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Mass Spectra of Chlorinated Organophosphorus Pesticides

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염소화 유기인제 농약의 질량 분석법

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ABSTRACT : Fragmentation patterns on electron impact of 8 chlorinated organophosphorus pesticides were investigated. In most cases, characteristic ions could be identified and the peak clusters due to the ^{35}Cl and ^{37}Cl isotopes in the fragment ions were found to be highly characteristic. The fragmentation patterns of phosphorus moiety were coincident with previous report in the aspect of mechanism.

요약 : 8종의 염소화유기인제 농약에 대한 전자충돌식으로 이온화시킨 질량분석법에 대하여 연구하였다. 대부분의 경우, 염소 원소를 포함하는 특성이온들은 그들의 동위원소에 기인하는 ^{37}Cl 피크에 의해 쉽게 확인되어진다. 즉 깨어진 이온의 염소 동위원소(^{37}Cl)에 기인하는 피크량의 비를 측정함으로써 염소 원자수를 알 수 있다. 또한, 유기인제 부분은 과거에 보고되었던 질량분석 메카니즘과 비교하였을 때, 대체로 잘 일치함이 관측되었다.

Key Words : Mass fragmentation pattern, chlorinated organophosphorus pesticides.

1. Introduction

The importance of gas chromatography / mass spectrometry (GC/MS) for pesticides chemistry, particularly for the identification of samll quantities encountered in residues, is rapidlly being recognized.

Several classes of pesticides have been investigated and fragmentation patterns on various ionization methods were analyzed with high resolution mass spectrometry.[1-3]

In general, chlorinated pesticides are well suited for mass spectral residue analysis[4,5] because these

compounds usually yield intense characteristic ions due to the isotopic peaks of chlorine atoms. Fragmentation patterns of organophosphorus pesticides[5,7] have been studied according to phosphorus groups such as phosphates, phosphorothioates and phosphorodithioates.

We have been interested in determining the pesticides for obtaining structural information without high resolution mass spectrometry which is very expensive and non-popular instrument. We have chosen to study the chlorinated organophosphorus pesticides because these compound produce the isotopic clusters due to chlorine atom and also produce the characteristic ions of phosphorus group that can be resolved by quadrupole-type mass spectrometry.

In this study, we suggested the fragmentation pathways of the chlorinated organophosphorus pesticides on the basis of the presence of chlorine atoms which produce the isotopic peaks and utilizing information from the previously reported fragmentation patterns for organophosphorus groups.

2. Experimental

Chemicals Eight standard pesticides were obtained as test substances from Dr. Ehrenstorfer (Germany) and Chem Service(U.S.A) with 97~99% purity. Acetone and hexane were purchased from J. T. Baker(U.S.A).

Instrumentation Mass spectrometry was performed using a Hewlett-Packard 5970A mass selective detector with a Hewlett-Packard 5890 gas chromatograph. For the gas chromatographic separation a bonded fused-silica capillary column(HP-1, 30m×0.2mm, i. d.) was used which was coupled directly the ion source. Helium was used as the carrier gas at 0.9ml/min flow rate. The GC injection port temperature was 270℃, interface region was maintained at 300℃, and ion source was set at 200℃. The mass spectrometer was tuned with the calibration reagent of perfluorotributylamine(PFTBA) for the selected ion of m/z 69, 219 and 502. The electron energy was 70eV.

3. Results and Discussion

The standard chlorinated organophoshorus pesticides produced acceptable gas chromatographic properties as shown in the total ion chormatogram of *Figure* 1.

The basic fragmentation patterns of three major classes(phosphates, phosphorothioates and phosphorodithioates) of organophosphorus pesticides have been published in earlier report[6]. The study on fragmentation pathways for simple organophosphorus esters have focused on the phosphorus moiety. The pathways for the production of fragments with organophosphorus moiety proposed by Pritchard[7] are shown in Scheme 1. In their studies, the ion at m/z 109 $[(CH_3O)_2P=O]^+$ from molecular ion of dimethyl phosphorochlorodate fragments to give ions at m/z 79 and m/z 49, as shown in Scheme 1. Unlike the dimethylester of the phoshate compounds which undergo successive losses of formaldehyde, diethyl ester lost ethylene molecule and thus retain the oxygen atoms on phosphorus.

Dichlorvos The mass spectrum of dichlorvos has shown a weak intensity of molecular ion (4%) and its isotopic pead (M+2, 3%), as shown in *Figure* 2. *Scheme* 2 indicates that the base peak of m/z 109 is related to the formation of $(CH_3O)_2P=O$ due to inductive cleavage of phosphate group. The ion of m/z 79 is produced by loss of aldehyde molecule from the base peak ion. The loss of the chlorine radical from molecular ion generated m/z 185 and its isotopic peak m/z 187.

Trichlorfon Trichlorfon failed to yield a molecular ion peak and produced only a few significant

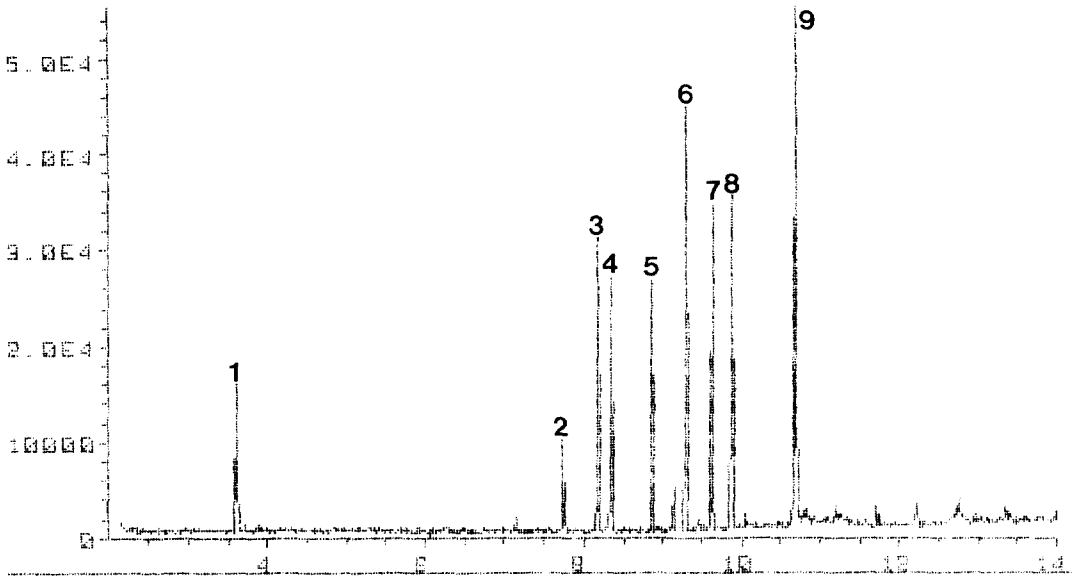
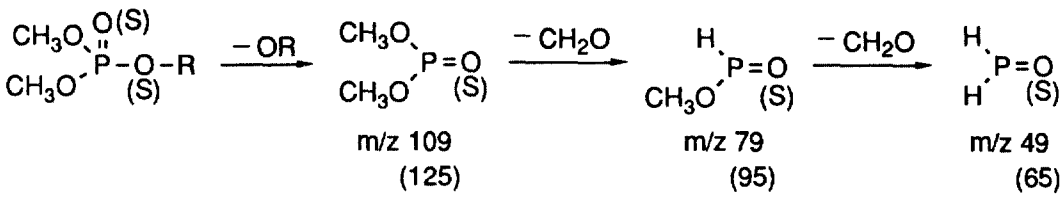
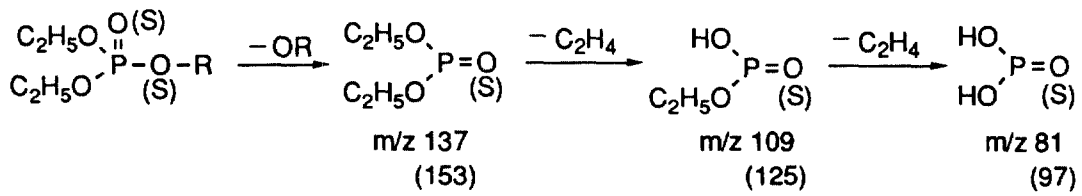


Figure 1. Total ion chromatogram of eight chlorinated organophosphorus pesticides: 1. dichlorvos 2. trichlorphon 3. cis-phosphamidon 4. trans-phosphamidon 5. chlorpyrifos-methyl 6. chlorpyrifos 7. tetrachlorvinfos 8. profenofos 9. carbofenothion.

A. In the case of dimethyl phosphate or phosphorothioate



B. In the case of dimethyl phosphate or phosphorothioate



Scheme 1. Basic fragmentation pattern of dimethyl and diethyl phosphate groups.

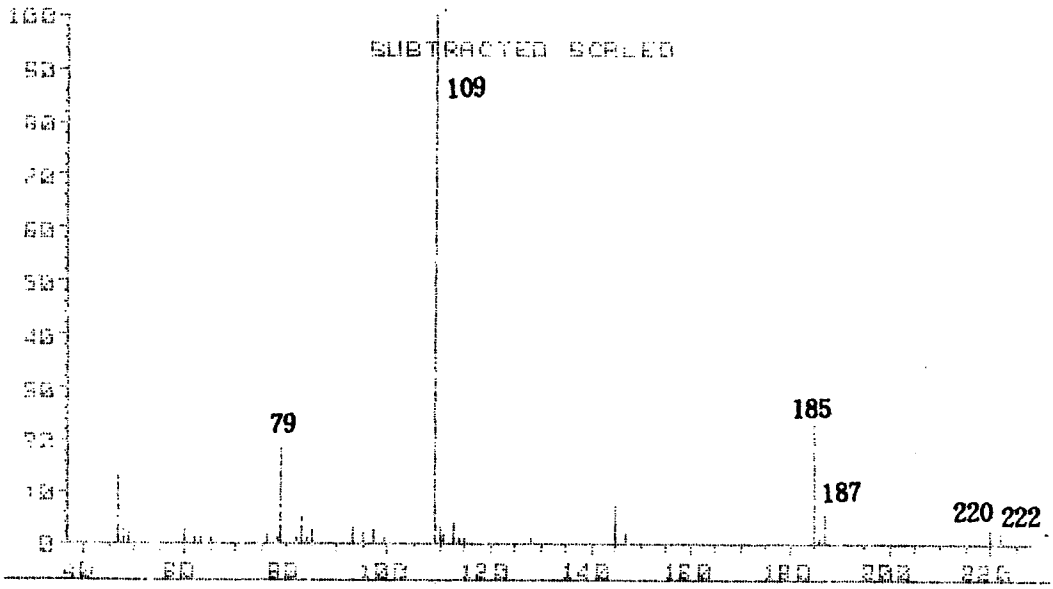
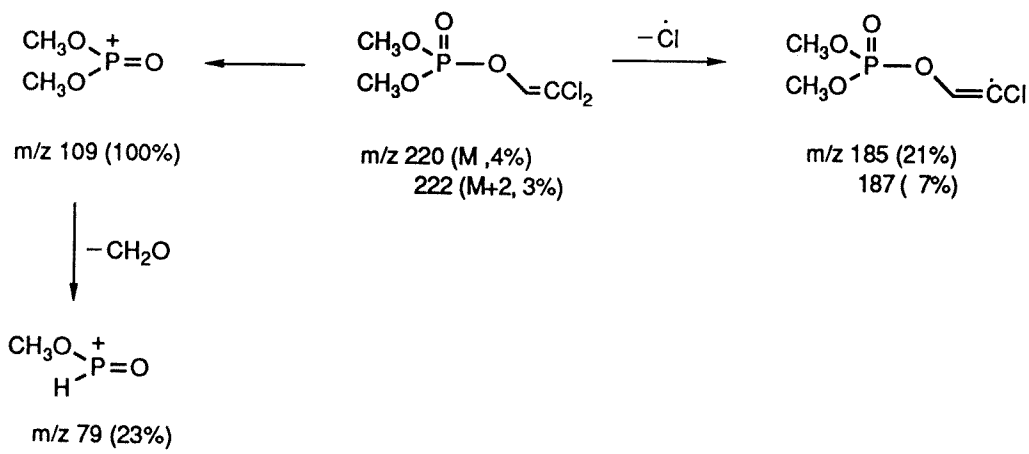


Figure 2. Mass spectrum of dichlorvos.



Scheme 2. Mass spectral fragmentation of dichlorvos.

ions as shown in its mass spectrum(*Figure* 3). The base peak at m/z 109 which usually appears in the spectra of compounds with dimethyl phosphorus moiety was produced by the inductive-cleavage with charge initiation at oxygen of hydroxy group followed by removal of CH_2O to yield the ion of m/z 79, as indicated in *Scheme* 3. Another significant ion at m/z 139 was formed by the loss of CCl_3 radical from the molecular ion through the alpha cleavage. The loss of all the chlorine atoms is appar-

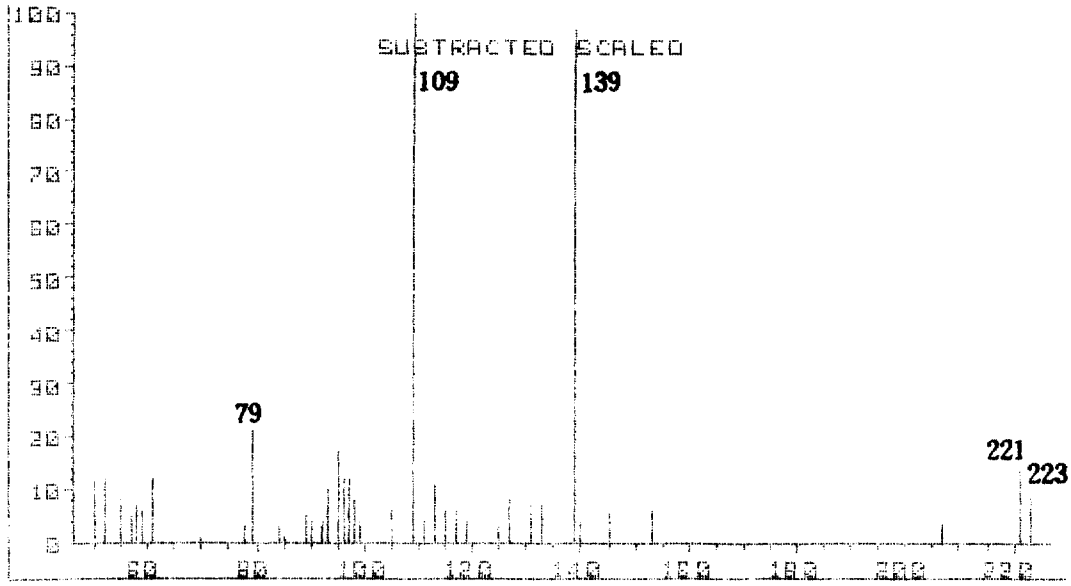
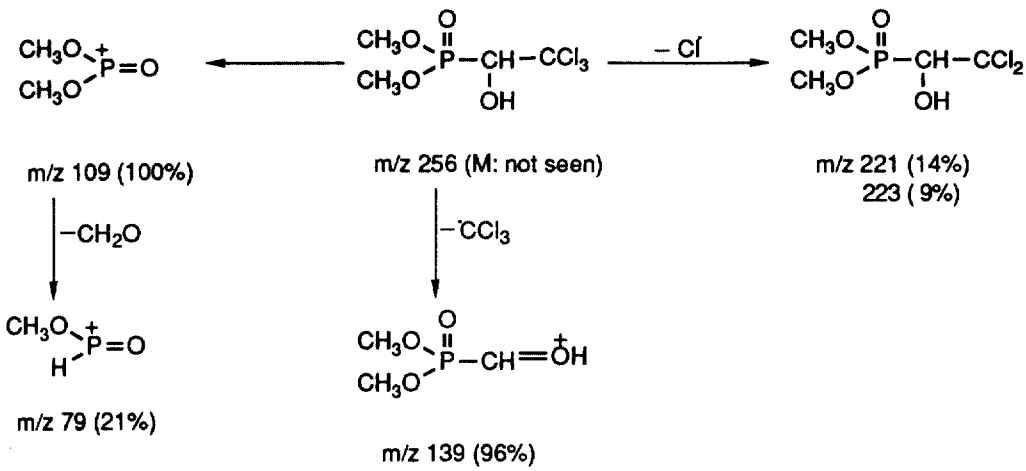


Figure 3. Mass spectrum of trichlorphon.



Scheme 3. Mass spectrum fragmentation of trichlorphon.

ent from the absence of isotopic clusters. The elimination of the chlorine radical from the molecular ion gives the ion of m/z 221.

Phosphamidon The molecular ion did not appear in the mass spectra of cis-and trans-phosphamidon. In general, cis-and trans-isomers demonstrate essentially identical mass spectra, but the mass spectra of phosphamidon isomers display slightly different abundance for some characteristic

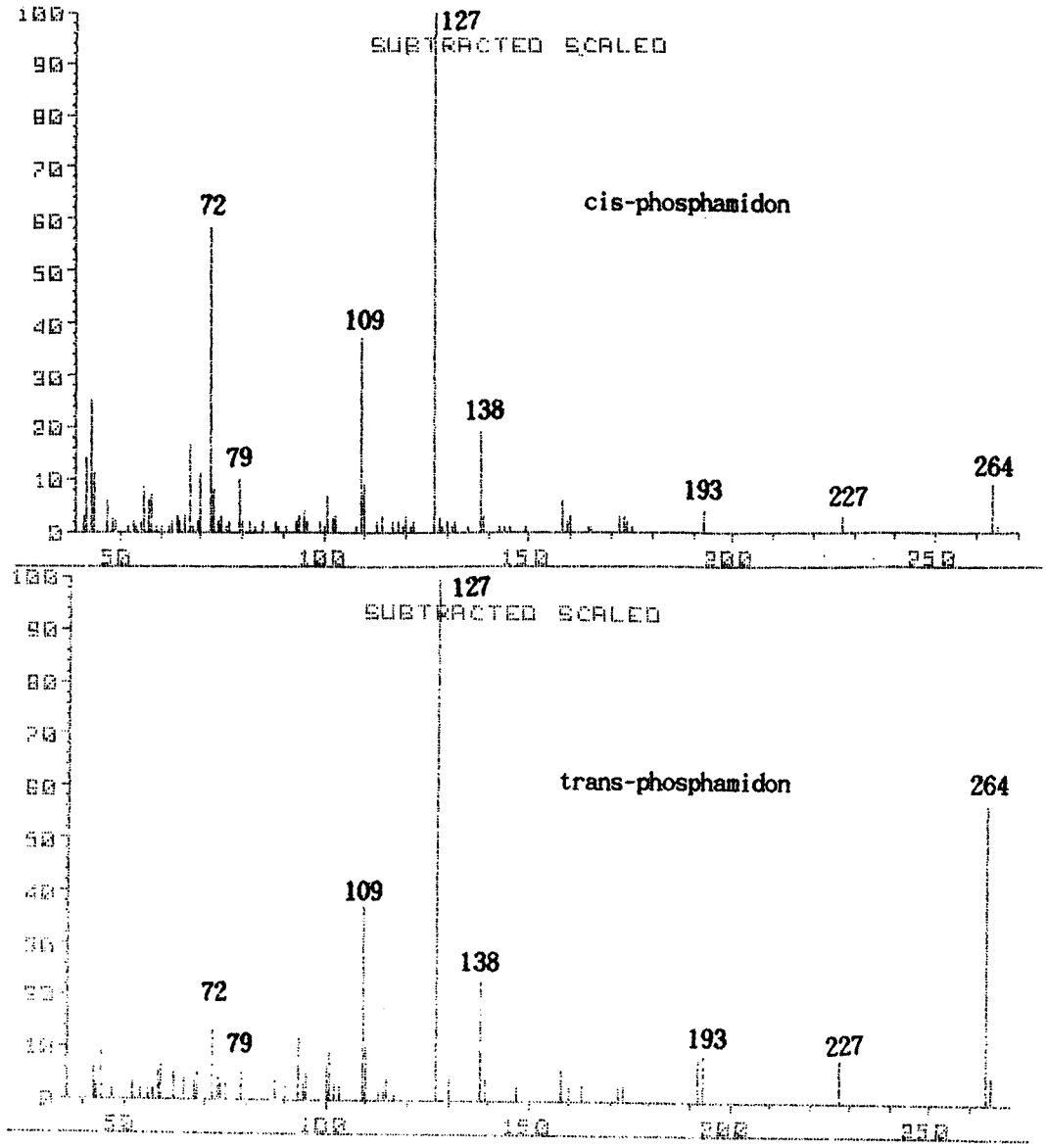
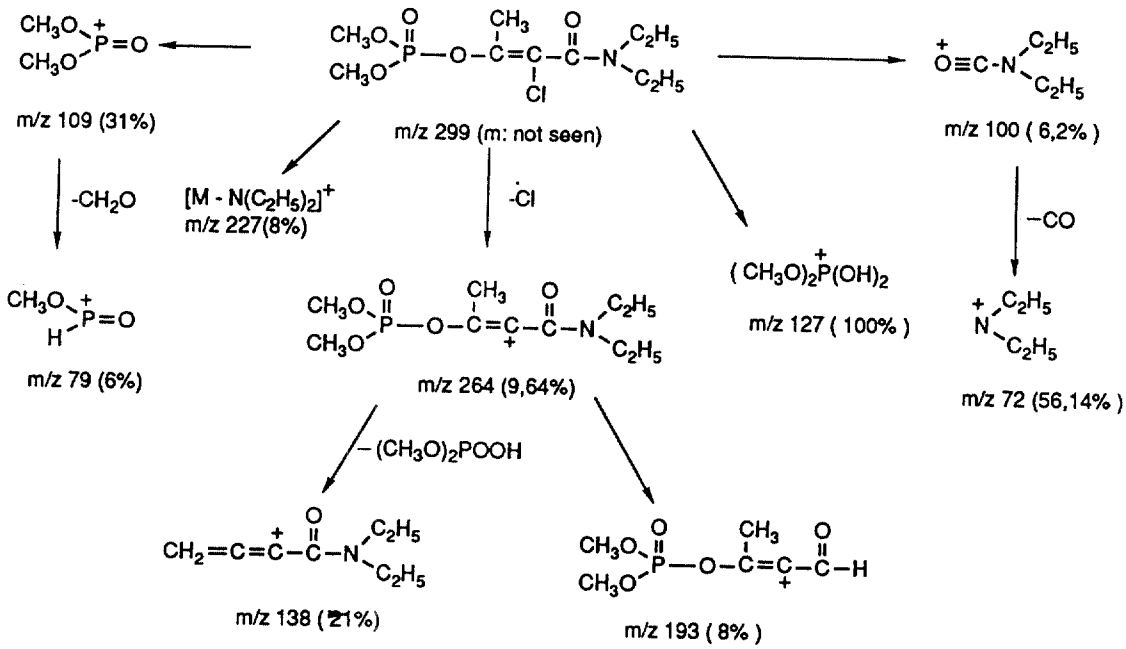


Figure 4. Mass spectrum of cis-and trans-phosphamidon.

ions such as m/z 72 and m/z 264 etc. as shown in *Figure* 4. *Scheme* 4 displays that the base peak of m/z 127 is expected to be $[(CH_3O)_2P(OH)_2]^+$ ion. This fragment ion was generated by a double hydrogen rearrangement from the substituted vinyl moiety to the phosphorus oxygen skeleton. The formation of this ion was confirmed by Holmstead[3] with deuterium labeled-methane chemical ionization mode. Significantly abundant ion at m/z 264 is observed corresponding to the loss of the chlorine radical from the molecular ion. The ion at m/z 100 corresponding to the N, N-diethyl



Scheme 4. Mass spectral fragmentation of phosphamidon.

isocyanate ion has a very weak intensity peak(1%) whereas the ion at m/z 72 which was formed by the loss of carbon monoxide from diethyl isocyanate ion appeared as relatively abundant ion. Fragment ion m/z 138 may be explained by the loss of phosphoric acid from dechlorinated molecular ion.

Chlorpyrifos-methyl Because of the ease of chlorine radical fragmentation, chlorpyrifos-methyl gives the weak molecular ion cluster together with a few significant ions(*Figure* 5). As showm in *Scheme* 5, the base peak at m/z 125 was produced by the inductive cleavage of phosphorothioate group. The small fragment ions in mass spectrum of chlorpyrifos-methyl were produced by the fragmentation of dimethyl phosphorothioate group through the elimination and rearrangement process which is indicated in *Scheme* 1.

The loss of the chlorine radical has produced the base peak at m/z 286 with its isotopic clusters at m/z 288 and 290. The ion cluster(m/z 197, 199 and 201) can be assigned as trichloropyriol ion which is formed through gamma hydrogen rearrangement. This ion cluster appeared also in mass spectrum of chlorpyrifos.

Chlorpyrifos The chemical structure of chlorpyrifos is very similar to that of chlorpyrifos-methyl, while its fragmentation pattern is different from that of the latter, as shown in *Figure* 5 and *Figure* 6. Various fragment appear in the spectrum of chlorpyrifos because of successive elimination of ethylene *via* four centered hydrogen rearrangement of diethyl phosphate group, as shown in *Scheme* 6. The molecular ion easily loses chlorine radical producing the strong intensity ion cluster(m/z 314, 316 and 318). The $(M-Cl)^+$ ion also fragments with a successive loss of C_2H_4 molecule to give characteristic ion cluster. The trichloropyriol ion which appeared with low intensity in the mass spectrum

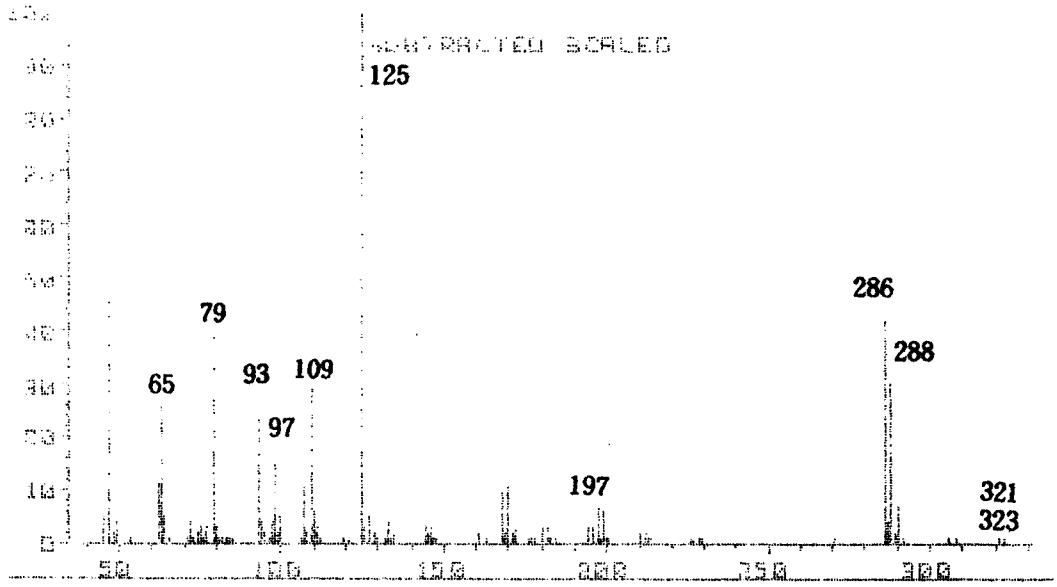
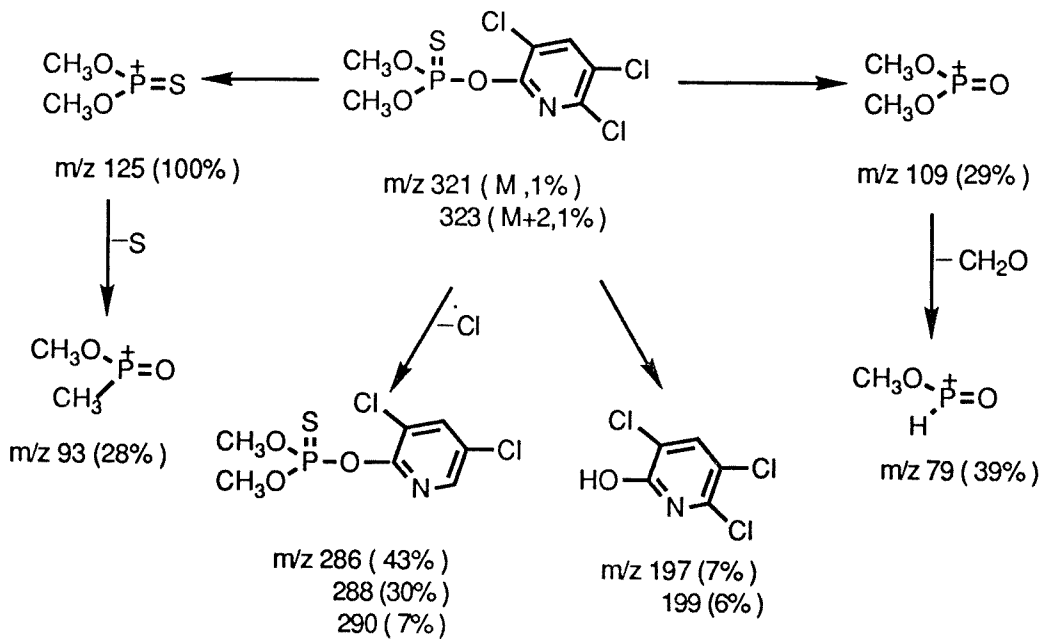


Figure 5. Mass spectrum of chlorpyrifos-methyl.



Scheme 5. Mass spectral fragmentation of chlorpyrifos-methyl.

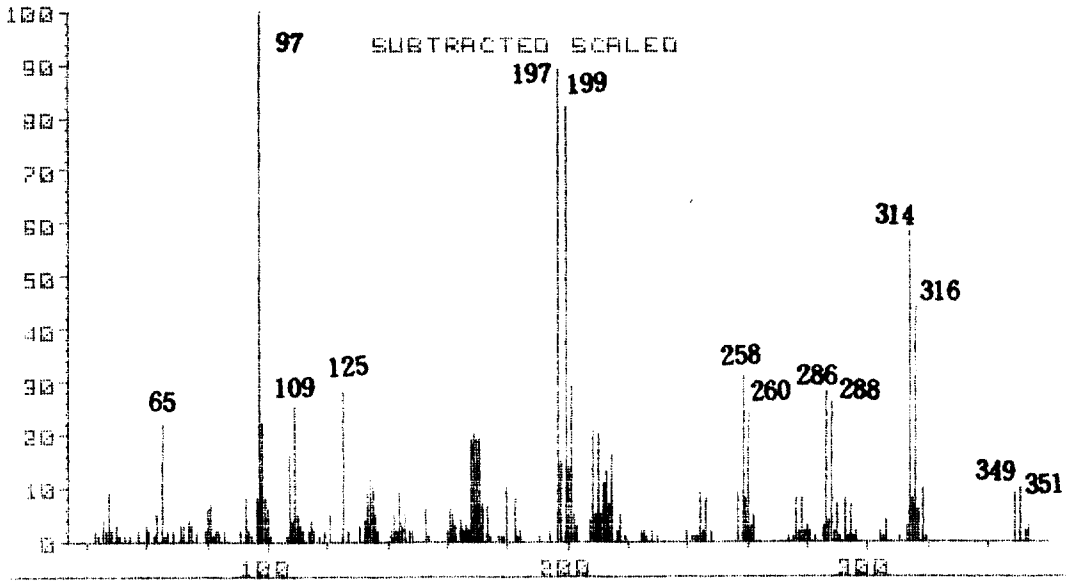
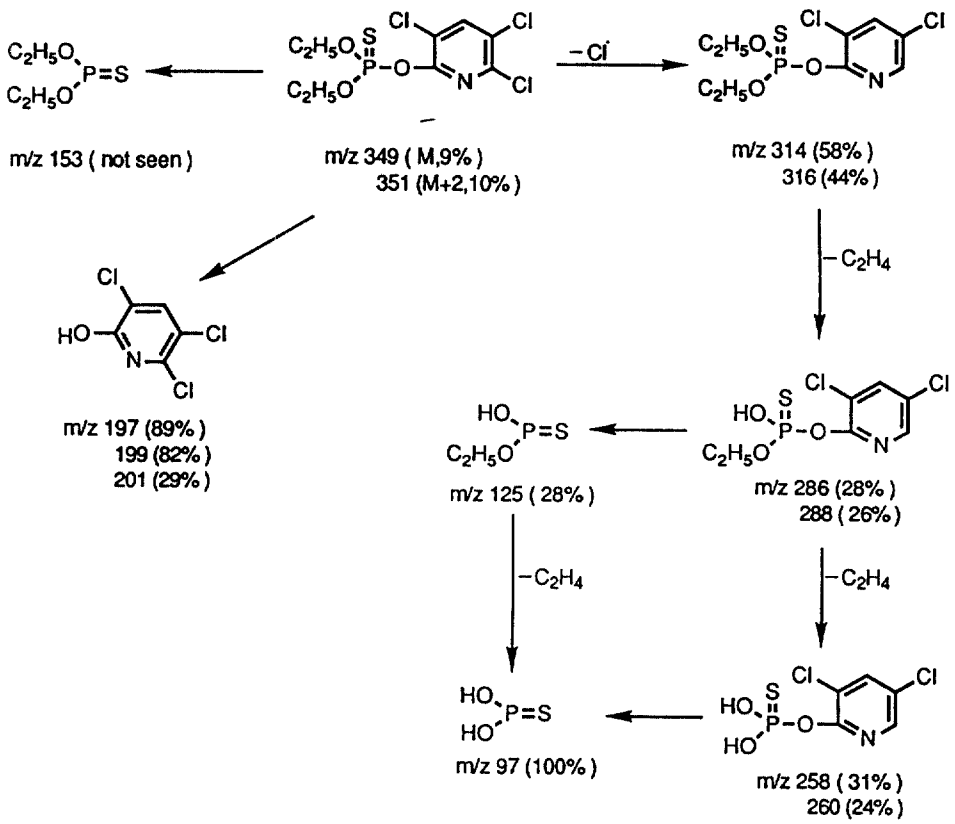


Figure 6. Mass spectrum of chlorpyrifos.



Scheme 6. Mass spectral fragmentation of chlorpyrifos.

of chlorpyrifos-methyl appeared prominently in the spectrum of chlorpyrifos. It is tempting to suggest the formation of trichloropyriol in chlorpyrifos by hydrogen migration from diethyl group to oxygen atom attached to benzene ring *via* six-membered rearrangement which that in chlorpyrifos-methyl is generated by hydrogen transfer of dimethyl group through four centered rearrangement. The other abundant low mass ions were formed due to fragmentation of diethyl phosphorothioate group.

Tetrachlorvinphos Tetrachlorvinphos yielded a weak molecular ion and produced only a few significant ions in its mass spectrum(*Figure* 7). *Scheme* 7 shows that the base peak of m/z 331 is formed by the loss of chlorine radical from the molecular ion. The second abundant ion at m/z 109 was formed by the alpha cleavage of phosphate group. The ion cluster(m/z 238, 240 and 242) must have arisen *via* the overall elimination of phosphoric acid, accompanied by hydrogen transfer from the ethylene moiety. The above pathways are supported by the existence of the chlorine isotopic peaks.

Profenofos As seen in *Figure* 8, profenofos gives a strong molecular ion cluster and several significant peaks are detected in its mass spectrum becaues of the presence of phosphorothioate group containing chlorine and bromine substituted on benzene ring. Most of the ions containing the aromatic ring are of significant intensity. The stability imparted to the molecule by the aromatic system is evident from the molecular ion intensity. The dominant ion cluster at m/z 206 and 208 can be assigned to 2-chloro, 4-bromo-phenol ion based on the isotope analysis. The abundant ion at m/z 339 is due to the ^{81}Br isotopic peak of m/z 337 ion which is formed by the loss of chlorine radical from molecular ion. As shown in *Scheme* 8, other significant ions can be easily identified by the observing the isotopic abundance of each ion.

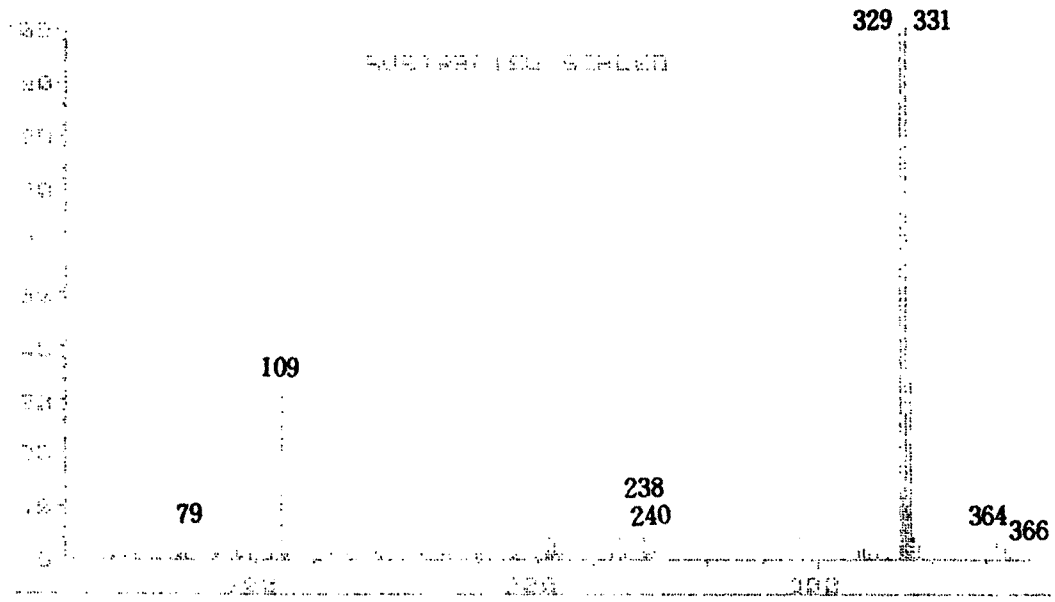
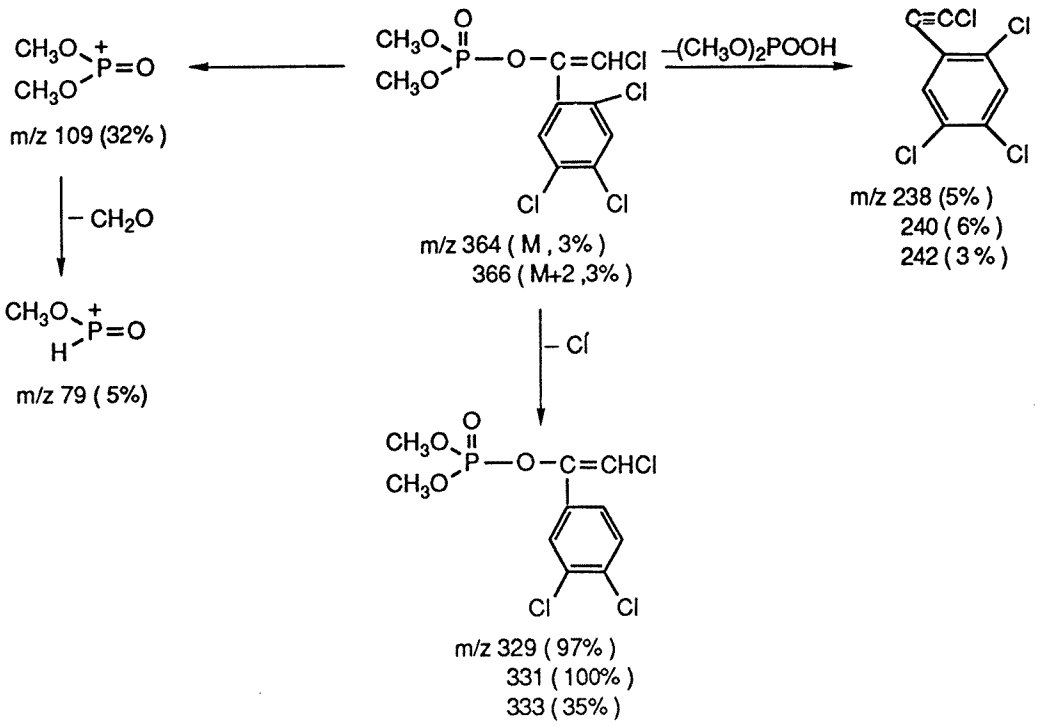


Figure 7. Mass spectrum of tetrachlorvinphos.



Scheme 7. Mass spectral fragmentation of tetrachlorvinphos.

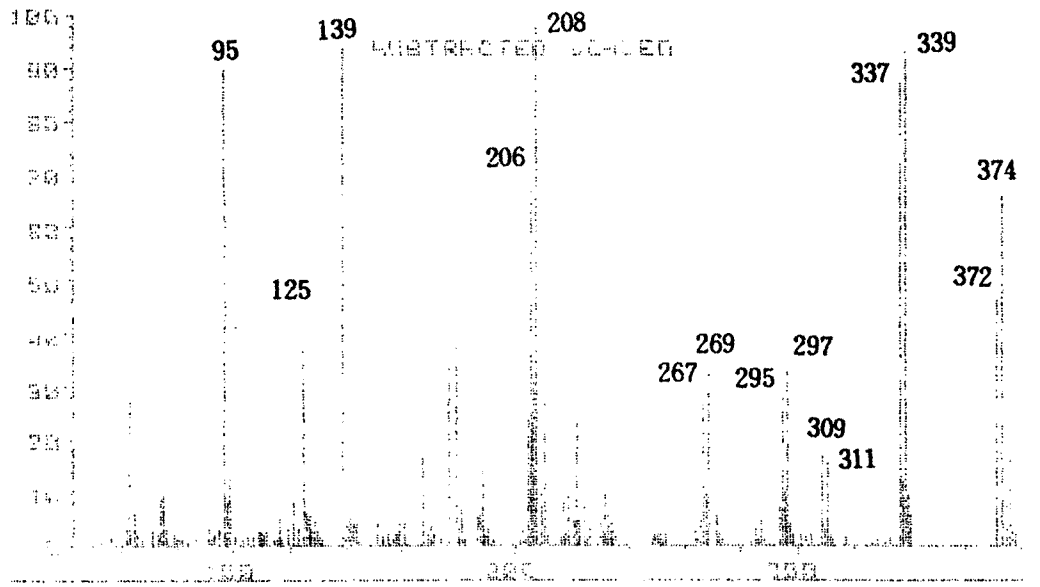
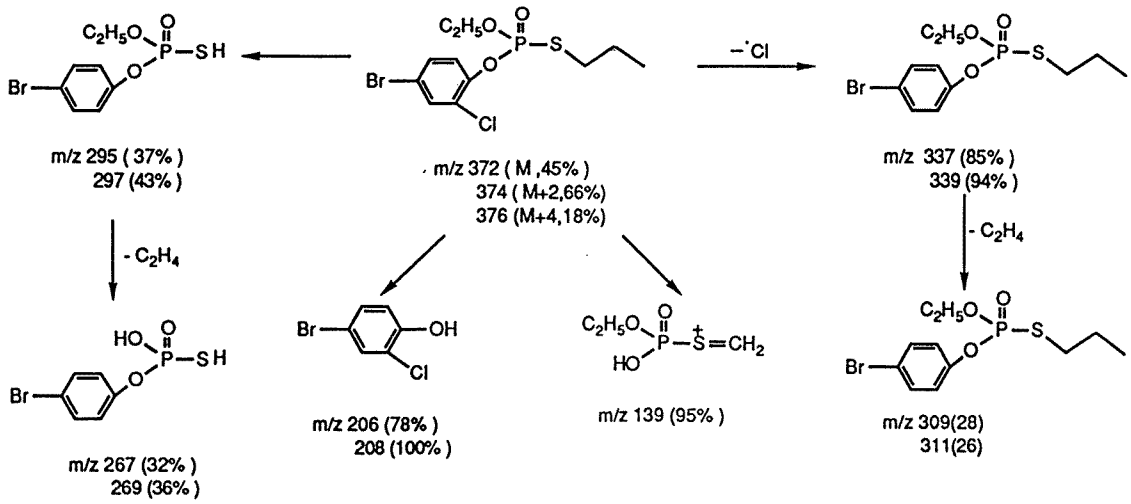


Figure 8. Mass spectrum of profenofos.



Scheme 8. Mass spectral fragmentation of profenofos.

Carbophenothion *Figure* 9 presents the mass spectrum of carbophenothion. The molecular ion was observed as base peak. As shown in *Scheme* 9, the abundant fragment ions at m/z 157 was formed by the alpha-cleavage with charge retention on the sulfur atom attached to benzene ring. The formation of m/z 199 is explained by a charge initiation on sulfur atom of phosphorodithioate group followed by an alpha-cleavage. The diethyl phosphorodithioate group of carbophenothion exhibited the typical fragmemtation patten for diethyl phosphorothioate under EI-condition; consecutive elimin-

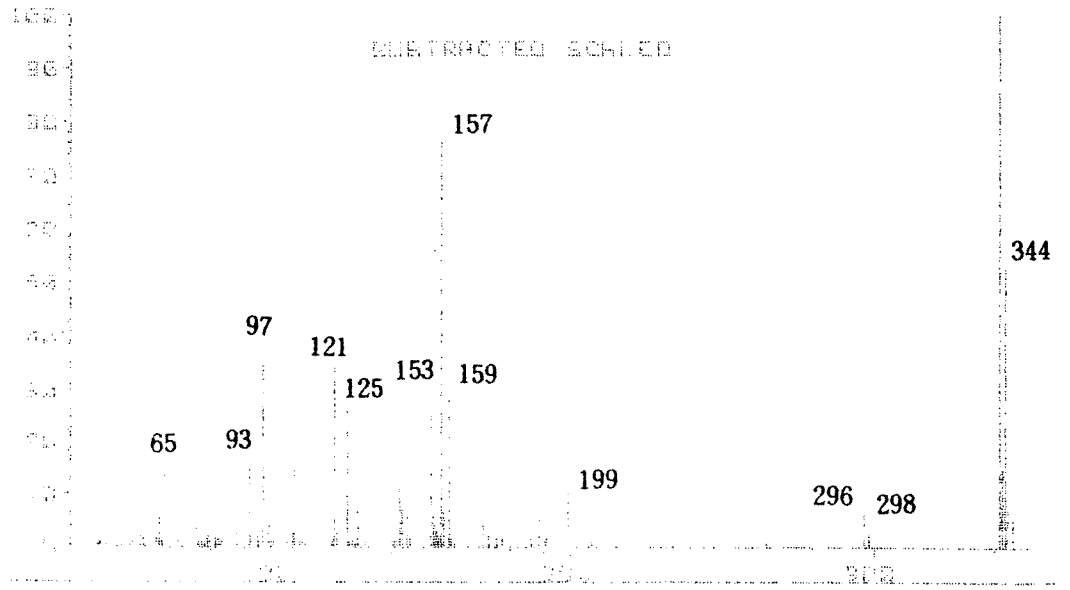
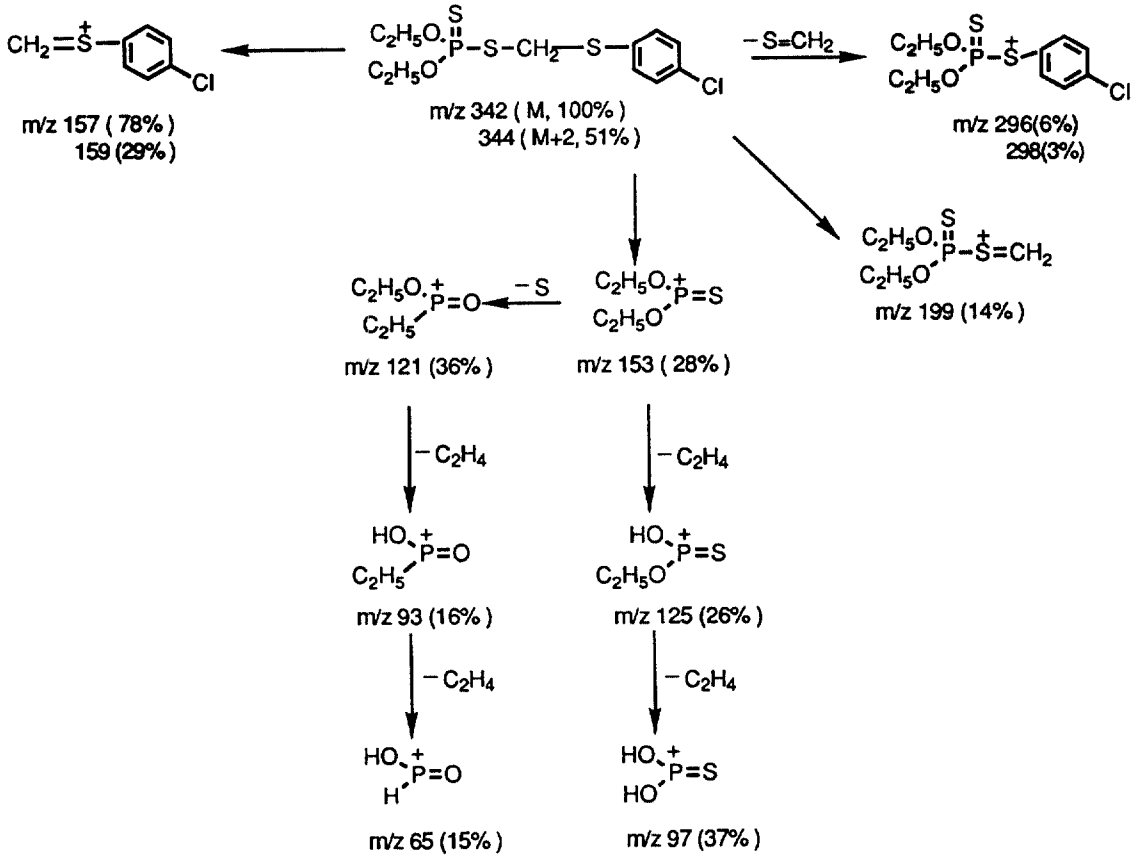


Figure 9. Mass spectrum of carbophenothion.



Scheme 9. Mass spectral fragmentation of carbophenothion.

Table 1. Characteristic Ions of 8 chlorinated Organophosphorus Pesticides.

Compound	Mol. Wt.	base peak	other ions
Dichlorvos	220	109	185 187 79 220 222
Trichlorphon	256	109	139 79 221 223
Phosphamidon	299	127	109 138 193 79 72 227
Chlorpyrifos-methyl	321	286	286 288 79 109 65 93 321 323
Chlorpyrifos	349	97	314 316 197 199 286 288 258 260
Tetrachlorvinphos	364	331	329 109 79 238 240 364 366
Profenofos	372	208	206 337 339 372 374 139 95 125
Carbophenothion	342	342	344 157 199 153 121 125 93 97

ation of ethene molecule. In particular, the conversion of the ion m/z 153 to the ion m/z 121 through the removal of sulfur diradical and then the rearrangement of oxygen atom is an ambiguous mechanism proposed by Pritchard.[6] The other significant ion at m/z 296 which is not intense was

produced by the elimination of CH_2=S *via* four centered rearrangement. The formation of this ion is aided by the presence of chlorine isotopic ion at m/z 298.

The mass fragmental pathways for chlorinated phoshorus pesticides have been suggested with the use of ^{37}Cl isotope peak and mass spectral information of phosphorus moiety which have been reported. The mechanism for these chlorinated organophosphorus pesticides may be extended to interpret the spectra of other pesticides. The characteristic ions of these compound are listed in *Table* 1.

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