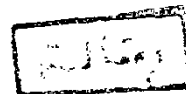
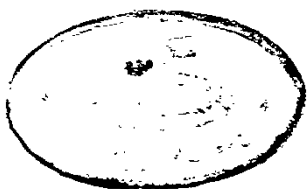


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RESIDUAL ANALYSIS OF INSECTISIDES RECENTLY USED IN EGYPT



THESIS

**Presented For The
Degree of M. Sc.**

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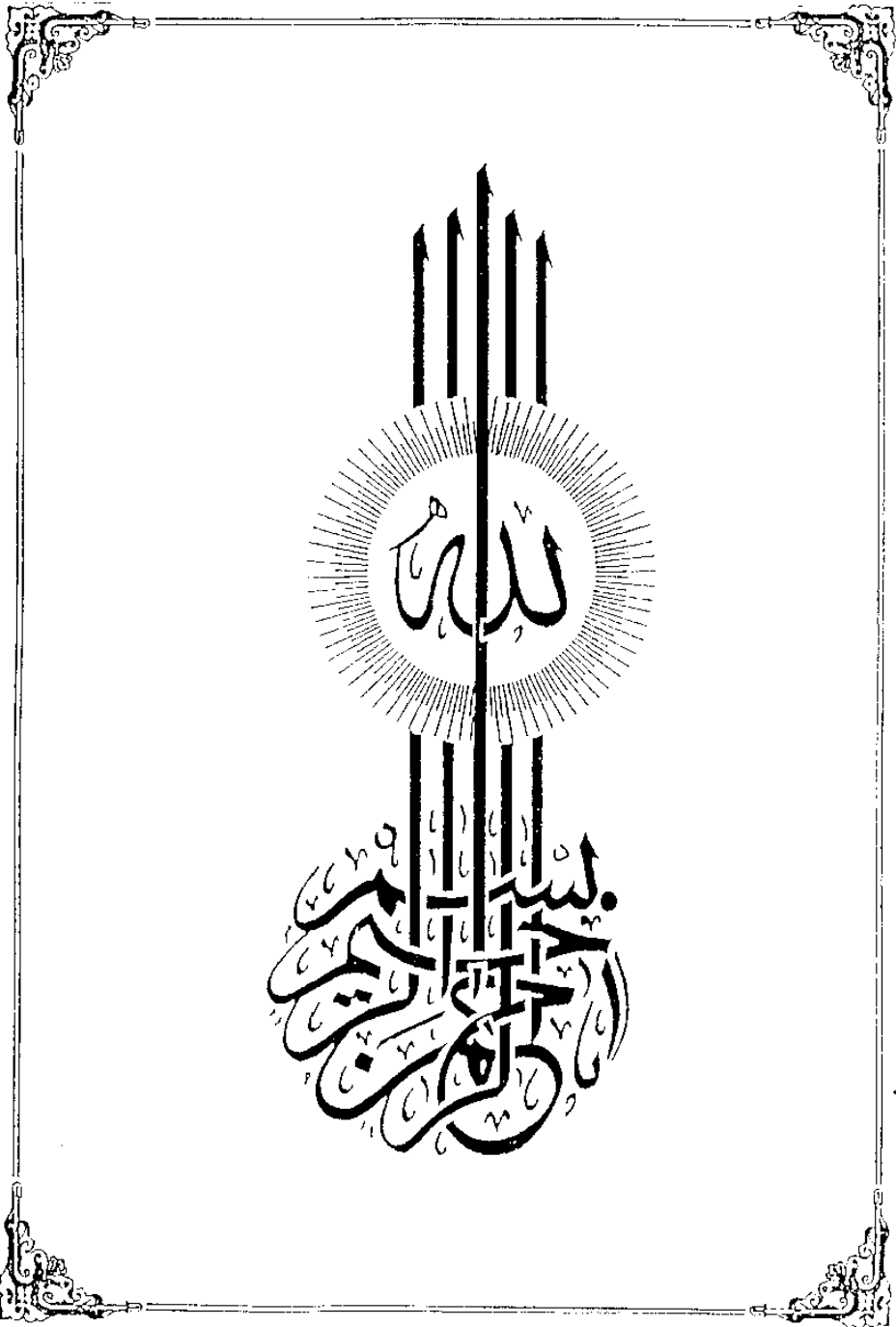
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NOTE

Besides the work carried out in this, the candidate had attended post-graduate courses for one year in the following topics:

- 1- physical Organic Chemistry.
- 2- Chemical Spectroscopy.
- 3- Advanced Heterocyclic Chemistry.
- 4- Analytical Chemistry; Instrumental Analysis.
- 5- Advanced Organic Chemistry.
- 6- Quantum Chemistry.
- 7- Macromolecular Chemistry.

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PART I

*INTRODUCTION

*COMPOUNDS STUDIES

INTRODUCTION

Pests control is an integral part of the development of every country. Since chemical control of pests is so successful, there has been an explosive expansion in the development of synthetic organic pesticides. Except for the organochlorine compounds, most of these chemicals persist for only few weeks or months in the environment. However as a result of the continued use of pesticides, appreciable quantities of pesticide residues and their degradation products accumulate in the biota. These accumulations lead to several environmental problems such as contamination of natural water causing destruction of aquatic microorganisms, soil pollution through persistence of insecticides and their detrimental influence on microbial population and soil fertility, serious injuries inflicted upon invertebrate and vertebrate animals and food contaminations causing toxic hazards to man and livestock. In Egypt the data obtained showed that the total quantity of pesticides which were used since 1952 to 1984 is 617507 metric tons.⁽¹⁹⁾ All the groups of pesticides "Chlorinated hydrocarbons, substituted phenols, organophosphorus compounds, carbamates, pyrethroids, natural organic compounds, organic oils, organic sulphur compounds, dinitrophenols, antifeedants, organothiocyanate etc... were used.

All methods of applications for pesticide were also used i.e hand atomizer, bucket pumps, knapsack sprayers, barrel - sprayers, power sprayers, knapsack air carrier sprayers, mist sprayers, mid size air carrier sprayers, aircraft were used. So, every one can imagine the quantity of pesticide residues which can be formed after this extensive use of pesticides in our agricultural environment. As a result of this, monitoring of residues of pesticides in the environment has become a very important aspect of pesticide technology and application.

As insecticide residues occur in a very low concentrations, and the residues persisting on plants and crops as well as the time required for an initial residue to decay to an acceptable level may be variable at the different locations, this needs a good evaluations, accurate and reproducible methods to detect and identify the nature and behaviour of such residues and finally what the decay leads to. Since there are different categories of insecticides, a varieties of analytical methods are used.

In this work we are tested two different types of insecticides i.e. the carbamate, Methomyl (Lannate) and

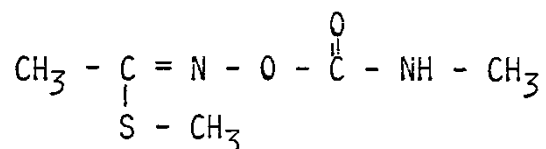
the synthetic pyrethroid Fenvalerate (sumicidin). The study was planned to cover four steps involved generally during the course of analysis i.e. extraction of the residues from the sample matrix, removal of interfering co-extractives and estimation of the insecticides in the cleaned-up extract. Thin-layer chromatography, gas liquid chromatography and ultra-violet spectrophotometry⁴ are used as tools of analysis. Moreover, the residual activity of the Methomyl and Fenvalerate insecticides in soil, water, and plants under the local conditions of Embaba, Giza governorate at different periods was studied. This aimed to clarify the role of insecticides on polluting the existing ecosystem contaminating water supplies, plant and human environment. Hopefully the study may contribute us to decrease the use of insecticides that cause pollution and hazards.

COMPOUNDS STUDIED*

1. METHOMYL

Lannate, Nudrin, SD 14999, Griffin NU-Bait II.

S-Methyl-N(methylcarbamoy)oxy)-thioacetimidate.



White crystalline solid, with slightly sulfurous odour melting point 78-79°C. Solubility in water, 5.8g/100g; in ethanol, 42g/100g; in methanol, 100g/100g.

Toxicity:-

Oral LD₅₀ for rat 17 mg/kg (male) and 24 mg/kg (female), For rabbit, dermal LD₅₀ 5880 mg/kg and 0.3 mg/L through inhalation for 4 hours.

Uses:-

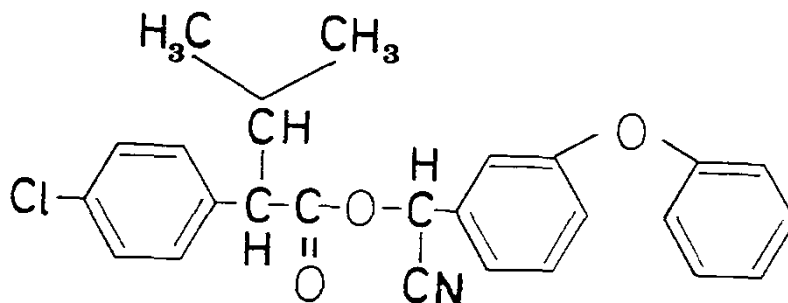
Broad-spectrum control of insects in many vegetables, soybeans, cotton and other field, crops, certain fruit crops, and ornamentals.

* "FARM CHEMICALS HAND BOOK 1982" Published by FARM CHEMICALS magazine, Willoughby.

4. FENVALERATE:

Sumicidin, Belmark, Ectrin, Pydrin, S-5602,
sanmarton, SD 43775 (shell chemical), Sumifly, Sumipower.

Cyano (3-phenoxyphenyl) methyl 4-chloro-alpha-(1-methylethyl) benzeneacetate, or α -cyano-3-phenoxybenzyl 2-(4-chlorophenyl)-3-methylbutyrate.



Molecular Weight, 419.9; physical form at 23°C, a clear viscous liquid, yellow in color, density at 23°C, 1.17g/ml; V.P at 25°C, 1.1×10^{-8} mm Hg. More stable in acidic solution than in alkaline solution. Moderately soluble in a range of organic solvents, High thermal stability. Relatively non-volatile. Stable to heat, moisture and in most organic solvents except

alcohols. Soluble in acetone, alcohol, ether, xylene, and kerosene. Insoluble in water.

Toxicity:-

Acute oral LD₅₀ (rat), 451 mg/kg (DNSO), 3200 mg/kg (aqueous suspension), acute dermal LD₅₀ (rabbit) 2500 mg/kg, (rat) 5000 mg/kg. Highly toxic to fish.

Uses:-

Pydrin was conditionally registered by EPA in early 1979 for use on cotton, and in late 1980 for use on peanuts, potatoes, and pears (dormant). Tolerances have been established for cotton, peanuts, potatoes, pears, fat of milk, and meat byproducts. Ectrin used in dairy and beef cattle. Eartags for control of hornflies, faceflies, Gluf Coast, ticks, spinose ear ticks, and as an aid to control stable flies and house flies. Belmark is used for control of insects on cotton and a wide range of other crops. Sumicidin has a broad spectrum of activity, chiefly effective against Lepidoptera, Diptera, Orthoptera, Hemiptera, and Coleoptera, and is widely used for pest control in other fields.

PART II

THE ANALYTICAL PART :

Thin-Layer Chromatography

Gas-Liquid Chromatography

Ultraviolet Absorption Spectrophotometry

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Thin - Layer chromatography

Thin - layer chromatography was known since 1938 as chromatoplates⁽¹⁾ and was adopted by few workers^(2,3) Stahl⁽⁴⁾ in 1956 succeeded in simplifying and standardizing the technique, since then, thin-layer chromatography has become an integral and important method in modern pesticide residue analysis^(5,6,7,8,9,10). In addition thin - layer may be used as a screening procedure followed by confirmation and quantitation using gas chromatography^(9,10,11,12) or ultra-violet spectrophotometry^(5,7,13). Extraction, clean-up and concentration steps normally precedes thin-layer chromatography determination.

Careful examination of the literature revealed that thin-layer chromatography was used as a technique for residual analysis of methomyl^(7,11,13,14,15,16) and Fenvalerate^(17,18,19). The main adsorbents used were silica gel of different varieties^(5,7,11,15,16), alumina^(7,17,19) and polyamide. The solvents used were acetone- cyclohexane, pentane, hexane and benzene⁽⁵⁾, (19: 1 v/v) ether-acetone⁽¹⁴⁾, acetone - hexane (1:4), (9:1) benzene-ethylacetate⁽¹⁵⁾, (9:1) chloroform-hexane, hexane-benzene (45-55) and hexane - chloroform (60-40 v/v).⁽¹⁷⁾