

SENSORY CHEMICAL PESTICIDE WARNING SYSTEM

**EXPERIMENTAL, SUMMARY
AND RECOMMENDATIONS**

JULY 1976

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WASHINGTON, D.C. 20460**



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" SENSORY CHEMICAL PESTICIDE
WARNING SYSTEM

Experimental, Summary
and Recommendations

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I. INTRODUCTION

The period covered by this report is June 13, 1974 through July 12, 1975.

The main purpose of this program was to develop a warning system which would alert individuals against premature reentry into areas treated with organophosphate and carbamate pesticides.

Restrictions on the use of persistent organochlorine insecticides have led to increased use of organophosphate and carbamate insecticides as substitutes. Many of these substitutes are highly toxic substances, manifesting their toxicity through inhibition of cholinesterase which permits the accumulation of acetylcholine to reach toxic levels. Thus, the danger in the use of certain organophosphate and carbamate insecticides is inherent. Conditions for their safe use must be determined, and rules which assure that safe conditions prevail during use must be implemented.

The segment of the population of the United States which could conceivably be involved with these pesticides is large. An estimated 4.5 million persons are regularly employed in farm work, but twice that number may be engaged in some form of agriculture in the course of a year's time. The states of North Carolina, California, and Texas have great numbers of seasonal workers, many of whom move from field to field without establishing a permanent home in the areas where they are likely to be exposed to the pesticides. The three crops which probably use the largest amounts of these pesticides are cotton, citrus and tobacco.

Citrus fruit pickers are the highest risk group. Following are tobacco leaf pickers and handlers and "scouts," who enter cotton fields counting insects for the purpose of determining when an application of pesticide is required. Although no fatal poisonings have resulted from premature reentry, hundreds of cases varying from severe to slight in degree have been documented, especially in California. In view of this experience, minimum field reentry safety intervals have been set by law by the Environmental Protection Agency. Laws have been enacted in California which are even more stringent than EPA requirements. Facts indicate that the proper safe interval in one area or for one crop may not be suitable in another area or for another crop. Several factors influence the persistence and the threat of the dislodgeable residues. The two most important probably are quantity of pesticide applied and the atmospheric conditions prevailing after application. Wet weather tends to shorten the reentry safety interval, and cold weather tends to lengthen the interval.⁽¹⁾

Danger in the use of organophosphates and carbamates might be reduced substantially if a warning system were in effect in a treated area during the time that the pesticide residue remains at a health-threatening level. The work undertaken was directed toward the development of a warning system based on the incorporation, or simultaneous but separate

1. "Occupational Exposure to Pesticides," Report to the Federal Working Group on Pest Management from the Task Group on Occupational Exposure to Pesticides, Washington, D. C., January, 1974.

application, with the pesticide spray of chemical agents which were odoriferous or visible. Ideally, these agents would have volatility characteristics such that when they were no longer detectable, either by smell or sight, the level of residual insecticide would be low enough to permit safe reentry. Other desirable characteristics of the agents would be low toxicity and low cost. In addition to this approach, provision was made in the program to consider alternative approaches in an uninhibited fashion known as a blue-sky effort.

The three insecticides involved in this program were methyl parathion, carbofuran, and azinphosmethyl. These were chosen because they are in wide use, are substitute chemicals, representative of their chemical types, and have vapor pressures which are spread more than one order of magnitude, thus covering the range of vapor pressures of many of those pesticides commonly used in the United States.

By mutual agreement between representatives of the Criteria and Evaluation Division, EPA, and Southwest Research Institute, the first three months of the program were devoted almost exclusively to searching of the literature and the generation of experimental approaches, so that decisions could be made at the end of the first quarter as to the nature of the experimental program to be pursued in the remainder of the contract period.

The second, third, and fourth quarters were almost exclusively devoted to experimental work, although some literature searching and

studying were required throughout the program for the purposes of guidance and evaluation.

II. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

A. Odor Agents

The literature search did not reveal any odoriferous analogs of the pesticides of interest. By logical reasoning, these compounds, if they exist, offer the best chances of having physical and chemical properties similar to the pesticides. Compounds with unusually high boiling points tend to evoke milder odor responses in humans than many lower boiling compounds. It was necessary to compromise and trade off the desired high boiling point for increased odor intensity. In order to compensate for the too rapid volatilization of the more intensely odoriferous compounds, a means of retarding the evaporation of the odor compounds had to be employed. The odor agents chosen for work in this program finally were skatole, β -phenylethylphenylacetate, and 2-phenylethanol.

The design of our study was such that the disappearance times of the pesticides and odor agents (as well as visual agents) were determined under laboratory climatic conditions and for at least two different temperatures outdoors. The tests were designed to evaluate different sensory agents rather than to test one with varying climatic conditions. Final development of any sensory system for reentry purposes should be thoroughly tested under a wide variety of climatic situations.

The disappearance time for methyl parathion was matched quite well with the proper concentrations of the first two of these substances and not so well with the latter one. These substances, and probably most other useful odorant compounds, tend to tail off so that the end point as determined by human sniffing is not sharply defined. The disappearance times of Guthion and carbofuran were not well matched, generally.

Although the quantitative aspects of sensory odor agents are not as precise as desired, they do have a distinct advantage in that they are easily recognized by the general population. Even young children can be instructed to associate smell with danger and that they should avoid the area if the smell can be discerned. Some thought was given to the incorporation of odor agents in the insecticide formulation as an aid in preventing reuse of the formulation containers. This idea probably has to be rejected because of cost considerations and the difficulties and cost which might be encountered in getting government approval of adding a new chemical to the formulation. In this program, attempts were made to develop sensory agents which would assist in preventing premature reentry into sprayed fields by farmers and field workers and also less knowledgeable people such as young children. This program has clearly demonstrated that for pesticides with vapor pressures similar to methyl parathion, odor systems are feasible and provide a reasonable definition of the times when it is safe to reenter sprayed fields. For

pesticides like carbofuran and Guthion, the development of useful systems requires more work but it does appear feasible.

B. Visual Agents

The visual agents of importance to the program were polycyclic, aromatic hydrocarbons which fluoresce under ultraviolet irradiation. The compounds offering the best potential to this program were anthracene and phenanthrene. The disappearance of these substances, when used in properly selected quantities, matched the disappearance of methyl parathion quite well but not the disappearance times of Guthion and carbofuran. The end points of the visual agents tend to be sharper and more easily read than the end points of the odor agents.

The visual agents provide a more accurate end point because people have less variation in their sense of vision than they do for odors. These agents must be exposed to UV light in order to reveal their fluorescence. This requires more knowledge and special equipment on the part of the user, and, thus, it would be less useful for the general population. This program has demonstrated that for pesticides with vapor pressures similar to methyl parathion a relatively accurate visual system can be perfected. Additional feasibility studies are needed to evaluate visual agents for pesticides like carbofuran and Guthion.

C. Warning Systems

No distinct preference between the visual sensory item and the unpleasant sensory item was established by the opinion survey.

Similarly, no distinct preference for one of these two systems was established experimentally in tests involving methyl parathion. Only through additional experience could, perhaps, a distinct preference for either device become apparent.

Warning systems, both visual and odor, can probably be developed successfully for methyl parathion. With respect to the conceptualized methods for warning systems given in Part 2, Method 1 (skatole incorporated into methyl parathion formulation) is unacceptably expensive. Method 2 (skatole in perimeter signs) is less costly than Method 3 (anthracene or phenanthrene in perimeter signs). However, the deciding factor on which of these methods is best for general use is probably not a cost factor but, rather, which system evokes human response in the most effective and reliable manner. Both methods, from a cost standpoint, are acceptable for use in the cotton-growing regions where cost of application of methyl parathion is in the lower part of the range given. Probably neither would be acceptable in the higher part of the cost range given. (For cost analysis, see Part 2 of this report.)

D. Blue-Sky Portion

Ideas generated in this effort were not examined experimentally, except for a few which were tested to a minor extent. Although some of the proposed concepts were technically possible, none were sufficiently promising to warrant additional experimentation.

E. Additional Information Derived from the Program

The program developed some valuable adjunct information, especially disappearance times for all 3 pesticides in the laboratory and the field. The disappearance data for methyl parathion are within the span of data of other investigators. The disappearance times found in this program for Guthion and carbofuran are substantially longer than those found by other investigators.

III. LITERATURE SEARCHES

The literature search conducted in the first quarter of the program was initiated with the foremost objective being to ascertain whether or not odoriferous compounds were known among the analogs and derivatives of the pesticides of interest. Logical reasoning suggested that the best chances for finding compounds having physical and chemical properties similar to the pesticides lay in searching closely related families. Such compounds were especially attractive because they might have disappearance rates close to those of the pesticides. Computerized searches for these compounds were made through the following facilities:

CHEMCON
DOD Technical Searching Facility
NASA Scientific & Technical Information Facility
EPA Abstract Search Center at Research Triangle

The principal key words and the modifiers used in these searches are as follows:

Name of pesticide/analog or derivatives-odor
smell, odoriferous;

organophosphates-odor, smell, odoriferous;

pesticides or Insecticides-odor, smell, odoriferous.

Insertion of the modifiers "odor", "smell", or "odoriferous" always resulted in zero citations available for printout. These negative results offer the options for believing that there are no such compounds or, if

such compounds exist, their odoriferous characters are not cited as key pieces of information.

Extensive manual searching of the literature was carried out for both odor and visual agents. This search was broadened so as to no longer exclude any organic chemical family, as was done in the computerized searching. Chemical Abstracts was the prime search source. The volumes searched and the major search categories are shown below. The modifiers used to restrict these major categories are not shown because they vary with the category and were applied at the judgment of the index reviewer, keeping in mind the objectives of the search.

Chemical Abstracts 1947-56

Major search categories:

- organic compounds
- aroma
- odor, odorous substances, olfaction
- pesticides
- insecticides
- luminescent, luminescence
- fluorescence, fluorescent substances
- phosphorescence
- phosphoric acid
- thiophosphoric acid
- phosphorothioic acid
- phosphorodithioc acid

Chemical Abstracts 1957-61

Major search categories:

- same as for 1947-56, plus perfumes
- and N-methyl, -dimethyl, -ethyl, and -diethyl
- carbamic acid
- N-methyl, -dimethyl, -ethyl, and -diethyl
- dithiocarbamic acid

Chemical Abstracts 1962-73

Major search categories:

- organic compounds
- odor, odorous substances, olfaction
- perfumes
- pesticides
- insecticides
- fluorescence, fluorescent substances
- phosphorescence

Starting with the 1962 volume of Chemical Abstracts, the categories which were omitted from the earlier search lists were dropped from the search because of the voluminous entries, even when quite restrictive modifiers were applied, and the doubtful payoff experienced in searching these categories in the preceding period, 1957-61.

The actual number of abstracts which received cursory review is unknown. The number of abstracts which were copied and came under close scrutiny was between 700-800. Of these, approximately 50 of the corresponding primary references were obtained for study. Approximately 100 abstracts contained useful information on an "as is" basis. One primary reference is a French patent⁽²⁾ concerning an insecticide preparation containing a phosphorescent material which is reputedly active so long as an effective amount of insecticide remains available at the exposure site. The phosphorescent material is not

2. Michel, R. H. R., No. 1, 441, 972 (Cl.A01n) June 10, 1966.

identified in the patent. One of the abstracts of interest "as is" dealt with a Russian report of unsuccessful attempts to mark seed disinfectants with a strong and long-lasting odor material or with permanent dyes.⁽³⁾

In addition, a variety of reference works and books in the library of Southwest Research Institute were searched.

Contact with the Institute of Gas Technology (IGT) in Chicago resulted in the information that the gas trade currently uses dimethyl-sulfide, C₃ and C₄ mercaptans, and tetrahydrothiophene as odorants. C₅ mercaptan has been used in the past but has caused problems by condensing in transmission lines and fell into disfavor. IGT forwarded a private research report containing some information about their search for non-sulfur-containing compounds which they have considered as alternative odorants for natural gas. This report contained a variety of compounds and their odor thresholds, but most of the information had already been obtained from other sources.

During the program, questions were raised regarding the possible carcinogenic activity of the polynuclear hydrocarbons being used as fluorescing agents. Although such activity appears to be nil for the two compounds of most interest ultimately,⁽⁴⁾⁽⁵⁾ the desirability of having acceptable substitute agents from chemical families beyond any shadow

3. Chemical Abstracts, 72, 89170n (1970) Kulikov, A.I., et al, Byull, Vses. Nauch. -Issled. Inst. Zashch. Rast., 1969 (3) 15-17.

4. Steiner, P. E., Cancer Research, 15, 632-635 (1955).

5. Salaman, M. H. and Roe, R. J. C., Brit. J. Cancer, 10, 363-378 (1956).

of suspicion is obvious. Toward this end, another effort was made to find such compounds in the literature. However, it appears that the most effective fluorescing agents are in the polynuclear hydrocarbon groups.

The only other organized search effort was for the purpose of accumulating data of other investigators relative to the disappearance of the pesticides of interest after field application. These data are used in a subsequent report section in comparison with the disappearance data generated in this program.

IV. SELECTION OF ODOR AGENTS

Selection of candidate odor materials involved the factual and theoretical considerations mentioned in the following paragraphs.

The volatilities of the pesticides, as shown below, were thought to be of first importance:

<u>Pesticide</u>	<u>Vapor Pressure, 20°C, mm Hg</u>	<u>Concentration in Saturated Vapor, 20°C, ppb</u>
Methyl parathion	$0.97 \times 10^{-5(6)}$	12.8
Carbofuran	$0.46 \times 10^{-5*}$	10.
Guthion	$2.2 \times 10^{-7(6)}$	0.03

Note: *Extrapolated value based on vapor pressure data at higher temperatures supplied by manufacturer.

Requirements for ideal odorants were envisioned as follows:

1. Vapor pressures of the odorous substances should be close to the vapor pressures shown above for the three pesticides.
2. Molecular weights should not exceed 300 and, preferably, should be below 250. This requirement is based on the observation by Stoll⁽⁷⁾ that no odorous substance is known with a molecular weight above 300 and that the limit of perception, for many people, begins around 250.
3. Odor perception thresholds should be below the saturated vapor concentrations shown above for the three

6. Melnikov, N. N., "Residue Reviews," 36, Gunther & Gunther, Eds., Springer-Verlag, N. Y. (1971).

7. Stoll, M., "Molecular Structure and Organoleptic Quality," Soc. of Chem. Ind. Monograph No. 1, The Macmillan Co., N. Y. (1957).

pesticides. Preferably, the thresholds should be much below these values since the atmosphere sniffed in actual field conditions would never be saturated.

4. Chemical characteristics should be similar to the three pesticides since the rate of disappearance is thought to be the sum of losses from evaporation, hydrolysis, water solubility, photolysis, absorption, microbiological action, oxidation, isomerization, and other. Evaporation from surface deposits is thought to be a major route of disappearance for many pesticides.⁽⁸⁾

5. The materials should be relatively nontoxic originally and after they degrade.

6. Odors of the agents should evoke a sharp human response.

7. The agents should not leave toxic residues.

The literature search did not reveal any candidate odor compounds from the same chemical families as the pesticides. Although the pesticides of interest were noted to have appreciable odors themselves, discussions with representatives of the manufacturers (Monsanto Company, Chemagro Division of Baychem Corporation, and the Agri-Chem Division of the FMC Corporation) disclosed that the odors present were probably from low molecular weight, volatile compounds present as impurities.

8. Spencer, W. F., et al, Pesticide Volatilization, "Residue Reviews," 49, Gunther & Gunther, Eds., Springer-Verlag, N. Y. (1973).

In the case of methyl parathion, methyl mercaptan is released by hydrolysis of the thioester isomer which forms from the parent compound at a slow rate at room conditions. Attempts to take advantage of this phenomenon to attain the objectives of this program are described elsewhere in this report.

At this point in the selection process, with the theoretically most promising chemical categories having been eliminated, attention was turned toward compiling a list of odoriferous compounds, with emphasis on those boiling above 275°C and having, or estimated as having, low odor thresholds. The compounds are given in Table IV-1. During the time that Table IV-1 was being compiled, the following firms were contacted for suggestions for compounds to be included in the list of candidates:

International Flavors and Fragrances, Inc. (U.S.)
Givaudan Corporation
S. B. Penick and Company
Chemessence, Inc.
J. Manheimer, Inc.
Evans Chemetics, Inc.
Fritzsche, Dodge & Olcott, Inc.
Petro-Tex Chemical Corp.

None of the contacted firms could suggest any outstandingly odoriferous compounds boiling above 300°C, except in the musk family. Four of the companies expressed an interest in the problem and sent samples for evaluation.

While a number of very odoriferous substances are listed in Table IV-1, only some members of the musk family, benzyl salicylate,

TABLE IV-1. CANDIDATE ODOR AGENTS

Compound	Mol. Wt.	Boiling Point ⁽⁹⁾		Odor Thresh., ppb (v/v) ⁽¹⁰⁾	Odor Character
		t, °C	pr., mm Hg		
artificial musk, 1-tertbutyl-3-methyl-2, 4, 6-trinitrobenzene	283	m.96-7	—	0.001	like natural musk
typical synthetic macrocyclic musk, 11-oxahexadecanolide	256	m.35	—	—	like natural musk
musk ambrette	268	25	2.5×10^{-5}	—	like natural musk
musk xylene	297	25	1×10^{-5}	—	like natural musk
musk ketone	294	25	2.4×10^{-6}	—	like natural musk
muscone-active principle in natural musk, 3-methylcyclopentadecanone	238	328 130	760 0.5	—	natural musk
civetone, 9-cycloheptadecen-1-one	250	342 159	742 2	—	disgustingly obnoxious, becoming pleasant in extreme dilutions
2-hexyl-3-methoxypyrazine	194	—	—	0.001 ⁽¹¹⁾	like fresh bell pepper
2-isopropyl-3-methoxypyrazine	152	—	—	0.002	like fresh bell pepper
2-isobutyl-3-methoxypyrazine	166	—	—	0.002	like fresh bell pepper
2-propyl-3-methoxypyrazine	152	—	—	0.006	like fresh bell pepper
alpha-ionone, beta-ionone	192	127 81 250	12 1 760	0.013	like cedar wood in strong dilutions like violets in extreme dilutions.
vanillin	152	285 170	atm. 15	0.016	like vanilla
ethyl vanillin	166	25	1.7×10^{-4}	—	like vanilla
deca-trans, trans-2, 4-dienal	152	—	—	0.070 ⁽¹²⁾	like fried chicken
2-methoxynaphthalene	158	272	atm.	0.12	like old nerolin
coumarin	146	298 139	atm. 5	0.28	like vanilla
methyl coumarin	161	305	760	—	like vanilla
methyl anthranilate	151	135	15	0.65	like concord grapes
1, 7, 7-trimethylbicyclo [4.4.0]-decan-3-one	195	87	0.001	—	can be used in perfumes
1, 7, 7-trimethylbicyclo [4.4.0]-decan-3-formate	224	85	0.01	—	can be used in perfumes
decan-3-acetate	238	90	0.01	—	can be used in perfumes
decan-3-propionate	252	100	0.02	—	can be used in perfumes
decan-3-butyrate	266	115	0.05	—	can be used in perfumes
decan-3-acrylate	250	86	0.01	—	can be used in perfumes

TABLE IV-1. CANDIDATE ODOR AGENTS (Cont'd)

Compound	Mol. Wt.	Boiling Point ⁽⁹⁾		Odor Thresh., ppb (v/v) ⁽¹⁰⁾	Odor Character
		t, °C	pr., mm Hg		
alpha-(2-hydroxycyclohexylmethyl) butyrolactone	196	203	3	—	like peppermint
alpha-(4-hydroxycyclohexylmethyl) butyrolactone	196	203	3	—	like peppermint
1-(phenylethoxy)adamantane	256	176	1	—	can be used in perfumes
gamma-decalactone	170	281	atm.	—	like peach
gamma-undecalactone	184	286	atm.	—	like peach
gamma-dodecalactone	198	170	11	—	like peach
benzophenone	182	305	760	—	—
β -phenylethyl phenylacetate	240	324	760	—	rose-hyacinth
benzyl cinnamate	238	350	760	—	sweet odor of balsam
hexyl cinnamic aldehyde	216	305	760	—	—
benzyl benzoate	212	323	760	—	faint, pleasant, aromatic
benzyl salicylate	228	368	760	—	pleasant
o-bromophenol	170	194	760	0.001	unpleasant
alpha and beta-santalol	220	302	760	—	like sandalwood

Note: Compounds for which no odor threshold data are presently available were included in the above list on the basis of actual or estimated high boiling points and indicated odorous character.

9. Appel, L., *Am. Perfumer Cosmet.*, **79**, 25-39 (1964).
10. Dravnieks, A., Report No. IITRI-C8140-1, IIT Research Institute Technology Center, Chicago, Illinois, March 10, 1969.
11. Seifert, R. M., *et al*, *J. Agr. Food Chem.*, **18**, 246-249 (1970).
12. Buttery, R. G., *et al*, *J. Agr Food Chem.*, **17**, 1322-1327 (1969).

and benzyl cinnamate have vapor pressures which approach those of the pesticides. On this basis alone, these compounds appeared to be the best candidates for inclusion in the pesticide formulations for application simultaneously with the pesticides and over the identical area. If application of the signal odorant were to be in some manner other than by inclusion in the pesticide formulation and by a means which retarded its normal evaporation rate, then numerous other odoriferous compounds, including ones not listed, might be potentially useful. For example, vanillin, ethyl vanillin, coumarin, methyl coumarin, and gamma dodecalactone appeared to be in this category.

Odor perception thresholds for some typical odoriferous compounds are presented in Table IV-2 for the purpose of comparison with those of the odor agent candidates which are given in Table IV-1.

TABLE IV-2. ODOR PERCEPTION THRESHOLDS FOR
SOME TYPICAL ODORIFEROUS COMPOUNDS

(for purposes of comparison with odor agent candidates)

Compound	Odor Threshold ppb (v/v)
hydrogen sulfide	1 to 5
methyl mercaptan	1 to 8
n-butyl mercaptan	0.5
butyric acid	0.4
crotonaldehyde	34
pyridine	10 to 12
p-toluidine	3.1
eugenol	3.5
methyl salicylate	0.6
skatole	0.3
p-chlorophenol	0.2

V. SELECTION OF VISUAL AGENTS

There are many compounds which exhibit some degree of photoluminescence. The potential use of inorganic phosphors, dyes, and nonvolatile luminescent substances is treated in the blue-sky section of this report. This section is concerned with the search for organic compounds which exhibit some form of photoluminescence and have normal boiling points similar to those estimated for the pesticides of interest. Availability of photoactive compounds having normal boiling points matching those of the pesticides was, of course, no guarantee that such compounds would have vapor pressures matching the pesticides at the usual laboratory and field temperatures. However, since vapor pressure data at ambient temperatures are not available for most of these materials, most of which are solids at ambient temperatures, no better criteria for potential usefulness were known than matching the normal boiling points.

The search for such compounds in the journal literature was difficult and not as productive as had been hoped for. Journal articles treating photoluminescent phenomena are not often concerned with the vapor pressures of the compounds under study. Books, reference works, and contacts with industrial firms were more helpful sources of information.

The field of fabric brighteners seemed very attractive, initially. However, as information was obtained, it became apparent that most of the compounds employed were of exceedingly low volatility or had

insufficient stability when subjected to prolonged, intense sunlight.

Companies which were contacted in this regard are:

American Cyanamid Company
Ciba-Geigy, Inc.
Crompton and Knowles Corp.
American Hoechst Corp.
United States Radium Corp.
Hercules, Inc.

A few samples were received from these organizations for experimental evaluation.

Some attention was given to natural substances which fade or darken under sunlight. An example of this category would be carotene, which fades. However, such action is a function of time and seems to be no better than a timepiece.

Table V-1 is a listing of candidate visual agents which span the boiling point range of interest. Most of these were taken from chemistry handbooks and other books, although one journal article was outstandingly useful,⁽¹³⁾ and at least two more helpful.⁽¹⁴⁾⁽¹⁵⁾ The compounds selected for screening first were: trans-stilbene, anthracene, carbazole, tri-phenylmethane, 2,5-diphenyloxazole, fluoranthene, 9-phenylanthracene, o,o'-quaterphenyl, and 1,2,7-trihydroxyanthraquinone.

The possibility of using the photoluminescent character of the pesticides themselves was considered but did not appear promising. Guthion and carbofuran exhibit some phosphorescence, barely in the

13. Furst, M., et al, J. Chem. Physics, 26, 1321-1332 (1957).

14. Kirkbright, G. F., et al, Anal. Chim. Acta, 52, 237-246 (1970).

15. Williams, R. T., J. Roy. Inst. Chem., 83, 611-626 (1959).

TABLE V-1. CANDIDATE VISUAL AGENTS

Compound	Boiling Point, °C
trans-stilbene	305 (720 mm Hg)
anthracene	340
phenanthrene	340
acridine	345-6
alpha-benzyl-naphthalene	350
para-benzyl-naphthalene	350
1,4-diphenylbutadiene	350 (720 mm Hg)
4-methoxybenzophenone	354-5
carbazole	355
triphenylmethane	358-9
2,5-diphenyloxazole	360
1,1,2,2-tetraphenylethane	360
2-hydroxybenzothiazole	360
diphenylurethane	360
triphenyl phosphite	360
quinazolinone	360
benzimidazole	360
1,2-benzophenazine	360
1,1'-binaphthyl	360+
1,3,5-trinitronaphthalene	364 (explodes)
1-naphthyl-2-tolyl ketone	365
m-terphenyl	365
diphenylene disulfide	366
phenothiazine	371
thioxanthone	372
fluoranthene	375
p-terphenyl	376

TABLE V-1. CANDIDATE VISUAL AGENTS (Cont'd)

Compound	Boiling Point, °C
anthraquinone	377
diphenylsulfone	379
melene	380
triphenylmethanol	380
retene	390
pyrene	393
N-benzylsuccinimide	395
4,4'-dibromobenzophenone	395
4,4'-ditolylsulfone	405 (714 mm Hg)
1,2-benzofluorene	413
9-phenylanthracene	417
o,o'-quaterphenyl	420
tetraphenylethylene	420
triphenylene	425
9,10-benzophenanthrene	425
1,2-dihydroxyanthraquinone	430
tetraphenylmethane	431
1,2-benzanthracene	435
1,8-dinitronaphthalene	445 (decomposes)
chrysene	448
2,2-binaphthyl	452
1,3,5-triphenylbenzene	459 (717 mm Hg)
1,2,6-trihydroxyanthraquinone	459
1,2,7-trihydroxyanthraquinone	462
11,12-benzofluoranthene	480
picene	519

visible range, but methyl parathion does not. However, the p-nitrophenol produced upon hydrolysis of methyl parathion does phosphoresce in the visible range,⁽¹⁶⁾ although inadequately for the purpose of this program.

16. Moye, H. A., and Winefordner, J. D., J. Agr. Food Chem., 13, 516-518 (1965).

VI. LABORATORY DISAPPEARANCE TESTS

In these tests, the objective was to develop sensory systems (odor and visual) which would match the disappearance rates of three pesticides. Ideally these rates would match under variable weather conditions of temperature, wind speed, humidity, and rainfall. The intent of the program is to provide a sensory system which will indicate when the pesticide is at a level which will allow safe reentry into the field. Stated in another way, the systems will warn individuals not to enter as long as the sensory agent is detectable. The "safe" level of pesticide (on plants) which has been used for the studies reported herein is when 90% of the original level has dissipated. This is an arbitrary value used in lieu of more definitive data. The actual residue levels of different pesticides on plants, soils, etc. which are considered safe for reentry are being developed under other EPA programs. The sensory agents developed under this contract should be sufficiently adaptable so that by minor changes of delivery system they will meet the safe levels when established.

A. Pesticides

1. From Glass Plates

In order to follow the disappearance of the pesticides, an analytical capability of adequate sensitivity was established using a gas chromatograph equipped with a flame ionization detector. No interferences were experienced in the detection and measurement of the target pesticides or their degradation products.

Carbofuran was found to chromatograph satisfactorily on a 20-inch, 1/8-inch diameter SS tube packed with 10% UC-W98 (methyl silicone gum containing 1% vinyl) on Chromosorb WAW-DMCS (80-100 mesh) at an oven temperature of 150°C. A short column (20-inch) was used to reduce the times required for analyses and to minimize the exposure of carbofuran to high temperature. Carbofuran has been found difficult to chromatograph directly, but the conditions given in this paragraph produced good, reproducible instrument response to this pesticide. Other conditions are: carrier gas flow - 30 ml/min.; H₂ flow = 30 ml/min.; O₂ flow = 240 ml/min.; injection port temperature = 200°C, and detector temperature - 200°C. Methyl parathion was analyzed on the same column at the conditions above except an oven temperature of 160°C was preferable. Guthion was also chromatographed on this column but at temperatures of 250°C for the injection port and detector and 200°C for the oven. Retention times for the three pesticides are as follows: methyl parathion - 8.5 min. at 160°, 12.7 min. at 150°; carbofuran - 6.6 min. at 150°; Guthion - 14.7 min. at 200°.

The first disappearance work encountered the problem of uneven distribution of the substance under study. A dilute solution of a substance in a volatile solvent does not deposit the substance uniformly if permitted to evaporate unmolested on a flat surface. Uneven distribution, of course, leads to unequal disappearance times for the

areas of relatively heavy and light deposits. Miniature spray devices (e.g. DeVilbiss, No. 15, modified) were found difficult to control when spraying the small areas needed in the studies, and the stray spray droplets required safety precautions which were burdensome.

Eventually, a system was developed which visually gave a fairly uniform distribution of pesticides and sensory agents on glass plates which were then exposed to controlled conditions in the laboratory. A four-inch frosted glass square was rotated on a turntable at 175 rpm while a selected volume of agent or pesticide in solution in toluene was applied to the center of the plate by means of 100- μ l syringe. Perfect reproduction of area covered and perfect uniformity of the deposit were not achieved, but the system gave fair-to-good reproducibility and was very useful. When the amount of solution deposited is 50 microliters, the area covered is approximately 30 cm². When all factors involved except concentration are constant, then the amount of substance deposited per cm² becomes dependent upon the concentration of substance in the solution.

In order to determine the amount of pesticide present on the glass plates at the desired intervals after application, a plate was rinsed with a stream of dichloromethane which was collected, as it ran from the corner of the plate, in a small glass beaker. The rinse was evaporated, without heating, under a stream of nitrogen to a predesignated volume and compared with a standard solution by gas chromatographic analysis.

Working with pesticide formulations commonly used in field applications, the rate of disappearance was determined for Methyl Parathion E-4, Furadan 4 Flowable (carbofuran), and Guthion 2L (azinphosmethyl). Disappearance was studied at a temperature of 23°C (73°F) with an air velocity over the exposed plates of 8 kph (5 mph). Figures VI-1, VI-2, and VI-3 are plots of the replicate amounts of pesticide remaining on the plates after the passage of various intervals of time. Two levels of deposit of each pesticide were applied in this work, 10 $\mu\text{g}/\text{cm}^2$ (0.88 lb/acre) and 5 $\mu\text{g}/\text{cm}^2$ (0.44 lb/acre), simulating high and medium applications in the field. At both levels of application, only about 3% of the methyl parathion remained on the plate after 24 hours had passed. The high level of Furadan showed about 20% remaining after 15 days and the medium level about 3% remaining after 12 days. The high level of Guthion showed about 60% remaining after 30 days with this dropping to around 12% after 60 days. The medium level of Guthion was not followed beyond the 28-day mark, at which point about 20% remained.

In order to be certain that the chromatographic peak representing methyl parathion is truly methyl parathion and not methyl paraoxon, the latter was synthesized by the method of Lichtenstein, et al⁽¹⁷⁾ and injected into the chromatograph. Figure VI-4 shows sufficient separation between the methyl paraoxon and methyl parathion to prevent

17. Lichtenstein, E. P., et al, J. Agr. Food Chem., 21, 416-424 (1973).

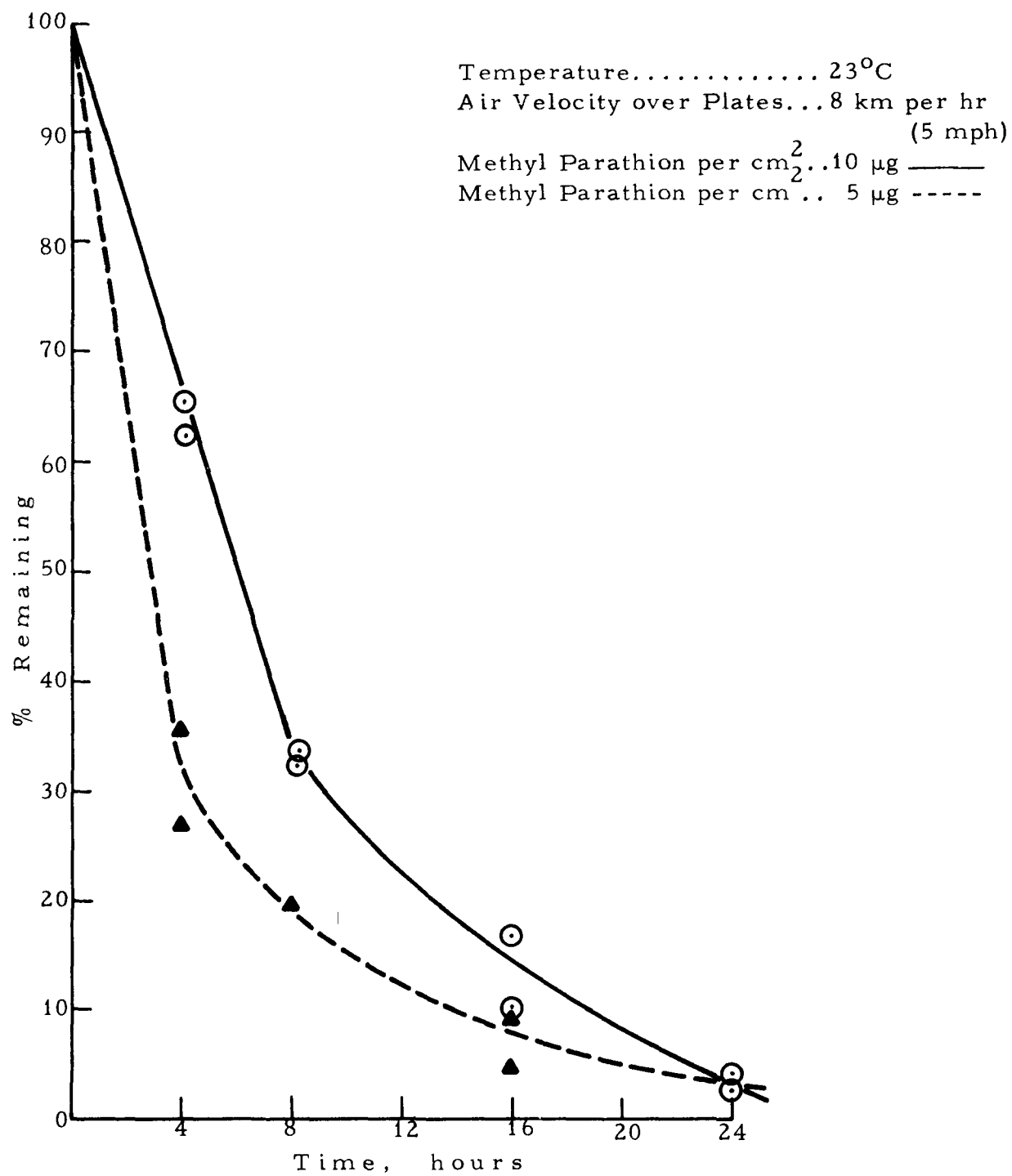


Figure VI-1. Disappearance of Methyl Parathion from Glass Plates

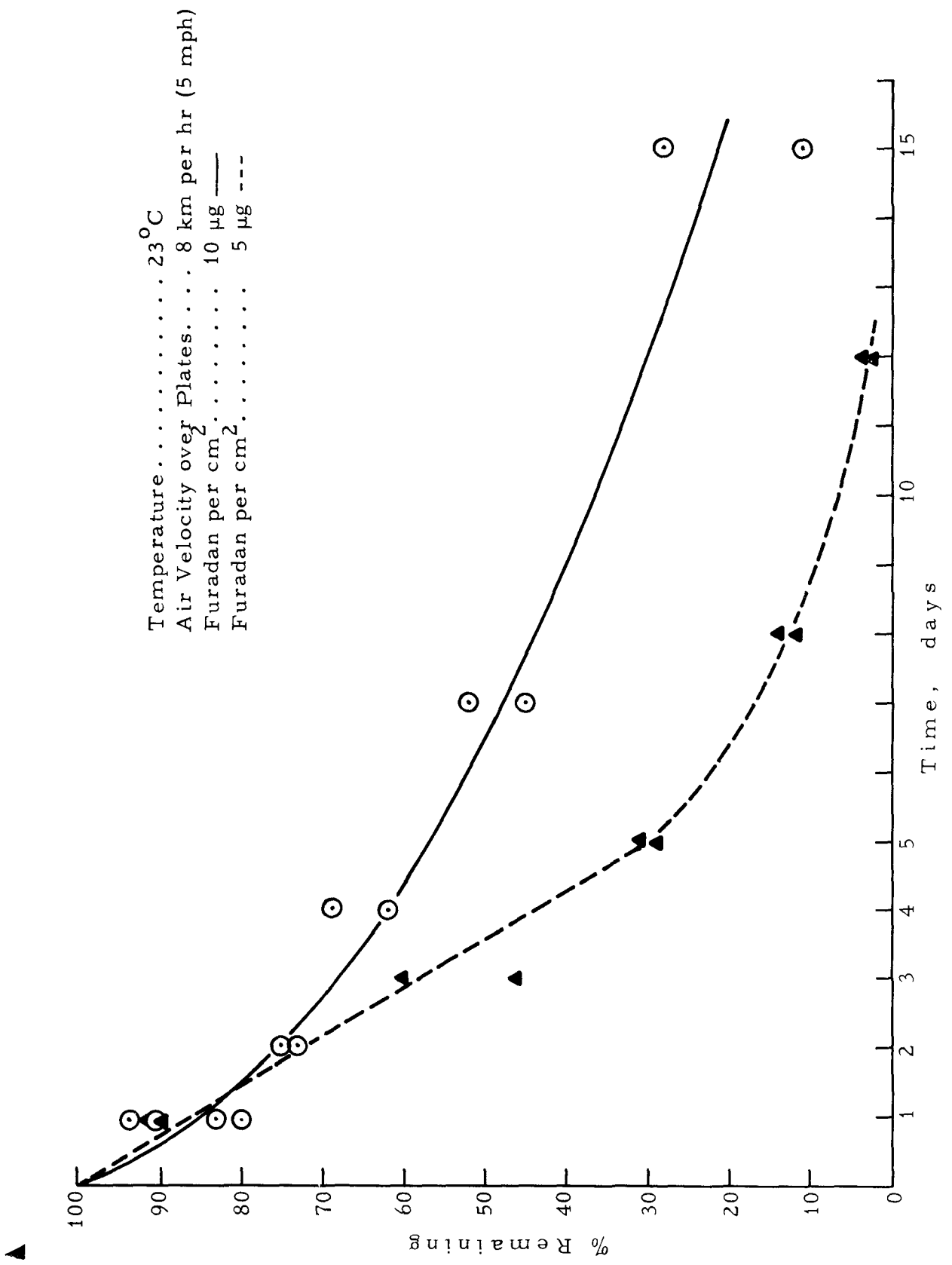


Figure VI-2. Disappearance of Furadan from Glass Plates

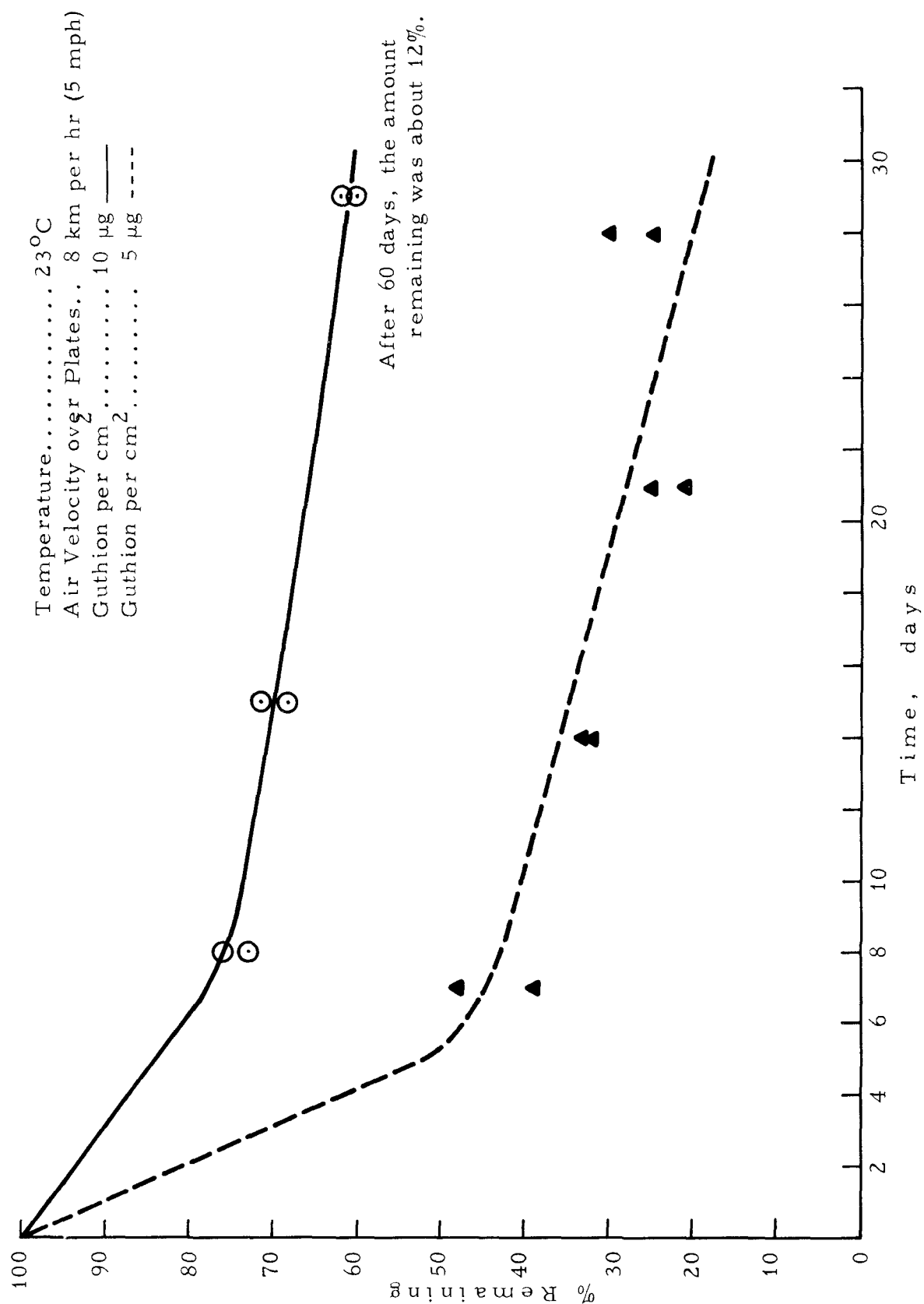


Figure VI-3. Disappearance of Guthion from Glass Plates

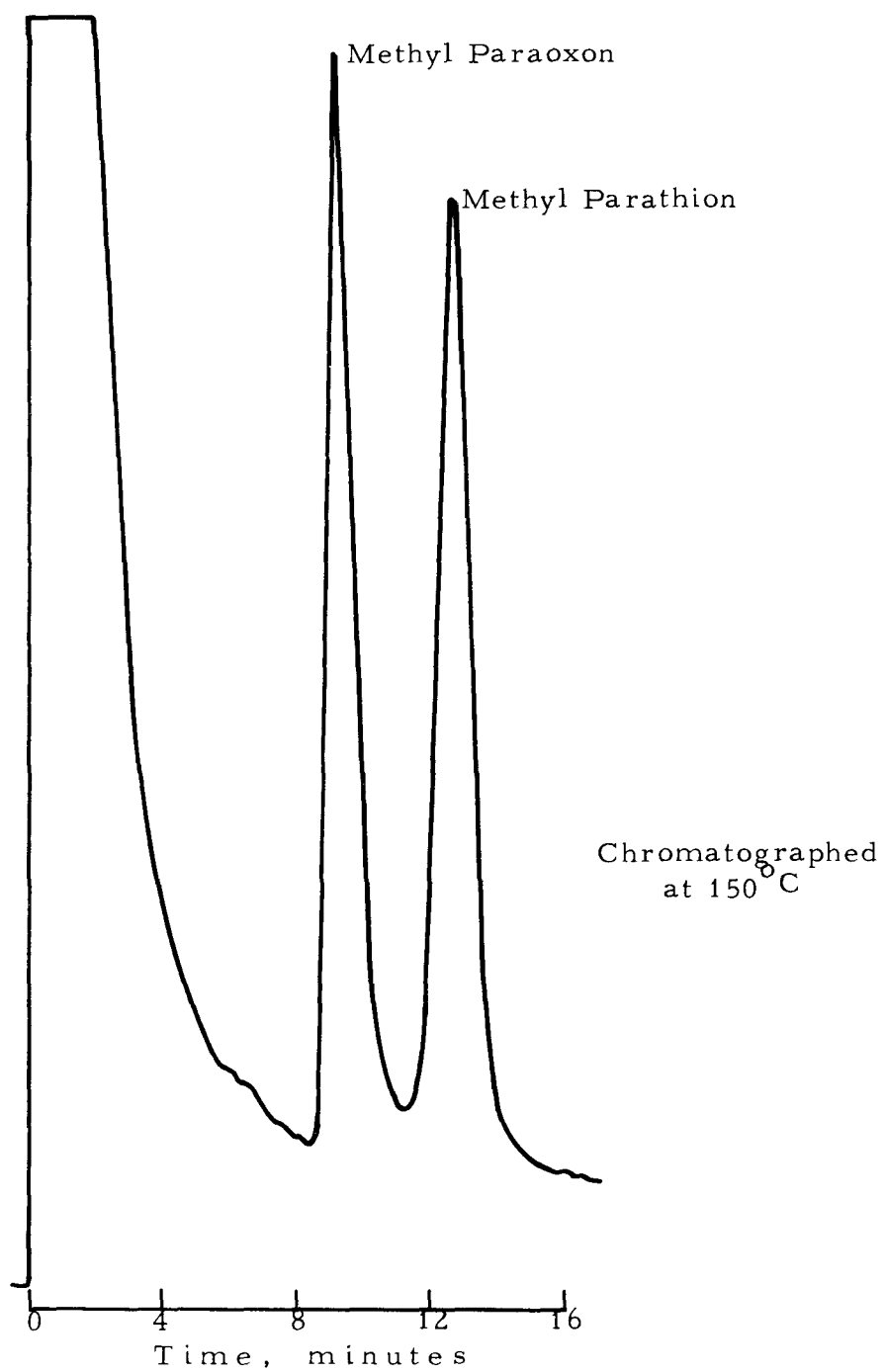


Figure VI-4. The Separation of Methyl Paraoxon and Methyl Parathion

confusion of identities. Although this figure was constructed from chromatography at 150°C, we have found that at our normal operating temperature of 160°C the differential retention times for paraoxon (6.2 minutes) and parathion (8.5 minutes) provide adequate resolution. Thus, it is probable that the disappearance study of methyl parathion dealt with the parent compound.

Furadan 4 Flowable, as received, is an aqueous suspension of the pesticide and insoluble, finely divided solid. In order to conduct the disappearance study mentioned above, it was necessary to extract the Furadan from the aqueous suspension with toluene so that it could be applied in the same manner as the Methyl Parathion E-4 and Guthion 2L. Of course, the extract did not contain the finely divided solid which, if it served as a good adsorbent, could affect the rate of disappearance of the Furadan. This effect would likely reduce the rate of disappearance of the Furadan, resulting in a longer staying time than that determined in this experiment.

The lack of precision and inconsistencies in the data in Figure VI-2 and VI-3 require some comment. These imperfections are thought to be the result of three factors: (1) the difficulty in obtaining uniform distribution of the pesticide on the plants, as mentioned earlier; (2) changes in analytical sensitivity which occasionally occurred in an unpredictable pattern, decreasing precision obtained despite the frequent

use of standards. The source of this difficulty was tentatively identified as resulting from the accumulation of deposits of unknown materials in the injection port, for example, possibly the emulsifiers in the pesticide formulation. Cleaning the injection port after every ten injections was found to lessen the problem; (3) This factor applies to Figure VI-3 only. The more rapid rate of loss of Guthion in the second 30-day period versus the first 30-day period could possibly be explained by temperature change brought on by failure of the laboratory air conditioning system. Repairs could not be effected until several days had passed. Nevertheless, the data procured in these tests were sufficiently accurate to allow continuation of the work of matching pesticide disappearance times with those of odor and visual agents.

2. From Soil

Two soil types were used: (1) a dark brown silty clay (Lewisville silty clay) and, (2) a tan sandy loam (Venus clay loam). The large lumps were crushed, and then the soil was sieved to provide a fraction with particles ranging from 0.5 to 2.4 mm. This fraction was exposed in a 1/4-inch layer to an atmosphere at 50% relative humidity and a temperature of 24°C (75°F) for a period of 3 days, or more, before use.

Forty grams of soil were placed in petri dish (area = 63.6 cm), and 318 µg of methyl parathion was applied in 2 ml of aqueous spray emulsion, a volume of just the right amount to wet the surface of the soil sample thoroughly. The application rate of methyl parathion was 5 µg/cm² (0.44 lb/acre).

Methyl parathion was recovered from the soil samples by placing the soil on filter paper in a Buchner funnel and washing 5 times with approximately 30-ml portions of acetone. Suction was applied briefly to strip the acetone from the soil after each application of acetone. The filtrate, amounting to about 150 ml, was evaporated to a known volume of less than 5 ml, placed in a small vial, and shaken with enough NaCl to cause any water present to separate from the acetone. The amount of methyl parathion recovered was estimated from injections into the gas chromatograph of the sample solution, a standard solution, and a soil blank solution. Average recovery from the brown silty clay was 75% and from the tan sandy clay loam was 61.5%. The brown soil was also spiked with methyl paraoxon, and a recovery of 69.5% was obtained.

The spiked soil samples were placed in a laboratory hood in an air current of about 8 km/hr (5 mph) and at a temperature of approximately 23°C (73° F). Recovery of the methyl parathion was made periodically. The loss of methyl parathion from the brown soil amounted to about 25% during the first day of exposure, and the residue remained essentially unchanged through the next 16 days. The loss of methyl parathion from the tan soil amounted to about 10% during the first day of exposure, and the residue remained essentially unchanged through the next 8 days.

At the end of 30 days, the loss from the tan soil amounted to 27%. The loss from the brown soil was not determined after the

16-day loss point. The chromatograms of the spiked samples of both soils, after 8 days of exposure, showed small peaks which have an elution time coincident with methyl paraoxon. This peak is about the same size after 16 days of exposure of the brown soil and, also, after 30 days of exposure of the tan soil.

The leveling off of the loss of methyl parathion may result from strong adsorption of the layer of molecules resting on the soil and the diffusion limited access of molecules from the recesses to the outside layer or surface where evaporation occurs. Perhaps, then, decomposition of the adsorbed molecules does not occur owing to the low water content of the soil and a consequent lack of microorganism action.

B. Visual Agents

Of the fluorescing substances named in this portion of the report, only chrysene appears to be carcinogenic. Steiner ⁽⁴⁾ has reported this substance to be a weak carcinogen. On the basis of this information, no further work was conducted with chrysene after the screening tests on glass plates.

1. From Glass Plates

The same technique used to apply the pesticides for disappearance determinations was used to apply fluorescing chemicals for disappearance tests. The same conditions of temperature and air velocity used in the pesticide work prevailed in the fluorescence studies. The visual agents were detected by 2 or more individuals observing the plates under short wave (254 nm) ultraviolet light. The objective of the

study was to develop agents which were to be detected by sensory means. All of the laboratory and field tests were conducted using observers (for both visual and odor agents) rather than using some type of chemical or instrumental method. Prospective fluorescent agents were first screened at an application level of $10 \mu\text{g}/\text{cm}^2$ (0.88 lb/acre) (see Table VI-1), but an additional two levels were added in an effort to develop information more quickly relating disappearance time and level of application. This work is summarized in Table VI-2. The information contained in these two tables and in Figures VI-1, VI-2, and VI-3 served as the basic data from which to proceed in matching disappearance times of pesticide and fluorescing substance.

In the course of the first experiments conducted in which Guthion was mixed with a fluorescing substance, it was observed that two out of six of the prospective visual agents were quenched by the Guthion (see Table VI-3). These observations led to the hope that a useful system employing the quenching phenomenon could be developed rather quickly, perhaps. As a result of this thinking, combinations of the three pesticides and four fluorescing substances were prepared and applied to glass plates. The results are shown in Table VI-4. The most consistent observation that was made is that the quenching effect observed at or near the start of a test never changes, i.e., the quenching effect does not diminish appreciably with time and the fluorescent property of the sensory agent does not return. The basis for this effect is not understood, but quenching as a mechanism for employing a

TABLE VI-1. DISAPPEARANCE OF FLUORESCING AGENTS

Fluorescing Agent	Visual Fluorescing Strength*						
	0 Hr	24 Hr	48 Hr	72 Hr	96 Hr	120 Hr	144 Hr
Carbazole	S	S	S	S	S	S	S
Triphenylmethane	W	very W	0	—	—	—	—
Trans-Stilbene	S	W-0	0	—	—	—	—
6-Methylcoumarin	W-0	0	—	—	—	—	—
Fluoranthene	S	S	W	W	W	0	—
Anthracene	S	S	S-M	W	W	W	W
2,5-Diphenyloxazole	S	S-M	W	W	W	0	—
Chrysene	S	S	S	S	S	S	S
Pyrene	S	S	S-M	S-M	S-M	W-0	0
o-Quaterphenyl	S	S	S	S	S-M	S-M	S-M

*S—strong; M—moderate; W—weak; 0—none.

Note: Fluorescing agent applied at rate of $10 \mu\text{g}/\text{cm}^2$.

TABLE VI-2. DISAPPEARANCE OF FLUORESCING AGENTS

Fluorescing Agent	Application Rate, $\mu\text{g}/\text{cm}^2$	Visual Fluorescing Strength at Hours*											
		0	16	24	40	48	64	72	88	96	112	120	
Chrysene	10	S	S	S	S	S	S	S	S	S	S	S	
Chrysene	1	S	S	S	S	S	S	S	S	S	S	S	
Chrysene	0.1	M	M	M	M	M	—	VW	VW	VW	VW	VW	
Carbazole	10	S	S	S	—	S†	S†	S†	S†	S†	S†	S†	
Carbazole	1	S	S	S	—	0	—	—	—	—	—	—	
Carbazole	0.1	M	M	M	—	0	—	—	—	—	—	—	
Fluoranthene	10	S	S	S	S†	S†	S†	0	—	—	—	—	
Fluoranthene	1	S	0	—	—	—	—	—	—	—	—	—	
Fluoranthene	0.1	VW	0	—	—	—	—	—	—	—	—	—	
Anthracene	10	S	S	S	S‡	S‡	S‡	0	—	—	—	—	
Anthracene	1	S	0	—	—	—	—	—	—	—	—	—	
Anthracene	0.1	VW	0	—	—	—	—	—	—	—	—	—	
Phenanthrene	10	S	0	—	—	—	—	—	—	—	—	—	
Phenanthrene	1	M	0	—	—	—	—	—	—	—	—	—	
Phenanthrene	0.1	VW	0	—	—	—	—	—	—	—	—	—	
p-Terphenyl	10	S	S	S	S	S	S	S	S	S	S	S	
p-Terphenyl	1	M	M	M	M	M	M	M	M	M	W	W	

*S—strong, M—moderate, W—weak, VW—very weak, 0—none.

†Spotty, some left after 600 hours

‡Spotty

TABLE VI-3. DISAPPEARANCE OF FLUORESCING AGENTS
MIXED WITH GUTHION

Fluorescing Agent	Visual Fluorescing Strength*				
	0 Hr	24 Hr	48 Hr	72 Hr	96 Hr
Carbazole (1/2)	S	S-M	S-M	M	M-W
Anthracene (1/2)	S	W	very W	0	—
Chrysene (1/2)	S	S	S	S	S
Pyrene (1/2)	q	q	q	q	q
Fluoranthene (1)	S	S-M	M	W	W
2,5-Diphenyloxazole (1)	q	q	q	q	q

*S—strong; M—moderate; W—weak; 0—none; q—quenched.

Note: Fluorescing agent applied at same concentration as insecticide (1) or at half the concentration of the insecticide (1/2) from solution containing both insecticide and fluorescing agent. Insecticide used was Guthion 2L sprayable emulsion. Insecticide application rate = $10 \mu\text{g}/\text{cm}^2$ (0.9 lb/acre) of active ingredient.

TABLE VI-4. QUENCHING STUDIES OF PESTICIDES IN TOLUENE

Fluorescer	Pesticide	Application Rate, $\mu\text{g}/\text{cm}^2$		Visual Appearance at Hours*				
		Fluorescer	Pesticide	0	16	24	40	64
p-Terphenyl	E-4 Methyl parathion	0.5	5	q	q	q	q	q
p-Terphenyl	Guthion	0.5	5	q	sl	sl	sl	sl
p-Terphenyl	Furadan	0.5	5	sl	sl	sl	sl	sl
Chrysene	E-4 Methyl parathion	0.5	5	sl	M	M	M	M
Chrysene	Guthion	0.5	5	q	sl	sl	sl	sl
Chrysene	Furadan	0.5	5	S	S	S	S	S
Carbazole	E-4 Methyl parathion	0.5	5	q	q	q	q	q
Carbazole	E-4 Methyl parathion	5	5	S	S	S	S	S
Fluoranthene	E-4 Methyl parathion	10	10	q†	S	S	—	—

*q—quenched, sl—slight, M—moderate, S—strong.

(†) Quenched initially but strongly fluorescent in spots within 1 hr and virtually continuously covered with fluorescence within 16 hrs.

fluorescing agent does not appear promising, based on limited compounds studied.

The possibility of matching disappearance times of pesticide and fluorescer appeared to be greatest for a system involving methyl parathion. For this reason, a number of tests were conducted with methyl parathion and three promising fluorescing substances in combination. The observations made in these tests are summarized in Table VI-5. The reproducibility is certainly influenced by the uniformity of the coating obtained, the texture of the frosted glass plate surface, and by the size of the crystals formed as the toluene evaporates from the solution applied to the plate. Also, the presence of methyl parathion on the same plate as the fluorescer quenches fluoranthene and, in the case of anthracene and phenanthrene, reduces the length of time of fluorescence to some extent. This last effect can be offset by adding more fluorescing substance to the mixture than is required when the fluorescing substance alone is applied. The three fluorescing substances were judged useful at the following application rates: anthracene, 2-3 $\mu\text{g}/\text{cm}^2$; fluoranthene, 2-4 $\mu\text{g}/\text{cm}^2$; and phenanthrene, 45-50 $\mu\text{g}/\text{cm}^2$. Fluoranthene apparently cannot be combined with methyl parathion because of the quenching which occurs at these low levels.

In addition to the above three fluorescing substances, trans-stilbene was found to fluoresce for about 24 hours when applied at a coverage of 10 $\mu\text{g}/\text{cm}^2$. This was of interest inasmuch as it also very nearly matched the disappearance of methyl parathion. However, this

TABLE VI-5. DISAPPEARANCE OF FLUORESCING AGENTS WITH AND WITHOUT
SIMULTANEOUS APPLICATION OF METHYL PARATHION E-4

Fluorescing Agent	Application Rate, $\mu\text{g}/\text{cm}^2$	Application Rate of Methyl Parathion E-4, $\mu\text{g}/\text{cm}^2$	Visual Fluorescing Strength at Hours*							
			0	16	20	24	30	40	44	48
Phenanthrene	20.0	0	S	0	—	—	—	—	—	—
Phenanthrene	20.0	5	S	0	—	—	—	—	—	—
Phenanthrene	40.0	0	S	M	M-W	barely visible	—	—	—	—
Phenanthrene	40.0	5	S	M	W	0	—	—	—	—
Phenanthrene	40.0	0	S	W	W	0	—	—	—	—
Phenanthrene	40.0	5	S	0	—	—	—	—	—	—
Phenanthrene	45.0	0	S	S	S	0	—	—	—	—
Phenanthrene	45.0	5	S-M	0	—	—	—	—	—	—
Phenanthrene	50.0	0	S	—	—	S	W	—	0	—
Phenanthrene	50.0	5	S	—	—	W	0	—	0	—
Fluoranthene	2.5	0	S	—	W	barely visible	—	—	—	—
Fluoranthene	2.5	5	q	—	0	0	—	—	—	—
Fluoranthene	3.0	0	S	—	W	0	—	—	—	—
Fluoranthene	5.0	0	S	S	—	M	—	W	0	—
Fluoranthene	5.0	5	q	barely visible	—	barely visible	—	0	—	—
Anthracene	5.0	0	S	S	—	M	—	W	W	0
Anthracene	5.0	5	S	S	—	M	—	W	W	0
Anthracene	3.0	0	S	—	S	S	M	—	0	—
Anthracene	3.0	5	M	—	W	W	W	—	0	—
Anthracene	2.0	0	S	—	0	—	—	—	—	—
Anthracene	2.0	5	S	—	0	—	—	—	—	—

*S—strong, M—moderate, W—weak, 0—none.

substance was reported by a manufacturer to be sensitive to UV radiation, and preliminary tests in which exposure was made outdoors indicated a much quicker loss of fluorescence than was observed indoors. This is probably due to isomerization of the "trans" form to the inactive "cis" form, brought about by the increased intensity of UV radiation received in the outdoors exposure. It might be possible to increase the residence time of the trans form to the useful range by increasing the amount applied per unit area.

2. From Soil

Soil samples, identical with those in VI, A,2, were sprayed similarly with aqueous emulsions of anthracene. Compared to the amounts required for foliage, 10 to 15 times as much anthracene was required to give a satisfactory visual response, initially. This may be the result of molecules penetrating the interstices of the soil where they can neither receive nor emit light. However, the fluorescence lasted less than 3 days. Amounts up to 50 times that which was effective on foliage gave fluorescence for only 4 days. A similar observation was made when carbazole, a long-lasting fluorescing substance in the laboratory, was applied to the soil samples; the highest concentration provided a strong to finally weak fluorescence for a 7-day period, and weak fluorescence continued for an additional 7-day period.

The use of fluorescing agents on soil does not appear promising because of the large quantities of fluorescing agents required to give a satisfactory signal for significant periods of time.

C. Odor Agents

1. From Glass Plates and Polymer Films

Various odorous substances (see Table VI-6) were applied to the frosted glass plates by the same technique mentioned earlier to deposit pesticides and/or fluorescent substances. The agents were detected by 2 or more individuals sniffing the plates. The odorants were applied at a coverage of $10 \mu\text{g}/\text{cm}^2$ (0.88 lb/acre) and were exposed to the same temperature and air velocity given earlier in this report. None of the odorants tested in this manner gave much of a residual odor after 24 hours of exposure to the test conditions.

One of the ways to increase residence times of the candidate odorants is to add more of the substance per unit of area. By doubling the amount added to $20 \mu\text{g}/\text{cm}^2$ (1.76 lb/acre), the residence times of vanillin and several musks, as examples, were increased to a 1- to 3-day period.

Another approach to extending the residence time of a substance is to mix it with a fixative. A variety of substances were mixed with equal parts of mineral oil or Galaxolide (a synthetic musk by International Flavors & Fragrances) without any substantial benefit being realized, however.

A third approach followed to increase residence times was to mix odorants and polymers in solution and then cast the solution in thin films.

TABLE VI-6. CANDIDATE ODOR AGENTS SUBJECTED
TO SCREENING TESTS

Benzyl cinnamate	Pentadecanolide
Benzyl salicylate	Anisyl acetate
beta-Phenylethylphenylacetate	Terpineol
Coumarin	Laurine
Ethyl vanillin	Jasmonyl
2-Methoxynapthalene	Methyl eugenol
Santalol	Geraniol
Methyl anthranilate	Anisyl alcohol
Ethyl anthranilate	Acetanisole
Ethyl salicylate	Galaxolide (musk)
Eugenol-- USP--prime	6-Methylcoumarin
Sandela	gamma-Dodecalactone
Musk ketone	Skatole
Musk ambrette	alpha-choroacetophenone
Musk xylol	alpha-bromoacetophenone
Heptaldehyde	Dimethyl sulfide
2-Phenylethanol	Several proprietary perfume oils and odor masking agents.

Some difficulties apparent in the development of an odorant sensory system are these:

- (1) The odor agents investigated thus far tend to "tail off" in intensity without giving a sharp end point.
- (2) The known compounds of highest boiling points and lowest odor thresholds tend to be mildly odoriferous (e.g., the natural and synthetic musks) in character rather than strongly odoriferous (e.g. hydrogen sulfide and the mercaptans).
- (3) Strongly odoriferous compounds, when applied by themselves, do not have adequate residence times.
- (4) Wide variation in the individual human response.

The best approach appeared to be a compromise in which the desired high boiling point characteristic is traded off in favor of increased odor intensity. Some odorants which fit this category and were investigated are: menthol, eugenol, heptaldehyde, dimethyl disulfide, skatole, alpha-chloroacetophenone (lachrymator), alpha-bromoacetophenone (lachrymator), 2-phenylethanol, and some proprietary perfume oil products. In order to use such substances, which are quite volatile relative to the pesticides, especially Guthion and carbofuran, the evaporation must be retarded in some manner such as may be achieved through incorporation into polymer films (see Table VI-7), or by some other device, which restricts the treated area being exposed to evaporation. Mixing with polymers was the route followed with the

TABLE VI-7. ODOR IN POLYMERS

Formulation: 13.6% Ethocel (10 cps), 9.1% odorant, 77.3% Toluene/isopropyl alcohol 70/30.

Odor	Blade Setting, mils	Odor Strength at Hours*													
		0	16	24	40	48	64	72	88	96	112	120	160	184	208
Floral Bouquet GD-5280 (Givaudan)	10	S	S	S	S	S	S	S	S	S	S	S	S	S	S
	2	S	S	S	S	S	S	S	S	S	S	S	S	—	—
Eugenol USP Prime (Givaudan)	10	S	S	S	S	S	S	S	S	S	S	S	S	S	S
	2	S	S	S	S	S	S	S	S	S	S	S	S	—	—
	1	S	VW	—	—	—	—	—	—	—	—	—	—	—	—
Violet Perfume Oil GF-2417 (Givaudan)	10	S	S	S	S	S	S	S	S	—	—	M	M	M	M
	2	S	S	S	—	M	M	M	M	M	M	M	M	—	—
Odamask C-1245 (S.B. Penick & Co.)	10	S	S	S	S	S	S	S	S	S	S	S	S	M	M
	2	S	S	S	S	S	S	S	S	—	M	M	M	—	—
	1	S	S	S	S	S	S	S	S	S	S	S	—	—	—
Alpha-chloroaceto- phenone†	1.5	S	VW	0											
Alpha-bromoaceto- phenone†	1.5	S	W	0											
Eugenol‡	2.0	S	S	S	S	S	S	S	S						

*S—strong, M—moderate, W—weak, VW—very weak.

†Contains 0.9% odorant.

‡Contains 4.5% odorant.

investigations involving Guthion and carbofuran. With methyl parathion, adjusting the quantities of odorant applied to glass or paper strips or incorporated into the spray formulation provided adequate variation in the residence time.

2. From Soil

Soil samples as identified earlier in this report were also sprayed with skatole emulsions. The quantity of skatole required to evoke a satisfactory small response after 3 days of exposure is at least two times that required for foliage. Three and 6 times the amount required for foliage were found to provide an odor for 10 days and 21 days, respectively.

The use of skatole on soil does not appear promising because of the large quantity of the substance required to evoke a satisfactory response for a significant period of time.

VII. OUTDOOR DISAPPEARANCE TESTS

When the laboratory disappearance tests were complete, disappearance tests were conducted outdoors using a small number of plants. These tests were conducted to determine if the laboratory matched sensory agents and pesticides would perform satisfactorily in a less controlled environment and to investigate possible problems which might be encountered in a limited field test planned later in the program.

The plants used were *Euonymus japonica* (also called *Aucuba japonica*, gold spot euonymus, and gold dust plant). This variety of plant was chosen because it is readily available at the local nurseries, is hardy, and has large leaves of a shape and texture that permit easy sampling. The plants were sprayed at recommended coverage rates given by the pesticide supplier for general use.

A. Methyl Parathion

The plants were sprayed outdoors with a compressed air sprayer and were kept outdoors for periods of time ranging from 4 to 7 hours per day. For the rest of the 24-hour period, the plants were placed in a greenhouse to prevent damage by freezing during the night. Two tests were conducted, each being of 3 days' duration, each using 3 plants. Temperature extremes during the outside exposure periods ranged from 4° to 24°C (40° to 76°F). Every day, except one, was sunny or

partly cloudy. The relative humidity was generally low. Winds varied from calm to 24 kph (15 mph). The greenhouse, where the plants were kept most of the time, was maintained within the temperature range of 25° to 29°C (78° to 85°F), with high relative humidity.

The methyl parathion formulation applied was procured from the Thompson-Hayward Company and is labeled Methyl Parathion E-4 (four pounds per gallon). The directions on the label recommend use from one-half to one pint per acre (one-quarter to one-half pound per acre) in most applications. This is within the typical use range given by Melnikov.⁽⁶⁾ The calculated deposit of methyl parathion applied would be $5.0 \mu\text{g}/\text{cm}^2$, assuming uniform coverage (or 0.44 lb/acre). However, the values found under our spraying conditions varied considerably from the calculated value.

The sensory agents were incorporated into the spray, by dissolving them in the E-4 formulation with additional solvent (toluene) as required and additional wetting agent (Triton X-45) as required to produce a satisfactory emulsion for spraying. Anthracene was applied at $3 \mu\text{g}/\text{cm}^2$ (0.26 lb/acre) and phenanthrene at $50 \mu\text{g}/\text{cm}^2$ (4.4 lb/acre). Skatole was applied at $15 \mu\text{g}/\text{cm}^2$ (1.32 lb/acre in Test 1 and $10 \mu\text{g}/\text{cm}^2$ (0.88 lb/acre) in Test 2.

The plants were sprayed to run off, and pools of liquid were dislodged from the leaves by tilting the plants from the vertical position and shaking gently. When the spray had dried, about 30 minutes later, the first plant leaf sample was obtained, and this time was designated as

zero time. At predesignated subsequent time intervals, leaf samples were taken.

Leaf samples were analyzed for surface residues of methyl parathion and visual agent (anthracene or phenanthrene) by rinsing the leaves thoroughly with dichloromethane, concentrating the rinse under nitrogen flow, and injecting an aliquot into a gas chromatograph. Phenanthrene and anthracene chromatograph well under the same conditions used for methyl parathion (given earlier in this report). Retention times at 160° are 5.8 min. for phenanthrene and 6.1 min. for anthracene. The area of the leaf sample was determined by tracing the outline of the leaf on paper, then measuring the outlined area with a planimeter. The presence of the visual agent on the plant was also followed qualitatively by observing the plant, at sampling times, under ultraviolet light in a darkened room. The presence of the odor agent was determined by the sense of smell, using 2 to 7 human subjects.

Test 1 involved the E-4 methyl parathion formulation with incorporated phenanthrene or skatole applied as sprays. The disappearance times of methyl parathion and phenanthrene matched very well. The residual odor of skatole was judged to be too strong when the methyl parathion was essentially gone. The results of Test 1 are given in Table VII-1.

In test 2, the E-4 methyl parathion formulation with incorporated anthracene, or two-thirds of the amount of skatole used in Test 1, were applied as sprays. The disappearance times of methyl parathion and

TABLE VII-1. RESULTS OF TEST 1

Time Elapsed, hr	Plant 1		Plant 2		Plant 3	
	$\mu\text{g}/\text{cm}^2$ of Leaf		$\mu\text{g}/\text{cm}^2$ of Leaf		$\mu\text{g}/\text{cm}^2$ of Leaf	
	Methyl Parathion		Methyl Parathion	Phenanthrene	Methyl Parathion	Odor from Skatole on Plant
0	7.7		9.4	76.0	17.9	strong
4	8.4		5.1	67.0	10.9	strong
24	6.9		3.0	34.0	5.6	strong
30	9.1		1.6	17.5	0.9	moderate
48	1.1		0.9	9.3	2.9	moderate
72	1.4		0.9	19.0	1.0	moderate

anthracene matched very well, and the matching of methyl parathion with skatole was much better than in Test 1 and was considered satisfactory.

Also in Test 2, anthracene, phenanthrene, skatole, eugenol, and α -bromoacetophenone (a lachrymator) were applied to glass plates which were exposed side by side with the plants. The eugenol and α -bromoacetophenone were applied to the plates in solutions of Ethocel (Dow ethylcellulose - 48 to 49.5% ethoxyl content - 10 cps.), using doctor blade settings of 1 and/or 2 mils. The Ethocel was used to reduce the volatility of these two odorants. The other agents applied to the glass plates were in solution in toluene. Fairly good correlation between the disappearance of the agents on the plates, as determined by human response, and the disappearance of methyl parathion from the plant, as determined analytically, was attained.

The results of Test 2 are given in Table VII-2a and 2b.

Figure VII-1 is the disappearance curve of methyl parathion from the 6 test plants. Each point is based on the average of the amount of methyl parathion found on one leaf from each of the plants at the times indicated. The percentage of the initial dosage remaining at 72 hours is 4.8. Although phenanthrene and anthracene were also determined by gas chromatography, only one leaf from the sprayed plant was analyzed at each time point, which was insufficient to give data smooth enough to plot well owing to the lack of uniformity of the spray application. The comments in Tables VII-1 and VII-2a and VII-2b give a better depiction of the eye response to the fluorescing plants.

TABLE VII-2a. RESULTS WITH METHYL PARATHION AND SENSORY
AGENTS ON PLANTS IN TEST 2

Time Elapsed, hr	Plant 1		Plant 2		Plant 3	
	$\mu\text{g}/\text{cm}^2$ of Leaf Methyl Parathion	$\mu\text{g}/\text{cm}^2$ of Leaf Methyl Parathion	Anthracene	Fluorescence on Plant (visual obser.)	$\mu\text{g}/\text{cm}^2$ of Leaf Methyl Parathion	Odor from Skatole on Plant (subject response)
0	7.6	14.8	12.5	strong	30.8	strong
4	4.7	5.2	5.1	strong	22.5	strong
24	2.4	3.6	4.2	strong-moderate	9.2	strong-moderate
30	1.1	1.6	1.5	isolated spots strong to weak	1.2	weak-none
48	0.9	3.0	2.8	weak isolated spots-95% gone	0.5	—
72	0.2	0.5	0.4	—		

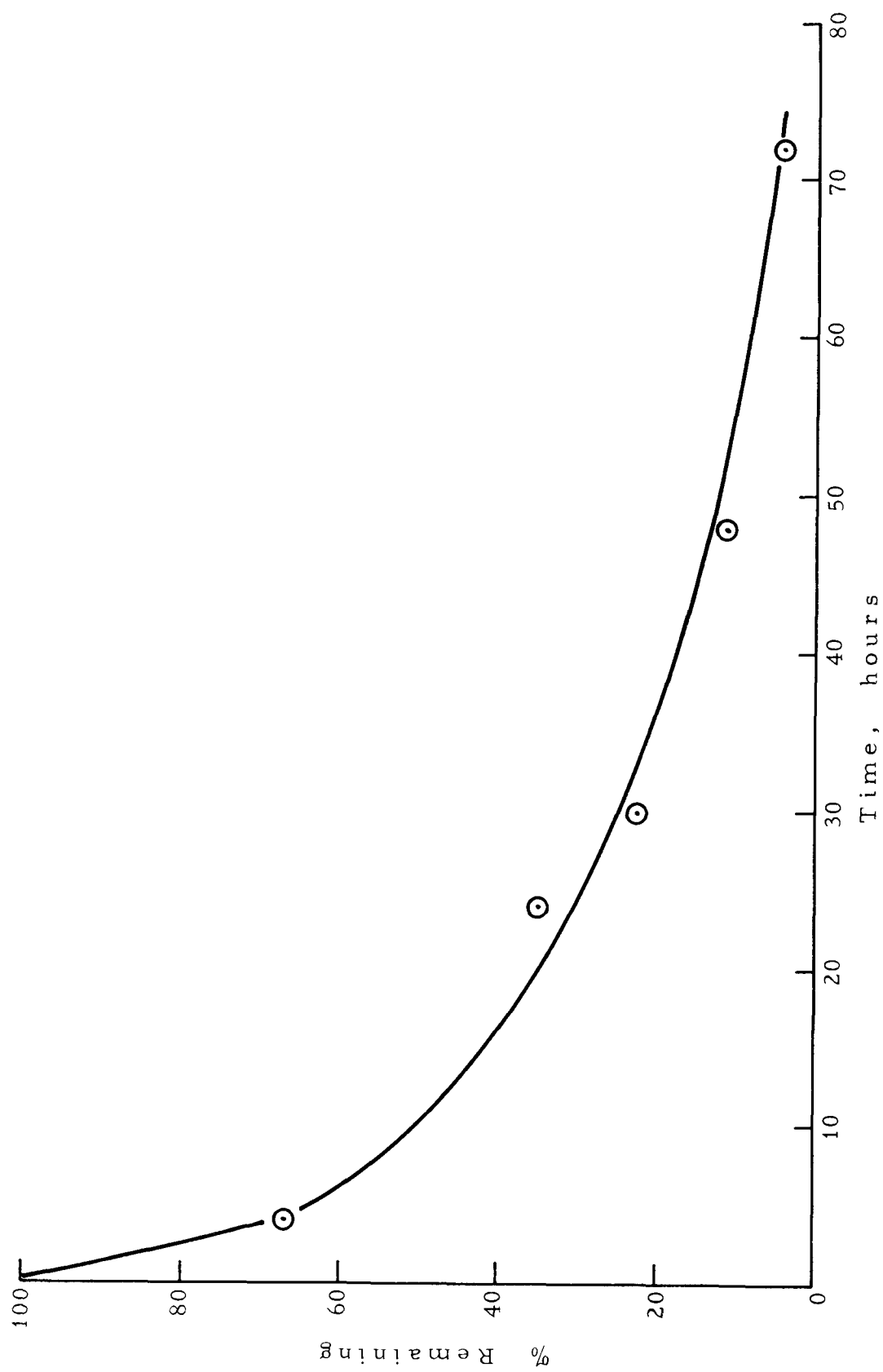


Figure VII-1. The Disappearance of Methyl Parathion from Euonymus Plants

B. Azinphosmethyl (Guthion 2L)

The product used was Guthion 2L Emulsifiable Insecticide from Chemagro Division, Baychem Corporation. Two plants were sprayed as prescribed by the supplier for a coverage of $10 \mu\text{g}/\text{cm}^2$ (0.88 lb/acre) and then shaken free of excess spray as in the methyl parathion tests. The plants were kept outside continuously after spraying, since the possibility of damage by freezing at night was slight. At night when rain threatened, the plants were placed under a shelter which consisted of a protective roof without sides.

Thus, the plants were sheltered from direct rainfall but exposed to other atmospheric factors. The effect of a large amount of rainfall directly on the plants was unknown, but it was suspected that it would remove much of the Guthion. By shielding the plants, the disappearance time obtained should be at a maximum with respect to the prevailing other atmospheric factors. The plants were wetted often with condensed moisture during foggy weather and when the dew point was reached. During the 55-day test period, the following general statements about the weather apply:

- . Temperature extremes were 0.5° (33°F) and 32°C (90°F).
- . Wind speeds were most often 16-40 kph (10-25 mph) with occasionally gusty periods where the wind speed reached as high as 75 kph (45 mph).
- . The relative humidity was usually moderate; however, extremes were experienced.
- . Cloudy skies prevailed more than 50% of the time.

Leaf samples were analyzed for Guthion using the same basic procedure described in the methyl parathion tests, except that rectangular leaf samples were cut from the whole leaves with scissors. This was done so that the area of the sample could be determined by measurements with a ruler rather than a planimeter.

The amounts of Guthion found on the leaves of the plants is as follows for the 55 days of the test:

<u>Elapsed time, days</u>	<u>Guthion found, avg of 2 detns., $\mu\text{g}/\text{cm}^2$</u>
0	13.1
1	13.9
5	11.2
12	8.3
19	7.0
28	5.4
35	4.0
55	4.0

These data are presented in graphical form in Figure VII-2, with $13.5 \mu\text{g}/\text{cm}^2$ taken as the zero time amount. This value is the average of the values for day 0 and day 1. Between 25 and 30% is found to remain at the end of the test period.

At the same time that the plants were sprayed, glass plates on which Ethocel films containing the fluroescing agents anthracene and phenanthrene or the odor agent skatole had been laid down were exposed side by side with the plants.

During the first few days of the test, fog and frequent dew point conditions resulted in condensed water being deposited on the plants and the plates, despite the use of the sheltering roof mentioned earlier.

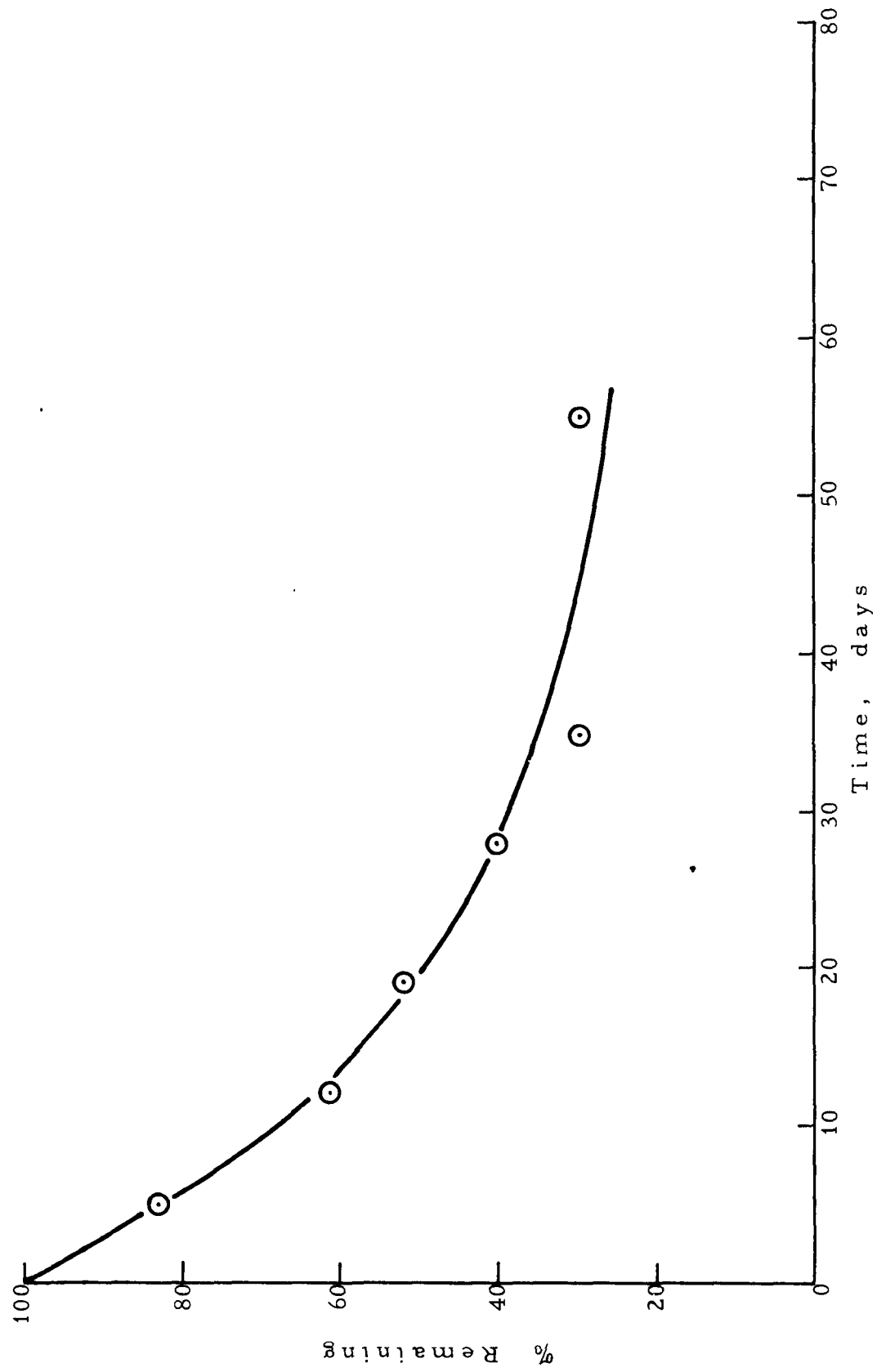


Figure VII-2. The Disappearance of Guthion from Euonymus Plants

Skatole, being water-soluble, was leached from the plastic films so that no odor remained after 5 days. The fluorescing agents, being water insoluble, were not subject to leaching and continued to fluoresce. However, all films, containing skatole or fluorescing agent, were loosened from the glass plates, and large pieces of them were blown away by the wind. This means of exposing the sensory agents for prolonged periods to the outside environment was, at this point, obviously unacceptable.

A new means of exposing the sensory agents was developed. This consisted of dipping strips of filter paper and strips of glass fiber filter medium in polymer solutions of fluorescing agents or odor agents, dried to a tack-free state, then sprayed with a water repellent before exposure alongside the plants under test. The strips were suspended from wooden rods held by clamps to an ordinary laboratory support stand. Anthracene and phenanthrene were again the fluorescing agents tested. Carbazole, which had been found to be a promising long-lasting fluorescing agent in the laboratory tests conducted earlier in the program, had since been found to be unsuited for outdoor use.

β -Phenylethylphenylacetate and 2-phenylethanol were substituted for the odor agent skatole. This was done because it had become increasingly evident that skatole was not suitable for prolonged exposure outdoors because of changes occurring in the basic odor or premature loss of odor entirely, whereas the other two agents were apparently superior in these respects. In addition to the Ethocel polymer, the copolymer

Vynlite VYHH (Union Carbide copolymer of 86% vinyl chloride and 14% vinyl acetate) was put under test. The visual and odor agents were dissolved in solutions of the two polymeric substances and applied to the paper and glass substrates as indicated above. In all, 24 paper strips and 24 glass strips were tested, representing the 4 test substances at 3 different amounts on the 2 substrates.

Within 5 to 7 days, the anthracene treated strips were quite yellow (especially the glass fiber ones) and fluoresced with a yellow color under a UV lamp rather than the original purple-blue color. Phenanthrene exhibited a similar but not identical change after about two weeks of exposure. After 3 weeks of exposure, it was necessary to prepare fresh strips to use as controls to determine whether or not the exposed strips still fluoresced. It was found that the strips still fluoresced at this point but with colors different from the original colors as well as with lessened intensities. The changes in color and intensity of fluorescence made the state of the strips difficult to assess, even with the prepared control strips at hand, and the reading of the strips is complicated to some extent by the inherent fluorescence of the substrate materials. The test strips were exposed for a total of 40 days, but there were essentially no changes observed after the 3-week point.

The odor strips retained their characteristic odors through the first 3 weeks. At this point, the odor of the strips with the least amount of odorant became undetectable to about half of the persons sniffing them. The other strips, with the greater amounts, were

regarded to be faint to strong, depending upon the individual sniffer. The principal problem with this approach is that the end point is not sharply defined. These strips were kept on test for 40 days also, with the intensity of the odors weakening slowly. Most of the strips containing the largest amounts of odorants were weakly odorous at the end of the 40-day period.

C. Carbofuran (Furadan 4 Flowable)

The product used was Furadan 4 Flowable Insecticide manufactured by the Agri-Chem Division, FMC Corporation. Two plants were sprayed to the dripping-wet state; then the excess was shaken free as in the methyl parathion test. The intended coverage was $10 \mu\text{g}/\text{cm}^2$ (0.88 lb/acre); however, the actual amount found initially was much higher for reasons unknown. It should be appreciated that large variations are often encountered in amount deposited per unit area by spraying. These plants were exposed alongside of the plants sprayed with Guthion 2L and the sensory agents described above. Therefore, the comments made about the weather and the sensory agents apply also to the test with Furadan 4 Flowable.

The amounts of Furadan found on the leaves of the plants is as follows for the 55-day test:

<u>Elapsed time, days</u>	<u>Furadan found, avg. of 2 detns., $\mu\text{g}/\text{cm}^2$</u>
0	28.4
1	24.0
5	19.0
12	12.6
19	7.5
28	4.4
35	3.2
55	0.9

These data are presented in graphical form in Figure VII-3.

Between 3 and 4% is found to remain at the end of the test period.

D. Limited Field Test

A limited field test was conducted on a cotton farm near Batesville, Texas. The cotton plants, in the early blooming stage, were sprayed by airplane with methyl parathion at an intended dosage of $17 \mu\text{g}/\text{cm}^2$ (1.5 lb per acre) and Galecron at an intended dosage of $0.95 \mu\text{g}/\text{cm}^2$ (0.083 lb per acre). The main purpose of the test was to follow the disappearances of the methyl parathion from the cotton leaves and of visual and odor agents placed alongside the field. Leaf samples were taken at 20 min., 2, 4, 8, 22.5, and 48 hours after application. Observations of the sensory agents were made at the 4, 8, 22.5 and 48-hour points.

Spraying was completed at approximately 8 A.M. At that time, the wind was blowing at an estimated 30-40 kph (18.5 - 25 mph). During that day and the remainder of the test period, the wind blew steadily at that velocity, or slightly higher, with frequent gusts to 56 kph (35 mph),

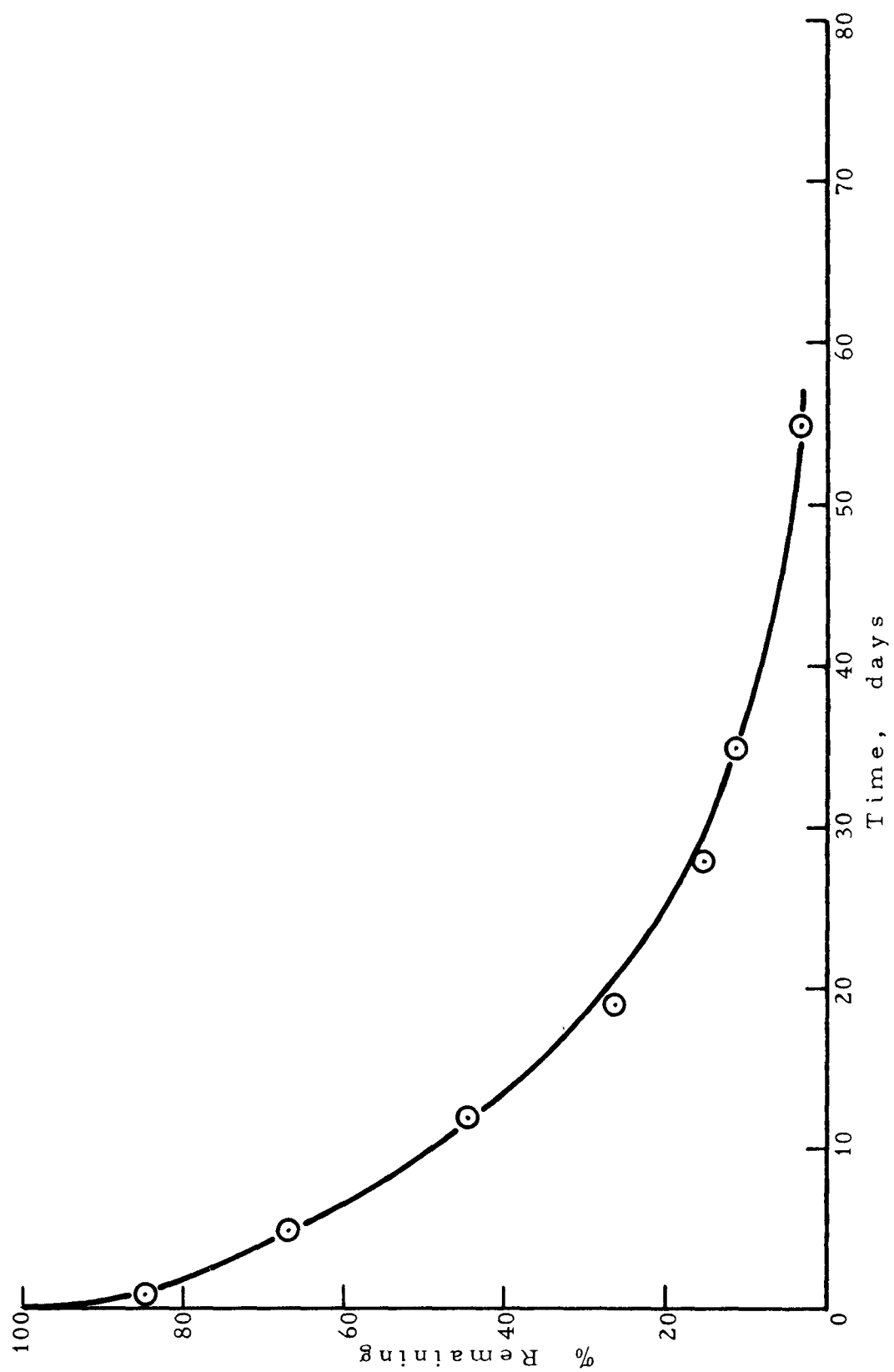


Figure VII-2. The Disappearance of Furadan from Euonymus Plants

except for the periods near dawn when the velocity dropped to the 8 to 16 kph (5-10 mph) range. The days were sunny with only scattered light clouds. The temperature span during the test period was from 25.6° to 34.4°C (78° to 94°F). The relative humidity ranged from high in the mornings to moderately low in the afternoons. No rainfall occurred during the test period.

Prior to the spraying, a small table was erected approximately 150 meters into the field so that the table top was essentially at cotton plant height. Twelve glass plates, 5 x 5 cm square, were fastened to the table top by placing them on strips of tape having adhesive on both sides. This was done so that the turbulent air streams from the spraying airplane could not dislodge the plates from the table top. The purpose of the plates was to collect spray for analysis and comparison with leaf samples and the sensory agents on glass plates. After the first samples were taken, the table top was removed from the supporting legs and kept in the shade of the cotton plants. It had been found in earlier preparatory tests that exposure in the shade more closely matched the disappearance of a substance from a glass plate with the disappearance of that same substance from a plant in the sun.

At the time that the table with the glass plates was set up, 10 cotton plants surrounding the table (none closer than 3 meters, none farther away than 20 meters) were tagged with white cloth strips. This was done so that sample leaves would always be taken from the tagged plants or the ones on either side of them.

After spraying was completed, sampling consisted of removal of 2 of the glass plates and one canopy leaf from the windward side of each of the designated plants (or the ones on either side of them). The upper sides (exposed to the aerial spraying) of the plates were washed thoroughly with a small stream of dichloromethane (DCM), and the washings were collected in a single glass bottle for transport to the laboratory for analysis. The leaves were placed on top of each other, making a stack 10-high, on a polyethylene-covered board. A No. 15 laboratory cork borer was used to cut through the leaves, giving a circular sample of each leaf of about 2 cm in diameter. This sample was ejected from the borer into a glass beaker, and the process was repeated 2 times, with each set of leaf samples being put into a different beaker. Each set of 10 circles was washed 3 times with 15 ml of DCM, using a small stainless steel spatula to make sure that agglomerates of leaf circles were broken up and each circle contacted by the solvent. The washings from each set of 10 circles were bottled in glass bottles and transported to the laboratory for analysis.

At the laboratory, each bottle of DCM washings was reduced to the standard volume of 3 ml under a stream of nitrogen without heating. Two μ l of the concentrate were injected into a gas chromatograph (GC) equipped with a flame ionization detector and a column consisting of a 20-inch x 1/8-inch SS tube packed with 10% UC-W98 on Chromosorb WAW-DMCS (80-100 mesh). The GC oven was kept at 160°C. Other conditions were carrier gas flow, 30 ml/min.; H₂ flow, 30 ml/min.;

O₂ flow, 240 ml/min.; injection port temperature, 250°C; and detector temperature, 250°C. The concentration of methyl parathion in each sample was calculated from peak height measurements on the chromatograms of the samples and a standard solution of methyl parathion. This value was used to determine the amount of methyl parathion present on a per-square-centimeter basis of upper leaf surface or upper plate surface. Samples of leaves taken before spraying showed no detectable interference on the chromatograms at the points of interest.

Results of analyses are shown in Table VII-3 and Figure VII-4. The 3 values for leaf samples at each sampling time were averaged before the disappearance curves in Figure VII-4 were constructed. Methyl parathion disappeared more rapidly from the cotton leaves than from the glass plates. At 24 and 48 hours, approximately 3% and 1%, respectively, remained on the leaves, while about 14% and 4% remained on the plates at those time points.

Just before the spraying commenced, 2 visual agents and 3 odor agents were put under test in a shaded area beside the cotton field. The visual agents were anthracene and phenanthrene. The odor agents were skatole, 2-phenylethanol, and β -phenylethylphenylacetate. The visual agents were applied to frosted glass plates only. The odorant skatole was applied to a frosted glass plate and to paper strips, also. The other two odorants were applied only to paper strips. Table VII-4 gives the amounts or concentrations applied and the observations made during the test by the two men conducting the test. Attempts were made

TABLE VII-3. METHYL PARATHION ANALYTICAL DATA FROM FIELD TEST (Cotton Plants)

Time After Application	Sample	$\mu\text{g}/\text{cm}^2$ *	Percent Remaining†
20 min	Plate No. 1	8.50	97.7
	Leaf 1a	7.22	
	1b	12.74	
	1c	6.02	
	Leaf Avg.	8.66	97.3
2 hr	Plate No. 2	7.93	91.1
	Leaf 2a	7.93	
	2b	5.72	
	2c	6.72	
	Leaf Avg.	6.79	76.3
4 hr	Plate No. 3	3.97	45.6
	Leaf 3a	5.52	
	3b	4.01	
	3c	5.62	
	Leaf Avg.	5.05	56.7
8 hr	Plate No. 4	2.73	31.4
	Leaf 4a	1.77	
	4b	2.38	
	4c	1.38	
	Leaf Avg.	1.84	20.7
22.5 hr	Plate No. 5	1.20	13.8
	Leaf 5a	0.33	
	5b	0.14	
	5c	0.29	
	Leaf Avg.	0.25	2.8
48 hr	Plate No. 6	0.36	4.1
	Leaf 6a	0.05	
	6b	0.10	
	6c	0.10	
	Leaf Avg.	0.08	0.9

*Based on area of one side of leaf sample only.

†Based on zero time amounts (obtained by extrapolation—see Figure VII-4) of $8.70 \mu\text{g}/\text{cm}^2$ for plates and $8.90 \mu\text{g}/\text{cm}^2$ for leaves.

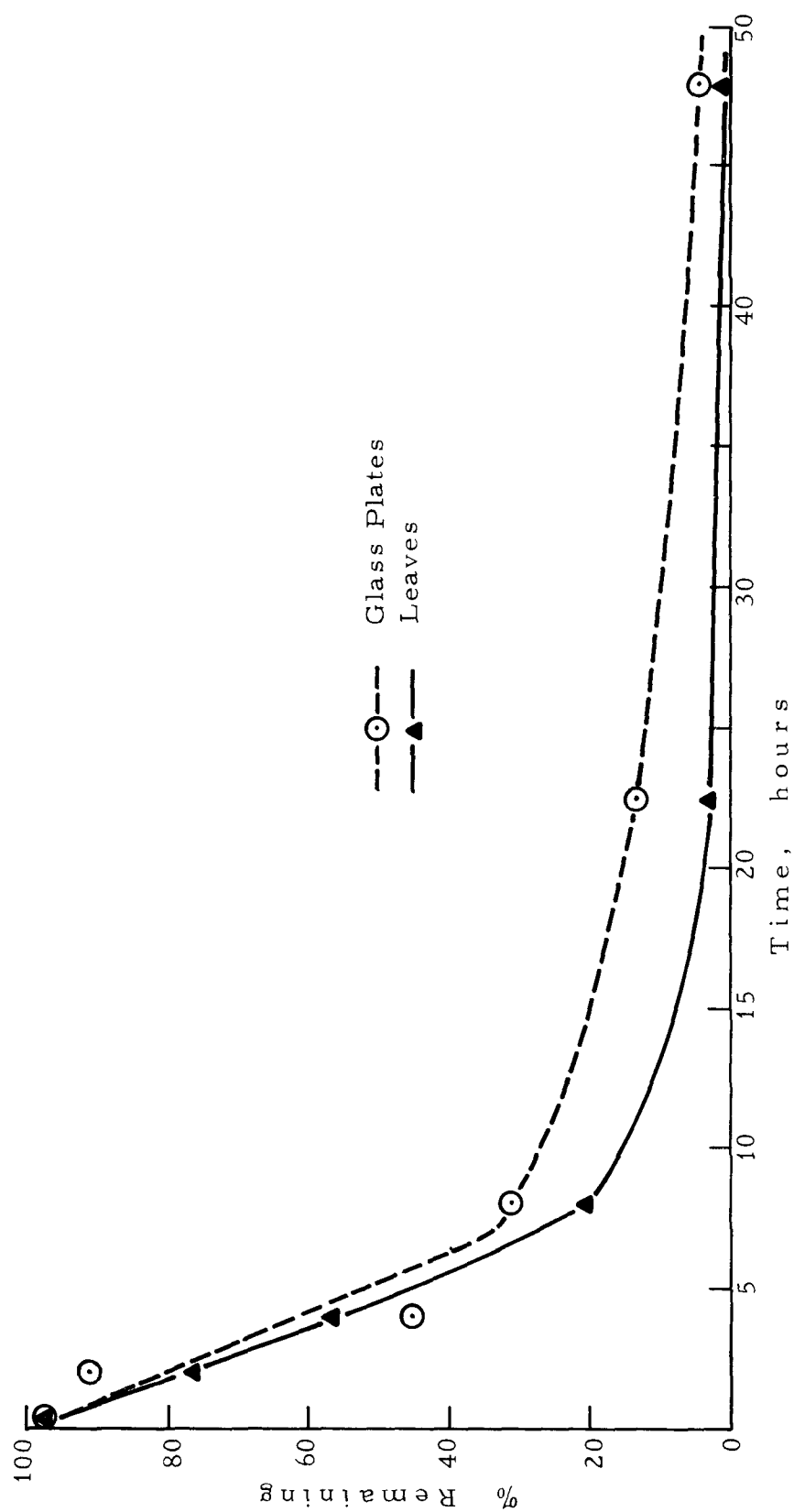


Figure VII-4. The Disappearance of Methyl Parathion from Cotton Leaves and Glass Plates

TABLE VII-4. OBSERVATIONS MADE ON SENSORY ITEMS
DURING BATESVILLE FIELD TEST

Conc, $\mu\text{g}/\text{cm}^2$	Time, hr				
	0	4	8	22.5	48
<i>Anthracene</i>					
3	S	W	E		
5	S	S	W	E	
7.5	S	S	S	I ₁	E
10	S	S	S	I ₂	E
<i>Phenanthrene</i>					
40	S	W	E		
50	S	W	E		
60	S	W	E		
<i>Skatole (on plate)</i>					
40	S	S	S/W	W/E	E

Conc, g/l	Time, hr				
	0	4	8	22.5	48
<i>Skatole (on paper)</i>					
6	S	S/W	W/E	E	
9	S	S	S/W	E	
12	S	S	S	W/E	E
24	S	S	S	M	VW
<i>2-Phenylethanol</i>					
1	S	S	S/W	M	VW
3	S	S	S	M	M
6	S	S	S	M	M
9	S	S	S	M	M
<i>β-Phenylethyl-Phenylacetate</i>					
1	S	S	W/E	E	
3	S		(paper strip lost)		
6	S	S	S	M	M
9	S	S	S	M	M

S — strong

M — moderate

W — weak

VW — very weak

E — extinct

I₁ — irregular pattern, 90% of material gone

I₂ — irregular pattern, 75% of material gone

/ — gives individual responses when disagreement of the observers occurred

to procure disinterested observers from the population in the vicinity, but the remoteness of the field made such arrangements unworkable. As a consequence, the opinions of 5 field workers on the sensory items were collected at a different site.

The observations made by the two men conducting the test are given in Table VII-4 in terms of whether or not a definite visual or odor response was noted and the intensity of that response or signal. It may be noted that disagreement occurred rather frequently between the two men with regard to the odor evaluations. This disagreement is noted in the table by slash lines, with each half showing an individual response. Whatever time for safe reentry is chosen between the 8-hr and 48-hr points in Figure VII-4, the time is matched or bracketed by the anthracene quantities used. The phenanthrene quantities employed are useful only at the 8-hr point. The skatole on the plate matches the 22.5-hr point fairly well. The concentrations of skatole on paper cover the time span with about the same options as the anthracene. The 2-phenylethanol concentrations used were too strong and did not match well. The lowest concentration of β -phenylethylphenylacetate matches the 8-hr point fairly well, and the next concentration would probably have been in the useful range but this remains a speculation since the test paper was blown away by the strong wind.

The responses received in the opinion survey are given in Table VII-5. Some of the panel did not detect the fluorescent light source immediately, and many indicated that the light source was dim

TABLE VII-5. RESULTS OF PANEL EVALUATION OF SENSORY WARNING DEVICES

Device #1 -- Visual		Device #2 -- Phenylethanol		Device #3 -- Skatole		Preference	
1. See?	% Answers	1. Smell	% Answers		1. Like Best	% Answers	
Yes	40	Yes	100		Skatole	40	
No	40	No	0-		Phenylethanol	20	
Unc.	20	Unc.	0-		Visual	40	
2. Color?		2. Pleasant			2. Most Confidence		
Green	0-	Pleasant	80		Skatole	40	
Yellow	0-	Unpleasant	20		Phenylethanol	0-	
Blue/Purp.	100	Unc.	0-		Visual	60	
Other	0-						
Unc.	0-						
3. Brightness		3. Strength			3. Best Warning		
Very Bright	0-	Strong	0-		Skatole	40	
Bright	40	Weak	80		Phenylethanol	0-	
Dim	60	None	0-		Visual	60	
Barely Seen	0-	Unc.	20				
Not Seen	0-						
Uncertain	0-						
4. Easily Noticed		4. Easily Noticed			4. Useful for Children		
Yes	40	Yes	20		Yes	100	
No	40	No	80		No	0-	
Unc.	20	Unc.	0-		Uncertain	0-	
5. Warning Indicated		5. Warning Indicated			5. Best for Children		
Yes	80	Yes	40		Skatole	60	
No	20	No	40		Phenylethanol	0-	
Unc.	0-	Unc.	20		Visual	40	

and not easily noticed. All recognized the color of the light source. Most of the panel said that a warning was indicated. Concerning the unpleasant smelling device (skatole), all of the panel detected a smell, and most indicated that the smell was strong. All said that the smell was easily noticed, and most said that a warning was indicated.

Relative to the pleasant smelling device (2-phenylethanol), all of the panel detected a smell and most indicated the smell was weak. Most said the smell was not easily noticed and approximately one-half said that a warning was indicated. Virtually none of the panel preferred the pleasant smelling device (2-phenylethanol). The panel was evenly distributed between preferring the unpleasant smelling device (skatole) and the visual device. All indicated that the unpleasant smelling device (skatole) would be useful and effective for the protection of children.

E. Other Investigators' Disappearance Data

A literature search was conducted to find outdoor disappearance data of other investigators for the 3 pesticides of concern in this program. The information obtained is presented in Tables VII-6, VII-7, and VII-8. Variations in weather conditions, quantity applied, plant species involved, length of tests, and analytical procedures make exact comparisons impossible. For this reason, appropriate information and data other than disappearance figures have been extracted from the journal articles and are included in the tables to help in the evaluation of

TABLE VII-6. DISAPPEARANCE DATA FOR METHYL PARATHION
(% Remaining on foliage 3 days after application)

Source of Information	Percent Remaining	Application Rate	Plant Species	Comments
Shipp, <i>et. al.</i> (18)	1.9*	5.7 $\mu\text{g}/\text{cm}^2$ (0.5 lb/acre)	Cotton	Half-life is approximately 24 hr. Temp extremes, 19-34°C (67-94°F); some rain fell.
Quinby, <i>et. al.</i> (19)	<5 after 24 hr	5.7 $\mu\text{g}/\text{cm}^2$ (0.5 lb/acre)	Cotton	Half-life is less than 1 hr. Temp extremes 15-36°C (59-97°F).
Ware, <i>et. al.</i> (20)	19.4	5.7 $\mu\text{g}/\text{cm}^2$ (0.5 lb/acre)	Cotton	Temp extremes, 17-37°C (62-98°F). No rainfall.
Fahey, <i>et. al.</i> (21)	20	est. at 3 $\mu\text{g}/\text{cm}^2$ (0.26 lb/acre)	Apple	Temp extremes 14-23°C (58-74°F). Rainfall during test periods 6.6-8.6 cm (2.6 to 3.4 inches).
Pass and Dorrough (22)	4.2 6.4	5.7 $\mu\text{g}/\text{cm}^2$ (0.5 lb/acre) 11.4 $\mu\text{g}/\text{cm}^2$ (1.0 lb/acre)	Alfalfa	Temp extremes, 18-28°C (64-82°F); no rainfall during first 3 days.
Waldron and Goleman (23)	16 23	5.7 $\mu\text{g}/\text{cm}^2$ (0.5 lb/acre) 11.4 $\mu\text{g}/\text{cm}^2$ (1.0 lb acre)	Alfalfa	Temp extremes, 5-23°C (41-73°F). Some rain from 0.3-3 cm (0.1 to 1.2 in.).
Ware, <i>et. al.</i> (24)	1.9	11.4 $\mu\text{g}/\text{cm}^2$ (1.0 lb/acre)	Cotton	Temp extremes, 26-42°C (78-108°F), windy and dry.
Ware, <i>et. al.</i> (25)	1.1	11.4 $\mu\text{g}/\text{cm}^2$ (1.0 lb/acre)	Cotton	Temp extremes, 20-42°C (68-108°F); No rain.
Ware, <i>et. al.</i> (26)	4.8	11.4 $\mu\text{g}/\text{cm}^2$ (1.0 lb/acre)	Cotton	Temp extremes, 22-39°C (71-103°F); no rain.

References noted on following page.

TABLE VII-6. DISAPPEARANCE DATA FOR METHYL PARATHION (Cont'd)
(% Remaining on foliage 3 days after application)

Source of Information	Percent Remaining	Application Rate	Plant Species	Comments
SwRI	4.8 (avg.)	5.7 $\mu\text{g}/\text{cm}^2$ (0.5 lb/acre)	Euonymus	Temp extremes, 4-29°C (40-85°F); no rain. Sunny 2 of the 3 days. Winds varied from calm to 24 kph (15 mph). Humidity varied from low to high.
SwRI	1.0	17.1 $\mu\text{g}/\text{cm}^2$ (1.5 lb/acre)	Cotton	Temp. extremes, 25.6-34.4°C (78°-94°F). No rain—sunny. Winds from 8 to 56 kph (5 to 35 mph). Humidity varied from low to high.

*Analytical determinations on ppm basis (i.e. $\mu\text{g}/\text{g}$ of whole plant or leaves).

18. Shipp, O.E., *et. al.*, *J. Econ. Entomol.*, **56**, 793-798 (1963).
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TABLE VII-7. DISAPPEARANCE DATA FOR AZINPHOSMETHYL (GUTHION 2L)
(% Remaining on foliage 4 days after application)

Source of Information	Percent Remaining	Application Rate	Plant Species	Comments
Quinby, <i>et. al.</i> (19)	<50	5.7 µg/cm ² (0.5 lb/acre)	Cotton	Half-life is 2-4 days; Temp extremes, 15-36°C (59-97°F)
Ware, <i>et. al.</i> (24)	17.7	5.7 µg/cm ² (0.5 lb/acre)	Cotton	Temp extremes, 26-42°C (78-108°F); windy and dry.
Ware, <i>et. al.</i> (25)	16.7	5.7 µg/cm ² (0.5 lb/acre)	Cotton	Temp extremes, 20-42°C (68-108°F); no rain.
Ware, <i>et. al.</i> (26)	22.4*	5.7 µg/cm ² (0.5 lb/acre)	Cotton	Temp extremes, 22-39°C (71-103°F); no rain.
Scott, <i>et. al.</i> (27)	46†	0.7 µg/cm ² (0.0625 lb/acre)	Cotton	Very low application rate. No weather conditions given.
SwRI	86†	10 µg/cm ² (0.88 lb/acre)	Euonymus	Temp extremes 7-29°C (48-85°F); no rain on plants. Winds were calm to 24 kph (15 mph). Humidity varied from low to high. Two of the 4 days were sunny.

* Analytical determinations on ppm basis (i.e., µg/g of whole plant or leaves).

† By straight line interpolation.

19. Quinby, G.E., *et. al.*, *J. Econ. Entomol.*, **51**, 831-838 (1958).
24. Ware, G.W., *et. al.*, *Bull. Environ. Contam. Toxicol.*, **11**, 434-437 (1974).
25. Ware, G.W., *et. al.*, *Bull. Environ. Contam. Toxicol.*, **13**, 334-337 (1975).
26. Ware, G.W., *et. al.*, *Bull. Environ. Contam. Toxicol.*, **8**, 361-362 (1972).
27. Scott, W.P., *et. al.*, *J. Econ. Entomol.*, **67**, 408-410 (1974).

TABLE VII-8. DISAPPEARANCE DATA FOR CARBOFURAN (FURADAN 4 FLOWABLE)
(% Remaining on foliage 14 days after application)

Source of Information	Percent Remaining	Application Rate	Plant Species	Comments
Fahey, <i>et. al.</i> (28)	<0.4*	5.7 $\mu\text{g}/\text{cm}^2$ (0.5 lb/acre) 11.4 $\mu\text{g}/\text{cm}^2$ (1.0 lb/acre)	Alfalfa	Maximum daily temp about 31°C (87°F). Rain after 14th day of test.
SwRI	39†	10 $\mu\text{g}/\text{cm}^2$ (0.88 lb/acre)	Euonymus	Temp extremes, 7-29°C (45-85°F); no rain on plants. Winds were calm to 24 kph (15 mph). Two of the four days were sunny. Humidity varied from low to high.

*Analytical determinations on ppm basis (i.e., $\mu\text{g}/\text{g}$ of whole plant or leaves).

†By straight line interpolation.

28. Fahey, J.E., *et. al.*, *J. Econ. Entomol.*, 63, 589-591 (1970).

the disappearance figures. The length of time after application is given at the top of each table. This time point was chosen so as to accommodate the maximum number of references. In this program, the amount of methyl parathion remaining 3 days after application was 4.8% of the amount applied on the euonymus plants and less than 1% on the cotton plants. Extremes found in the literature for the same time period were 23% and 1.1%. In a similar comparison, but for a 4-day period, 86% of the azinphosmethyl was found on the plants in this program, whereas the high and low figures from the literature were 46% and 16.7%. For carbofuran, the comparison had to be made after 14 days had passed. In this program, 39% was found to remain. Only one value could be found in the literature, and it was less than 0.4%.

In this program, azinphosmethyl and carbofuran were found to disappear much more slowly than other investigators have found. However, the disappearance rates from plants outdoors were not out of line with the disappearance rates from glass plates in a laboratory environment. The disappearance rates of methyl parathion from plants, as determined in this program, are substantially in the span of the data of others.

Since carbofuran has most frequently been applied to soil rather than to plant foliage, only one reference was found which had data suitable for comparison with the data generated in this program. Another interesting reference on carbofuran gives the half-life in soil, under field conditions, as ranging from 46 to 117 days. (29)

29. Caro, J.H., et. al., J. Agr. Food Chem., 21, 1010-1015 (1973).

VIII. BLUE-SKY EFFORT

Several meetings were held with groups of Institute personnel to discuss the problem of time of safe reentry into fields which had been sprayed with toxic pesticides named in this report. Present in the various groups were chemists, physicists, plant physiologists, and engineers. It was explained that, although low cost, simple devices were desired, the discussions were not to be limited by these factors, as the ideas were to be screened later. It is possible that, during the screening process, new and simple practical ideas might be developed from the more complicated and less practical suggestions. The following suggestions were made.

1. As the pesticides under consideration are cholinesterase inhibitors, it should be possible to develop a nonspecific test for the pesticides which would relate to the actual residual pesticide activity. An article, entitled "Test for Anticholinesterase Materials in Water", published by Ganison, et al,⁽³⁰⁾ describes such a test. The test involves a color development by uninhibited cholinesterase. In the presence of pesticides, inhibition of the enzyme occurs, and there is no color development. A rapid and continuous system for monitoring organophosphates in water has been developed by Dr. Louis H. Goodson of Midwest Research Institute. This system is based upon the determination of the activity of an immobilized enzyme in an electrochemical cell.

30. Ganison, R.M., et. al., Environ. Sci. Technol., 7, 1137-1140 (1973).

It could possibly be adapted to make a fairly simple piece of inexpensive test equipment for spot tests.

2. A cursory check of the literature indicates that it may be possible to develop simple color tests for some of the pesticides. Further search of the literature and some experimental work may confirm this.

3. The ability of methyl parathion and parathion to isomerize to compounds which hydrolyze readily might be used to detect these compounds. Heating of methyl parathion to 100°C rapidly isomerizes it to a product which hydrolyzes readily to form methylmercaptan which could be easily detected by its odor. A similar reaction occurs with parathion and might occur with Guthion. The equipment required for such a test would be simple, inexpensive, and readily available. As mercaptans have low odor thresholds, the test should be capable of detecting small quantities of the pesticides, although the quantities encountered in use conditions might require concentrating to reach the level of perception.

4. The use of small retroreflective glass beads offer a possibility as an indicator for safe reentry into a sprayed field. The retroreflective characteristics of these beads are usually very low or nonexistent when wetted with a liquid. The pesticide might act as such a material, and the retroreflective characteristics return on loss of the pesticide. A good flashlight would be the only equipment required.

5. When dyes are in solution, they frequently exhibit a color which differs from that of the solid dye. This principle might be used as an indicator for the presence or absence of the pesticide.

6. The fluorescence and phosphorescence of some materials can be quenched by the addition of certain materials. If the pesticide has this quenching property with some light emitting materials, a system could be devised for indicating the absence of pesticide. It would be rather simple to experimentally check a number of light emitting compounds with the pesticides.

7. A chemiluminescent system in which one of the reactants has the desired rate of disappearance could be used as an indicator for the disappearance of the pesticide from foliage. This reactant could be coated on the foliage with or without the pesticide. In determining if any of the reactant remains, the other component or components of the system could be sprayed on the foliage periodically. When all of the indicator reactant has disappeared, a chemiluminescent reaction would no longer take place, and no light would be emitted.

8. If contaminated air from the sprayed field is passed through a cage containing insects which are sensitive to the pesticide under consideration, the death rate or number of insects killed could be used as an indication of pesticide concentration. Tests such as this are generally not sufficiently reproducible or sufficiently rapid to be of value.

9. A test similar to that suggested in 8., but use contaminated foliage in place of contaminated air.

10. If the fluorescence of the pesticide is sufficiently strong, this property could be utilized to indicate concentration.

11. A laser could be utilized as a strong, concentrated light source. Either fluorescence or light absorption could be utilized to determine presence or absence of pesticide. This type of equipment would be relatively expensive and complicated.

12. Convert the thio-compounds to hydrogen sulfide which could be identified by odor or lead acetate test paper. This conversion would require equipment considered too complicated and expensive for general field application.

13. Use insect attractants (bug lights or chemicals) to attract insects into the area and determine kill. This would be difficult to reproduce, as it would depend upon the concentration and type of insects found in the area.

14. React thio-compounds with copper and determine sulfide formation by reflectance or color change.

15. The pesticide molecules could be activated with a laser beam and the Raman spectra determined. The Materials Research Center of the Allied Chemical Corporation has developed such a remote gas analysis system. Measurements can be made in the kilometer range. However, this equipment is bulky and expensive.

16. The laser beam could be used to volatilize the pesticide from the foliage and the concentration of pesticide measured. Such a treatment would undoubtedly destroy the foliage and interfere with the analysis.

17. The conductivity of solutions formed by passing air through a solvent may be a measure of the pesticide concentration. In a similar manner, the conductivity of solutions formed by washing the foliage in a solvent, preferably one with a low solvent power for inorganic materials could be utilized. Disadvantage of such a test is the presence of interfering materials in the environment.

18. The adaptation of infrared photography would be useful in surveying pesticide concentration from an airplane or helicopter.

19. Adaptation of the infrared sniperscope to examine the sprayed foliage would be useful for determining concentration of pesticide.

20. Same as 19, but use ultraviolet light.

21. A condensation nuclei detector in conjunction with a chromatographic column could be used. This method would be expensive.

22. As the flame photometric detector is selective for sulfur and phosphorus, it may be possible to adapt it to a device for detecting pesticides containing these elements without the use of a chromatographic column. The equipment would be expensive and would require a hydrogen and oxygen source.

23. If enzymes that emit odor from substrates are sensitive to pesticides, they could be adapted to detection of pesticides.

24. Changes in conductivity of the surface of semi-conductors might be useful as this method is capable of detecting extremely small quantities of material. The disadvantage of this method is its lack of selectivity.

25. The contaminated foliage could be fed to a rabbit which would be observed for neurological changes indicating toxicity. Trained personnel would be required for such a test.

26. Samples could be pyrolyzed and the products analyzed with a coulometric detector. Equipment would be relatively expensive and complicated.

27. It was suggested that the action of atropine in the treatment of phosphate ester poisoning be determined and adapted to pesticide determination if possible. Information given in a medical book indicates that this is not possible.

28. As a method of sampling, a nonabsorbent tape would be stretched across a portion of the field prior to spraying. After spraying, the tape could be reeled in slowly or periodically for examination by a suitable detection system.

It was suggested that the first 7 ideas be considered for further checking for feasibility and the feasible ones be considered for development.

It was the consensus of all personnel questioned that, as there are too many factors affecting the concentration of pesticide in air and as the concentration of the pesticide in air is so low, adaptation of the various ideas to foliage examination would be more practical than air examination.

A small amount of experimental work was done attempting to utilize the phenomenon of heat isomerization of methyl parathion to the thio ester with subsequent hydrolysis to yield methyl mercaptan. Heating of small quantities of methyl parathion to 160-180°C in an air atmosphere in a test tube permits oxidation to the oxygen analog, and no methyl mercaptan is obtained on hydrolysis. If this procedure is to be successfully applied, relatively sophisticated equipment for heating and cooling the pesticide in an inert atmosphere would have had to be developed. Avoidance of sophisticated equipment was one of the objectives of this program. It was noted that on hydrolysis of either the unheated or heated and oxidized parathion, the p-nitrophenol formed gives a light yellow color to the alkaline hydrolysate. On acidification, the yellow color disappears.

Small amounts of experimental work were also done in other areas. Sawicki, et al.⁽³¹⁾ reported 4-(p-nitrobenzyl)-pyridine to be a sensitive reagent for the determination of alkylating agents. The work done at SwRI indicates this reagent offers some promise for determining the presence of residual methyl parathion at levels down to 1 µg. By using several leaf washings and concentrating the washings, if necessary, this test is thought to offer some promise in determining methyl parathion at the low levels of interest.

Attempts to quench small retroreflective beads with pesticides, as mentioned in suggestion 4, above, were without success. Similarly,

31. Sawicki, E., et al., Anal. Chem., 35, 1479-1486 (1963).

inorganic phosphors, dyes, and other nonvolatile luminescent substances were not quenched by the pesticides and no useful way to use their luminescent properties was devised.

A literature notation ⁽³²⁾ that the 3-keto derivative of carbofuran fluoresced in an intensely blue manner suggested that maybe this compound could be synthesized by a simple oxidative procedure under field conditions. However, neither hydrogen peroxide, bis (4-t-butylcyclohexyl) peroxydicarbonate, diisopropylbenzene hydroperoxide, nor NaOCl produced positive results. The literature method of producing this compound by prolonged heating with chromium trioxide in glacial acetic acid was not effective when the reaction time was reduced to a few minutes.

Another reference ⁽³³⁾ stated that heating organic compounds in the presence of ammonium bicarbonate often produced a fluorescent residue. Methyl parathion was heated with ammonium bicarbonate for one hour at 110°C without success.

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