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PESTICIDE RESIDUES IN FRUITS AND VEGETABLES

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ABSTRACT

Oranges andappleswere investigated for fruitssamples while the tomatoes were investigated for vegetable. Thesewere obtained from the Oja Oba market of Akure, Ondo State, Nigeria. Pesticide residual concentration were determined using acetonitrile extraction procedure.The quantity of the pesticides was determine instrumentally using Gaschromatography/mass spectrometry (GC/MS). Factors investigated include retention time, relative abundance, limit of quantification, polarity, elution time, molecular weight and concentration and maximum residue limit. The result indicated that faster elution was associated with low molecular weight pesticides than the high molecular weight pesticides. Pesticides identified include Chlorothalonil, Chlorpyrifos, Flumioxazin, Diazinone, Heptachlor-epoxideetc.Glycophosphate was found in all the samples, with retention time ranging from 3.100 – 3.425 seconds. The pesticides concentrations in the studied samples ranged from 0.006 ppb in Glycophosphate to 0.090 ppb in Chlorpyrifos andwere found to be below maximum pesticides residue limits as prescribed by FAO/WHO, 1993.

KEYWORDS: Pesticide, Acetonitrile, GC-MS, Spectrometry, Extraction, Fruits, Vegetables.

INTRODUCTION

Fruits serves as supplement for different classes of food and important nutrient. Fruits and vegetables intake has been known for vitamin deficiency prevention and cancer prevention [1]. Pesticides and insecticides known as chemicals used by farmers for the prevention of crops against pesthas led to increase in the yields of crops demand of over growing population [2]. The use of pesticides is known with theirfast action, infecting organisms' reduction and reduced farmers' labor [3]. However, after pesticides are used, their residuals are maintained in the fruit sprayed. Unfortunately, not all farmers follow legal use of thepesticides on fruit and vegetable production [4]. Manypesticides are toxic in very small concentrations; while exposure to a sufficient amount of almost all pesticides can also be toxic. Problems associated to it include respiratory disease, cancer, depression, etc.[5].

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Since pesticides are hazardous to human health, therefore, pesticides residue in fruits and vegetables will pose danger to humans [6]. Considering the problem caused by pesticide to human health, it is therefore important to investigate the pesticides which can be ingested through fruits and vegetables after pesticides spray.This research is a pesticide residue study aimed at investigating the concentration of pesticides in fruits and vegetables samples.

MATERIALS AND METHODS

SAMPLING

A total number of one hundred and fifty (150) fruits and vegetables (40 apples, 30 oranges and 80 tomatoes) were bought from the Oja Oba market in Akure, Ondo State. These fruits and vegetables were collected in there (3) baskets weighing 35kg each.

EXTRACTION OF PESTICIDE RESIDUES FROM FRUITS AND VEGETABLES

Quechers method was used to extract the pesticide residues from fruits and vegetables samples as described by [7]. For each sample 20 g was taken and 20 ml of distilled water was added. 50 ml of acetonitrile was added after left to stand for 15minutes and then the sample was homogenized by crushing in a mortar and pestle and then filtered. 20 ml of acetonitrile was added to the residue in filter paper and homogenized refiltered by suction. Both filtrates were combined together and the volume was increased to 100 ml by using acetonitrile for makeup. From this which 10 g of NaCl and 20 ml of 0.5 mol/L of phosphate of buffer (pH 7.0) was added and shaken was added to 20mL of the solution. The aqueous layer was partitioned out by allowing it to stand for a period of time.The organic layer was dried over anhydrous sodium sulphate and filtered. The filtrate was dried at40^{0}C from which 2 ml were added to mixture of toluene/acetonitrile in ratio of 3:1.Gas Chromatography Mass Spectroscopy (GC/MS model GP 2010, Shimadzu) was used for the instrumental analysis.

RESULTS AND DISCUSSION

SPECTRA OF EXPERIMENTS

The result of molecular weights of the pesticides residual were compared with GC/MS data library for identification confirmation. And from the elution time of pesticides base on their spectra, it was found that the elution time of the lower molecular weight pesticide were lower than the higher molecular weight pesticides, which showed a good agreement with the observation of Gil Garcia [8].

The spectra peaks indicated the relative abundance of each pesticide. Peaks were only shown in the spectra of fruits sprayed with pesticides. Glycophosphate was the common pesticides found in all sprayed fruit samples. A full list of pesticide found in Apple, Tomato and Orange samples are presented in Tables I,II and III Respectively, along with their retention times, elution times, relative abundance, molecular weights, limits of detention, limits of qualification, maximum residue level and concentration.

In table I below, Glycophosphate was found to elute at 2.806 seconds and the retention time was 3.425 seconds in the sample. This is confirmed by the findings of Watanabe [9]. Its use as a broad spectrum systematic herbicide for killing weeds allows for its leaves or the trees stumps absorption. Its mode of action is only effective on actively growing plant since it inhibits an enzyme involved in aromatic amino acid, tyrosine tryptophan and phenylalan-inesynthesis. As the samples were taken at random, the recovery rates of Glycophosphate were much less than those reported for

fortified samples [9]. The residual presence of heptachlor-epoxide in apple sample is an insecticide whoseaction is known by accelerating moulting process. The metabolic pathway for degradation of heptachlor-epoxide in fruits suggests that the parent compound contribute to the large residual percentage [10].

RESIDUES OF GLYOPHOSPHATE, HEPTACHLOR-EPOXIDE, DIAZIONE AND FLUMIOXAZIN IN APPLES

Table 1.Pesticides identified in Apple by GC/MS

Pesticides	Retention Time	Elution Time	LOD ($MgKg^{-1}$)	LOQ ($MgKg^{-1}$)	Relative Abundance (%)	Molecular Weight	Concentration (ppb)	MRLs (ppm)
Glyco phosphate	3.425	2.806	0.0015	0.005	1-2	169	0.006	0.50
Heptachlor-epoxide	19.433	19.575	0.0015	0.005	10	368	0.040	0.70
Diazinone	19.017	18.106	0.0015	0.005	30	300	0.049	3.00
Flumioxazin	19.675	19.400	0.0015	0.005	2	355	0.058	5.00

The higher residual concentration of Diazinone as shown in table I above, can be attributed to the insecticide activities of Juvenile hormone analog [JHA] as also reported by Miyamoto [11].The residual amounts of flumioxazin according to the table, suggest its rapid degradation to 6-amino-fluoro-4-[2propynyl]-1 4-benzoxazin-3[2H] -one [APF] and 3, 4, 5, 6, tetrahydrophthalic acid [THPA]. This confirmed the report of Jaga [12].

The spectra of Glyophosphate, Heptachlor-epoxide, Diazione and Flumioxazin in Apples are as shown in appendix 1 (a-d), with each residue having a peak at its retention time.

RESIDUES OF CHLOROTHALONIL AND CROTOXYPHOS IN ORANGES

In table II below, Chlorothalonil, Crotoxyphos and Glycophosphate residues were found to be present in orange sample, with retention time of 16.275 seconds, 17.283 seconds and 3.175 seconds respectively. The residues were eluted at 17.661 seconds, 17.901 seconds and 3.165 seconds respectively. This was similar to the earlier report given by Patil and Shingare [13]. Chlorothalonil is a pesticide synergist. It is an active cytochrome C450 and a non-specific esterase inhibitor in action. The principle of its mechanism permits higher unmetabolised systemic concentrations of the active insecticide to remain within the target species for long time. Excess Crotoxyphos can lead cholinesterase inhibition which may result in inhibition of acetylcholinesterace, resulting from enantioselectivity of the chiral OPs in non-target organisms [14].The spectra of Chlorothalonil and Crotoxyphos in Oranges are as shown in appendix 2 (a-c), with each residue having a peak at its retention time.

Table 2.Pesticides identified in Orange by GC/MS

Pesticides	Retention Time	Elution Time	LOD ($MgKg^{-1}$)	LOQ ($MgKg^{-1}$)	Relative Abundance (%)	Molecular Weight	Concentration (ppb)	MRLs (ppm)
Chlorothalonil	16.275	17.661	0.0015	0.005	2-3	325	0.012	0.20
Crotoxyphos	17.283	17.901	0.0015	0.005	3-4	338	0.041	1.00
Glyco phosphate	3.175	3.165	0.0015	0.005	2-3	169	0.007	0.50

RESIDUES OF CHLORPYRIFOS IN TOMATOES

As showed in table III above, Chlorpyrifos [1,1-diethyl-3,5,6-trichloropyridin-2-yl phosphoro thiote] which is a crystalline organophosphate insecticide, eluted at 15.204 seconds and its retention time is 13.673 seconds. This is similarly reported by Abdalla [15]. Chlorpyrifos is an organophosphate insecticides and is moderately toxic to humans and exposure has been linked to neurological effects [16]. Chlorpyrifos has a tolerance of 0.1 ppb residue on all food items.

The spectra of Chlorpyrifos and Glycophosphate in Tomatoes are as shown in appendix 3 (a-c), with each residue having a peak at its retention time.

Table 3.Pesticides identified in Tomato by GC/MS

Pesticides	Retention Time	Elution Time	LOD ($MgKg^{-1}$)	LOQ ($MgKg^{-1}$)	Relative Abundance (%)	Molecular Weight	Concentration (ppb)	MRLs (ppm)
Glyco phosphate	3.100	3.139	0.0015	0.005	1-2	169	0.016	0.50
Chlorpyrifos	13.673	15.204	0.0015	0.005	3-4	342	0.090	1.00

CONCLUSION

The findings showed that seven pesticides residues were found in the studied samples.The concentration of pesticides was found to be homogenously distributed. This showed the farmers were continuing to use the same type of pesticide since past, as revealed from the present study. The vegetable and fruit samples were discovered to be contaminated with different pesticides (Glycophosphate, Heptachlorepoxide, Diazinone, Flumioxazin, Chlorpyrifos, Chlorothalonil and Crotoxyphos.) at different concentrations. The concentration of the pesticide residues concentrationwas from 0.006 ppb in Glycophosphate to 0.090 ppb in Chlorpyrifos, and were all found to be below the maximum residue limits as prescribed by FAO/WHO, 1993.

Analyses by GC/MS gave good recoveries, indicating good performance of extraction, clean up and chromatographic parameters for the pesticide residues analysis in fruit and vegetable samples. Owing to the risk assessment results showing positiveindication, the potential health risk associated with the consumption of fruits and vegetables sprayed with pesticides cannot be neglected, therefore. there is a need for continuous investigation to ensure the continuous safety of fruit and vegetable consumers.

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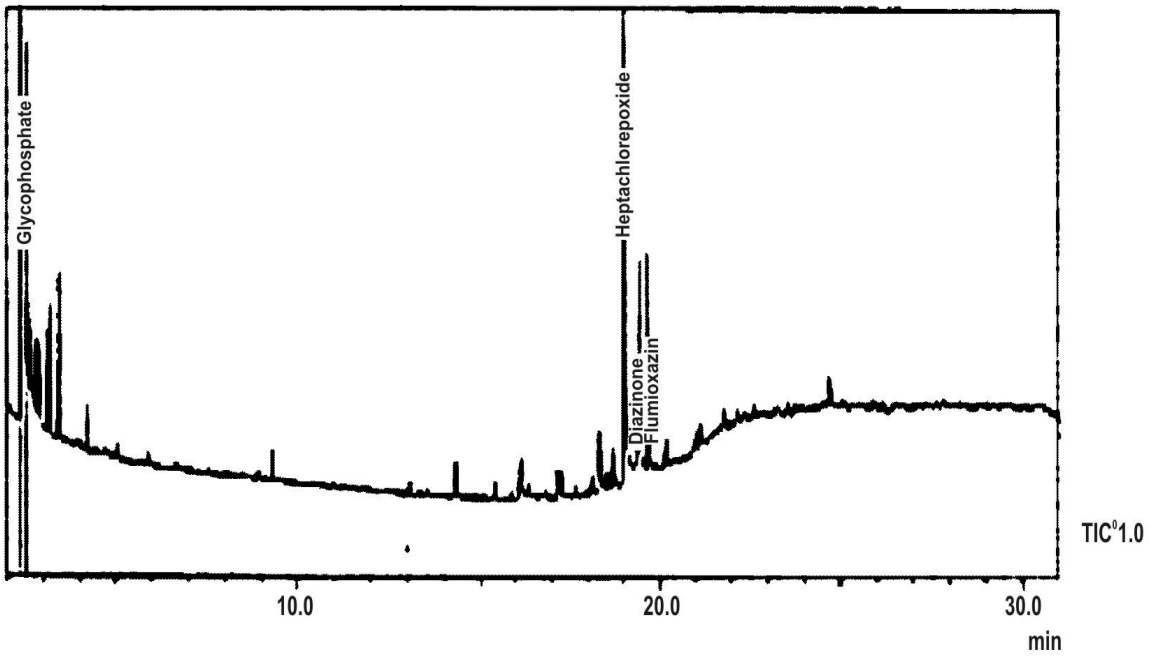
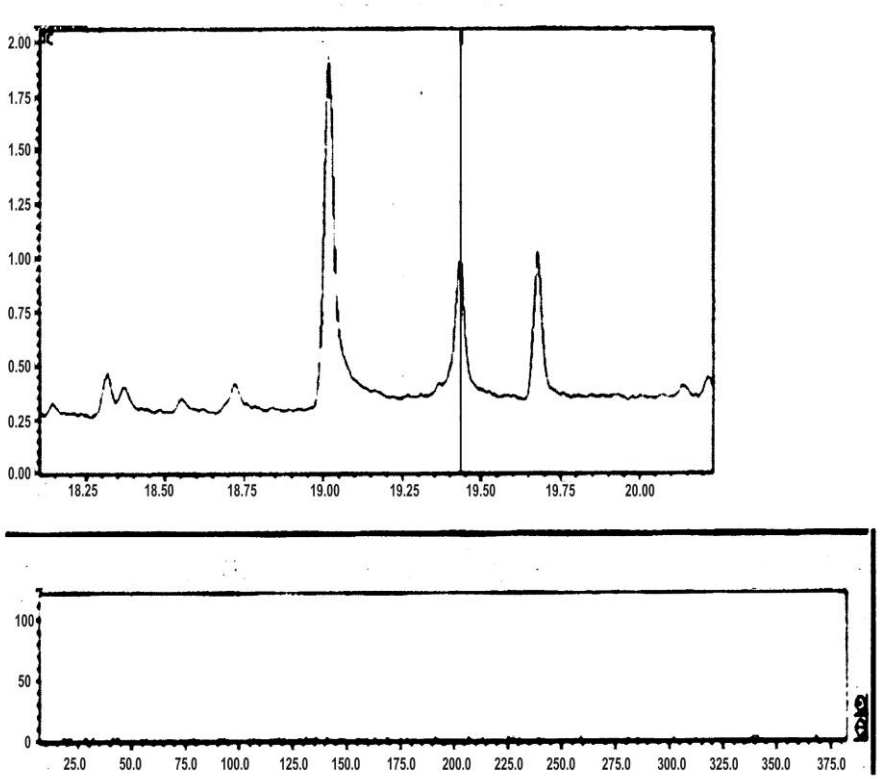
APPENDIX 1.GC/MS Spectra of Apple Sample

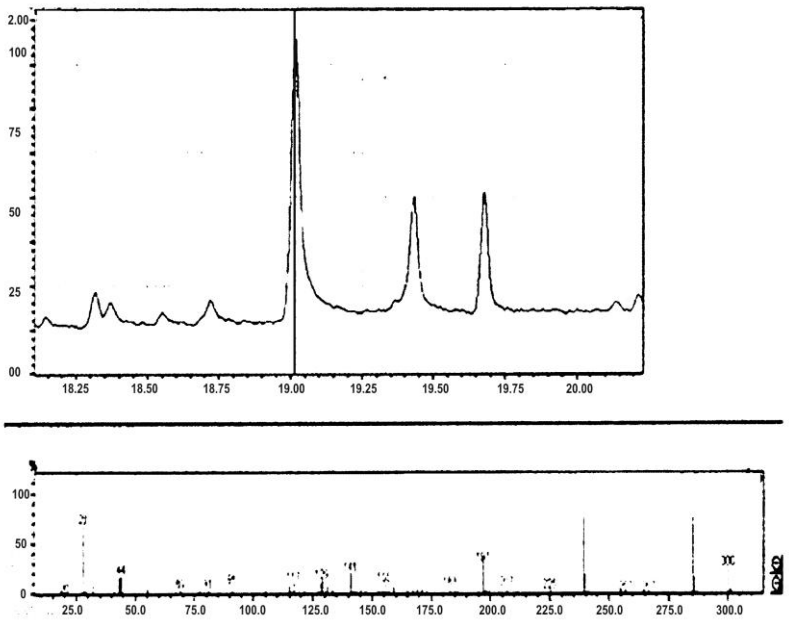


Spectrum

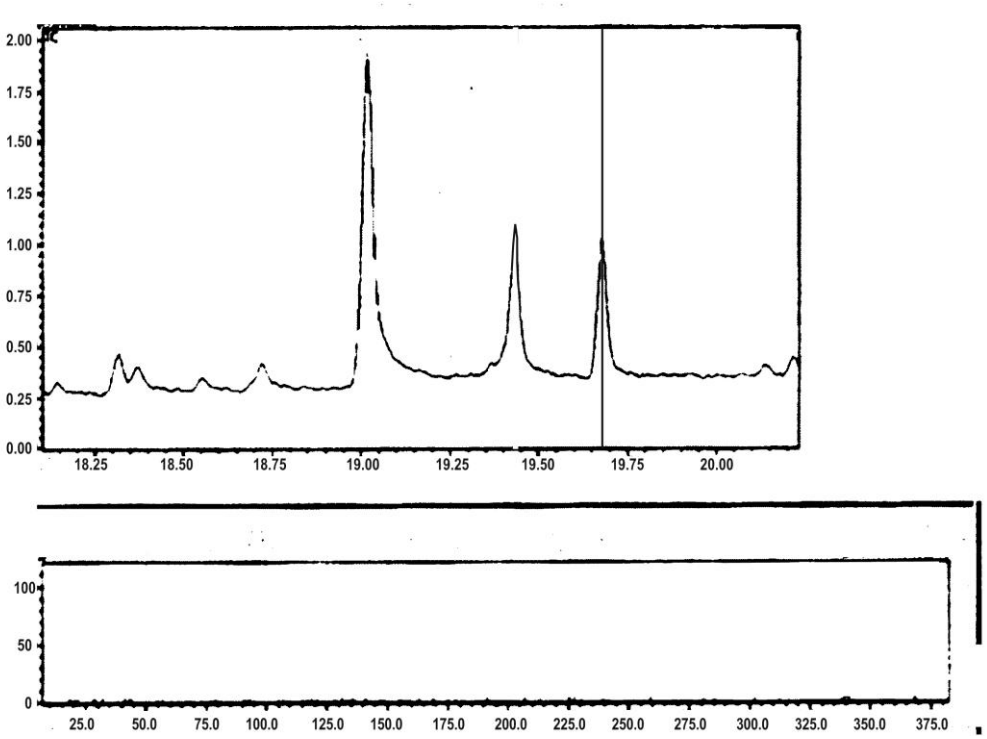
Appendix 1(A)



Appendix 1(B).Heptachlor-Epoxide

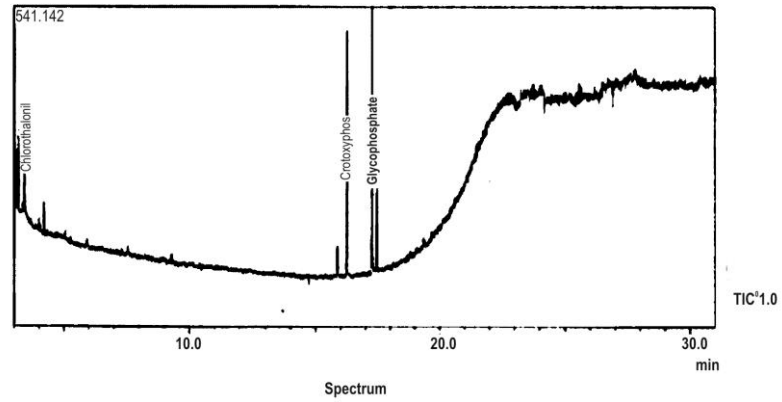


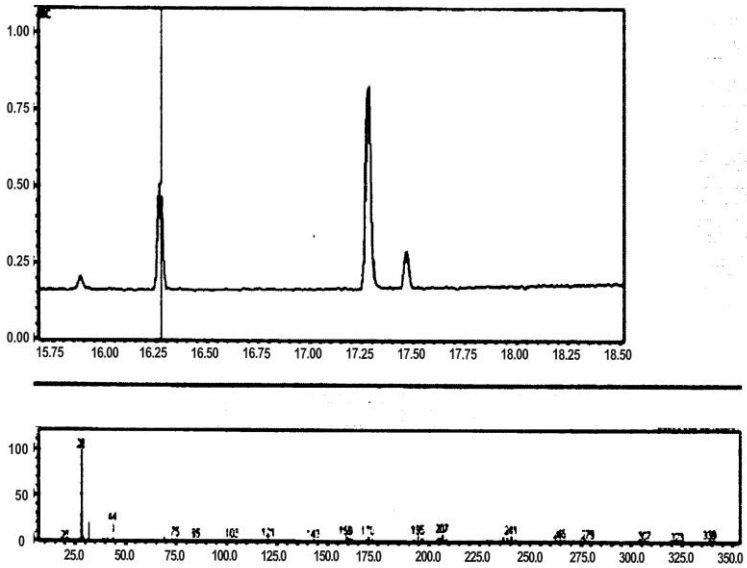
Appendix 1(C).Diazinone



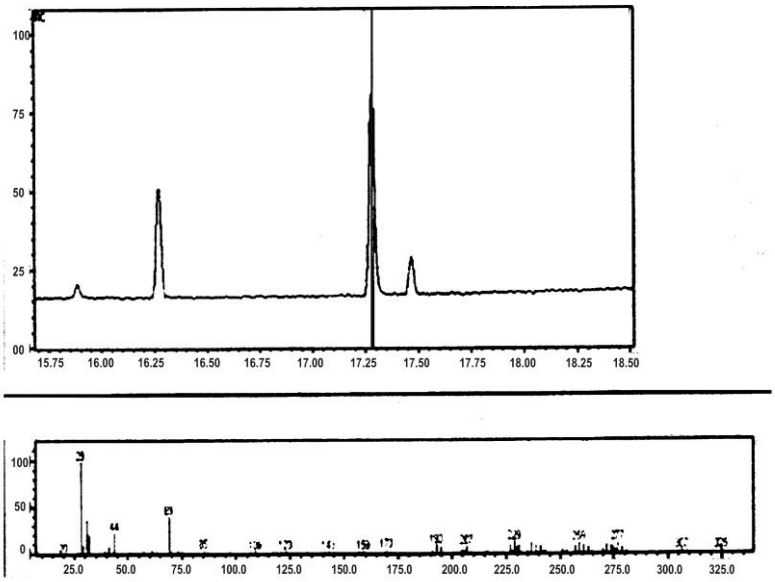
Appendix 1(D).Flumioxazin

APPENDIX 2: GC/MS SPECTRA OF ORANGE SAMPLE



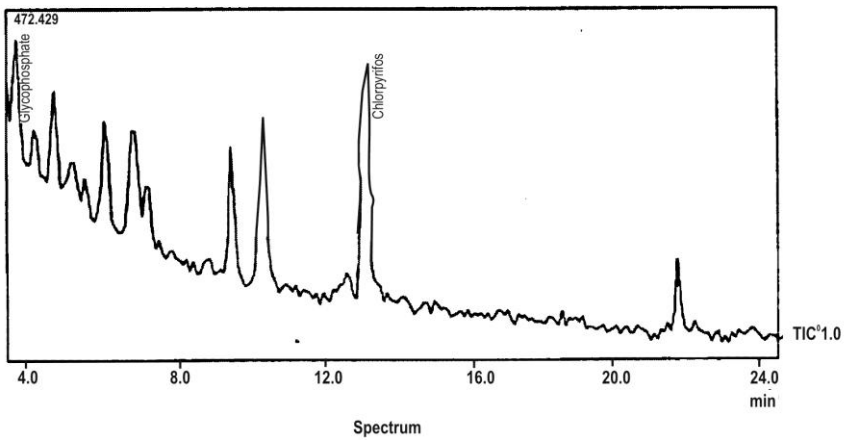


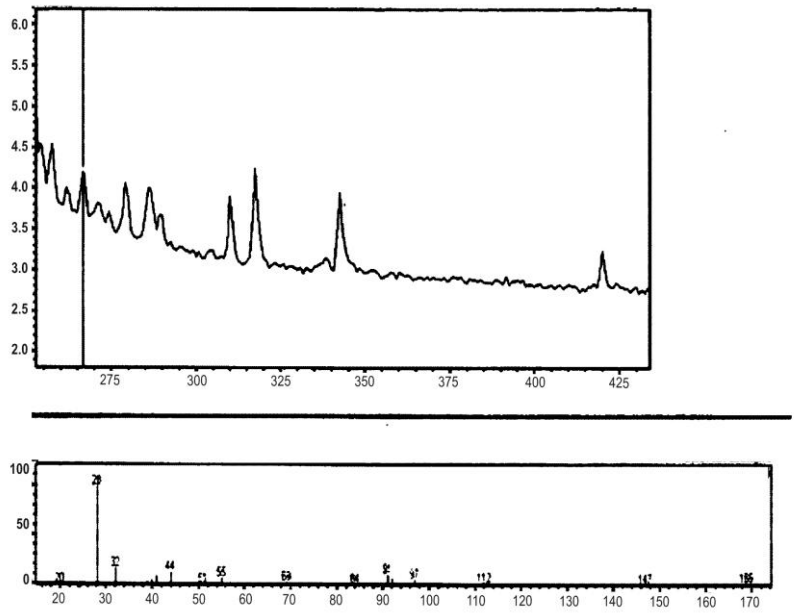
Appendix 2(b).Chlorothalonil



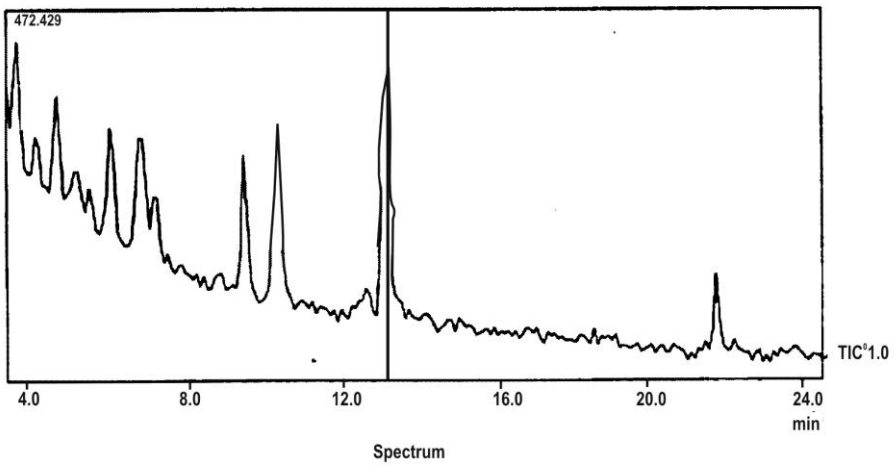
Appendix 2(c).Crotoxyphos

APPENDIX 3.GC/MS SPECTRA OF TOMATO





Appendix 3(b).Glyophosphate



Appendix 3(c).Chlorpyrifos

