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GAS CHROMATOGRAPHY OF ORGANOPHOSPHATE INSECTICIDE RESIDUES IN STORED GRAINS, I. COMPARATIVE PERFORMANCE OF TWO DETECTION SYSTEMS ILLUSTRATED WITH MALATHION AND PIRIMIPHOS-METHYL[1]

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Residues of malathion and pirimiphos methyl on stored grains were determined by gas chromatography using the electron capture (ECD-GLC) and alkali flame ionization detectors (AFID-GLC).

Extraction with benzene cleanup with Florisil column chromatography and analysis by ECD-GLC gave a recovery of 75.4% for malathion on spiked samples. Extraction with methanol and analysis by AFID-GLC without cleanup gave a high recovery of 92.6% for pirimiphos methyl. The merits of AFID-GLC over ECD-GLC is discussed relative to the work done.

Malathion residues in the corn samples stored for three, six, and nine months in sacks treated with 2% and 4% malathion decreased with longer storage time from 1.2 to 1.0 ppm and 1.4 to 1.0 ppm, respectively, which is lower than the USFDA tolerance limit of 7 ppm. Pirimiphos methyl admixed with corn grains at approximately 10, 15, and 30 ppm gave a residue range of 0.6 to 2.6 ppm and 0.4 to 2.5 ppm after three and six months storage which is again lower than the FAO/WHO Recommended Residue Tolerances.

Grain admixture and sack treatment with insecticides are presently employed for the control of insect pests of stored grains. These insecticides are being used to protect stored grains without any knowledge of the residue levels present. Since grains are in close proximity to insecticides, the residue occurring after definite time intervals should be established in relation to the degree of control so that at the same time that we are protecting the grains from the insects, we are also protecting the public from harmful residues.

This study was conducted to determine the residue levels of some organophosphate insecticides used in the control of insect pests of stored grains. Evaluation of two commonly used detection systems and related procedures, namely

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electron capture gas chromatography (ECD-GLC) and alkali flame ionization gas chromatography (AFID-GLC), for their utility in residue analysis in stored grains was done as a logical preliminary step to full-scale residue analysis work.

MATERIALS AND METHODS

Insecticide Treatment and Storage. The stored grains used in the experiment were prepared and treated by the Stored Grain Laboratory of the Department of Entomology, UPLB. Corn grains used were from initial weevil infestations and maintained at 14 percent moisture content before treatment with insecticide.

For evaluation of malathion residues in stored corn, the grains were stored in sacks dipped in two percent and four percent aqueous emulsions of malathion.

Pirimiphos methyl (emulsifiable concentrate and dust) were applied by ordinary hand spraying or dusting to leave a deposit of approximately 10, 15 and 30 parts per million (ppm) of the insecticide on shelled corn.

After three, six and nine months, 200-g samples were removed after evaluation of degree of insect infestation, placed in plastic bags, and stored in the freezer until ready for analysis.

Analysis. a. *Malathion.* The procedure used was modified from that recommended by the Stored Products Research Laboratory, Atlanta, Georgia. Samples (50 g) were shaken in 100 ml benzene with a mechanical shaker. After allowing the solutions to stand for 10 min, it was filtered and the filtrate was concentrated to about one ml with a stream of air and cleaned up by column chromatography using Florisil partially deactivated by adding water to 10 per cent by weight. The insecticide was eluted with 40 ml of 1:1 ether-petroleum ether.

The eluate was concentrated to about five ml, made to five ml and analyzed by ECD-GLC using the following conditions:

Column: 4 feet, glass, with 10% DC-200 on 60/80 Gas Chrom Q
Detector T: 195°C
Injector: 225°C
Column T: 200°C

b. *Pirimiphos methyl.* The method used is essentially that recommended by Imperial Chemicals Industries, Ltd., Jealott's Hill Research Station. Samples (50 g) were shaken with 125 ml methanol in a mechanical shaker for 10 min and the mixture was allowed to stand for two hours with occasional stirring.

After filtration, the extract was analyzed directly by AFID-GLC using the following conditions:

Column: 3 feet, aluminum, with 7% QF-1 on 80/100 Gas Chrom Q
Column T: 190°C
Injector T: 200°C
Detector T: 200°C

Gas flow: N_2 = 21 ml/min
H_2 = 38 ml/min
Air = 200 ml/min

Identity confirmation of pirimiphos methyl was done by using another column (1:1 10% DC-200 + 10% QF-1 on 80/100 Gas Chrom Q) and thin layer chromatography with bromcresol green and silver nitrate as chromogenic reagents.

RESULTS AND DISCUSSION

Although the ECD-GLC has remained one of the most sensitive detection methods in pesticide residue analysis, its non-specific response has made it unsuitable for some analysis work. A rigorous cleanup procedure is also required and this generally results in lower recoveries. As a result of this limitation and also because of the decreasing uses of organochlorines, the trend is towards the more specific detectors such as the AFID for organophosphates. Because of the more specific responses of these detectors to heteroatoms in the molecule and detection limits about equal that of the ECD for some compounds, no cleanup or at most not-so-rigorous cleanup is required. This results in higher recoveries and greater data reproducibility. It must be stressed however, that contrary to popular belief the ECD can also be used for the analysis of organophosphate insecticide residues and so its utility is not limited to the organochlorines.

The AFID is a simple detector consisting of a flame enclosed by an alkali salt bead. Samples are burned in the flame and this causes signals due to an increase in the number of ions reaching the collector anode. These signals are amplified and transmitted to a recorder. Figure 1 shows the schematic diagram of the AFID marketed by Varian Aerograph (Walnut Creek, California).

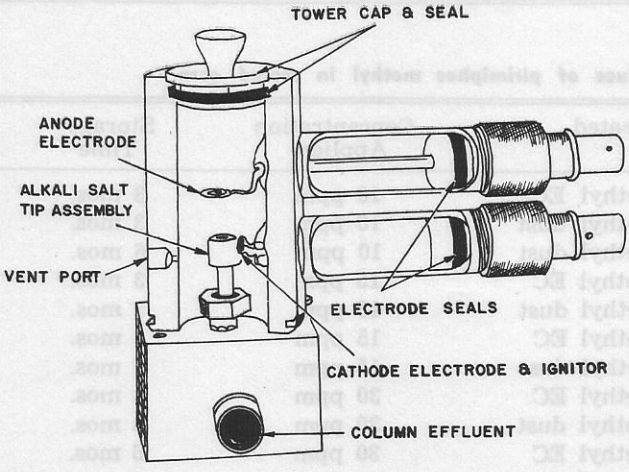

Fig. 1. Cross-sectional view of the alkali flame ionization detector.

The minimum detection limits of the two methods are comparable; ECD-GLC detect as low as 0.2 ppm of malathion while AFID-GLC was able to detect 0.01 ppm pirimiphos methyl. As expected, a higher recovery was obtained with pirimiphos methyl (92.6%) than with malathion (75.4%). The whole procedure for pirimiphos methyl took just as much time (3-4 hrs) as for malathion but about three times more pirimiphos methyl samples can be done in one day than malathion. The procedure for pirimiphos methyl is also less tedious.

Tables 1 and 2 show the residue data obtained with malathion and pirimiphos methyl, respectively. The gas chromatograms obtained are shown in Figures 2 and 3. At three months, malathion residues averaged 1.4 ppm for the four percent treatment and this went down to 1.0 ppm after nine months. It is seen in Figure 4 that the same trend occurs for the two percent treatment. Pirimiphos methyl application at 10, 15, and 30 ppm gave residues ranging from 0.6 to 2.8 ppm and 0.4 ppm to 2.5 ppm after three and six months storage, respectively. In general, the pirimiphos methyl dust formulation gave lower residues than the emulsifiable concentrates. The expected N-dealkylated metabolite was not detected.

TABLE 1. **Malathion residues in stored corn after storage in sacks dipped in insecticide solution.**

Concentration Insecticide	Storage Time	Residue level (ppm)
2%	3 months	1.2
2%	6 months	1.0
2%	9 months	1.0
4%	3 months	1.4
4%	6 months	1.2
4%	9 months	1.0

TABLE 2. **Residues of pirimiphos methyl in stored corn.**

Insecticide Treated	Concentration Applied	Storage Time	Residue level (ppm)
Pirimiphos methyl EC	10 ppm	3 mos.	1.3
Pirimiphos methyl dust	10 ppm	3 mos.	0.6
Pirimiphos methyl dust	10 ppm	6 mos.	0.4
Pirimiphos methyl EC	15 ppm	3 mos.	1.5
Pirimiphos methyl dust	15 ppm	3 mos.	1.5
Pirimiphos methyl EC	15 ppm	6 mos.	1.3
Pirimiphos methyl dust	15 ppm	6 mos.	1.2
Pirimiphos methyl EC	30 ppm	3 mos.	2.2
Pirimiphos methyl dust	30 ppm	3 mos.	2.8
Pirimiphos methyl EC	30 ppm	6 mos.	2.3
Pirimiphos methyl dust	30 ppm	6 mos.	2.5

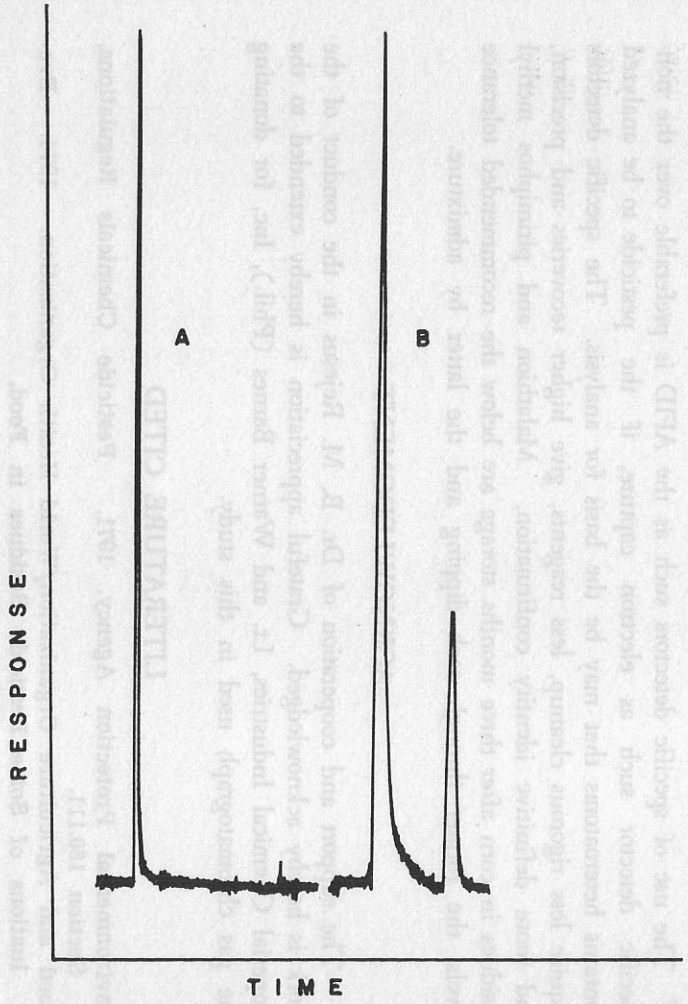

Fig. 2. Typical gas chromatogram using the alkali flame ionization detector. A-control, B-fortified.

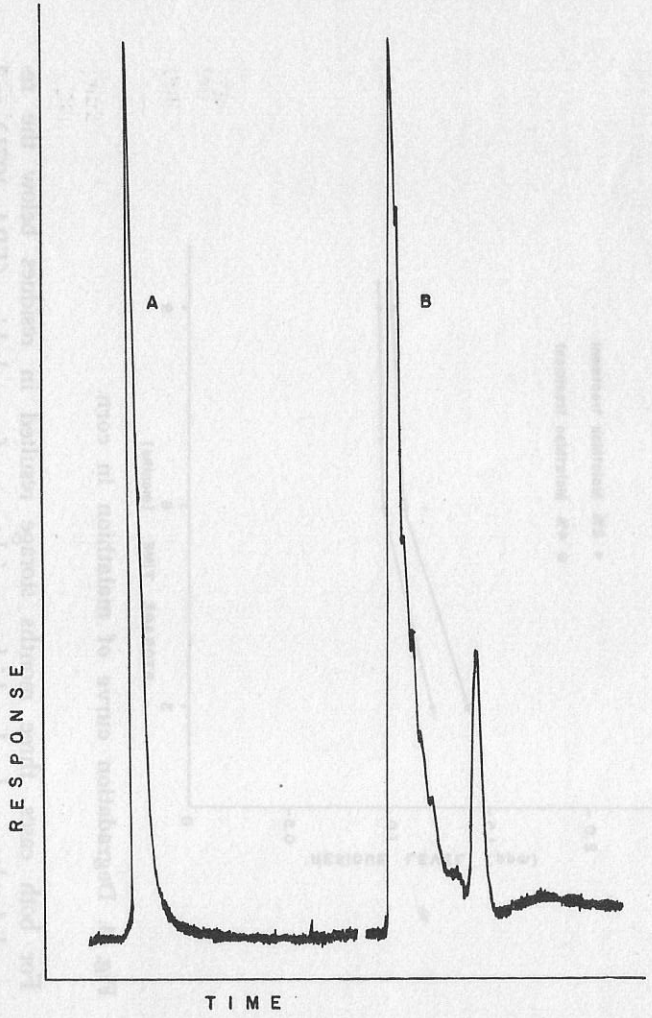

Fig. 3. Typcal gas chromatogram using the electron capture detector. A-control, B-fortified

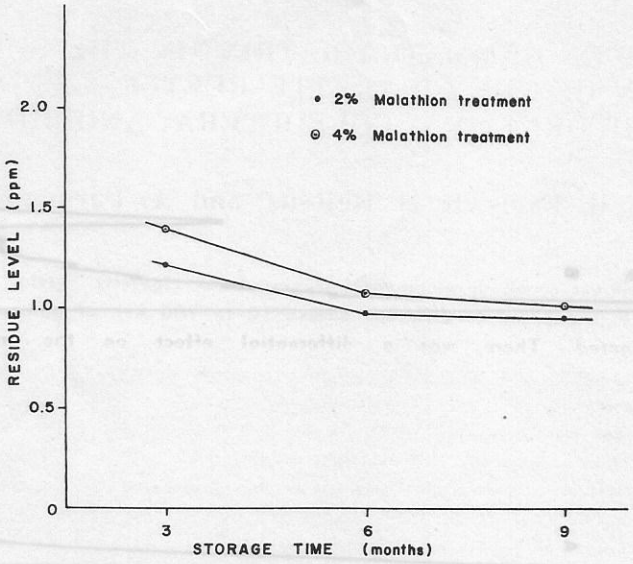

Fig. 4. Degradation curve of malathion in corn.

For both cases, three months storage resulted in residues below the recommended tolerance levels which are eight ppm for malathion (EPA, 1971) and seven ppm for pirimiphos methyl (FAO/WHO, 1974).

CONCLUSION

The use of specific detectors such as the AFID is preferable over the non-specific detector such as electron capture, if the pesticide to be analyzed contains heteroatoms that may be the basis for analysis. The specific detectors require less rigorous cleanup, less reagents, give higher recoveries and precision, and more definitive identity confirmation. Malathion and pirimiphos methyl residues in corn after three months storage are below the recommended tolerance levels, the former through sack dipping and the latter by admixture.

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