentadiene ring, while peaks with retention times from 17.06 to 20.90 min seem to be isomers of partially dechlorinated Dech Plus, or Dech Plus itself.

GC/MS results for the volatile products of a pyrolyzed 90:10 Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture appear in Figures 19-1 through 19-3. The peak with the retention time of 13.48 min is yet to be identified, in part because of its failure to display a parent ion in its mass spectrum. The two small peaks with retention times in the neighborhood of 20 to 21 min are thought to be isomers of Dech Plus.

In attempts to understand the thermal behavior of Dech Plus in the presence of Sb<sub>2</sub>O<sub>3</sub>, some reactions of hexachlorocyclopentadiene were studied for purposes of comparison. GC/MS results for pure hexachlorocyclopentadiene (unheated) are shown in Figures 20-1 and 20-2. The peak with the retention time of 7.22 min is hexachlorocyclopentadiene, which comprises 98% of the sample. The peak with the retention time of 9.08 min is octachlorocyclopentene, the major impurity (2%). These data were referred to later for comparisons.

Figures 21-1 through 21-3 show GC/MS results for pure hexachlorocyclopentadiene that had been heated at 250-260 °C for 19.7 h.

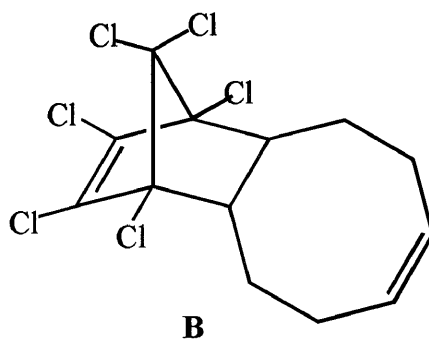
The hexachlorocyclopentadiene peak, which has a retention time of 7.07 min here, has been reduced from 98% to 60%, while octachlorocyclopentene, the major impurity, now constitutes 37% of the sample. It is not clear how the octachlorocyclopentene forms, because there is no source of chlorine here except the hexachlorocyclopentadiene. Among the new substances that formed upon heating is a dechlorinated dimer of hexachlorocyclopentadiene, which corresponds to the peak with the retention time of 13.53 min. This compound, decachlorobis-2,4-cyclopentadienyl, comprises 0.8% of the products.

Figures 22-1 and 22-2 show GC/MS results for the 90:10 hexachlorocyclopentadiene/Sb<sub>2</sub>O<sub>3</sub> mixture that was heated at 250-260 °C for 19.7 h in a sealed tube. The hexachlorocyclopentadiene, which corresponds to the peak with the retention time of 7.08 min, amounts to 31% of the mixture, while the major impurity, octachlorocyclopentene, which corresponds to the peak with the retention time of 9.10 min, has increased to 53%. Also, the dechlorinated dimer of hexachlorocyclopentadiene, decachlorobis-2,4-cyclopentadienyl, which corresponds to the peak with the retention time of 13.71 min, has increased to 6.0%. The most interesting observation, however, is the apparent formation of a pentachlorobutene isomer that corresponds to the peak with the retention time of 4.44 min and constitutes 5.3% of the products. It is not yet known how this substance forms.

The GC/MS results in Figures 23-1 and 23-2 are for a 50:50 hexachlorocyclopentadiene/Sb<sub>2</sub>O<sub>3</sub> mixture that was heated at 250-260 °C for 4 h in a sealed tube. The peak with the retention time of 6.96 min indicates that the amount of hexachlorocyclopentadiene has been reduced from 98% to 11%. On the other hand, the major product is, suprisingly, the supposed pentachlorobutene that corresponds to the peak with the retention time of 4.46 min and constitutes 81% of the mixture.

Another 50:50 mixture of hexachlorocyclopentadiene and antimony trioxide was heated at 250-260 °C for 19.7 h. The GC/MS results for this experiment are shown in Figures 24-1 and 24-2. With the longer period of heating, the amount of hexachlorocyclopentadiene was reduced from 98% to 1.4%. The major product is the “pentachlorobutene” that corresponds to the peak at 4.47 min and constitutes 98.6% of the soluble products.

GC/MS results for a neat hexachlorocyclopentadiene/1,5-cyclooctadiene mixture (1:4 mole ratio) that was refluxed at 100 °C for 4 h are shown in Figure 25. The peaks with retention times of 3.38, 7.02, and 8.92 min are from starting materials. They are 1,5-cyclooctadiene, hexachlorocyclopentadiene and the impurity in the latter material (see above). The peak with the retention time of 12.08 min is the product (**B**) of a Diels-Alder reaction between hexachlorocyclopentadiene and the octadiene.



The retention time of **B** and its mass spectrum were very useful for comparison in our attempts to identify the volatile materials formed from Dech Plus in the pyrolysis experiments described above.



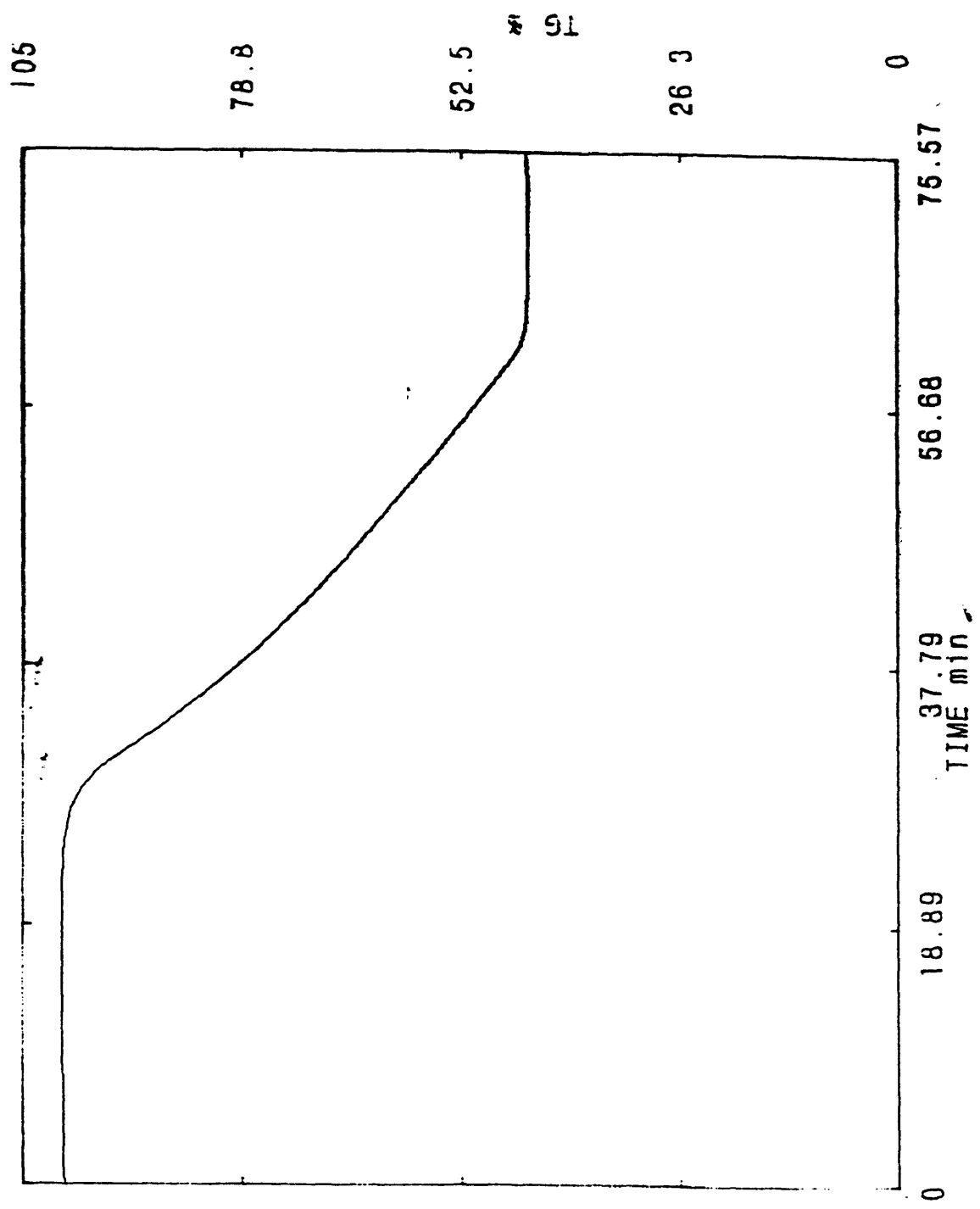


Figure 6. TGA curve of Dech Plus

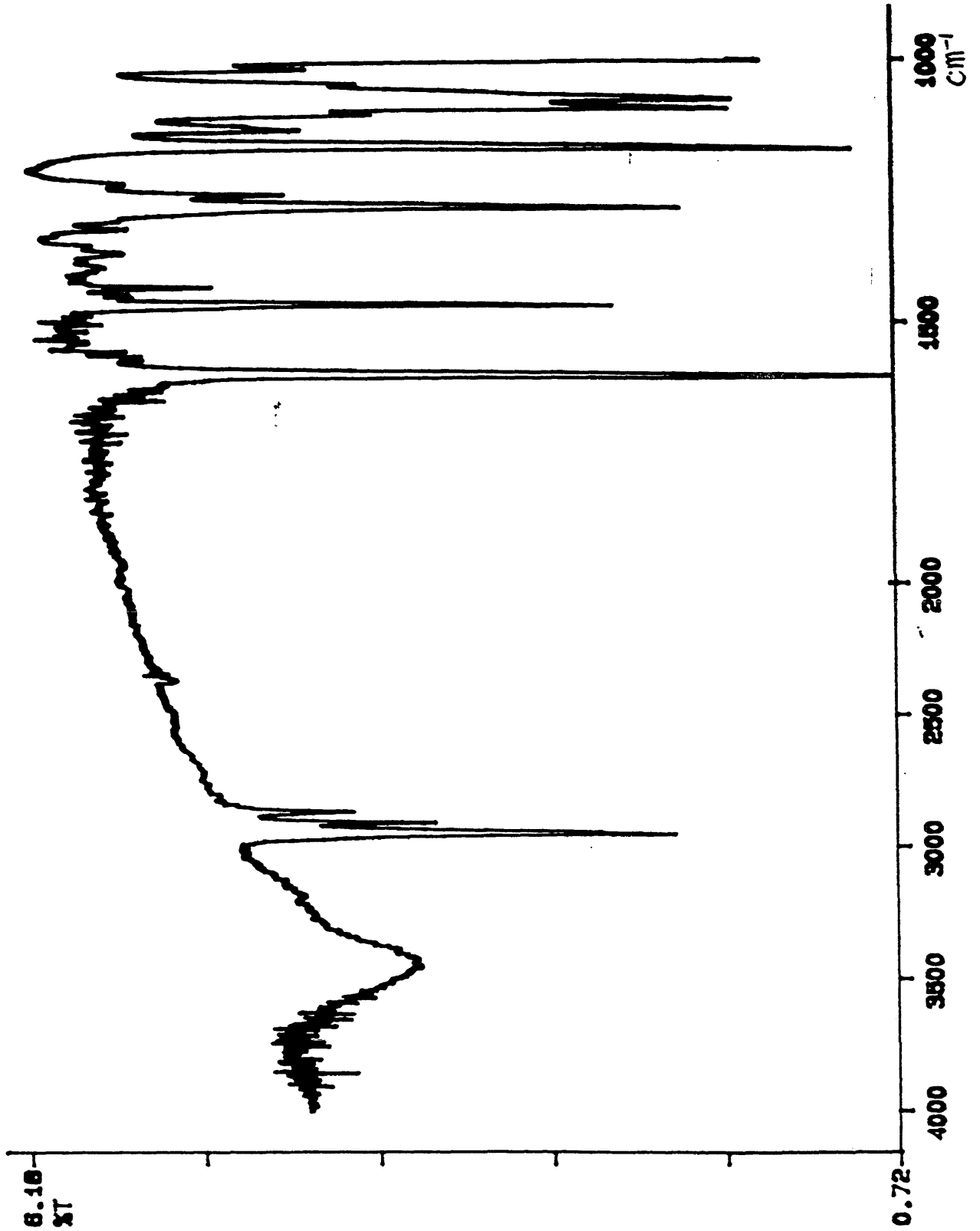


Figure 7. IR spectrum of Dech Plus

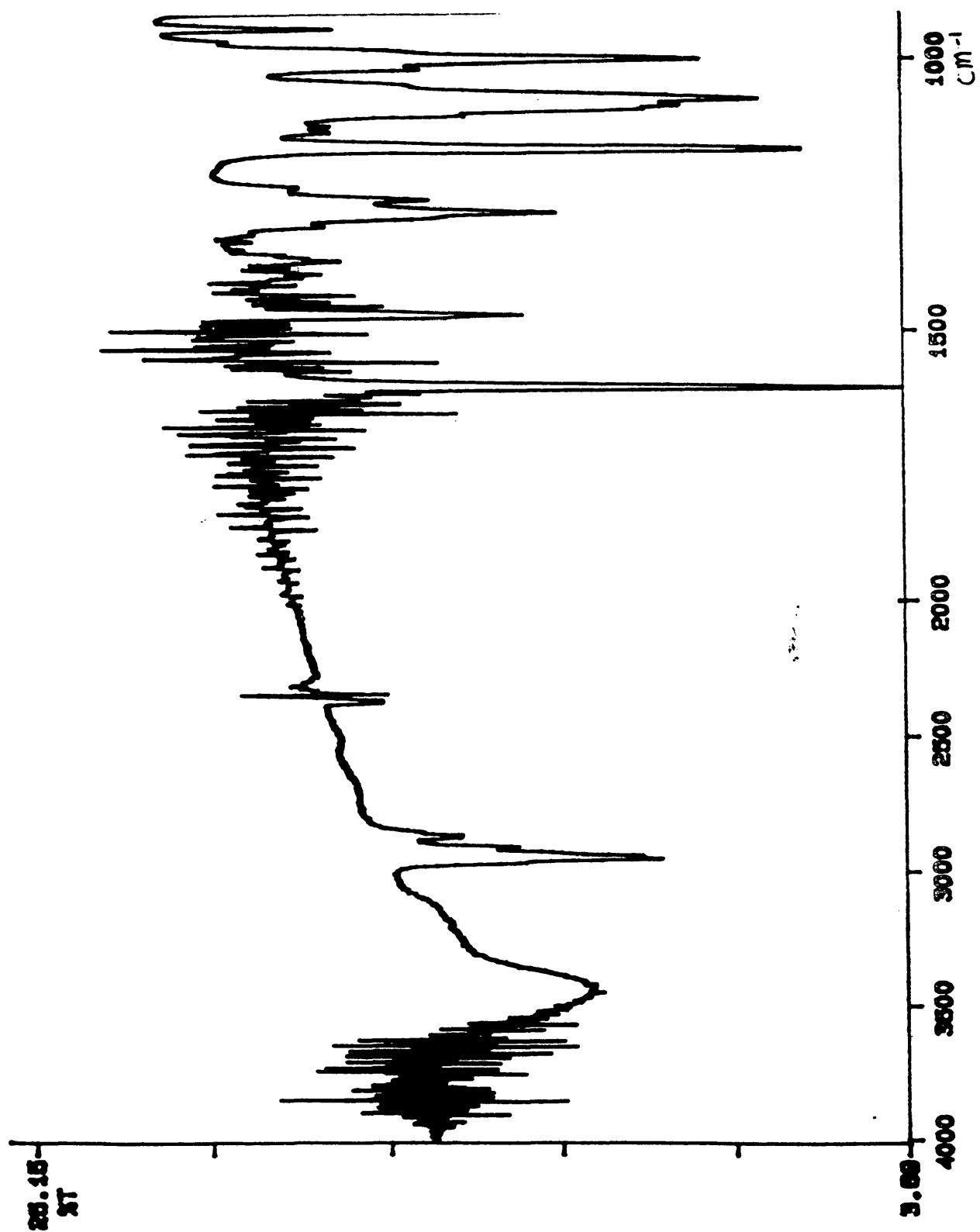
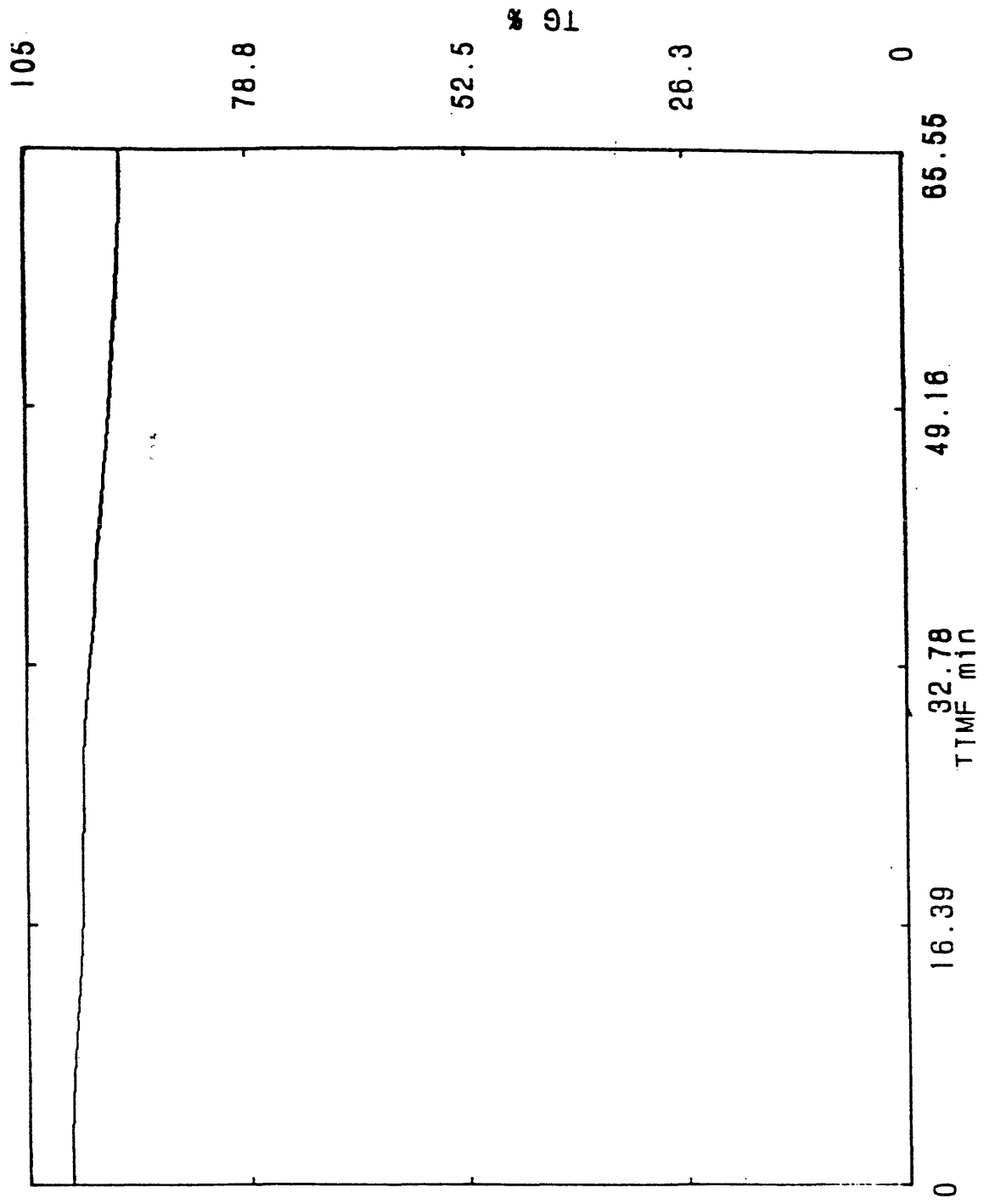


Figure 8. IR spectrum of sublimed Dech Plus



**Figure 9.** TGA curve of Nylon 66

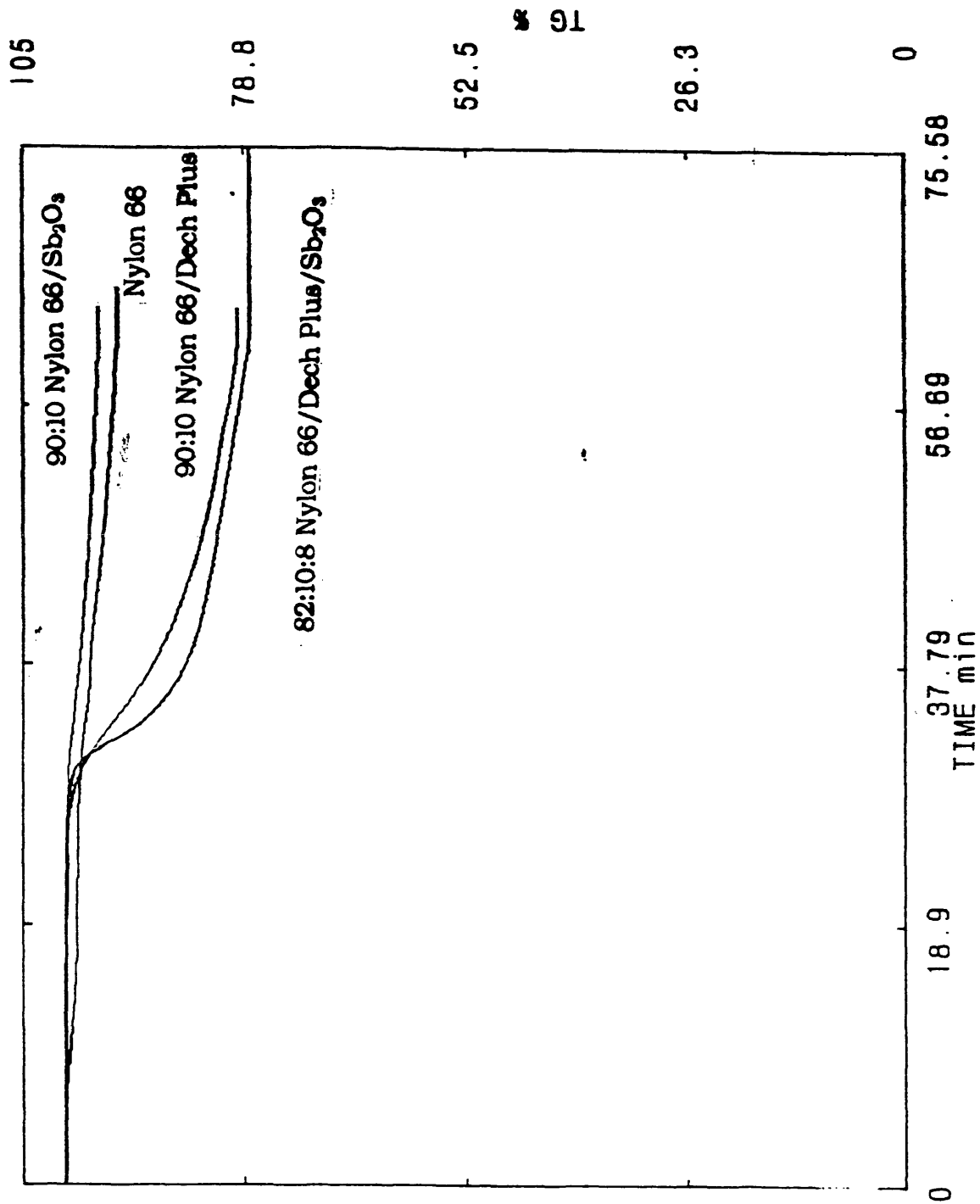
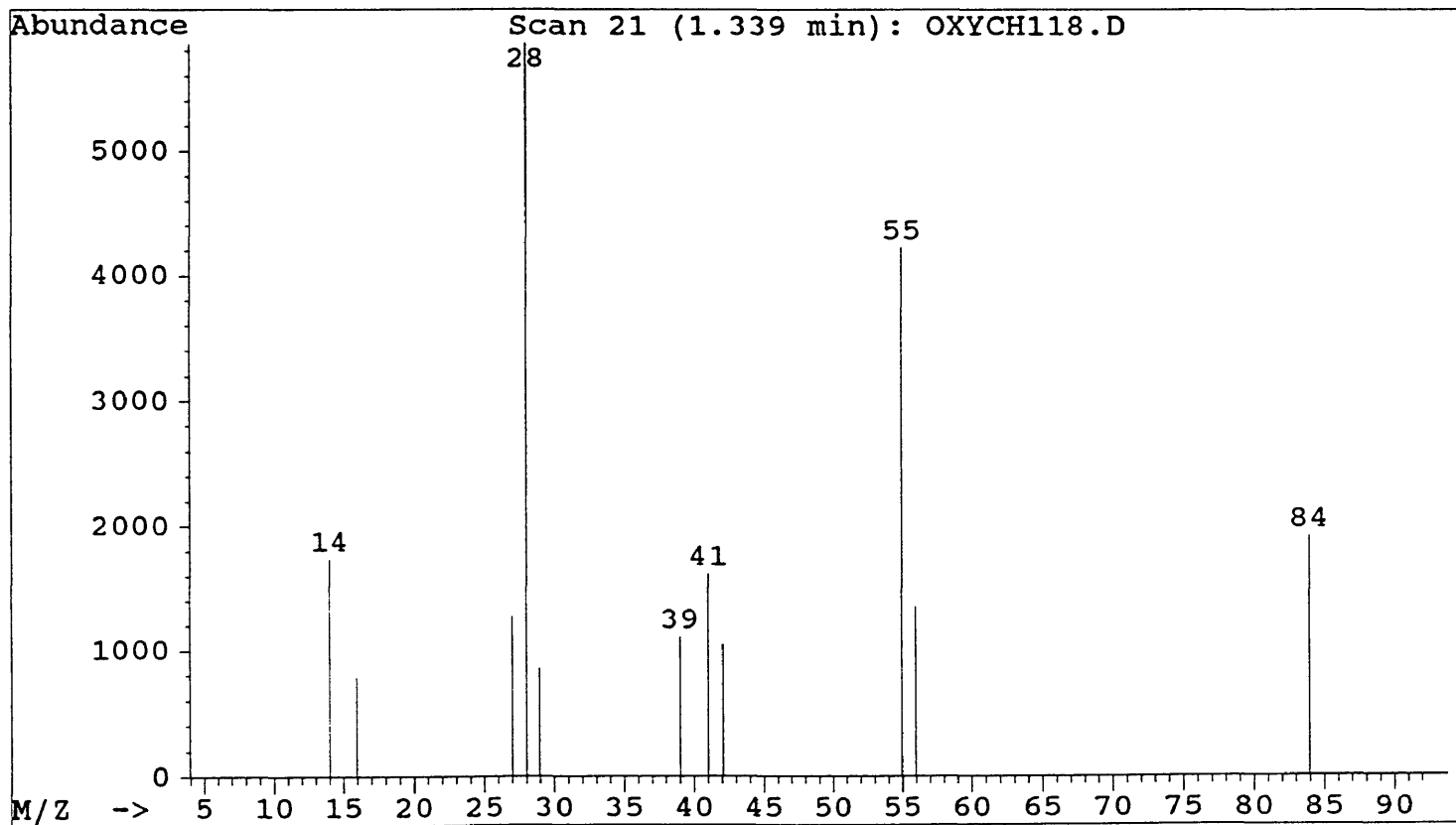
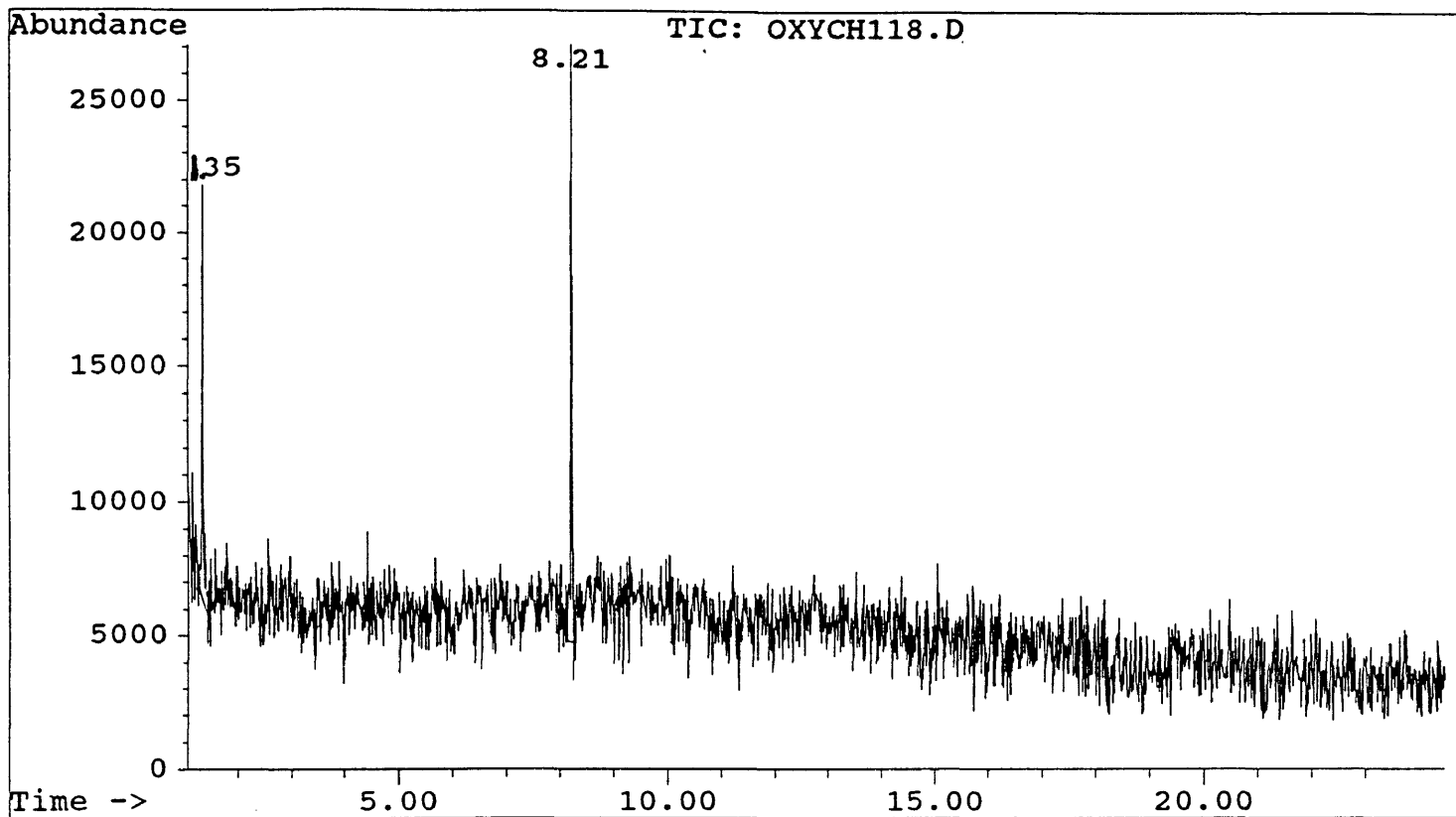
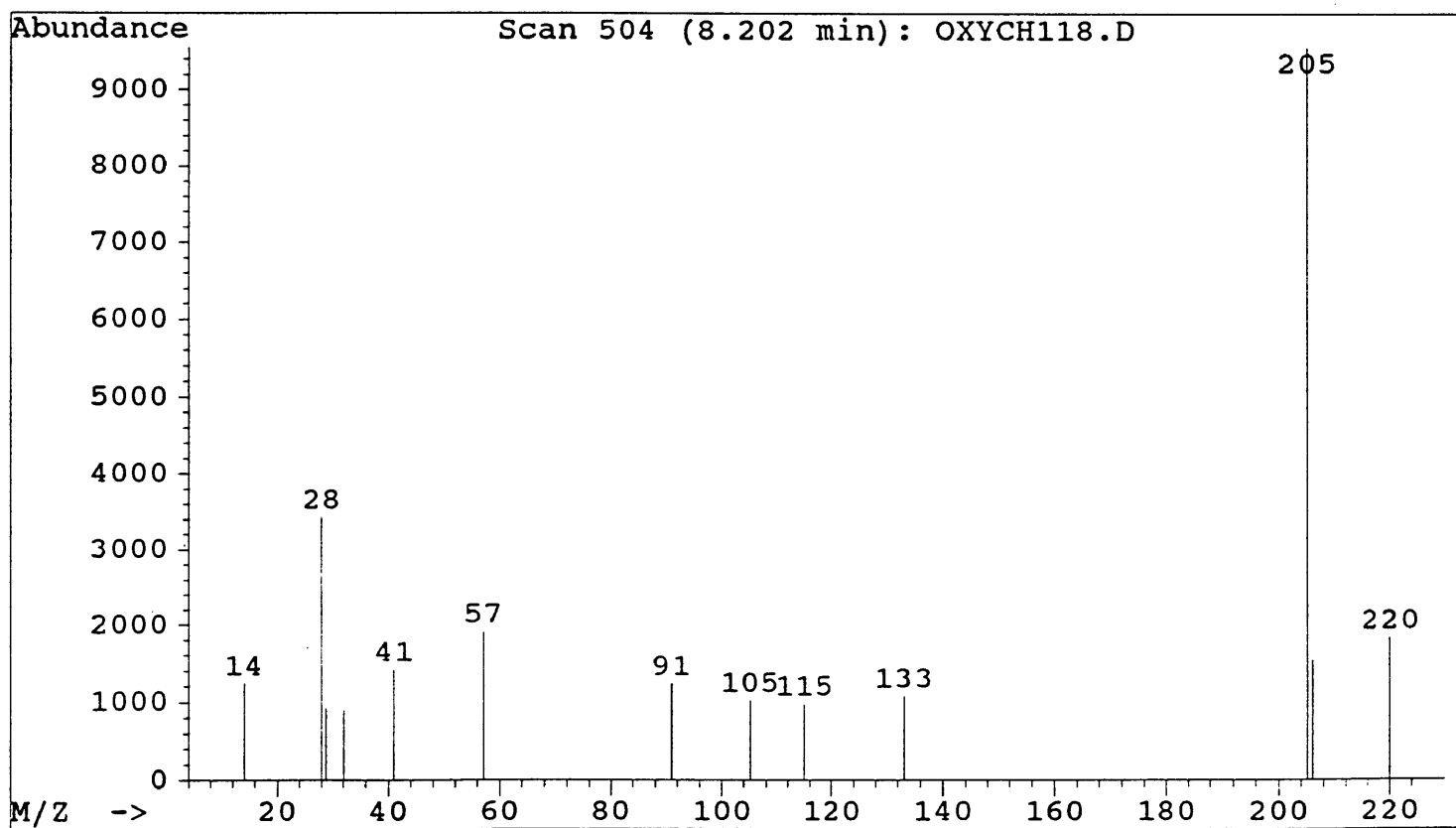
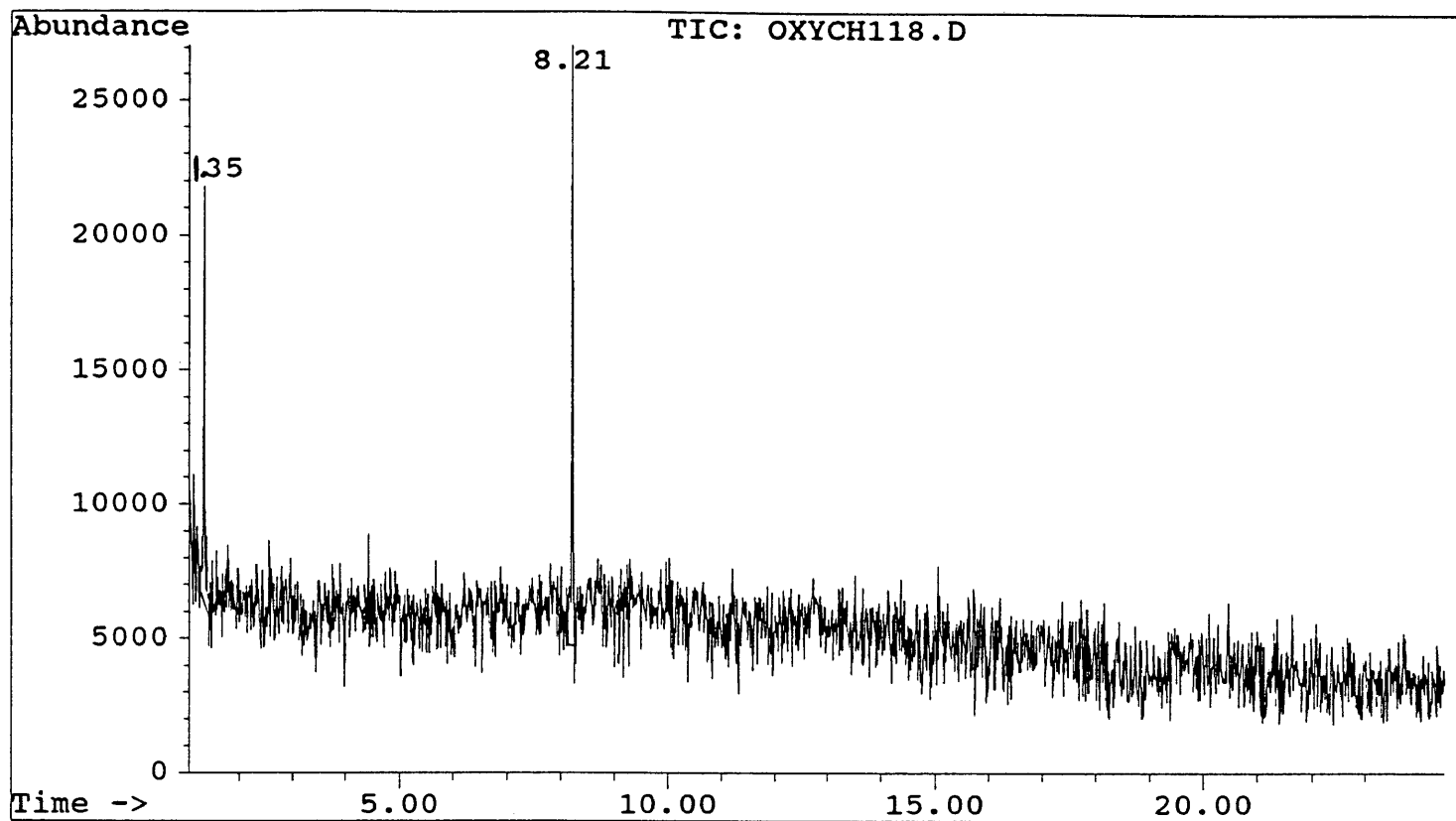


Figure 10. Overlaid TGA curves



**Figure 11-1.** GC/MS analysis of volatile products from pyrolyzed Nylon 66



**Figure 11-2.** GC/MS analysis of volatile products from pyrolyzed Nylon 66

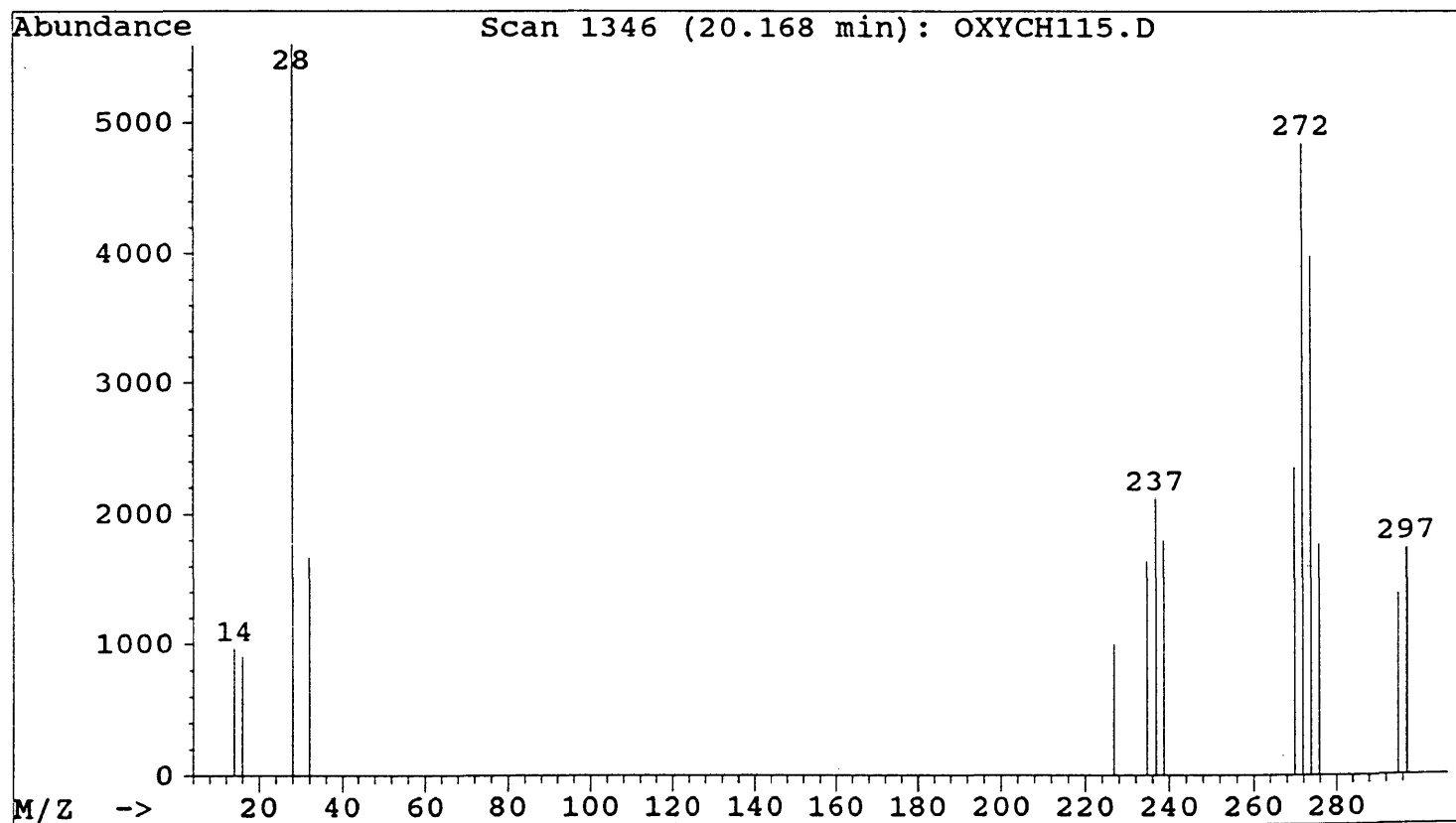
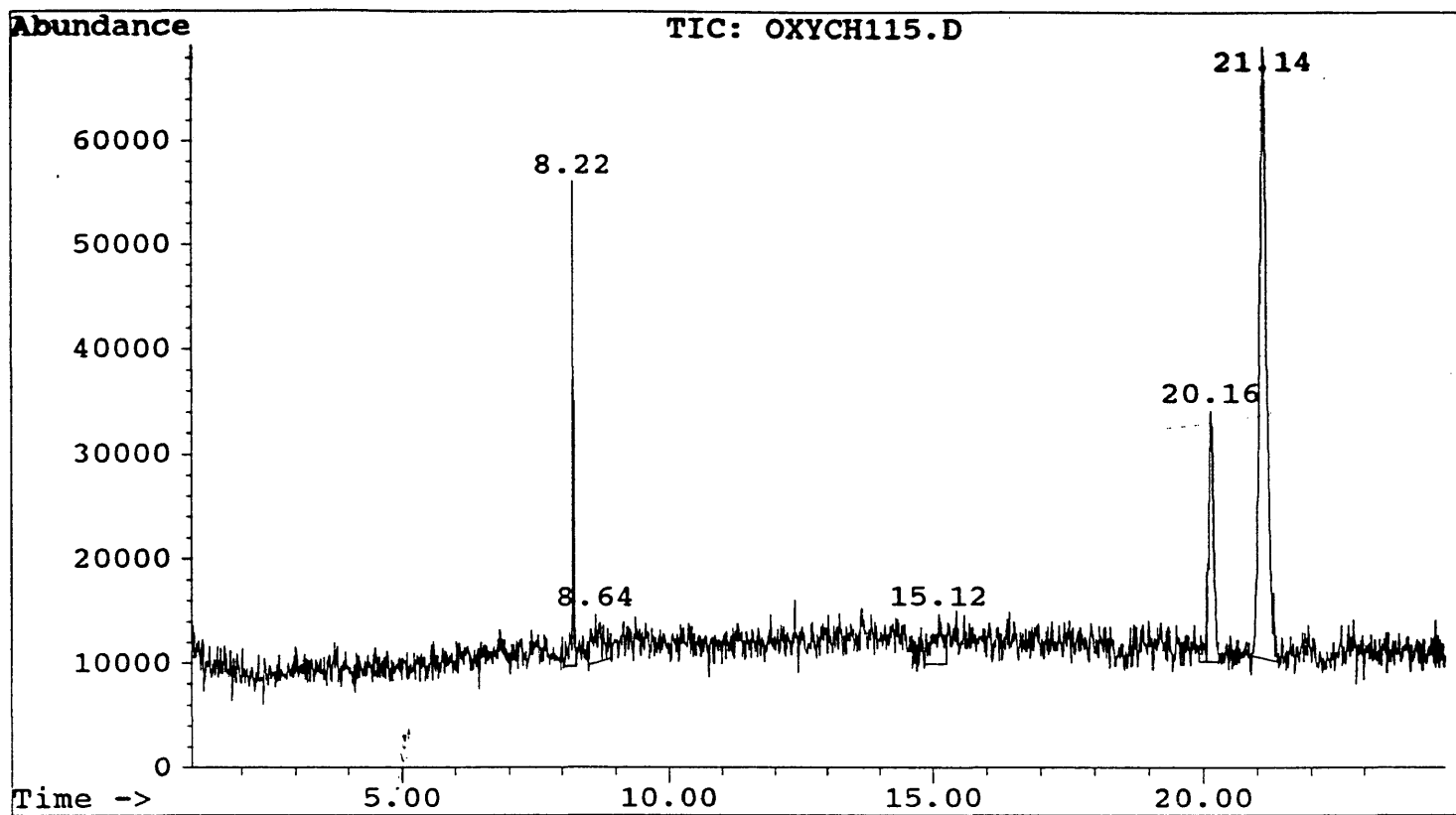


Figure 12-1. GC/MS analysis of Dech Plus



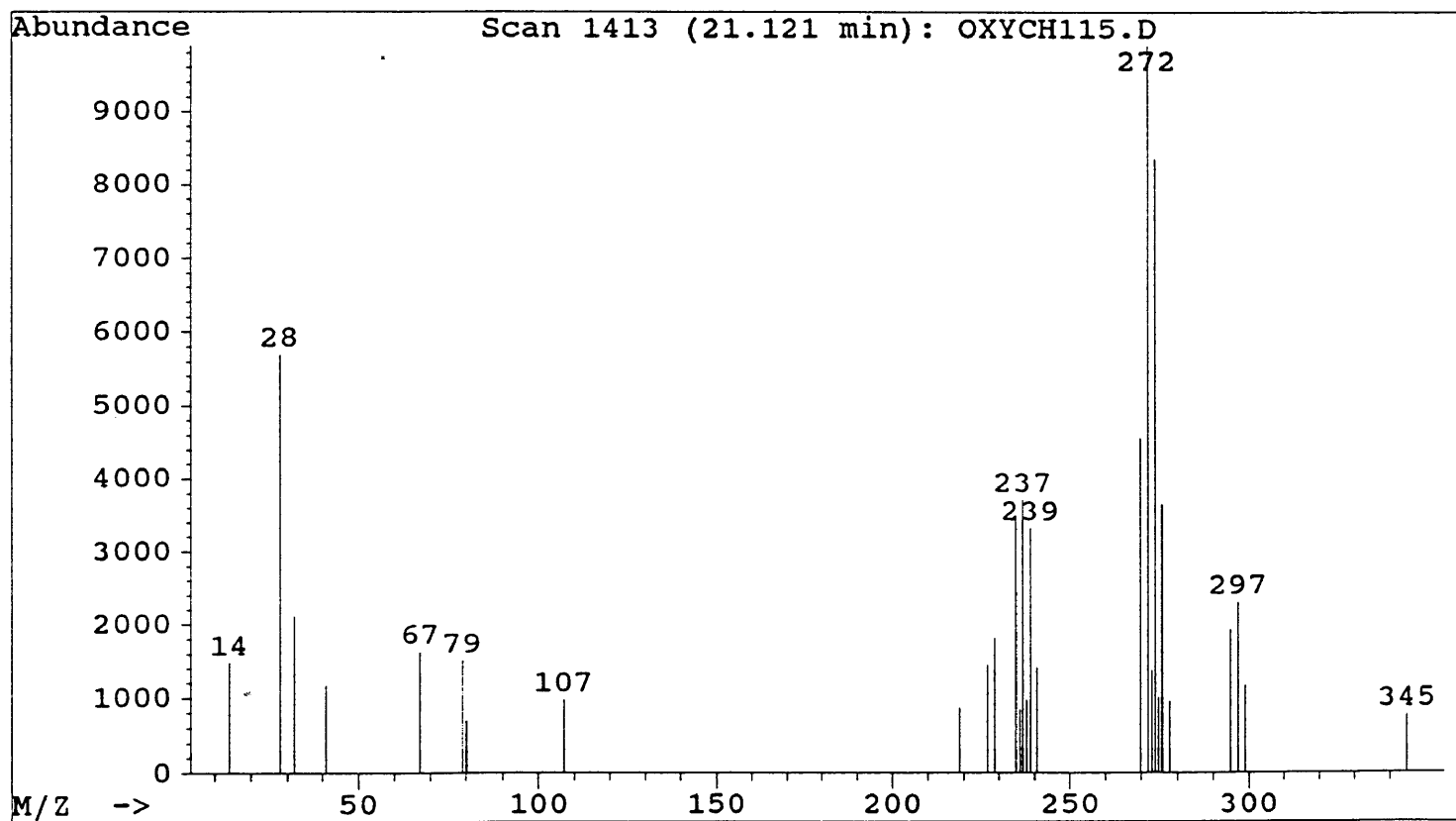
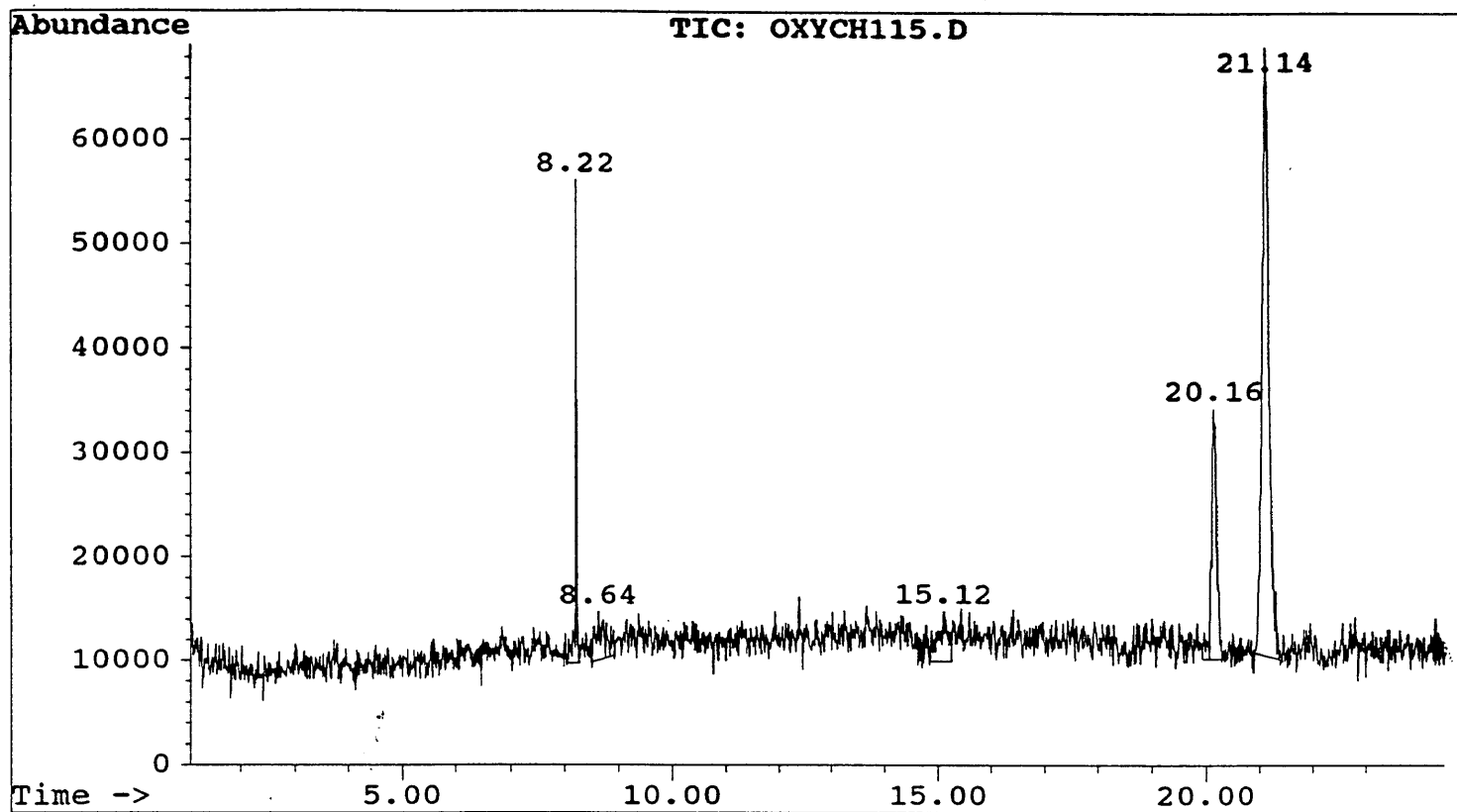
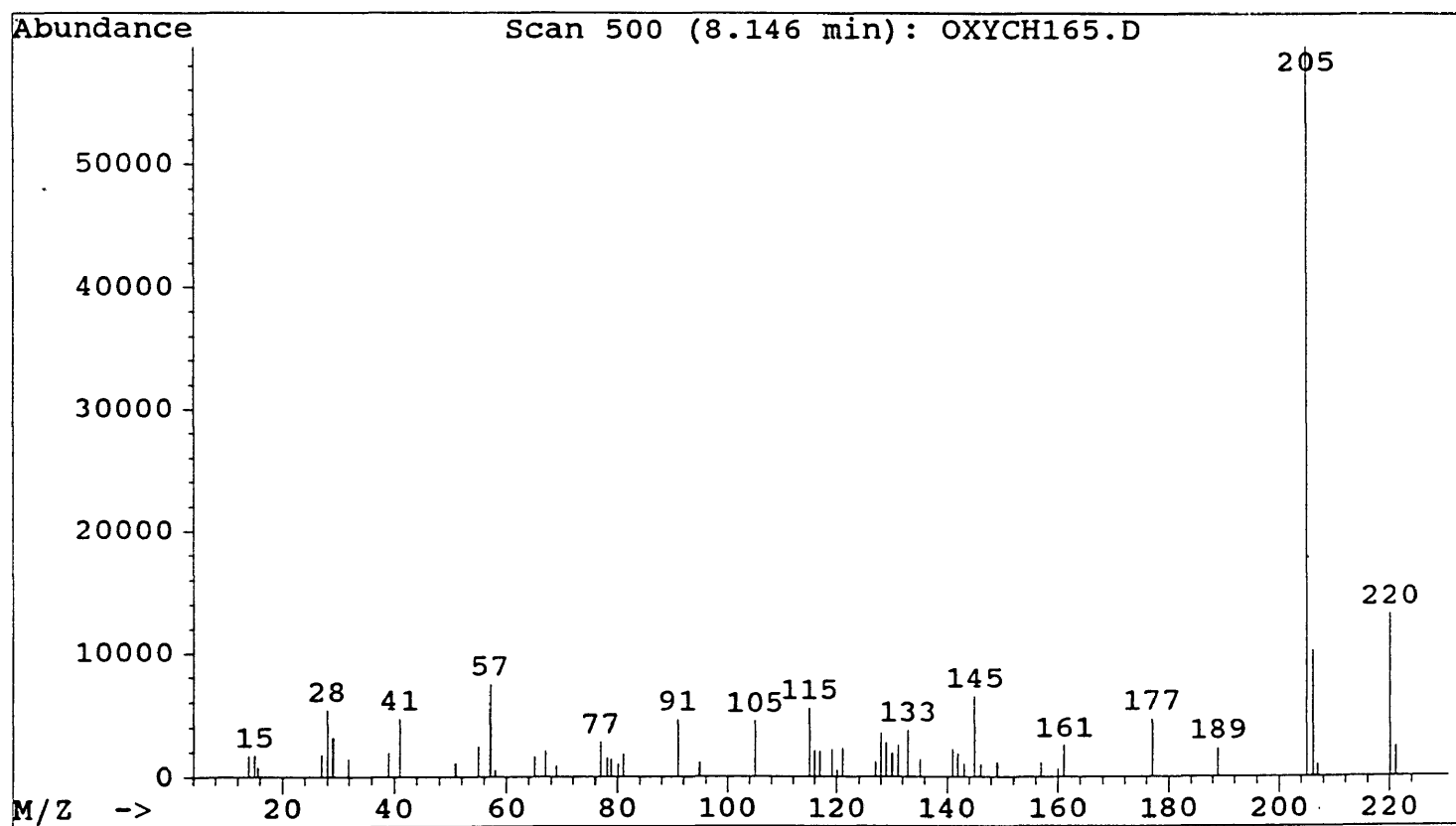
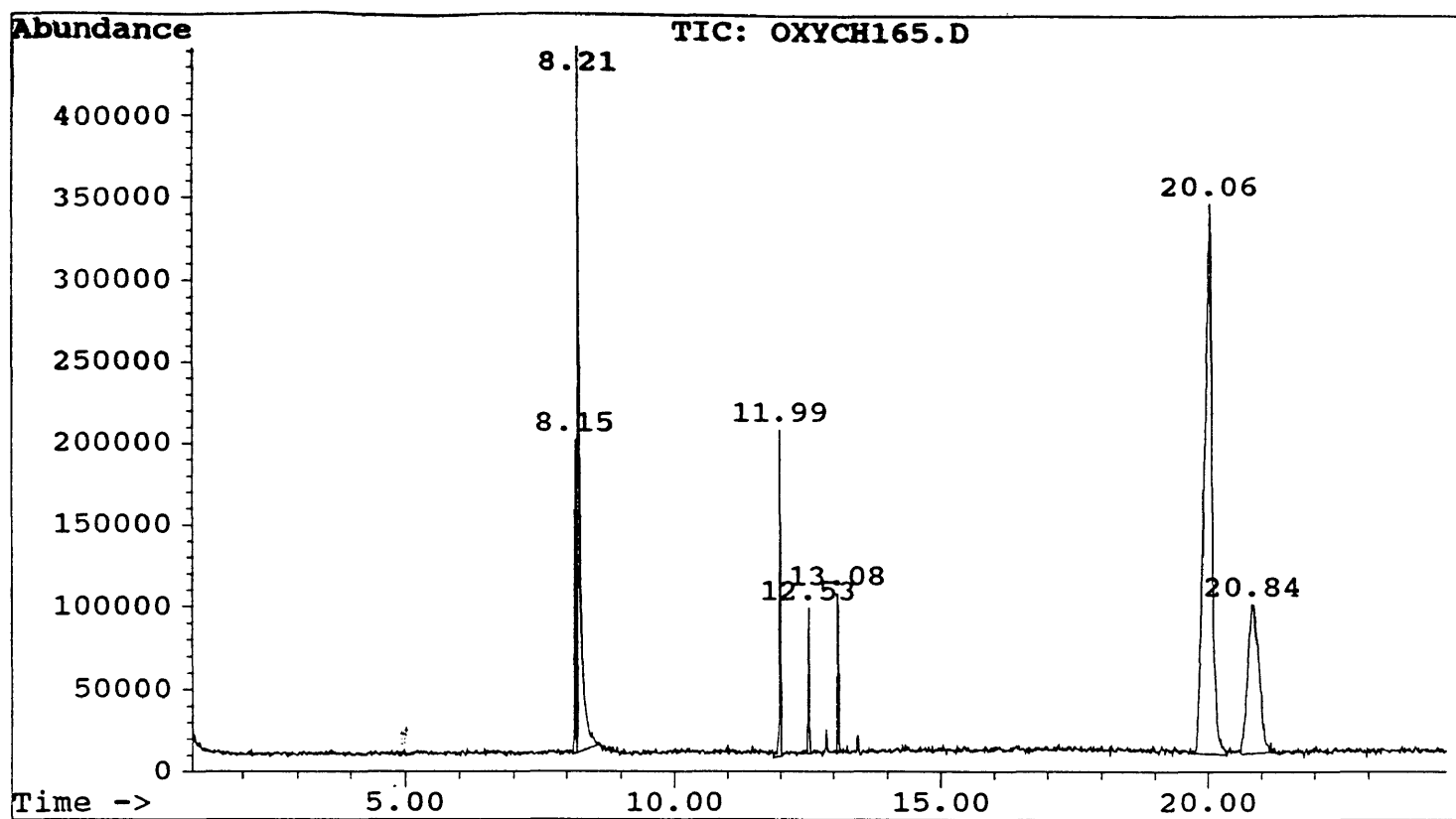


Figure 12-2. GC/MS analysis of Dech Plus



**Figure 13-1.** GC/MS analysis of Dech Plus heated in a sealed tube @ 320-370 °C for 22 h

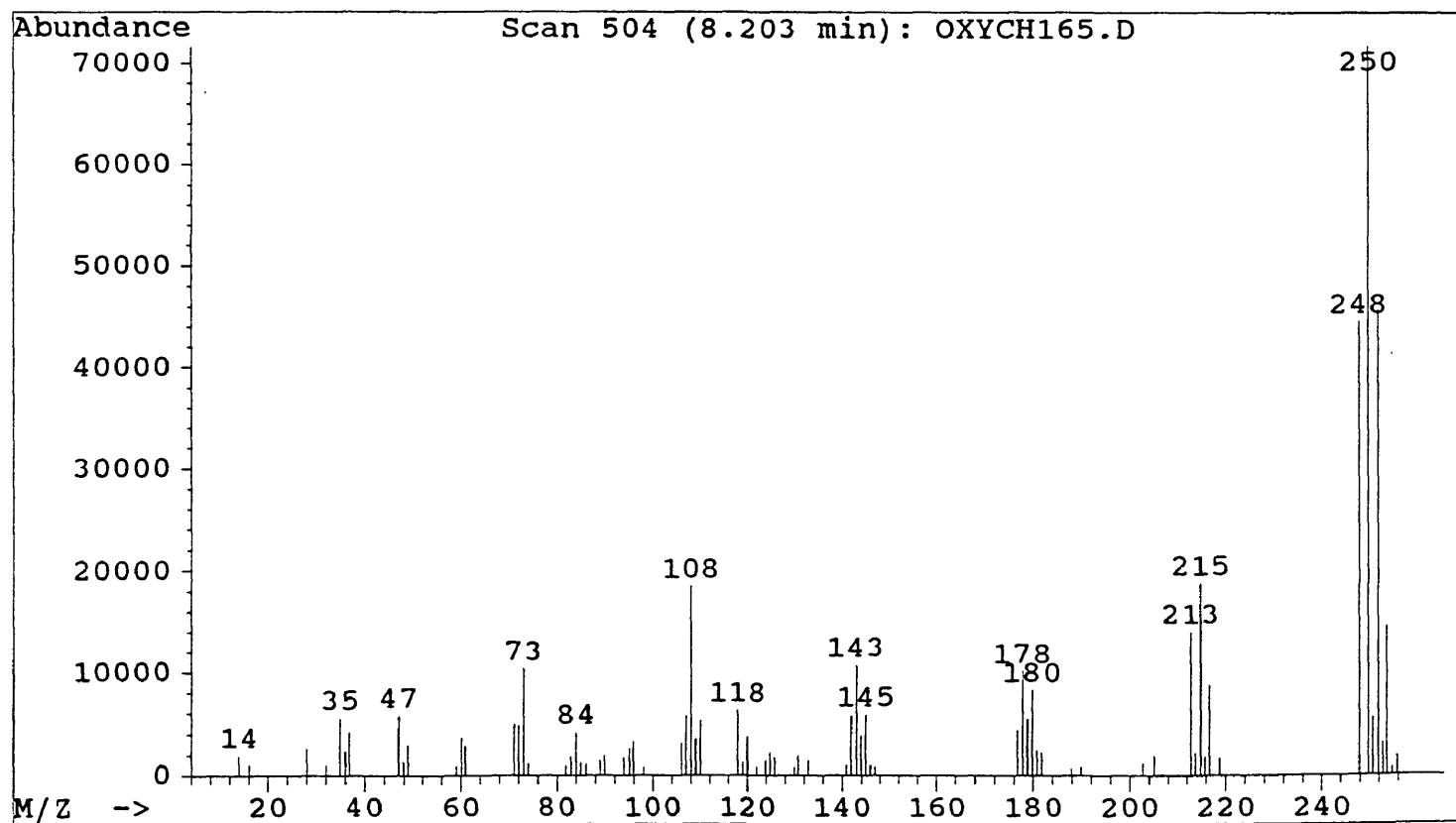
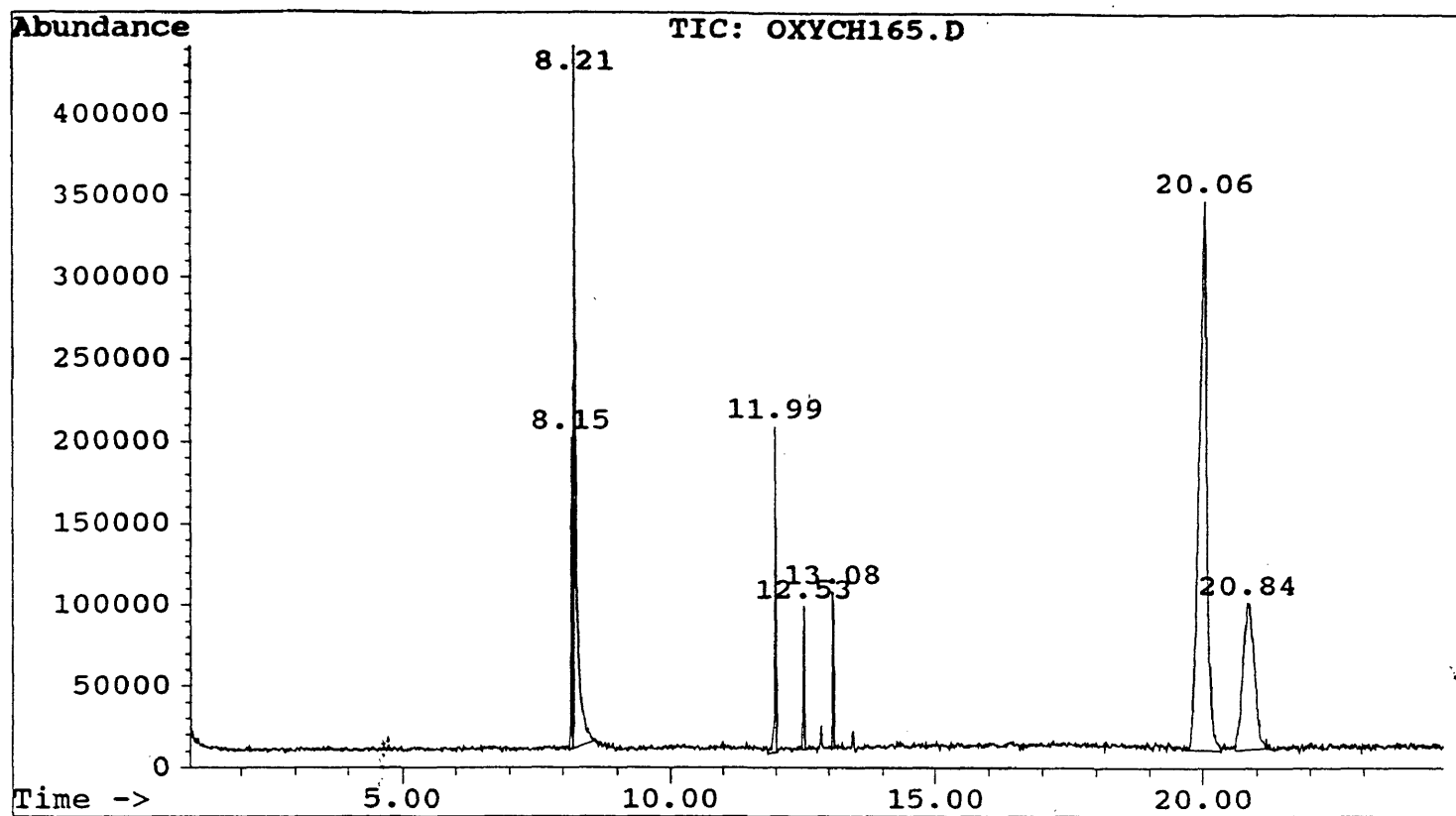
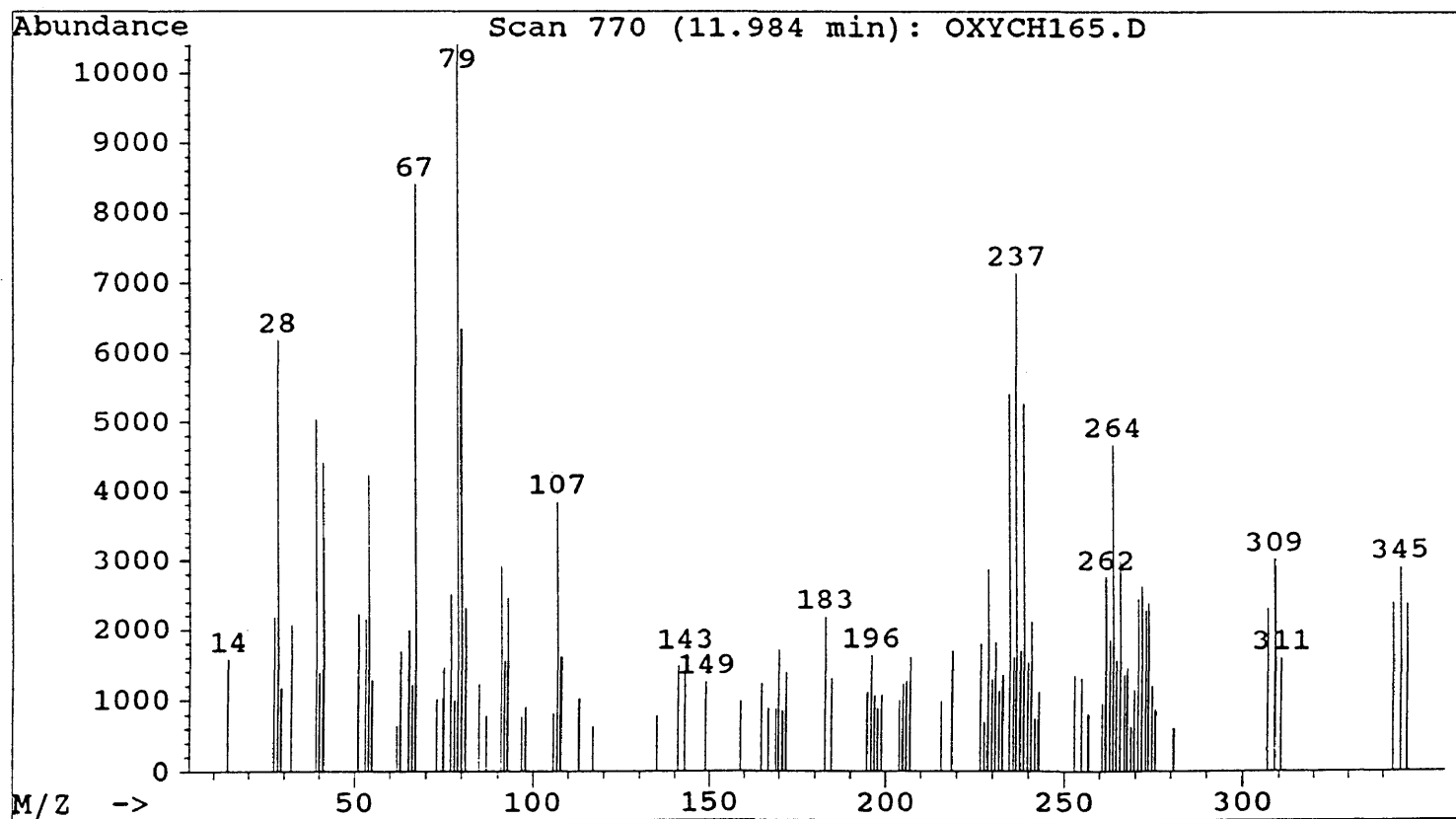
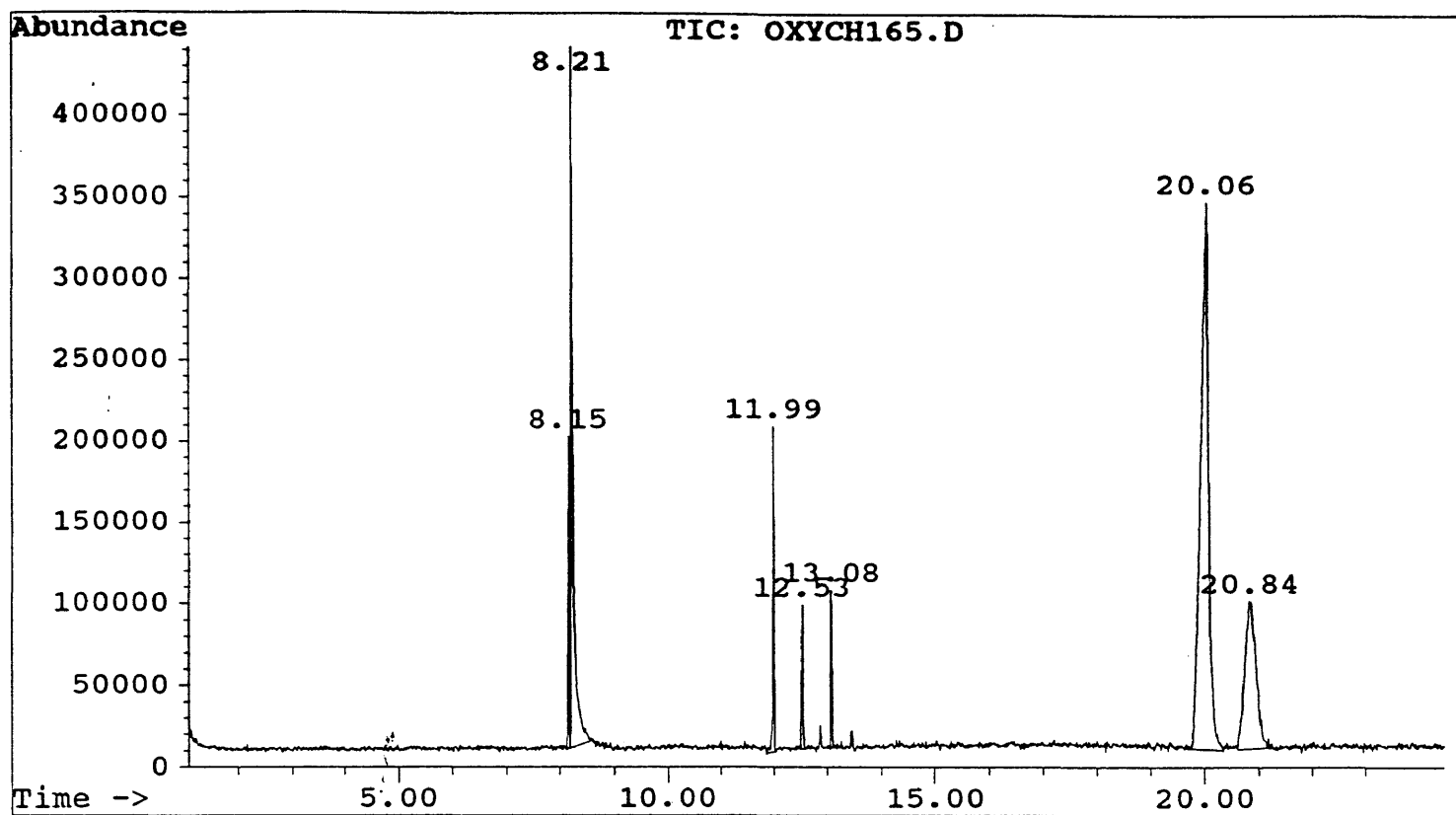
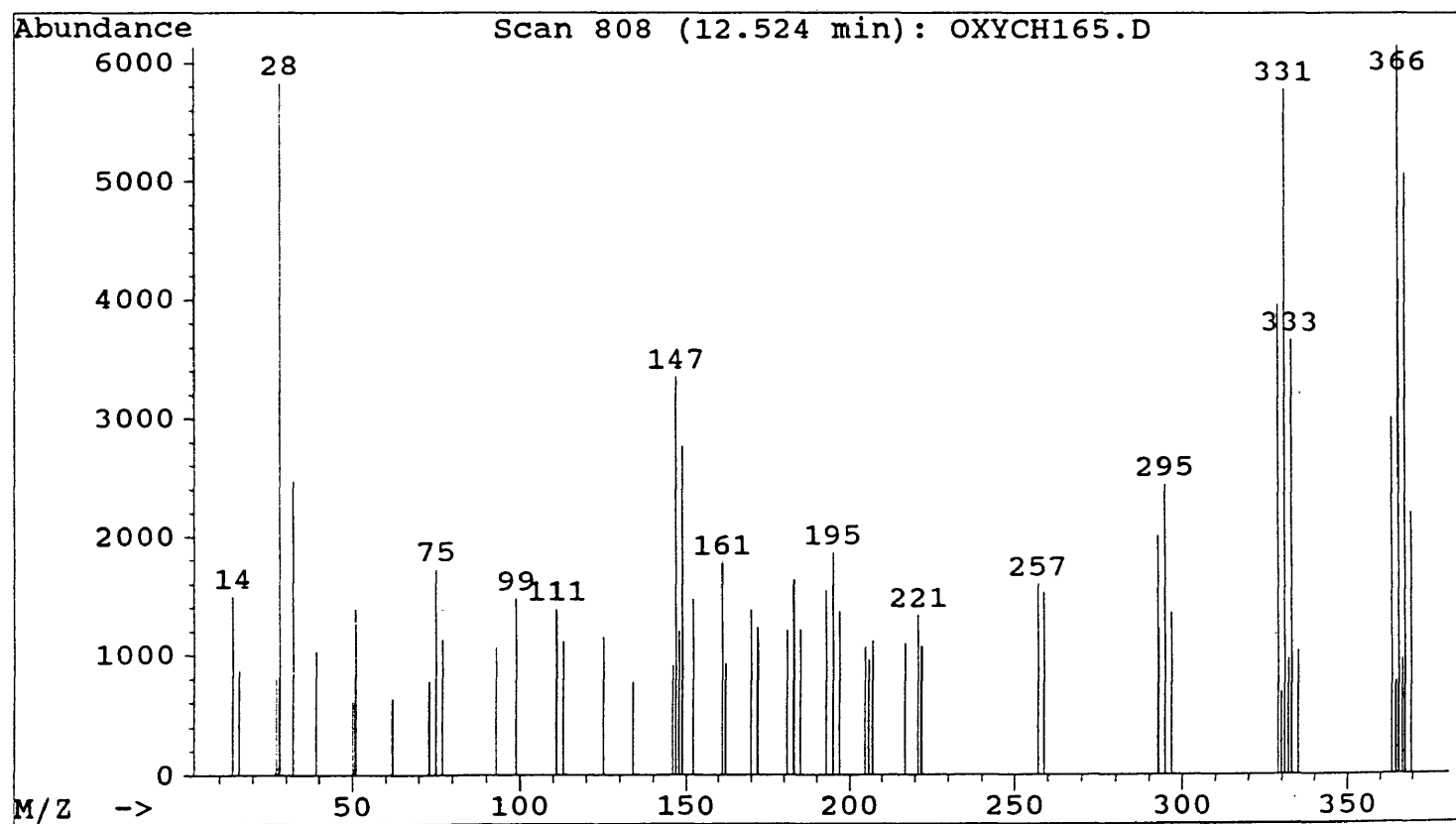
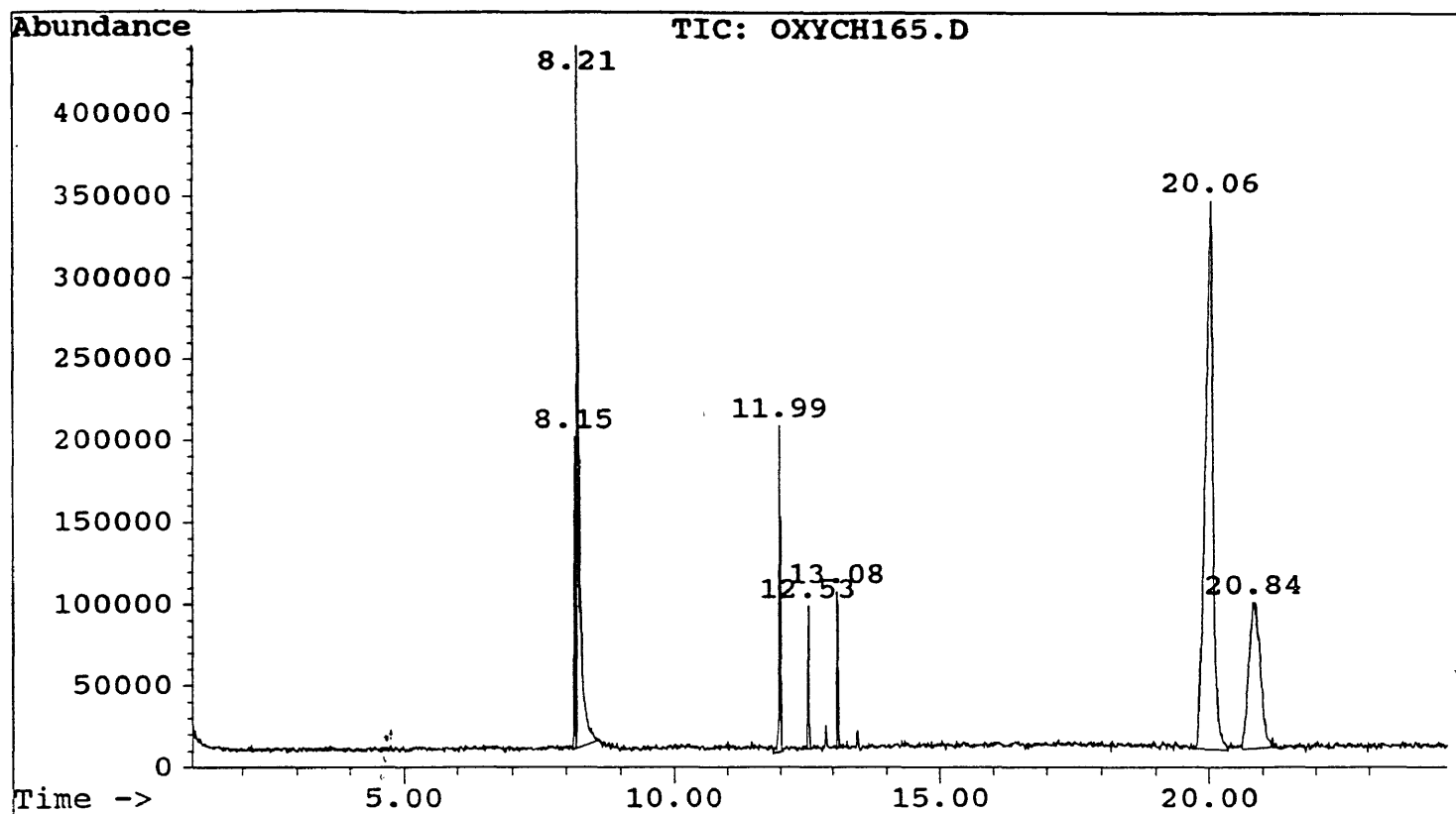


Figure 13-2. GC/MS analysis of Dech Plus heated in a sealed tube @ 320-370 °C for 22 h



**Figure 13-3.** GC/MS analysis of Dech Plus heated in a sealed tube @ 320-370 °C for 22 h



**Figure 13-4.** GC/MS analysis of Dech Plus heated in a sealed tube @ 320-370 °C for 22 h

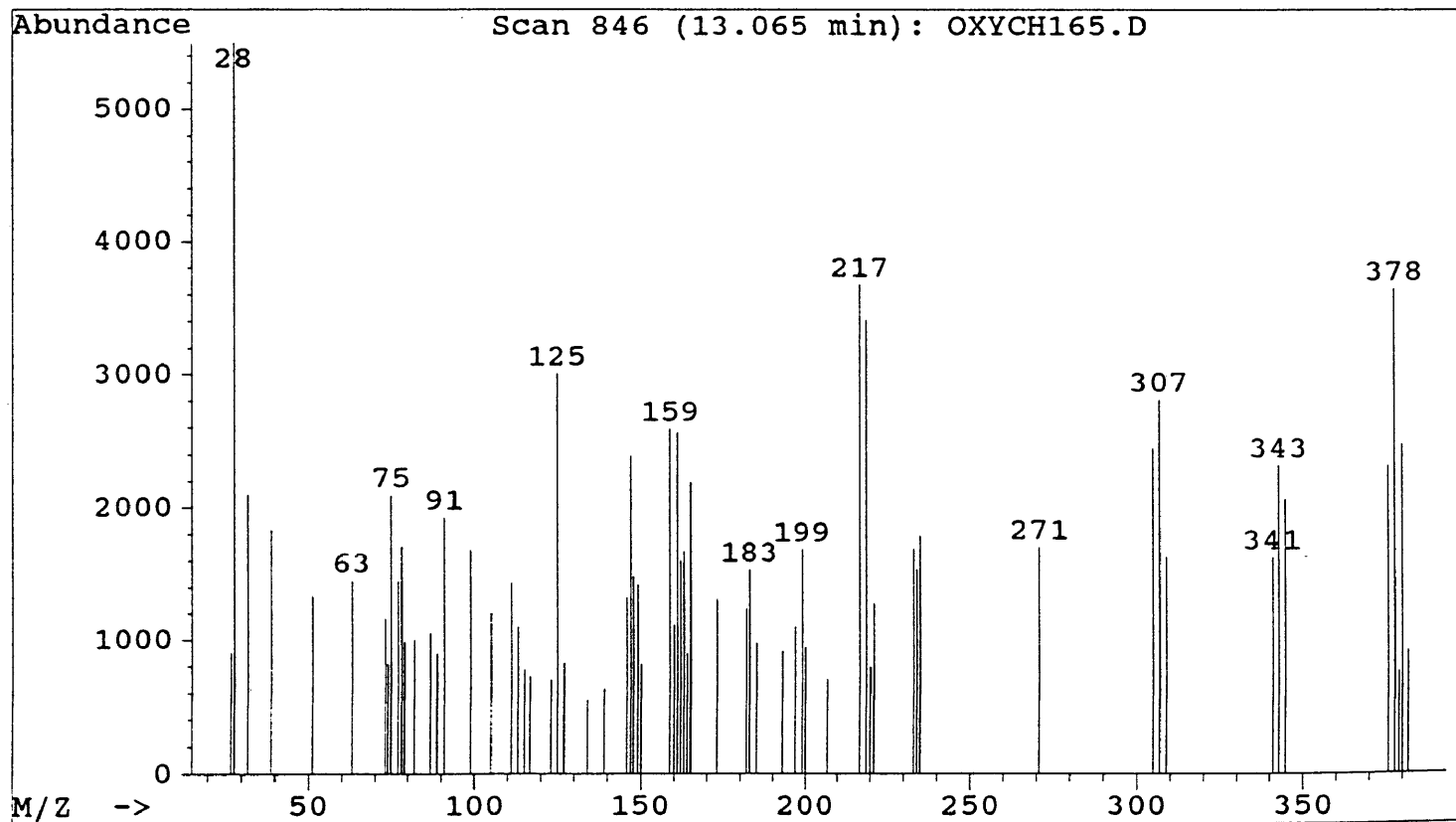
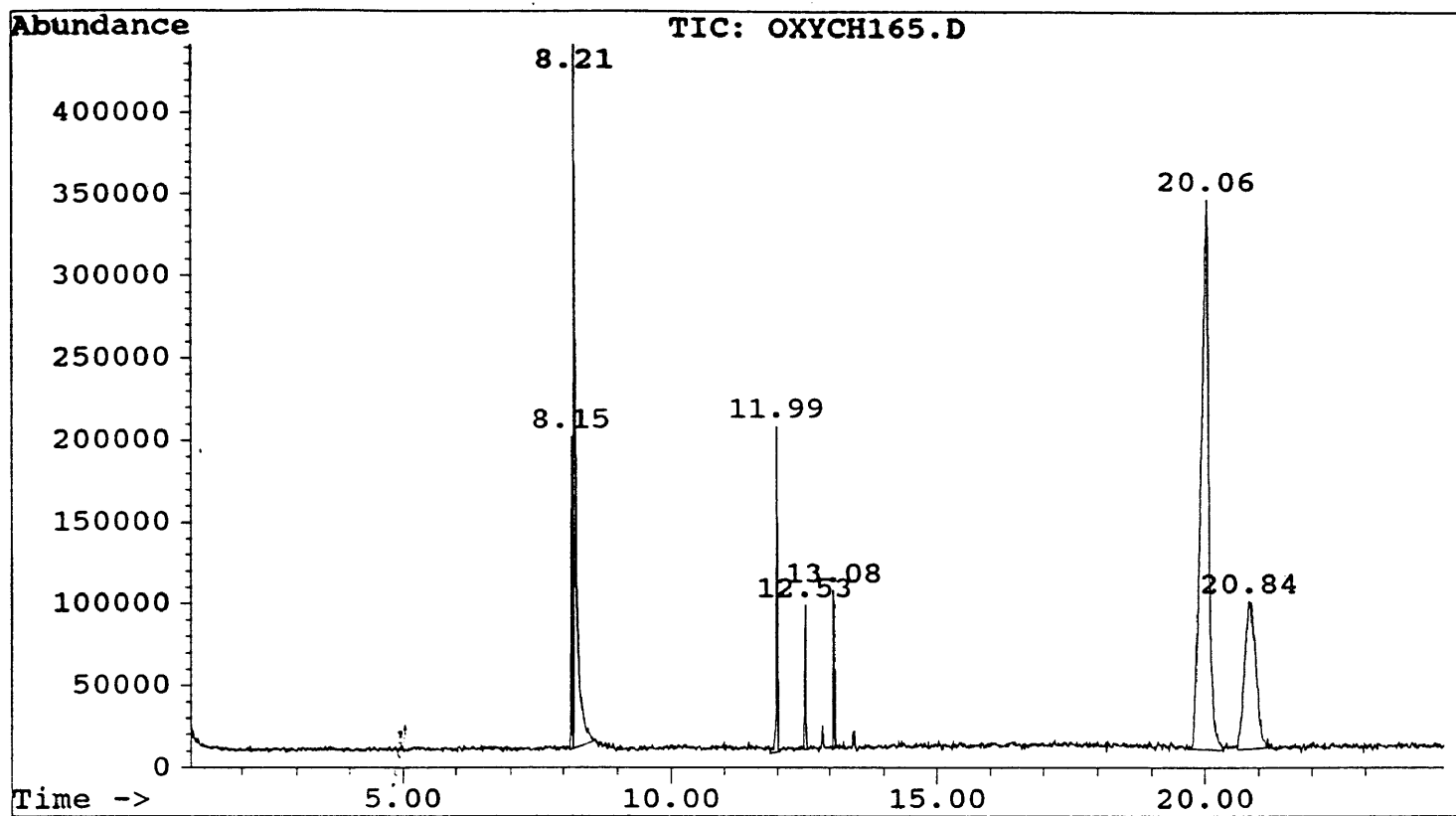
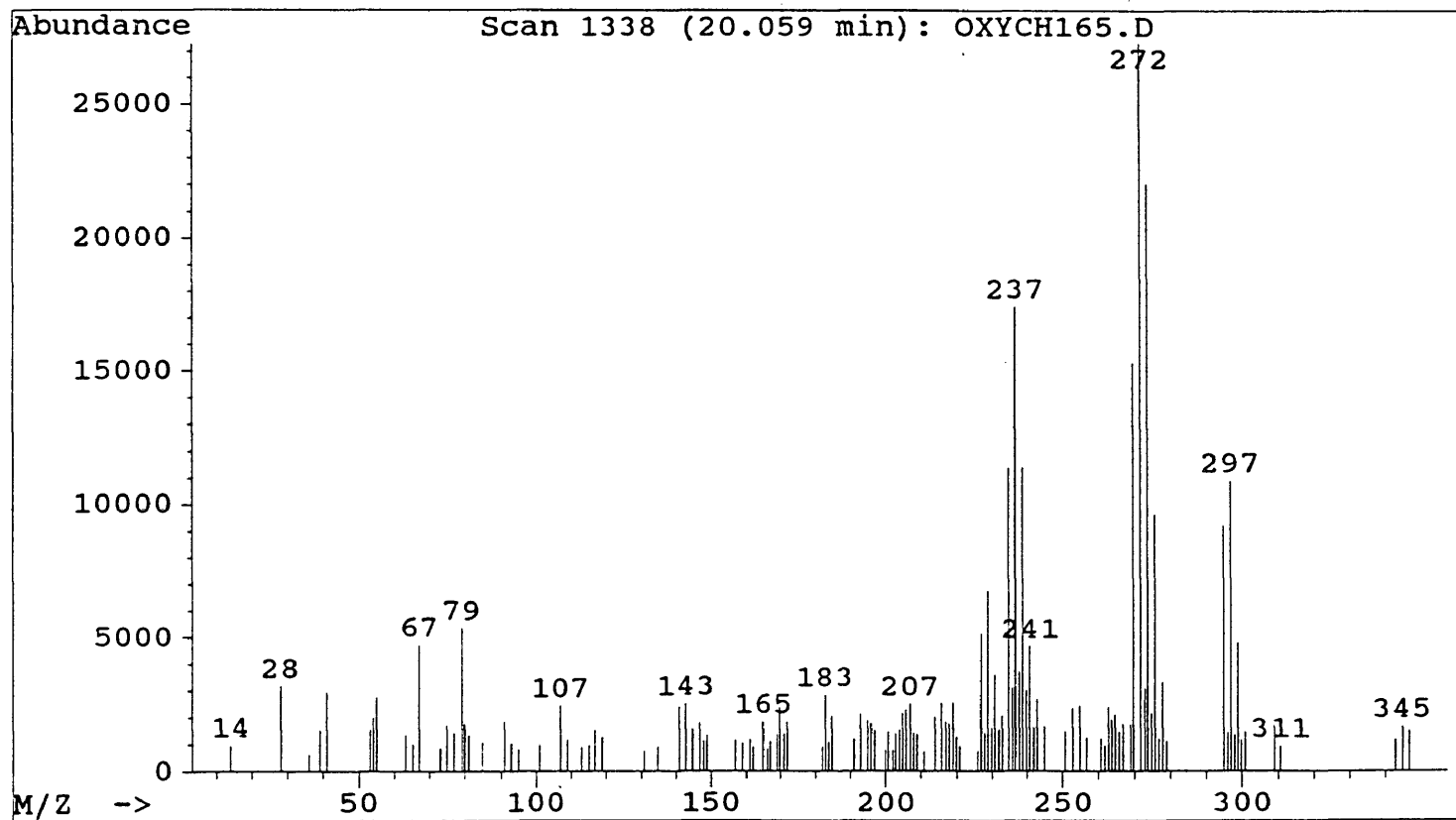
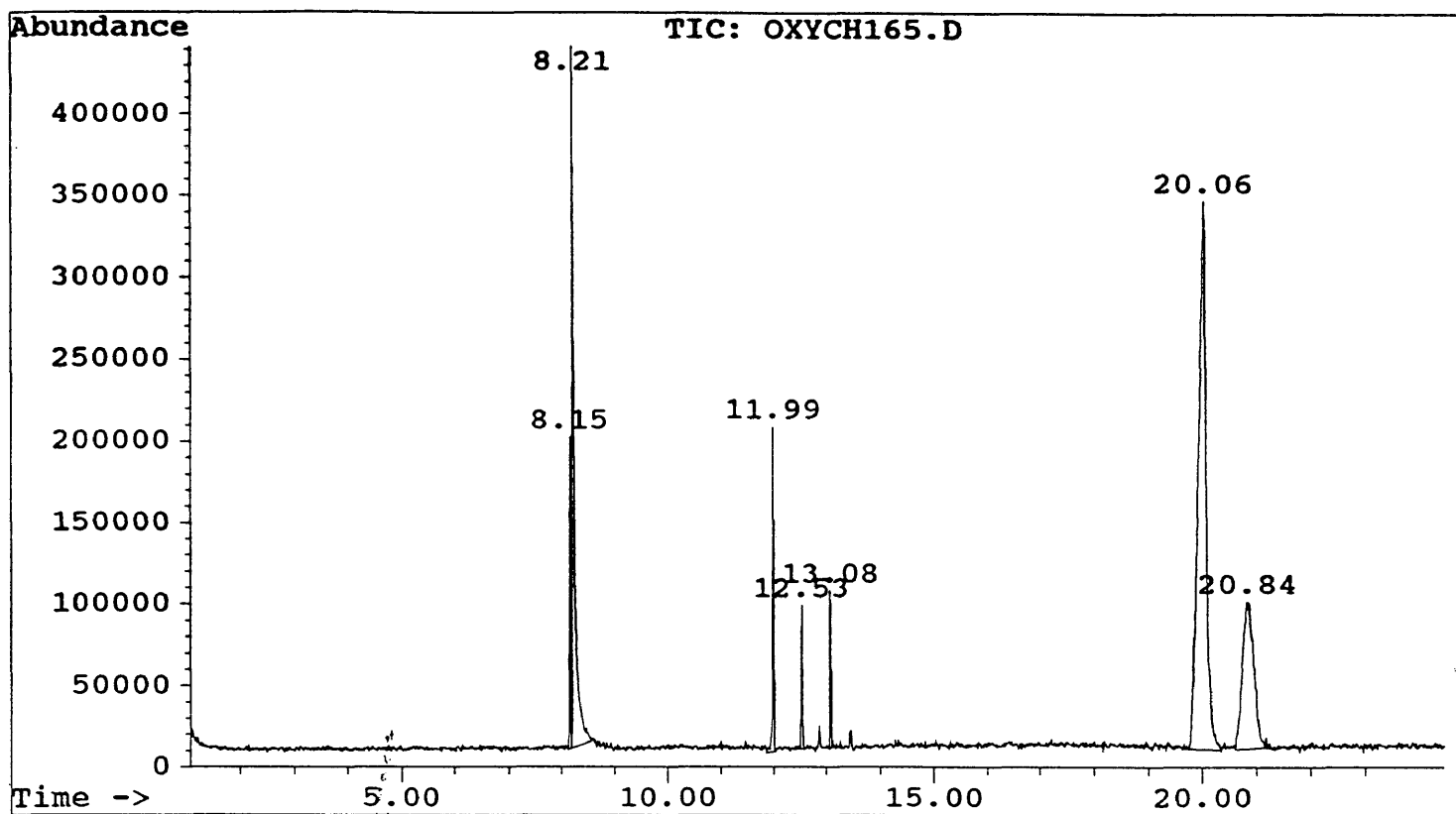


Figure 13-5. GC/MS analysis of Dech Plus heated in a sealed tube @ 320-370 °C for 22 h



**Figure 13-6.** GC/MS analysis of Dech Plus heated in a sealed tube @ 320-370 °C for 22 h

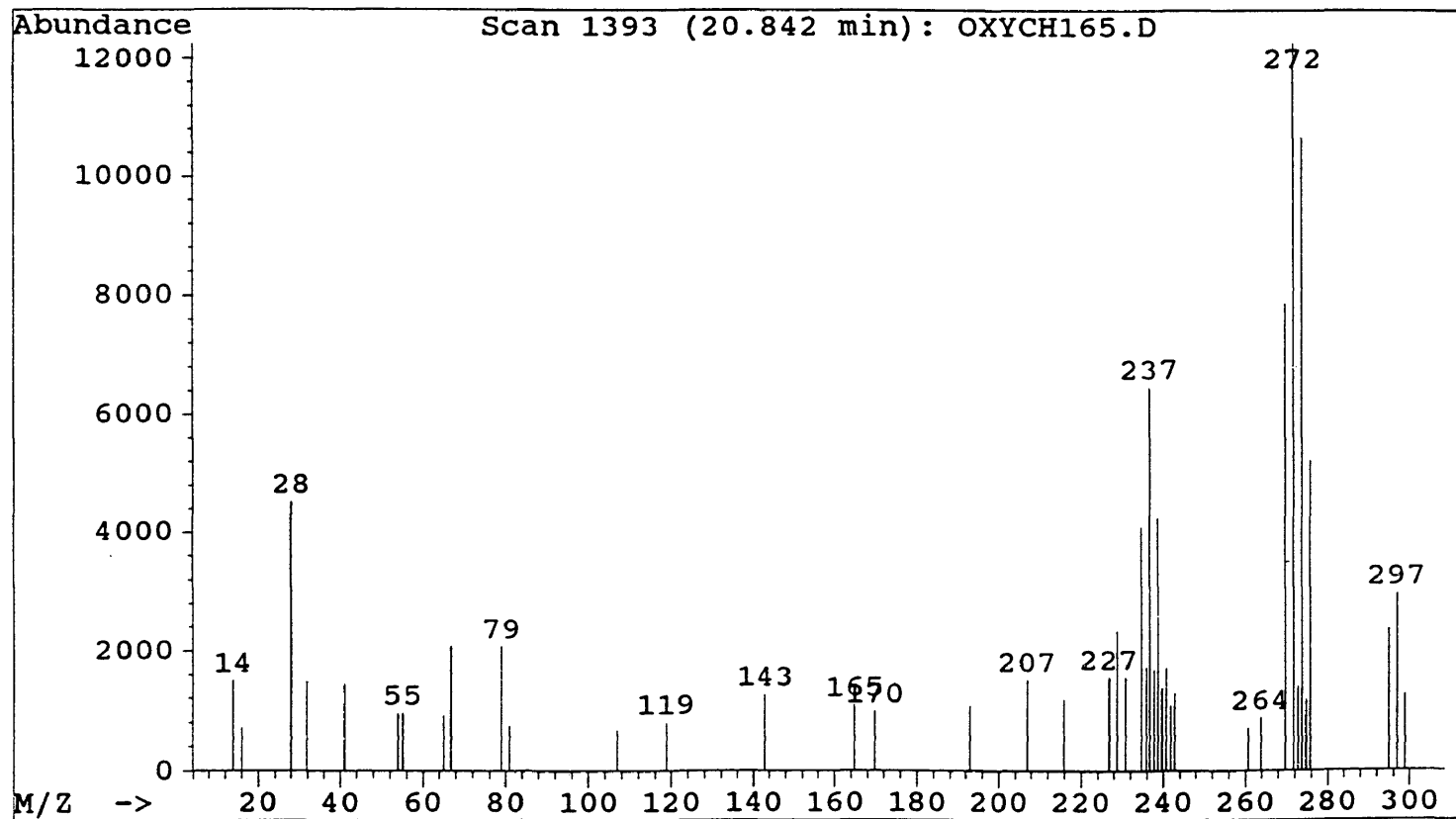
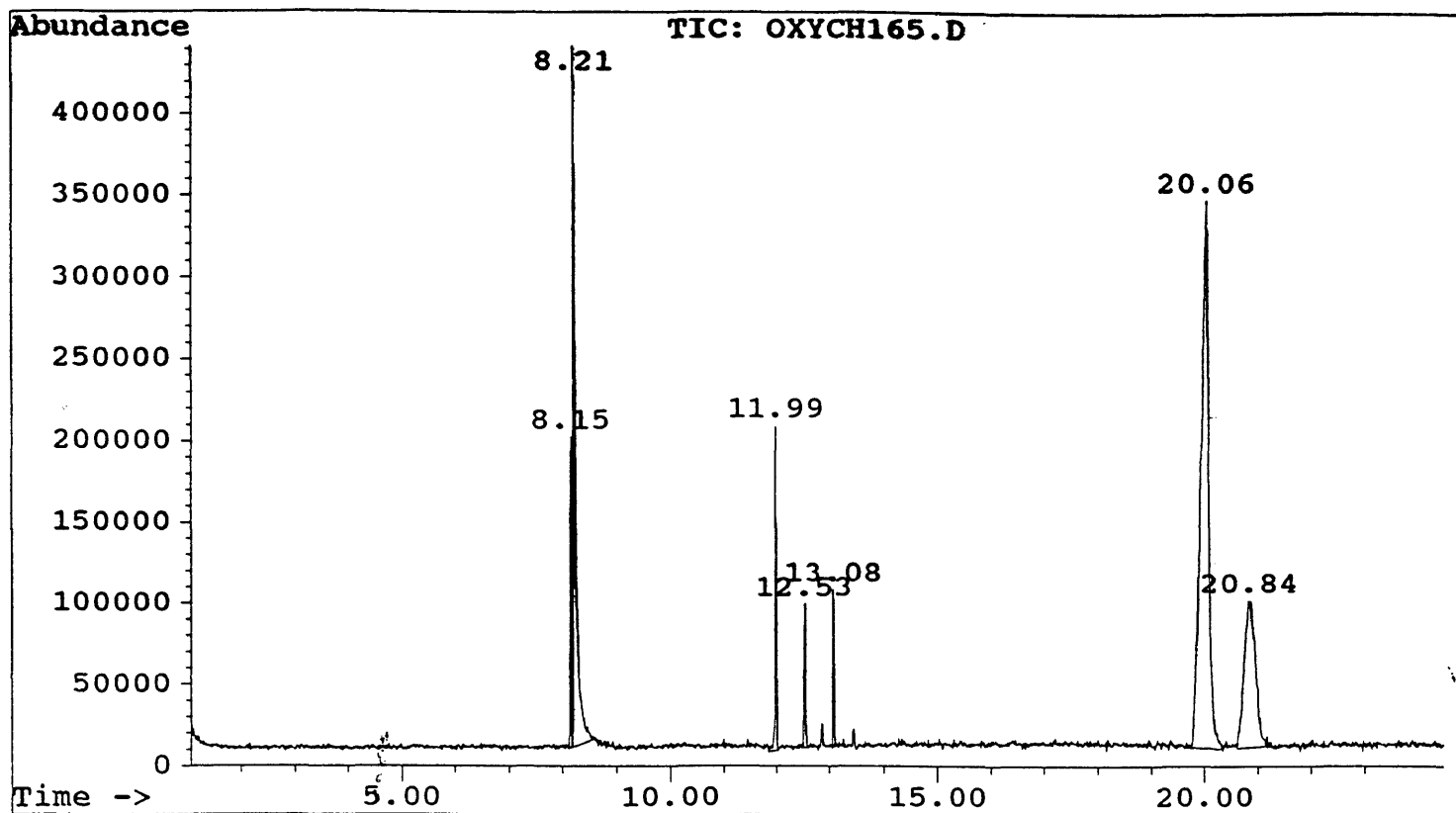
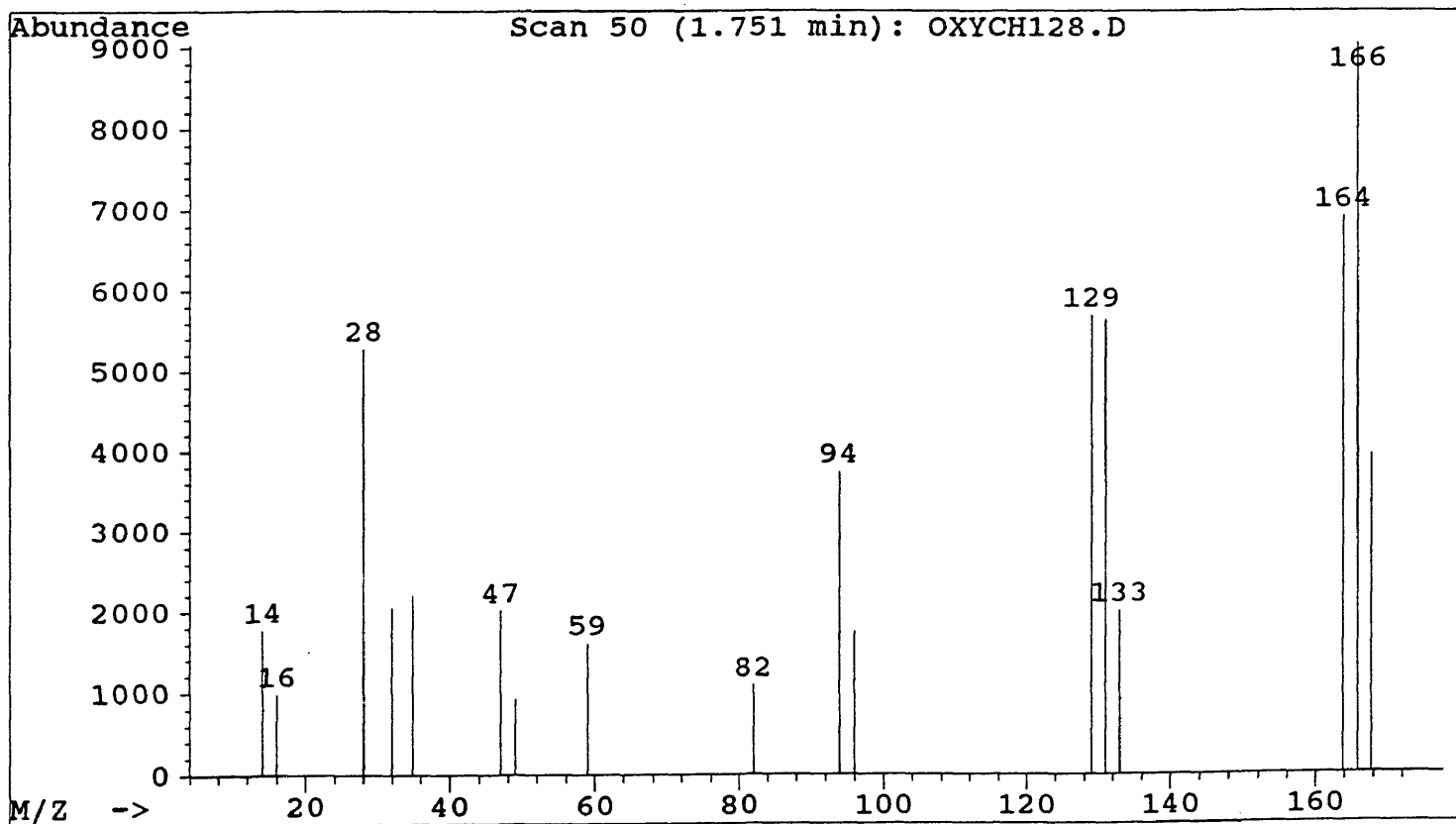
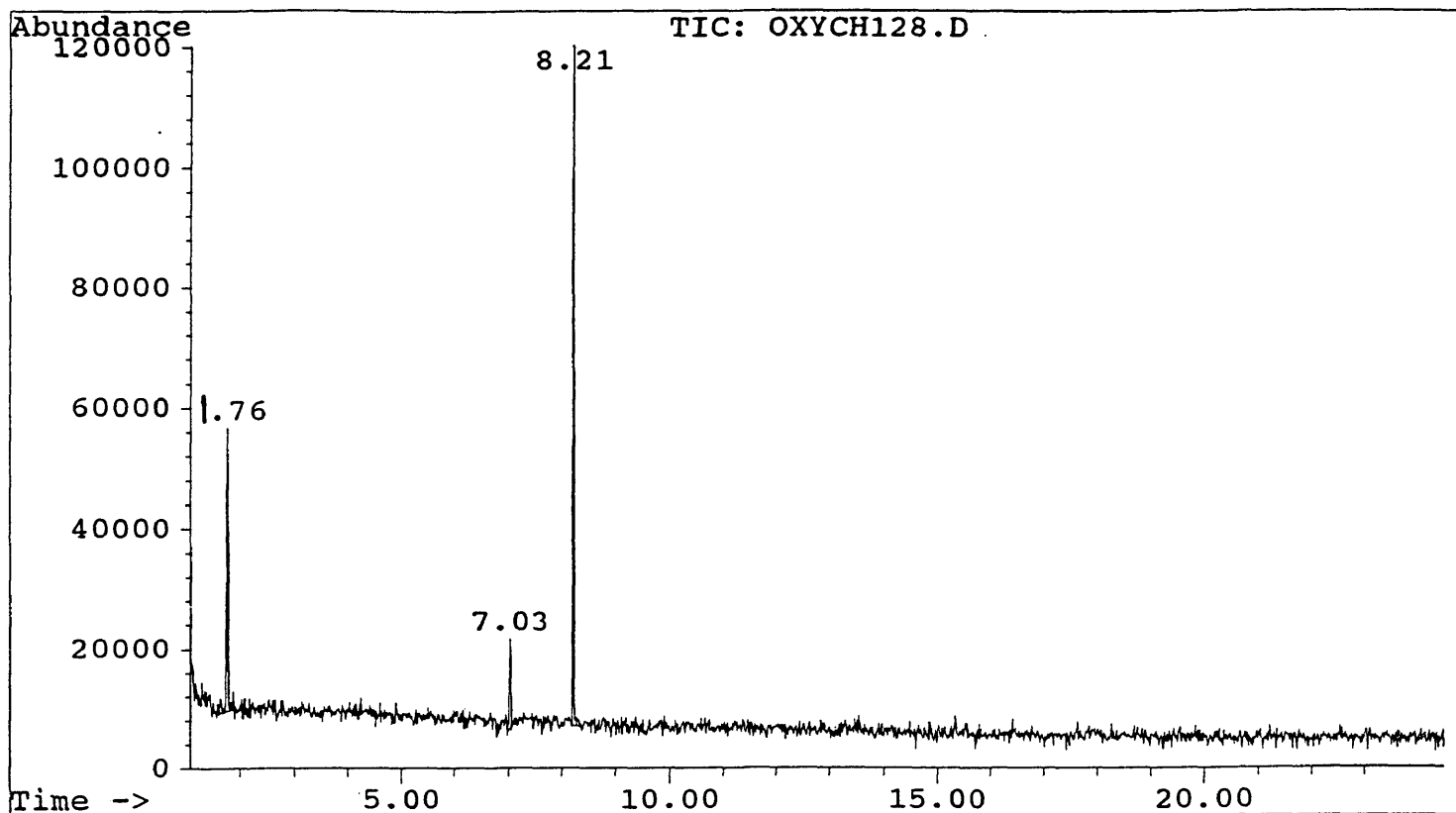
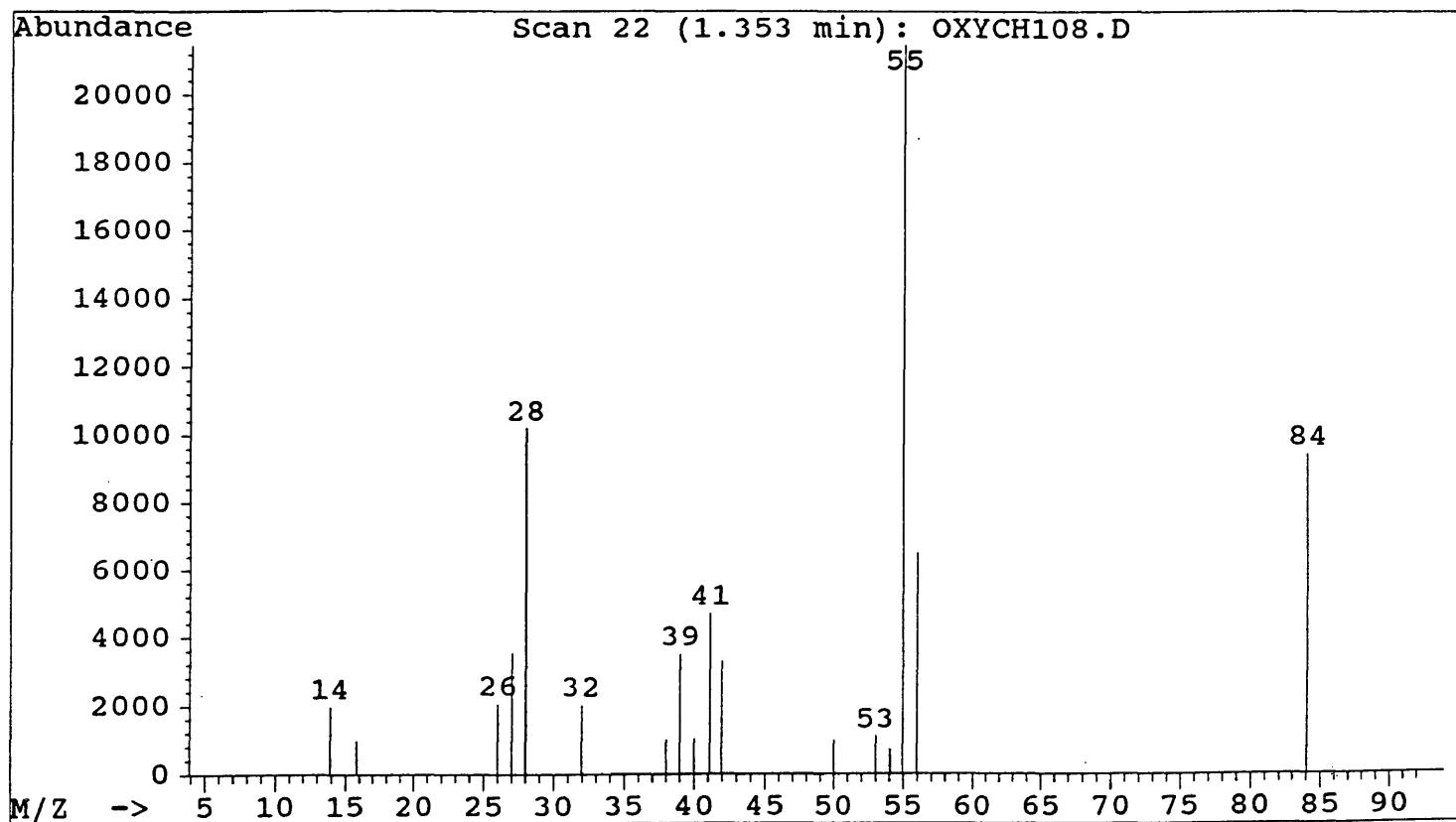
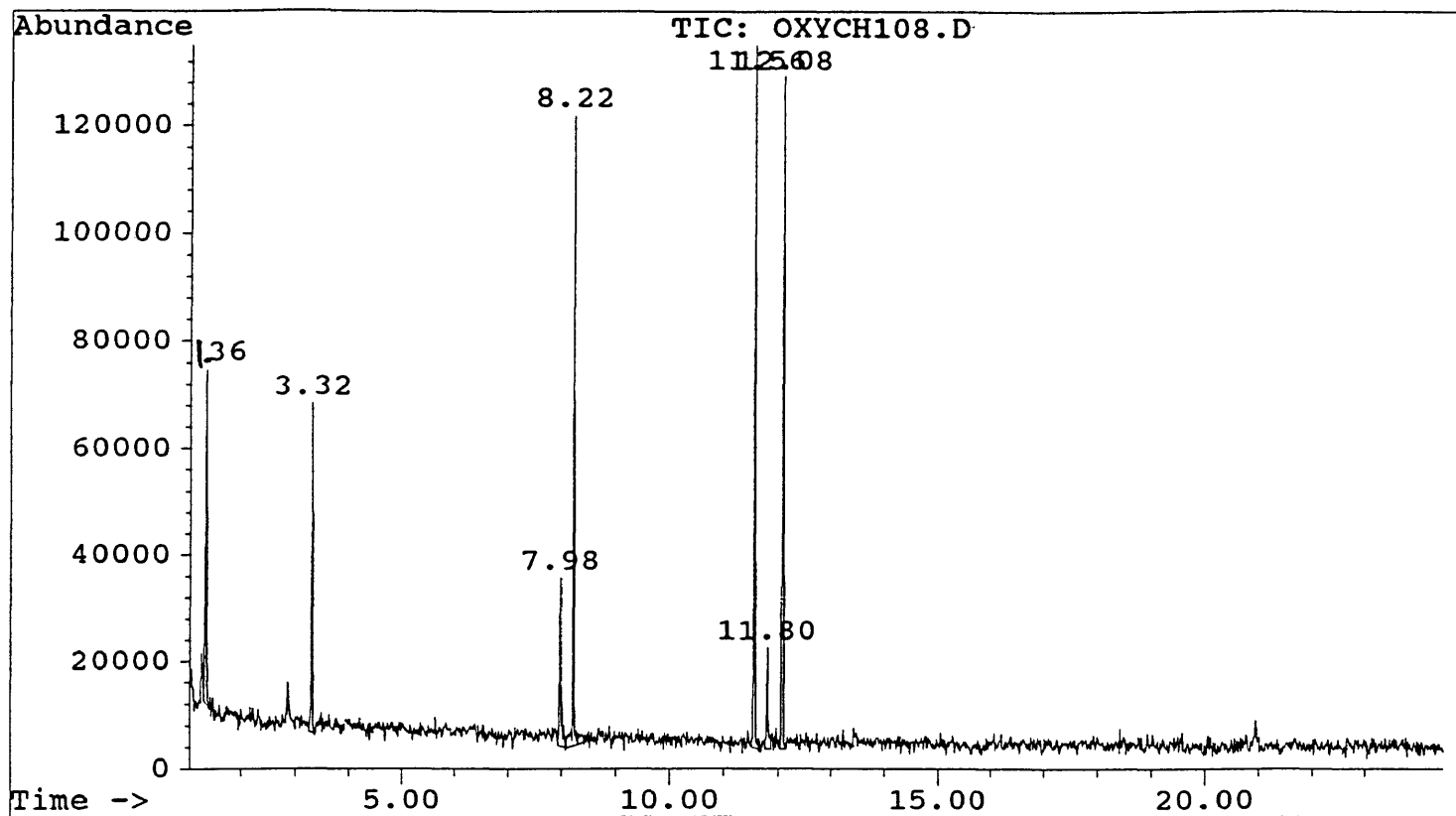


Figure 13-7. GC/MS analysis of Dech Plus heated in a sealed tube @ 320-370 °C for 22 h

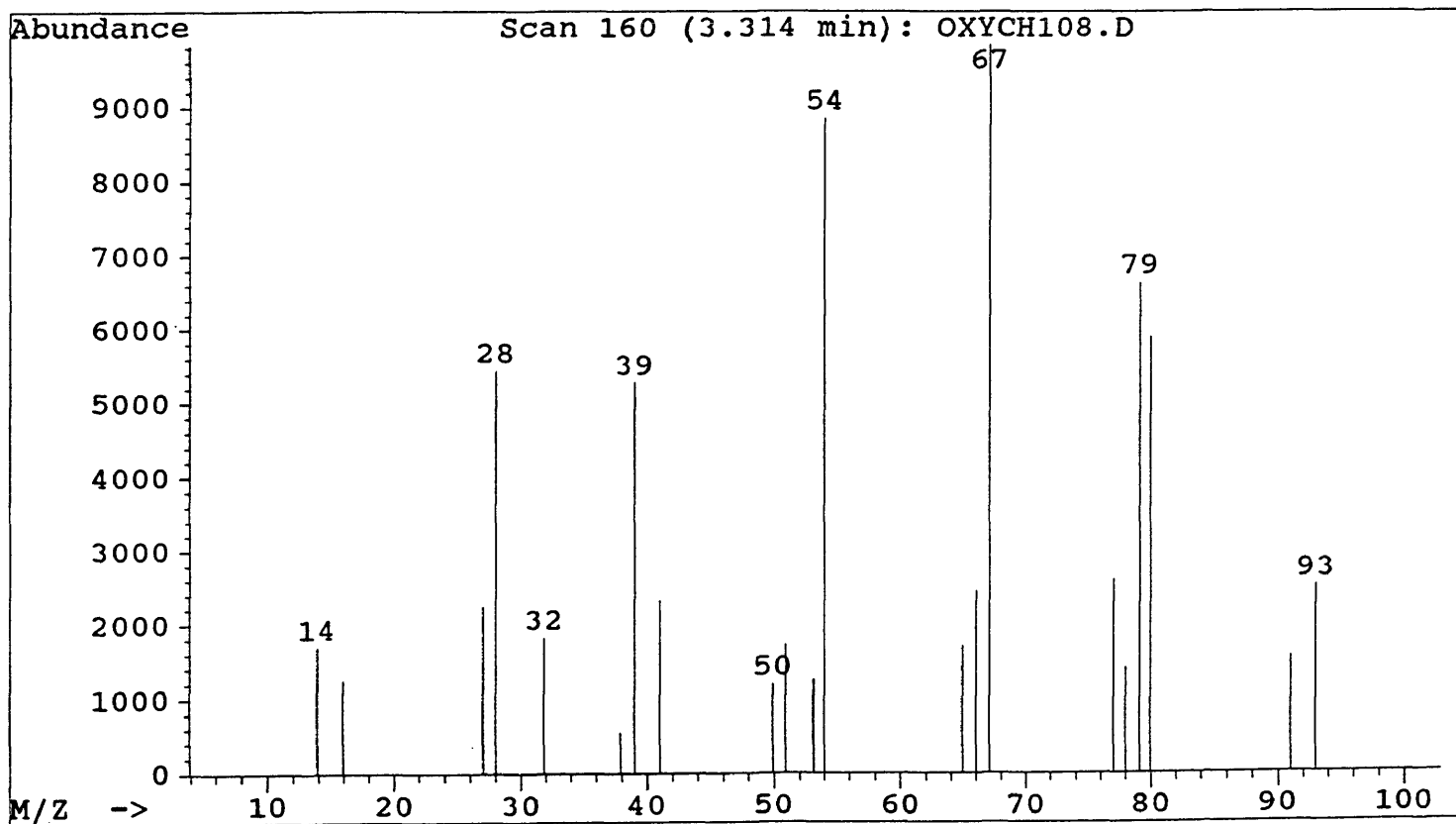
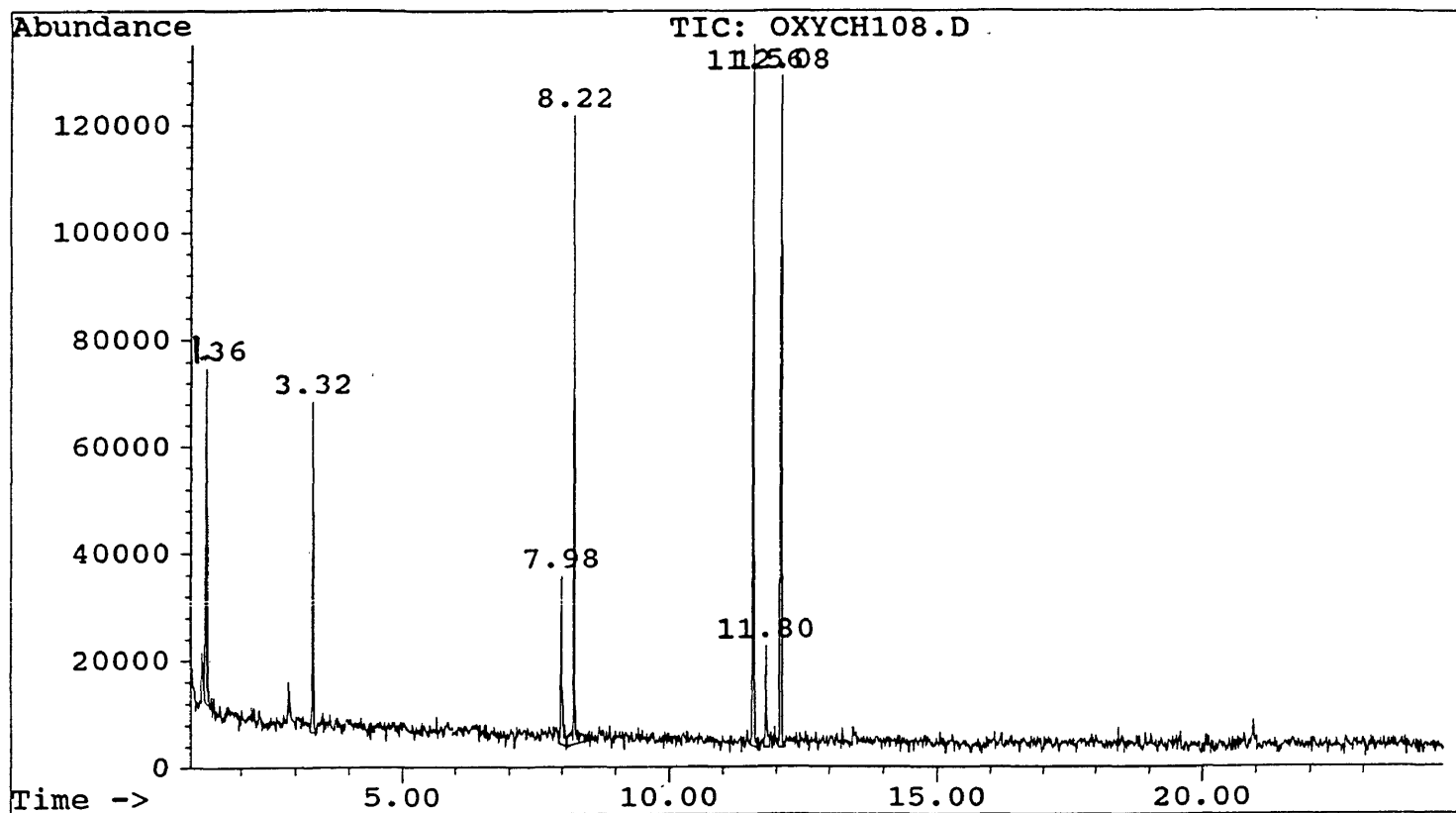




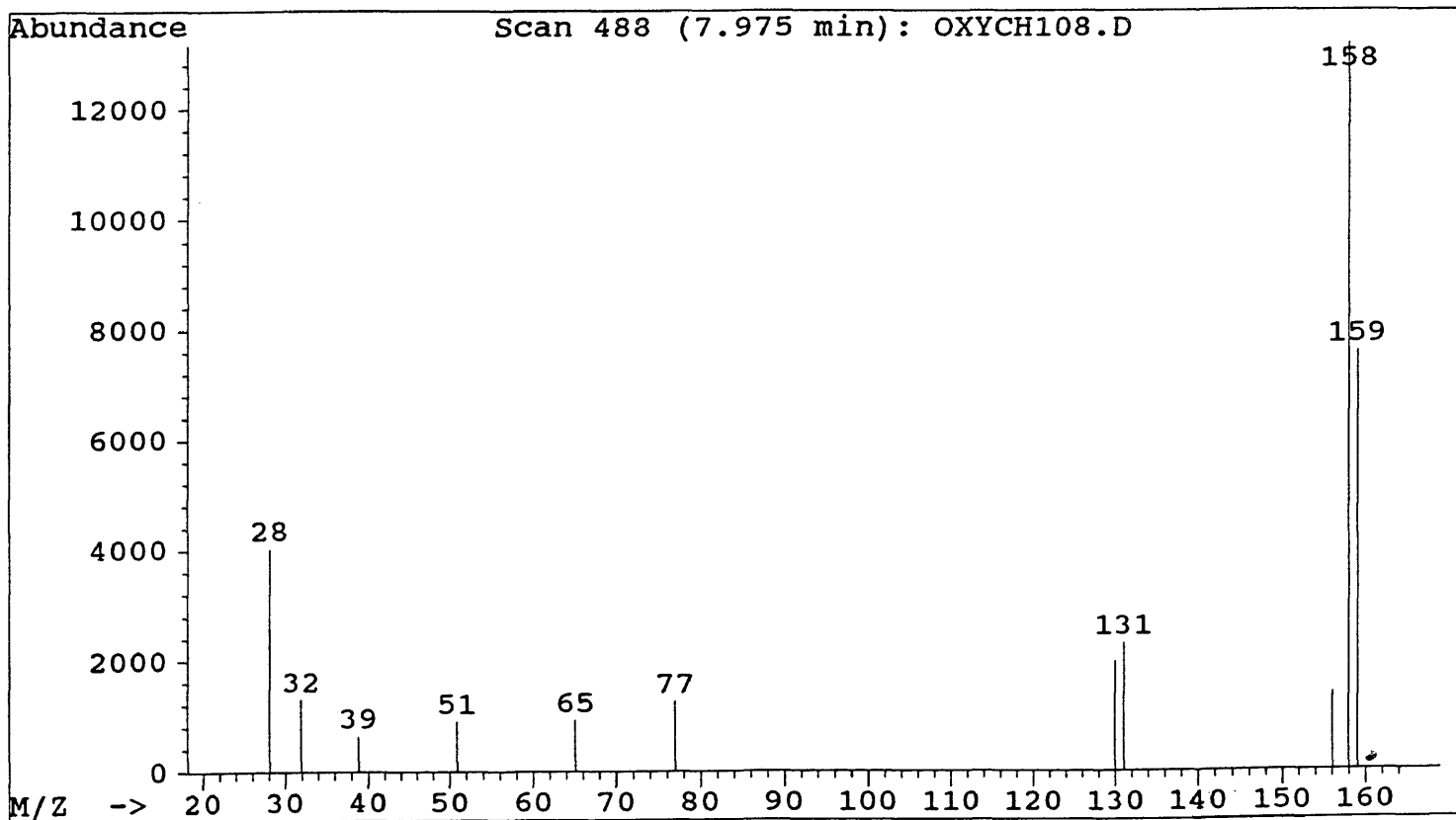
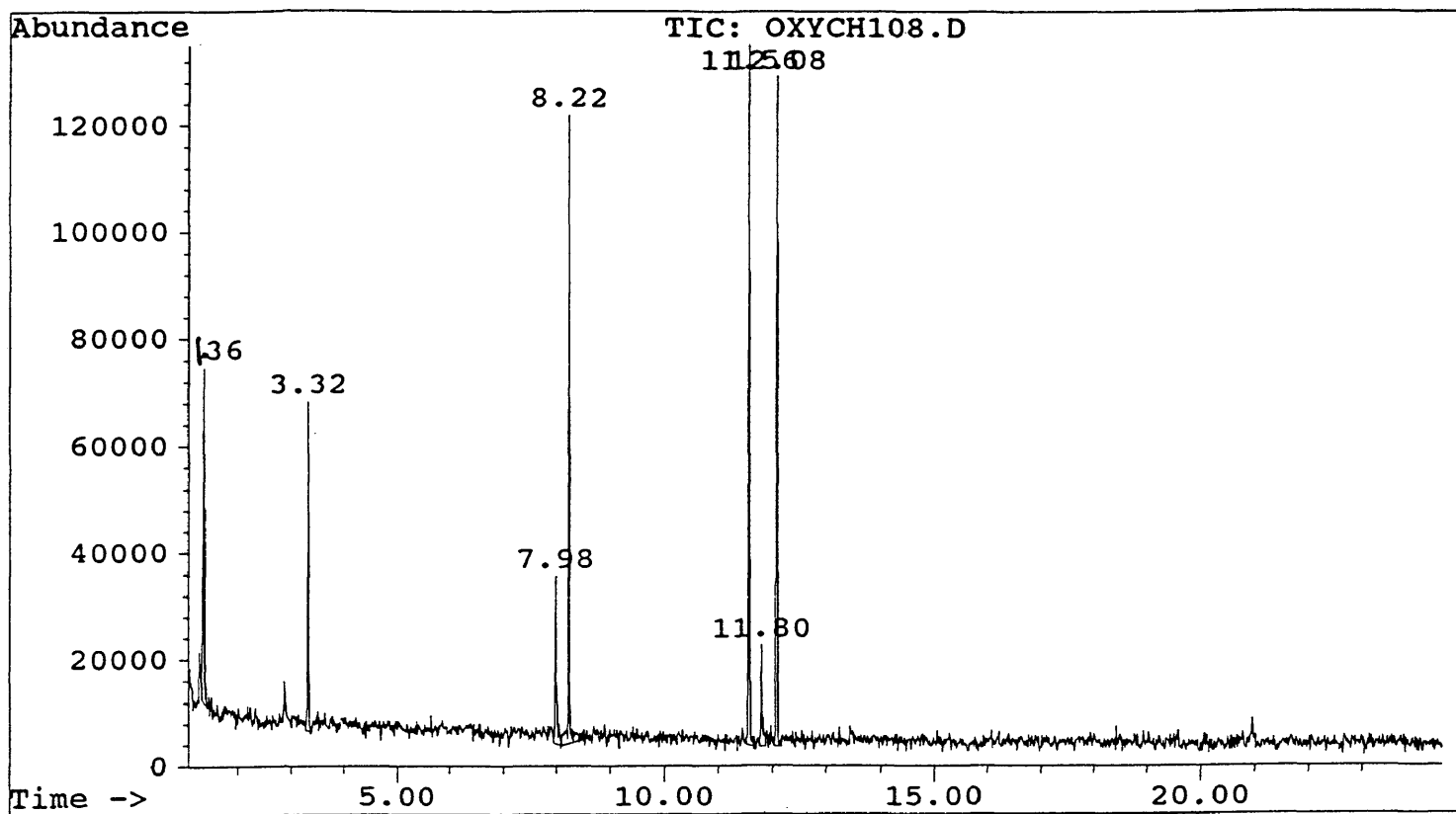
**Figure 14.** GC/MS analysis of volatile products from pyrolyzed Dech Plus



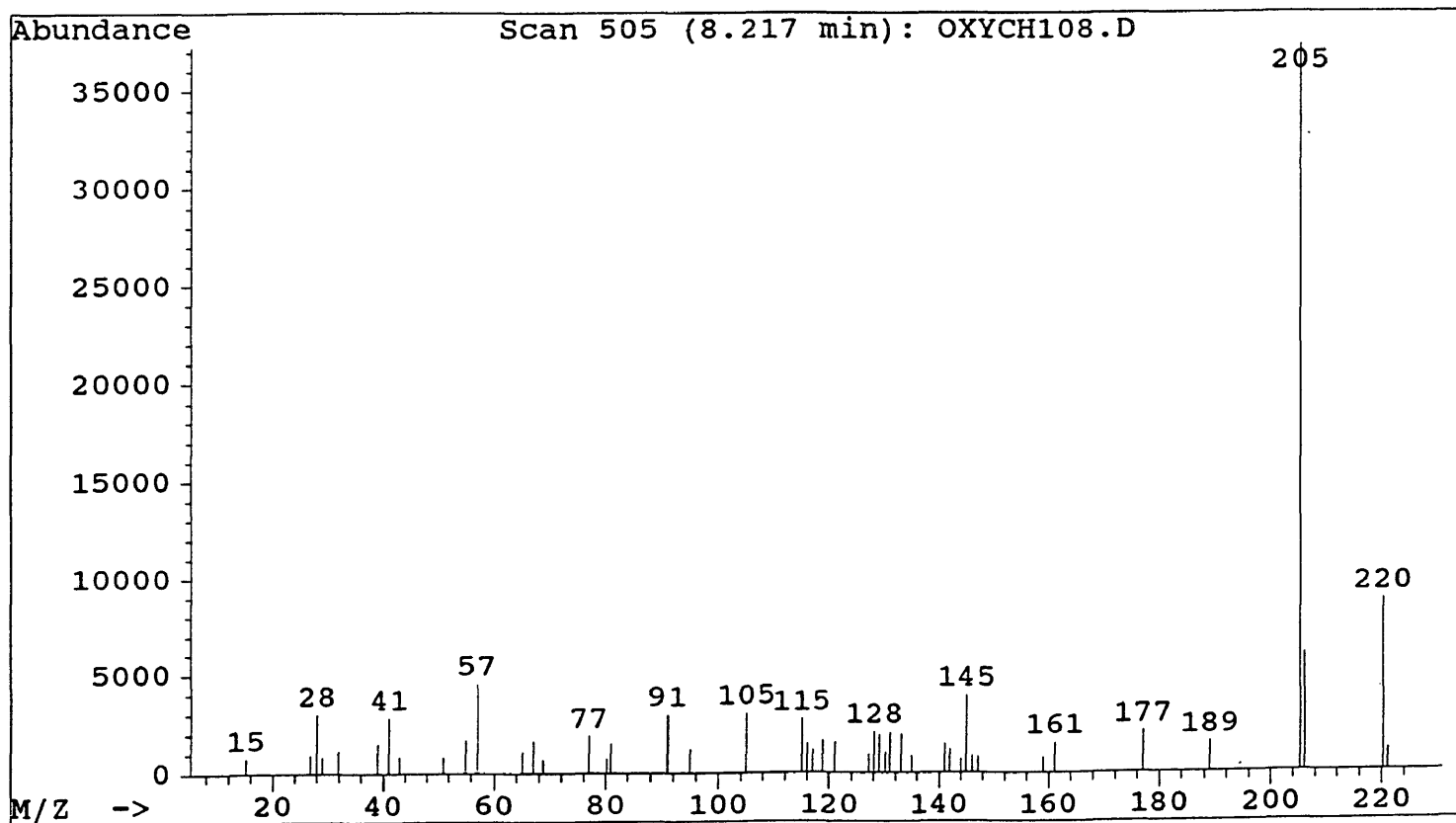
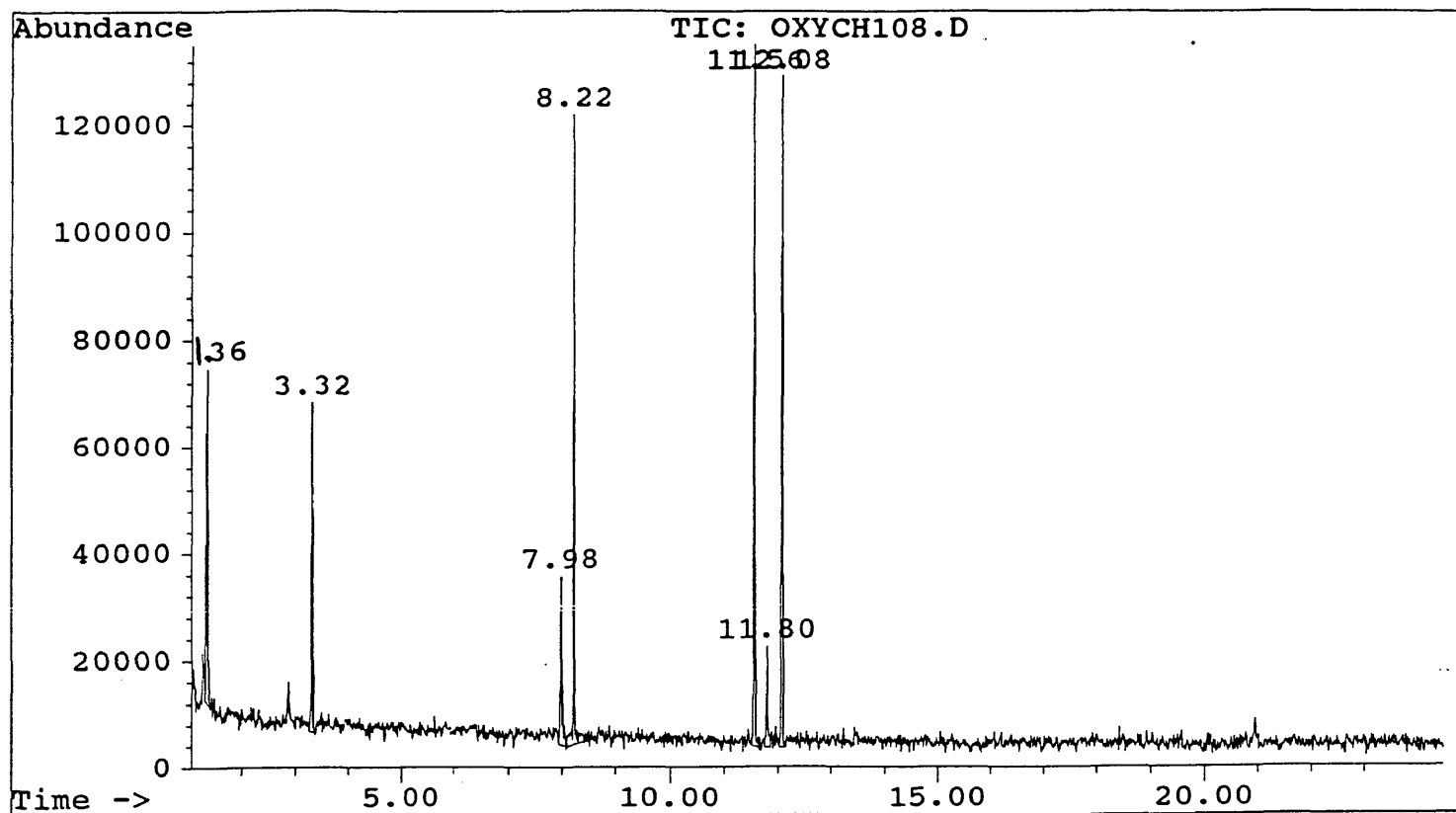
**Figure 15-1.** GC/MS analysis of volatile products from a pyrolyzed 90:10 Nylon 66/Dech Plus mixture



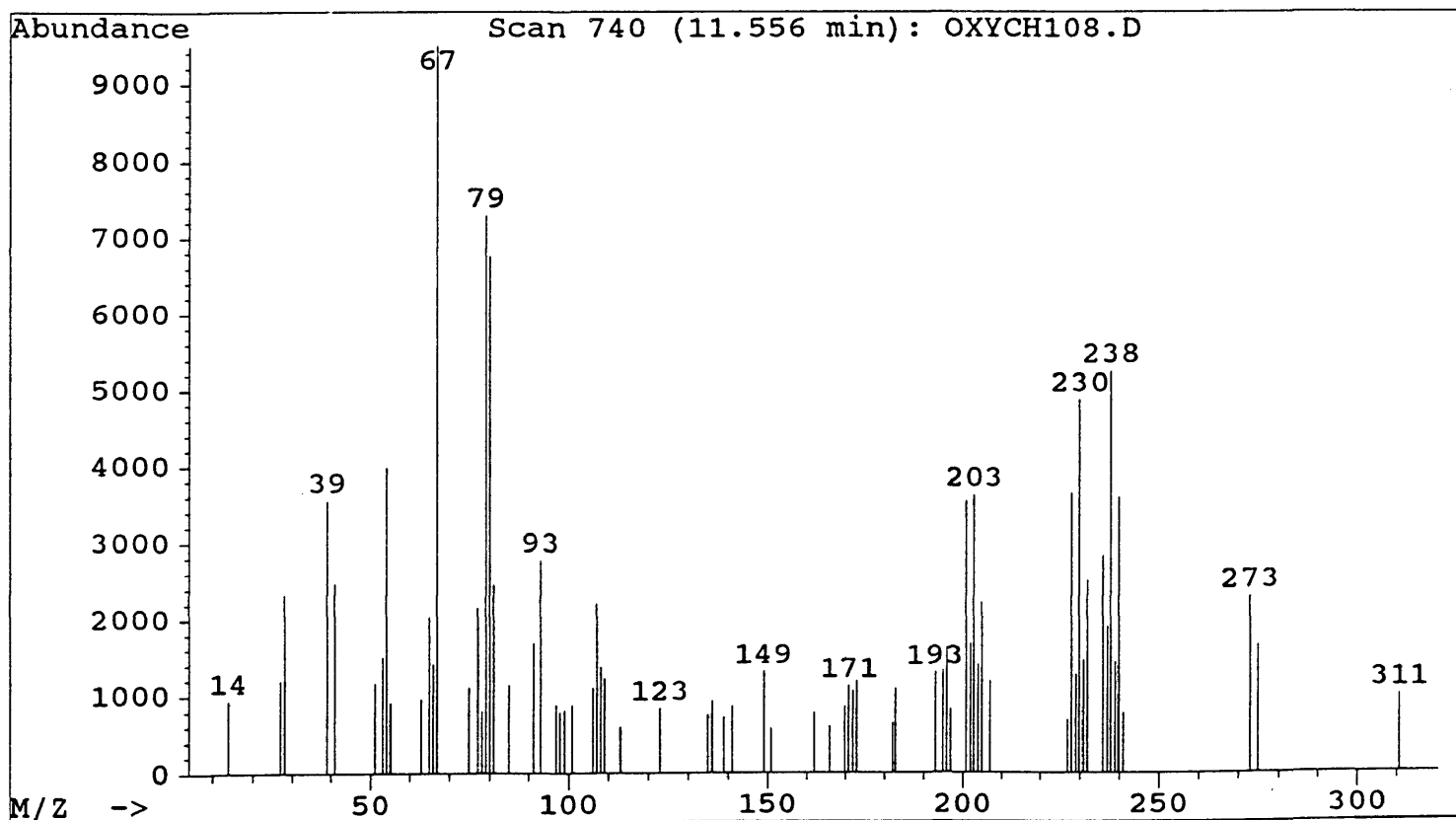
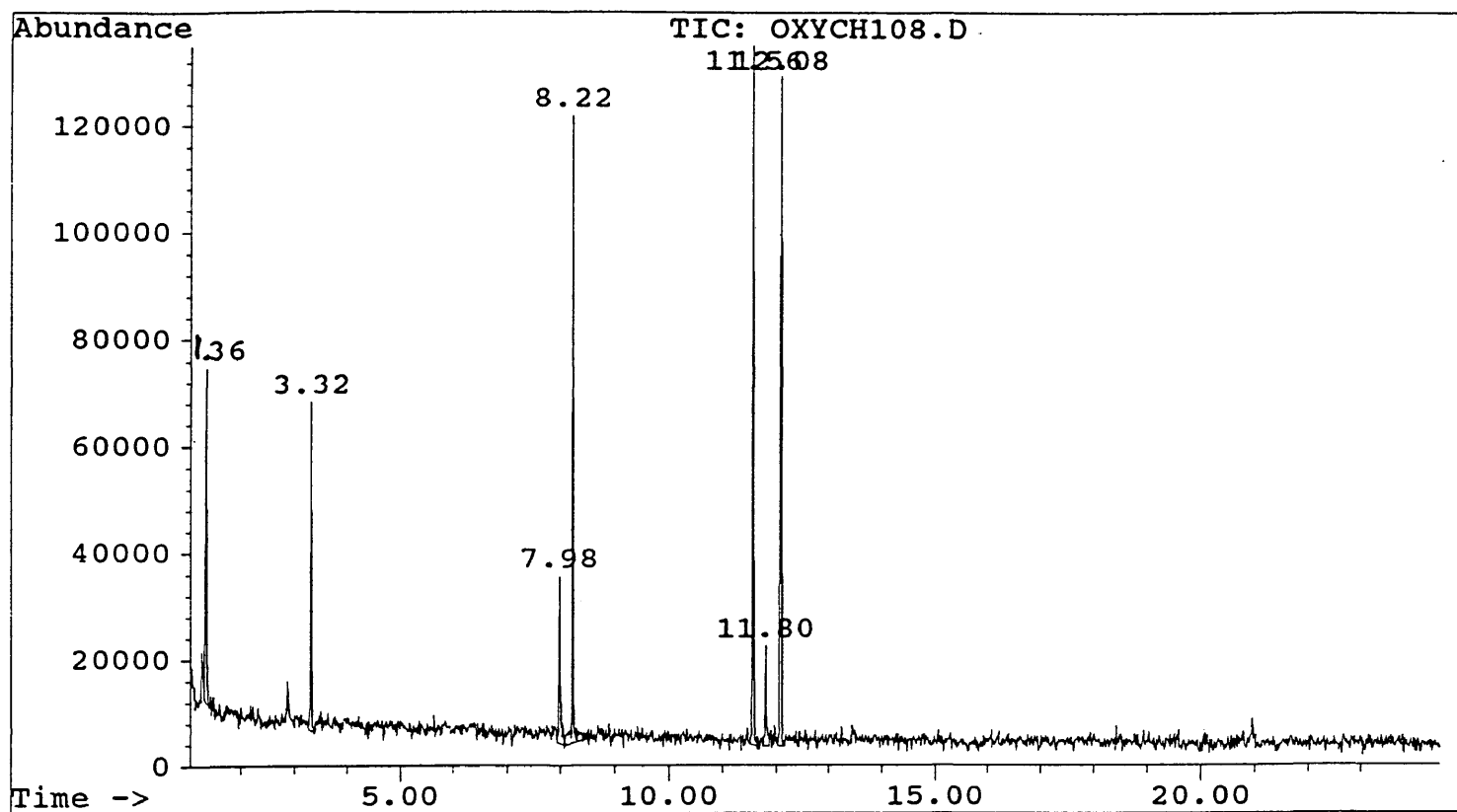
**Figure 15-2.** GC/MS analysis of volatile products from a pyrolyzed 90:10 Nylon 66/Dech Plus mixture



**Figure 15-3.** GC/MS analysis of volatile products from a pyrolyzed 90:10 Nylon 66/Dech Plus mixture



**Figure 15-4.** GC/MS analysis of volatile products from a pyrolyzed 90:10 Nylon 66/Dech Plus mixture



**Figure 15-5.** GC/MS analysis of volatile products from a pyrolyzed 90:10 Nylon 66/Dech Plus mixture

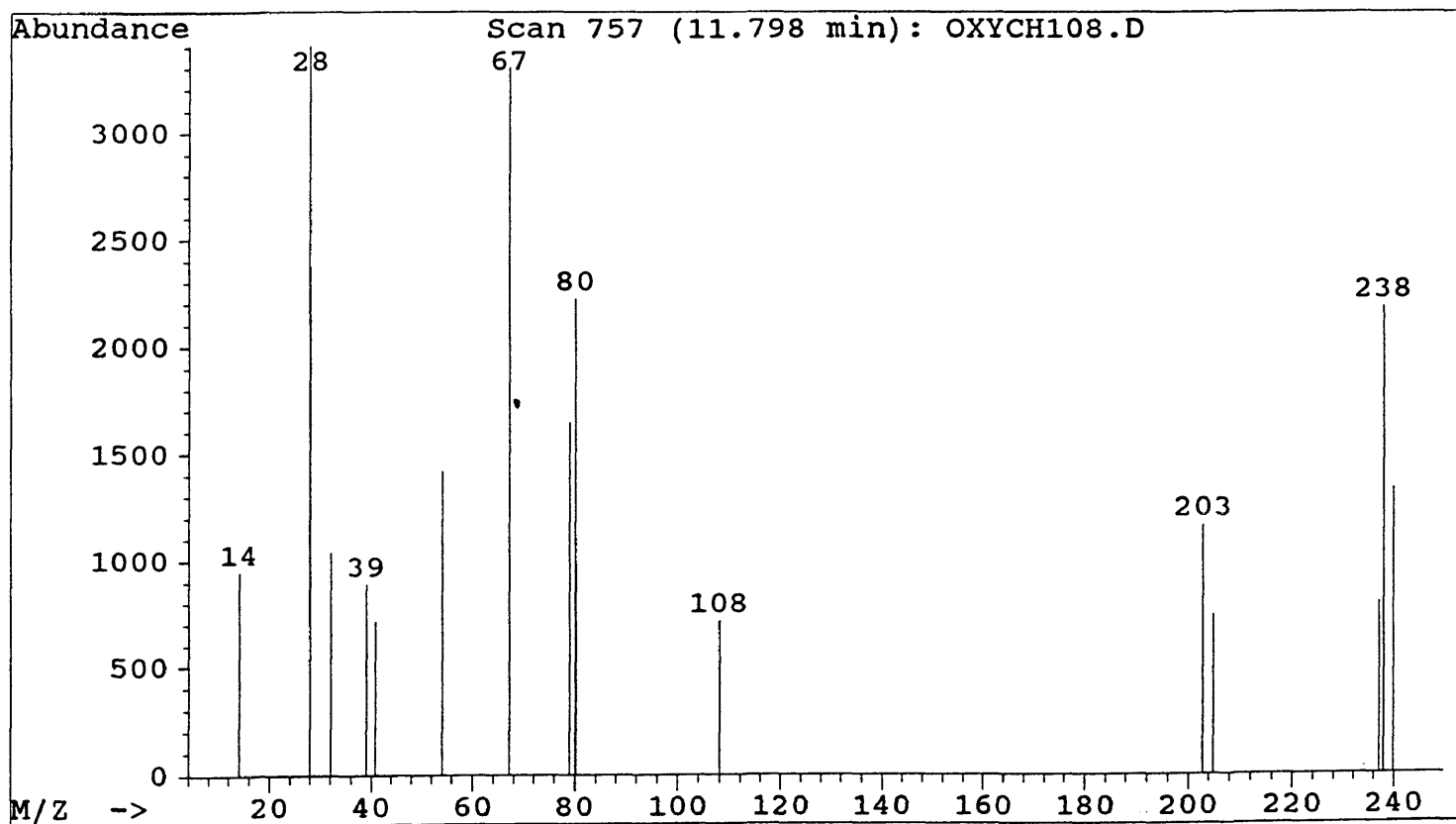
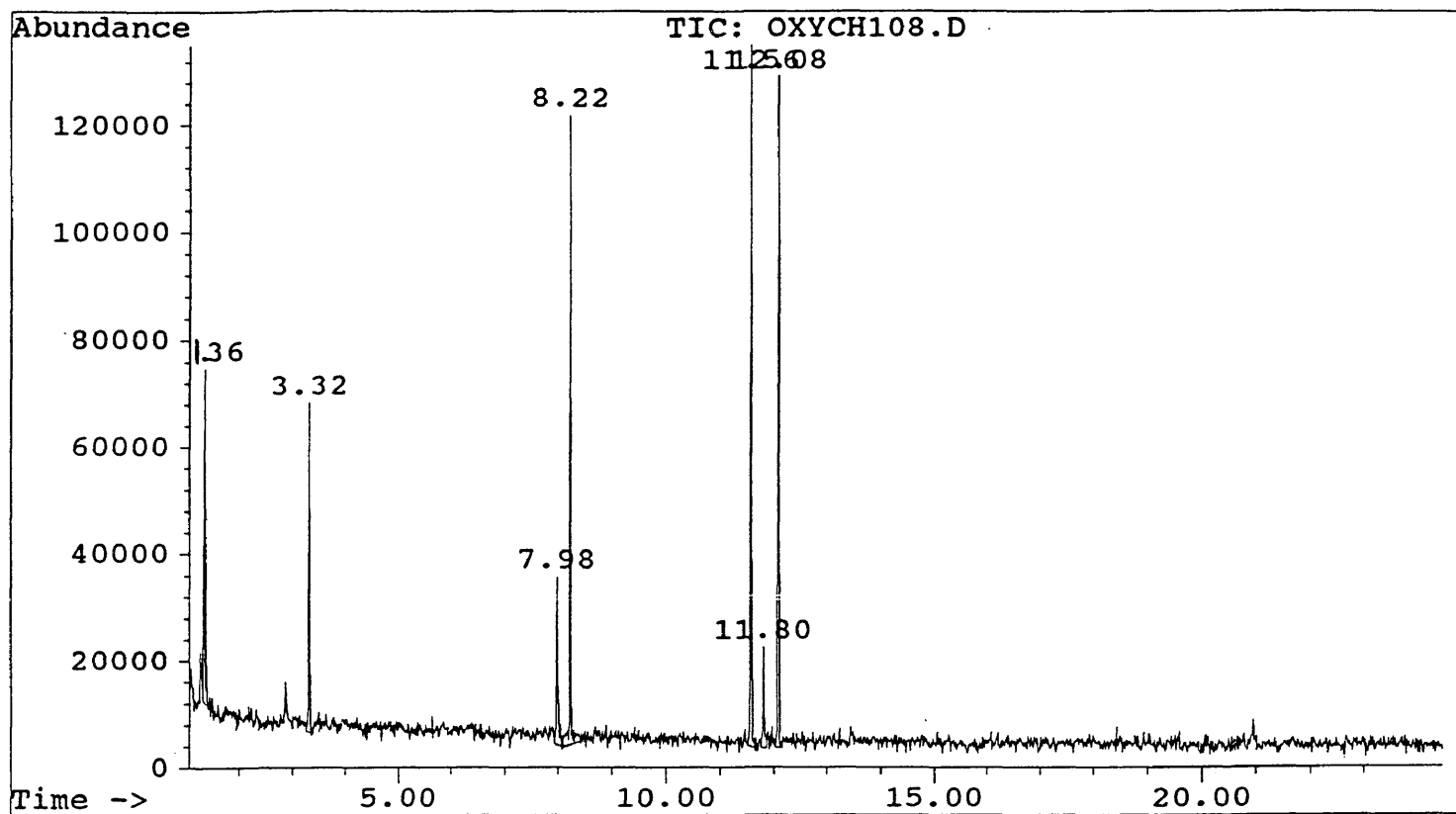


Figure 15-6. GC/MS analysis of volatile products from a pyrolyzed 90:10 Nylon 66/Dech Plus mixture

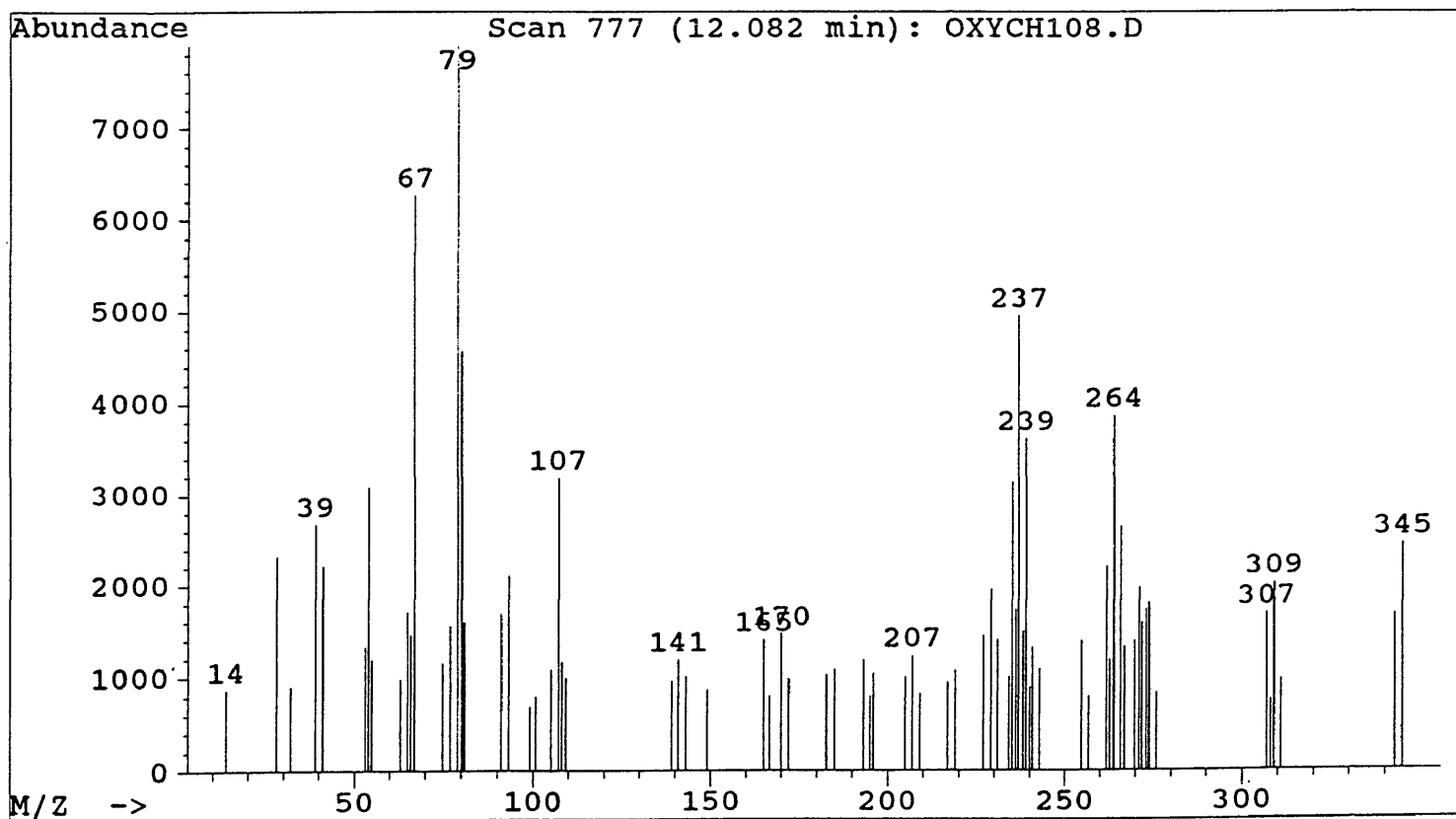
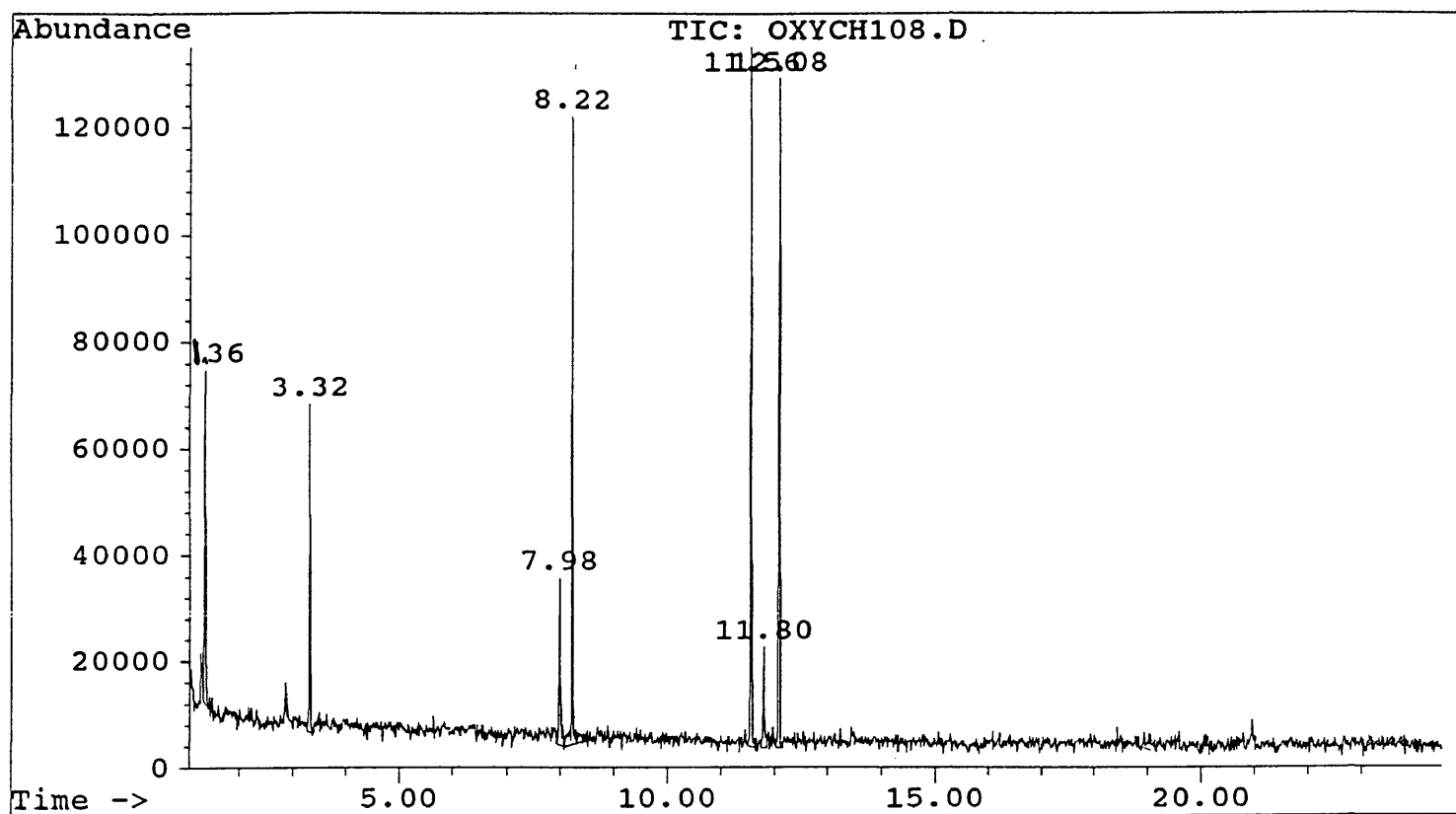
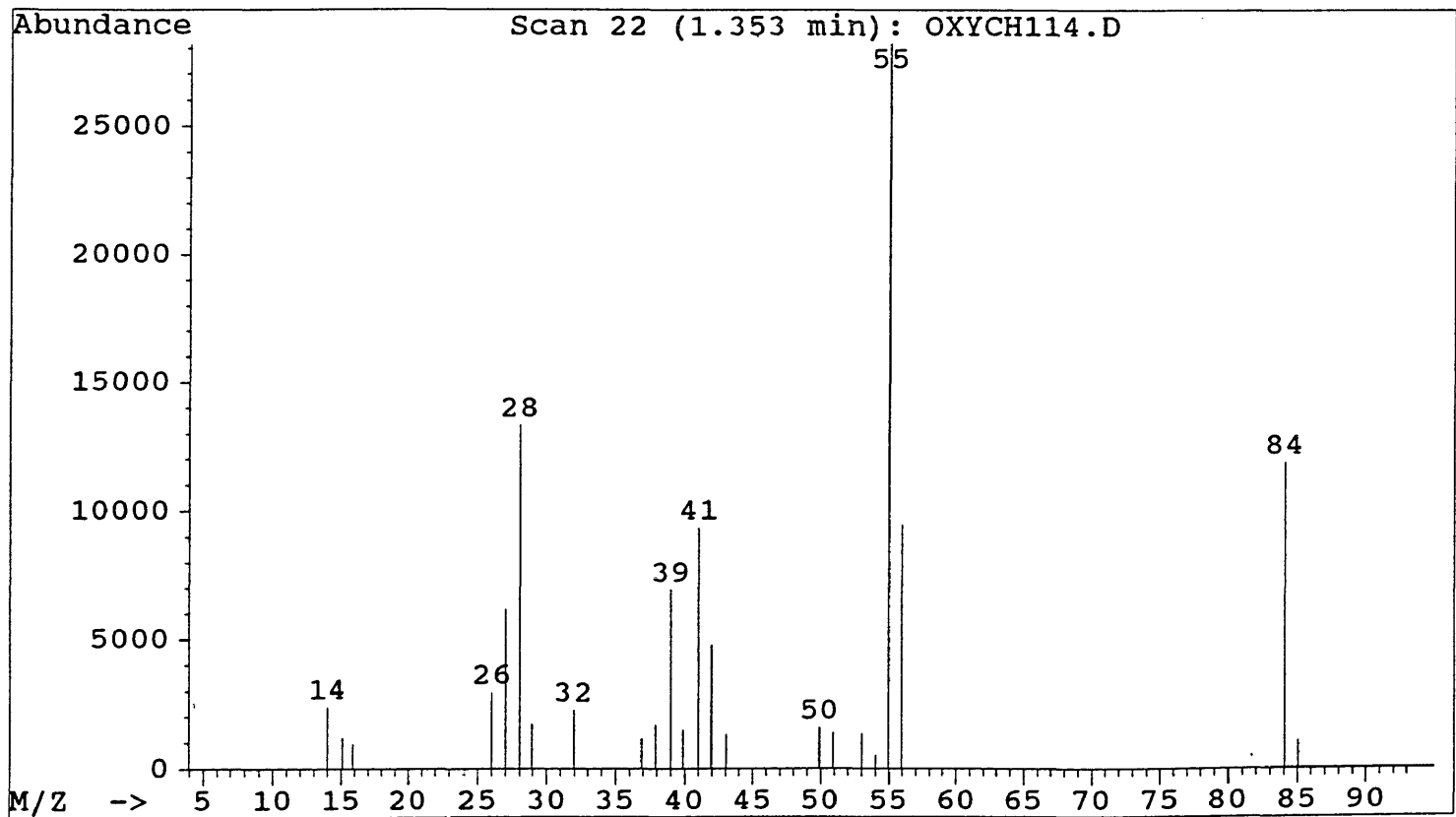
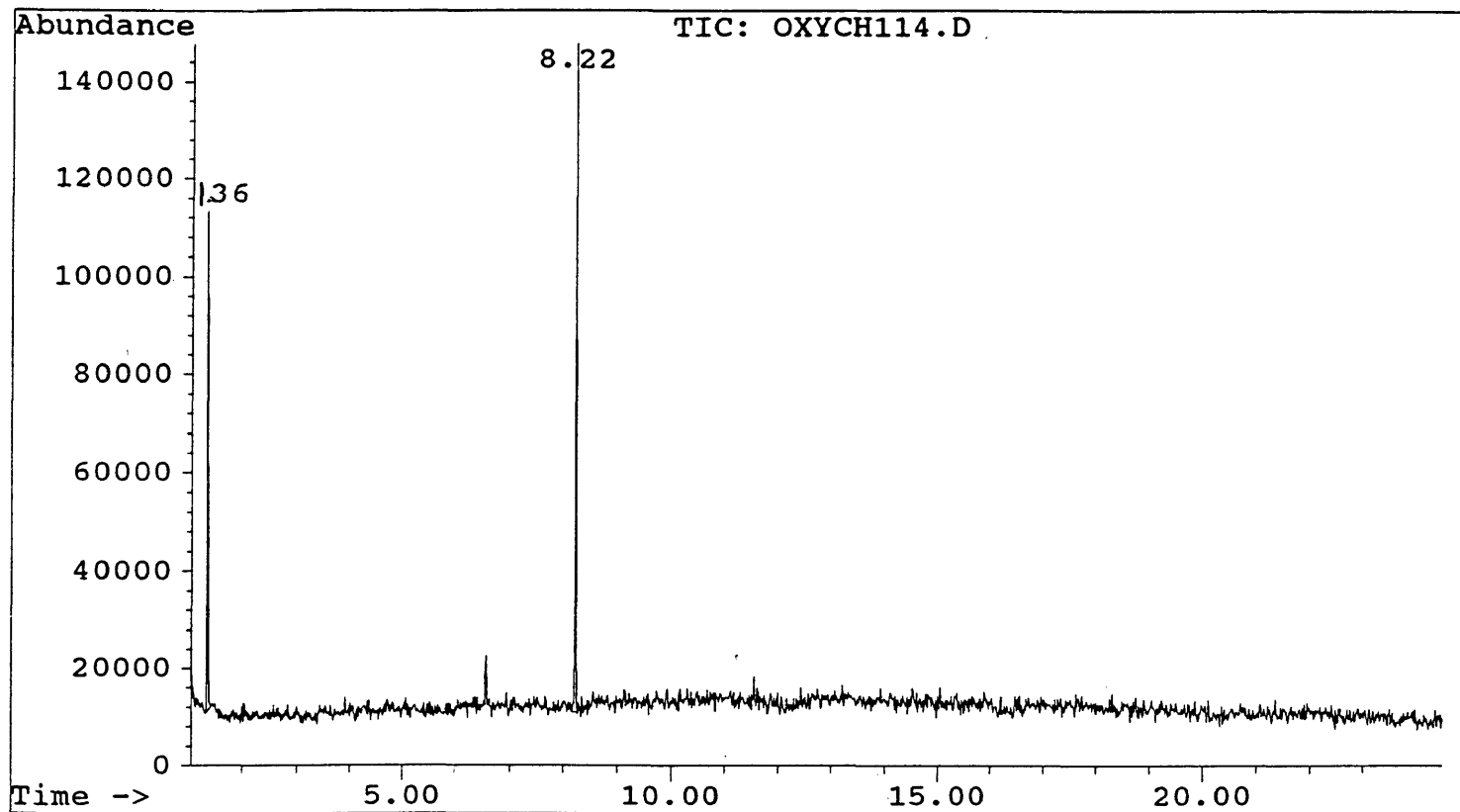
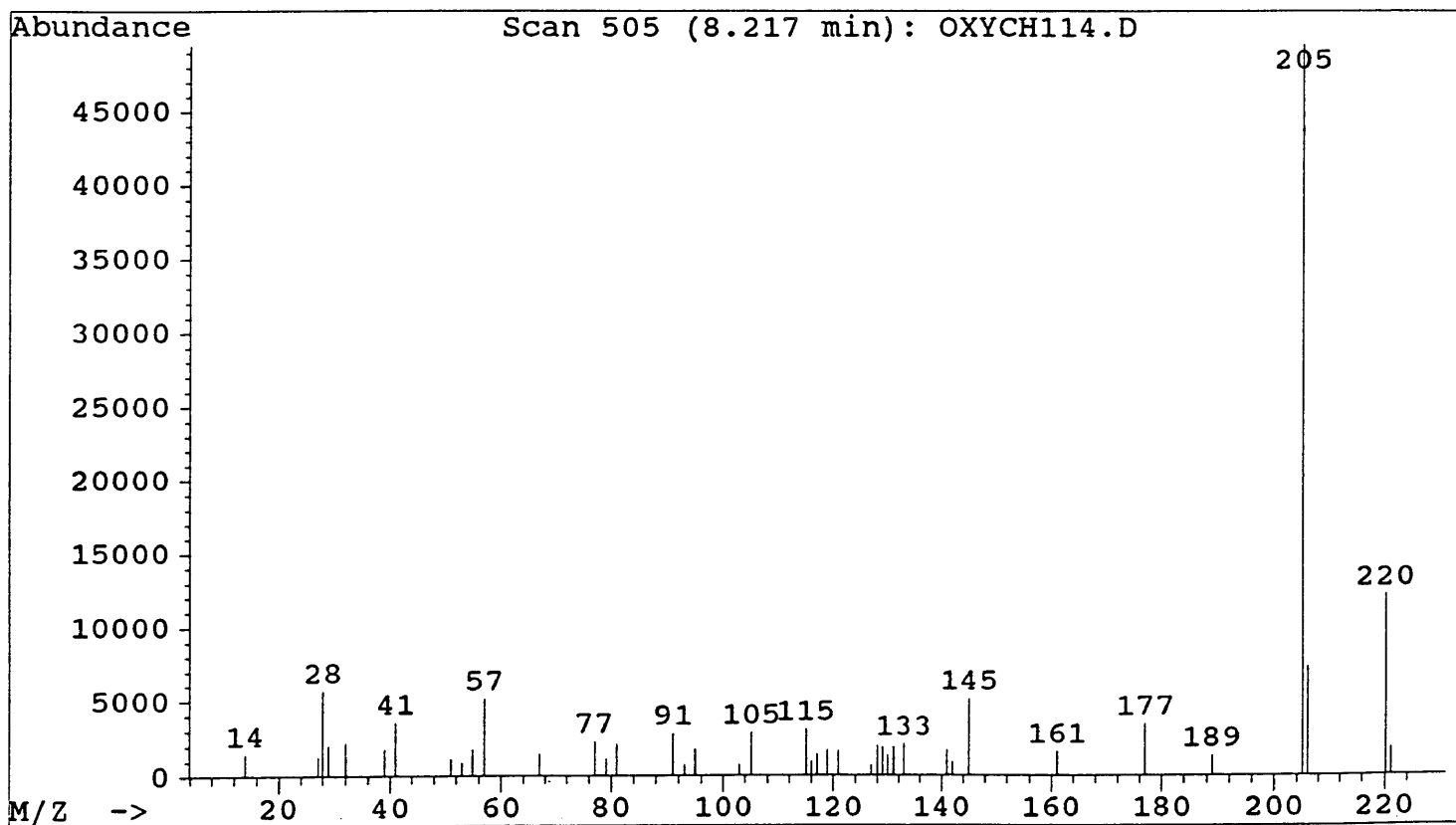
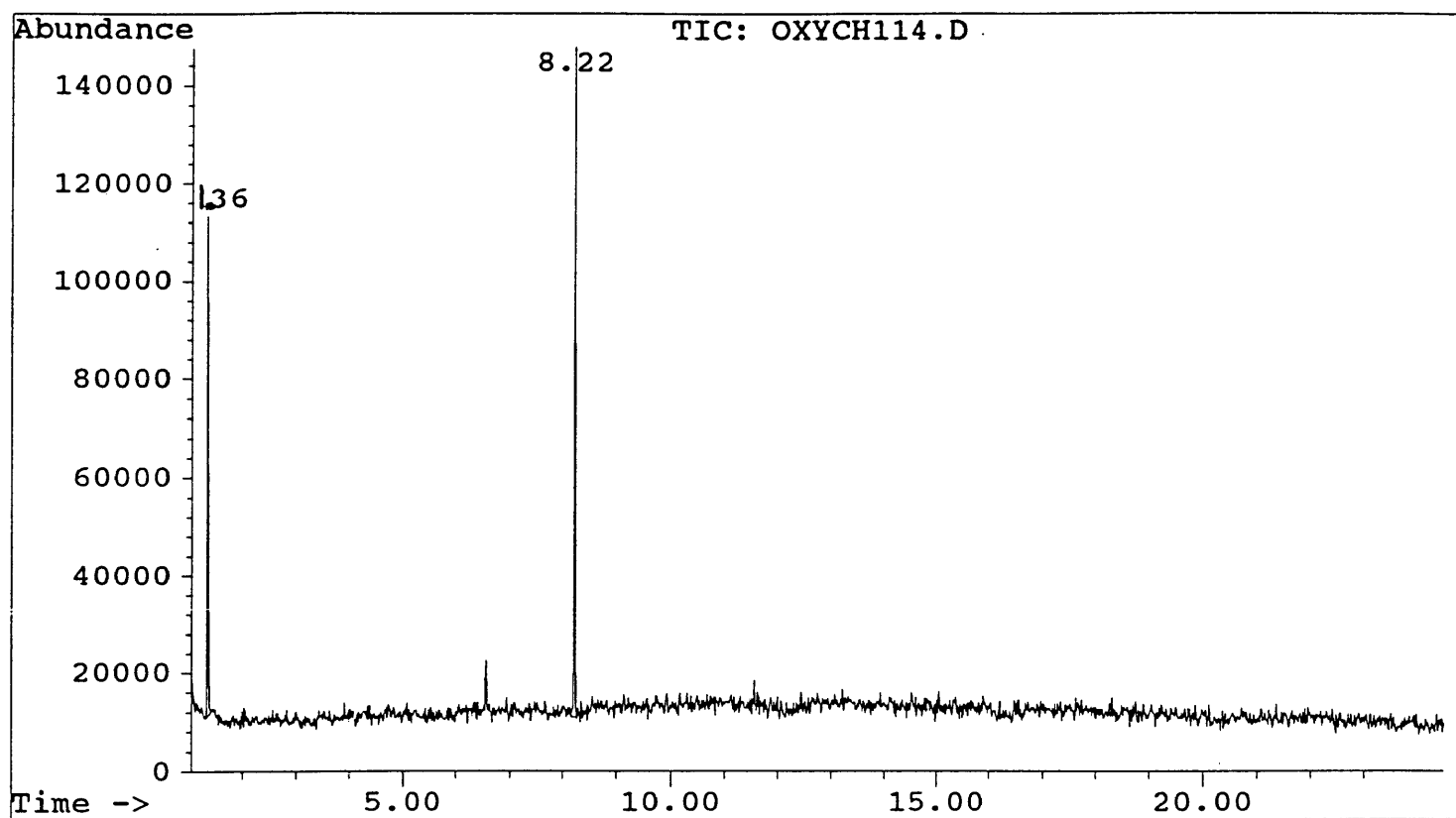


Figure 15-7. GC/MS analysis of volatile products from a pyrolyzed 90:10 Nylon 66/Dech Plus mixture

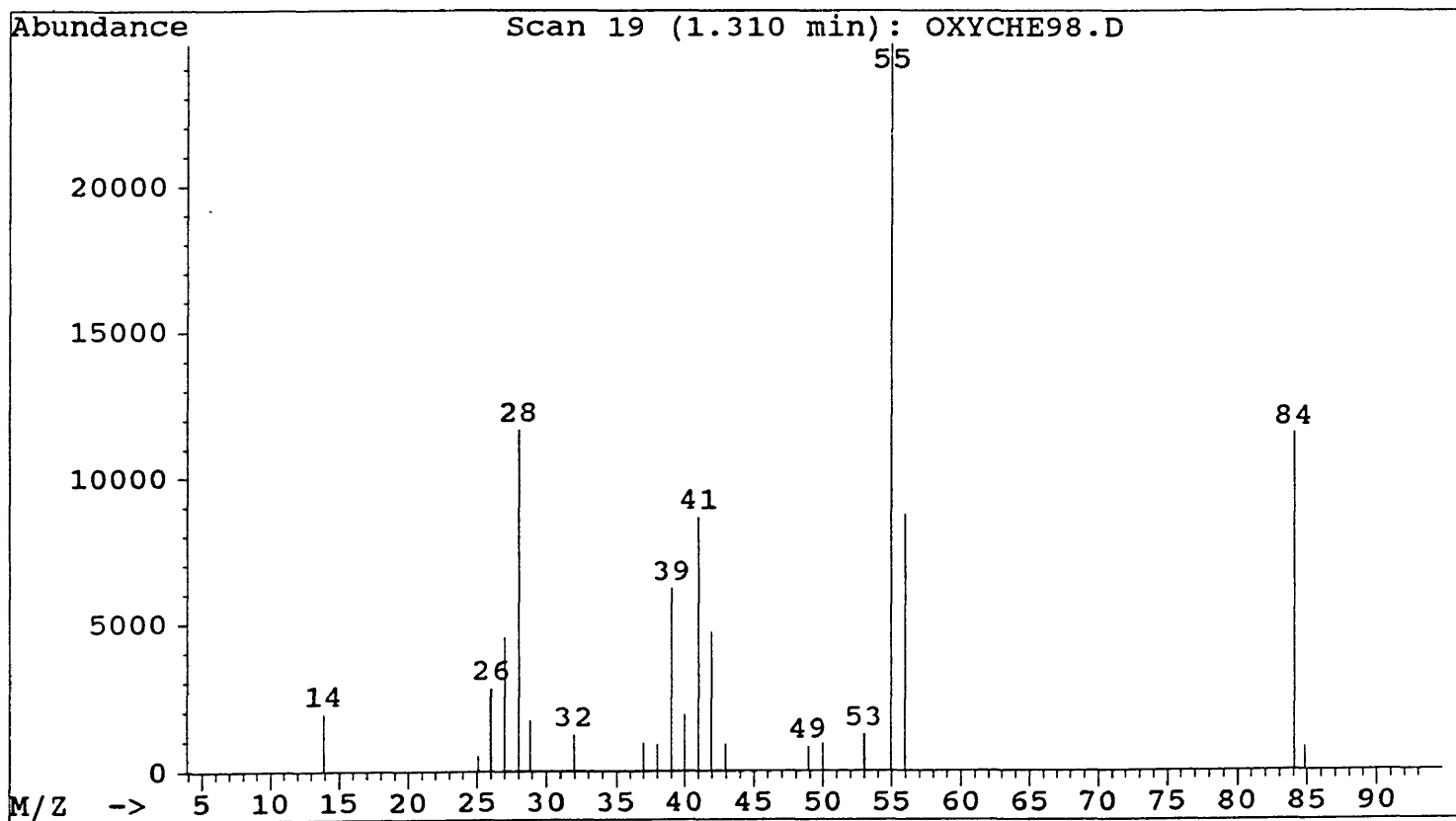
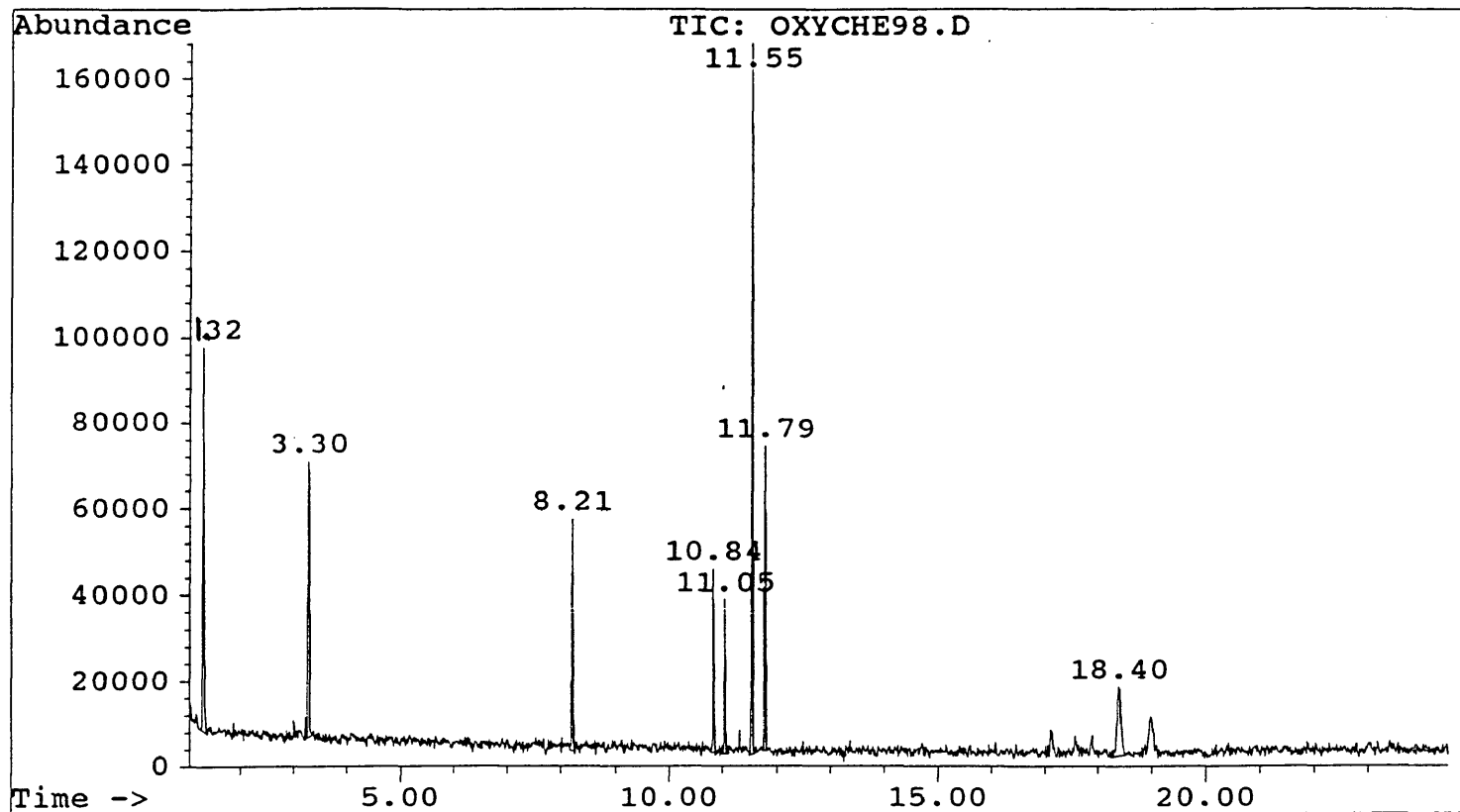




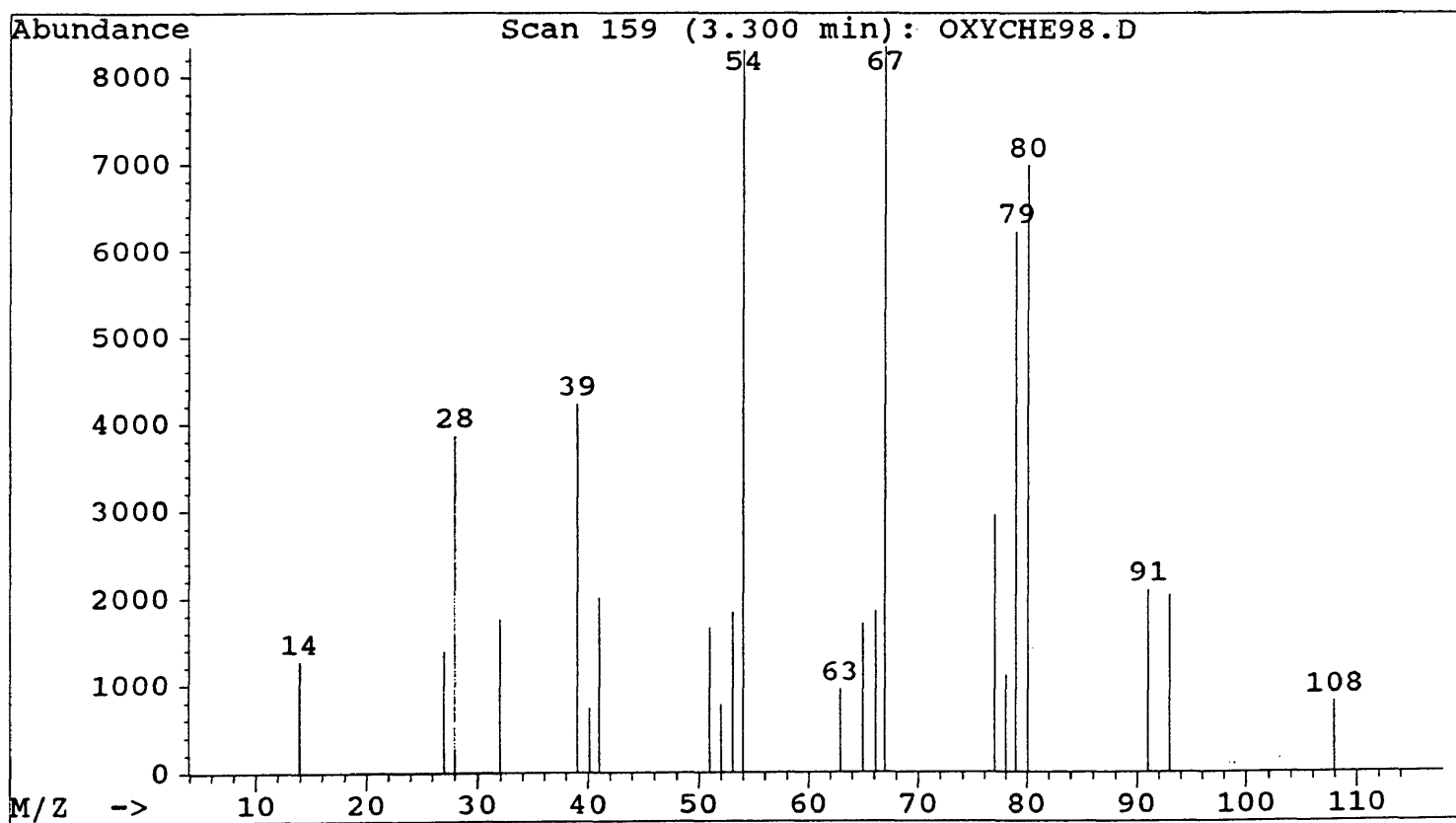
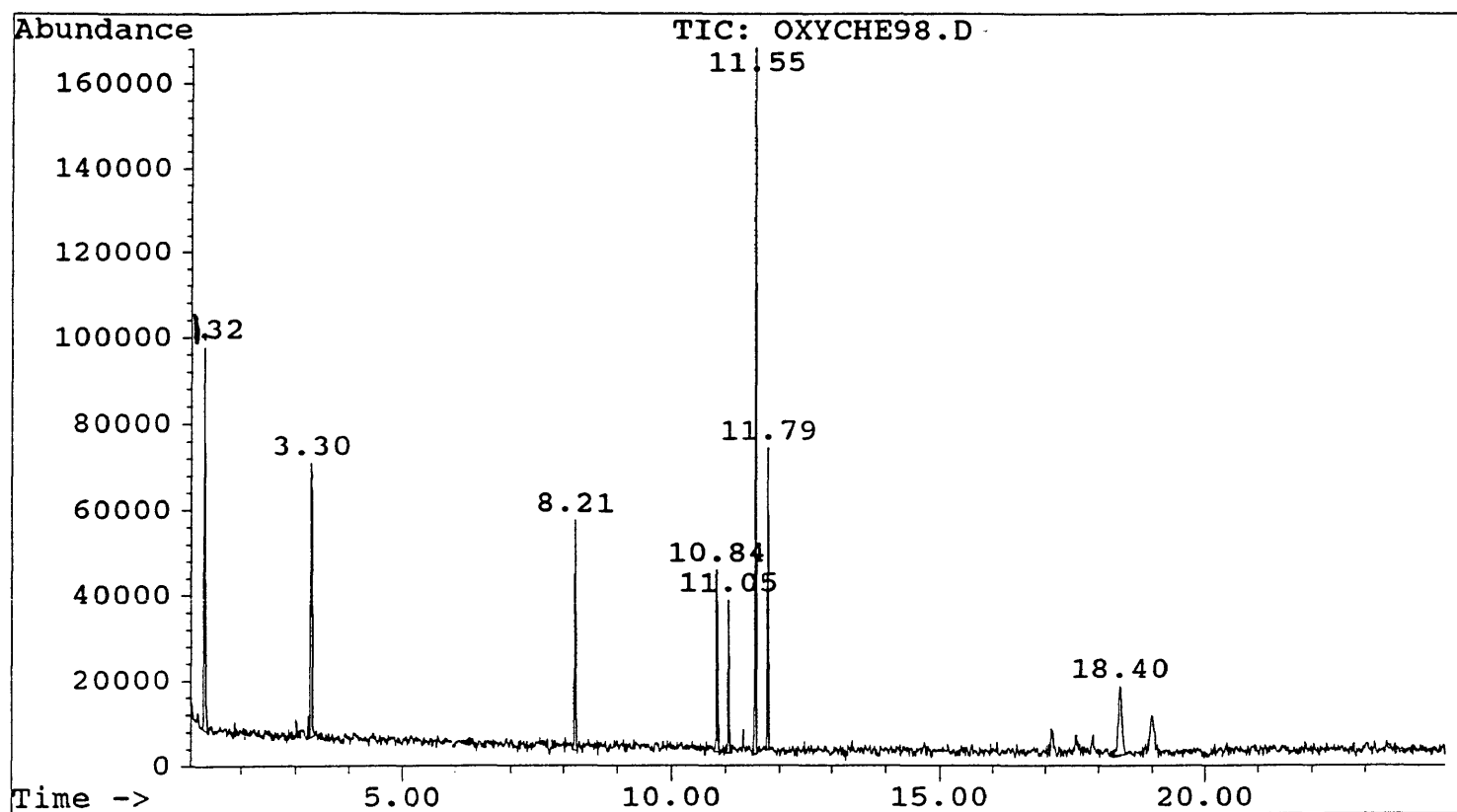
**Figure 16-1.** GC/MS analysis of volatile products from a pyrolyzed 90:10 Nylon 66/Sb<sub>2</sub>O<sub>3</sub> mixture



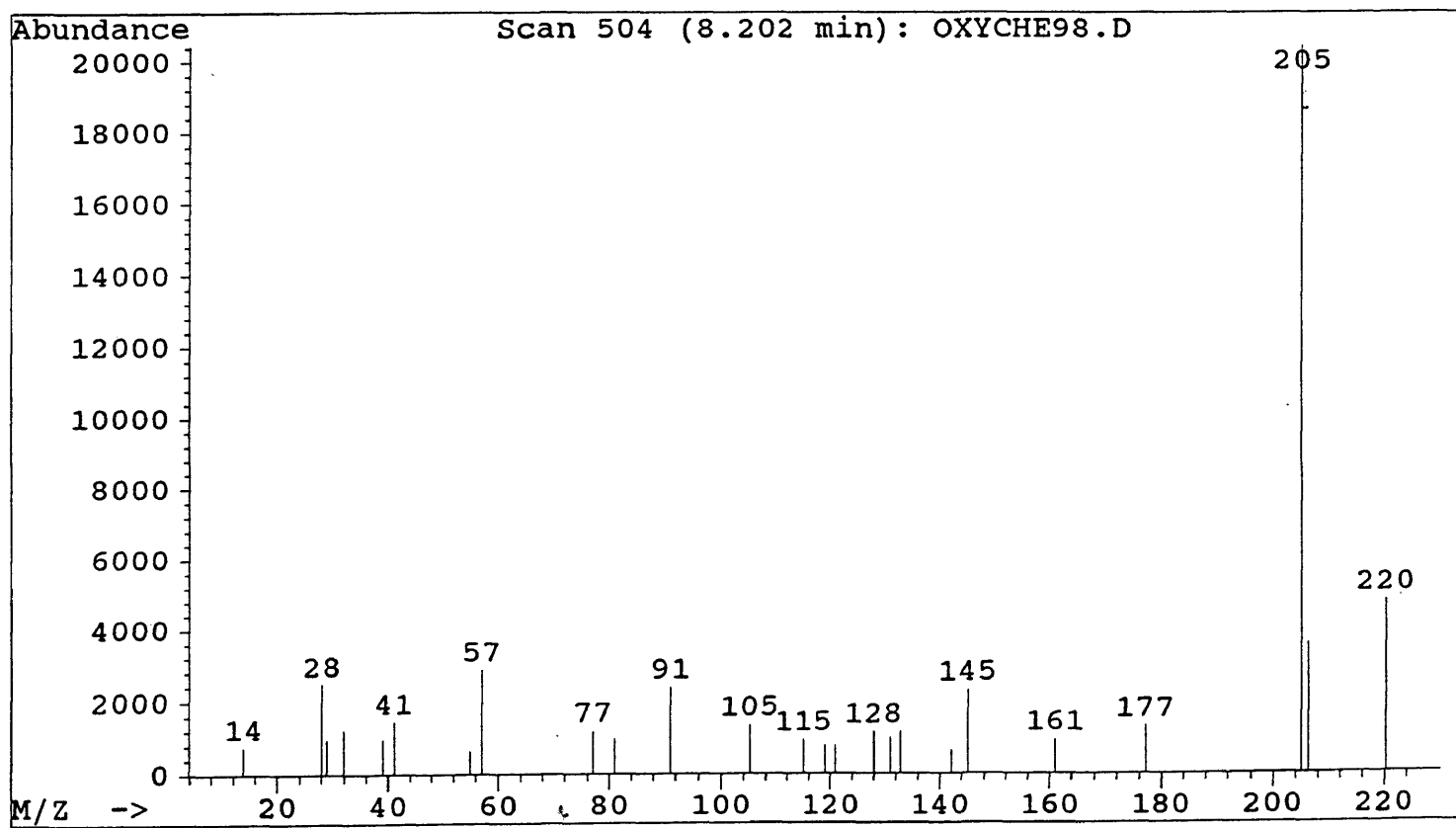
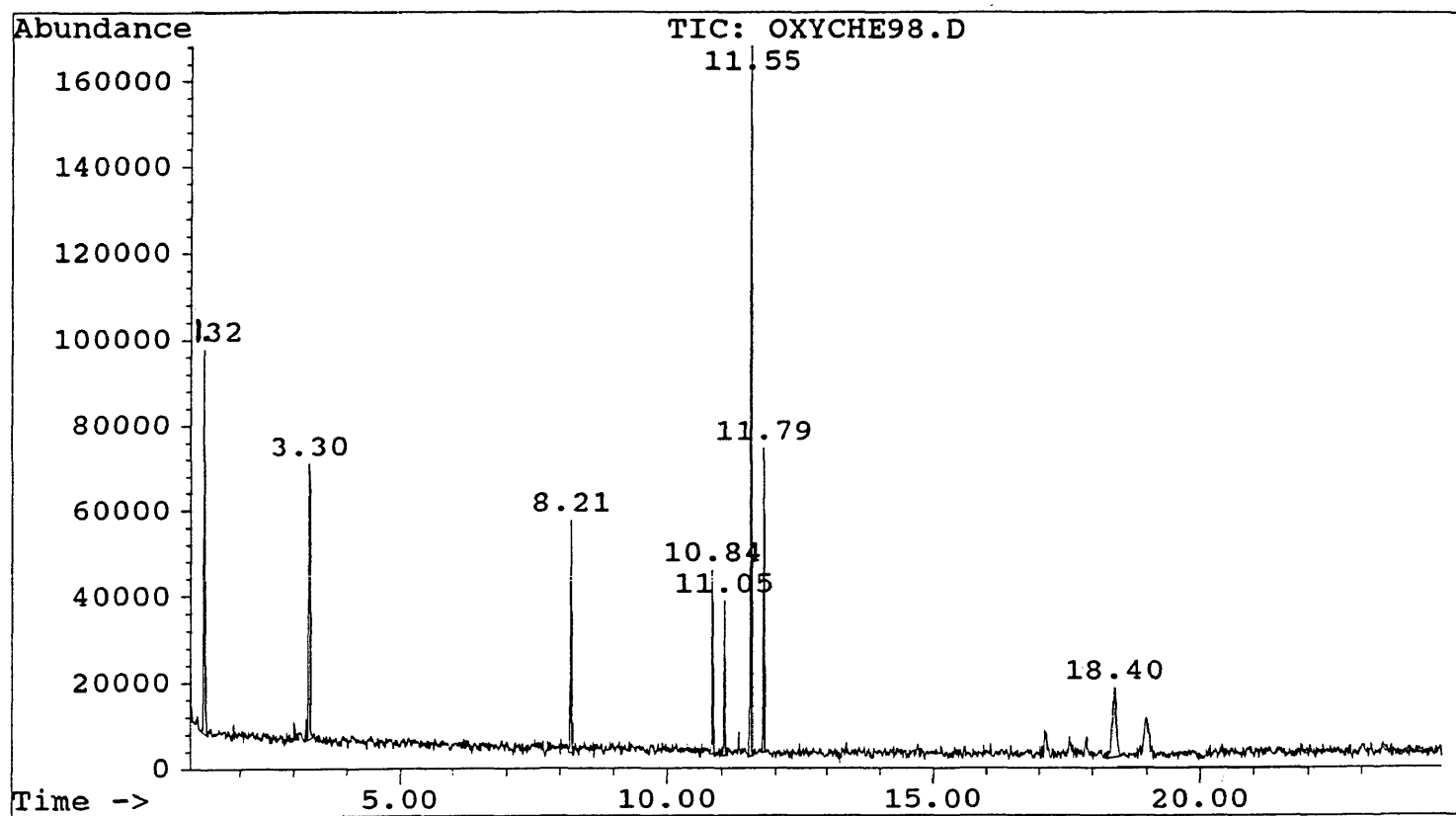
**Figure 16-2.** GC/MS analysis of volatile products from a pyrolyzed 90:10 Nylon 66/Sb<sub>2</sub>O<sub>3</sub> mixture



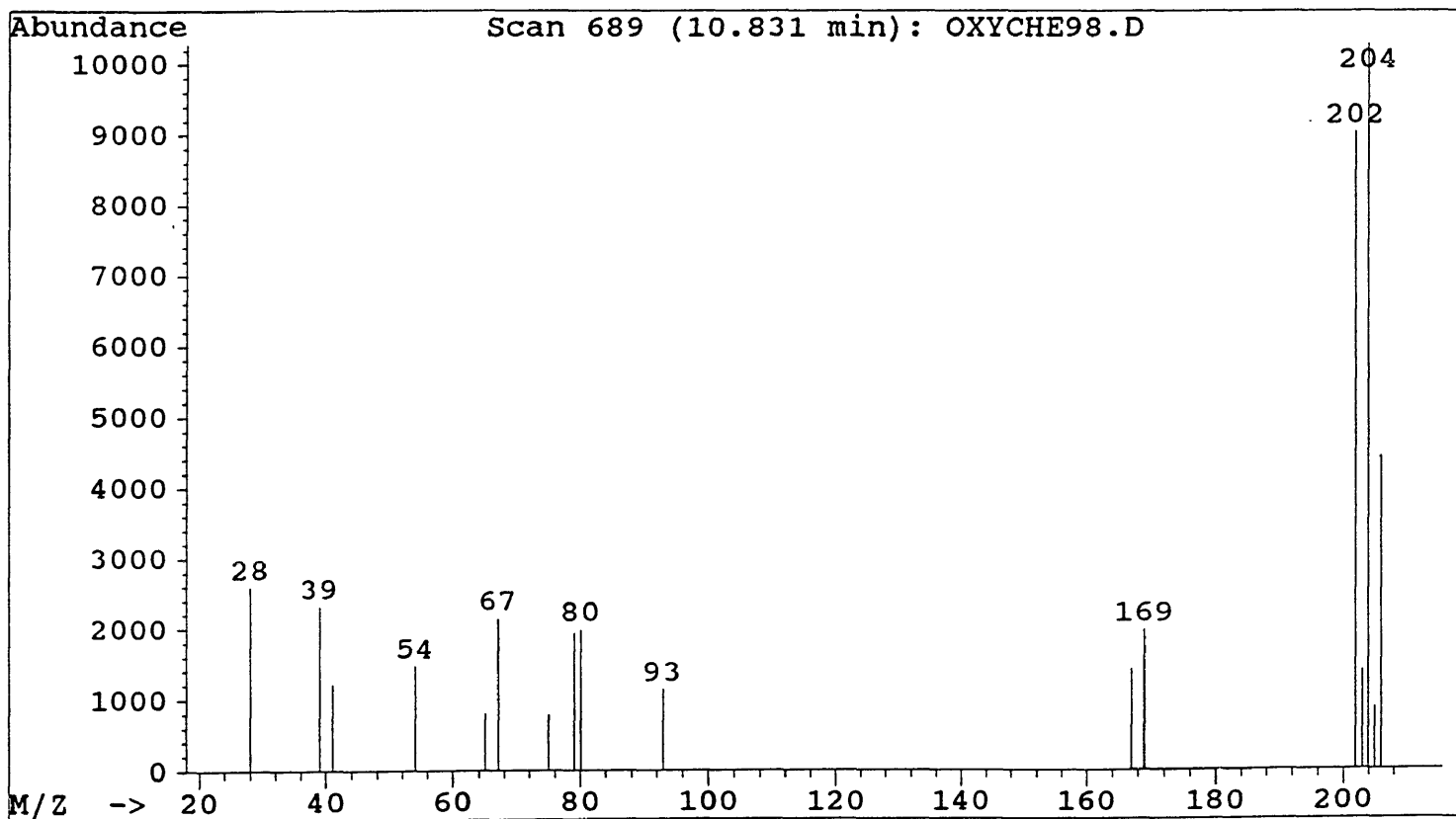
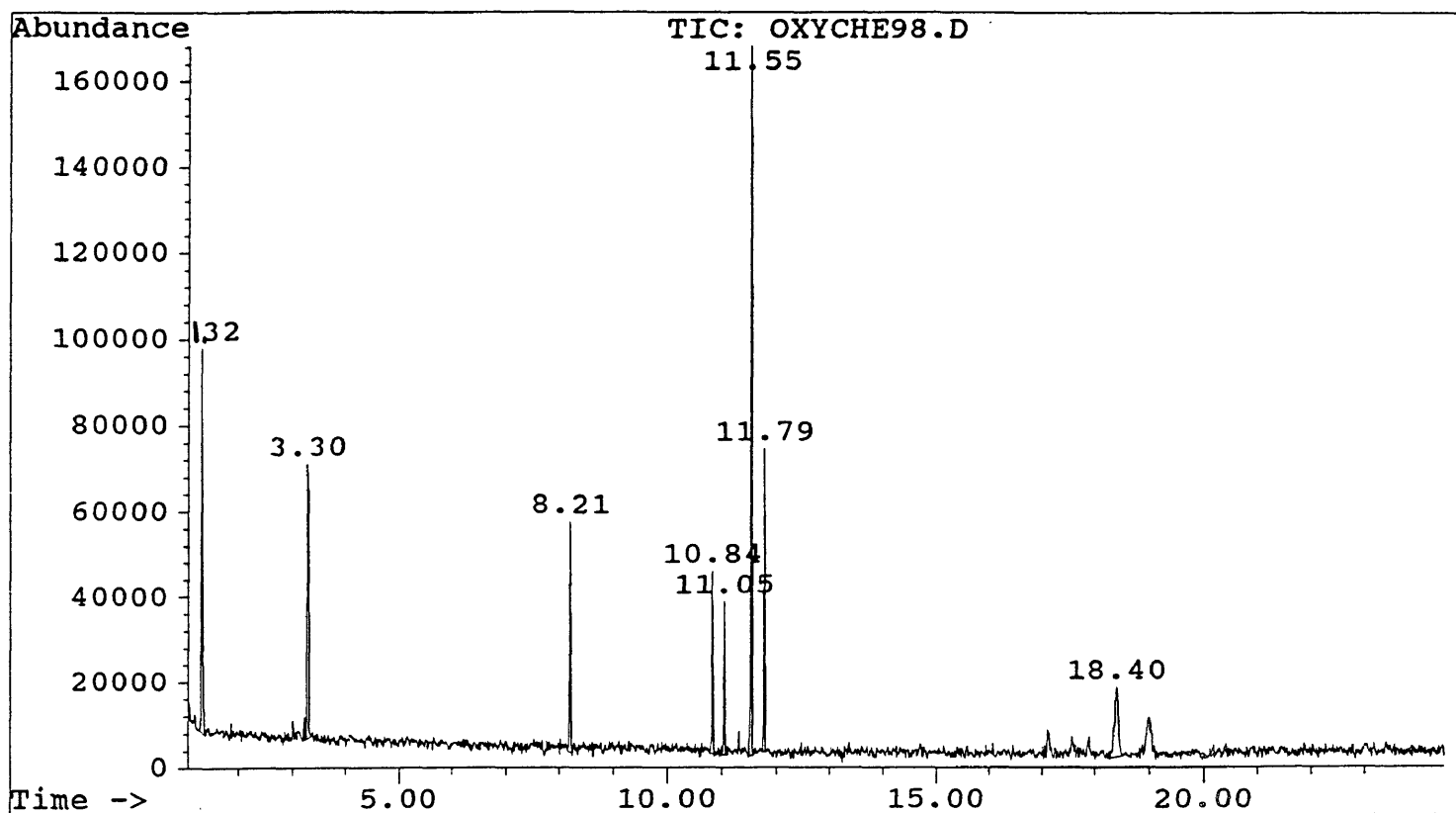
**Figure 17-1.** GC/MS analysis of volatile products from a pyrolyzed 82:10:8 Nylon 66/Dech Plus/  $\text{Sb}_2\text{O}_3$  mixture



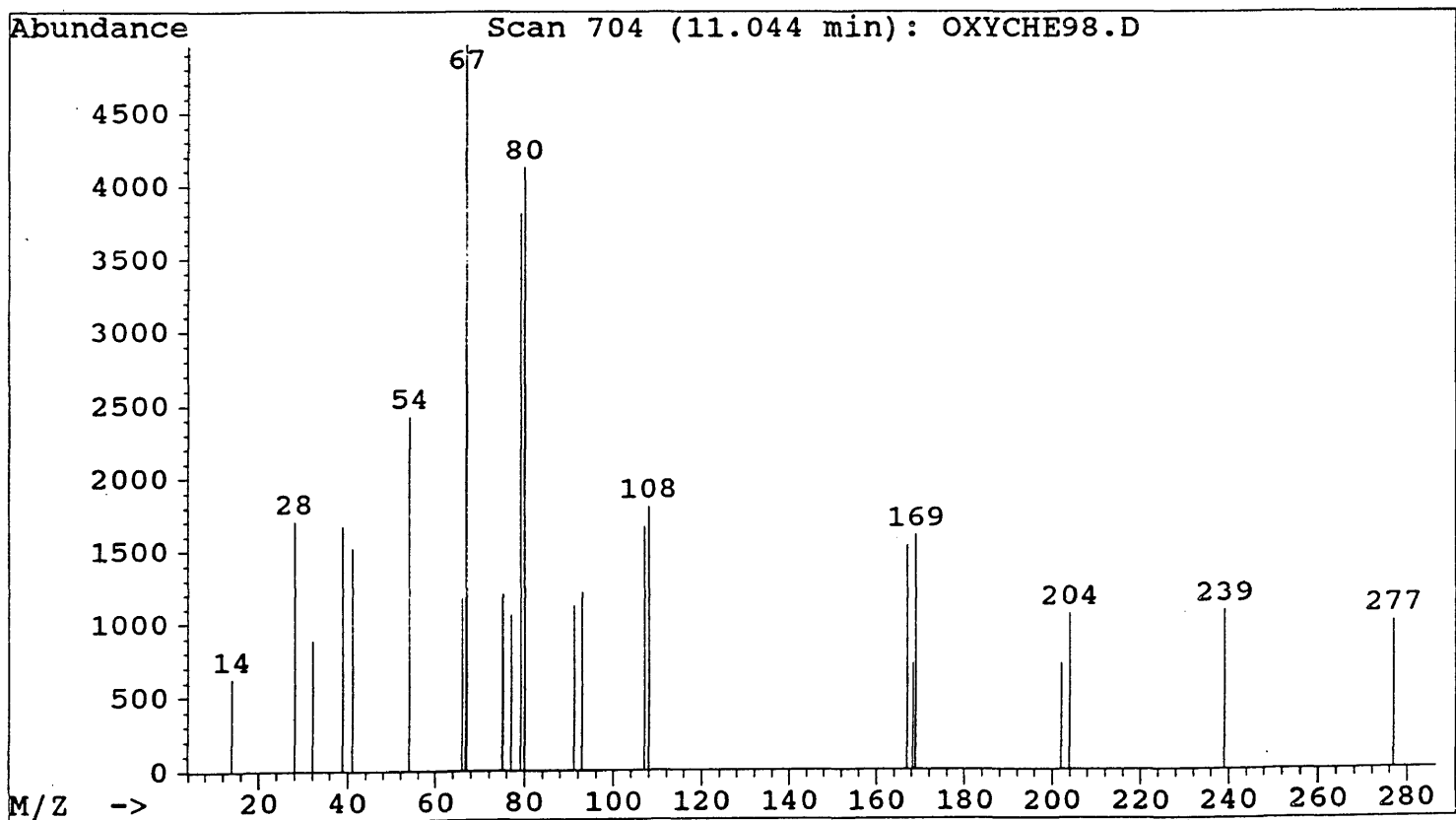
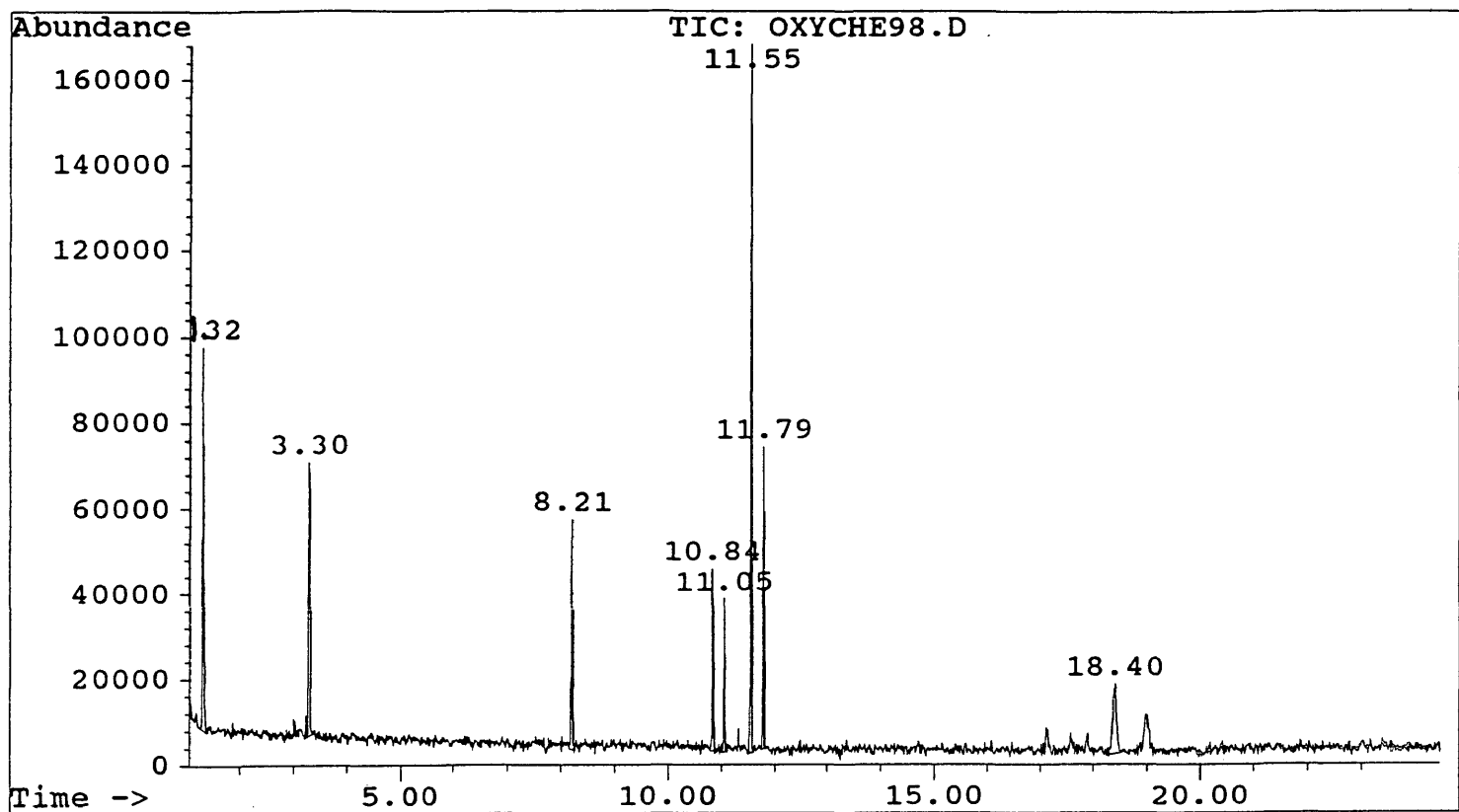
**Figure 17-2.** GC/MS analysis of volatile products from a pyrolyzed 82:10:8 Nylon 66/Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture



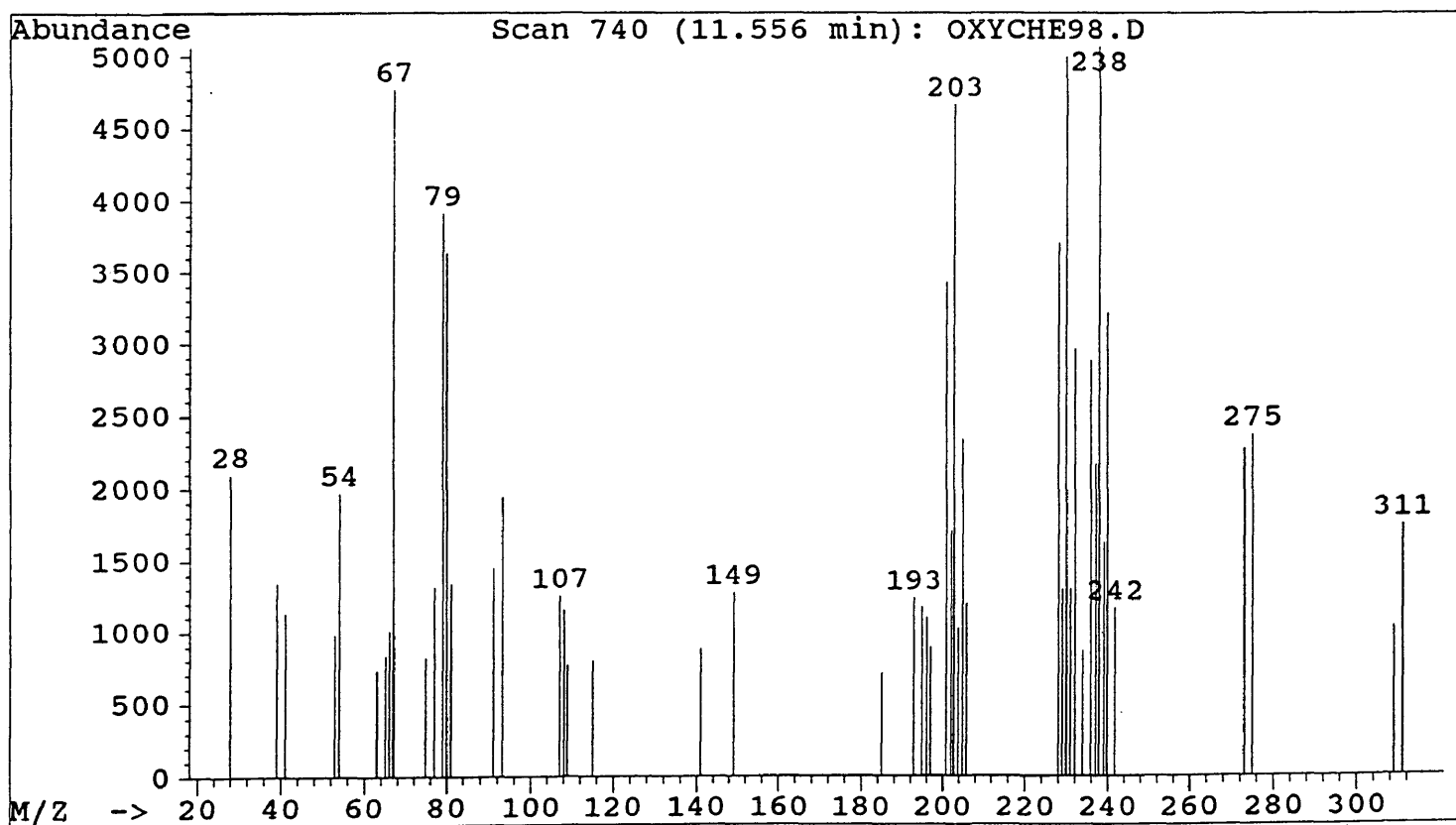
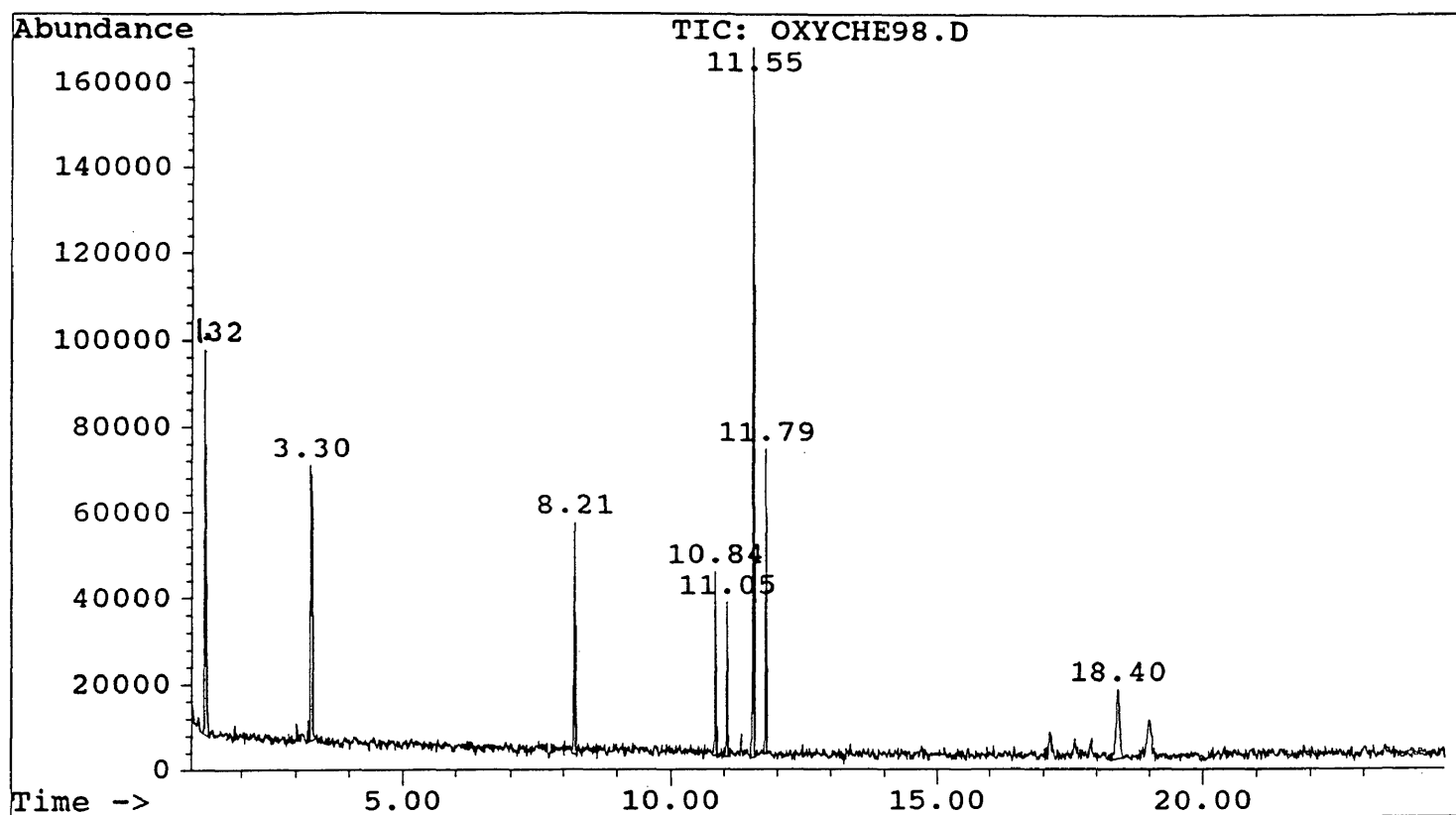
**Figure 17-3.** GC/MS analysis of volatile products from a pyrolyzed 82:10:8 Nylon 66/Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture



**Figure 17-4.** GC/MS analysis of volatile products from a pyrolyzed 82:10:8 Nylon 66/Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture

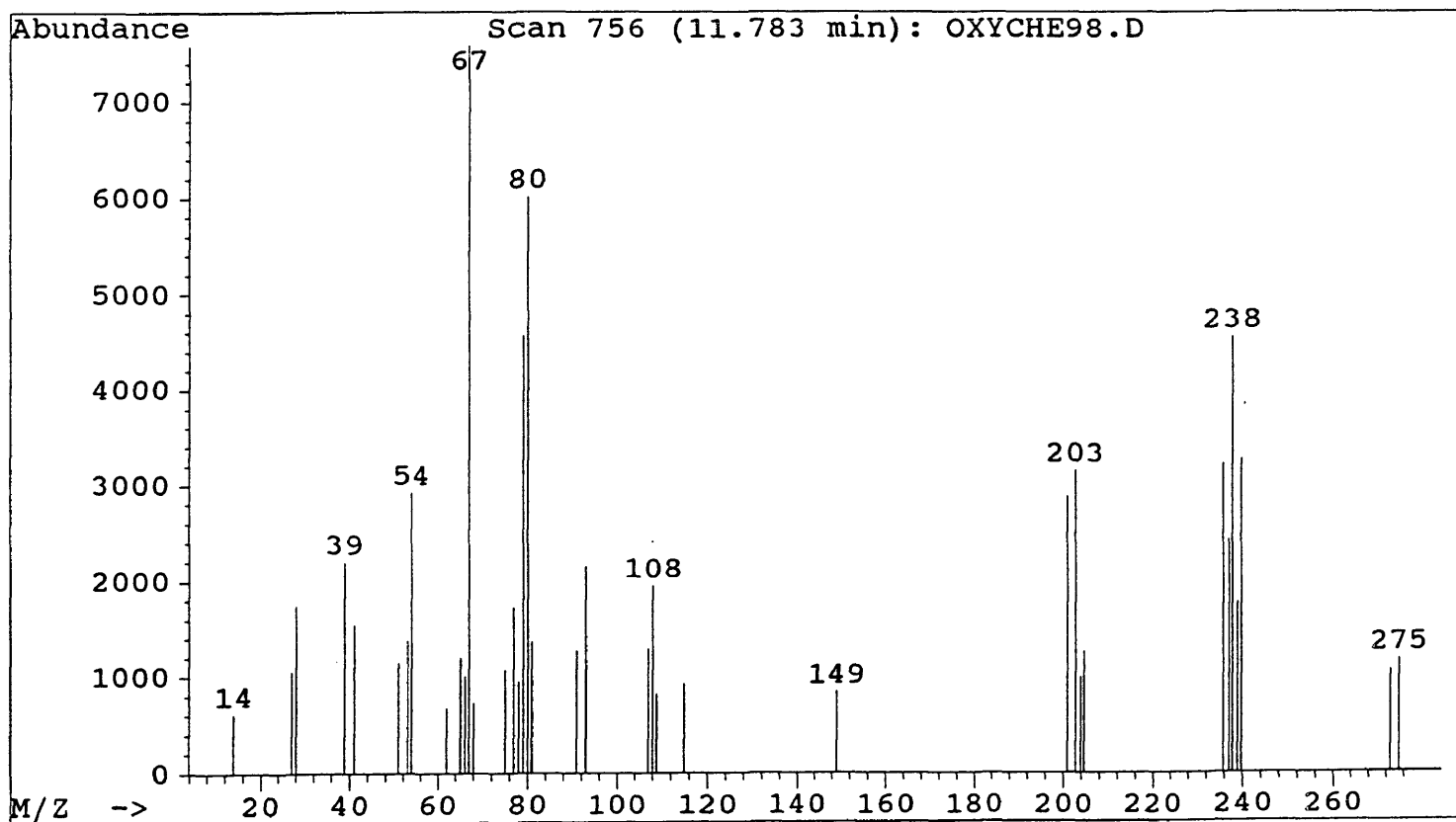
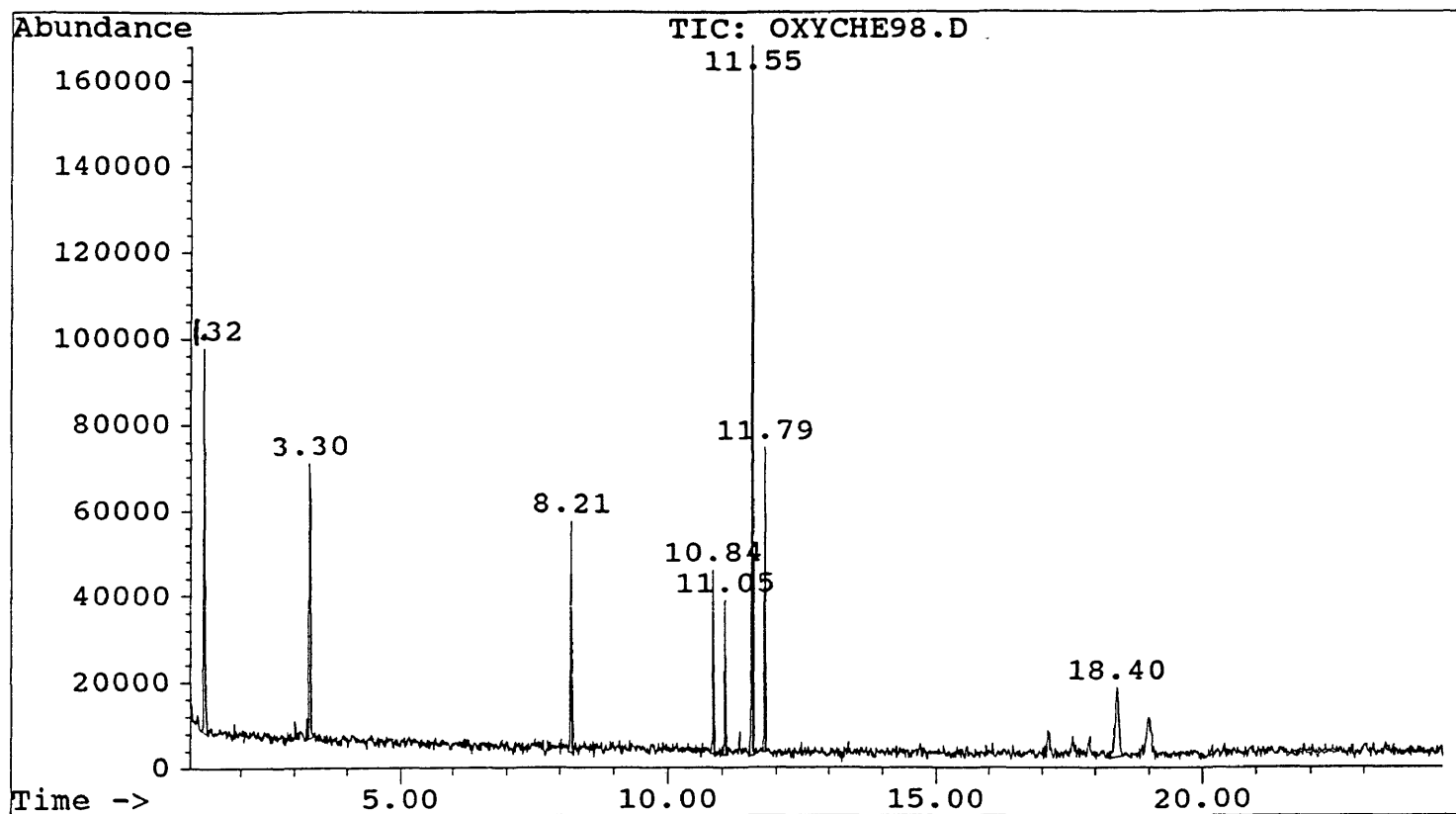


**Figure 17-5.** GC/MS analysis of volatile products from a pyrolyzed 82:10:8 Nylon 66/Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture

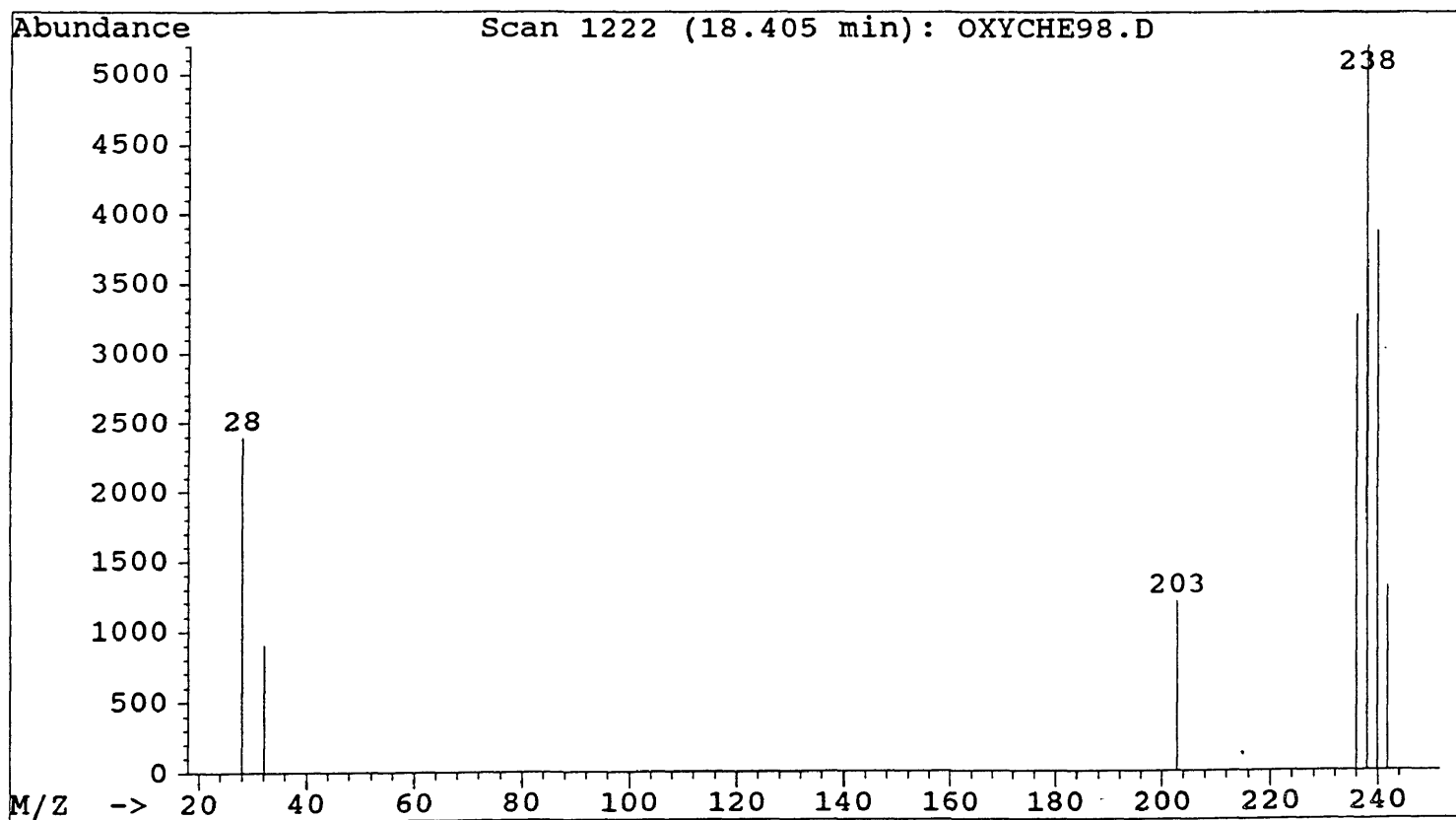
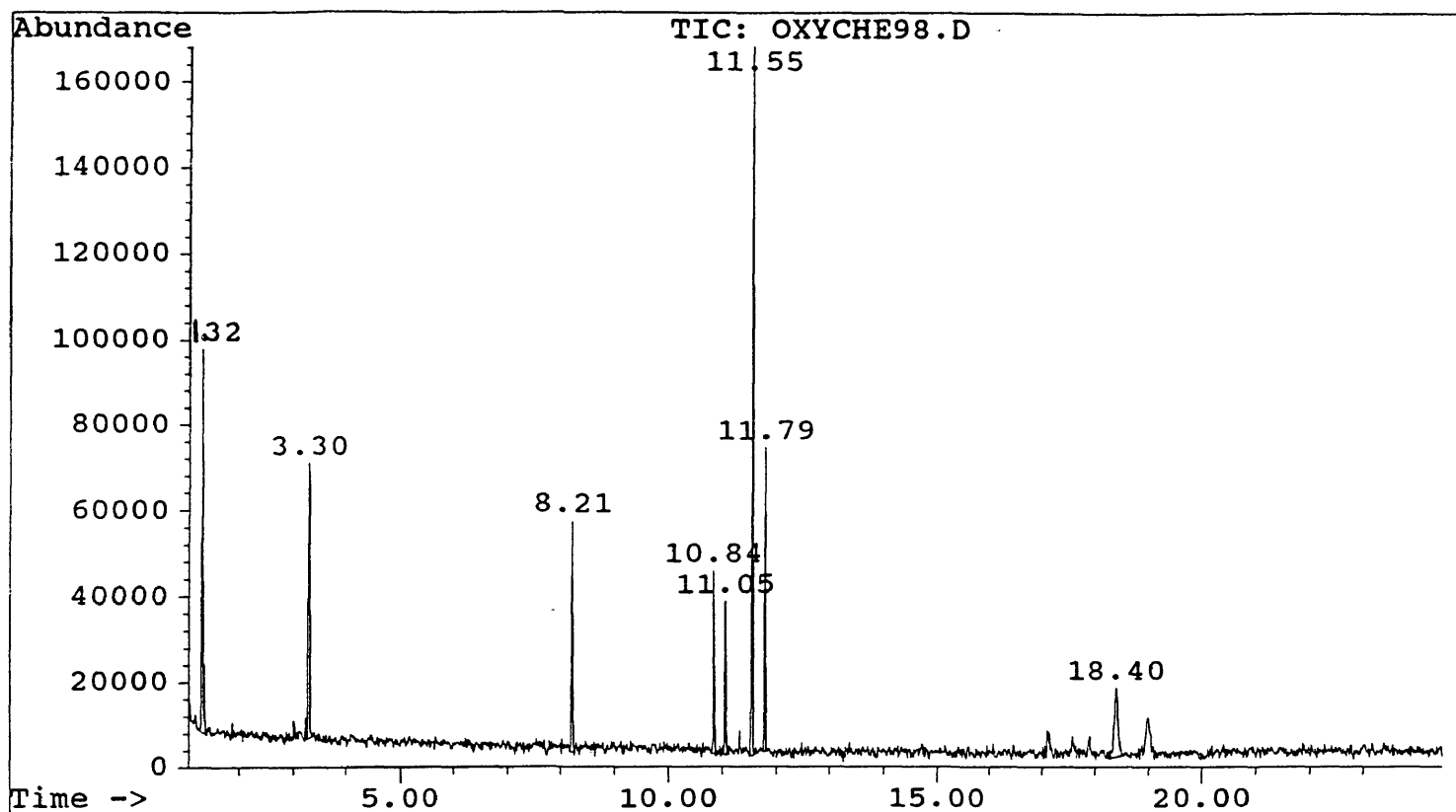


**Figure 17-6.** GC/MS analysis of volatile products from a pyrolyzed 82:10:8 Nylon 66/Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture

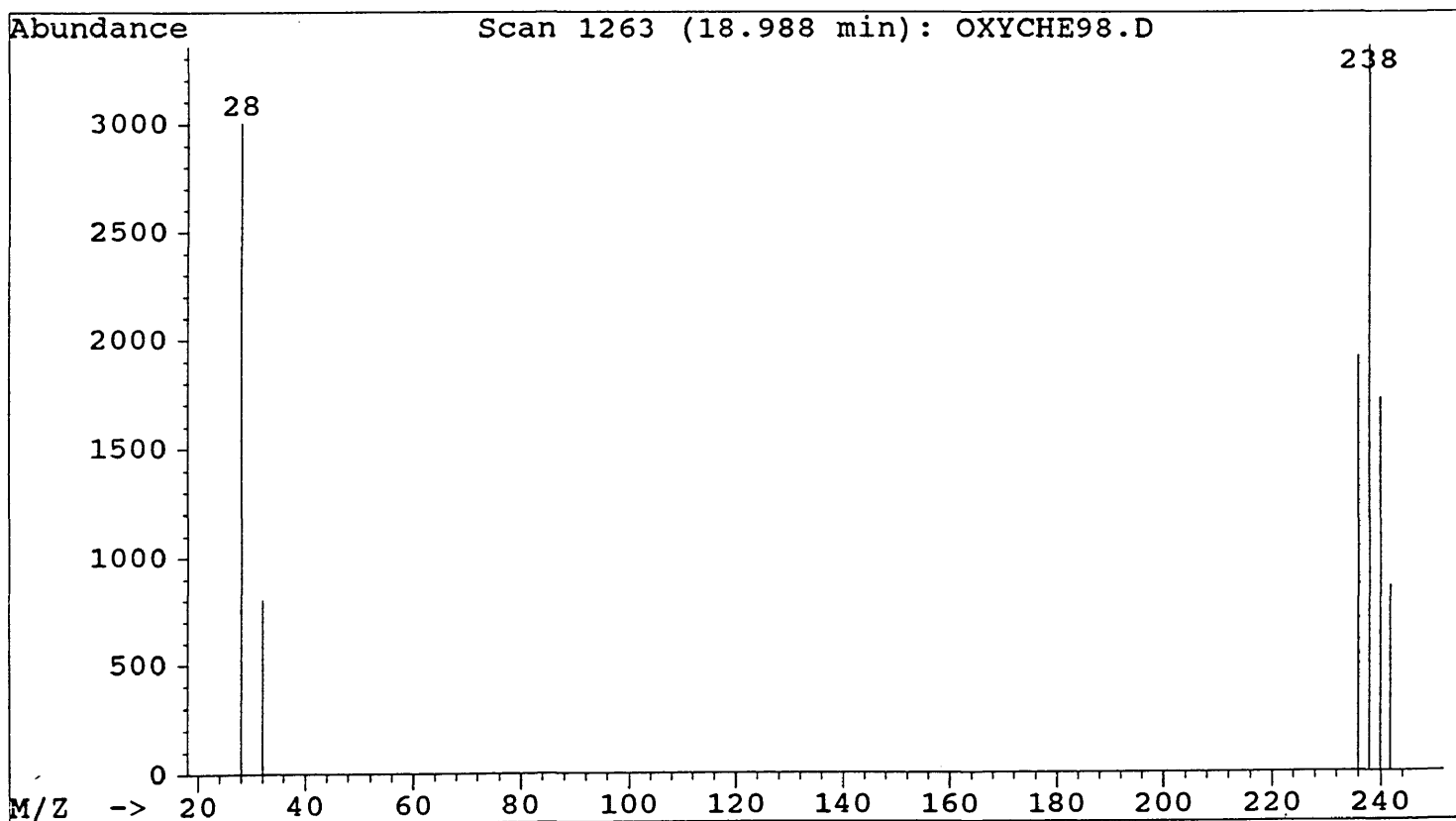
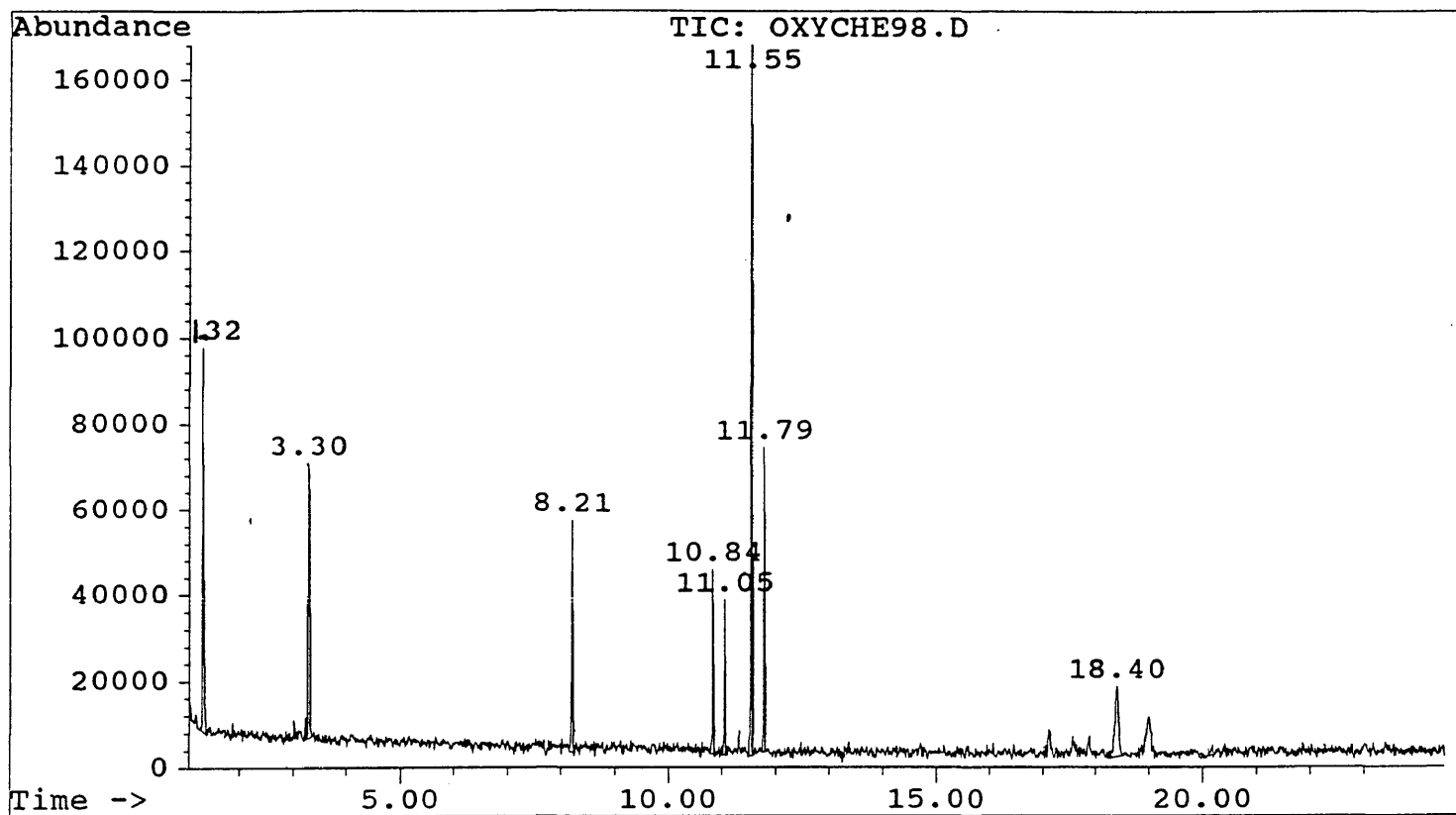




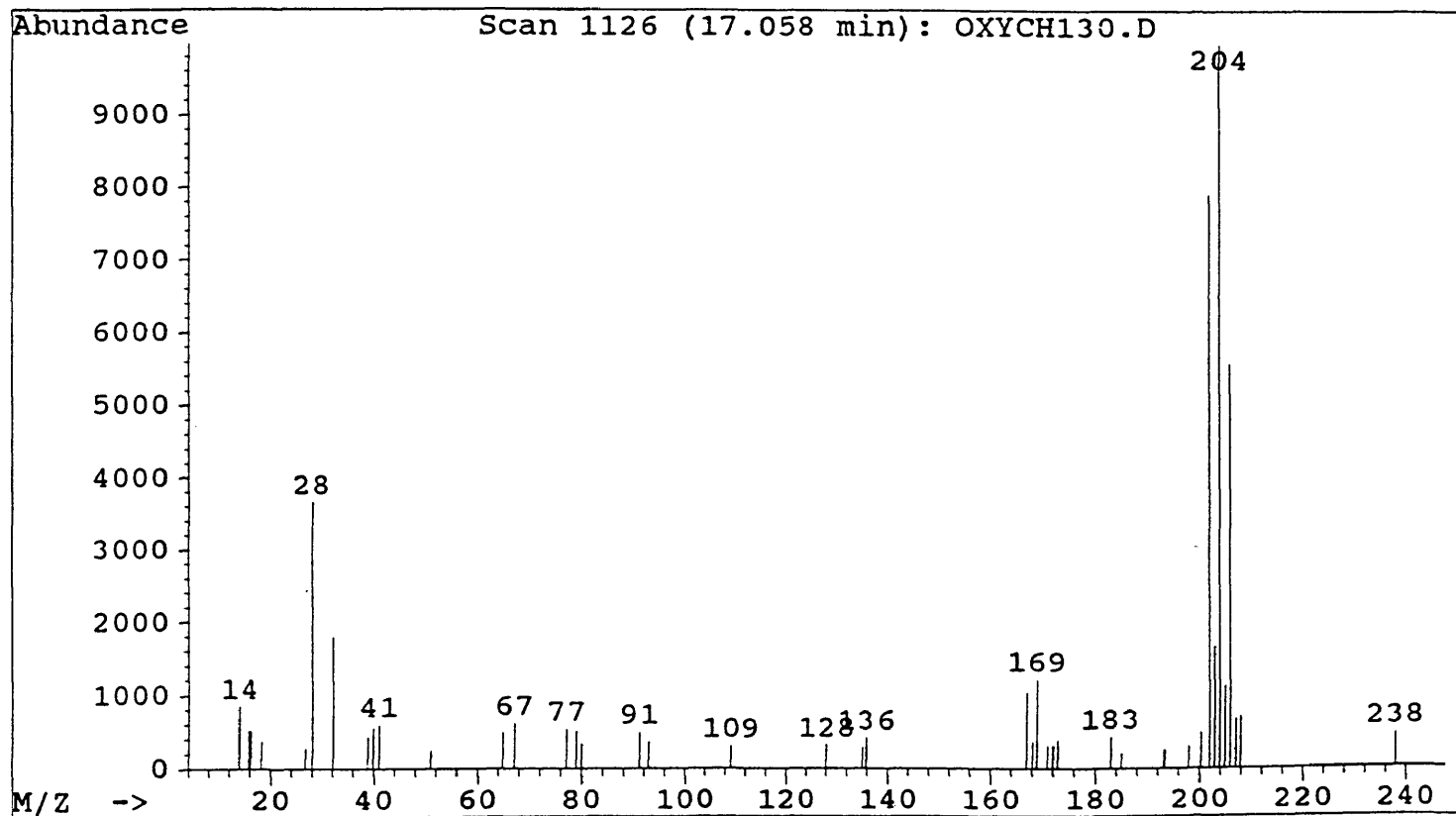
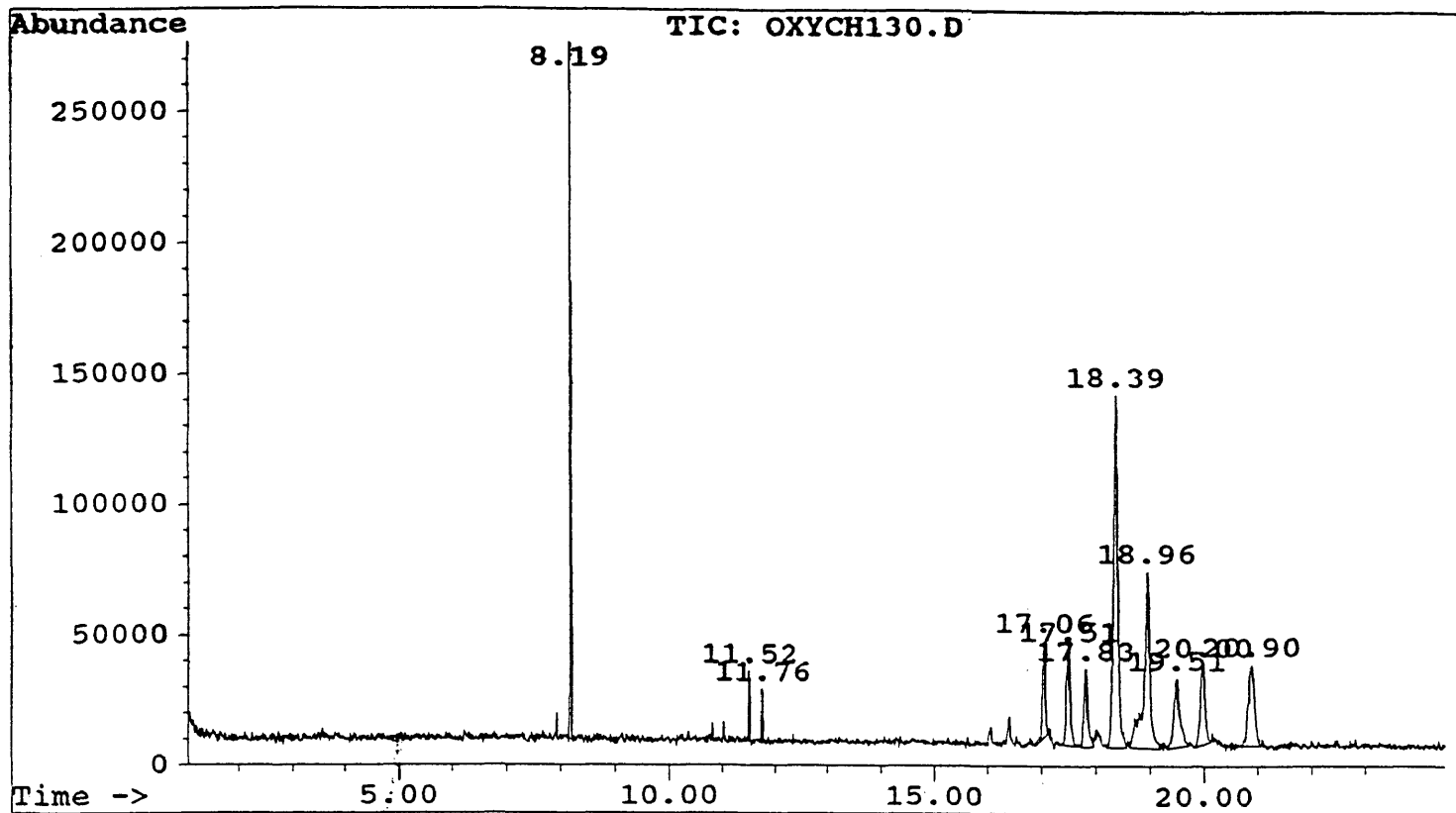
**Figure 17-7.** GC/MS analysis of volatile products from a pyrolyzed 82:10:8 Nylon 66/Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture



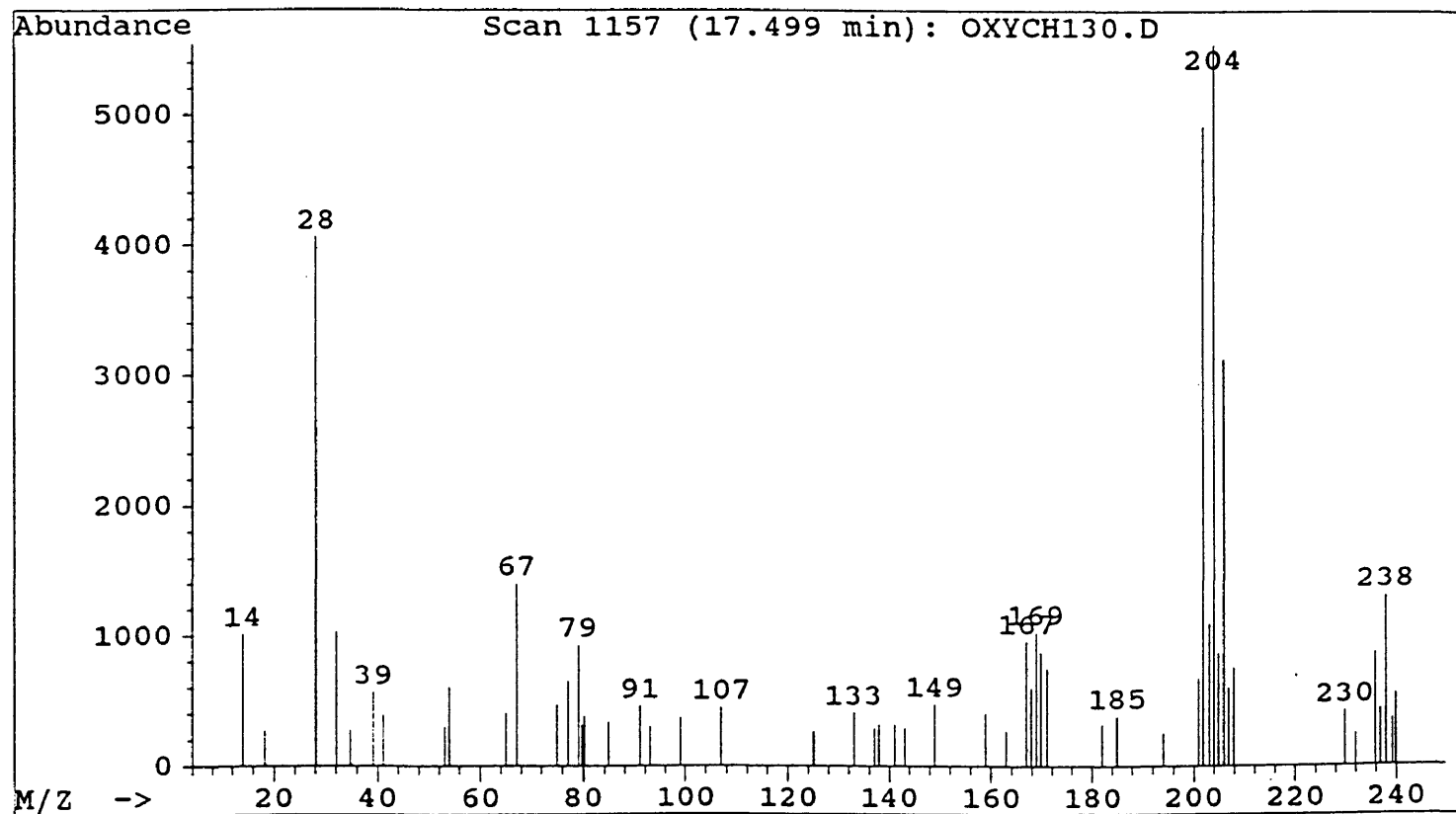
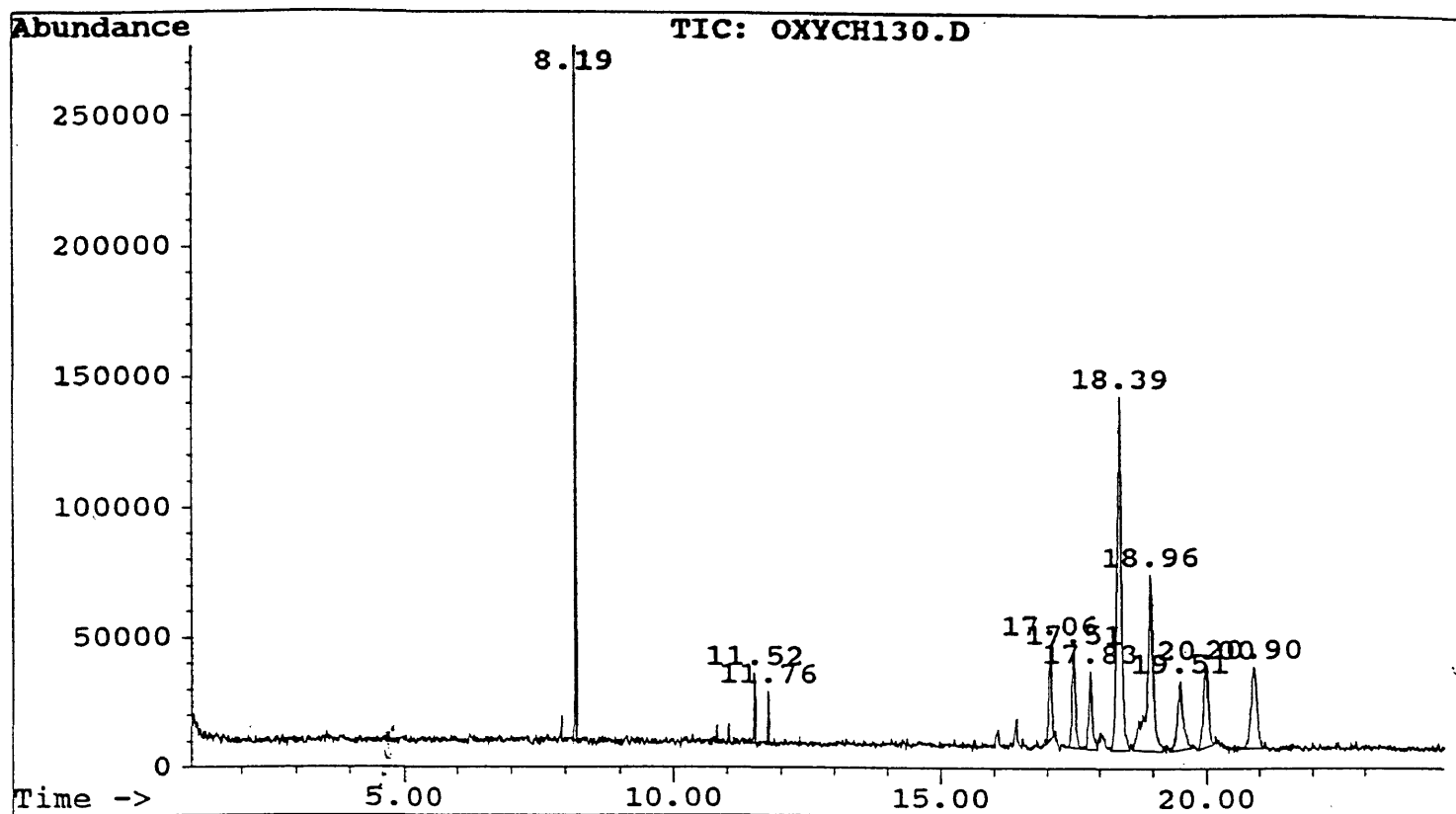
**Figure 17-8.** GC/MS analysis of volatile products from a pyrolyzed 82:10:8 Nylon 66/Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture



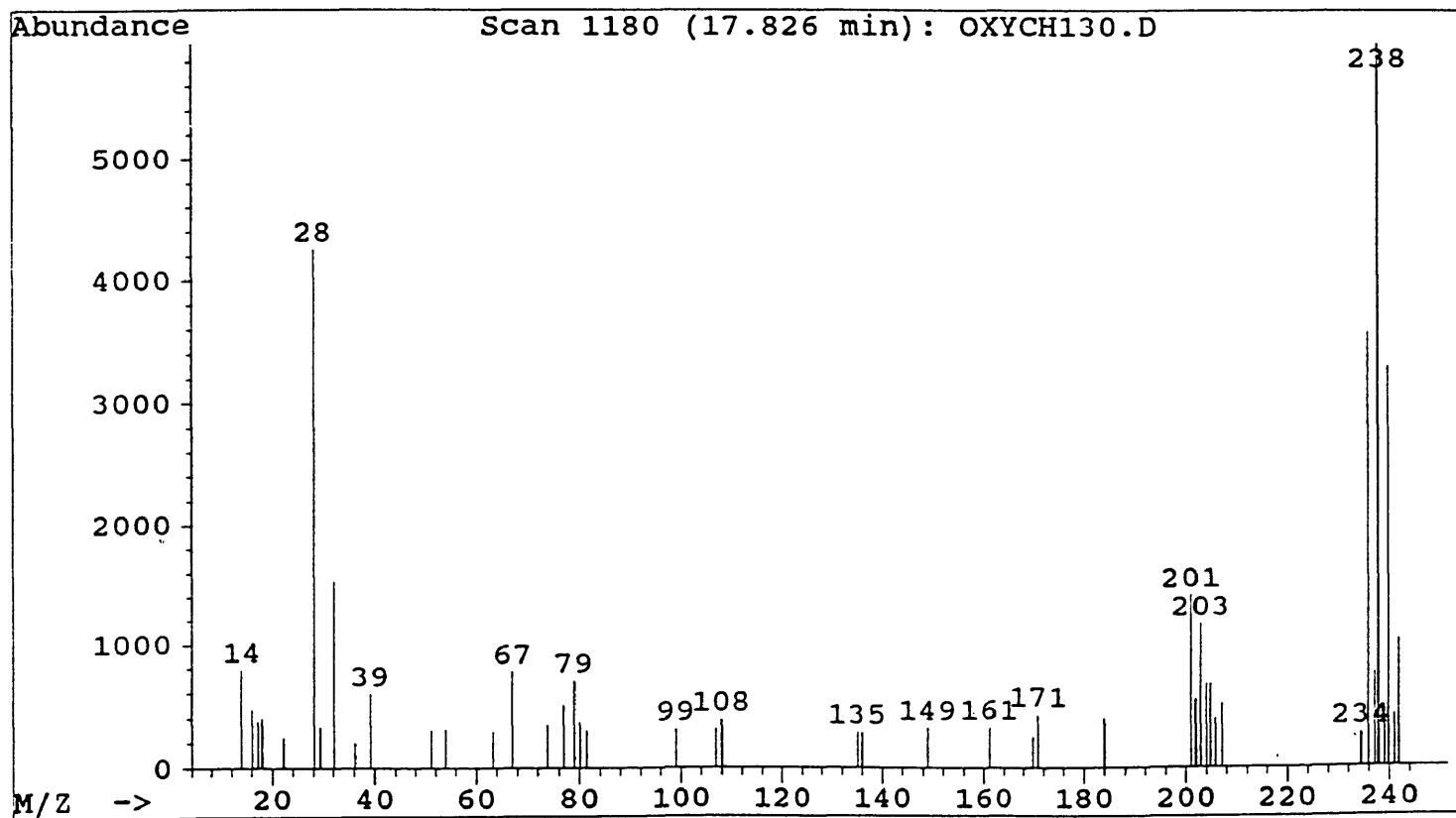
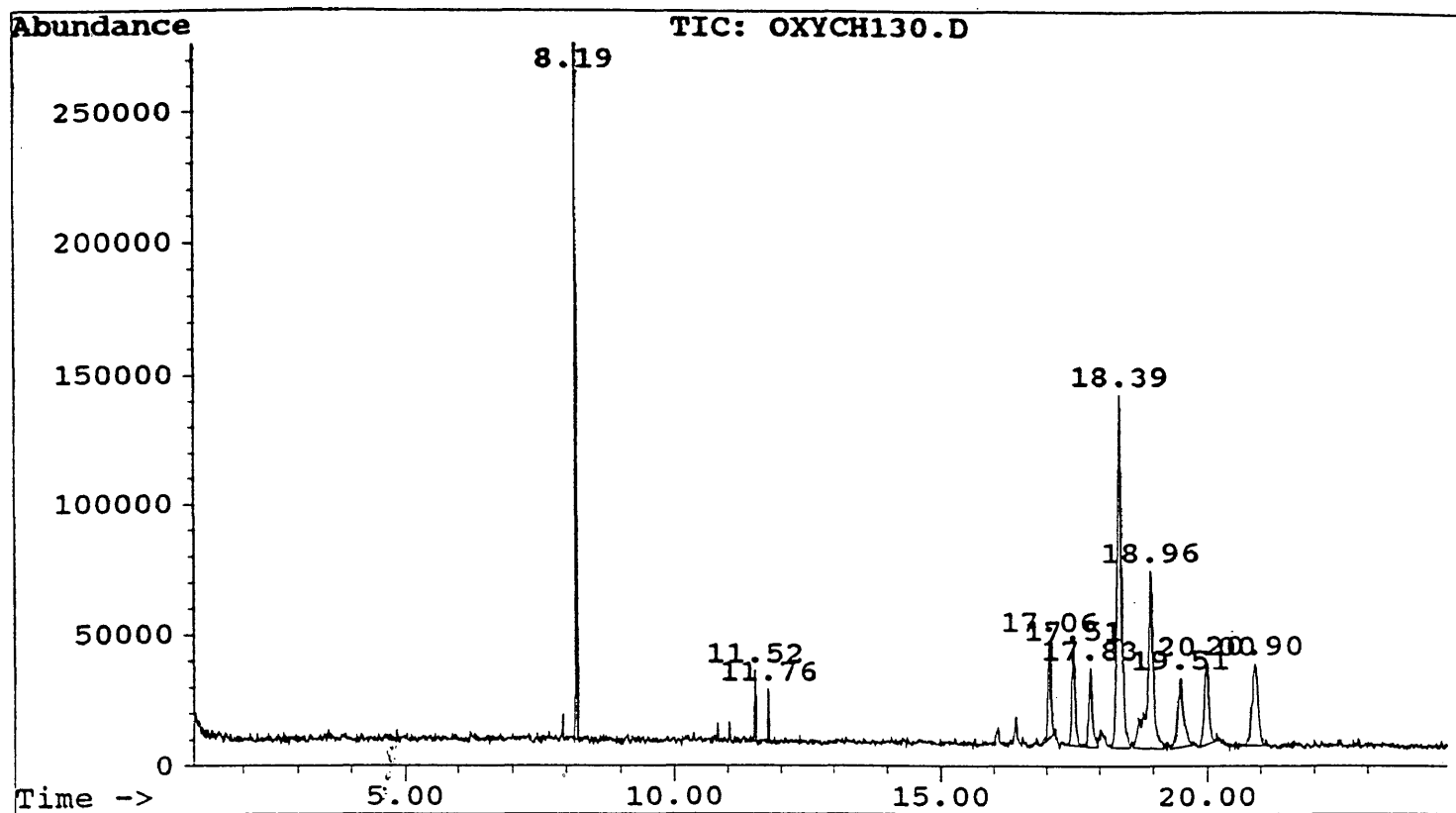
**Figure 17-9.** GC/MS analysis of volatile products from a pyrolyzed 82:10:8 Nylon 66/Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture



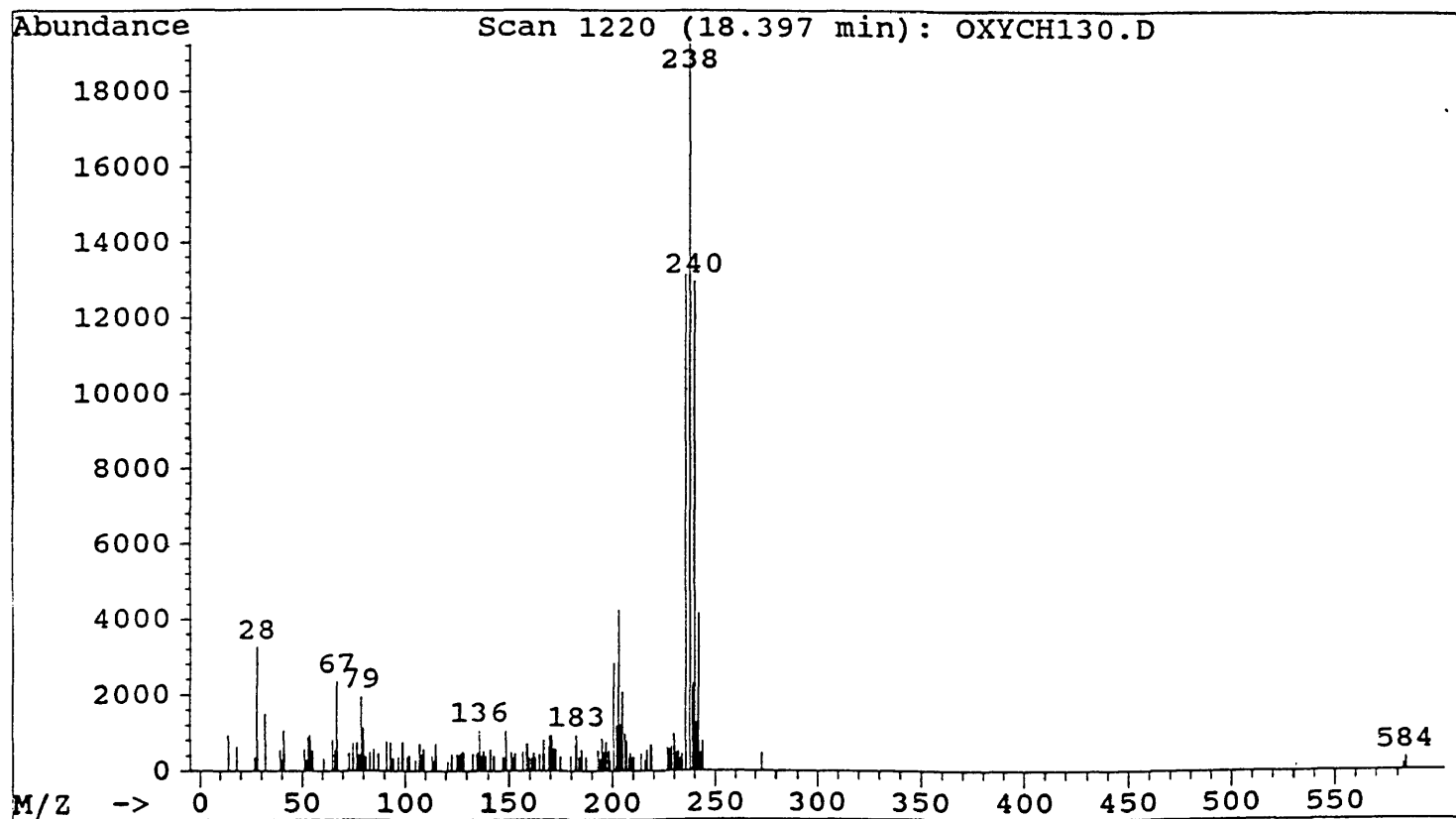
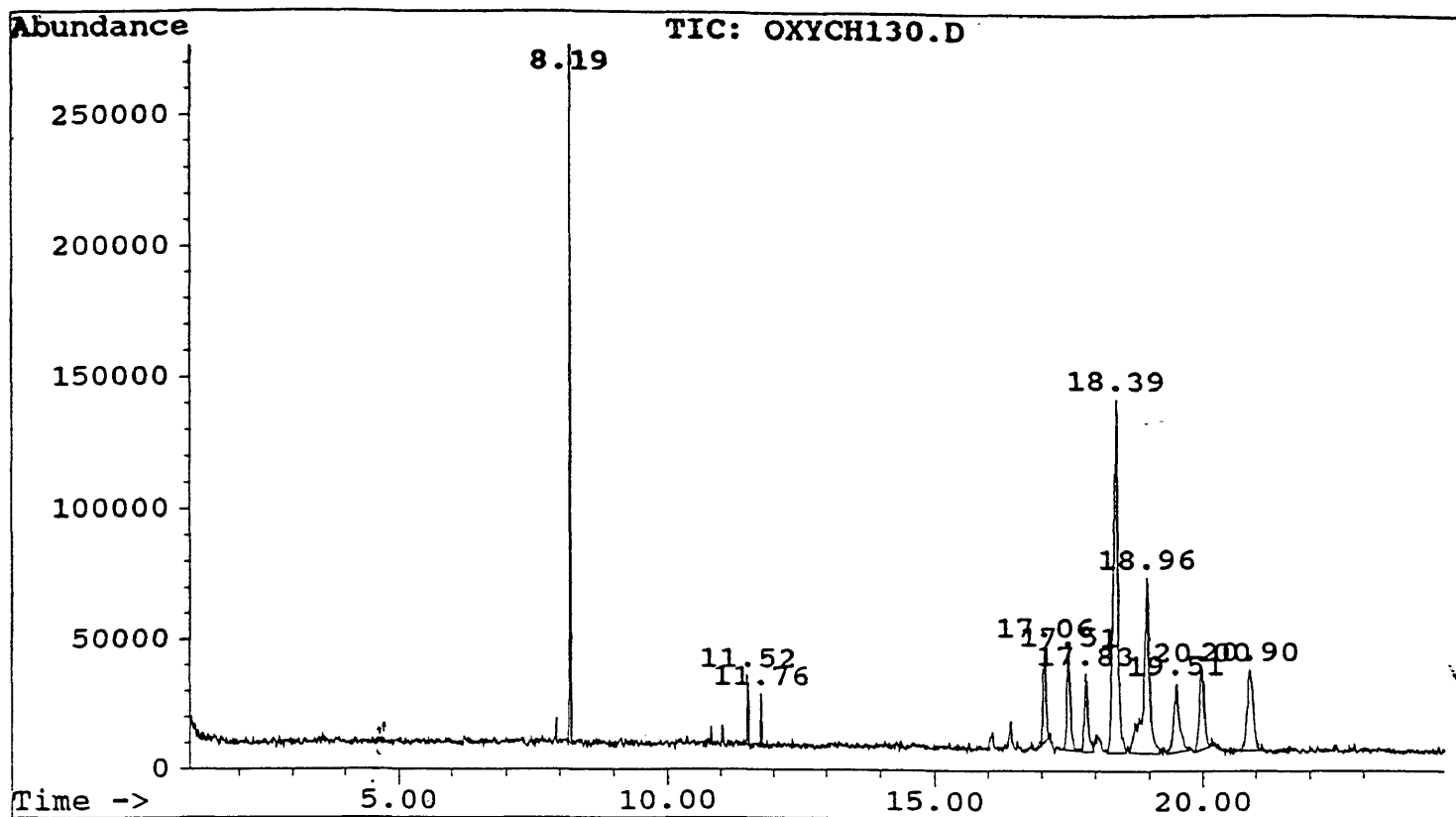
**Figure 18-1.** GC/MS analysis of residue from a pyrolyzed 82:10:8 Nylon 66/Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture



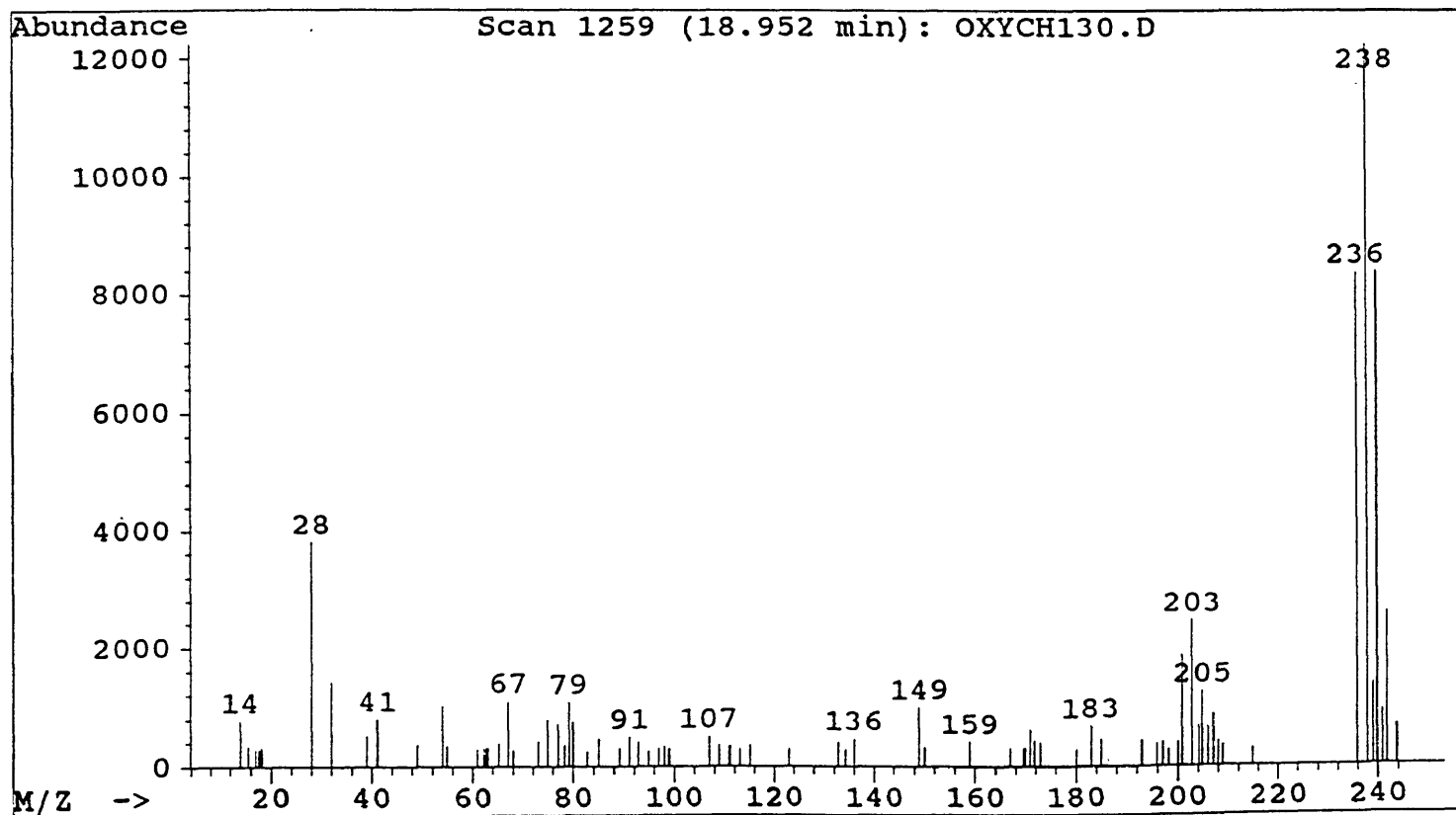
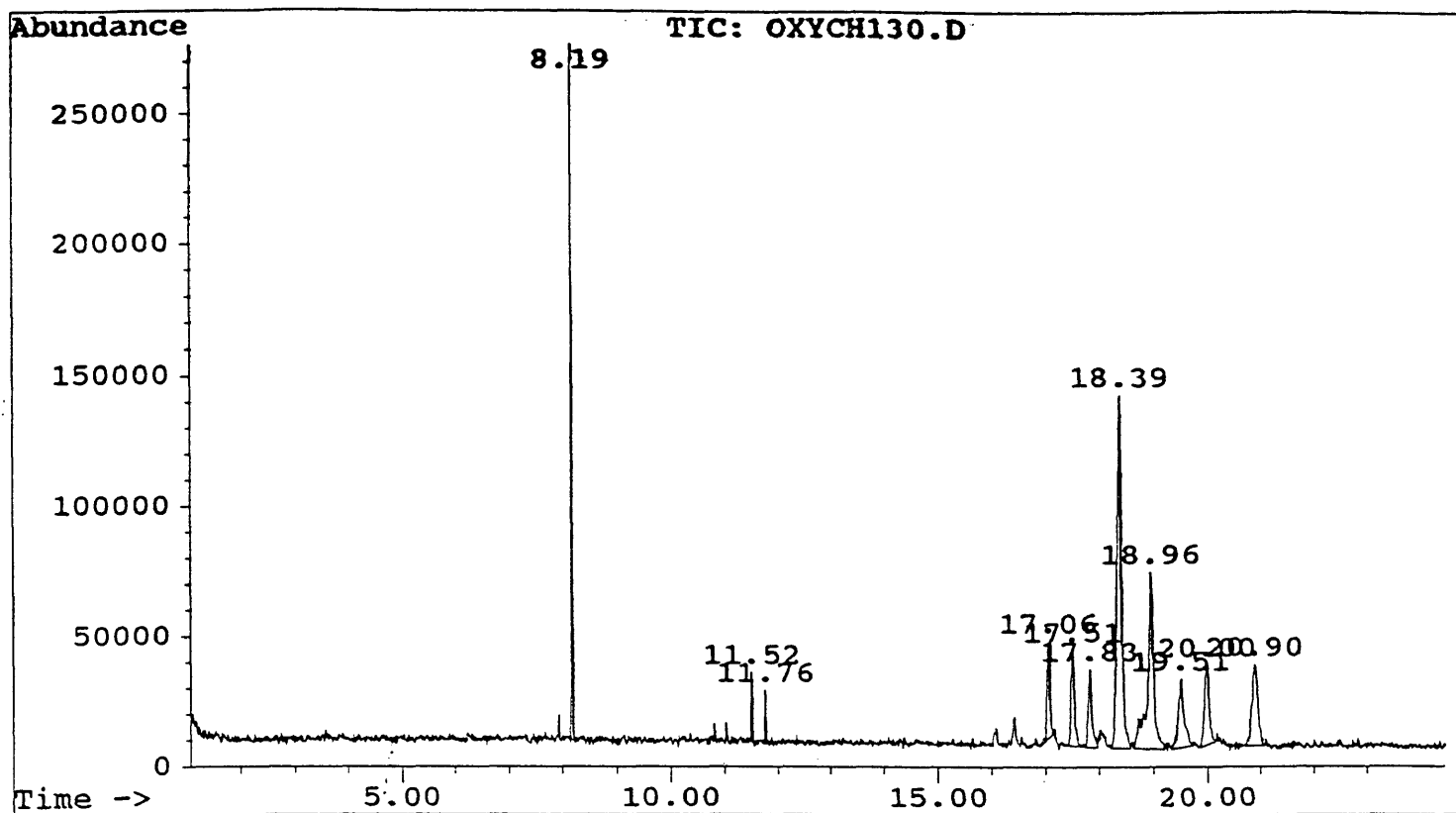
**Figure 18-2.** GC/MS analysis of residue from a pyrolyzed 82:10:8 Nylon 66/Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture



**Figure 18-3.** GC/MS analysis of residue from a pyrolyzed 82:10:8 Nylon 66/Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture

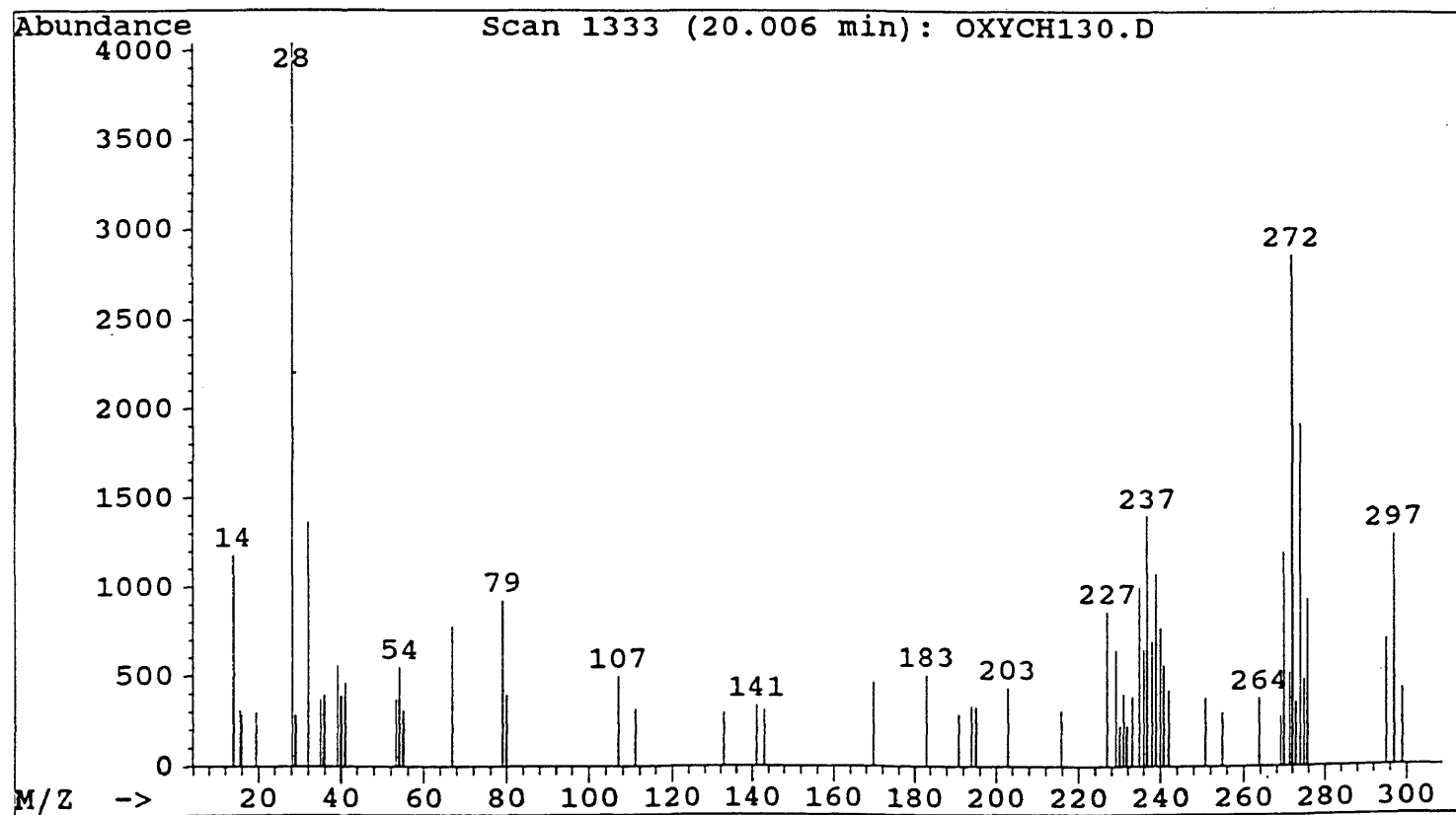
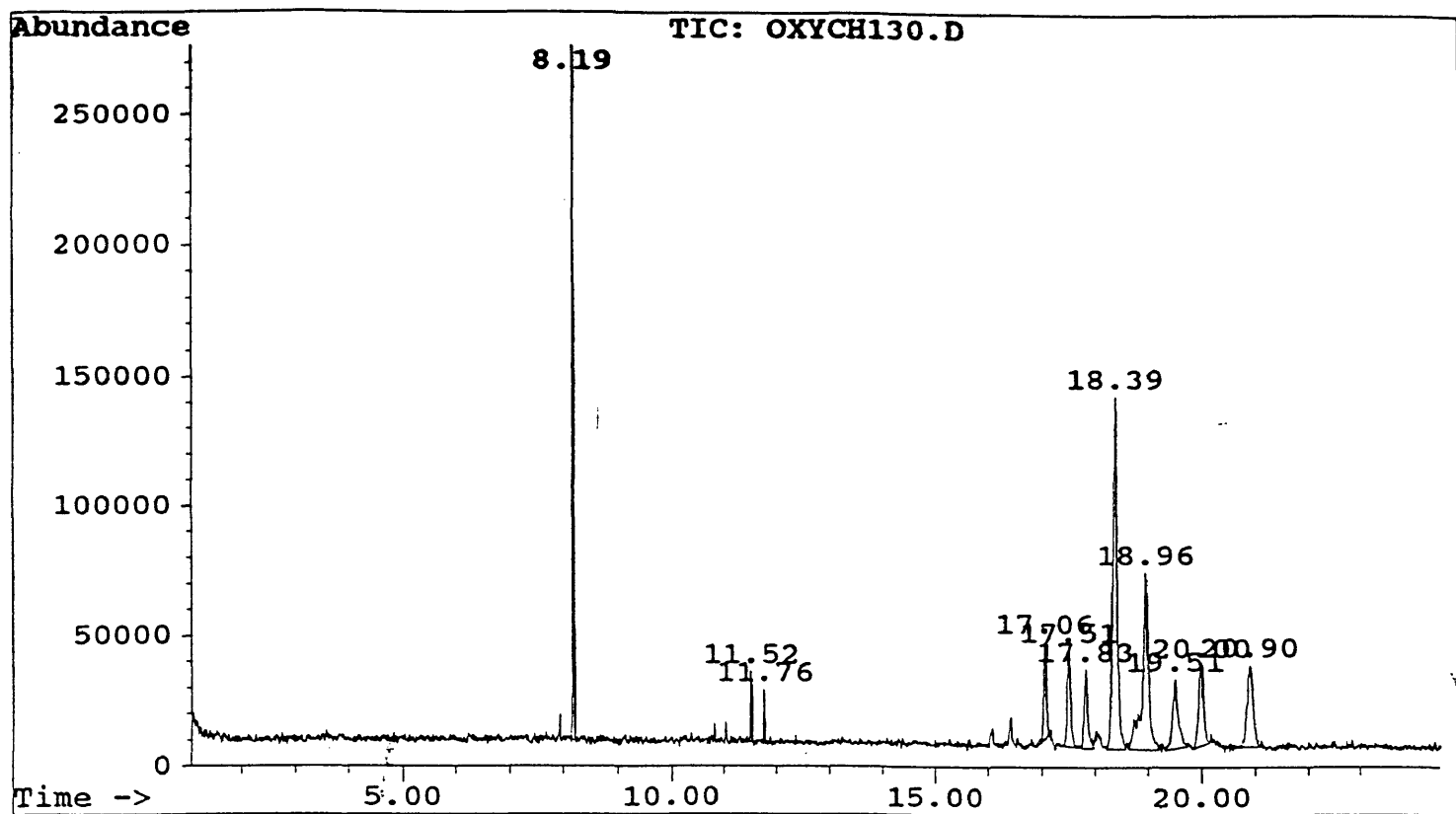


**Figure 18-4.** GC/MS analysis of residue from a pyrolyzed 82:10:8 Nylon 66/Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture

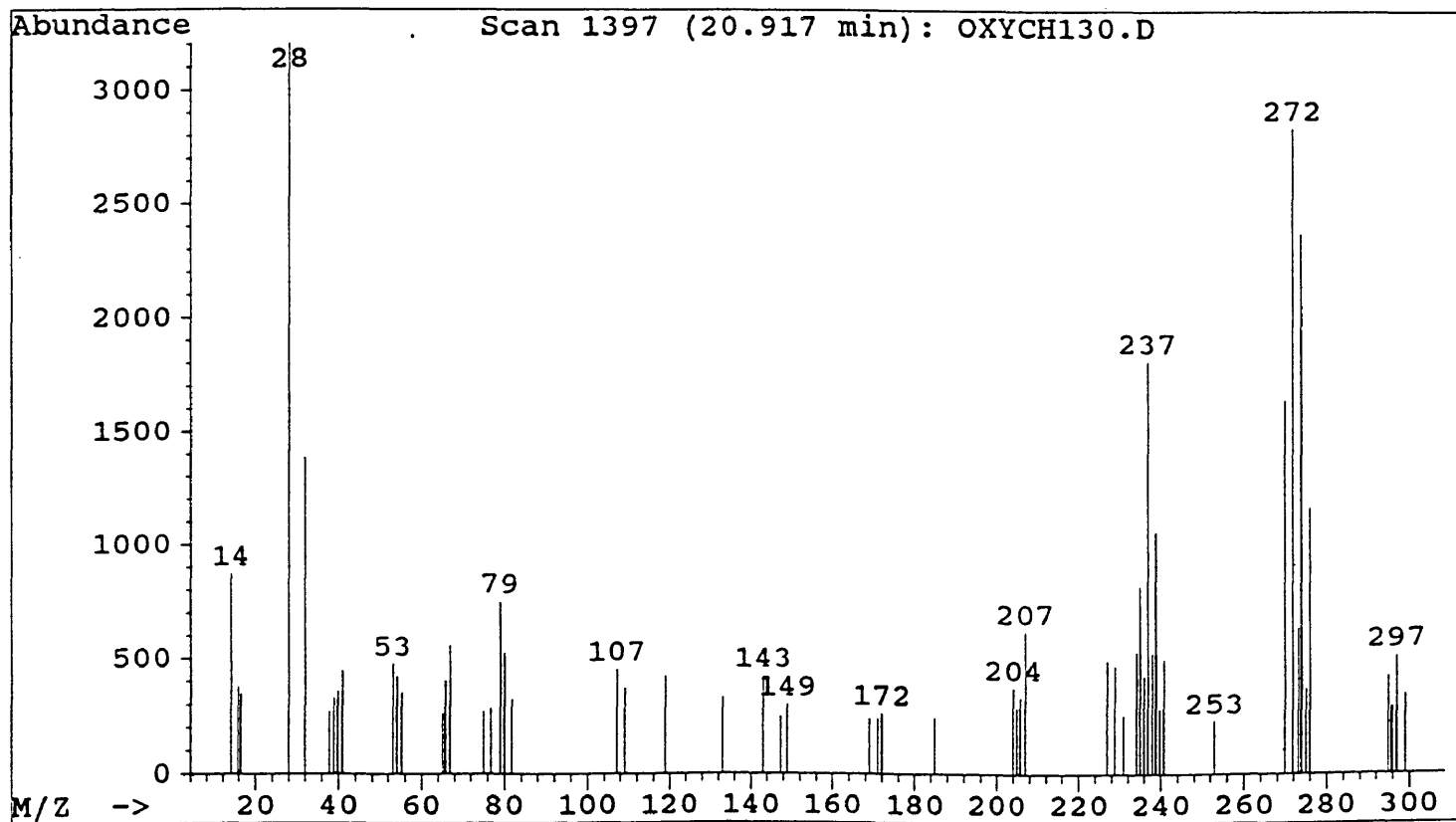
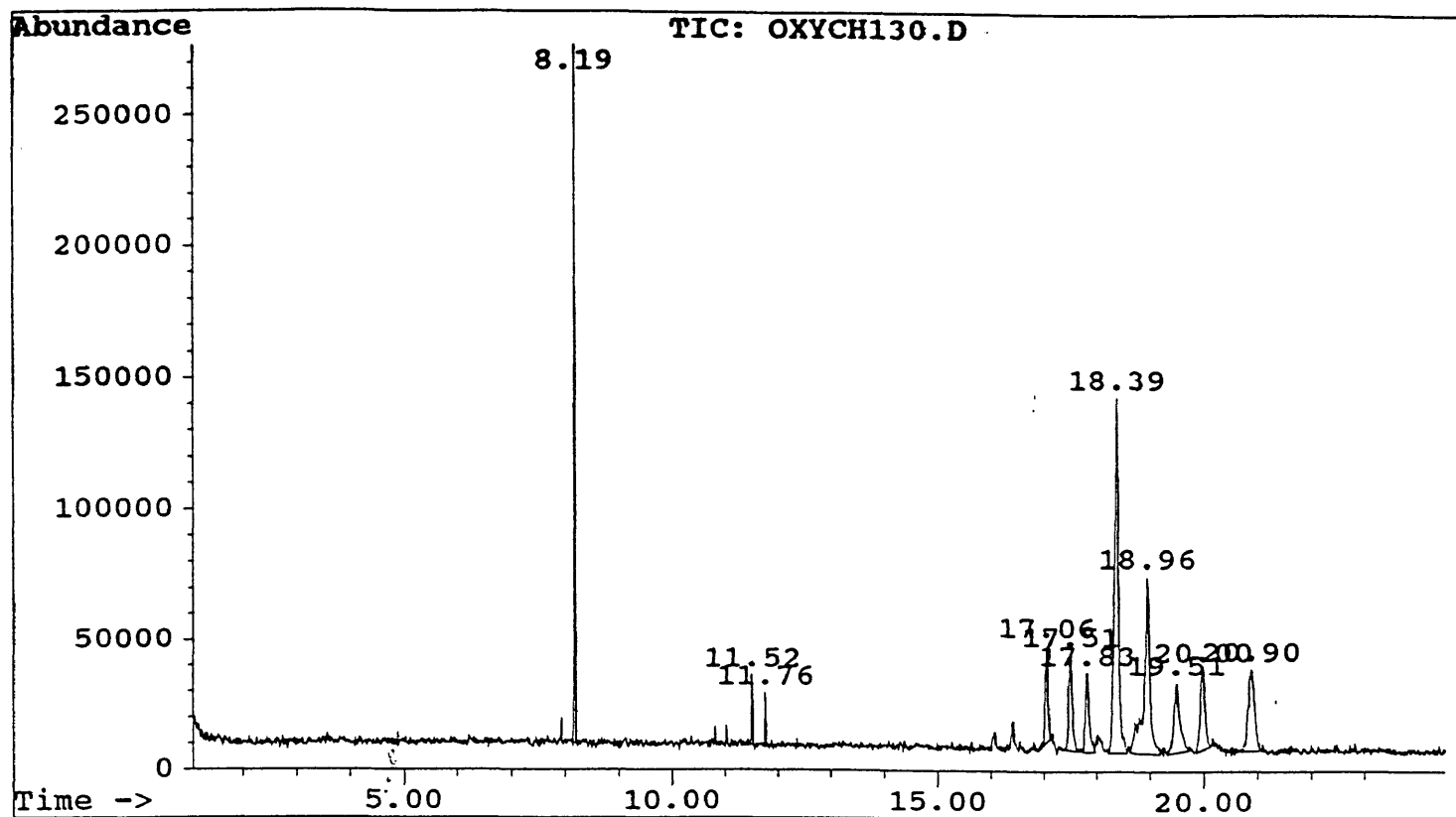


**Figure 18-5.** GC/MS analysis of residue from a pyrolyzed 82:10:8 Nylon 66/Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture

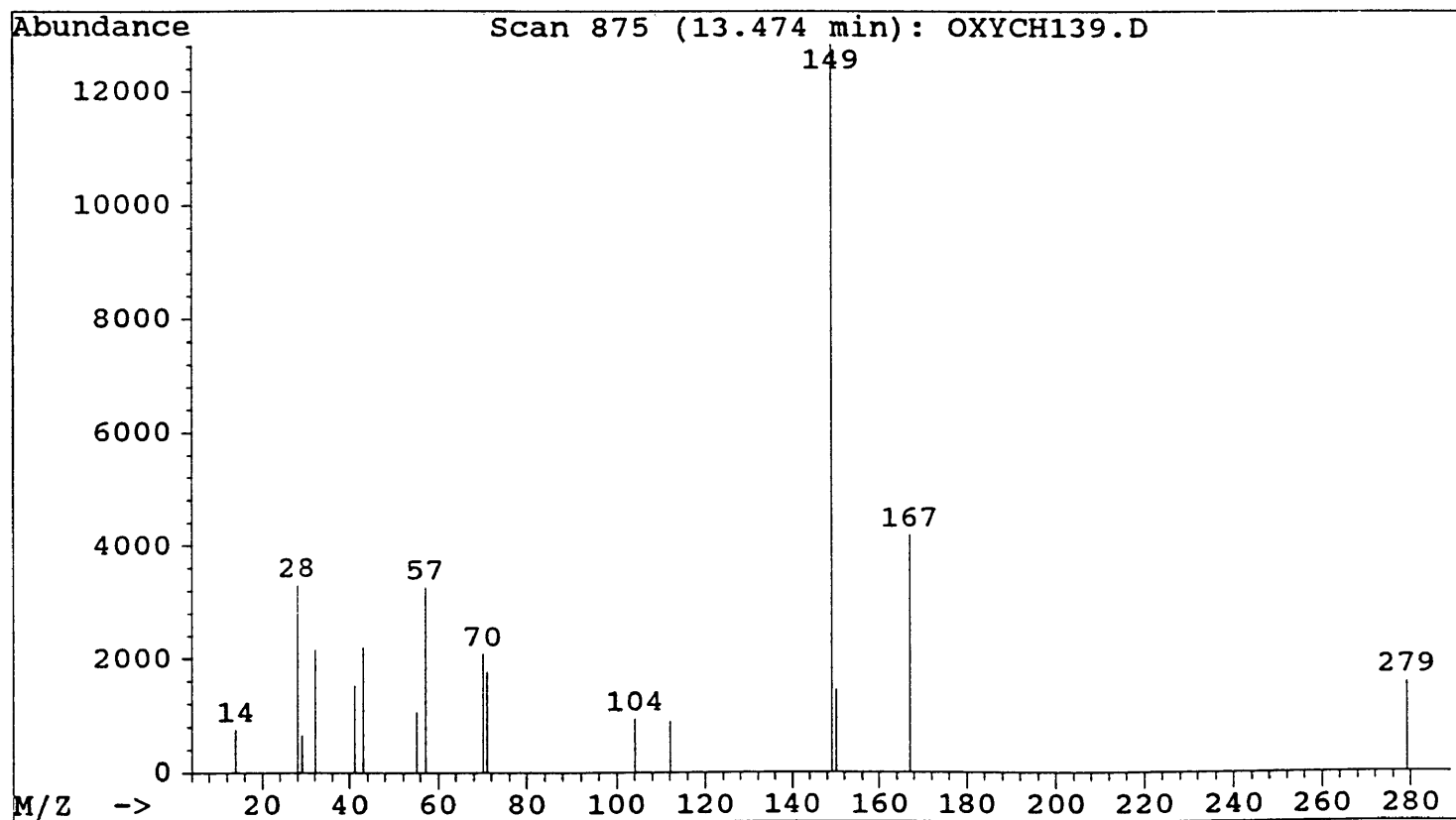
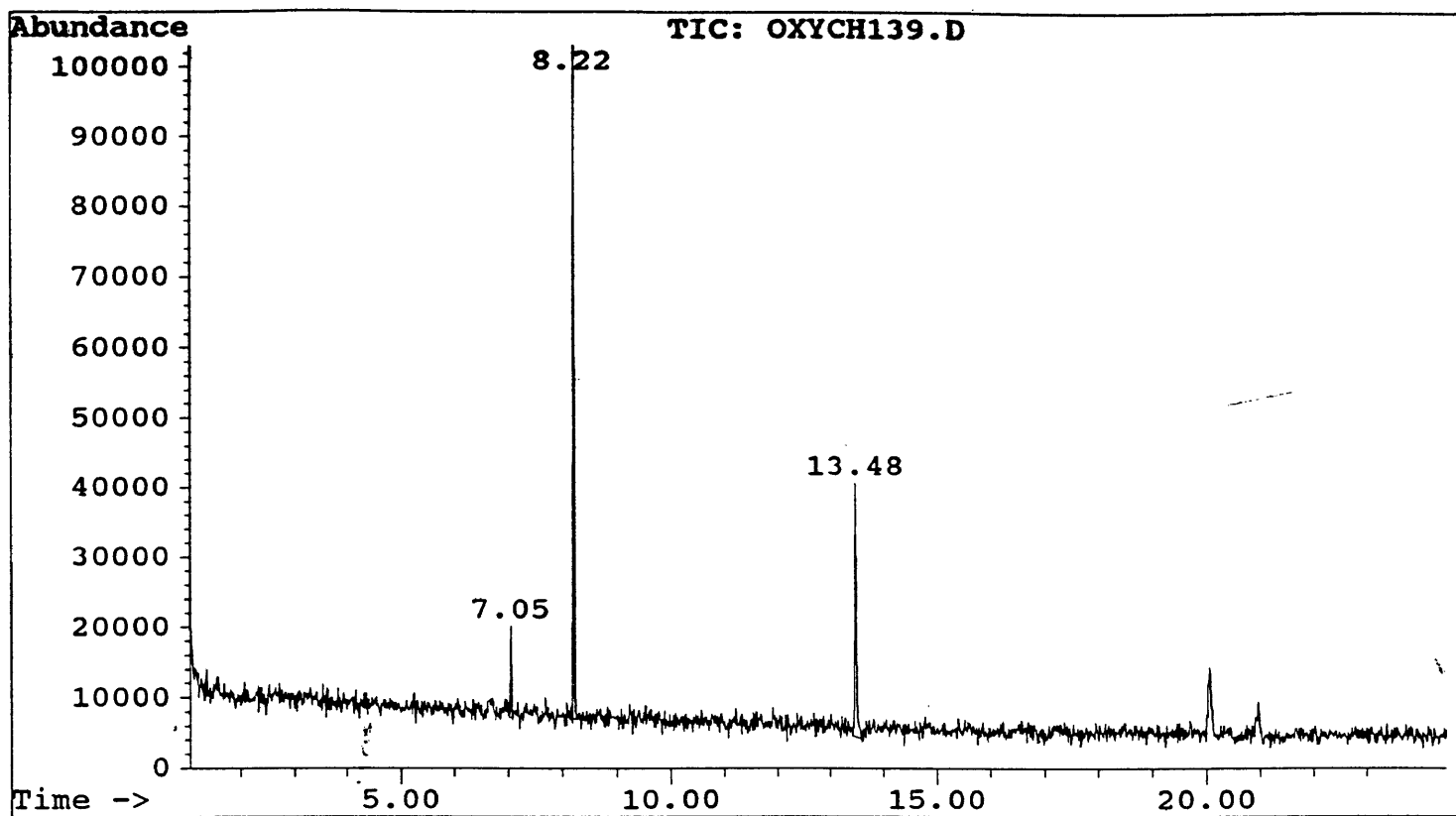




**Figure 18-6.** GC/MS analysis of residue from a pyrolyzed 82:10:8 Nylon 66/Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture



**Figure 18-7.** GC/MS analysis of residue from a pyrolyzed 82:10:8 Nylon 66/Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture



**Figure 19-1.** GC/MS analysis of volatile products from a pyrolyzed 90:10 Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture

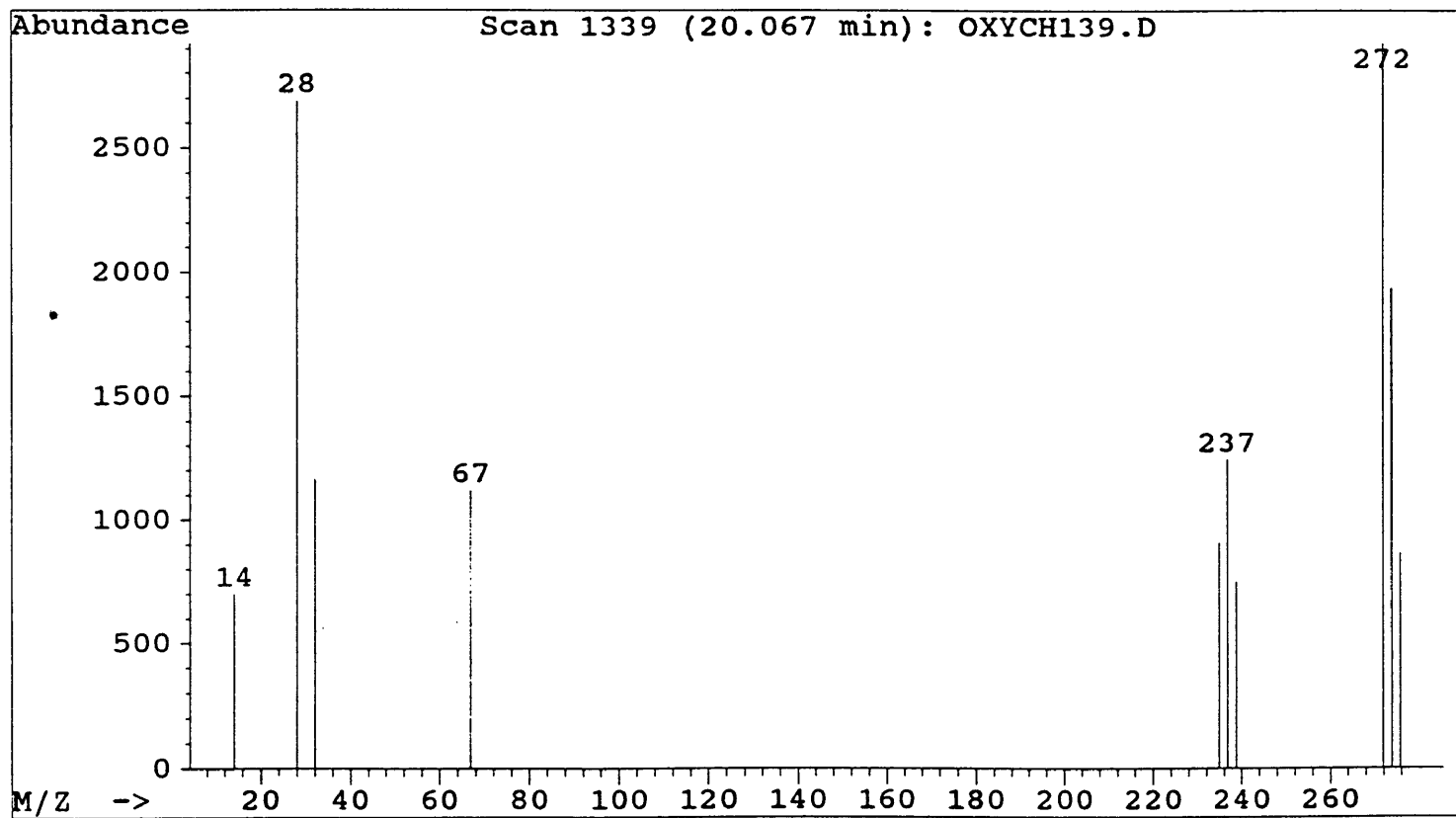
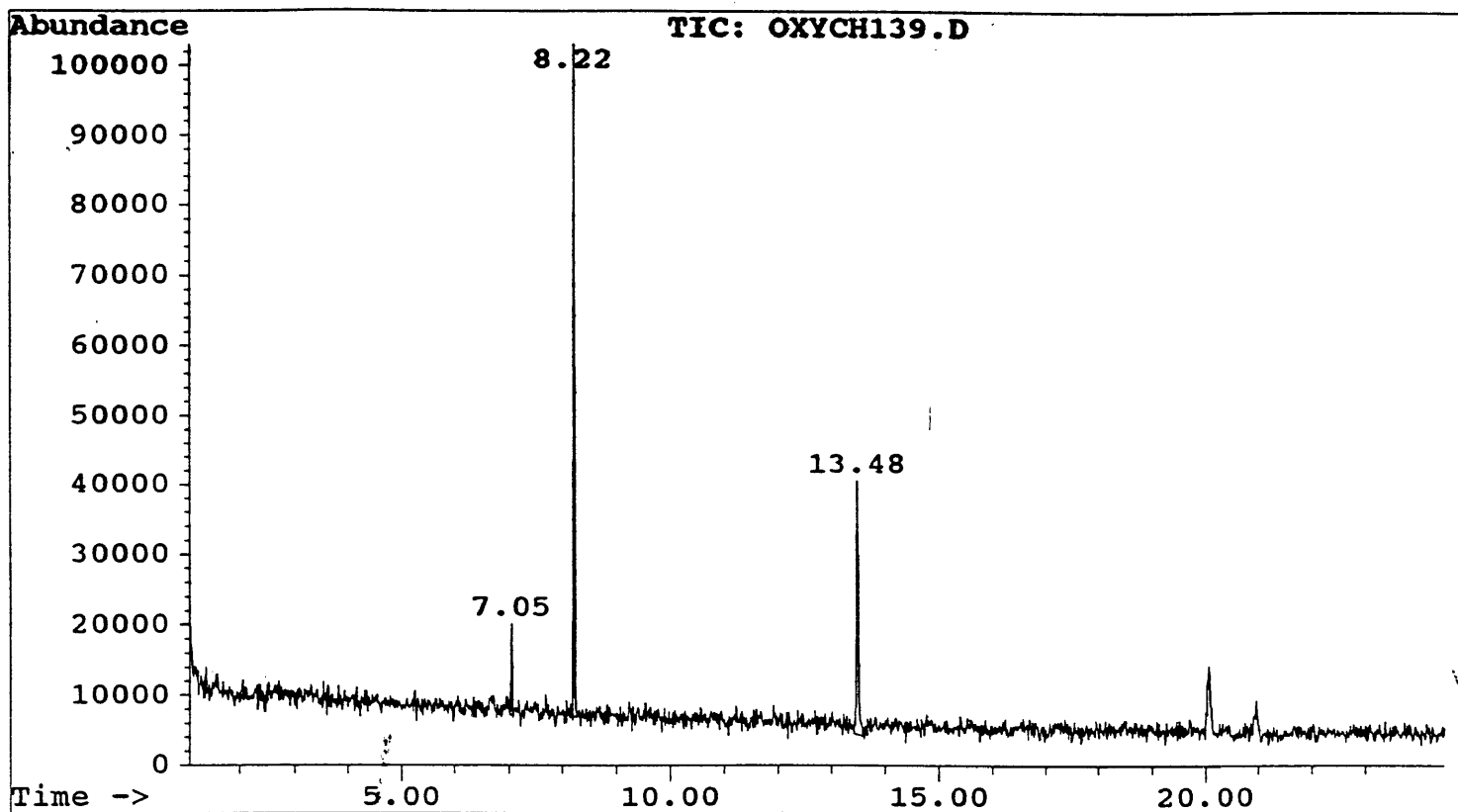
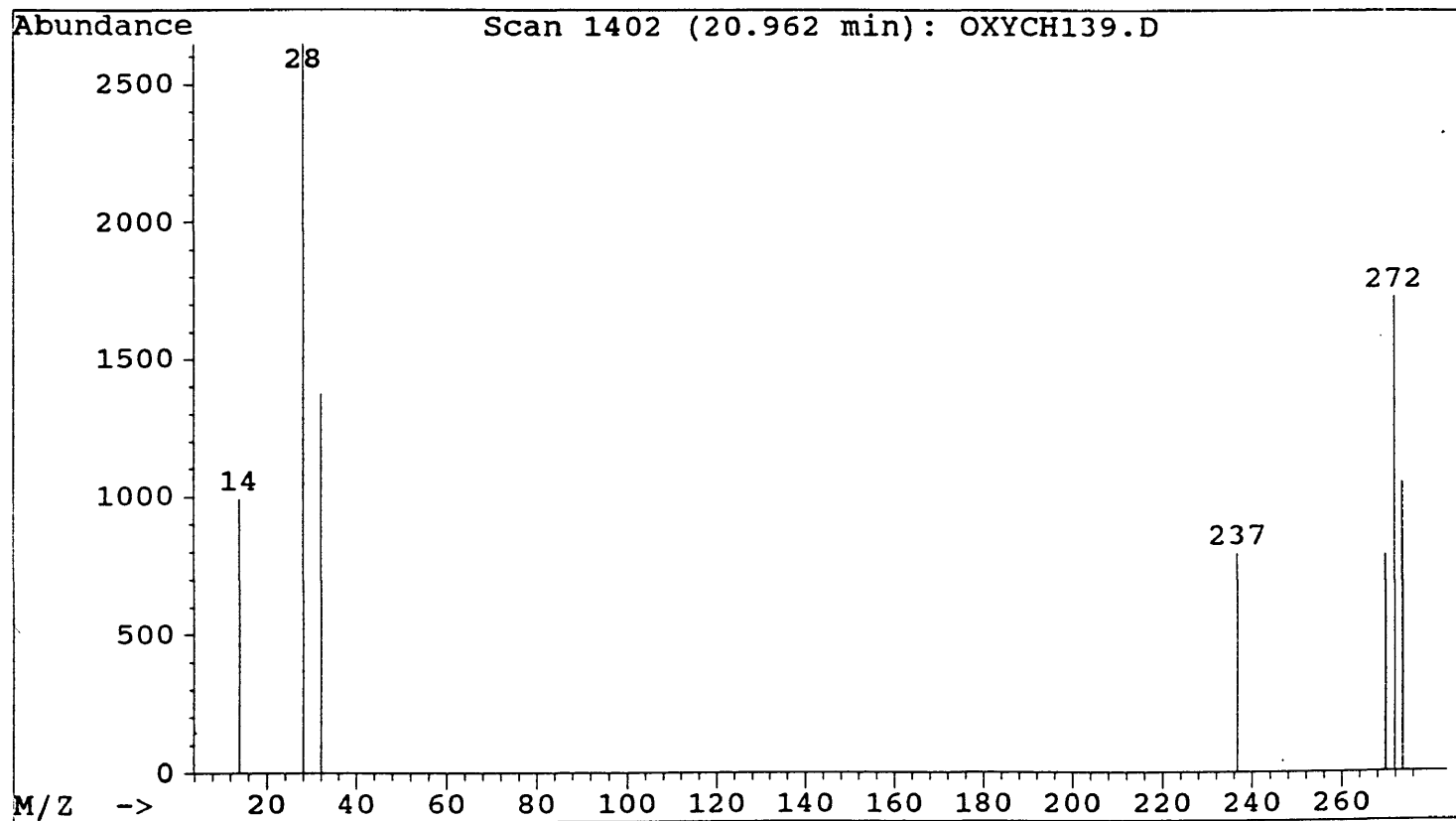
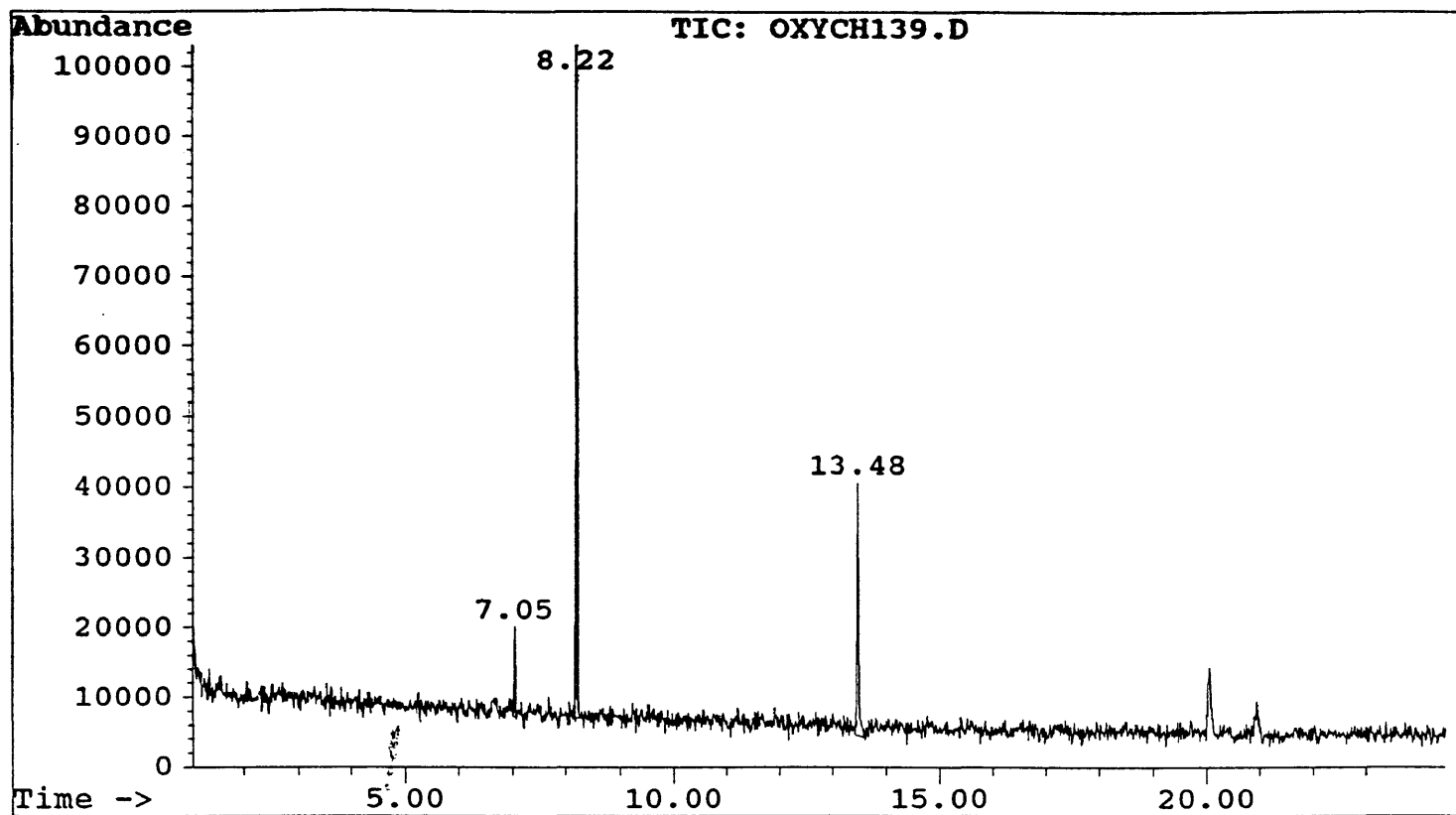


Figure 19-2. GC/MS analysis of volatile products from a pyrolyzed 90:10 Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture



**Figure 19-3.** GC/MS analysis of volatile products from a pyrolyzed 90:10 Dech Plus/Sb<sub>2</sub>O<sub>3</sub> mixture

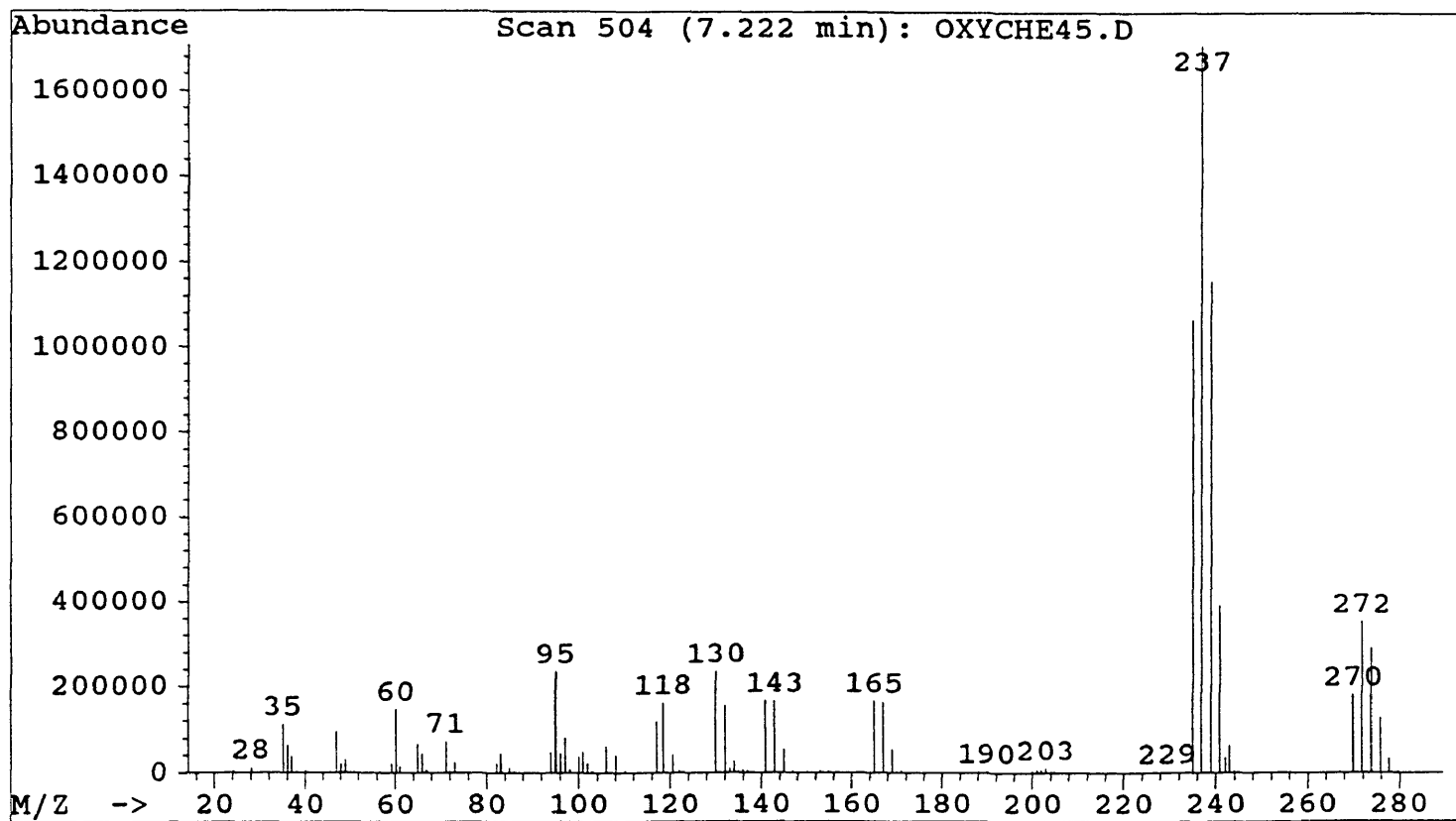
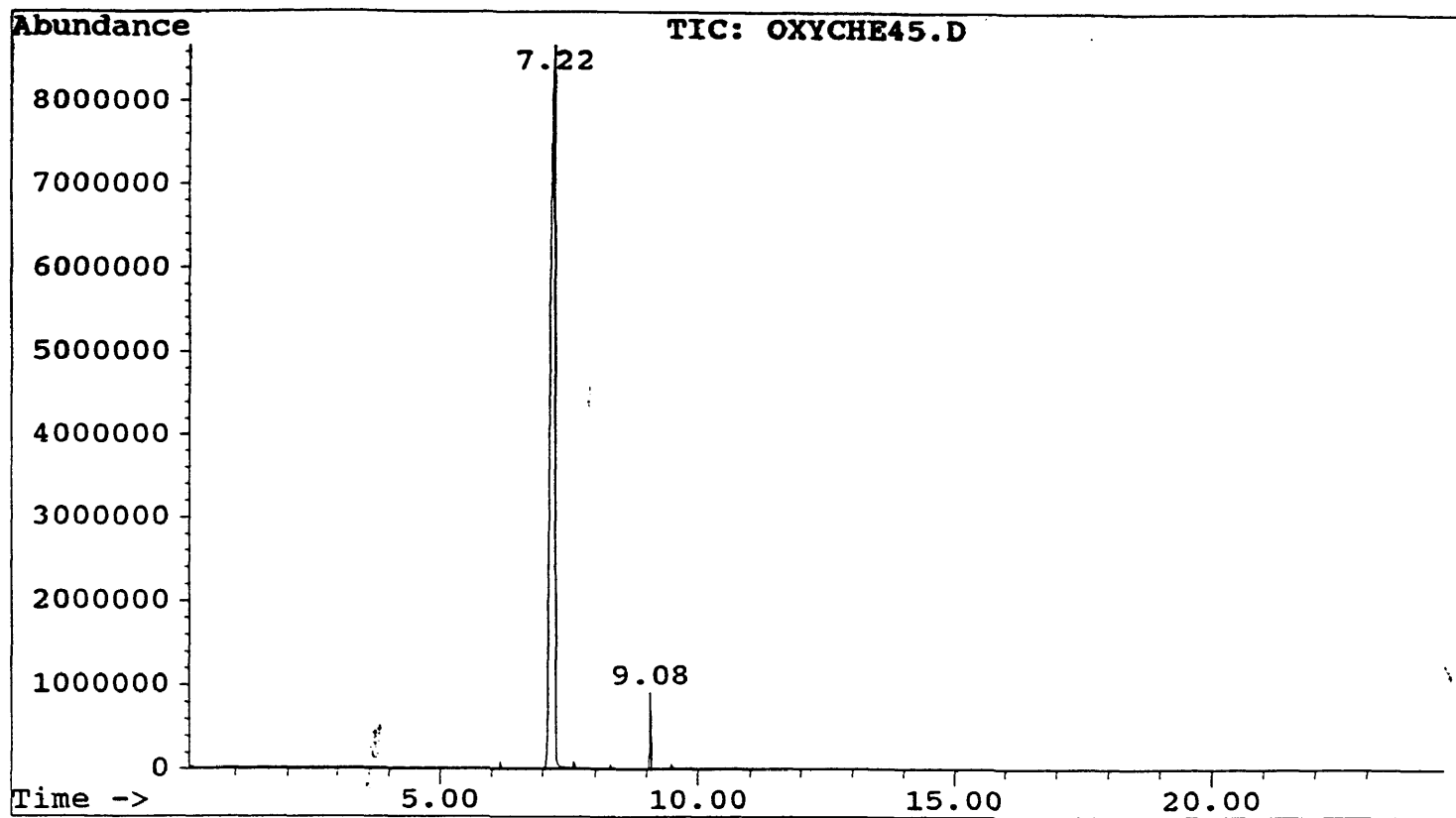


Figure 20-1. GC/MS analysis of hexachlorocyclopentadiene

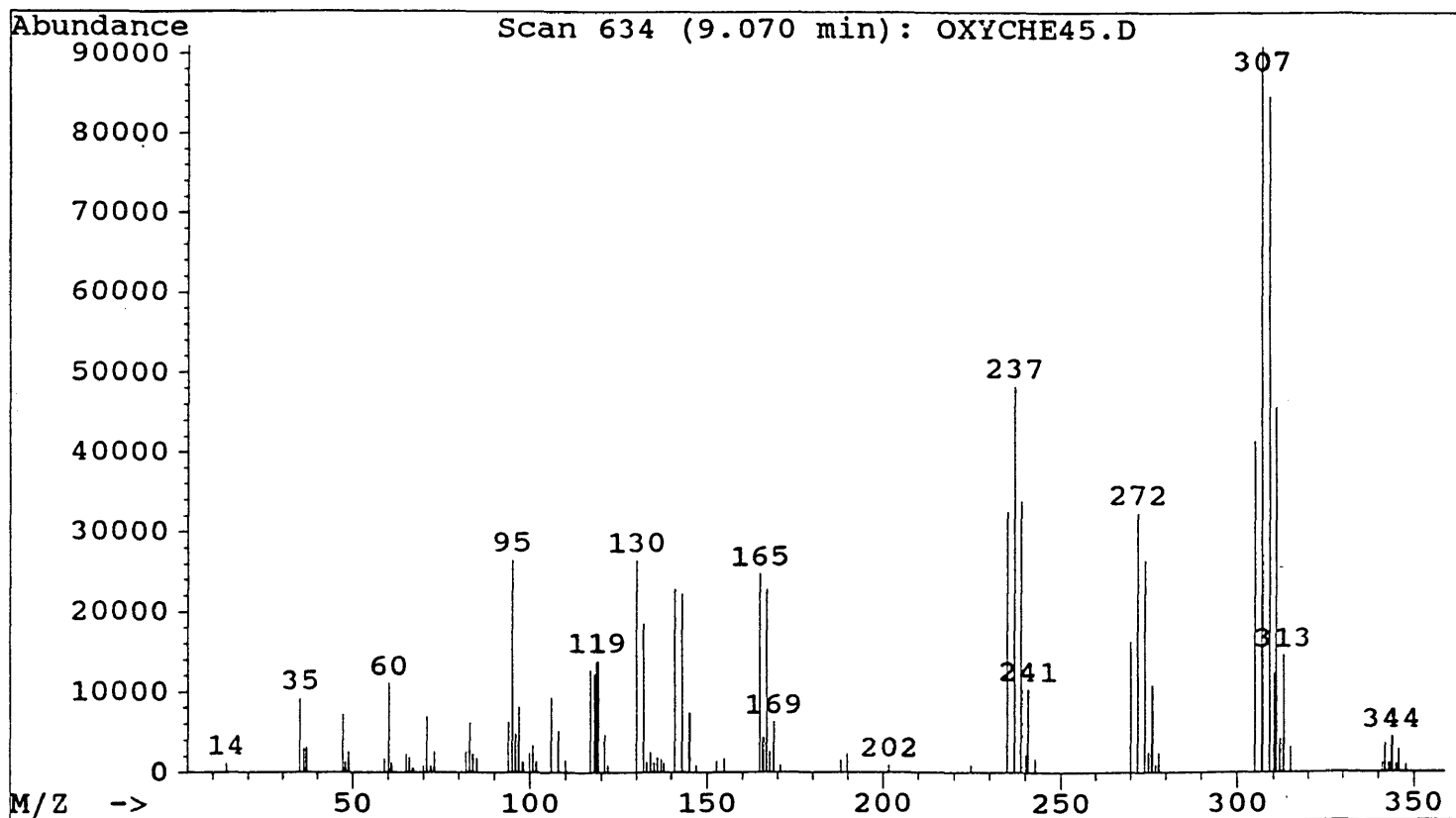
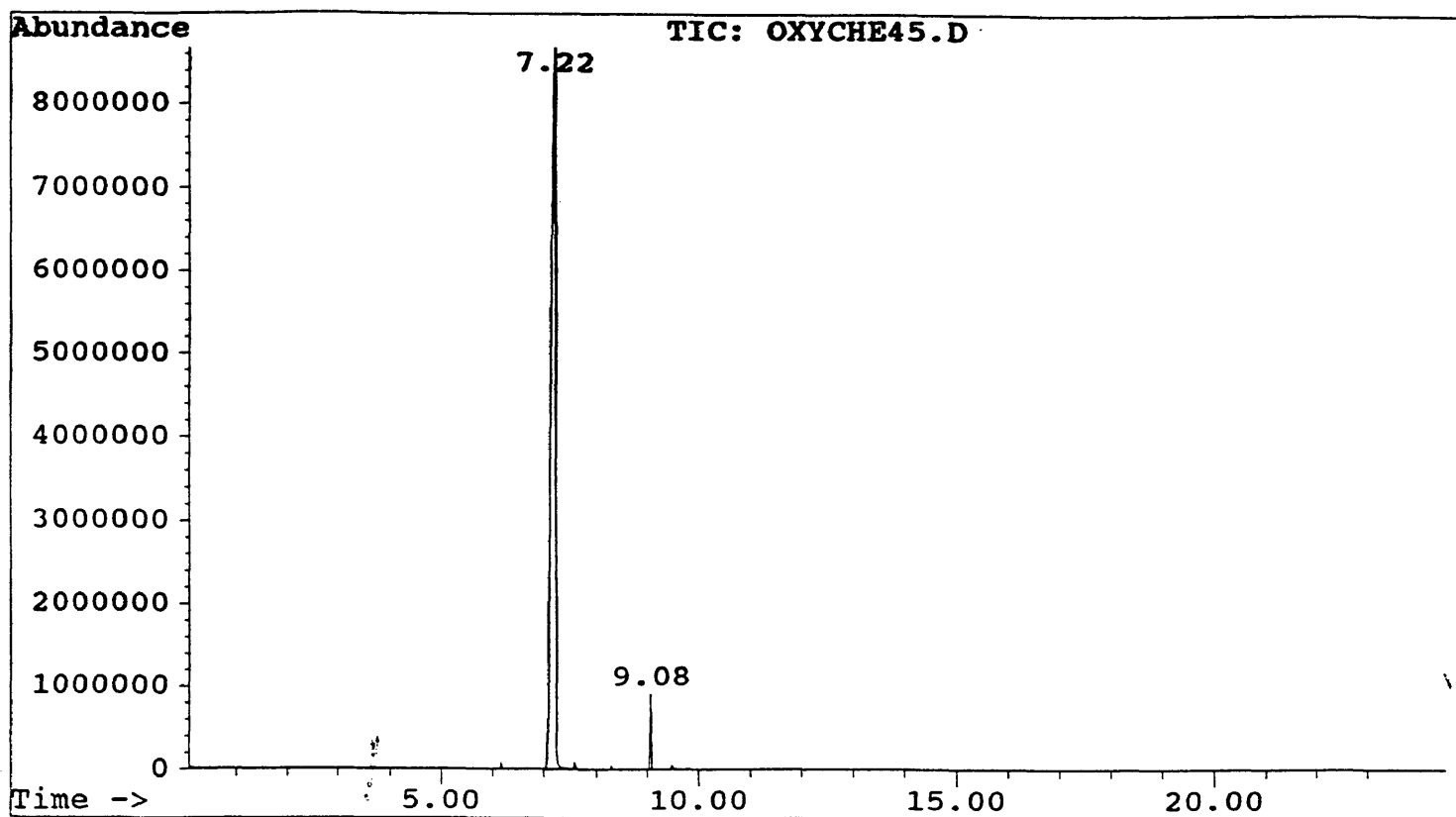
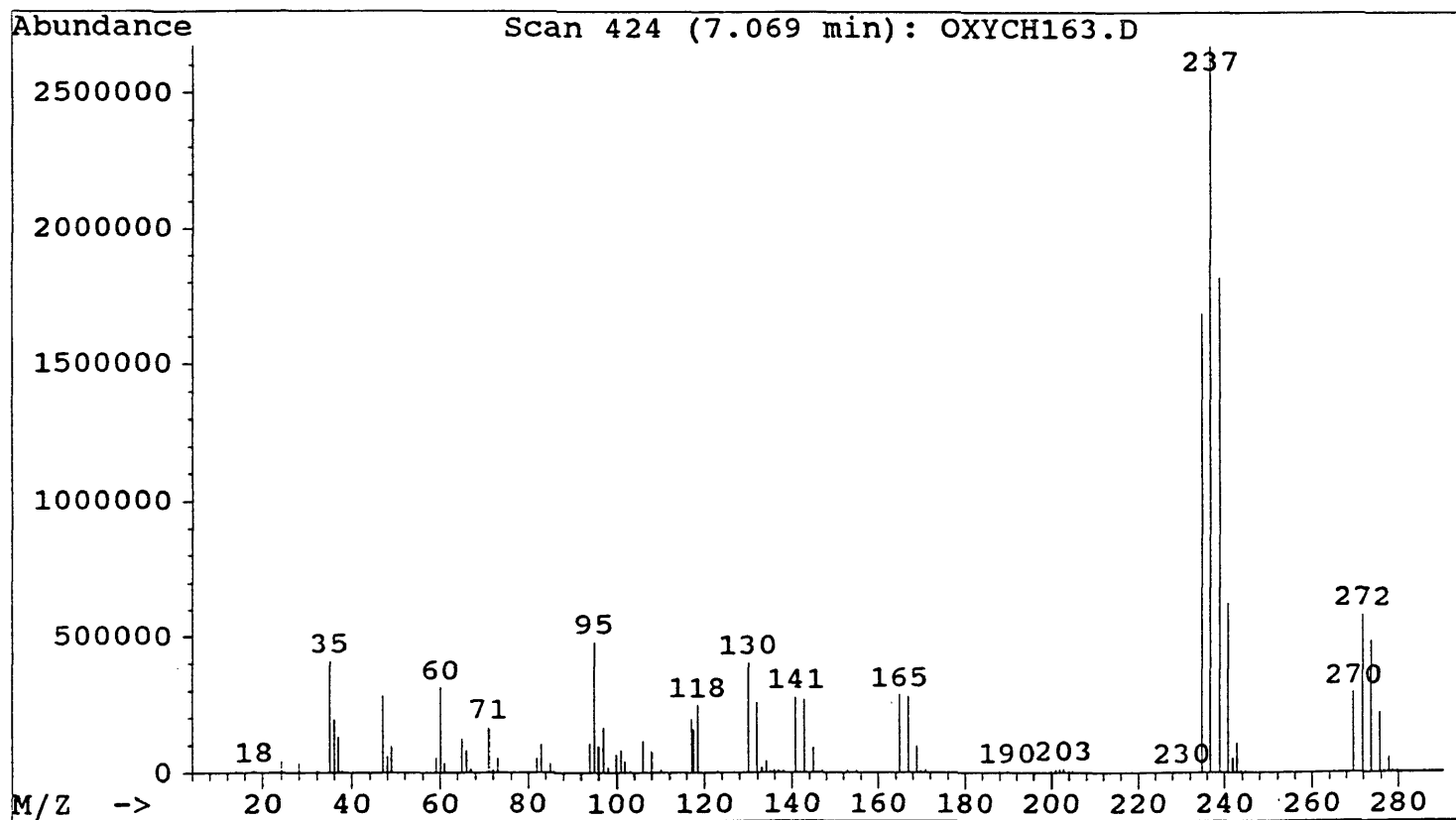
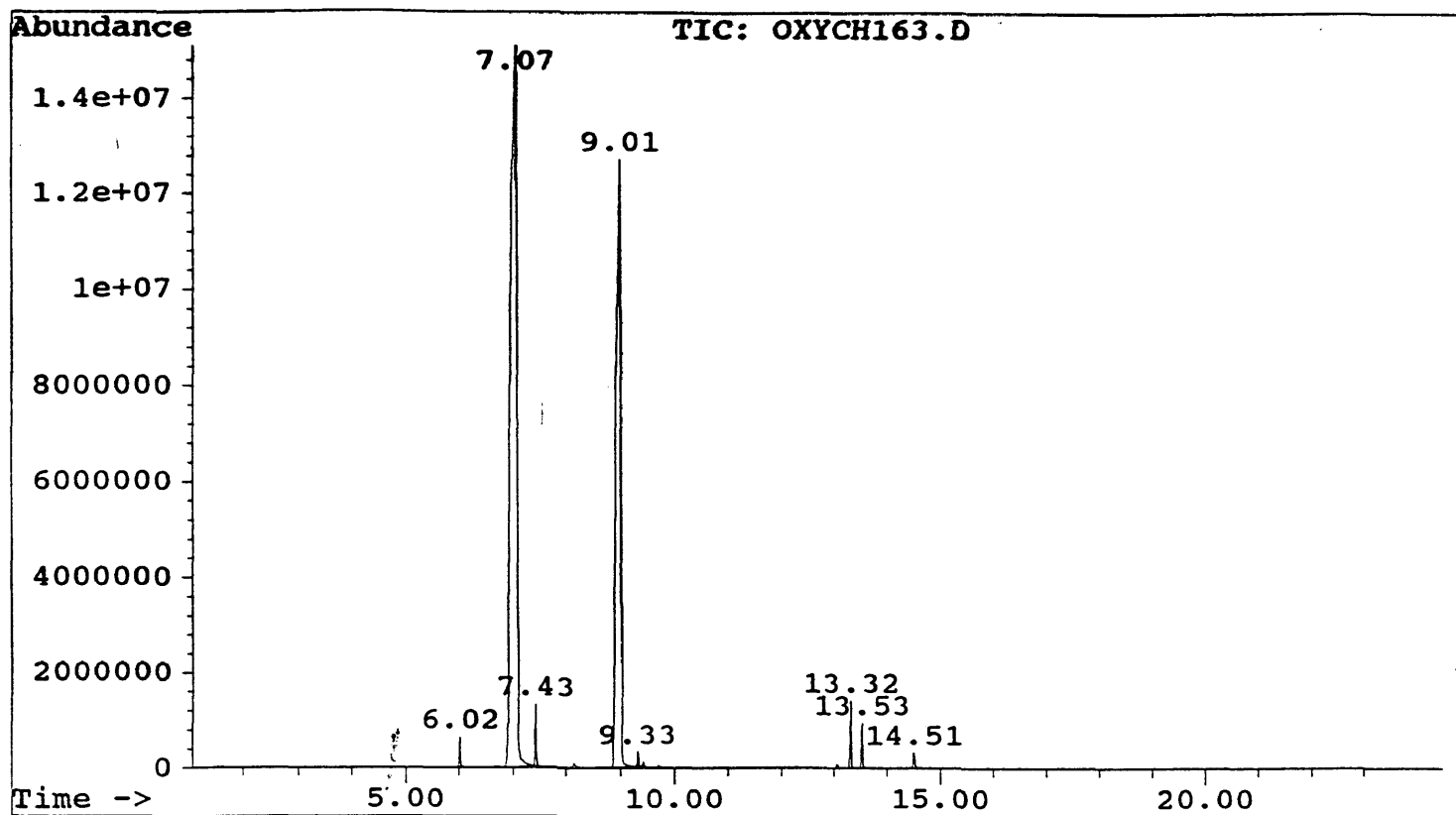
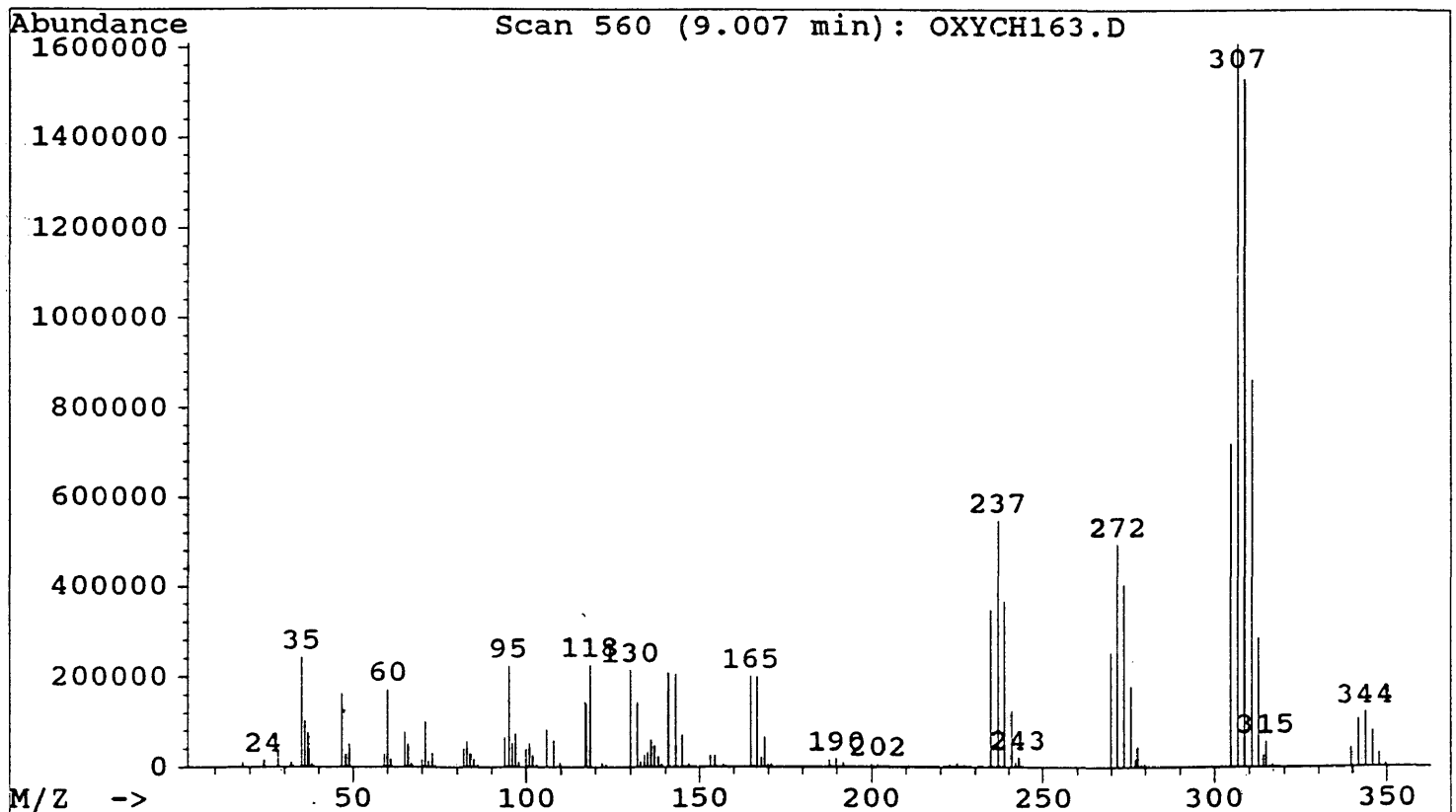
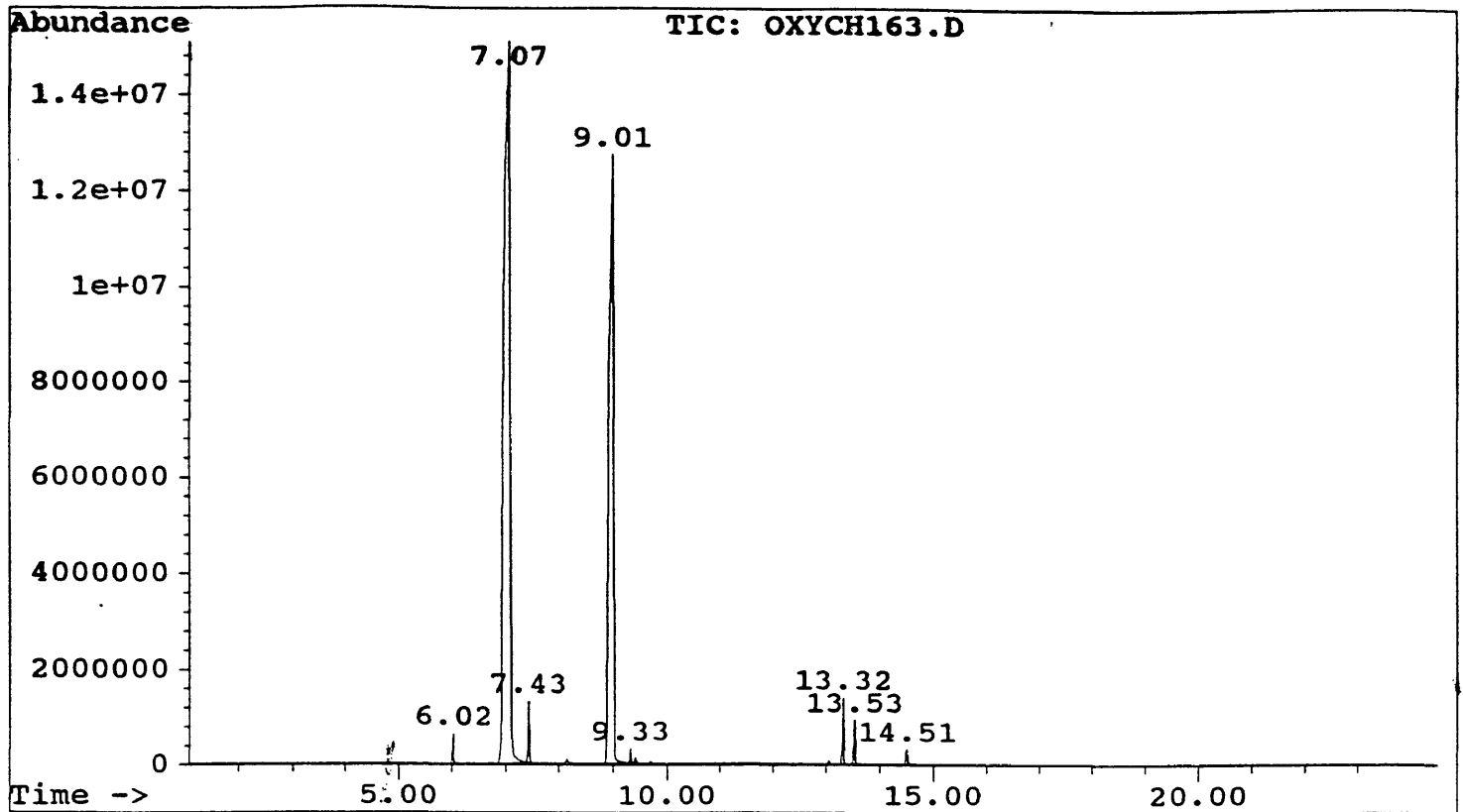


Figure 20-2. GC/MS analysis of hexachlorocyclopentadiene

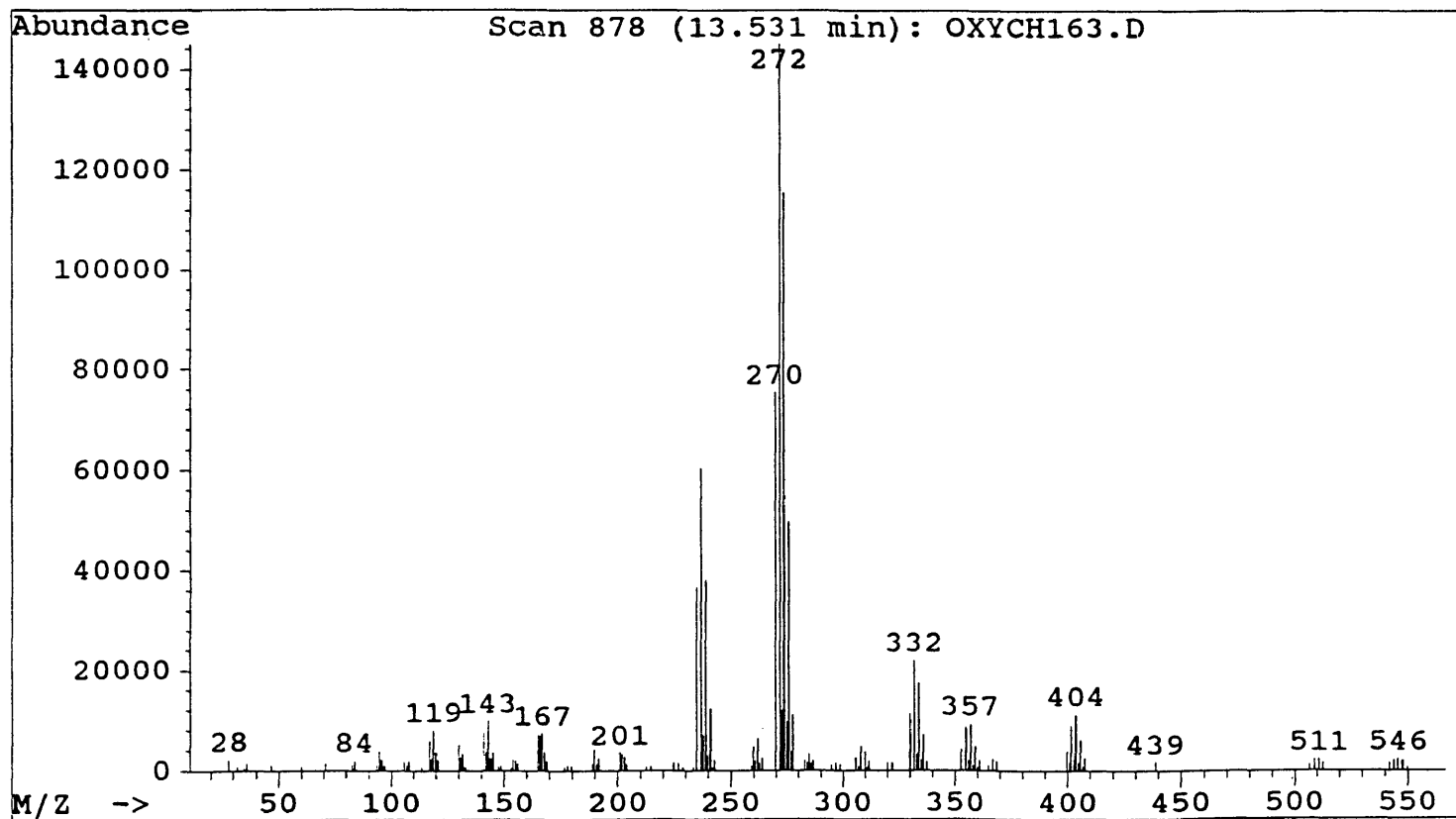
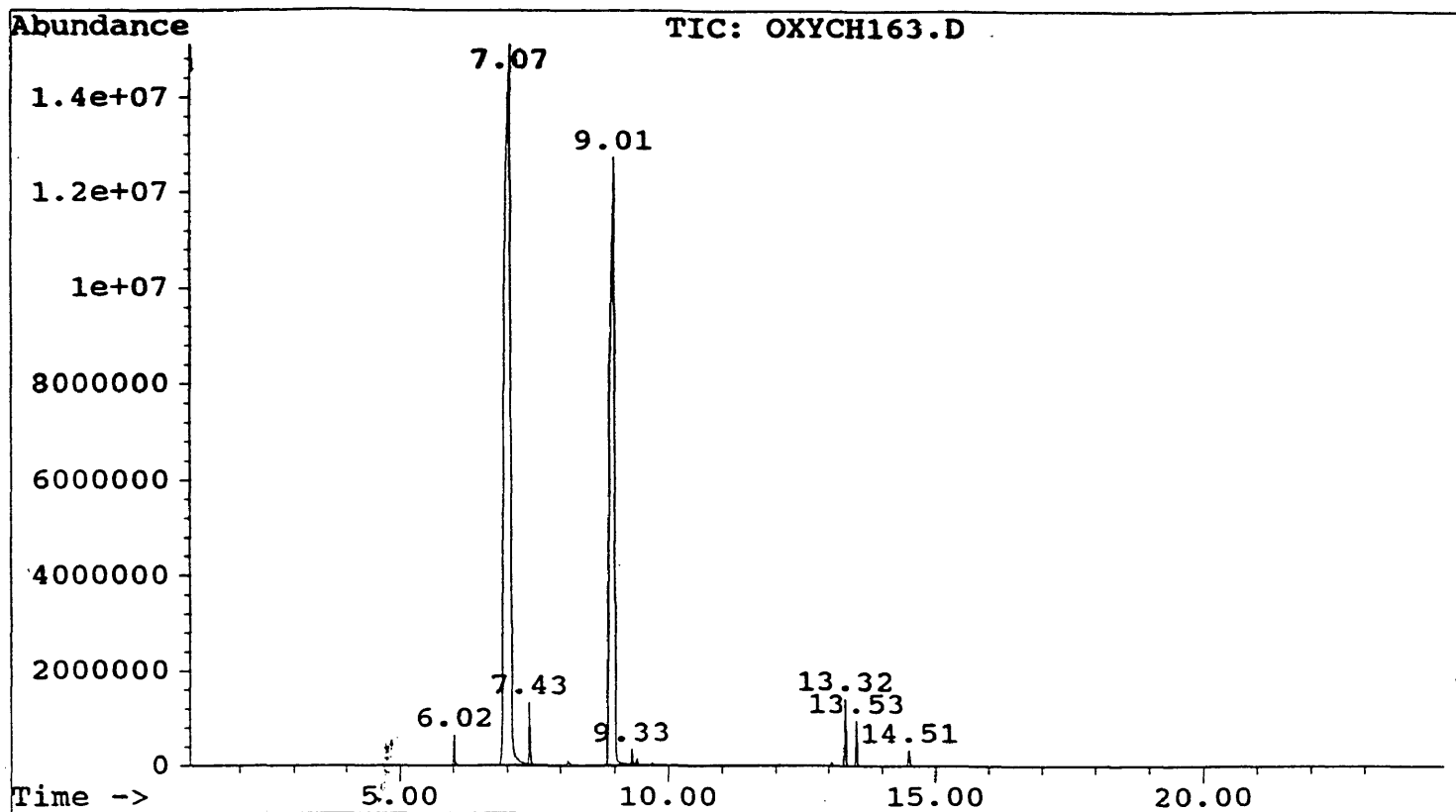


**Figure 21-1.** GC/MS analysis of hexachlorocyclopentadiene heated @ 250-260° C for 19.7 h

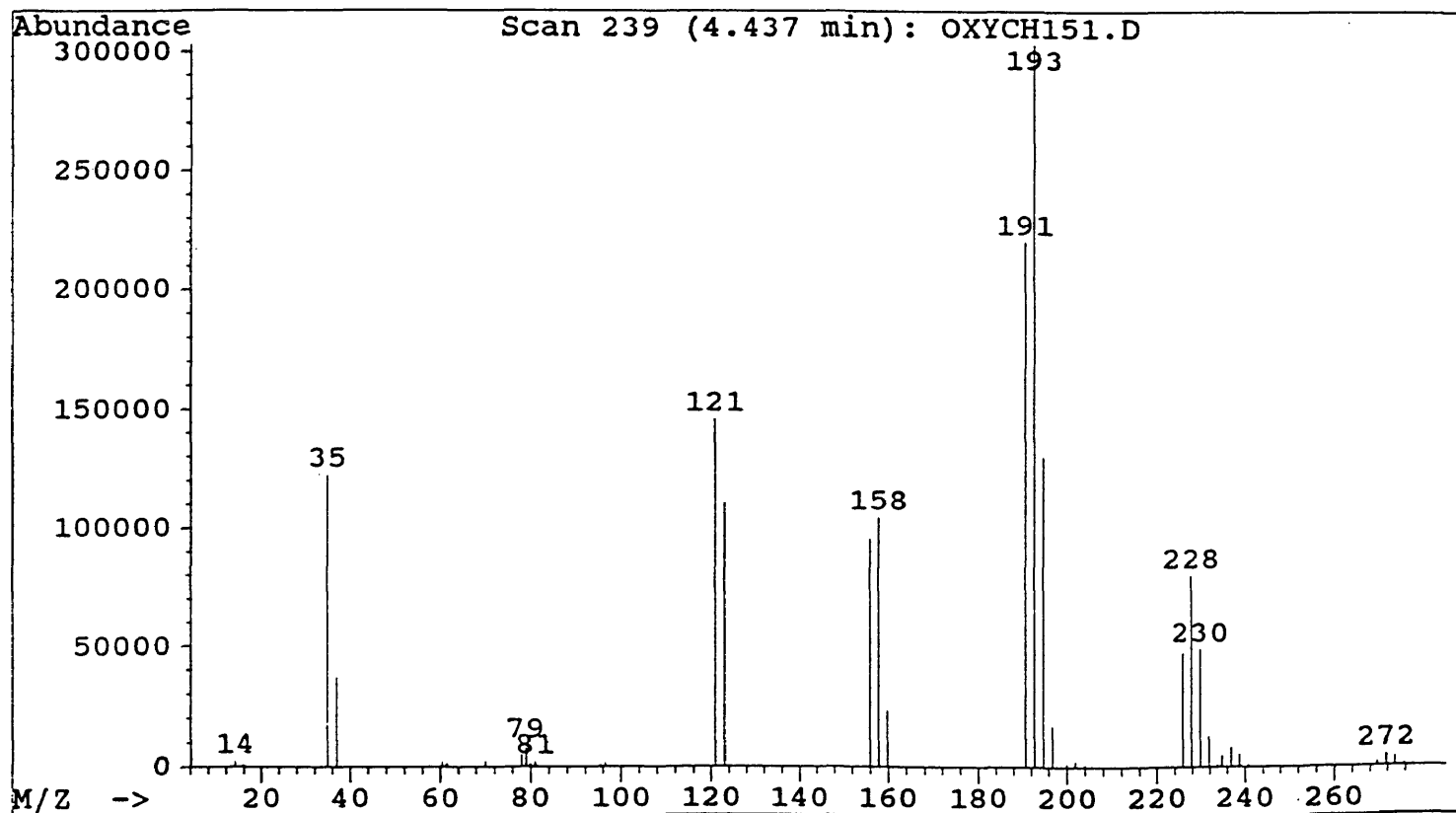
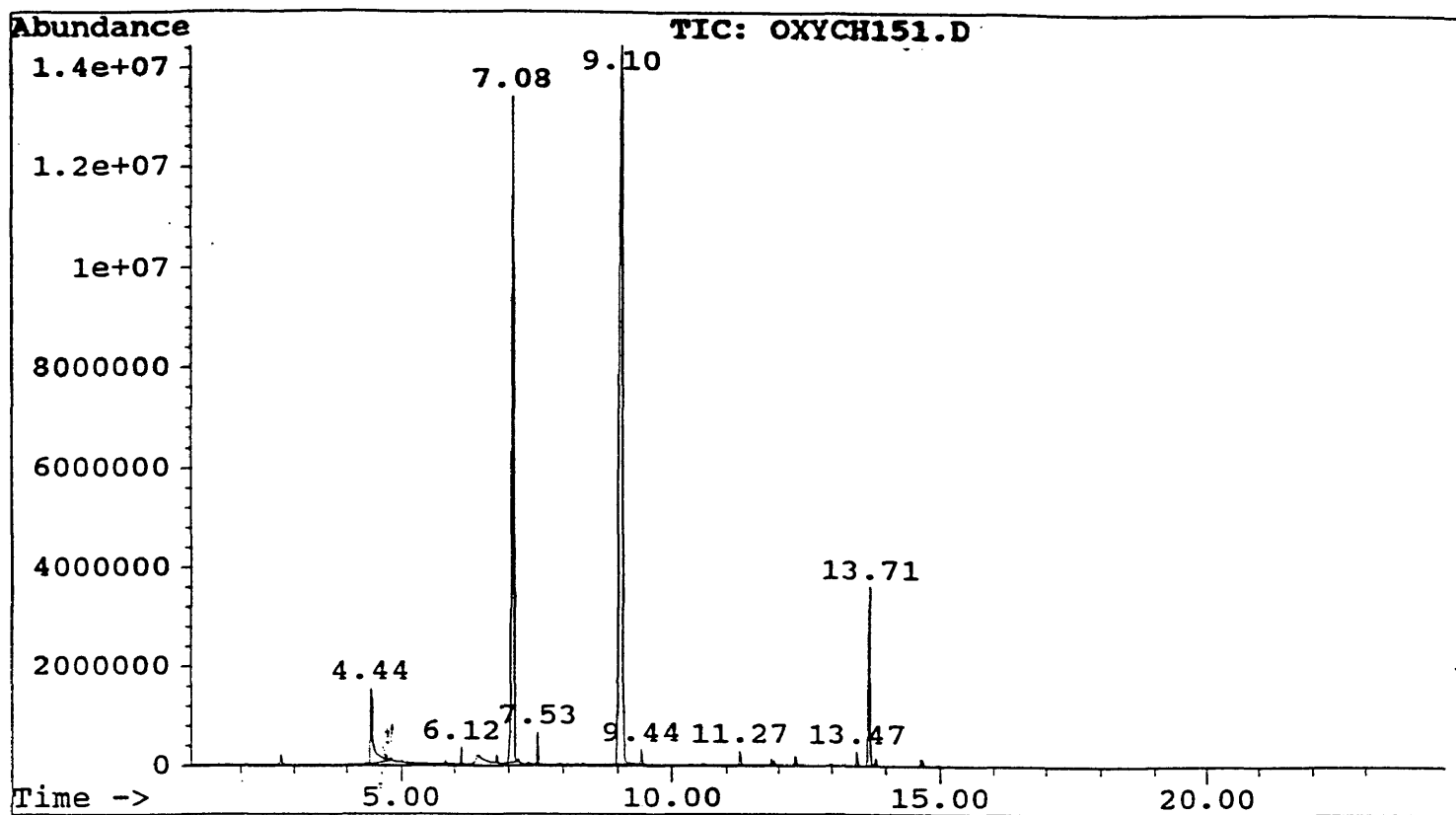




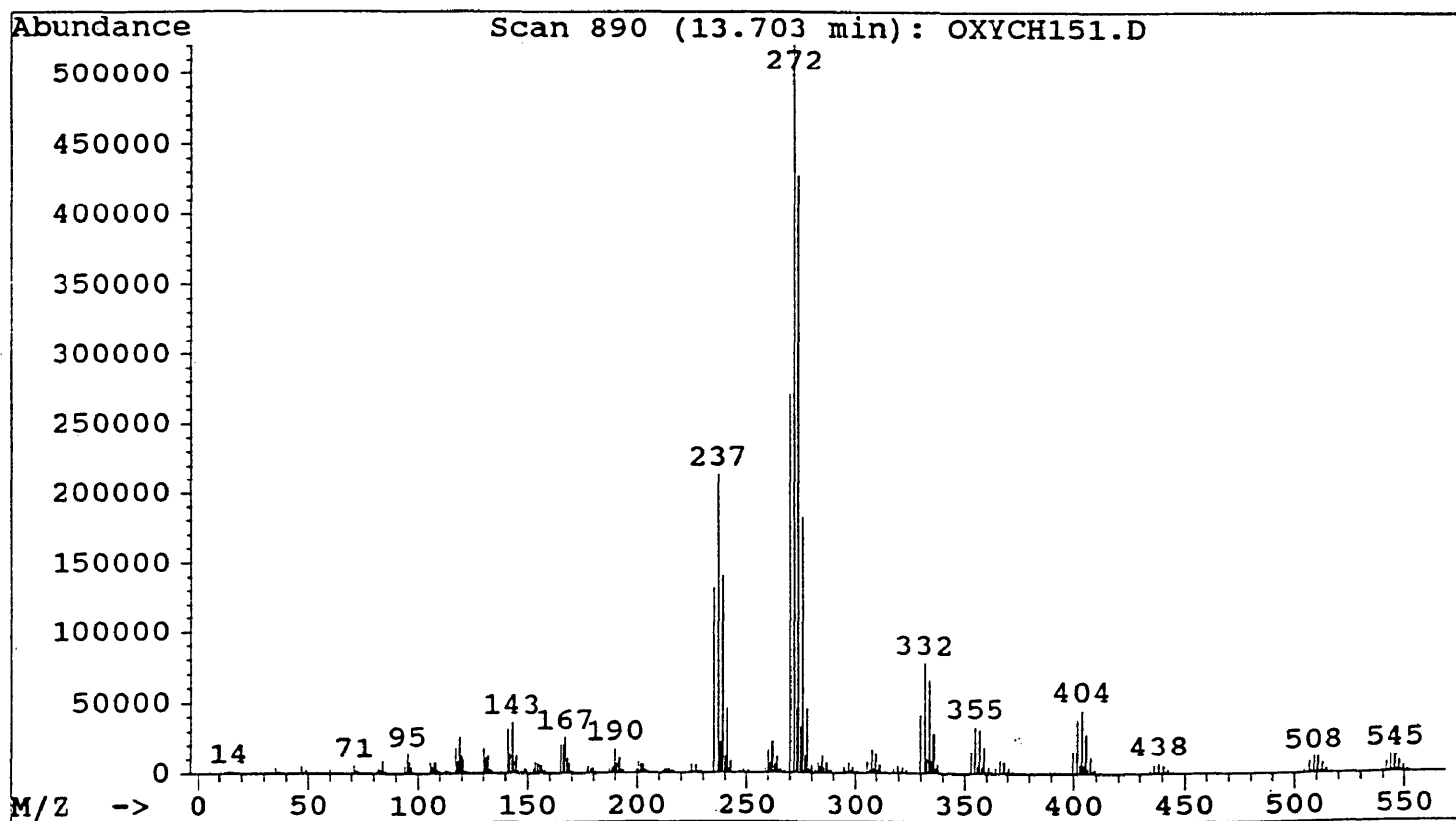
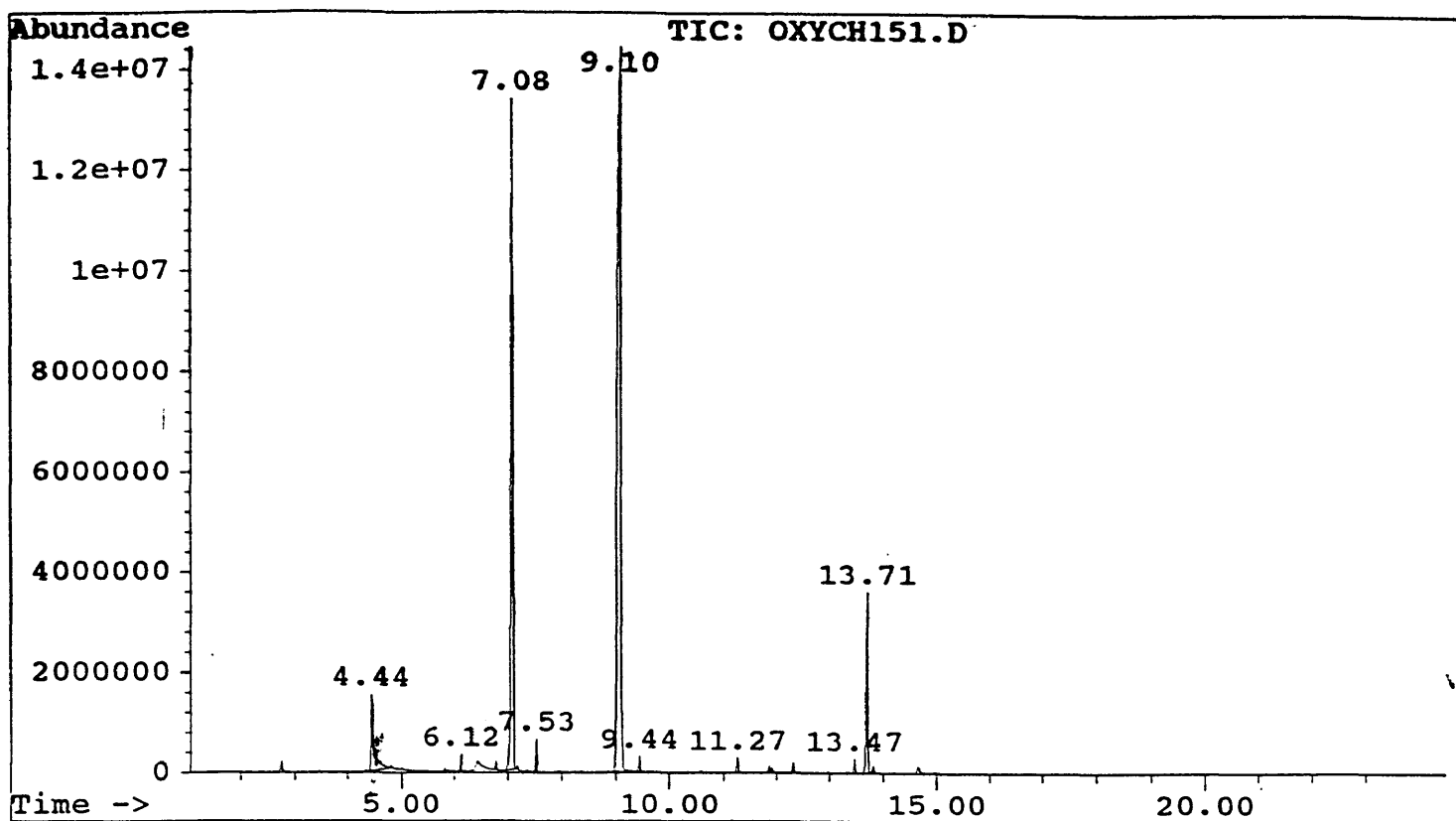
**Figure 21-2.** GC/MS analysis of hexachlorocyclopentadiene heated @ 250-260 °C for 19.7 h



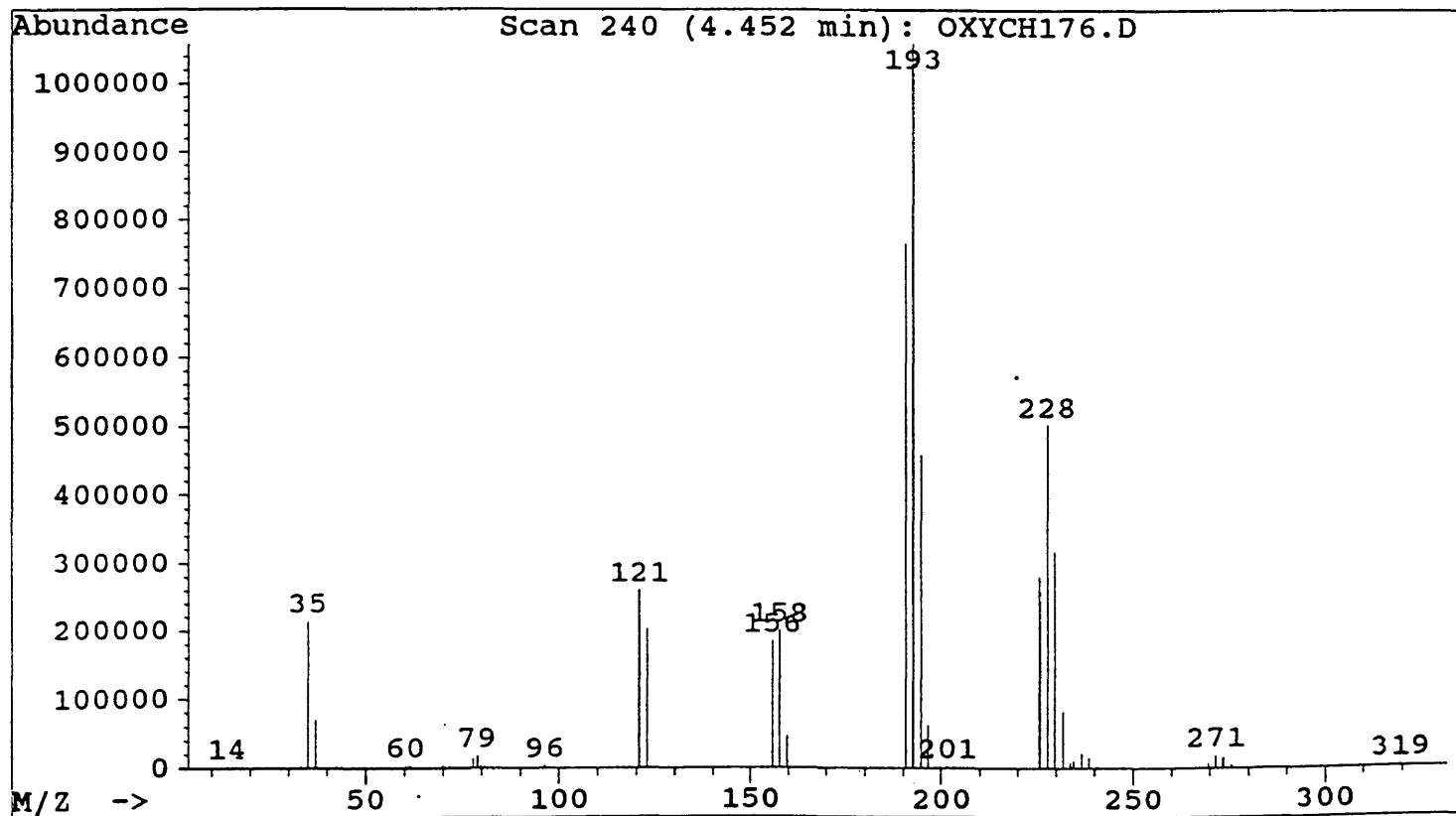
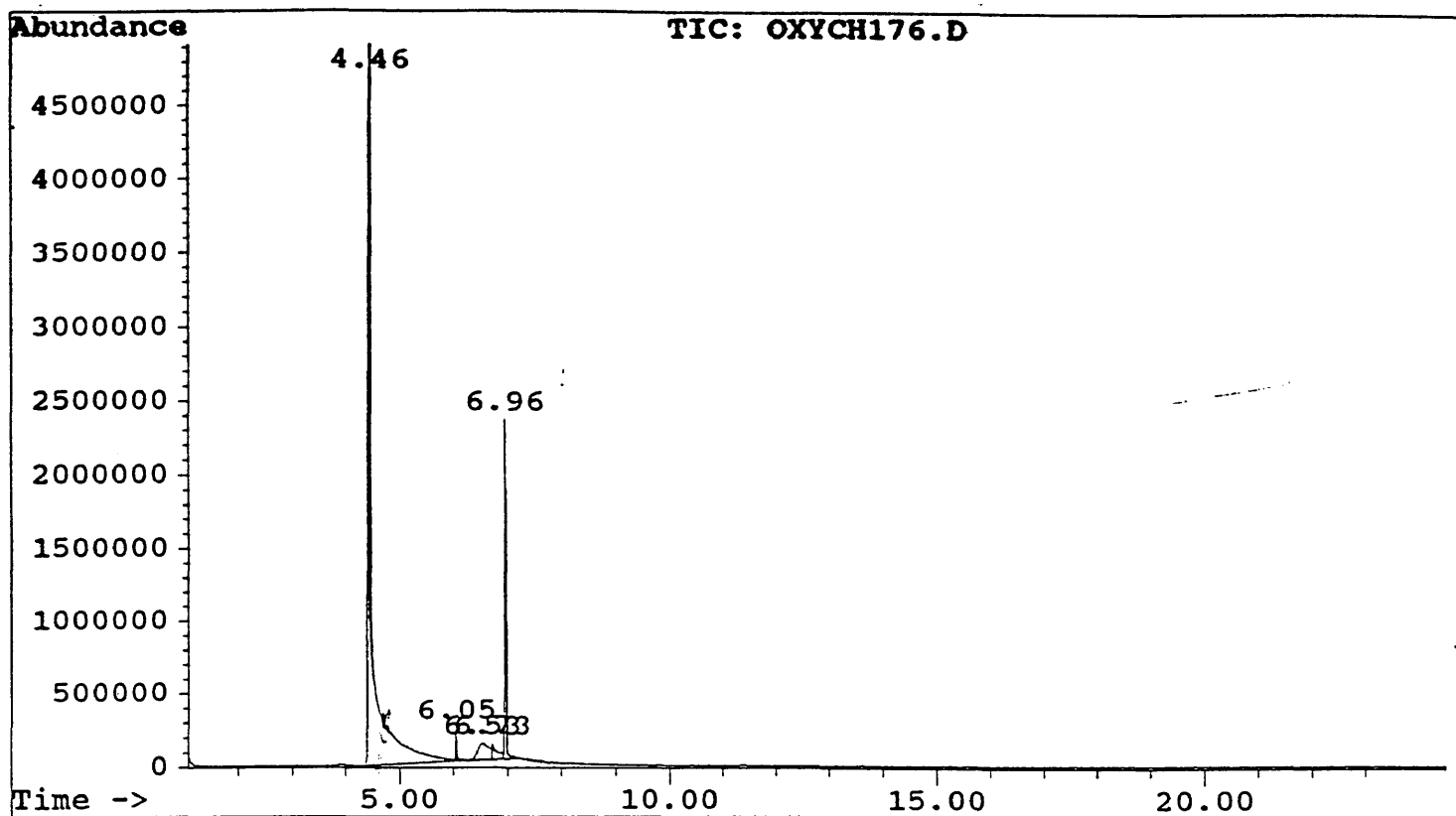
**Figure 21-3.** GC/MS analysis of hexachlorocyclopentadiene heated @ 250-260 °C for 19.7 h



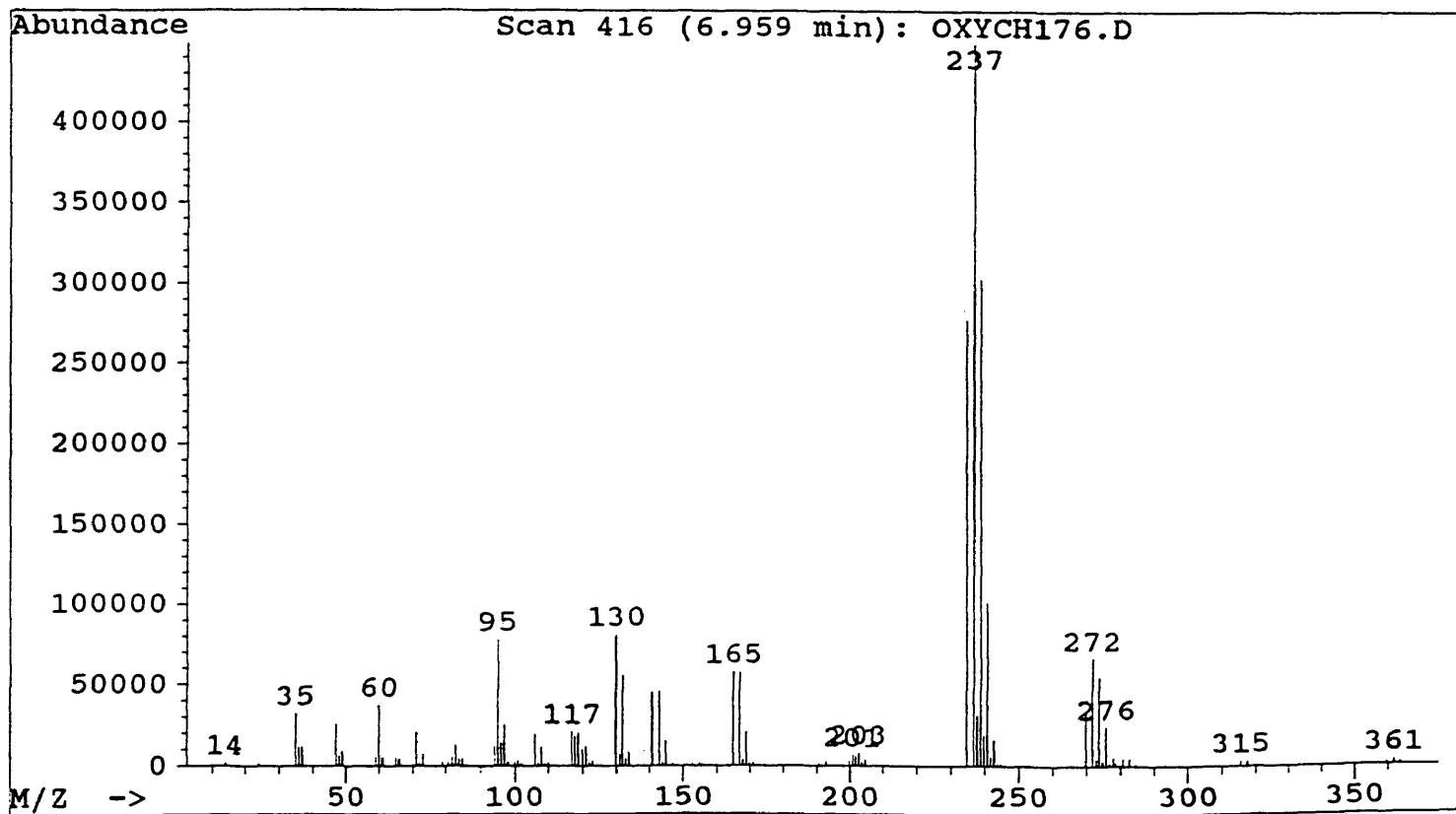
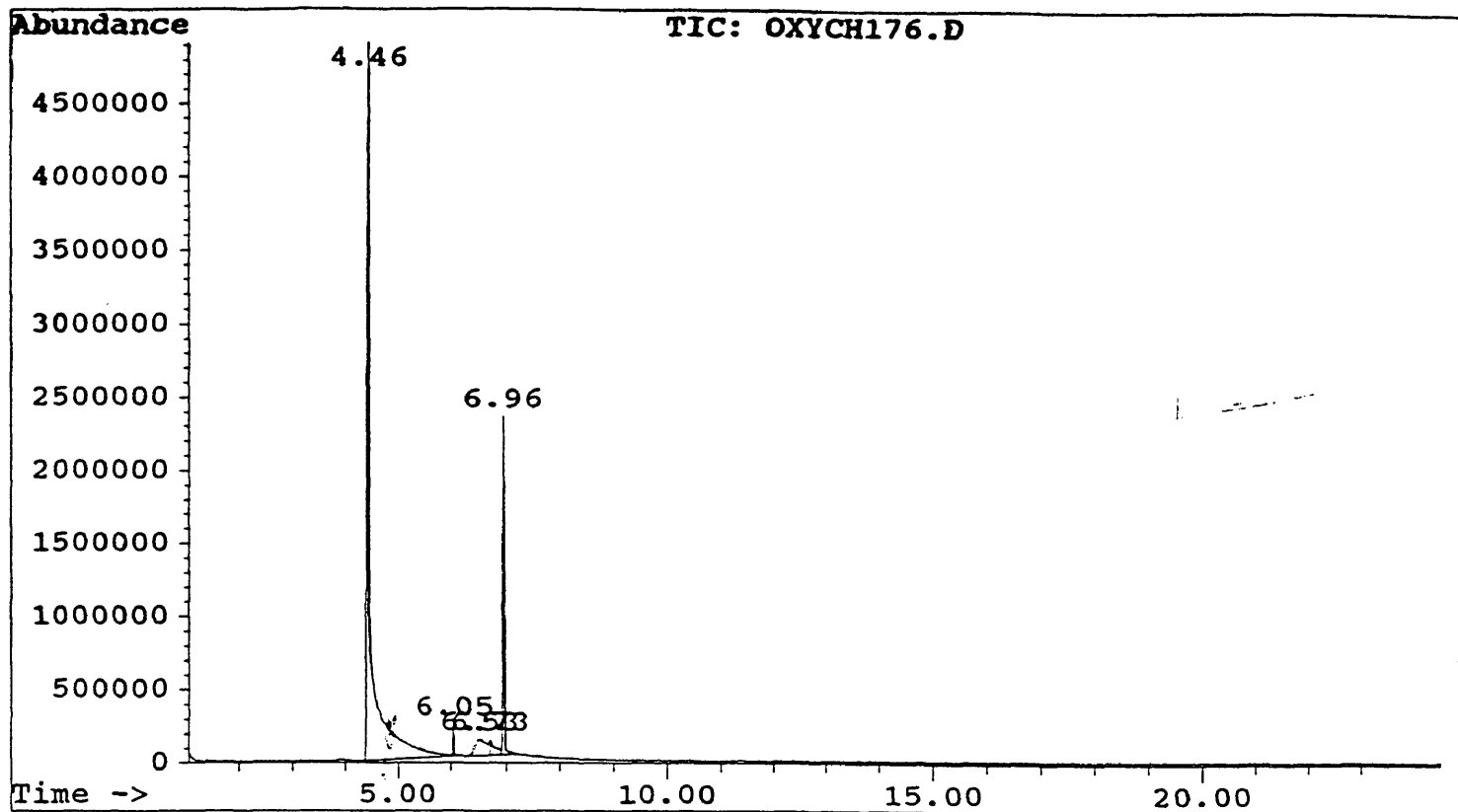
**Figure 22-1.** GC/MS analysis of 90:10 hexachlorocyclopentadiene/  
Sb<sub>2</sub>O<sub>3</sub> mixture heated @ 250-260 °C for 19.7 h



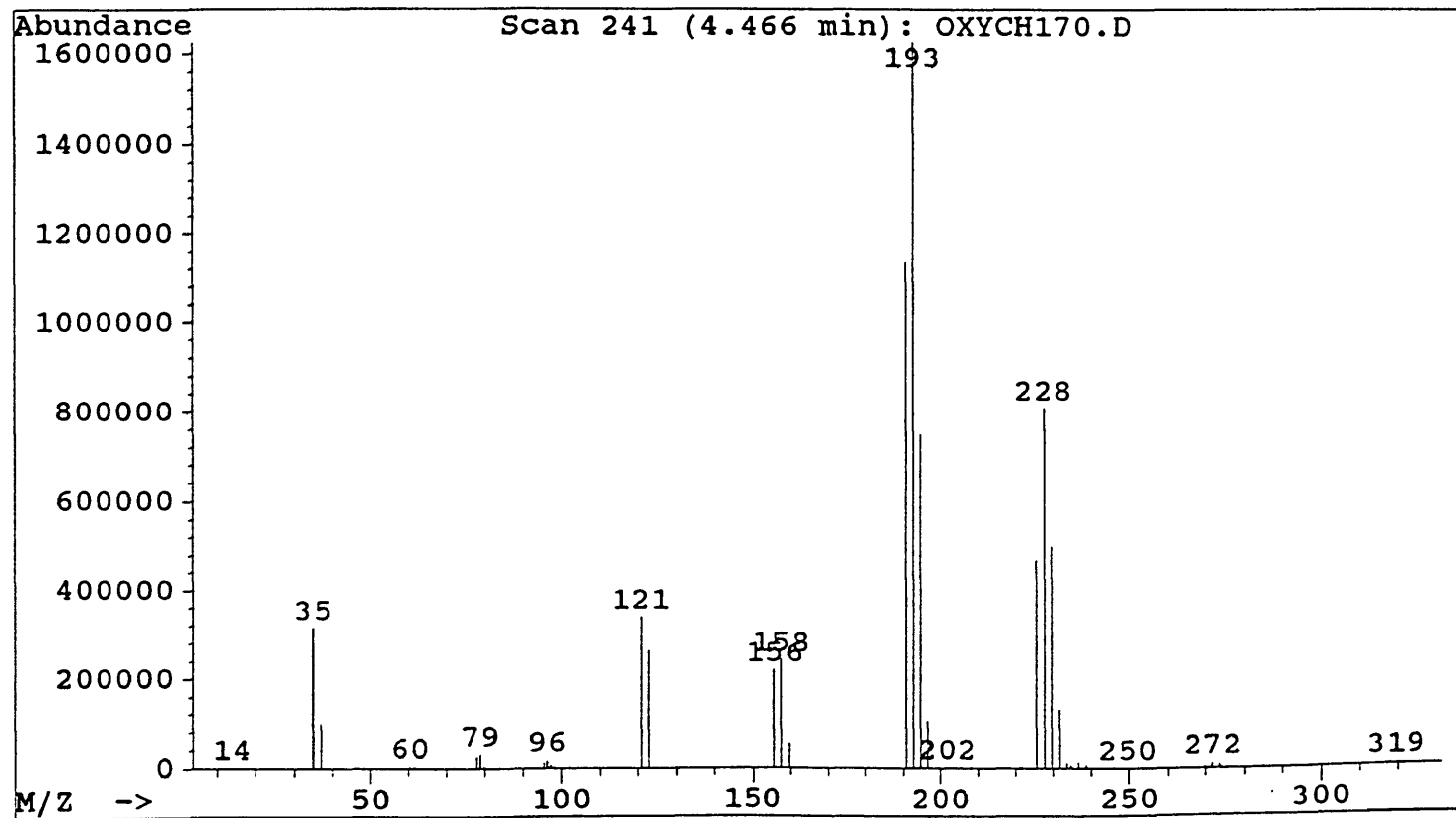
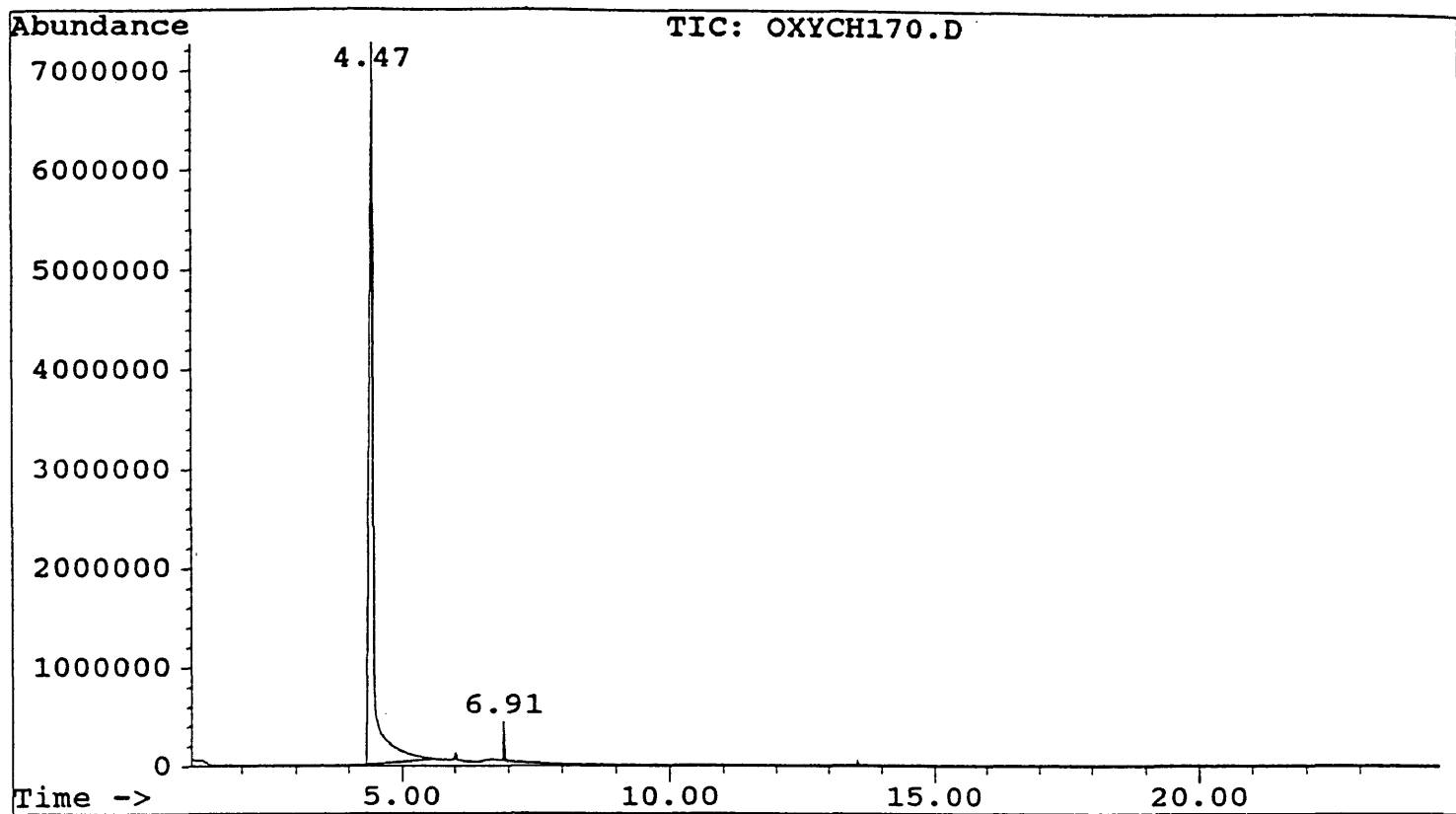
**Figure 22-2.** GC/MS analysis of 90:10 hexachlorocyclopentadiene/  
Sb<sub>2</sub>O<sub>3</sub> mixture heated @ 250-260 °C for 19.7 h



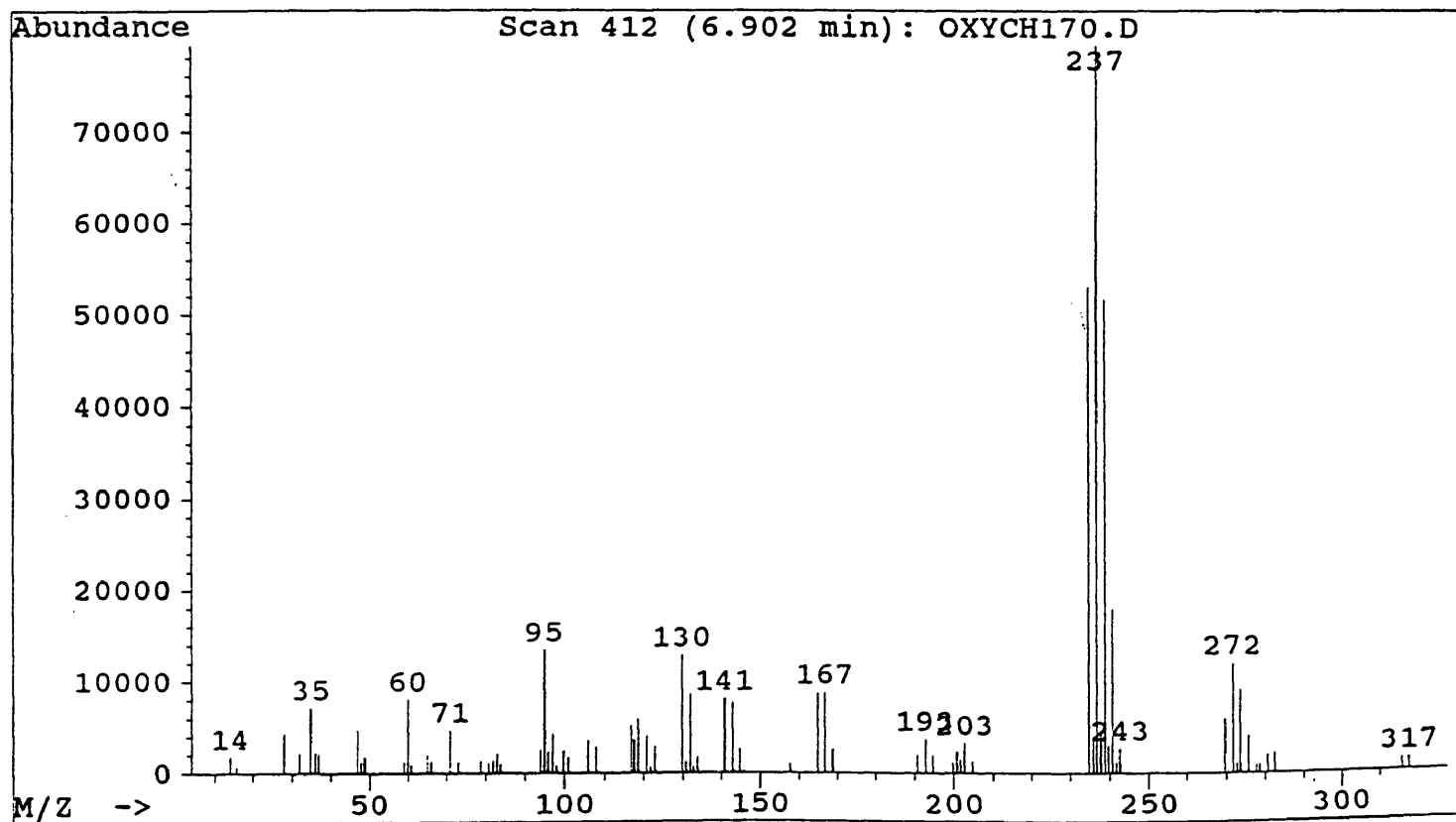
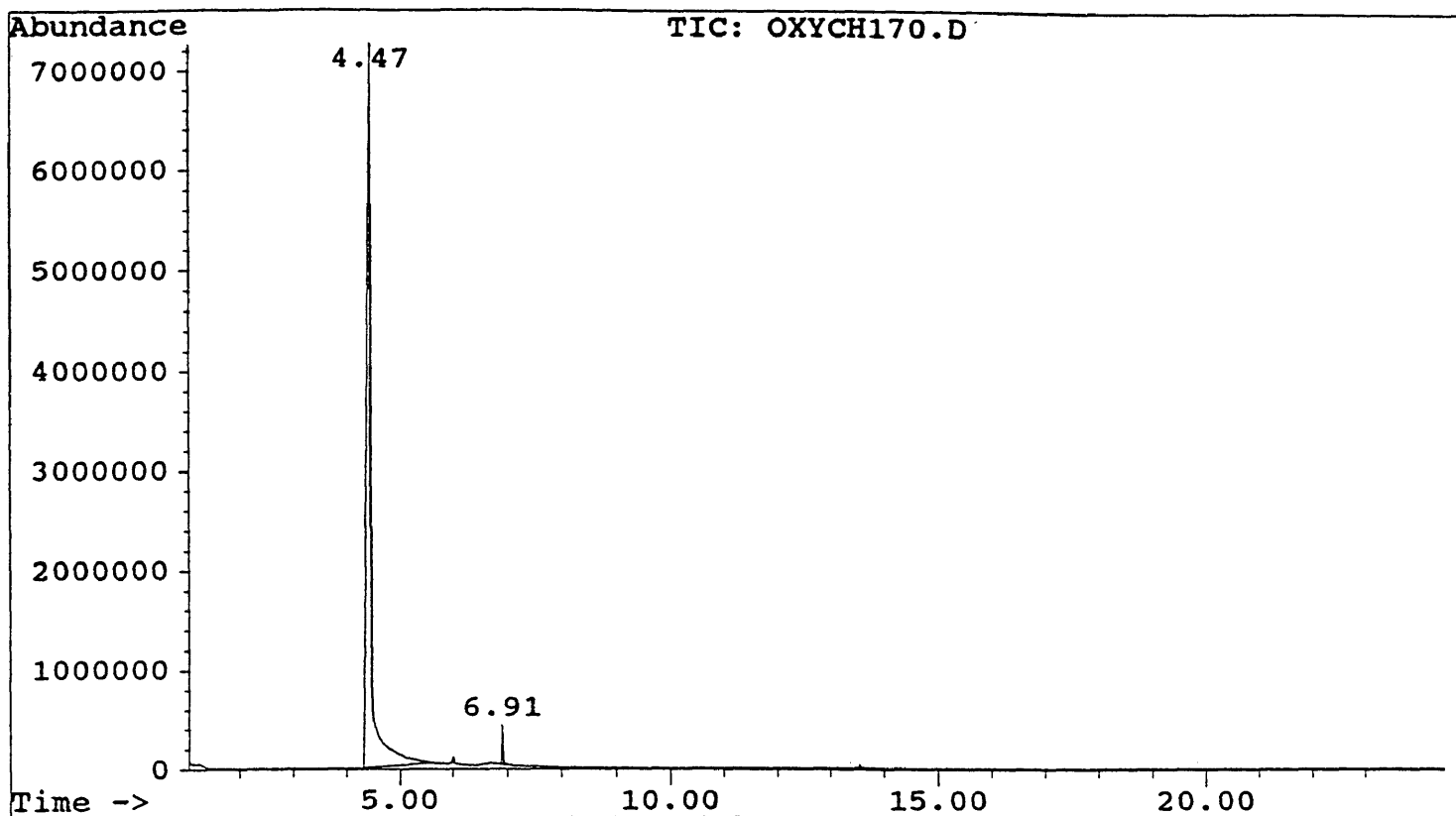
**Figure 23-1.** GC/MS analysis of 50:50 hexachlorocyclopentadiene/  
Sb<sub>2</sub>O<sub>3</sub> mixture heated @ 250-260 °C for 4 h



**Figure 23-2.** GC/MS analysis of 50:50 hexachlorocyclopentadiene/  
Sb<sub>2</sub>O<sub>3</sub> mixture heated @ 250-260 °C for 4 h

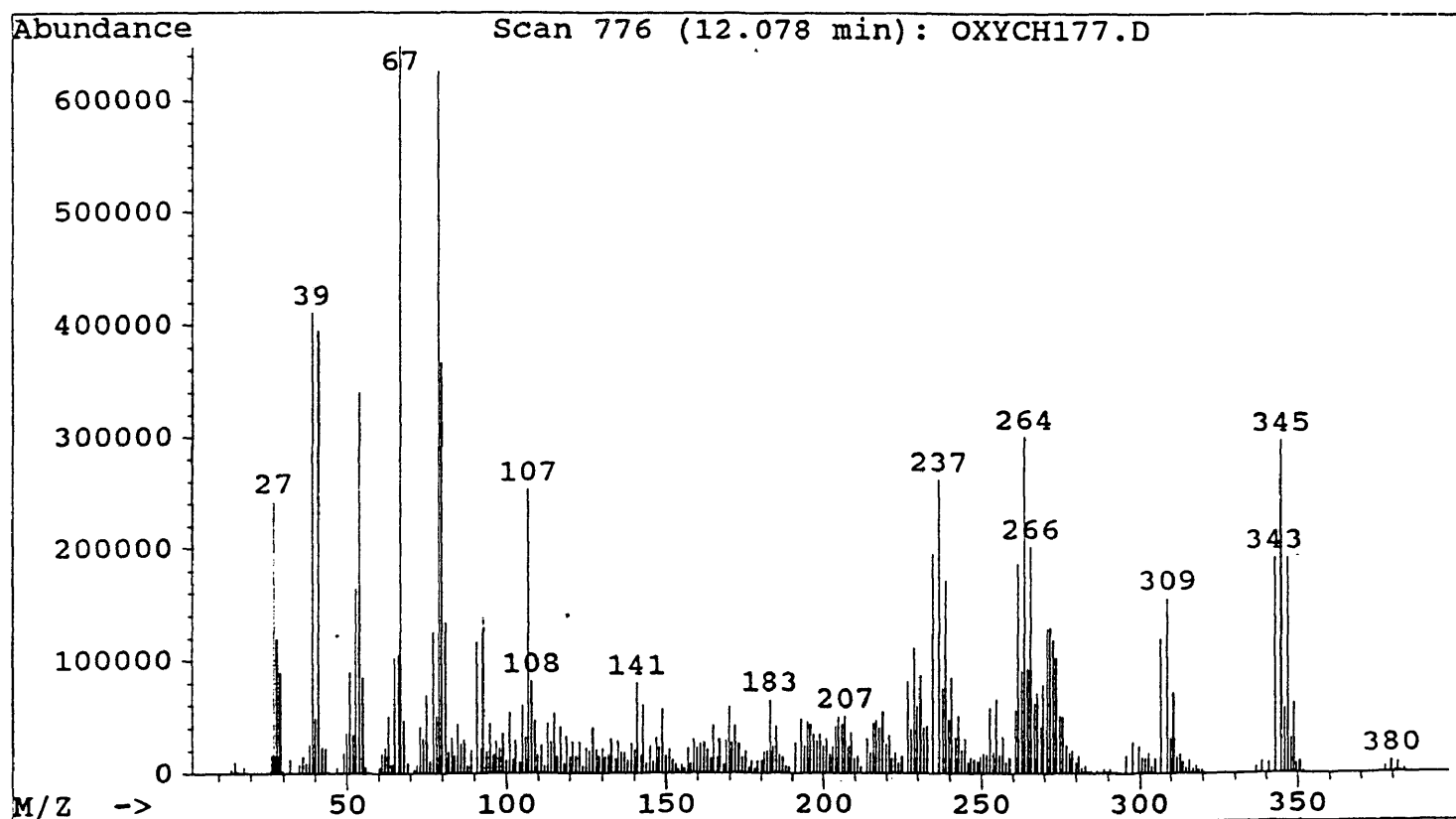
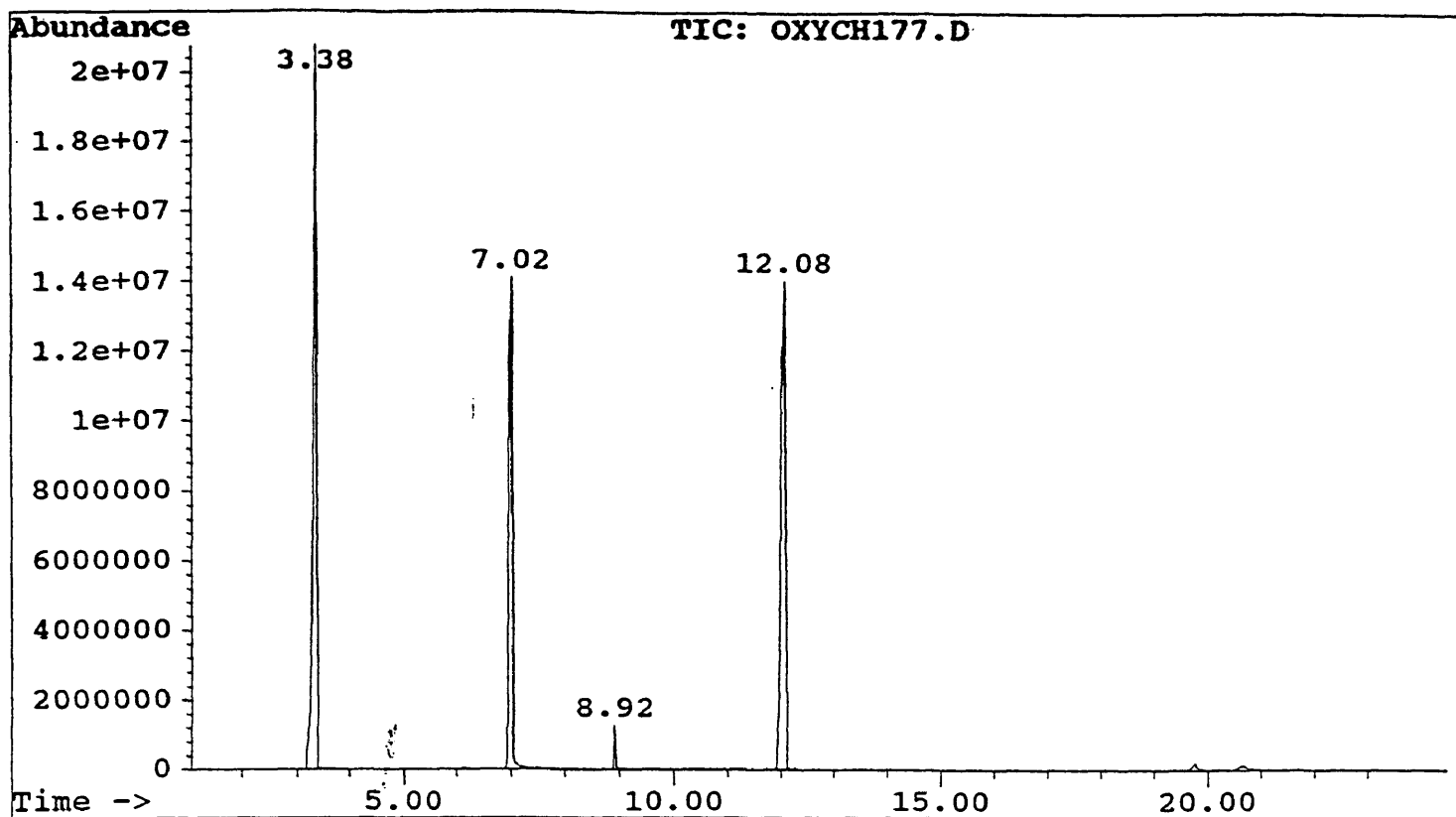


**Figure 24-1.** GC/MS analysis of 50:50 hexachlorocyclopentadiene/  
Sb<sub>2</sub>O<sub>3</sub> mixture heated @ 250-260 °C for 19.7 h



**Figure 24-2.** GC/MS analysis of 50:50 hexachlorocyclopentadiene/  
Sb<sub>2</sub>O<sub>3</sub> mixture heated @ 250-260 °C for 19.7 h





**Figure 25.** GC/MS analysis of 1:4 hexachlorocyclopentadiene/  
1,5-cyclooctadiene mixture refluxed @ 100 °C for 4 h

#### IV. CONCLUSIONS

In Nylon 66 formulations, Dechlorane Plus (Dech Plus) reacts with antimony trioxide in ways that are highly unusual and were previously unsuspected. A major feature of this new chemistry is reductive dechlorination. This process forms partially reduced isomers of Dech Plus, as well as partially reduced isomers of compound **B**, which is the product of a retro-Diels-Alder reaction. The mechanism of the dechlorination has not yet been determined, although some preliminary attempts to understand it were made in the present work. A possible mechanism for the retro-Diels-Alder process involves the reaction of antimony trioxide with a C-Cl bond in a  $-CCl_2-$  bridge, in order to form a carbanion that loses a pentachlorocyclopentadienyl anion very rapidly ( see Figure 4 ). However, this mechanism also remains to be confirmed.

The dechlorination of Dech Plus and its conversion into products that are more volatile may account for the deleterious effects of antimony trioxide on the fire-retardant properties of this useful material. Further work is needed in order to understand fully the very rich chemistry that now has been found in this system, and to devise ways of preventing its occurrence in Nylon 66.

## REFERENCES

1. Avento, J. M.; Touval, I. *Encyclopedia of Chemical Technology*, 4<sup>th</sup> ed.; Wiley-Interscience: New York, **1991**; Vol. 10, p 934.
2. Landrock, A. *Handbook of Plastics Flammability and Toxicology*; Park Ridge Noyes: New Jersey, **1983**; Chapter 3.
3. Einhorn, I. N. In *Reviews in Polymer Technology*; Skeist, I., Ed.; Marcel Dekker: New York, **1972**; Vol. 1, p 113.
4. McNeil, I. C. *Makromol. Chem., Macromol. Symp.* **1993**, 74, 11.
5. Gann, R. G.; Dipert, R. A.; Drews, M. J. *Encyclopedia of Polymer Science and Engineering*, 2<sup>nd</sup> ed.; Wiley-Interscience: New York, **1987**; Vol. 7, p 154.
6. Cullis, C. F.; Hirschler, M. M. *The Combustion of Organic Polymers*; Oxford: New York, **1981**; Chapter 3.
7. Chamberlain, D. C. *Flame Retardancy of Polymeric Materials*; Kuryla, W. C.; Papa, A. J., Eds.; Marcel Dekker: New York, **1978**; Vol. 4, Chapter 2.
8. Camino, G.; Costa, L.; Luda di Cortemiglia, M. P. *Polym. Degrad. Stab.* **1991**, 33, 131.
9. Grassie, N.; Scott, G. *Polymer Degradation and Stabilization*; Cambridge University: New York, **1985**; Chapter 6.
10. Ebdon, J. R., Jones, M. S. In *Polymeric Materials Encyclopedia*; Salamone, J., Ed.; CRC Press: New York, **1996**; Vol. 4, p 2397.

11. Avento, J. M.; Touval, I. *Encyclopedia of Chemical Technology*, 3<sup>rd</sup> ed. ; Wiley-Interscience: New York, **1980**; Vol. 10, p 355.
12. Camino, G.; Costa, L. *Polym. Degrad. Stab.* **1988**, 20, 271.
13. Pearce, E. M.; Shalaby, S. W.; Baker, R. H. In *Flame-Retardant Polymeric Materials*; Lewin, M.; Atlas, S. M.; Pearce, E. M., Eds.; Plenum Press: New York, **1975**; Vol. 1, p 239.

**VITAE**

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